

### 1. Method for transitioning between incompatible olefin polymerization catalyst systems

By Meier, Gerhardus; Mihan, Shahram

From [U.S. \(2013\)](#), [US 8481658 B2 20130709](#), Language: English, Database: CAPLUS

A method for transitioning from a Ziegler-Natta to a **Phillips catalyst** system for the olefin polymn. reaction in one reactor, preferably a gas phase reactor, is described. The method comprises the steps of a) discontinuing a first olefin polymn. reaction performed in the presence of the Ziegler-Natta **catalyst** system; b) performing a second olefin polymn. reaction in the presence of a further **catalyst** system comprising **catalyst** components (A) and (B) producing, resp., a first and a second polyolefin fraction, wherein the  $M_w$  of the first polyolefin fraction is less than the  $M_w$  of the second polyolefin fraction and the initial activity of **catalyst** component (A) exceeds the initial activity of **catalyst** component (B); and c) performing a third olefin polymn. reaction the presence of the **Phillips catalyst** system. Thanks to this method, there is no need to empty the reactor after each olefin polymn. reaction, and the transitioning time needed to attain the desired quality of the polyolefin obtained in each olefin polymn. reaction subsequent to the first one is sufficiently short to permit a quick and reliable change of prodn.

#### ~0 Citings

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### 2. Reduction of the **Phillips catalyst** by various olefins: Stoichiometry, thermochemistry, reaction products and polymerization activity

By Potter, Kelsey C.; Beckerle, Connor W.; Jentoft, Friederike C.; Schwerdtfeger, Eric; McDaniel, Max P.

From [Journal of Catalysis \(2016\)](#), [344](#), [657-668](#). Language: English, Database: CAPLUS,

DOI:10.1016/j.jcat.2016.10.031

The adsorption, reaction and desorption of ethylene or hexenes on Cr(VI)/SiO<sub>2</sub> contg. 1 or 3 wt.% chromium were monitored by thermogravimetry, differential scanning calorimetry and mass spectrometry. Reaction of Cr(VI)/SiO<sub>2</sub> with ethylene at 200 °C always included some oligomerization, making it impossible to identify the stoichiometry of the initial redox reaction. Reaction of Cr(VI)/SiO<sub>2</sub> with 1-hexene or cyclohexene at 150 °C indicated an adsorption stoichiometry of one olefin per chromium. Heats of reaction were consistent with oxidn. of the olefin to an aldehyde or ketone, or even to a carboxylic acid or ester. Oxidn. products were retained on the surface. Thermal desorption of surface products resulted in CO<sub>2</sub> evolution at temps. of 265-285 and 390-415 °C, with the co-products indicating decompn. of formate and acetate species, resp. Redn. of Cr(VI) with ethylene led to sites active for ethylene polymn. after thermal desorption of the redox products, whereas redn. with hexenes did not generate active sites irres. of thermal desorption of products.

#### ~0 Citings

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### 3. Activation and Deactivation of **Phillips Catalyst** for Ethylene Polymerization Using Various Activators

By Zeng, Yanning; Chammingkwan, Patchanee; Baba, Ryuki; Taniike, Toshiaki; Terano, Minoru

From [Macromolecular Reaction Engineering \(2016\)](#), [Ahead of Print](#). Language: English, Database: CAPLUS,

DOI:10.1002/mren.201600046

The present article reveals important roles of metal alkyl activators in tuning the performance of the **Phillips catalyst** in ethylene polymn. The addn. of aluminum alkyl aids the activation of the **catalyst**, while excess addn. leads to the loss of the activity. The balance between the activation and deactivation depends on the type of employed aluminum alkyl, and tri-n-octylaluminum offers the most efficient **catalyst** usage by preferentially suppressing the deactivation. The passivation of aluminum trialkyl with a hindered phenol mildens not only the deactivation but also chain transfer reactions, leading to an increment of high mol. wt. fractions.

#### ~0 Citings

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### 4. Reactivity of Hydrosilanes with the CrII/SiO<sub>2</sub> **Phillips Catalyst**: Observation of Intermediates and Properties of the Modified CrII Sites

By Barzan, Caterina; Bordiga, Silvia; Quadrelli, Elsje Alessandra; Groppo, Elena

From [Topics in Catalysis \(2016\)](#), [59\(19-20\)](#), [1732-1739](#). Language: English, Database: CAPLUS,

DOI:10.1007/s11244-016-0694-8

The reaction of hydrosilanes (both silane and triethylsilane) with  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalyst has been investigated in detail by anal. of the gaseous byproducts, temp.- and pressure- resolved FT-IR spectroscopy and deuterium exchanges. We found that the reaction proceeds via two steps, passing through intermediates characterized by elongated Si-H bonds and transient Cr-hydride species leading to the release of  $\text{H}_2$  in the gas phase. These exptl. evidence allowed us to advance an hypothesis of the reaction mechanism, which validates our previous proposal for the structure of the modified chromium sites. Furthermore, based on the intermediates of the reaction mechanism, we have also tested the ability of the modified "homogeneous-like"  $\text{Cr}^{\text{II}}$  sites toward  $\text{H}_2$  ( $\text{D}_2$ ) activation, demonstrating that, contrarily to the unmodified  $\text{Cr}^{\text{II}}$  species, such reactivity is present.

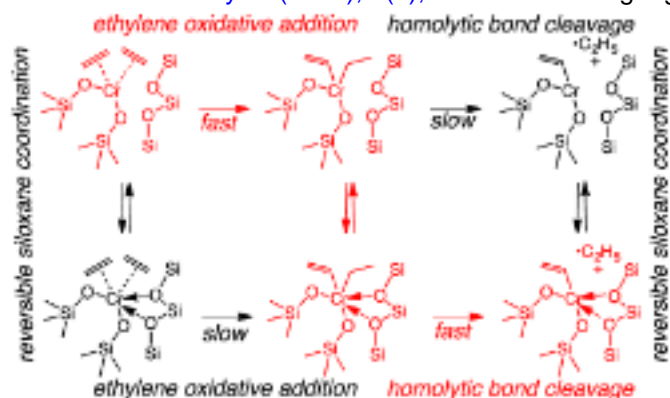
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## 5. One-Electron-Redox Activation of the Reduced Phillips Polymerization Catalyst, via Alkylchromium(IV) Homolysis: A Computational Assessment

By Fong, Anthony; Peters, Baron; Scott, Susannah L.

From *ACS Catalysis* (2016), 6(9), 6073-6085. Language: English, Database: CAPLUS, DOI:10.1021/acscatal.6b01728



In ethylene polymn. by the Phillips catalyst, inorg.  $\text{Cr}(\text{II})$  sites are believed to be activated by reaction with ethylene to form (alkyl) $\text{Cr}^{\text{III}}$  sites, in a process that takes about 1 h at ca. 373 K. The detailed mechanism of this spontaneous self-initiation has long remained unknown. It must account both for the formation of the first Cr-C bond and for the one-electron oxidn. of  $\text{Cr}(\text{II})$  to  $\text{Cr}(\text{III})$ . In this study, we used d. functional theory to investigate a two-step initiation mechanism by which ethylene oxidative addn. leads first to various (organo) $\text{Cr}^{\text{IV}}$  sites, and subsequent Cr-C bond homolysis gives (organo) $\text{Cr}^{\text{III}}$  sites capable of polymg. ethylene. Pathways involving spin crossing, C-H oxidative addn., H atom transfer, and Cr-C bond homolytic cleavage were explored using a chromasiloxane cluster model. In particular, we used classical variational transition theory to compute free energy barriers and est. rates for bond homolysis. A viable route to a four-coordinate bis(alkyl) $\text{Cr}^{\text{IV}}$  site was found via spin crossing in a bis(ethylene) $\text{Cr}^{\text{II}}$  complex followed by intramol. H atom transfer. However, the barrier for subsequent Cr-C bond homolysis is a formidable 209 kJ/mol. Increasing the Cr coordination no. to 6 with addnl. siloxane ligands lowers the homolysis barrier to just 47 kJ/mol, similar to reported homolysis paths in mol.  $[\text{CrR}(\text{H}_2\text{O})_5]^{3+}$  complexes. However, siloxane coordination also raises the barrier for the prior oxidative addn. step to form the bis(alkyl) $\text{Cr}^{\text{IV}}$  site. Thus, we suggest that hemilability in the silica "ligand" may facilitate the homolysis step while still allowing the oxidative addn. of ethylene.

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## 6. Real-time Analysis of a Working Triethylaluminium-Modified Cr/Ti/SiO<sub>2</sub> Ethylene Polymerization Catalyst with In Situ Infrared Spectroscopy

By Cicmil, Dimitrije; Meeuwissen, Jurjen; Vantomme, Aurelien; Weckhuysen, Bert M.

From *ChemCatChem* (2016), 8(11), 1937-1944. Language: English, Database: CAPLUS, DOI:10.1002/cctc.201600200

A diffuse reflectance IR Fourier-transform (DRIFT) study was conducted at 373 K and 1 bar on an industrial  $\text{Cr}/\text{Ti}/\text{SiO}_2$  Phillips-type catalyst modified with, and without, triethylaluminum (TEAL) as co-catalyst. The reaction rate of the polymn. of ethylene, as monitored by the increase in the methylene stretching band of the growing polyethylene (PE), was investigated as a function of the titanium content. After an initial period of mixed kinetics, with the reaction rate significantly higher for the TEAL-modified catalysts compared with the non-modified catalysts, the polymn. proceeded as a pseudo-zero-order reaction with a reaction rate that increased as a function of titanium loading. Furthermore, it was found that the higher Ti loading caused the appearance of more acidic hydroxyl groups and modified the Cr sites by making them more Lewis acidic, ultimately shortening the induction time and increasing the initial polymn. rate.

~0 Citings

## 7. Ti-modified silica supported Cr-Mo hybrid **Phillips catalyst** for ethylene polymerization

By Ma, Yue; Cheng, Rui-hua; He, Xue-lian; Liu, Zhen; Zhao, Ning; Liu, Bai-ping

From [Huadong Ligong Daxue Xuebao, Ziran Kexueban \(2016\), 42\(2\), 163-170, 253](#). Language: Chinese, Database: CAPLUS, DOI:10.14135/j.cnki.1006-3080.2016.02.003

**Phillips catalyst** ( $\text{CrO}_x/\text{SiO}_2$ ) is an important industrial high d. polyethylene **catalyst**. In this work, a Ti-modified Cr-Mo hybrid **Phillips catalyst** ( $\text{CrMo/TiSi}$ ) was prepd. and tested to improve the ethylene polymn. performance.  $\text{CrMo/TiSi}$  and  $\text{CrMo/Si}$  catalysts were compared and studied by the temp.-program redn., X-ray photoelectron spectrometer and d. function theory. Due to the Ti-modification, the redn. peak shifted to the lower temp. and the binding energy of the Cr species increased, which reflected that the Cr species were easier to be reduced. The ethylene polymn. performances over the  $\text{CrMo/TiSi}$  and  $\text{CrMo/Si}$  catalysts at different conditions were investigated. The Ti-modification increased the activity and the **catalyst** produced the polymer with higher mol. wt. ( $M_w$ ). Detd. by high temp.  $^{13}\text{C}$ -NMR, the copolymer by the Ti-modified **catalyst** exhibited higher 1-hexene incorporation. However, the amt. of short chain branches for the copolymer decreased in the high  $M_w$  part, according to the temp. rising elution fractionation cross successive self-nucleation and annealing (TREF + SSA) results.

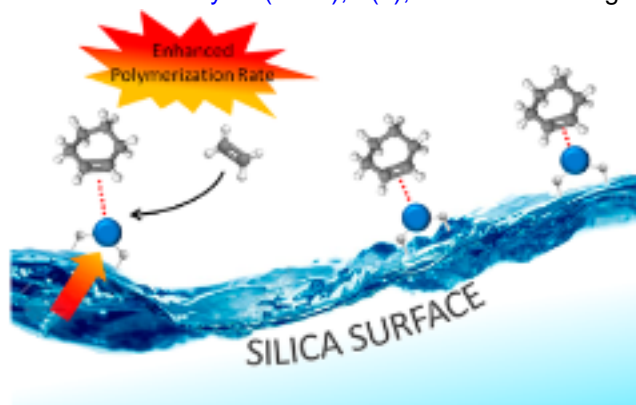
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## 8. Toward the Understanding of the Comonomer Effect on $\text{Cr}^{\text{II}}/\text{SiO}_2$ **Phillips Catalyst**

By Barzan, Caterina; Bordiga, Silvia; Groppo, Elena

From [ACS Catalysis \(2016\), 6\(5\), 2918-2922](#). Language: English, Database: CAPLUS, DOI:10.1021/acscatal.6b00147



The origin of the "comonomer effect" (i.e., the enhancement of ethylene polymn. rate in the presence of  $\alpha$ -olefin comonomer) on  $\text{Cr}^{\text{II}}/\text{SiO}_2$  **Phillips catalyst** was investigated by means of in situ FT-IR and Diffuse Reflectance UV-vis spectroscopies. A nonpolymg. olefin, cyclohexene, was chosen as "comonomer" and introduced on the **catalyst** prior the monomer injection in order to produce only homopolymers. The exptl. data showed that  $\alpha$ -olefin (ethylene, propene, and 1-hexene) homopolymn. is enhanced up to a factor of 5. The exptl. data also provided the first direct evidence that the comonomer strongly interacts with all the  $\text{Cr}^{\text{II}}$  sites and that it is responsible for their structural and electronic rearrangement at a mol. scale, as proposed for the "trigger mechanism". The data also proved that the fraction of Cr active sites do not retain the comonomer during the olefin polymn., meaning that the increased reactivity is due to a modification influencing all the **catalyst** Cr sites.

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## 9. Activation of the **Phillips** polymerization **catalyst** by ethylene oxidative addition followed by homolysis: A computational assessment

By Fong, Anthony; Scott, Susannah L.; Peters, Baron

From [Abstracts of Papers, 251st ACS National Meeting & Exposition, San Diego, CA, United States, March 13-17, 2016 \(2016\), CATL-8](#). Language: English, Database: CAPLUS

The mechanism of ethylene polymn. by the widely used **Phillips catalyst** remains controversial. In this work, we compare initiation, propagation, and termination pathways computationally using small chromasiloxane cluster models for several previously proposed and new mechanisms. Prohibitively high activation barriers for propagation rule out previously proposed chromacycle ring expansion and alternating alkylidene/chromacycle mechanisms. A new oxachromacycle ring expansion mechanism has a plausible propagation barrier, but initiation is prohibitively slow. On sites with adjacent bridging hydroxyls, either  $\text{Si}(\text{OH})\text{Cr}^{\text{II}}\text{-alkyl}$  or  $\text{Si}(\text{OH})\text{Cr}^{\text{III}}\text{-alkyl}$ , initiated by proton transfer from ethylene, chain growth by a Cossee-Arlman-type mechanism is fast. However, the initiation step is uphill and extremely slow, so essentially all sites remain trapped in a dormant state. In addn., these sites only make oligomers, because when all pathways are considered, termination is faster than propagation. A monoalkylchromium(III) site without an adjacent proton,  $(\text{ident.}\text{SiO})_2\text{Cr-alkyl}$ , is viable as an active site for polymn. Initiation may occur with oxidative addn. of ethylene with spin-crossing, followed by Cr-C homolysis.

~0 Citings

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## 10. Not all long chain branching in polyethylene is created equal

By Yu, Youlu

From [Abstracts of Papers, 251st ACS National Meeting & Exposition, San Diego, CA, United States, March 13-17, 2016 \(2016\), PMSE-485](#). Language: English, Database: CAPLUS

Long-chain branching (LCB) is a very important polymer architectural attribute for polyethylene resins and has been extensively studied since the creation of the first polyethylene resin made using peroxide catalyst under high temp. and high pressure (i.e. The presence of LCB not only affects polymer processability but also polymer mech. properties. Depending on applications, the right amt., type, and distribution of LCB are necessary in order to produce products that meet the desired processability and end-use properties. In this talk, we will present LCB characterization of LDPE, and polyethylene resins made using the Phillips catalyst, Ziegler-Natta catalyst and metallocene catalyst under low pressure and low temp. using size-exclusion chromatog. (SEC, also known as gel-permeation chromatog., GPC) hyphenated with multi-angle light scattering (MALS) (i.e. SEC-MALS) in conjunction with other spectroscopic, rheol. and fractionation techniques. Some of these results will be compared to those obtained via asym. flow field-flow fractionation (AF4) coupled with MALS (i.e. AF4-MALS). Polymer architectural characteristics of these four types of PE resins will also be discussed in this presentation.

~0 Citings

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## 11. Homogeneous models for heterogeneous chromium-based ethylene polymerization catalysts

By Theopold, Klaus

From [Abstracts of Papers, 251st ACS National Meeting & Exposition, San Diego, CA, United States, March 13-17, 2016 \(2016\), PMSE-222](#). Language: English, Database: CAPLUS

Heterogeneous chromium catalysts play an important role in the industrial polymn. of ethylene. The Phillips catalyst, in particular, is notable both for its com. impact as well as the mystery surrounding its active site and mechanism of action. As part of our program of investigating paramagnetic organometallics, we have prepd. a series of mols. that serve as structural and functional models for chromium based polymn. catalysts. These studies have - inter alia - addressed the issues of the active oxidn. state, the propensity to incorporate  $\alpha$ -olefins, and effect of ligands on polymer microstructure. More recently, we have also addressed the mechanism of the selective oligomerization of ethylene, which produces comonomers for the prodn. of LLDPE.

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## 12. Pre-reduction of the Phillips Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst by cyclohexene: A model for the induction period of ethylene polymerization

By Barzan, Caterina; Damini, Alessandro A.; Budnyk, Andriy; Zecchina, Adriano; Bordiga, Silvia; Groppo, Elena

From [Journal of Catalysis \(2016\), 337, 45-51](#). Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2016.01.013

The pre-redn. of the industrially relevant Cr<sup>VI</sup>/SiO<sub>2</sub> Phillips catalyst by cyclohexene at room temp. was investigated by means of operando XANES, Diffuse Reflectance UV-Vis and transmission FT-IR spectroscopies. It was found that cyclohexene efficiently reduces the surface chromates sites (Cr<sup>VI</sup>) at room temp. to give mainly divalent chromium sites and aldehyde byproducts, which are rapidly converted in ester species. These byproducts remain in strong interaction with the reduced chromium sites, defining a complex and tunable ligand sphere, which controls the entrance of incoming mols., including ethylene. Unlike the Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst, the cyclohexene-reduced Cr/SiO<sub>2</sub> catalyst polymerizes ethylene already at room temp. with no induction time. The reactivity of cyclohexene with the Cr<sup>VI</sup> species mimics that of ethylene during the induction period on Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst, simplified by the absence of the further polymn. step. Hence, the results discussed in this work are potentially useful to understand what happens during the induction period in the presence of ethylene.

~2 Citings

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## 13. Reprint of: Effect of Mo-modification over Phillips CrOx/SiO<sub>2</sub> catalyst for ethylene polymerization



By Ma, Yue; Cheng, Ruihua; Li, Jiajun; Zhong, Lei; Liu, Zhen; He, Xuelian; Liu, Boping  
From [Journal of Organometallic Chemistry \(2015\), 798\(Part\\_2\), 317-327](#). Language: English, Database: CAPLUS,  
DOI:10.1016/j.jorganchem.2015.11.002

**Phillips**  $\text{CrO}_x/\text{SiO}_2$  **catalyst** is an important **catalyst** for industrial prodn. of polyethylene. In this work, a Mo-modified **Phillips catalyst** for ethylene polymn. (defined as CrMo/Si) was developed. The characterizations of the **Phillips catalyst** (defined as Cr/Si) and the CrMo/Si **catalyst** by temp. programmed redn. (TPR) and XPS showed an obvious interaction between the chromium and molybdenum components on the silica support. The ethylene polymn. performances at different conditions, in terms of  $\text{H}_2$  responds, polymn. temps., and the copolymn. with 1-hexene were systematically investigated. Although the polymn. activity of the CrMo/Si **catalyst** was lower, the copolymer presented a higher mol. wt. (MW) and a broader mol. wt. distribution (MWD). The Mo-modified **Phillips catalyst** (CrMo/Si) exhibited 67% higher 1-hexene incorporation ability as detd. by  $^{13}\text{C}$  NMR. Moreover, the short chain branch distribution (SCBD) of the copolymer obtained via the CrMo/Si **catalyst** was also improved as confirmed by temp. rising elution fractionation (TREF) cross successive self-nucleation and annealing (SSA) methods. The results of TREF and SSA showed that the amt. of short chain branches for the copolymer was increased in the high MW part, which would benefit for the long term mech. property of polyethylene.

~0 Citings

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#### 14. Stretched porous membrane made of an ultra-high molecular weight polyethylene composition

By Inatomi, Takashi; Abe, Shigehiko  
From [Jpn. Kokai Tokkyo Koho \(2015\), JP 2015199828 A 20151112](#), Language: Japanese, Database: CAPLUS

The invention relates to a stretched microporous membrane manufd. by using an ultra-high mol. wt. polyethylene compn. having excellent abrasion resistance, high heat resistance, strength, and good appearance. The stretched microporous membrane is made of an ultra high mol. wt. polyethylene compn. comprising (A) 100 parts of an ultra-high mol. wt. polyethylene which has an intrinsic viscosity 7-35 dL/g and a stress at break (MTS) 1MPa or less when melt-stretched at 150 °C and (B) 5-900 parts of an ultra-high mol. wt. polyethylene which has an intrinsic viscosity is 15-60 dL/g and a break stress (MTS) 2MPa or more when melt-stretched at 150 C. The ultra-high mol. wt. polyethylene (A) is obtained by homopolymn. or copolymn. of ethylene in the presence of Ziegler **catalyst** or **Phillips catalyst**.

~0 Citings

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#### 15. Polyethylene with Reverse Co-monomer Incorporation: From an Industrial Serendipitous Discovery to Fundamental Understanding

By Cicmil, Dimitrije; Meeuwissen, Jurjen; Vantomme, Aurelien; Wang, Jian; van Ravenhorst, Ilse K.; van der Bij, Hendrik E.; Munoz-Murillo, Ara; Weckhuysen, Bert M.  
From [Angewandte Chemie, International Edition \(2015\), 54\(44\), 13073-13079](#). Language: English, Database: CAPLUS, DOI:10.1002/anie.201506718

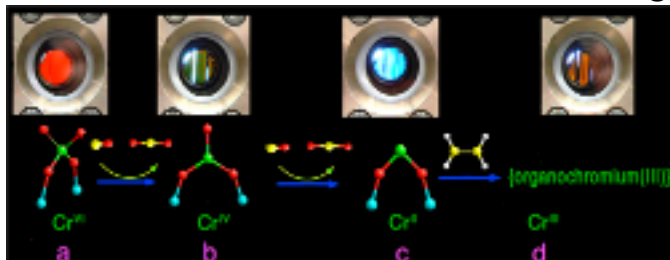
A triethylaluminum(TEAL)-modified **Phillips** ethylene polymn. Cr/Ti/SiO<sub>2</sub> **catalyst** has been developed with two distinct active regions positioned resp. in the inner core and outer shell of the **catalyst** particle. DRIFTS, EPR, UV-Vis-NIR DRS, STXM, SEM-EDX and GPC-IR studies revealed that the **catalyst** produces simultaneously two different polymers, i.e., low mol. wt. linear-chain polyethylene in the Ti-abundant **catalyst** particle shell and high mol. wt. short-chain branched polyethylene in the Ti-scarce **catalyst** particle core. Co-monomers for the short-chain branched polymer were generated in situ within the TEAL-impregnated confined space of the Ti-scarce **catalyst** particle core in close proximity to the active sites that produced the high mol. wt. polymer. These results demonstrate that the **catalyst** particle architecture directly affects polymer compn., offering the perspective of making high-performance polyethylene from a single reactor system using this modified **Phillips catalyst**.

~4 Citings

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#### 16. Mechanism of Initiation in the **Phillips** Ethylene Polymerization **Catalyst**: Redox Processes Leading to the Active Site

By Brown, Carole; Krzystek, J.; Achey, Randall; Lita, Adrian; Fu, Riqiang; Meulenberg, Robert W.; Polinski, Matthew; Peek, Nathan; Wang, Youhong; van de Burgt, Lambertus J.; et al  
From [ACS Catalysis \(2015\), 5\(9\), 5574-5583](#). Language: English, Database: CAPLUS, DOI:10.1021/acscatal.5b00927



The detailed mechanism by which ethylene polymn. is initiated by the inorg. **Phillips catalyst** ( $\text{Cr/SiO}_2$ ) without recourse to an alkylating cocatalyst remains one of the great unsolved mysteries of heterogeneous catalysis. Generation of the active **catalyst** starts with redn. of  $\text{Cr}^{\text{VI}}$  ions dispersed on silica. A lower oxidn. state, generally accepted to be  $\text{Cr}^{\text{II}}$ , is required to activate ethylene to form an organoCr active site. In this work, a mesoporous, optically transparent monolith of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  was prepd. using sol-gel chem. in order to monitor the redn. process spectroscopically. Using in situ UV-vis spectroscopy, we obsd. a very clean, stepwise redn. by CO of  $\text{Cr}^{\text{VI}}$  first to  $\text{Cr}^{\text{IV}}$ , then to  $\text{Cr}^{\text{II}}$ . Both the intermediate and final states show XANES consistent with these oxidn. state assignments, and aspects of their coordination environments were deduced from Raman and UV-vis spectroscopies. The intermediate  $\text{Cr}^{\text{IV}}$  sites are inactive toward ethylene at 80 °C. The  $\text{Cr}^{\text{II}}$  sites, which have long been postulated as the end point of CO redn., were obsd. directly by high-frequency/high-field EPR spectroscopy. They react quant. with ethylene to generate the organo $\text{Cr}^{\text{III}}$  active sites, characterized by X-ray absorption and UV-vis spectroscopy, which initiate polymn.

~6 Citings

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## 17. Organometallic chromium catalysts in olefin polymerization

By Alliger, Glen E.

From [Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, 2015 \(2015\), PMSE-153](#). Language: English, Database: CAPLUS

Chromium has a rich history in olefin polymn., and continues to play an important role today, as nearly half of the world's HDPE is made using the **Phillips catalyst**. This **catalyst**, however, being heterogeneous, generally gives polyethylene featuring a broad mol. wt. distribution. In an effort to exert greater control over the properties of the polymer yielded, we have been investigating single-sited chromium catalysts, both in homogeneous soln. and as supported species, for olefin polymn. Reported here will be the results of our investigations, and the advantages and disadvantages of this approach relative to a purely heterogeneous one will be discussed.

~0 Citings

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## 18. Effect of Mo-modification over **Phillips** $\text{CrOx/SiO}_2$ **catalyst** for ethylene polymerization

By Ma, Yue; Cheng, Ruihua; Li, Jiajun; Zhong, Lei; Liu, Zhen; He, Xuelian; Liu, Boping

From [Journal of Organometallic Chemistry \(2015\), 791, 311-321](#). Language: English, Database: CAPLUS, DOI:10.1016/j.jorganchem.2015.05.058

**Phillips**  $\text{CrO}_x/\text{SiO}_2$  **catalyst** is an important **catalyst** for industrial prodn. of polyethylene. In this work, a Mo-modified **Phillips catalyst** for ethylene polymn. (defined as  $\text{CrMo/Si}$ ) was developed. The characterizations of the **Phillips catalyst** (defined as  $\text{Cr/Si}$ ) and the  $\text{CrMo/Si}$  **catalyst** by temp. programmed redn. (TPR) and XPS showed an obvious interaction between the chromium and molybdenum components on the silica support. The ethylene polymn. performances at different conditions, in terms of  $\text{H}_2$  responds, polymn. temps., and the copolymn. with 1-hexene were systematically investigated. Although the polymn. activity of the  $\text{CrMo/Si}$  **catalyst** was lower, the copolymer presented a higher mol. wt. (MW) and a broader mol. wt. distribution (MWD). The Mo-modified **Phillips catalyst** ( $\text{CrMo/Si}$ ) exhibited 67% higher 1-hexene incorporation ability as detd. by  $^{13}\text{C}$  NMR. Moreover, the short chain branch distribution (SCBD) of the copolymer obtained via the  $\text{CrMo/Si}$  **catalyst** was also improved as confirmed by temp. rising elution fractionation (TREF) cross successive self-nucleation and annealing (SSA) methods. The results of TREF and SSA showed that the amt. of short chain branches for the copolymer was increased in the high MW part, which would benefit for the long term mech. property of polyethylene.

~0 Citings

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## 19. Ultra-high molecular weight polyethylene compositions and molded articles therewith

By Inatomi, Takashi; Abe, Shigehiko

From [Jpn. Kokai Tokkyo Koho \(2015\)](#), [JP 2015140369 A 20150803](#), Language: Japanese, Database: CAPLUS

Provided is a ultra-high mol. wt. polyethylene compn. and molded article having excellent heat resistance, high moldability, and mech. strength, comprising (A) 100 parts ultra-high mol. wt. polyethylene having intrinsic viscosity of 7-35 dL/g when melt-stretched at 150° at break stress (MTS) of  $\leq 1$  MPa and (B) 5-900 parts ultra-high mol. wt. polyethylene having intrinsic viscosity of 15-60 dL/g, when melt-stretched at 150° at break stress of at least 2 MPa.

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## 20. The effect of the electronic nature of spectator ligands in the C-H bond activation of ethylene by Cr(III) silicates: an ab initio study

By Nunez-Zarur, Francisco; Comas-Vives, Aleix

From [Chimia \(2015\)](#), [69\(4\)](#), 225-229. Language: English, Database: CAPLUS, DOI:10.2533/chimia.2015.225

The **Phillips catalyst**, chromium oxides supported on silica, is one of the most widely used catalysts for the industrial prodn. of polyethylene. We recently synthesized a well-defined mononuclear Cr(III) silicate as active site model of the **Phillips catalyst**. The catalytic activity of this well-defined **catalyst** was similar to the industrial **Phillips catalyst**. We proposed that C-H bond activation of ethylene over a Cr-O bond initiates polymn. in this Cr(III) **catalyst**. Our results also showed that the presence of a second ethylene olefin in the coordination sphere of Cr decreases the intrinsic energy barrier of the C-H activation of ethylene. In order to understand the effect of this addnl. ligand in the C-H activation of ethylene by the Cr(III) **catalyst**, we evaluated the energetics of this step with different spectator ligands ( $C_2H_4$ ,  $C_2F_4$ ,  $N_2$  and CO) coordinated to the Cr center. The Charge Decomn. Anal. of the bonding interactions between the Cr(III) **catalyst** and the ligands showed that the intrinsic energy barrier for the C-H activation of ethylene decreases with the increasing electron-donor properties of the spectator ligand.

~0 Citings

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## 21. A molecular approach to well-defined metal sites supported on oxides with oxidation state and nuclearity control

By Delley, Murielle F.

From [Chimia \(2015\)](#), [69\(4\)](#), 168-171. Language: English, Database: CAPLUS, DOI:10.2533/chimia.2015.168

A mol. understanding of the catalytically active site is essential to rationally develop metal-contg. heterogeneous catalysts. The controlled grafting of mol. precursors on pre-treated supports, often referred to as surface organometallic chem., is an approach to prep. well-defined heterogeneous catalysts with complex org. functionalities. However, many heterogeneous catalysts do not contain org. ligands coordinated to their active sites. To model such sites, the principles of surface organometallic chem. therefore have to be adapted. Here, we describe a method, which provides access to molecularly-defined metal sites supported on oxides, which do not contain org. functionalities and are uniform in oxidn. state and nuclearity. By consecutive grafting of suitable mol. precursors and controlled thermal treatment, we prepd. and characterized well-defined dinuclear Cr(II) and Cr(III) species and mononuclear Cr(III) species supported on silica. We also investigated the polymn. activity of these materials in view of the well-known ethylene polymn. **catalyst** based on  $CrO_x/SiO_2$ , the so-called **Phillips catalyst**. This study led to new insights on the catalytically active sites in ethylene polymn., which are based on Cr(III), not Cr(II).

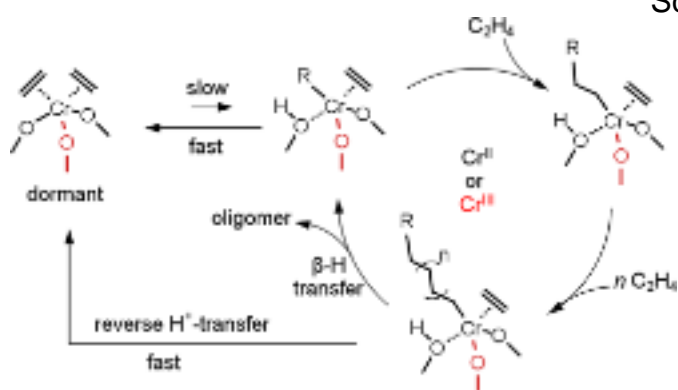
~1 Citing

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## 22. Computational Kinetic Discrimination of Ethylene Polymerization Mechanisms for the **Phillips (Cr/SiO<sub>2</sub>) Catalyst**

By Fong, Anthony; Yuan, Ye; Ivry, Sam L.; Scott, Susannah L.; Peters, Baron

From [ACS Catalysis \(2015\)](#), [5\(6\)](#), 3360-3374. Language: English, Database: CAPLUS, DOI:10.1021/acscatal.5b00016



The mechanism of ethylene polymn. by the widely used **Phillips catalyst** remains controversial. In this work, we compare initiation, propagation, and termination pathways computationally using small chromasiloxane cluster models for several previously proposed and new mechanisms. Where possible, we consider complete catalytic cycles and compare predicted kinetics, active site abundances, and polymer mol. wts. to known properties of the **Phillips catalyst**. Prohibitively high activation barriers for propagation rule out previously proposed chromacycle ring expansion and Green-Rooney (alternating alkylidene/chromacycle) mechanisms. A new oxachromacycle ring expansion mechanism has a plausible propagation barrier, but initiation is prohibitively slow. On sites with adjacent bridging hydroxyls, either  $\equiv\text{Si}(\text{OH})\text{Cr}^{\text{II}}\text{-alkyl}$  or  $\equiv\text{Si}(\text{OH})\text{Cr}^{\text{III}}\text{-alkyl}$ , initiated by proton transfer from ethylene, chain growth by a Cossee-Arlman-type mechanism is fast. However, the initiation step is uphill and extremely slow, so essentially all sites remain trapped in a dormant state. In addn., these sites make only oligomers because when all pathways are considered, termination is faster than propagation. A monoalkylchromium(III) site without an adjacent proton,  $(\equiv\text{SiO})_2\text{Cr-alkyl}$ , is viable as an active site for polymn., although its precise origin remains unknown.

~10 Citings

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### 23. Heterolytic Activation of C-H Bonds on Cr(III)-O Surface Sites Is a Key Step in Catalytic Polymerization of Ethylene and Dehydrogenation of Propane

By Conley, Matthew P.; Delley, Murielle F.; Nunez-Zarur, Francisco; Comas-Vives, Aleix; Coperet, Christophe  
From *Inorganic Chemistry* (2015), 54(11), 5065-5078. Language: English, Database: CAPLUS,  
DOI:10.1021/ic502696n



The authors describe the reactivity of well-defined chromium silicates toward ethylene and propane. The initial motivation for this study was to obtain a mol. understanding of the **Phillips catalyst**. The **Phillips catalyst** contains reduced chromium sites on silica and catalyzes the polymn. of ethylene without activators or a preformed Cr-C bond. Cr<sup>II</sup> sites are commonly proposed active sites in this **catalyst**. We synthesized and characterized well-defined chromium(II) silicates and found that these materials, slightly contaminated with a minor amt. of Cr<sup>III</sup> sites, have poor polymn. activity and few active sites. In contrast, chromium(III) silicates have 1 order of magnitude higher activity. The chromium(III) silicates initiate polymn. by the activation of a C-H bond of ethylene. D. functional theory anal. of this process showed that the C-H bond activation step is heterolytic and corresponds to a  $\sigma$ -bond metathesis type process. The same well-defined chromium(III) silicate catalyzes the dehydrogenation of propane at elevated temps. with activities similar to those of a related industrial chromium-based **catalyst**. This reaction also involves a key heterolytic C-H bond activation step similar to that described for ethylene but with a significantly higher energy barrier. The higher energy barrier is consistent with the higher pK<sub>a</sub> of the C-H bond in propane compared to the C-H bond in ethylene. In both cases, the rate-dtg. step is the heterolytic C-H bond activation.

~14 Citings

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### 24. Effect of surface hydroxylation on the catalytic activity of a Cr(II)/SiO<sub>2</sub> model system of **Phillips catalyst**

By Budnyk, Andriy; Damin, Alessandro; Groppo, Elena; Zecchina, Adriano; Bordiga, Silvia  
From *Journal of Catalysis* (2015), 324, 79-87. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2015.01.016



Cr/SiO<sub>2</sub> systems (0.1 wt% of Cr) in the form of high surface area glasses have been synthesized. After proper activation in the 823-1023 K range, they transformed to Cr(VI)/SiO<sub>2</sub> and then to Cr(II)/SiO<sub>2</sub> due to CO redn. (performed at 623 K). Subsequently, C<sub>2</sub>H<sub>4</sub> polymn. activity on these samples has been followed. Surprisingly, ethylene polymn. proceeds faster on samples obtained at 823 K, those ones coming from activation at 1023 K resulting less performing. UV-Vis and FT-IR spectroscopies revealed that the progressive increase of activation temp. leads to even more defined and protruding Cr(II) species at highly de-hydroxylated silica surface: this opens new questions on features of active sites and on the role of silica in prepg. such species. Finally, the obtained exptl. data have been used as refs. to validate models and methods adopted to simulate the Cr(II)/SiO<sub>2</sub> system, foreseeing to further investigation of the reactivity of Cr(II) toward ethylene.

~2 Citings

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## 25. High-resolution XPS and DFT investigations into Al-modified Phillips CrOx/SiO<sub>2</sub> catalysts

By Ma, Yue; Wang, Lisong; Liu, Zhen; Cheng, Ruihua; Zhong, Lei; Yang, Yun; He, Xuelian; Fang, Yuwei; Terano, Minoru; Liu, Boping

From [Journal of Molecular Catalysis A: Chemical](#) (2015), 401, 1-12. Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2015.01.020

The effects of Al-modification on Phillips catalysts were studied by high-resoln. XPS and the performance in ethylene polymn. reactions. D. functional theory (DFT) method was used to achieve a deeper mechanistic understanding. The decreased Cr 2p binding energies (BE), related with an increase in electron d. of Cr by Al-modification, were confirmed by the DFT calcn. The ethylene polymn. activity over the Al-modified Phillips catalyst was increased. The mol. wt. (MW) of polymer was decreased with the expansion of mol. wt. distribution (MWD) to low MW side, which was in agreement with the decreased energy barrier difference between the chain transfer and chain propagation in DFT calcn. The initiation step undergoing a metallacycle reaction pathway was found through a spin crossover from the quintet energy surface via a min. energy crossing point (MECP) to the triplet energy surface. Modeling results indicated that the promotion effect on polymn. activity from Al-modification for Phillips catalyst was mainly originated from the chain initiation reaction with lowered energy barrier for Al-modified Cr active sites. Improved environmental stress-crack resistance (ESCR) of polymer derived from the Al-modified catalyst could be expected from the less short chain branches (SCBs) distribution in the low MW side.

~4 Citings

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## 26. Phillips Cr/Silica Catalyst for Ethylene Polymerization

By Cheng, Ruihua; Liu, Zhen; Zhong, Lei; He, Xuelian; Qiu, Pengyuan; Terano, Minoru; Eisen, Moris S.; Scott, Susannah L.; Liu, Boping

From [Advances in Polymer Science](#) (2013), 257(Polyolefins: 50 Years after Ziegler and Natta I), 135-202. Language: English, Database: CAPLUS, DOI:10.1007/12\_2013\_222

A review. The Phillips Cr/silica catalyst, discovered by Hogan and Banks at the Phillips Petroleum Company in the early 1950s, is one of the most important industrial catalysts for polyethylene prodn. In contrast to its great com. success during the past half-century, academic progress regarding a basic understanding of the nature of the active sites and polymn. mechanisms is lagging far behind. During the last decade, increasing research efforts have been performed on the Phillips catalyst through various approaches, including spectroscopic methods, polymn. kinetics, heterogeneous model catalysts, homogeneous model catalysts, and mol. modeling. Much deeper mechanistic understanding, together with successive catalyst innovations through modifications of the Phillips catalyst, has been achieved.

~8 Citings

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## 27. Active sites and ethylene polymerization mechanisms of Phillips catalyst

By Zhong, Lei

From [No Corporate Source data available](#) (2013), 127 pp.. Language: Chinese, Database: CAPLUS

~0 Citings

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**28. Recent progress on molecular modeling of ethylene polymerization/oligomerization catalyzed by chromium-based catalysts**

By Liu, Zhen; Cheng, Ruihua; He, Xuelian; Tian, Zhou; Liu, Boping

From [Huaxue Fanying Gongcheng Yu Gongyi](#) (2014), 30(3), 218-228. Language: Chinese, Database: CAPLUS

**Phillips** chromium-based catalysts are widely used in industrial prodn. of polyethylene and  $\alpha$ -olefins through ethylene selective oligomerization. Recently, mol. modeling has been playing more and more important role in understanding the mechanism of ethylene polymn. and selective trimerization. From this point of view, the active site transformation from polymn. to metathesis during the induction period of the **Phillips catalyst**, the effect of Ti-modification on the **Phillips catalyst**, the transformation from ethylene polymn. to selective trimerization of the Cr(III) 2-EH/PIBAO/DME system, and the effect of deprotonation and Cr oxidn. states in the Cr-SNS system on the ethylene selective trimerization were reviewed. A much profound mechanistic understanding has been achieved through combination of mol. modeling with expts.

~0 Citings

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**29. Ethylene polymers with good durability, moldability, and short crystallization time, their moldings, and pipes and joints comprising them**

By Hiramoto, Tomoki; Fukuda, Masaki; Monoi, Hisashi; Kuzuha, Yuichi; Yamamoto, Kazuhiro; Fukuda, Tetsuro

From [Jpn. Kokai Tokkyo Koho](#) (2014), JP 2014208770 A 20141106, Language: Japanese, Database: CAPLUS

The ethylene polymers show high-load MFR (HLMFR; 190°, 21.6 kg load) 8-30 g/10 min, d. 0.947-0.960 g/cm<sup>3</sup>, breaking time in full-notch creep test (FNCT; 80°, 5 MPa) ≥300 h, peak-top time in isothermal crystn. at 121.5° (Tp; by DSC) ≤300 s, flexural modulus at 23° ≥950 MPa, and melt tension at 190°(MT) ≥100 mN. Thus, a compn. comprising polyethylene prepd. using Ziegler **catalyst** 60, polyethylene prepd. using metallocene **catalyst** 35, and polyethylene prepd. using **Phillips catalyst** 5% showed HLMFR 15 g/10 min, d. 0.952 g/cm<sup>3</sup>, flexural modulus 1200 MPa, Tp 210 s, FNCT 370 h, and MT 110 mN. A pipe comprising the compn. showed no surface scratch.

~1 Citing

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**30. A practical method of neutralizing Cr(VI) in **Phillips** polymerization catalysts**

By Collins, Kathy S.; McDaniel, Max P.

From [ACS Symposium Series](#) (2014), 1163(Academia and Industrial Pilot Plant Operations and Safety), 73-83.

Language: English, Database: CAPLUS, DOI:10.1021/bk-2014-1163.ch007

A review. The **Phillips** Cr/silica **catalyst**, which has great worldwide industrial importance, also involves Cr(VI) at one stage in its prepn. Consequently workers must be protected from exposure and strict decontamination procedures are required. In this paper various ways of neutralizing the Cr(VI) in the **catalyst** are evaluated with regard to efficiency of redn., cost and other practical considerations. One reducing agent seems esp. well suited to this application, ascorbate (vitamin C). A method of detection of ppm levels of hexavalent chromium on work surfaces is also discussed.

~0 Citings

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**31. Effect of polymerization **catalyst** technology on the melt processing stability of polyethylenes. Part 3: Additives blends performance**

By Sanchez, Karmele del Teso; Allen, Norman S.; Liauw, Christopher M.; Edge, Michelle

From [Journal of Vinyl and Additive Technology](#) (2016), 22(2), 117-127. Language: English, Database: CAPLUS,

DOI:10.1002/vnl.21421

This article considers the interaction between additives that occur during the stabilization process. The simultaneous effects of the additives and assocd. interactions on melt processing stability and processing discoloration were of particular interest. Melt stability is an important factor to consider because phys. changes in the processed polymer can occur during the compounding and fabrication steps. Furthermore, discoloration is one of the most important problems affecting com. polymers. Most discoloration manifests itself as yellowing, esp. in the case of polyolefins. Although yellowing can often be assocd. with degrdn. processes caused by various agents, such as light or heat, this is not always the case; yellowing can also be due to the interaction of additives in the stabilizer packages. Blends of primary antioxidants (AOs), secondary AOs, and hindered amine light stabilizers have been studied with the intention of further improving stabilization performance together with cost redn. of the stabilized polymer. Although synergism between AOs and a stabilizer is fairly common, antagonism was also obsd. in terms of melt flow protection and in color stability in some of the AOs tested. The effects of a range of thermal and light stabilizers on the melt stability (investigated via multiple pass extrusion) and color stability of three different polyethylenes (PEs) were examd. The PEs varied in terms of the catalyst system used to synthesize the polymers and included a high-d. polyethylene (HDPE) produced by using a chromium-based Phillips catalyst and two linear low-d. polyethylenes (LLDPEs) produced via chromium-based metallocene and titanium-based Ziegler-Natta catalysts. The apparent lack of influence of polymn. catalyst system on the mode of stabilizer interaction should lead to the reassessment of stabilizer formulation strategies in relation to PE type/catalyst system and assocd. com./economic considerations.

~0 Citings

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### 32. Proton transfers are key elementary steps in ethylene polymerization on isolated chromium(III) silicates

By Delley, Murielle F.; Nunez-Zarur, Francisco; Conley, Matthew P.; Comas-Vives, Aleix; Siddiqi, Georges; Norsic, Sebastien; Monteil, Vincent; Safonova, Olga V.; Coperet, Christophe

From [Proceedings of the National Academy of Sciences of the United States of America](#) (2014), 111(32), 11624-11629. Language: English, Database: CAPLUS, DOI:10.1073/pnas.1405314111

Mononuclear Cr(III) surface sites were synthesized from grafting [Cr(OSi(OtBu)<sub>3</sub>)<sub>3</sub>(tetrahydrofurano)<sub>2</sub>] on silica partially dehydroxylated at 700 °C, followed by a thermal treatment under vacuum, and characterized by IR, UV-visible, ESR, and X-ray absorption spectroscopy (XAS). These sites are highly active in ethylene polymn. to yield polyethylene with a broad mol. wt. distribution, similar to that typically obtained from the Phillips catalyst. CO binding, EPR spectroscopy, and poisoning studies indicate that two different types of Cr(III) sites are present on the surface, one of which is active in polymn. D. functional theory (DFT) calcns. using cluster models show that active sites are tricoordinated Cr(III) centers and that the presence of an addnl. siloxane bridge coordinated to Cr leads to inactive species. From IR spectroscopy and DFT calcns., these tricoordinated Cr(III) sites initiate and regulate the polymer chain length via unique proton transfer steps in polymn. catalysis.

~29 Citings

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### 33. Chromium catalysts for ethylene polymerization and oligomerization

By Liu, Zhen; He, Xuelian; Cheng, Ruihua; Eisen, Moris S.; Terano, Minoru; Scott, Susannah L.; Liu, Boping

From [Advances in Chemical Engineering](#) (2014), 44(Catalysis and Kinetics), 127-191. Language: English, Database: CAPLUS, DOI:10.1016/B978-0-12-419974-3.00003-8

A review. Chromium-based catalysts are the most important ethylene polymn. and oligomerization catalysts widely applied for industrial prodn. of polyethylene and 1-hexene. Phillips chromium catalyst is a well-known heterogeneous catalyst for com. prodn. of HDPE products, which accounts for more than 40% of world prodn. annually. The Chevron-Phillips Cr-based homogeneous catalyst system is the first commercialized catalyst for the prodn. of 1-hexene through selective ethylene oligomerization. Although a great success with these Cr-based catalysts has been achieved in industrial applications, there are still many debates in the academic field concerning the precise structure of active chromium species, the oxidn. states of chromium center, the effects of cocatalysts/ligands and the catalytic mechanisms. During the last decades, a step-forward mechanistic understanding has been achieved through extensive and successive investigations on these Cr-based catalysts for ethylene polymn./oligomerization. In addn., the progress in mechanistic understanding on alkyne cyclotrimerization by the same Phillips catalyst and ethylene polymn. over Mo-based catalyst are also covered. The later might be served as an alternative green catalyst for the industrial prodn. of polyethylene.

~5 Citings

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### 34. Polymerization on CO-Reduced Phillips Catalyst initiates through the C-H bond Activation of Ethylene on Cr-O Sites

By Delley, Murielle F.; Conley, Matthew P.; Coperet, Christophe  
From [Catalysis Letters](#) (2014), 144(5), 805-808. Language: English, Database: CAPLUS, DOI:10.1007/s10562-014-1238-0

Abstr.: Investigation of the polymn. of ethylene on CO-reduced **Phillips catalyst** (1 wt% chromium) by IR spectroscopy reveals the presence of new OH bands. In particular, an OH-band appears at 3,605 cm<sup>-1</sup>, consistent with the interaction of the SiOH group with an adjacent Lewis acidic chromium center, Si-(μ-OH)-Cr. Polymn. with d<sub>4</sub>-ethylene leads to the formation of the isotopically shifted band at 2,580 cm<sup>-1</sup>, consistent with heterolytic C-H activation of ethylene over a Cr-O bond to generate the first Cr-C bond in ethylene polymn. with **Phillips catalyst**, as recently obsd. on well-defined Cr(III) silicates.

~14 Citings

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### 35. Well-defined chromium silicates as efficient ethylene polymerization catalysts in the absence of co-catalyst: A clue in the **Phillips catalyst**

By Conley, Matthew P.; Delley, Murielle; Siddiqui, Georges; Lapadula, Giuseppe; Norsic, Sebastien; Monteil, Vincent; Safonova, Olga V.; Coperet, Christophe  
From [Abstracts of Papers, 247th ACS National Meeting & Exposition, Dallas, TX, United States, March 16-20, 2014](#) (2014), INOR-452. Language: English, Database: CAPLUS

The **Phillips catalyst**, which contains chromium dispersed on silica, accounts for 40 - 50 % of global high d. polyethylene (PE) prodn. The active catalytic sites of the **Phillips catalyst** remains unknown, though X-ray Absorption Spectroscopy shows that Cr(II) species are formed, inferring that they are responsible for catalysis. We grafted [Cr(OSi(OtBu)<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and thermally removed the org. ligands to generate well-defined silica supported dimeric Cr(II) species, which are converted into Cr(III) silicates by treatment with N<sub>2</sub>O according to XAS and model mol. studies. While the Cr(II) species is hardly active in ethylene polymn., the Cr(III) species exhibits activities exceeding those of the **Phillips catalyst**, though the PE produced by these two materials is very similar in terms of mol. wt. and dispersity indicating similar active sites. The mononuclear Cr(III) analogs can be prepd. from [Cr(OSi(OtBu)<sub>3</sub>)<sub>3</sub>] via the same approach, and it also displays high activity in the polymn. of ethylene. These results lay the foundation to design new supported Cr(III) ethylene polymn. catalysts.

~0 Citings

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### 36. Polymerization of Ethylene by Silica-Supported Dinuclear CrIII Sites through an Initiation Step Involving C-H Bond Activation

By Conley, Matthew P.; Delley, Murielle F.; Siddiqui, Georges; Lapadula, Giuseppe; Norsic, Sebastien; Monteil, Vincent; Safonova, Olga V.; Coperet, Christophe  
From [Angewandte Chemie, International Edition](#) (2014), 53(7), 872-1876. Language: English, Database: CAPLUS, DOI:10.1002/anie.201308983

The insertion of an olefin into a preformed metal-carbon bond is a common mechanism for transition-metal-catalyzed olefin polymn. However, in one important industrial **catalyst**, the **Phillips catalyst**, a metal-carbon bond is not present in the precatalyst. The **Phillips catalyst**, CrO<sub>3</sub> dispersed on silica, polymerizes ethylene without an activator. Despite 60 years of intensive research, the active sites and the way the first Cr-C bond is formed remain unknown. We synthesized well-defined dinuclear Cr<sup>II</sup> and Cr<sup>III</sup> sites on silica. Whereas the Cr<sup>II</sup> material was a poor polymn. **catalyst**, the Cr<sup>III</sup> material was active. Poisoning studies showed that about 65 % of the Cr<sup>III</sup> sites were active, a far higher proportion than typically obsd. for the **Phillips catalyst**. Examn. of the spent **catalyst** and isotope labeling expts. showed the formation of a Si-(μ-OH)-Cr<sup>III</sup> species, consistent with an initiation mechanism involving the heterolytic activation of ethylene at Cr<sup>III</sup>-O bonds.

~14 Citings

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### 37. The Effect of Hydrosilanes on the Active Sites of the **Phillips Catalyst**: The Secret for In Situ α-Olefin Generation

By Barzan, Caterina; Gianolio, Diego; Groppo, Elena; Lamberti, Carlo; Monteil, Vincent; Quadrelli, Elsje Alessandra; Bordiga, Silvia  
From [Chemistry - A European Journal](#) (2013), 19(51), 17277-17282. Language: English, Database: CAPLUS, DOI:10.1002/chem.201303156



Despite com. and fundamental interest in the hydrosilane-modified **Phillips** catalysts presented above, no direct observation of the modified catalytic sites was reported so far. A mol.-level spectroscopic study of a hydrosilane-modified  $\text{CrII/SiO}_2$  **catalyst** active in LLDPE prodn. is presented. The data shown are related to triethylsilane (TES) as a modifying agent, but other hydrosilane compds. have shown similar modifications, both in terms of polyethylene product and of the chromium sites.

#### ~8 Citings

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### 38. Manufacture and application of metal oxide **catalyst** with double active centers loaded for polymerization of ethylene

By Cheng, Ruihua; Liu, Boping; Xue, Xin; He, Yun; Dong, Xuan; He, Xuelian; Liu, Zhen; Liu, Weiwei; Wang, Lisong; Sun, Qiaoqiao

From *PCT Int. Appl.* (2013), WO 2013155982 A1 20131024, Language: Chinese, Database: CAPLUS

The **catalyst** compn. comprises inorg. carrier and two supported active components, wherein the two active components comprise chromium oxide and vanadium oxide. The **catalyst** further comprises modifying component selecting from one of titanium dioxide and fluorine. The invention further provides a method for prepg. the **catalyst**: carrying a titanium or fluorine compd., vanadium salt and chromium salt on the inorg. carrier by a proportion, different sequences and methods, then roasting the carrier with high temp. to obtain the **catalyst**. The method may further comprise adding org. metallic cocatalyst to pre-reduce the **catalyst**. The supported metal-oxide double-active-center **catalyst** for ethylene polymn. of the invention is a **catalyst** which can produce polyethylene with high efficiency, and can be used to produce ethylene homopolymer or ethylene -alpha-olefin copolymer. The **catalyst** has the advantages of high catalytic activity, superior hydrogen regulation sensitivity, good copolymn. performance, and wide mol. wt. distribution of the polyethylene product, and so on. The title **catalyst** comprises inorg. carriers and two active components. The active components comprise chromium oxide and vanadium oxide. Method for manufg. the **catalyst** comprises the steps of: impregnating inorg. carriers with chromium salt and vanadium salt step by step or simultaneously, drying, and roasting with a high temp. The **catalyst** relates to a process for introducing vanadium active components to **Phillips** chromium-type **catalyst**. The **catalyst** can be used for manufg. homopolymer of ethylene or copolymers of ethylene and  $\alpha$ -alkenes, and has high efficiency and polymn. activity. Polyethylene product manufd. with the **catalyst** has wide distribution of mol. wt., good sensitivity to hydrogen regulation and copolymn. performance. The method does not need reconstruction of existing app. used for manufg. polyethylene with **Phillips catalyst**, and is convenient to apply.

#### ~0 Citings

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### 39. Study of the coordinative nature of alkylaluminum modified **Phillips** $\text{CrO}_x/\text{SiO}_2$ **catalyst** by multinuclei solid-state NMR

By Zhang, Qin-Hui; Yan, Fang; Xia, Wei; Liu, Chenguang

From *Petroleum Science* (2013), 10(4), 577-583. Language: English, Database: CAPLUS, DOI:10.1007/s12182-013-0309-y

Solid-state NMR spectroscopy was used to investigate the coordinative states of surface Al species on various alkylaluminum-modified **Phillips**  $\text{CrO}_x/\text{SiO}_2$  catalysts. The alkylaluminum-modified **Phillips**  $\text{CrO}_x/\text{SiO}_2$  catalysts were examd. via ethylene homopolymn.  $^1\text{H}$  and  $^{27}\text{Al}$  magic angle spinning (MAS) NMR (NMR) spectra clearly demonstrated that the existing states of surface Al species in alkylaluminum-modified catalysts strongly depended on the type of alkylaluminum cocatalyst, concn. of alkylaluminum and the calcination temp.  $^1\text{H}$  MAS NMR spectra of alkylaluminum-modified **Phillips**  $\text{CrO}_x/\text{SiO}_2$  catalysts, calcined at two different temps., exhibited similar trends in peak shift.  $^1\text{H}$  spectra showed that with an increase of Al/Cr ratio and calcination temp., the main peak shifted to high field, indicating that the dominant surface proton species changed from hydroxyl to ethoxyl and Et groups.  $^{27}\text{Al}$  MAS NMR spectra showed the presence of three different coordination states (6-, 5-, and 4-coordinated Al species) in the alkylaluminum-modified **Phillips** catalysts. In comparison of different alkylaluminum cocatalysts, it was found that the reactivity of alkylaluminum modified **Phillips catalyst** decreased in the order of TEA > DEAH > DEAE. The amt. of 4-coordinated Al species of **Phillips** catalysts modified by TEA, DEAE and DEAH also decreased in the order of TEA > DEAH > DEAE, indicating that the presence of 4-coordinated Al species is related to the polymn. activity.

#### ~0 Citings

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### 40. Heterogeneous catalysts based on chromium sites: synthesis, characterization and applications

By Moreno, Jovita; Carrero, Alicia; Aguado, Jose

From *Materials Science Research Journal* (2011), 5(2-3), 285-297. Language: English, Database: CAPLUS

A review. The incorporation of chromium species on different catalytic supports has been widely described for developing numerous kinds of heterogeneous catalysts. Thus, chromium oxide supported on silica is the most famous **Phillips catalyst** for the ethylene polymn. at relatively low pressures. As well, chromium species supported on other inorg. carriers such as alumina, zirconia or several zeolites have shown excellent activity in dehydrogenation of alkanes, oxidn. and isomerization reactions, etc. This high versatility for catalytic applications comes from the wide spectrum of oxidn. states, coordination environments and d.p. that chromium species may present when they interact with the surface of the support. In this sense, numerous authors have focused their investigations on the elucidation of the chromium mol. structure existing on the heterogeneous catalysts surface in order to understand its relation with the catalytic activity. Spectroscopy techniques (UV-Vis, IR, Raman, XPS and EPR) and temp.-programmed redn. tests have been the most widely characterization techniques used for this purpose. Chromium species placed on the surface of a heterogeneous **catalyst** are deeply related to three variables: the chromium compd. used as precursor, the properties of the catalytic support (chem. compn., pore size and pore vol., surface area, etc.) and the method used for chromium incorporation. Regarding to the chromium precursor, trivalent oxide and nitrate are probably the most widely used due to their lower cost and toxicity. However, several applications require hexavalent precursors (highly toxic) or organometallic species (chromocene). Concerning to the catalytic supports, apart from zeolites and conventional amorphous materials (such as silica or alumina), mesostructured silicas discovered in early nineties featured by ordered mesopores with very narrow pore sizes distributions, have opened a new field for many researchers in order to synthesize novel and improved chromium catalysts. Finally, the incorporation of the chromium species on the support can be carried out by several ways. Incipient wetness impregnation is the most common method, but grafting, ion-exchange and chem. vapor deposition are other possibilities usually explored. Besides these post-synthetic methods, chromium species can be also introduced into silica framework by co-condensation processes leading to more stable and dispersed metal species. This contribution will conc. in reviewing the most relevant works existing about heterogeneous catalysts based on chromium sites emphasizing on the recent advances related to their synthesis, characterization and applications. Special attention will be focused to catalysts with significant industrial applications.

#### ~0 Citings

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#### 41. Cr-doped porous silica glass as a model material to describe **Phillips catalyst** properties

By Budnyk, Andriy; Damin, Alessandro; Barzan, Caterina; Groppo, Elena; Lamberti, Carlo; Bordiga, Silvia; Zecchina, Adriano

From [Journal of Catalysis](#) (2013), 308, 319-327. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2013.08.016

Cr-doped mesoporous silica glasses with Cr loading in the 0.01-0.5 wt% range were synthesized by one-pot acid catalyzed sol-gel route in form of monoliths. The absence of light scattering in the whole IR and UV-Vis-NIR region makes them ideal systems to investigate the optical and structural properties of grafted Cr sites by means of transmission spectroscopy, even in the highest dild. case, on which this contribution is mainly focused. For these reasons, Cr-doped porous silica monoliths are proposed here as models for the well-known **Phillips catalyst** for ethylene polymn. It is demonstrated that, even when chromium is extremely dild. (0.01 wt%), the electronic and structural properties of the Cr sites (both in the oxidized and reduced forms) are very similar to those of Cr sites on std., aerosil-based, **Phillips** catalysts (with a Cr content of 0.5 and 1 wt%): a distribution of Cr sites differing in the coordination ability is always present, irresp. of the Cr concn. and of the silica support. Nevertheless, the possibility to perform UV-Vis spectroscopy in transmission allowed to add unprecedented information on the relative intensity of bands due to charge transfer and d-d transitions. In situ ethylene polymn. was followed by means of both IR and UV-Vis spectroscopy in transmission on the sample having the lowest Cr loading (0.01 wt%), showing that the precursor species can be easily traced from the first steps of polymn. and that they are very similar to those obsd. on more concd. catalysts.

#### ~2 Citings

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#### 42. Effect of fluorination of silica support on initiation of ethylene polymerization during induction period over **Phillips catalyst**

By Zhong, Lei; Liu, Zhen; Cheng, Ruihua; He, Xuelian; Liu, Boping

From [Huagong Xuebao \(Chinese Edition\)](#) (2013), 64(2), 539-546. Language: Chinese, Database: CAPLUS, DOI:10.3969/j.issn.0438-1157.2013.02.018

In spite of great importance of **Phillips**  $\text{CrO}_x/\text{SiO}_2$  **catalyst** for com. polyethylene prodn. and long term research efforts, polymn. mechanism, esp. initiation mechanism, still remains unclear. The effect of surface fluorination of silica support on initiation of ethylene polymn. during induction period over **Phillips catalyst** adsorbed with different amts. of formaldehyde mols. was investigated with the d. functional theory. It was demonstrated that no reaction could be initiated over cluster models adsorbed with two formaldehyde mols. on account of steric hindrance. For cluster models adsorbed with one formaldehyde mol., ethylene dimerization to 1-butene and metathesis to propylene took place via chromacyclopentane intermediate, and fluorination of silica support showed minor influence on both reactions. After a complete desorption of formaldehyde mols., further ring expansion to chromacycloheptane occurred and surface fluorination of silica support showed improvement on this process. Fluorination of silica support was unfavorable to ring-opening of chromacycloheptane to give 1-hexene. It was also demonstrated that fluorination showed pos. effect on chain propagation over models of  $\text{Cr}^{\text{III}}$ -alkyl active sites during ethylene polymn.

~0 Citings

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#### 43. Development of a Hetero-Bimetallic **Phillips-Type Catalyst** for Ethylene Polymerization

By Zeng, Yanning; Matta, Akanksha; Dwivedi, Sumant; Taniike, Toshiaki; Terano, Minoru  
From [Macromolecular Reaction Engineering \(2013\), 7\(12\), 668-673](#). Language: English, Database: CAPLUS,  
DOI:10.1002/mren.201300119

In order to improve the ethylene polymn. activity and branching ability of **Phillips** catalysts, various bimetallic catalysts were synthesized on the basis of co-impregnation of chromium and second metal salts. The activity and branching ability of the catalysts were enhanced by the introduction of zirconium, zinc, and vanadium, while deteriorated by the introduction of molybdenum and tungsten. On the other hand, the structure of metal salt precursors did not greatly affect the catalytic performances. XPS clarified a tendency that second metal with lower electronegativity decreased the electron d. on chromium species, resulting in higher polymn. activity of the bimetallic catalysts plausibly due to enhanced ethylene activation. On the other hand, the branching ability of the **catalyst** improved as the **catalyst** activity increased due to more facile formation of  $\alpha$ -olefin co-monomer.

~2 Citings

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#### 44. Manufacture and application of metal oxide **catalyst** with double active centers loaded for polymerization of ethylene

By Cheng, Ruihua; Xue, Xin; Dong, Xuan; He, Yun; He, Xuelian; Liu, Zhen; Liu, Baiping  
From [Faming Zhuanli Shenqing \(2013\), CN 103145897 A 20130612](#), Language: Chinese, Database: CAPLUS

The title **catalyst** comprises inorg. carriers and two active components. The active components comprise chromium oxide and vanadium oxide. Method for manufg. the **catalyst** comprises the steps of: impregnating inorg. carriers with chromium salt and vanadium salt step by step or simultaneously, drying, and roasting with a high temp. The **catalyst** relates to a process for introducing vanadium active components to **Phillips** chromium-type **catalyst**. The **catalyst** can be used for manufg. homopolymer of ethylene or copolymers of ethylene and  $\alpha$ -alkenes, and has high efficiency and polymn. activity. Polyethylene product manufd. with the **catalyst** has wide distribution of mol. wt., good sensitivity to hydrogen regulation and copolymn. performance. The method does not need reconstruction of existing app. used for manufg. polyethylene with **Phillips catalyst**, and is convenient to apply.

~0 Citings

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#### 45. Ethylene/1-Hexene Copolymerization with A Novel $\text{SiO}_2$ -Supported Inorganic and Organic Hybrid Chromium-based **Catalyst**

By Zhang, Shiliang; Cheng, Ruihua; Dong, Qi; He, Xuelian; Wang, Quntao; Tang, Yan; Yu, Yongling; Xie, Kan; Da, Jianwen; Terano, Minoru; et al  
From [Macromolecular Reaction Engineering \(2013\), 7\(6\), 254-266](#). Language: English, Database: CAPLUS,  
DOI:10.1002/mren.201200075

Ethylene/1-hexene copolymn. with a novel  $\text{SiO}_2$ -supported inorg. and org. hybrid Cr-based **catalyst** was studied. This **catalyst** was prepd. using the residual surface hydroxyl groups in **Phillips catalyst** to support bis(triphenylsilyl) chromate (BC) to get the merits from 2 important Cr-based catalysts inorg. **Phillips** and org. S-2 catalysts. The influences of addn. amt. of 1-hexene and BC were systematically studied. With increasing 1-hexene from 0 to 7 vol.%, the activity of HCat-2 **catalyst** showed a decreasing tendency. Its copolymer also showed the better short chain branches distribution through the temp. rising elution fractionation cross successive self-nucleation and annealing characterization.

## ~10 Citings

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**46. Chemical modification of silica support to improve the branching ability of Phillips catalyst**

By Dwivedi, Sumant; Gujral, Satnam Singh; Taniike, Toshiaki; Terano, Minoru  
From [Pure and Applied Chemistry \(2013\), 85\(3\), 533-541](#). Language: English, Database: CAPLUS, DOI:10.1351/PAC-CON-12-03-10

A variety of modified Phillips catalysts were synthesized by employing 3 kinds of chem. modifiers for silica support: (1) org. modification with silane coupling agents, (2) Lewis acidic modification with typical metal alkyl or alkoxide, and (3) modification with transition-metal alkoxide. The activity and branching ability of these catalysts were investigated for ethylene polymn. It was revealed that the chem. modification of silica support was a good methodol. for controlling the catalyst activity as well as the branching level in resultant polyethylene.

## ~0 Citings

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**47. Effect of Al-alkyl cocatalyst on ethylene polymerization behavior using silyl chromate (SC)/SiO<sub>2</sub> catalyst**

By Li, Liuzhong; Wu, Yuxiang; Dong, Qi; Hao, Aiyu; Cheng, Ruihua; Zhong, Lei; Liu, Boping  
From [Asia-Pacific Journal of Chemical Engineering \(2013\), 8\(4\), 539-546](#). Language: English, Database: CAPLUS, DOI:10.1002/apj.1692

Cr/SiO<sub>2</sub> catalysts are important industrial ethylene polymn. catalysts, mainly including Phillips catalyst (also called oxo chromium/SiO<sub>2</sub>) and silyl chromate/SiO<sub>2</sub> systems (named as SC/SiO<sub>2</sub>, also called UCC S-2 catalyst). Compared with Phillips catalyst, SC/SiO<sub>2</sub> catalyst is not fully investigated. In this work, SC/SiO<sub>2</sub> catalyst was prepd., and triethylaluminum or triisobutylaluminum was used as cocatalyst for ethylene homopolymn. The effects of cocatalysts on polymn. kinetics and polymer microstructure were investigated. It is found that the kinetic curves using SC/SiO<sub>2</sub> catalyst in the presence of triethylaluminum or triisobutylaluminum seem to be a hybrid type composed of two types of basic polymn. kinetics: one is a fast built-up and fast decay type, and the other is a slow built-up and slow decay type, which indicates the existence of two types of polymn. active sites. Plausible mechanisms of the formation and transformation of active sites were proposed to rationalize the unique polymn. behavior. © 2012 Curtin University of Technol. and John Wiley & Sons, Ltd.

## ~1 Citing

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**48. Vanadium-Modified Bimetallic Phillips Catalyst With High Branching Ability for Ethylene Polymerization**

By Matta, Akanksha; Zeng, Yanning; Taniike, Toshiaki; Terano, Minoru  
From [Macromolecular Reaction Engineering \(2012\), 6\(8\), 346-350](#). Language: English, Database: CAPLUS, DOI:10.1002/mren.201200015

In order to improve the branching ability of Phillips catalyst for ethylene polymn., a new bimetallic Phillips catalyst was developed. In this work, a series of vanadium-modified Phillips catalyst were prepd. through co-impregnation by varying the pH of the impregnation soln., the vanadium loading and the vanadium precursors. A method to prep. bimetallic Phillips catalyst having good catalytic performance was proposed. Catalyst characterization by diffuse reflectance UV-Vis and x-ray photoelectron spectroscopies clarified the key role of specific interaction between chromium and vanadium components for the improvements in branching ability and catalyst activity.

## ~4 Citings

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**49. A novel SiO<sub>2</sub>-supported inorganic and organic hybrid chromium-based catalyst for ethylene polymerization**

By Zhang, Shiliang; Dong, Qi; Cheng, Ruihua; He, Xuelian; Wang, Quntao; Tang, Yan; Yu, Yongling; Xie, Kan; Da, Jianwen; Liu, Boping  
From [Journal of Molecular Catalysis A: Chemical \(2012\), 358, 10-22](#). Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2012.01.021



In this work, a novel SiO<sub>2</sub>-supported hybrid chromium-based catalyst for ethylene and ethylene/1-hexene polymn. was prepd. by using the residual surface hydroxyl groups in Phillips catalyst to further support bis(triphenylsilyl) chromate (BC) to get the merits from two important chromium-based catalysts namely inorg. Phillips and org. S-2 catalysts. By characterization of the catalysts, study of the polymn. behavior and the microstructures of polymers, several vital factors such as cocatalyst, the addn. amt. of BC, calcination temp., total chromium loading, polymn. temp., pressure and hydrogen were systematically studied. The proper addn. wt. amt. of BC was  $\text{Cr}_{\text{BC}} \leq 0.25 \text{ wt\%}$ . The suitable calcination temp. and total chromium loading were  $\leq 600 \text{ }^\circ\text{C}$  and  $\leq 0.5 \text{ wt\%}$ , resp. With increasing the relative addn. amt. of  $\text{Cr}_{\text{BC}}$  from 0 to 20, 50, 80 and 100 wt% (corresponding from Phillips to HCat-1, HCat-2, HCat-3 and S-2 catalysts), the copolymn. abilities of the above catalysts showed a decreasing tendency. By comparing different chromium catalysts, HCat-2 catalyst showed higher activity than S-2 catalyst and its polymer had higher av. mol. wt. (MW) than that obtained from Phillips catalyst. HCat-2 catalyst got well-balanced properties mainly including activity, MW of polymers and copolymn. ability.

~12 Citings

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## 50. Low temperature activation and reactivity of CO<sub>2</sub> over a Cr<sup>II</sup>-based heterogeneous catalyst: a spectroscopic study

By Groppo, Elena; Zecchina, Adriano; Barzan, Caterina; Vitillo, Jenny G.  
From [Physical Chemistry Chemical Physics](#) (2012), 14(18), 6531-6536. Language: English, Database: CAPLUS, DOI:10.1039/c2cp40524e

A new heterogeneous catalyst for CO<sub>2</sub> activation was identified in the Cr<sup>II</sup>/SiO<sub>2</sub> Phillips catalyst, one of the most important catalysts used industrially for olefin polymn. Interestingly, it was found that Cr<sup>II</sup>/SiO<sub>2</sub> strongly activates CO<sub>2</sub> already at room temp., making it available for chems. synthesis. A preliminary attempt in this direction was done by following the reaction of CO<sub>2</sub> with ethylene oxide at room temp. by means of FT-IR spectroscopy, which showed the formation of ethylene carbonate. Besides non-reductive CO<sub>2</sub> activation, Cr<sup>II</sup>/SiO<sub>2</sub> showed good performances in catalytic redn. of CO<sub>2</sub> to CO, when heated under mild conditions or irradiated with UV-Vis light. Both, in situ FT-IR and UV-Vis spectroscopy, were applied to highlight the redox process occurring at the Cr centers. These results open interesting perspectives to be developed in the field of CO<sub>2</sub> chem. fixation.

~0 Citings

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## 51. Active Site Transformation During the Induction Period of Ethylene Polymerization over the Phillips CrOx/SiO<sub>2</sub> Catalyst

By Zhong, Lei; Liu, Zhen; Cheng, Ruihua; Tang, Siyang; Qiu, Pengyuan; He, Xuelian; Terano, Minoru; Liu, Boping  
From [ChemCatChem](#) (2012), 4(6), 872-881. Language: English, Database: CAPLUS, DOI:10.1002/cctc.201100278

In spite of the great importance of the Phillips catalyst in com. polyethylene prodn. and long-term research efforts, the initiation mechanism of polymn. still remains unclear. The effect of formaldehyde desorption on the active site transformation during the induction period of the Phillips catalyst is studied over cluster models by using DFT. No reaction can be initiated over the cluster model coordinated with two formaldehyde mols., owing to steric hindrance and electronic donation. The first reaction over cluster models, on which either one or no formaldehyde mol. is adsorbed, follows the metallacyclic mechanism into chromacyclopentane. Subsequent dimerization to 1-butene and metathesis to propylene and ethylene are more favorable over the cluster model adsorbed with one formaldehyde mol. Only after a complete desorption of formaldehyde does further ring expansion to chromacycloheptane followed by 1-hexene formation become preferential. Spin state crossing from quintet diethylene-Cr<sup>II</sup> complex to triplet chromacyclopentane with a spin acceleration effect is revealed.

~12 Citings

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## 52. Unravelling the mechanism of polymerisation with the commercial Phillips catalyst

By McGuinness, D.; Davies, N.; Horne, J.; Ivanov, I.  
From [Pacifichem 2010, International Chemical Congress of Pacific Basin Societies, Honolulu, HI, United States, December 15-20, 2010](#) (2010), MACRO-118. Language: English, Database: CAPLUS

Around one-third of all polyethylene is produced using the Cr/silica **Phillips catalyst**, developed in the 1950s by Hogan and Banks [1], making this one of the worlds most important industrial catalysts for over half a century [2]. Despite the importance of this **catalyst**, it's mechanism of operation remains poorly understood. In a 1985 review of the **Phillips catalyst** [3], McDaniel described it as one of the most studied yet controversial systems ever, and stated that 'today we seem to be debating the same questions posed over thirty years ago, being no nearer to a common view.' A further two decades on, the mechanism of polymn. with this **catalyst** is still being debated [2,4]. There are three main proposals for the mechanism of chain growth with this **catalyst**; the Cossee-Arlman, Green-Rooney, and metallocycle mechanisms (below). Over the years evidence for all three proposals, and variants on these, has been presented [2], and a textbook mechanism for polymn. with this **catalyst** remains elusive. A criticism that has been levelled at past studies of the **Phillips catalyst** is that such investigations are often done under conditions which are quite removed from actual com. conditions, for instance at low temp. and at low ethylene pressure. In the present work we have therefore attempted to remain as close as possible to com. relevant conditions and catalysts. Herein we describe isotope labeling expts. which rule out two of the mechanisms shown below, and that are entirely consistent with the remaining proposal. (1) Hogan, J. P., J. Polym. Sci. A-1, 1970, 8, 2637 (2) Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. Chem. Rev. 2005, 105, 115. (3) McDaniel, M. P. Adv. Catal. 1985, 33, 47. (4) Theopold, K. H. Chemtech 1997, 27, 26.

~0 Citings

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### 53. Effects of polymerization **catalyst** technology on the melt processing stability of polyethylenes. part 2. single stabilizer performance

By del Teso Sanchez, Karmele; Allen, Norman S.; Liauw, Christopher M.; Edge, Michelle; Johnson, Brian; Catalina, Fernando; Corrales, Teresa  
From [Journal of Vinyl & Additive Technology](#) (2012), 18(1), 26-39. Language: English, Database: CAPLUS, DOI:10.1002/vnl.20288

The effects of a range of thermal and light stabilizers on the melt stability (studied via multiple pass extrusion) and color stability of three different polyethylenes (PEs) were examd. The PEs varied in terms of the **catalyst** system used to synthesize the polymers and included an HDPE produced by using a chromium-based **Phillips catalyst** and two LLDPEs produced via chromium-based metallocene and titanium-based Ziegler-Natta catalysts. The additive types included a range of phenolics of different functionality, phosphites, hindered piperidines, an hydroxylamine, and Vitamin E. The results obtained for the three PEs confirmed that primary antioxidants (AOs) such as highly hindered and less, hindered phenols or hydroxylamines promoted good melt stability but in some cases tended toward yellowing. The secondary AOs such as the phosphites or thioethers behaved in the opposite way; color suppression was good, but melt stabilization was poor. For different types of phenols (all with similar molar activity), reducing steric hindrance to the phenolic OH enhanced the tendency to form chromophoric groups and hence color led to better efficiency than high hindrance. Those phenol with higher molar activity (mol OH/kg AO) showed the best processing performance. J. VINYL ADDIT. TECHNOL., 2012. © 2012 Society of Plastics Engineers.

~0 Citings

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### 54. Ethylene polymerization on a SiH<sub>4</sub>-modified **Phillips catalyst**: detection of in situ produced $\alpha$ -olefins by operando FT-IR spectroscopy

By Barzan, Caterina; Groppo, Elena; Quadrelli, Elsie Alessandra; Monteil, Vincent; Bordiga, Silvia  
From [Physical Chemistry Chemical Physics](#) (2012), 14(7), 2239-2245. Language: English, Database: CAPLUS, DOI:10.1039/c2cp23269c

Ethylene polymn. on a model Cr(ii)/SiO<sub>2</sub> **Phillips catalyst** modified with gas phase SiH<sub>4</sub> leads to a waxy product contg. a bimodal MW distribution of  $\alpha$ -olefins ( $M_w < 3000 \text{ g mol}^{-1}$ ) and a highly branched polyethylene, LLDPE ( $M_w \approx 10^5 \text{ g mol}^{-1}$ ,  $T_m = 123^\circ$ ), contrary to the unmodified **catalyst** which gives a linear and more dense PE, HDPE ( $M_w = 86,000 \text{ g mol}^{-1}$  (PDI=7),  $T_m = 134^\circ$ ). Pressure and temp. resolved FT-IR spectroscopy under operando conditions ( $T = 130\text{-}230 \text{ K}$ ) allows us to detect  $\alpha$ -olefins, and in particular 1-hexene and 1-butene (characteristic IR absorption bands at 3581-3574, 1638 and 1598  $\text{cm}^{-1}$ ) as intermediate species before their incorporation in the polymer chains. The polymn. rate is estd., using time resolved FT-IR spectroscopy, to be 7 times higher on the SiH<sub>4</sub>-modified **Phillips catalyst** with respect to the unmodified one.

~15 Citings

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### 55. Size-exclusion chromatography coupled to multiangle light scattering detection of long-chain branching in polyethylene made with **Phillips catalyst**

By Yu, Youlu; Schwerdtfeger, Eric; McDaniel, Max

From *Journal of Polymer Science, Part A: Polymer Chemistry* (2012), 50(6), 1166-1173. Language: English, Database: CAPLUS, DOI:10.1002/pola.25877

Size-exclusion chromatog. coupled to multiangle light scattering (SEC-MALS) has been used to detect long-chain branching (LCB) in polyethylene (PE) from Cr/silica catalysts for the first time. The obsd. LCB response to several catalyst and reactor variables mostly confirms earlier conclusions drawn from rheol. measurements. However, SEC-MALS has also shed addnl. light on a few previously unanswered questions. Above all, SEC-MALS shows the placement of branching within the MW distribution, which was not previously known, and which may explain some of the unique molding behavior of Cr-derived PE. This new SEC-MALS data also provide insight into the mechanism of LCB formation, which is discussed. Like earlier studies based on rheol., this new study demonstrates that the commonly accepted view of macromer incorporation may be overly simplistic. Copyright 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem*, 2011.

~4 Citings

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## 56. Application of infrared spectroscopy in adsorption and catalysis. I

By Sarbak, Zenon

From *Wiadomosci Chemiczne* (2011), 65(5-6), 363-394. Language: Polish, Database: CAPLUS

The review presents some key results of IR investigations of adsorbents and catalysts, which were obtained in Lab. of Adsorption and Catalysis at Adam Mickiewicz University - conducted under the author guidance. After short introduction, review is divided into seven parts. In the first chapter, there was described an application of IR method devoted to examn. of structure of different types of zeolites, such as A, X, Y and mordenite as well as alumina and fly ashes and their modifications. Moreover, some results were presented on cobalt-molybdena catalysts supported on alumina. In the next chapter chemisorption of pyridine and t-butyl nitrile (TBN) mols. on the alumina and alumina modified with fluoride and sodium ions as well as Co(Ni)-Mo(W) catalysts supported on alumina were investigated. In the last case intensity of some spectra were correlated with catalytic activity for cumene cracking. Another set of expts. were devoted to transesterification on dealuminated mordenites contg. cations of alk. earths elements and correlation with IR results. In the next part of review, chemisorption of ethanol was presented. It was concluded, that during chemisorption of ethanol different surface species were produced on alumina, silica alumina and zeolites X and ZSM-5. In sep. chapter, it was considered oligomerization of different alkenes on Phillips catalyst using IR methods. In the last chapter, ways of chemisorption of dihydrobenzenes on cobalt-molybdena catalyst were examd. using IR reflectance spectra. It seems that above presented results based on IR examn. will help to better understand adsorbents and catalysts structure and their action during adsorption and catalytic reactions.

~0 Citings

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## 57. Elucidation of control factors of molecular weight distribution and branches in ethylene polymerization using phillips catalysts

By Tonosaki, Kiwamu; Tanhike, Toshiaki; Terano, Minoru

From *Kobunshi Ronbunshu* (2011), 68(5), 326-331. Language: Japanese, Database: CAPLUS, DOI:10.1295/koron.68.326

Comprehensive investigations based on exptl. and theor. approaches were undertaken to elucidate the control factors of branching and broad mol. wt. distribution (MWD) in polyethylene (PE) that was obtained using Phillips catalysts. It was found that the branch frequencies in PE are decided by the polymer yield, suggesting a branching mechanism by incorporation of in situ formed  $\alpha$ -olefins. Investigations on the effects of the chromium nuclearity using model catalysts proved a prominent enhancement in Me branching on dinuclear chromium species. On the other hand, the model catalysts produced PE with broad MWDs despite the uniform chromium nuclearity. Based on the results, the influence of the coordination environment of chromium, on the mol. wt. (MW) of PE was investigated by d. functional calcs. The MW of PE produced with monoalkyl-chromium(III) species is significantly sensitive to the coordination environment which is the origin of the broad MWD using Phillips catalysts.

~0 Citings

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## 58. Enhancing the Initial Rate of Polymerisation of the Reduced Phillips Catalyst by One Order of Magnitude

By Groppo, Elena; Damin, Alessandro; Otero Arean, Carlos; Zecchina, Adriano

From *Chemistry - A European Journal* (2011), 17(40), 11110-11114, S11110/1-S11110/5. Language: English, Database: CAPLUS, DOI:10.1002/chem.201101714

In summary, we have reported herein a procedure (based on controlled thermal treatment with N<sub>2</sub>O) that affords easy active-site engineering of the reduced **Phillips catalyst** leading to two novel results: (1) a large increase in the initial rate of polymn. of ethylene and (2) polymn. that readily proceeds at room temp., which could be highly relevant to the prodn. of some varieties of polyethylene. We think these are remarkable results that could lead to further studies on this highly interesting research field.

~16 Citings

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## 59. Structural investigation of Cr(II) sites in the **Phillips' CrOx/SiO<sub>2</sub> catalyst**

By Lee, Ming-Yung; Zhong, Lei; Liu, Boping; Scott, Susannah L.

From [Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011 \(2011\)](#), CATL-24. Language: English, Database: CAPLUS

The **Phillips'** (silica-supported chromium) **catalyst** is used to produce more than 40% of the world's high-d. polyethylene. Even after more than half a century of com. experience and published research, our understanding of the structure of the active-sites and the initiation mechanism for polymn. for this type of **catalyst** remains unclear. Well-defined, uniform Cr(II) sites can be prep'd. on a silica support via grafting of CrO<sub>2</sub>Cl<sub>2</sub> followed by heating at 300°C then redn. by CO. It has been reported that adsorbed CO and/or formaldehyde (from ethylene oxidn.) poisons the active sites. We have undertaken a d. functional theory study of the effect of formaldehyde adsorption on the active sites during the induction period of the **Phillips' catalyst**. When two formaldehyde mols. are adsorbed on a Cr(II) site, no reaction with ethylene takes place. The first reaction with ethylene over cluster models with or without one adsorbed formaldehyde mol. involves a metallacyclic mechanism, giving chromacyclopentanes. Subsequent dimerization to 1-butene and metathesis to propylene/ethylene are preferred over the cluster model with one formaldehyde mol. adsorbed. Only upon desorption of formaldehyde does further ring expansion to chromacycloheptane followed by 1-hexene formation become favored. These predictions about the active site structures and their partially and fully poisoned analogs were investigated exptl. using EXAFS at the Cr K-edge as well as in-situ IR spectroscopy.

~0 Citings

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## 60. Gas phase ethylene polymerization over SiO<sub>2</sub>-supported organosilyl chromate UCC S-2 **catalyst** using a high-speed stirred-autoclave reactor

By Li, Liuzhong; Hao, Aiyu; Cheng, Ruihua; Liu, Boping

From [Frontiers of Chemical Science and Engineering \(2011\)](#), 5(1), 89-95. Language: English, Database: CAPLUS, DOI:10.1007/s11705-010-0558-x

Although an important industrial **catalyst** for producing high d. polyethylene, the SiO<sub>2</sub>-supported organosilyl chromate UCC S-2 **catalyst** has not been fully investigated compared with the SiO<sub>2</sub>-supported oxo chromium **Phillips catalyst**. In this work, gas phase ethylene polymn. by S-2 catalysts (Cat-1, Cat-2, and Cat-3) was carried out in a high-speed stirred autoclave reactor. The effects of temp., time, and pressure on kinetics, activity, and product properties were studied. All kinetics were typical built-up types with slow decay. Compared to the simple phys. mixts. of Cat-1 and Cat-2, Cat-3 showed higher activity and its product had a broader mol. wt. distribution, indicating new active species induced during blending of Cat-1 and Cat-2 in n-hexane. The innovation by a simple **catalyst** technol. created a new application to meet market demands.

~0 Citings

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## 61. Polyethylene compositions suitable for high-speed molding for container covers

By Ibayashi, Kunihiro; Kagatani, Ippei; Hiramoto, Tomoki

From [Jpn. Kokai Tokkyo Koho \(2011\)](#), JP 2011052040 A 20110317, Language: Japanese, Database: CAPLUS



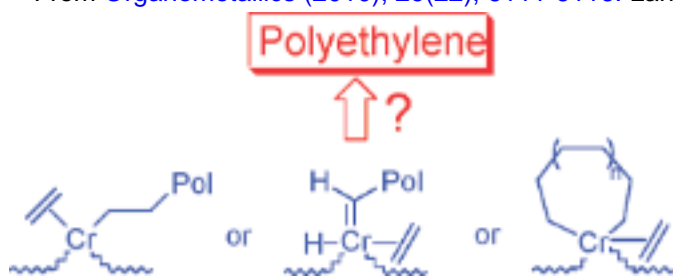
The title compns. comprise (A) 100 parts ethylene-based polymer compns. contg. (a)  $\geq 20$  to  $< 40\%$  Ziegler-catalyzed ethylene-based polymers having melt flow rate ( $190^\circ$ , 21.6 kg; HLMFR) 1-6 g/10 min, d. 0.930-0.945 g/cm<sup>3</sup> and (b)  $> 60$  to  $\leq 80\%$  Ziegler-catalyzed ethylene-based polymers having melt flow rate ( $190^\circ$ , 2.16 kg; MFR)  $\geq 200$  to  $< 400$  g/10 min and d.  $\geq 0.960$  g/cm<sup>3</sup> and (B) 4-40 parts Cr-catalyzed ethylene-based polymers having MFR  $\geq 0.1$  to  $< 0.4$  g/10 min and d. 0.945-0.960 g/cm<sup>3</sup> and satisfy (i) MFR 1-10 g/10 min, (ii) HLMFR 250-600 g/10 min, (iii) HLMFR/MFR = 60-140, and (iv) d. 0.960-0.970 g/cm<sup>3</sup>. Thus, 2-stage polymn. of ethylene and 1-butene and then ethylene gave an ethylene-based polymer compn. having MFR 8.5 g/10 min, melt flow rate ( $190^\circ$ , 11.1 kg; MLMFR) 170 g/10 min, and d. 0.963 g/cm<sup>3</sup>. The compn. was blended with ethylene-1-hexene copolymer that are prep'd. by using Cr-based **Phillips catalyst** and having MFR 0.25 g/10 min and d. 0.957 g/cm<sup>3</sup> and injection-molded to give test pieces showing MFR 4.4 g/10 min, HLMFR 450 g/10 min, d. 0.962 g/cm<sup>3</sup>, flexural modulus 1050 MPa, tensile yield strength 28 MPa, fixed strain (ESCR) 33 h, crystn. time 72 s, hydrocarbon volatile matter ( $130^\circ$ , 60 min) 28 ppm, and coeff. of static friction 0.20.

~1 Citing

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## 62. Unraveling the Mechanism of Polymerization with the **Phillips Catalyst**

By McGuinness, David S.; Davies, Noel W.; Horne, James; Ivanov, Ivan  
From *Organometallics* (2010), 29(22), 6111-6116. Language: English, Database: CAPLUS, DOI:10.1021/om100883n



The mechanism of polymer chain growth at the **Phillips catalyst** was studied, with the three prevailing mechanistic proposals, the Cossee-Arlman, Green-Rooney, and metallacycle mechanisms, considered. Through anal. of low mol. wt. oligomers/polymers formed during ethylene/ $\alpha$ -olefin copolymn. with labeled monomers, the isotopomer distribution is inconsistent with a metallacycle mechanism. Further anal. of polymer formed by copolymn. of labeled ethylene was used to rule out a Green-Rooney mechanism. The results support the notion of chain growth via a Cossee-Arlman process.

~17 Citings

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## 63. Experimental and theoretical studies on ethylene polymerization using SiO<sub>2</sub>-supported silyl chromate type catalysts prepared by a green method

By Li, Xiaofang; Cheng, Ruihua; Luo, Jun; Dong, Qi; He, Xuelian; Li, Liuzhong; Yu, Yongling; Da, Jianwen; Liu, Boping  
From *Journal of Molecular Catalysis A: Chemical* (2010), 330(1-2), 56-65. Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2010.07.002

SiO<sub>2</sub>-supported silyl chromate **catalyst** (UCC S-2 **catalyst**) is an important **catalyst** for the com. prodn. of polyethylene. Cann first reported a possible green synthesis route for the prepn. of S-2 **catalyst** through transformation from **Phillips catalyst** by addn. of triphenylsilanol (TPS) to avoid the use of toxic bis(triphenylsilyl) chromate (BC). In this work, this green synthesis route was further investigated by the combination of exptl. and theor. methods. The obtained **catalyst** was named as PS **catalyst** based on the incomplete conversion of **Phillips catalyst** to S-2 **catalyst**. Polymn. activity of PS1.5 **catalyst** was higher than that of S-2 **catalyst** with either TEA or MAO as cocatalyst. The existence of the simultaneously formed hydroxyl group and its coordination to the reduced Cr site was favorable to the PS **catalyst**, and this might attribute to the higher polymn. activity of PS **catalyst** than that of S-2 **catalyst**. A further modification of PS **catalyst** by a series of alkyl chlorosilane compds. showed that the role of the electron-withdrawing group only limited at a certain distance away from Cr active site. This preliminary study provided a solid basis for a further innovation of PS catalysts and final substitution of S-2 **catalyst** in com. processes.

~4 Citings

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## 64. High-resolution spectroscopy (XPS, 1H MAS solid-state NMR) and DFT investigations into Ti-modified **Phillips CrOx/SiO<sub>2</sub>** catalysts

By Cheng, Rui-Hua; Xu, Chen; Liu, Zhen; Dong, Qi; He, Xue-Lian; Fang, Yu-Wei; Terano, Minoru; Hu, Yatao; Pullukat, Thomas J.; Liu, Bo-Ping  
From *Journal of Catalysis* (2010), 273(2), 103-115. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2010.05.002

Ti-modified **Phillips catalyst** is a most important industrial **catalyst** widely used in ethylene polymn., but the mechanism still remains mysterious. In this work, Ti-modified **Phillips catalysts** were characterized by high-resoln. XPS and  $^1\text{H}$  magic-angle-spin solid-state NMR ( $^1\text{H}$  MAS solid-state NMR) combined with d. functional investigations into the effects of Ti-modification on promotion of polymn. activity and regulation of microstructures of the polymer chains. XPS data revealed Ti-modification caused increase in electron-deficiency and photo-stability of the surface chromate species.  $^1\text{H}$  NMR provided the first direct evidence of surface residual Ti-OH groups. Modeling results rationalized well the effects of Ti-modification on promotion of polymn. activity, extension of mol. wt. distribution (MWD) to lower MW region, improvement of the distribution of inserted co-monomer and enhancement of 2,1-insertion in regioselectivity of **Phillips catalysts**. It was the first time the Ti-modification on **Phillips catalysts** were theor. elucidated.

~20 Citings

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## 65. Method for transitioning between incompatible olefin polymerization **catalyst** systems

By Meier, Gerhardus; Mihan, Shahram

From [PCT Int. Appl. \(2010\), WO 2010072367 A1 20100701](#), Language: English, Database: CAPLUS

A method for transitioning from a Ziegler-Natta to a **Phillips catalyst** system for the olefin polymn. reaction in one reactor, preferably a gas phase reactor, is described. The method comprises the steps of (a) discontinuing a first olefin polymn. reaction performed in the presence of the Ziegler-Natta **catalyst** system; (b) performing a second olefin polymn. reaction in the presence of a further **catalyst** system comprising **catalyst** components (A) and (B) producing, resp., a first and a second polyolefin fraction, wherein the  $M_w$  of the first polyolefin fraction is less than the  $M_w$  of the second polyolefin fraction and the initial activity of **catalyst** component (A) exceeds the initial activity of **catalyst** component (B); and (c) performing a third olefin polymn. reaction the presence of the **Phillips catalyst** system. Thanks to this method, there is no need to empty the reactor after each olefin polymn. reaction, and the transitioning time needed to attain the desired quality of the polyolefin obtained in each olefin polymn. reaction subsequent to the first one is sufficiently short to permit a quick and reliable change of prodn.

~1 Citing

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## 66. Review of **Phillips chromium catalyst** for ethylene polymerization

By Mcdaniel, Max P.

Edited By: Hoff, Ray; Mathers, Robert T

From [Handbook of Transition Metal Polymerization Catalysts \(2010\), 291-446](#). Language: English, Database: CAPLUS, DOI:10.1002/9780470504437.ch10

A review on the complex chem. assocd. with the **Phillips catalyst** (silica-supported chromium oxide). It provides examples of how that chem. is controlled and exploited com. to produce a wide variety of ethylene polymer grades (HDPE, LDPE, some LLDPE). **Catalyst** prepn. as well as control of **catalyst** activity, mol. wt., and crystallinity, and other topics are discussed.

~0 Citings

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## 67. DFT and PIO study of the influences of Mo valance state and surface hydroxyl on supported-MoO<sub>x</sub> catalysts for ethylene polymerization

By Cao, Xiaochun; Cheng, Ruihua; Liu, Zhen; Wang, Lisong; Dong, Qi; He, Xuelian; Liu, Boping

From [Journal of Molecular Catalysis A: Chemical \(2010\), 321\(1-2\), 50-60](#). Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2010.01.018

**Phillips catalyst** ( $\text{CrO}_x/\text{SiO}_2$ ) is an important industrial **catalyst** for ethylene polymn., but the highly toxic chromium may contaminate the environment and do harm to human's health. Supported-MoO<sub>x</sub> **catalyst** with low toxicity has potential to replace **Phillips catalyst** if its catalytic performance could be improved. In this work, models of molybdenum active sites with different valence states (5+, 4+, 3+, 2+) supported on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , resp., were established to investigate the effects of the valence states and surface hydroxyl on the **catalyst** activity using the combination of d. functional theory (DFT) and paired interacting orbitals (PIO) methods. DFT results showed that supported  $\text{Mo}^{2+}$  center had the lowest energy barrier of ethylene insertion and thus possessed the highest activity for ethylene polymn. PIO method addnl. elucidated the orbital interaction and electron transformation between  $\text{Mo}^{2+}$  center and ethylene monomer. Hydroxyl on the support surface could poison the active center by coordination with Mo center. It had been demonstrated that pre-redn. of hexa-valent molybdenum into lower valence state +2 and elimination of surface hydroxyl groups of support were the key factors to obtain highly efficient ethylene polymn. **catalyst**. The mol. modeling results of this work provided theor. basis for further exptl. developments of green and highly efficient supported Mo-based polyethylene catalysts.

## ~13 Citings

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**68. Morphological modifications of Cr/SBA-15 and Cr/Al-SBA-15 ethylene polymerization catalysts: Influence on catalytic behaviour and polymer properties**

By Aguado, J.; Calleja, G.; Carrero, A.; Moreno, J.

From [Microporous and Mesoporous Materials](#) (2010), 131(1-3), 294-302. Language: English, Database: CAPLUS, DOI:10.1016/j.micromeso.2010.01.006

Mesostructured **Phillips** catalysts (Cr/SBA-15 and Cr/Al-SBA-15) with different morphologies were synthesized and tested in ethylene polymn. Morphol. properties of mesoporous supports were modified by changing some synthesis variables like stirring rate, concn. of silica source, mixt. acidity and the type of cosolvent mol. Obtained solids were calcined and characterized by N<sub>2</sub> adsorption-desorption, XRD, <sup>27</sup>Al NMR and SEM. By decreasing the stirring rate during the synthesis, the size and shape of SBA-15 particles changes from small fiber-like to larger irregular agglomerates. As well, a higher amt. of sphere-like particles were obtained by increasing TEOS/P123M ratio. On the contrary, for Al-SBA-15 material, agglomerated particles were obtained even at high stirring rate, but no sphere-like particles were obsd. by increasing the TEOS/P123M ratio. The increase of HCl/P123M ratio clearly modifies the SBA-15 particle morphol. but the structure becomes disordered. Cosolvent incorporation in the SBA-15 synthesis produces a swelling effect in the order trimethylbenzene > n-decane > toluene. Only the addn. of toluene affects SBA-15 morphol. from sphere-like to fiber-like particles. Chromium catalysts prepd. by impregnation of SBA-15 supports synthesized at lower stirring rates (50 rpm) present higher activity in ethylene polymn. and produce polymers with larger particle size. On the other hand, Cr/SBA-15 catalysts lead to polyethylenes with slightly lower mol. wt. and m.p. than traditional **Phillips catalyst** like Cr/SiO<sub>2</sub>.

## ~9 Citings

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**69. Polyethylene compositions and containers comprising them with good transparency, gloss, and surface smoothness**

By Hino, Toshitomo

From [Jpn. Kokai Tokkyo Koho](#) (2010), JP 2010047677 A 20100304, Language: Japanese, Database: CAPLUS

Title compns. comprising (A) 45-95% polyethylene (I) prepd. using **Phillips** catalysts and (B) 5-55% I prepd. using Ziegler catalysts show d. 0.942-0.953 g/cm<sup>3</sup>, MFR (190°, 2.16-kg load) 0.5-2.0 g/10 min, M<sub>w</sub>/M<sub>n</sub> (by GPC) 5.0-10.0, and haze [JIS K 7105:1981; as molding (%)] 50 to (1200D - 1064)[D = d. of molding (g/cm<sup>3</sup>)]. Thus, a compn. (d. 0.942 g/cm<sup>3</sup>, MFR 0.5 g/10 min, M<sub>w</sub>/M<sub>n</sub> 6.5) comprising 80% I prepd. using **Phillips catalyst** and 20% I prepd. using Ziegler **catalyst** was blow-molded to give a container showing light transmittance 70%, haze 61%, surface roughness (Ra) 0.9 μm, and good surface appearance.

## ~0 Citings

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**70. CRYSTAF Analysis of Polyethylene Synthesized with **Phillips Catalyst****

By Xia, Wei; Taniike, Toshiaki; Terano, Minoru; Fujitani, Tadahiro; Liu, Boping; Soares, Joao B. P.

From [Macromolecular Symposia](#) (2009), 285(Reaction Engineering of Polyolefins), 74-80. Language: English, Database: CAPLUS, DOI:10.1002/masy.200951110

Crystn. anal. fractionation (CRYSTAF) was used for the first time to investigate the soln. crystn. behavior of ethylene homopolymers and copolymers made with **Phillips** CrO<sub>x</sub>/SiO<sub>2</sub> **catalyst**. Interestingly, the crystn. peak temps. (T<sub>p</sub>) of copolymers of ethylene and cyclopentene increased with increasing cyclopentene molar fraction in the copolymer. Comparing two factors (short chain branches (SCBs) and cyclopentene incorporation), decreasing SCB frequency is proposed as the dominant factor to explain the increase of crystn. peak temps. with increasing cyclopentene incorporation. In addn., SCB frequency and mol. wt. might be the two significant factors detg. the crystn. temp. of polyethylene made with **Phillips** CrO<sub>x</sub>/SiO<sub>2</sub> **catalyst** with different cocatalysts (triethylaluminum and diethylaluminum ethoxide).

## ~3 Citings

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**71. Supporting mechanism of non-toxic chromium(III) acetate on silica for preparation of Phillips ethylene polymerization catalysts**

By Qiu, Pengyuan; Li, Xiaofang; Zhang, Shiliang; Cheng, Ruihua; Dong, Qi; Liu, Boping; Li, Liuzhong; Yu, Yongling; Tang, Yan; Xie, JianLing; et al  
From [Asia-Pacific Journal of Chemical Engineering](#) (2009), 4(5), 660-665. Language: English, Database: CAPLUS, DOI:10.1002/apj.314

Phillips catalyst is an important kind of industrial polyethylene catalyst. As early as in the late 1970s,  $\text{CrO}_3$  was substituted by chromium (III) acetate for the prepn. of Phillips catalyst on the industrial scale owing to health and environmental considerations. There is still considerable research focusing on the relations between the prepn. process and catalyst properties in academics. In this work, the supporting mechanism of chromium (III) acetate on silica has been studied by thermogravimetry-DTA (TG-DTA), and ESR, in comparison with that of supporting  $\text{CrO}_3$  on  $\text{SiO}_2$ . The basic chromium (III) acetate supported on high surface area silica gel decompd. differently from that for bulk basic chromium acetate when decompn. temp. was decreased by 15 °C. The decompn. temp. was 299 °C for  $\text{Cr}_3(\text{OH})_2(\text{Ac})_7/\text{SiO}_2$  catalyst precursor, which would be firstly transferred into  $\text{CrO}_3$  followed by supporting on silica surface as chromate species. The further wt. loss came from thermal inductive redn. of chromate species into  $\text{Cr}_2\text{O}_3$ , which was also supported by the results of colors of catalysts. Moreover, with the increase of chromium loading of  $\text{Cr}_3(\text{OH})_2(\text{Ac})_7/\text{SiO}_2$ , such thermal inductive redn. became more severe. ESR spectra of  $\text{Cr}_3(\text{OH})_2(\text{Ac})_7/\text{SiO}_2$  and  $\text{CrO}_3/\text{SiO}_2$  catalyst precursors showed that a small amt. of supported  $\text{Cr}^{5+}$  can exist stably on silica gel surface at temps. higher than 200 °C. Copyright © 2009 Curtin University of Technol. and John Wiley & Sons, Ltd.

~5 Citings

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**72. Ethylene polymers, hollow molded products using them, and their use**

By Kanazawa, Satoshi; Matsumoto, Katsuya; Monoi, Hisashi; Kuzuha, Yuichi; Hattori, Takaaki  
From [Jpn. Kokai Tokkyo Koho](#) (2009), JP 2009161615 A 20090723, Language: Japanese, Database: CAPLUS

Title polymers prepd. by the use of Cr-contg. polymn. catalysts satisfy d. 0.945-0.950 g/cm<sup>3</sup>, melt flow rate (190°, 21.6-kg load; HLMFR) 3.5-5.0 g/10 min,  $M_w/M_n \geq 25$  by GPC, failure time  $\geq 30$  h in the full notch creep test (FNCT), and Charpy impact strength  $\geq 9$  kJ/m<sup>2</sup>. Title molded products contain  $\geq 1$  ethylene polymer layer and are useful for fuel tanks, kerosene cans, drum cans, chem. containers, agrochem. containers, solvent containers, or bottles. Thus,  $\text{SiO}_2$ -supported Cr catalyst (Phillips catalyst) was activated at 450° for 20 h, supplied to a reactor with isobutane, and treated with ethylene, H, and 1-hexene to give 1800 g polymer/g-catalyst/h showing d. 0.947 g/cm<sup>3</sup>, HLMFR 4.0 g/10 min,  $M_w/M_n$  29, FNCT failure time 70 h, Charpy impact strength 10 kJ/m<sup>2</sup>,  $\lambda_{\text{max}}$  1.3, and flexural modulus 1060 MPa.

~1 Citing

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**73. Modeling CO and N2 Adsorption at Cr Surface Species of Phillips Catalyst by Hybrid Density Functionals: Effect of Hartree-Fock Exchange Percentage**

By Damini, Alessandro; Vitillo, Jenny G.; Ricchiardi, Gabriele; Bordiga, Silvia; Lamberti, Carlo; Groppo, Elena; Zecchina, Adriano  
From [Journal of Physical Chemistry A](#) (2009), 113(52), 14261-14269. Language: English, Database: CAPLUS, DOI:10.1021/jp902650m

In this article, we present a computational study of the structure and vibrational properties of the species formed by the interaction between Cr sites of Phillips catalyst and probe mols. ( $\text{CO}$ ,  $\text{N}_2$ ). The vibrational properties of these surface species, intensively investigated in the past, form a very rich and ideal set of exptl. data to test computational approaches. By adopting the  $\text{X}_4\text{Si}_2\text{O}_3\text{Cr}$  ( $\text{X} = \text{H}, \text{OH}, \text{F}$ ) cluster as a simplified model of the (equiv. $\text{SiO}_2$ )<sub>2</sub>Cr(II) species present at the surface of the real catalyst, we found that the B3LYP hybrid functional (contg. 20% of Hartree-Fock exchange), when applied to this model, is unable to reproduce with reasonable accuracy the currently available exptl. data (principally coming from IR spectroscopy). Better agreement is obtained when the percentage of Hartree-Fock exchange is increased (up to 35-40%).

~13 Citings

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**74. Multilayer blow moldings with good gloss, transparency, and impact resistance, and their manufacture**

By Hino, Toshitomo  
From [Jpn. Kokai Tokkyo Koho](#) (2009), JP 2009154472 A 20090716, Language: Japanese, Database: CAPLUS



The moldings are formed from laminates consisting of (A) surface and inner layers comprising metallocene-catalyzed polyethylene (I) with MFR (190°, 2.16 kg load) 1.0-15 g/10 min, d. 0.870-0.928 g/cm<sup>3</sup>, and M<sub>w</sub>/M<sub>n</sub> (GPC) 1.5-4.0, and (B) intermediate layers comprising **Phillips** or Ziegler **catalyst**-catalyzed I or I prepd. by high-pressure method with MFR (190°, 2.16 kg load) 0.1-5 g/10 min, d. 0.910-0.967 g/cm<sup>3</sup>, and M<sub>w</sub>/M<sub>n</sub> (GPC) 3.3-28. Thus, (A) metallocene-catalyzed I (MFR 1.0 g/10 min, d. 0.870 g/cm<sup>3</sup>, M<sub>w</sub>/M<sub>n</sub> 2.5) and (B) **Phillips catalyst**-catalyzed I (MFR 0.3 g/10 min, d. 0.935 g/cm<sup>3</sup>, M<sub>w</sub>/M<sub>n</sub> 9) were extruded into parison at A/B/A thickness ratio 15/70/15 and blow-molded to give a container showing surface gloss 42%, haze 32%, light transmittance 79%, and no peeling in pinch-off parts.

~0 Citings

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## 75. Olefin polymerization catalysts and manufacture of high-molecular-weight olefin polymers using them

By Yamamoto, Kazuhiro; Monoi, Hisashi

From [Jpn. Kokai Tokyo Koho \(2009\)](#), [JP 2009149708 A 20090709](#), Language: Japanese, Database: CAPLUS

The catalysts are obtained from components (A) selected from clays, clay minerals, and ion-exchangeable layered compds., compds. M(OR)<sub>n</sub> (B; M = Group 3-14 element; R = H, C<sub>1-20</sub> hydrocarbyl, silyl; n = valent of M), and Cr compds. (C) selected from chromic acid or its salts, dichromic acid or its salts, and chromate salts from Cr cations and halogen ions or inorg. or org. acid anions. Thus, activating a mixt. of K 10 (montmorillonite) 30, tetraethoxysilane 3.13, and Cr acetylacetonate 2.02 g at 730° for 6 h and polymg. 220 g ethylene in the presence of the resulting **catalyst** (conversion of C<sup>3+</sup> to C<sup>6+</sup> 98 wt.%) resulted in catalytic activity 1630 g/g-h and gave a polymer with HLMI 0.06 g/10 min and d. 0.952 g/cm<sup>3</sup>.

~0 Citings

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## 76. Synthesis of chromates in chromasiloxane ring structures as active site models for the **Phillips' catalyst**

By Scott, Susannah L.; Demmelmaier, Cori A.; White, Rosemary E.; Wanglee, Ying-Jen

From [Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009 \(2009\)](#), [CATL-018](#). Language: English, Database: CAPLUS

The reaction of chromyl chloride with silica results in the formation of supported chromates embedded in siloxane rings of different sizes. XANES and DRUV-vis spectra are consistent with the formation of low-strain 8-membered chromasiloxane rings when the silica is pretreated at 200 °C, and high-strain 6-membered chromasiloxane rings when the silica is pretreated at 800 °C. The former fail to initiate ethylene polymn., while the latter give an ethylene uptake profile with a pronounced induction period, similar to that obsd. for the heterogeneous **Phillips' catalyst** (Cr/silica). The use of silica itself as a ligand thus leads to insight not available from model mol. chromate compds. (e.g., with silsesquioxane ligands). The non-aq. grafting approach yields high site uniformity, permitting detailed structural anal. by vibrational spectroscopy and EXAFS.

~0 Citings

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## 77. Evidence for a chromasiloxane ring size effect in **Phillips** (Cr/SiO<sub>2</sub>) polymerization catalysts

By Demmelmaier, Cori A.; White, Rosemary E.; van Bokhoven, Jeroen A.; Scott, Susannah L.

From [Journal of Catalysis \(2009\)](#), [262\(1\)](#), 44-56. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2008.11.024

The ambient temp. reaction of CrO<sub>2</sub>Cl<sub>2</sub> with silica, followed by mild heating to induce formation of uniform grafted silylchromate diesters, was studied as a function of the silica pretreatment temp. The reactivity of the resulting chromate sites toward ethylene is qual. different: those formed on the silica pretreated at 200 °C are incapable of initiating polymn., while those formed on silicas pretreated at 450 and 800 °C spontaneously induce polymn. with kinetic profiles closely resembling that of the calcined **Phillips catalyst** (CrO<sub>x</sub>/SiO<sub>2</sub>). Comparison of their X-ray absorption spectra suggests subtle differences in the chromate-support interactions, which can be interpreted in terms of changes in the chromasiloxane ring size distribution. The unstrained sites favored on the highly hydroxylated silica surface are consistent with 8-membered chromasiloxane rings formed by attachment of the CrO<sub>2</sub> fragment to non-vicinal hydroxyls, while the strained sites on highly dehydroxylated silica surfaces are suggested to be 6-membered chromasiloxane rings created from vicinal hydroxyls located on adjacent silicon atoms. Simple computational models for these sites predict changes in the vibrational spectra and the XANES that are consistent with exptl. observations.

~43 Citings

**78. Copolymerization of ethylene and cyclopentene with the Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst in the presence of an aluminum alkyl cocatalyst**

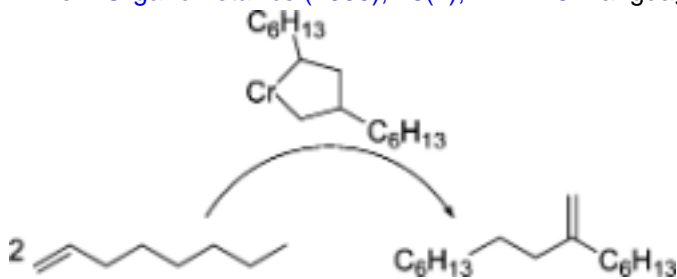
By Xia, Wei; Tonosaki, Kiwamu; Taniike, Toshiaki; Terano, Minoru; Fujitani, Tadahiro; Liu, Boping  
 From *Journal of Applied Polymer Science* (2009), 111(4), 1869-1877. Language: English, Database: CAPLUS,  
 DOI:10.1002/app.29207

The Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst is an important industrial catalyst for ethylene polymn. However, understanding of the state of active sites and chain propagation mechanisms concerning the Phillips catalyst is still waiting for conclusive evidence. In this work, the Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst, having been calcined, was used for investigating the copolymn. of ethylene and cyclopentene in the presence of triethylaluminum as a cocatalyst for the first time. The microstructures of the polymers were investigated with <sup>13</sup>C-NMR and gel permeation chromatog. methods. Because of the absence of internal double bond (C=C) in the copolymer main chain, the ring-opening metathesis polymn. of cyclopentene was excluded during the copolymn. stage of ethylene and cyclopentene. Also, the 1,2-insertion and 1,3-insertion of cyclopentene into the polyethylene main chain were confirmed. This evidence strongly implies that Cr=C species may not be the active sites for chain propagation; instead, the Cr-C active site model under the Cossee-Arlman chain propagation mechanism may be responsible for the chain propagation during the normal polymn. period.

~14 Citings

**79. Oligomerization of α-Olefins via Chromium Metallacycles**

By McGuinness, David S.  
 From *Organometallics* (2009), 28(1), 244-248. Language: English, Database: CAPLUS, DOI:10.1021/om8008348



Cr complexes that oligomerize and polymerize olefins via a metallacycle mechanism represent possible models for the com. important Phillips catalyst, which is still poorly understood mechanistically. Comparisons between the two might provide insight into the process, and as such the oligomerization of α-olefins (propene to 1-octene) with Cr(III)-pyridine-2,6-diylbis(3-R-1,3-dihydro-2H-imidazol-1-yl-2-ylidene) complexes (R = Me, *i*Pr, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in combination with MAO was studied. Linear α-olefins are homo-oligomerized, as well as cooligomerized with ethylene, via a mechanism most likely involving metallacycles. Homo-oligomerization of α-olefins leads predominantly to head-to-tail dimers with vinylidene unsatn., while a less favorable coupling leads to linear internal olefin dimers. With shorter chain monomers, trimerization and tetramerization become more significant, albeit still minor processes. The kinetics of 1-octene dimerization were studied and are 1st-order in Cr but zero-order in 1-octene concn. The results are interpreted in terms of the likely rate-detg. step of the reaction, and comparisons are drawn between the behavior of this system and the heterogeneous Phillips catalyst.

~27 Citings

**80. Simulation modeling on the coordination mechanism of ethylene monomer on various prereduced Cr(II)Ox/SiO<sub>2</sub> Phillips polyethylene model catalysts**

By Cheng, Rui-hua; Liu, Zhen; Qiu, Peng-yuan; Zhang, Shi-liang; Liu, Bo-ping  
 From *Chinese Journal of Polymer Science* (2008), 26(5), 579-587. Language: English, Database: CAPLUS,  
 DOI:10.1142/S0256767908003308

As one of the most important catalysts in polyethylene industry, the **Phillips catalyst** ( $\text{CrO}_x/\text{SiO}_2$ ) was studied with focus on activation by ethylene monomer, without activator, e.g., alkyl-aluminum or MAO. The coordination mechanism was studied using d. functional theory (DFT) calcns. combined with paired interacting orbitals (PIO) method for ethylene monomer and two model catalysts,  $\text{Cr(II)(OH)}_2$  (M1) and silsesquioxane-supported  $\text{Cr(II)}$  (M2) as surface  $\text{Cr(II)}$  active site precursors on **Phillips catalyst** at the early stage of ethylene polymn. Unexpected multiplicity of the coordination states of ethylene monomer on both M1 and M2 model catalysts was reported, on a mol. level. In general, increasing the coordination no. of ethylene, led to a decrease in binding energy per ethylene, for all the complexes. The supporting effect of chromium oxide on silica gel surface destabilized the complexes and decreased the no. of coordination states due to electronic and steric effects. Moreover, tri- and tetra- or higher ethylene coordination states could not form on the supported **catalyst**. The optimized complex geometries were adopted for detg. the intermol. orbital interactions. In-phase overlap orbital interaction for all the mol. complexes indicated favorable coordination between ethylene and  $\text{Cr(II)}$  sites. The MO origin of the  $\pi$ -bonded  $\text{Cr(II)}$ , and mono- and di- $\text{C}_2\text{H}_4$  M1 complexes was elucidated by the PIO method, showing high possibility of formation of metallacyclopropane or metallacyclopentane active sites in the subsequent initiation of polymn. stage.

~3 Citings

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### 81. Ethylene polymers for cyanoacrylate adhesive containers, and their containers with good deformation recovery

By Kurumi, Jiro

From [Jpn. Kokai Tokkyo Koho \(2008\), JP 2008101042 A 20080501](#), Language: Japanese, Database: CAPLUS

Title ethylene polymers satisfy (a) MFR (190°, 2.16 kg load) 0.05-100 g/10 min, (b) d. 0.930-0.970 g/cm<sup>3</sup>, (c) content of Group 17 element ≤10 ppm, (d) content of P antioxidants <100 ppm, (e) content of fatty acid metal salt antacids <100 ppm, and (f) content of inorg. antacids <100 ppm. Thus, Aron Alpha 201 (cyanoacrylate adhesive) in a container comprising ethylene-1-hexene copolymer (manufd. with **Phillips catalyst**) showed good storage stability and usability.

~0 Citings

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### 82. Nature of $\equiv\text{SiOCrO}_2\text{Cl}$ and $(\equiv\text{SiO})_2\text{CrO}_2$ Sites Prepared by Grafting $\text{CrO}_2\text{Cl}_2$ onto Silica

By Demmelmaier, Cori A.; White, Rosemary E.; van Bokhoven, Jeroen A.; Scott, Susannah L.

From [Journal of Physical Chemistry C \(2008\), 112\(16\), 6439-6449](#). Language: English, Database: CAPLUS, DOI:10.1021/jp7119153

The room-temp. reaction between chromyl chloride and Sylopol 952 silicas pretreated at 200, 450, and 800° was studied using IR, XANES, and EXAFS spectroscopy, as well as by DFT modeling. On the silicas pretreated at 200 and 450°, the structurally uniform sites formed by the reaction with one surface hydroxyl group are described as  $\equiv\text{SiOCrO}_2\text{Cl}$ . Unreacted silanols persist on these silicas even in the presence of excess  $\text{CrO}_2\text{Cl}_2$ , and on the  $\text{SiO}_2$  pretreated at 200° some participate in H bonding with the grafted monochlorochromate sites. On the  $\text{SiO}_2$  pretreated at 800°, both  $\equiv\text{SiOCrO}_2\text{Cl}$  and  $(\equiv\text{SiO})_2\text{CrO}_2$  sites are formed. The latter are produced despite the absence of H-bonded hydroxyl pairs on the support. The origin of the chromate sites probably is the reaction between  $\text{CrO}_2\text{Cl}_2$  and hydroxyl-substituted siloxane 2-rings. These rings are likely formed at 800° by condensation between a pair of vicinal silanols in which one of the silanols is also a member of a geminal pair.

~23 Citings

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### 83. Plausible mechanism for the formation and transformation of active sites on novel **Phillips type catalyst** with new organo-siloxane ligand

By Xia, Wei; Liu, Boping; Fang, Yuwei; Zhou, Daqing; Terano, Minoru

From [Studies in Surface Science and Catalysis \(2006\), 161\(Progress in Olefin Polymerization Catalysts and Polyolefin Materials\), 225-228](#). Language: English, Database: CAPLUS

A novel **Phillips type catalyst** with chiral organo-siloxane ligand was investigated for ethylene polymn. in the presence of triethylaluminum (TEA) cocatalyst. Plausible mechanism of the formation and transformation of active sites was proposed to rationalize its unique polymn. behavior.

~4 Citings

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**84. Computational approach on the interaction between CrO<sub>3</sub> and ethylene as a model for the understanding of Phillips catalyst**

By Liu, Boping; Xia, Wei; Terano, Minoru

From [Studies in Surface Science and Catalysis \(2006\)](#), 161(Progress in Olefin Polymerization Catalysts and Polyolefin Materials), 129-134. Language: English, Database: CAPLUS

Supporting of bulky CrO<sub>3</sub> onto SiO<sub>2</sub> surface is crucial for achieving activity for industrial Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst. However, mechanistic understanding of the supporting effect has not been achieved yet. In this work, the MO interaction between CrO<sub>3</sub> and ethylene was investigated using DFT and PIO methods. It was demonstrated that bulky CrO<sub>3</sub> without supporting onto SiO<sub>2</sub> surface is difficult to achieve activity for ethylene polymn. like Phillips catalyst because formation of stable  $\pi$ -bonded mol. complex between CrO<sub>3</sub> and ethylene monomer could block the whole activation process.

~3 Citings

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**85. One-step synthesis of chromium and aluminum containing SBA-15 materials. New Phillips catalysts for ethylene polymerization**

By Aguado, J.; Calleja, G.; Carrero, A.; Moreno, J.

From [Chemical Engineering Journal \(Amsterdam, Netherlands\) \(2008\)](#), 137(2), 443-452. Language: English, Database: CAPLUS, DOI:10.1016/j.cej.2007.06.022

New CrAISBA-15 mesoporous materials have been prepd. by direct synthesis and characterized by ICP-AES, XRD, N<sub>2</sub> adsorption, <sup>27</sup>Al NMR, TEM, UV-vis and H<sub>2</sub>-TPR. CrAISBA-15 materials exhibited high mesostructural order starting from chromium(III) nitrate (Si/Cr = 66; Si/Al = 35 at pH 3) and from chromium(III) acetate hydroxide (Si/Cr = 39; Si/Al = 51 at pH 1.5). The incorporation of chromium and aluminum into SBA-15 mesoporous structure is enhanced by increasing the pH and produces an increase in pore size and pore vol. After calcination, samples prepd. by one-step synthesis showed Cr(VI) centers well dispersed with a proportion of chromate species higher than Cr/AISBA-15 catalysts prepd. by impregnation and grafting. H<sub>2</sub>-TPR measurements showed that only the 80% of Cr(VI) ions incorporated into the SBA-15 structure were reduced, so part of chromium ions may be located in non-accessible positions inside the solid walls. CrAISBA-15 materials obtained by direct synthesis exhibited higher ethylene polymn. activity (381.1 kg PE/g Cr h) than Cr/AISBA-15 and conventional Cr/SiO<sub>2</sub> Phillips catalyst prepd. by impregnation (260.5 and 216 kg PE/g Cr h, resp.).

~29 Citings

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**86. Olefin polymerization method using chromium catalysts and cycloolefin monomers**

By Liu, Pai Ping; Sha, Wei; Terano, Minoru

From [Jpn. Kokai Tokkyo Koho \(2007\)](#), JP 2007302724 A 20071122, Language: Japanese, Database: CAPLUS

Title method involves polymg. ethylene-based olefin monomers in the presence of Cr polymn. catalysts and cycloolefin monomers. Thus, ethylene was polymd. in the presence of Phillips catalyst, Et<sub>3</sub>Al, and 5 vol% cyclopentene to give polymer with M<sub>w</sub> 8.11 × 10<sup>5</sup> and M<sub>w</sub>/M<sub>n</sub> 54.2.

~0 Citings

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**87. Activation of Phillips Cr/silica catalysts**

By McDaniel, M. P.; Collins, K. S.; Benham, E. A.

From [Journal of Catalysis \(2007\)](#), 252(2), 281-295. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2007.09.021

The satn. coverage behavior of Cr(VI) on silica has been used to study the mobility of hexavalent chromium during com. activation of the Phillips catalyst in a fluidized bed. Cr(VI) was found to migrate not only within each silica particle, but even between particles. The mechanism of transfer is thought to be particle-to-particle contact during the fluid bed calcining process, and Cr migration was obsd. at temps. as low as 300-400 °C in these expts. Transfer can take place even in the absence of oxygen, which suggests that redox cycling is probably not the main method of mobility. However, once the silica is calcined at high temps. the migration is stopped at low temps., indicating that the thermal history of the surface is important in the transfer process. Migration of Cr on and between alumina particles behaved in much the same way, and Cr transfer was also obsd. between silica and alumina in both directions. Cr(III) on deactivated com. Cr/silica catalysts could be reclaimed to Cr(VI) surprisingly easily by co-activation with virgin support. The spreading out of Cr(VI) onto a fresh unoccupied surface probably provides a powerful force to reoxidize the otherwise seemingly inert alpha-Cr<sub>2</sub>O<sub>3</sub> crystallites. The mobility has important consequences for com. manuf. and use of the catalyst.



## ~13 Citings

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**88. Reactivity of Cr Species Grafted on SiO<sub>2</sub>/Si(100) Surface: A Reflection Extended X-ray Absorption Fine Structure Study down to the Submonolayer Regime**

By Agostini, G.; Groppo, E.; Bordiga, S.; Zecchina, A.; Prestipino, C.; D'Acapito, F.; Van Kimmenade, E.; Thuene, P. C.; Niemantsverdriet, J. W.; Lamberti, C.

From [Journal of Physical Chemistry C](#) (2007), 111(44), 16437-16444. Language: English, Database: CAPLUS, DOI:10.1021/jp074066t

In situ X-ray absorption near-edge spectroscopy/extended X-ray absorption fine structure (XANES/EXAFS) expts. are conducted for the first time on a highly dild. Cr/SiO<sub>2</sub>/Si(100) system (2 Cr/nm<sup>2</sup>, representing a model of the **Phillips catalyst** for the ethylene polymn.) by exploiting the reflection EXAFS (RefLEXAFS) geometry. This expt., aimed to give a contribution in bridging the gap between surface science and catalysis, demonstrates that it is possible to follow the reversible red-ox reactivity of surface species grafted on a single well-defined surface, at a concn. limit that is far below the monolayer coverage level and for a highly sensitive sample. A further improvement on the impurity level of the RefLEXAFS chamber is however required in order to be able to follow in situ the polymn. reaction. Our results demonstrate that the red-ox ability of the isolated surface Cr species is not enough to make a polymn. active species.

## ~13 Citings

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**89. Triangular transition metal clusters supported by bridging triazacyclohexanes**

By Kohn, Randolph; Kociok-Kohn, Gabriele; Pan, Zhida; Tomas Laudo, Lorena

From [Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007](#) (2007), INOR-1123. Language: English, Database: CAPLUS

Our development of the co-ordination chem. of triazacyclohexanes with transition metals has lead us to the first good model system for the **Phillips catalyst** and the first selective  $\alpha$ -olefin trimerization **catalyst** based on chromium. This is probably due to the misdirected nitrogen lone pairs in  $\kappa^3$  complexes leading to inherent hemilability. We now found that the freed coordination sites can bind to two more metals to form triangular trimetal clusters: This was first discovered in copper reactions. Cu(I)<sub>3</sub> and Cu(II)<sub>3</sub> clusters were prepd. with or without addnl. donor substituents on the N-substituents. The donor substituents greatly facilitates the formation of such triangular tri-metal complexes. This presentation will give our latest results using different donor substituted ligands and different metals.

## ~0 Citings

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**90. Application and market status of polymerization catalysts**

By Shen, Gui-ying

From [Jingxi Yu Zhuanyong Huaxuepin](#) (2006), 14(22), 26-28. Language: Chinese, Database: CAPLUS

A review. The main catalysts for polymn. are single-site catalysts, Ziegler-Natta catalysts and **Phillips catalysts**. Single-site catalysts are the ones of the growth opportunities, the market for polymers made with single-site **catalyst** is growing globally. In Western Europe, about 70-75 % of polyethylene prodn. capacity uses a Ziegler-Natta **catalyst**, the 23-25 % installed capacity is based on **Phillips catalyst**, polypropylene is produced mainly by Ziegler-Natta **catalyst**. Advanced Ziegler-Natta catalysts can be readily applied to existing processes, and they are more firmly established in polypropylene prodn., so their use should continue to grow.

## ~0 Citings

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**91. Preparation, characterization and testing of Cr/AISBA-15 ethylene polymerization catalysts**

By Calleja, G.; Aguado, J.; Carrero, A.; Moreno, J.

From [Applied Catalysis, A: General](#) (2006), 316(1), 22-31. Language: English, Database: CAPLUS, DOI:10.1016/j.apcata.2006.09.012

Ethylene polymn. catalysts were prepd. by grafting chromium(III) acetylacetonate onto AISBA-15 (Si/Al =  $\infty$ , 156, 86 and 30) mesoporous materials. A combination of XRD, nitrogen adsorption, TEM, ICP-at. emission spectroscopy, H<sub>2</sub>-TPR, TGA, UV-vis and FT-IR spectroscopy, were used to characterize the prepd. Cr-AISBA-15 catalysts. Reducing the Si/Al ratio of the AISBA-15 supports increases the amt. of chromium anchored, promotes the stabilization of chromium species as chromate and decreases the redn. temp. of Cr<sup>6+</sup> ions detd. by H<sub>2</sub>-TPR. Attachment of Cr species onto the AISBA-15 surface results from the interaction of hydroxyl groups with the acetylacetonate ligands through H-bonds. On the contrary, a ligand exchange reaction may occur over siliceous SBA-15. The polymn. activity of Cr-AISBA-15 catalysts is significantly improved by increasing the aluminum content of the AISBA-15 supports. Particularly, the chromium catalyst prepd. with AISBA-15 (Si/Al = 30) support is almost four times more active than a conventional Cr/SiO<sub>2</sub> Phillips catalyst. Polymers obtained with all the catalysts showed melting temps., bulk densities and high load melt indexes indicating the formation of linear high-d. polyethylene.

### ~39 Citings

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## 92. Manufacture of polyolefins with good impact and environmental stress crack resistance using chromium catalysts

By Hasebe, Koichi; Shinko, Teruaki

From [Jpn. Kokai Tokkyo Koho \(2006\)](#), [JP 2006241257 A 20060914](#), Language: Japanese, Database: CAPLUS

The invention relates to polymn. method of olefins in the presence of polymn. catalysts comprising Cr oxide catalysts activated burned under nonredn. atm. and supported on SiO<sub>2</sub>-TiO<sub>2</sub> supports and org. Al compds. of R<sup>1</sup><sub>(3-n)</sub>AlL<sub>n</sub> (R<sup>1</sup> = C<sub>2-12</sub> alkyl; L = C<sub>1-8</sub> alkoxy or phenoxy; n 0-1). Polyolefins manufd. by the method are useful for blow molding. Thus, ethylene (I) was polymd. with 1-hexene (II) in the presence of a catalyst comprising a Cr acetate on a SiO<sub>2</sub>-TiO<sub>2</sub> support (EP 50) and a MeOH-trioctylaluminum compd. to give I-II copolymer showing activity 8800 g-catalyst/g-polymer/h, notched Charpy impact strength (JIS K 7111) 24 kg-cm/cm<sup>2</sup>, and b-ESCR (JIS K 6760) 50 h.

### ~0 Citings

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## 93. Unique polymerization kinetics obtained from simultaneous interaction of Phillips Cr(VI)Ox/SiO<sub>2</sub> catalyst with Al-alkyl cocatalyst and ethylene monomer

By Xia, Wei; Liu, Boping; Fang, Yuwei; Hasebe, Kouichi; Terano, Minoru

From [Journal of Molecular Catalysis A: Chemical \(2006\)](#), [256\(1-2\)](#), [301-308](#). Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2006.05.007

Introduction of metal-alkyl cocatalyst in different stages from catalyst prepn. to polymn. using Phillips catalyst significantly affects the active site formation, polymn. kinetics and polymer microstructure. However, the effect of the introduction of metal-alkyl cocatalyst in different stages has not been investigated systematically. In this work, ethylene homopolymn. was carried out using Phillips catalyst calcined at 600° (PC600). Different Al-alkyl cocatalysts (triethylaluminum (TEA) and diethylaluminum ethoxide (DEAE)) were introduced during polymn. stage with simultaneous interaction of catalyst with Al-alkyl cocatalyst and monomer. The polymn. kinetic curves using PC600/TEA catalyst systems seemed to be a hybrid type comprised of two types of basic polymn. kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type, which indicate the existence of two types of polymn. active sites. However, the polymn. kinetic curves using PC600/DEAE catalyst systems seemed to be a typical single type polymn. kinetics indicating only one type of polymn. sites that can be ascribed to Cr(II) species coordinated with Al-alkoxy formed by two ways. Plausible mechanisms of the formation and transformation of active sites were proposed to rationalize the unique polymn. kinetics and microstructures of polymers in terms of short chain branches (SCBs), mol. wt. (MW) and bimodal mol. wt. distribution (MWD). The metathesis mechanism proposed in our previous report got further exptl. support in this study.

### ~21 Citings

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## 94. XAS investigation of the precursor to the Phillips catalyst

By Demmelmaier, Cori A.; Scott, Susannah L.

From [Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006 \(2006\)](#), [INOR-864](#). Language: English, Database: CAPLUS

We have examd. the ability of chromyl chloride to react with silica to yield the desired surface chromate esters that are widely believed to be the initiation site of the **Phillips catalyst**.  $\text{CrO}_2\text{Cl}_2$  vapor reacts at 25 °C under reduced pressure with silica pretreated at 200, 450, and 800 °C. Grafting proceeds by reaction with the surface silanols, as confirmed by IR spectroscopy and formation of HCl. The primary product of this reaction is .ident.SiOCrO<sub>2</sub>Cl, as confirmed by XAS. The .ident.SiOCrO<sub>2</sub>Cl site does not initiate ethylene polymn. without heat treatment. However, EXAFS shows that conversion to the dichromate ester occurs spontaneously upon thermal treatment in vacuo, both by condensation with neighboring silanol groups and co-condensation of adjacent .ident.SiOCrO<sub>2</sub>Cl sites. Differences obsd. in the XAS spectra of the  $\text{CrO}_2\text{Cl}_2$ -treated silicas pretreated at different temps. provide insight into the dependence of polymn. activity on the thermal history of the **catalyst**.

~0 Citings

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## 95. Organoboron-treated fluorinated chromium polymerization catalysts, manufacture of ethylene polymers with good creep and impact resistance using them, and large-scale blow moldings comprising them

By Monoi, Hisashi; Yamamoto, Masakazu

From [Jpn. Kokai Tokkyo Koho \(2006\)](#), JP 2006182917 A 20060713, Language: Japanese, Database: CAPLUS

The catalysts are manufd. by prepg. Cr catalysts supported on inorg. carriers contg. F compds., activating under nonreducing conditions so as to at least partially convert Cr atoms into hexavalent, contacting the fluorinated Cr catalysts with  $\text{BR}^1\text{R}^2\text{R}^3$ ,  $\text{BR}^4\text{R}^5(\text{OR}^6)$ , or  $\text{R}^7\text{R}^8\text{BOBR}^9\text{R}^{10}$  ( $\text{R}^{1-10} = \text{C}_{1-18}$  alkyl,  $\text{R}^1$  and  $\text{R}^2$ , or  $\text{R}^4$  and  $\text{R}^5$  may be connected to form a ring). Thus, 1-hexene and ethylene were polymd. in the presence of a **catalyst** prepd. by activating a fluorinated Cr **catalyst** with F content 0.9% (Sylopol 7129) at 700°, then treating with  $\text{BEt}_3$  to give a copolymer [ $M_w$   $35.5 \times 10^{-4}$ ,  $M_w/M_n$  17.8, d. 0.944 g/cm<sup>3</sup>, and HLMFR (JIS K 7210; 190°, 21.60 kg-load) 6.4 g/10 min] at polymn. activity 4200 g/g **catalyst**-h. A test piece comprising the copolymer showed Charpy impact strength (JIS K 7111) 8.9 kJ/m<sup>2</sup> and breaking time 53 h in water at 80° and stress 6 MPa.

~2 Citings

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## 96. On the fraction of CrII sites involved in the C<sub>2</sub>H<sub>4</sub> polymerization on the Cr/SiO<sub>2</sub> **Phillips catalyst**: a quantification by FTIR spectroscopy

By Groppo, E.; Lamberti, C.; Cesano, F.; Zecchina, A.

From [Physical Chemistry Chemical Physics \(2006\)](#), 8(21), 2453-2456. Language: English, Database: CAPLUS, DOI:10.1039/b604515d

An estn. of the fraction of CrII sites involved in the C<sub>2</sub>H<sub>4</sub> polymn. on a CrII/SiO<sub>2</sub> **Phillips catalyst** has been obtained by means of in situ alternated CO adsorption and C<sub>2</sub>H<sub>4</sub> polymn. FTIR expts.: about 28% of the total surface sites react fast with C<sub>2</sub>H<sub>4</sub>, while a lower fraction, which depends upon the temp. reaction conditions, is more slowly involved, in agreement with XANES results.

~17 Citings

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## 97. In situ FTIR spectroscopy of key intermediates in the first stages of ethylene polymerization on the Cr/SiO<sub>2</sub> **Phillips catalyst**: Solving the puzzle of the initiation mechanism?

By Groppo, Elena; Lamberti, Carlo; Bordiga, Silvia; Spoto, Giuseppe; Zecchina, Adriano

From [Journal of Catalysis \(2006\)](#), 240(2), 172-181. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2006.03.006

We report here the first exptl. observation, by means of in situ FTIR spectroscopy, of key intermediate species in the ethylene polymn. on the Cr(II)/SiO<sub>2</sub> **Phillips catalyst**. We demonstrate that by adopting suitable strategies, it is possible to shed light on one of the remaining questions concerning the system responsible for one-third of the worldwide polyethylene prodn.: the puzzle of the initiation mechanism. "Anomalous" bands in the CH<sub>2</sub> stretching region are obsd. during the first steps of the polymn. reaction and assigned to small cycles on the Cr(II) sites, characterized by a structural strain decreasing with increasing ring dimension. These intermediate species are stable only in presence of a sufficiently high C<sub>2</sub>H<sub>4</sub> pressure and show a peculiar reactivity toward strong ligands, such as NO and O<sub>2</sub>. These results allow us to prove that the initiation mechanism follows a metallacycle route, similar to what occurs for several ethylene trimerization and tetramerization catalysts.

~49 Citings

**98. Various activation procedures of Phillips catalyst for ethylene polymerization**

By Fang, Y.; Liu, B.; Terano, M.

From *Kinetics and Catalysis* (2006), 47(2), 295-302. Language: English, Database: CAPLUS,

DOI:10.1134/S0023158406020224

Nowadays, the Phillips  $\text{CrO}_x/\text{SiO}_2$  catalyst is still attracting interest from both industrial and academic fields owing to its unique characteristics for HDPE prodn. Compared with other industrial catalysts for ethylene polymn., the Phillips catalyst can be activated by ethylene monomer, CO or Al-alkyl cocatalyst after a simple calcination process (thermal activation). In this work, a brief review of our recent new understanding on various activation procedures, including thermal activation, monomer activation, and CO activation, on industrial Phillips catalyst was presented. A new initiation mechanism, ethylene metathesis mechanism, was proposed according to some exptl. evidence during the induction period when ethylene monomer was used to activate the catalyst. Such an ethylene metathesis mechanism was also indirectly confirmed in CO-prereduced Phillips catalyst. The formation of short chain branches in polymer can be rationalized well by this newly proposed unique mechanism during ethylene homo- and copolymn. with hexene-1 using CO-prereduced Phillips catalyst in the presence of triethylaluminum cocatalyst.

~8 Citings

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**99. Theoretical investigation of novel silsesquioxane-supported phillips-type catalyst by density functional theory (DFT) method**

By Liu, B.; Fang, Y.; Xia, W.; Terano, M.

From *Kinetics and Catalysis* (2006), 47(2), 234-240. Language: English, Database: CAPLUS,

DOI:10.1134/S0023158406020121

In spite of great com. importance of the Phillips  $\text{CrO}_x/\text{SiO}_2$  catalyst and long term research efforts, the precise physicochem. nature of active sites and polymn. mechanisms still remains unclear. The difficulties in a clear mechanistic understanding of this catalyst mainly come from the complexity of the surface chem. of the amorphous silica gel support. In this work, novel silsesquioxane-supported Phillips Cr catalysts are utilized as realistic models of the industrial catalyst for theor. investigation using the d. functional theory (DFT) method in order to elucidate the effects of surface chem. of silica gel in terms of supporting of chromium compds. and fluorination of the silica surface on the catalytic properties of the Phillips catalyst. Both qual. and quant. aspects with respect to various electronic properties and thermodyn. characteristics of the model catalysts were achieved. The future prospects of a state-of-the-art catalyst design and mechanistic approaches for the heterogeneous  $\text{SiO}_2$ -supported Phillips catalyst has been demonstrated.

~10 Citings

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**100. The effect of temperature on ethylene polymerization over flat Phillips model catalysts**

By van Kimmenade, E. M. E.; Loos, J.; Niemantsverdriet, J. W.; Thuene, P. C.

From *Journal of Catalysis* (2006), 240(1), 39-46. Language: English, Database: CAPLUS,

DOI:10.1016/j.jcat.2006.03.002

The polymn. properties of a well-defined flat  $\text{CrO}_x/\text{SiO}_2/\text{Si}(100)$  catalyst were investigated. To compare this model system with the conventional Phillips catalyst based on porous silica, polymn. reactions were carried out at various temps. In contrast to the conventional Phillips catalyst, our model showed const. activity from the start of polymn. Both the activity and mol. wt. were tenfold higher for the flat catalyst. As expected, an increase in polymn. temp. led to an increase in activity; however, the mol. wt. distribution was only mildly affected. At a temp. around the m.p. of polyethylene, a sudden drop in both activity and mol. wt. was obsd. Based on our observations, we propose that chromium sites produce polymer chains in short bursts of high activity, followed by a dormant period, and that ethylene polymn. of active chromium sites can result in local ethylene depletions that limit both activity and mol. wt. This can severely affect the polymn. properties in the event of high active site d. and reduced mass transfer through the formed polymer layer.

~16 Citings

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**101. Effect of Phillips catalysts and polymerization conditions on the structure of polyethylene. II. Experiments**



By Janecska, Akos Laszlo; Nagy, Gabor; Fekete, Margit Hedvig; Suba, Peter; Tolveth, Janos  
From [Muanyag es Gumi \(2006\), 43\(2\), 73-80](#). Language: Hungarian, Database: CAPLUS

We have examd. the effect of **catalyst** sp. surface area, morphol., activation temp., and titanium content on the **catalyst** activity and the structure of the gained polyethylene polymn. We gave a clear picture how the general polymn. conditions, like monomer and comonomer concn. and residence time affect the above mentioned **catalyst** and polymer characteristics. We can state that the knowledge of interrelations among **catalyst** compn. - polymn. conditions - polymer structure is of paramount importance not only as a key to the successful product development but also as a guarantee toward the safe plant operation and const. product quality.

~0 Citings

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## 102. Novel SiO<sub>2</sub>-supported chromium **catalyst** bearing new organo-siloxane ligand for ethylene polymerization

By Fang, Yuwei; Xia, Wei; He, Man; Liu, Boping; Hasebe, Kouichi; Terano, Minoru  
From [Journal of Molecular Catalysis A: Chemical \(2006\), 247\(1-2\), 240-247](#). Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2005.11.052

Nowadays, SiO<sub>2</sub>-supported Cr-based catalysts mainly including oxo chromium (**Phillips catalyst**) and silyl chromate (UCC **catalyst**) systems are still important industrial catalysts for ethylene polymn. It was found that the addn. of tri-Ph silanol could transform **Phillips catalyst** into silyl chromate **catalyst**. In this work, a new chiral organo-silanol was synthesized and subsequently introduced to modify the **Phillips** catalysts in order to develop a new SiO<sub>2</sub>-support Cr-based **catalyst** with a chiral organo-siloxane ligand for ethylene polymn. The new **catalyst** was characterized by XPS and solid-state NMR methods. The new Cr-based catalysts with chiral organo-siloxane ligand presented as an active **catalyst** for ethylene polymn., and their kinetic characteristic is found to be similar with that of calcined **Phillips catalyst** combined with TEA cocatalyst. It was very interesting to find the existence of short chain branches (SCBs) in these ethylene homo-polymers. The introduction of the new chiral organo-siloxane ligand was also found to produce polyethylene with bimodal mol. wt. distribution and to enhance the amt. of SCBs, which might be due to the steric and/or electronic effect of such chiral ligand, indicating a new method to improve the performance of Cr-based **catalyst** for polyethylene prodn.

~15 Citings

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## 103. Activation processes and polyethylene formation on a **Phillips** model **catalyst** studied by laser ablation, laser desorption, and static secondary ion mass spectrometry

By Aubriet, Frederic; Muller, Jean-Francois; Poleunis, Claude; Bertrand, Patrick; Di Croce, Pascal G.; Grange, Paul  
From [Journal of the American Society for Mass Spectrometry \(2006\), 17\(3\), 406-414](#). Language: English, Database: CAPLUS, DOI:10.1016/j.jasms.2005.11.008

Since the discovery of the **Phillips** catalysts, there still is much uncertainty concerning their activation, their mol. structure, the nature of the active chromium sites, and the polymn. mechanisms. Surface techniques are not easy to be used for such study according to the nonconductive behavior of the support. Therefore, model **Phillips catalyst** is elaborated by spin coating a trivalent chromium precursor on a silicon wafer. The surface characterization of this model **catalyst** is conducted by laser ablation mass spectrometry (LA-MS), laser desorption/ionization mass spectrometry (LDI-MS), and static secondary ion mass spectrometry (s-SIMS), at different steps of its prepn. To validate our approach, a comparison is also made between the model and the real **Phillips catalyst**. Moreover, the model **catalyst** efficiency for polyethylene synthesis is evaluated and allows us to discuss the validity of the mechanisms previously proposed to explain the catalytic process. The characterization of **Phillips** model **catalyst** by mass spectrometry allows us to better understand the activation processes of such **catalyst**. Depending on the activation temp., chromium oxide species are formed and anchored at the support surface. They consist mainly in mono-chromium sites at high temp. The chromium valence is hexavalent. This model **catalyst** is active for the polymn. of ethylene. A pseudo-oligomer mol. wt. distribution is obsd. by LA-MS, whereas s-SIMS allows us to elucidate the anchorage of the polymer at activate chromium surface sites.

~4 Citings

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## 104. Effect of **Phillips** catalysts and polymerization conditions on the structure of polyethylene. I. Theory

By Janecska, Akos Laszlo; Nagy, Gabor; Fekete, Margit Hedvig; Suba, Peter; Tolveth, Janos Sandor  
From [Muanyag es Gumi \(2006\), 43\(1\), 3-8](#). Language: Hungarian, Database: CAPLUS

We have examd. the effect of **catalyst** sp. surface area, morphol., activation temp., and titanium content on the **catalyst** activity and the structure of the gained polyethylene polymers. We gave a clear picture how the general polymn. conditions, like monomer and co-monomer concn. and residence time affect the above mentioned **catalyst** and polymer characteristics. We can state that the knowledge of interrelations among **catalyst** compn.-polymn. conditions-polymer structure is of paramount importance not only as a key to the successful product development but also as a guarantee toward the safe plant operation and const. product quality.

~0 Citings

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### 105. Anatomy of catalytic centers in **Phillips** ethylene polymerization **catalyst**

By Zecchina, A.; Groppo, E.; Damin, A.; Prestipino, C.

From [Topics in Organometallic Chemistry \(2005\)](#), 16(Surface and Interfacial Organometallic Chemistry and Catalysis), 1-35. Language: English, Database: CAPLUS, DOI:10.1007/b138072

A review. A relevant fraction of the polyethylene produced in the world (about 30%) is obtained with the **Phillips** process. Many efforts in the last 30 years have been devoted to establish the valence state and the structure of the catalytically active species formed by redn. with ethylene. Only Cr(II) ions with the lowest coordination (which unfortunately are only a minor fraction of the total) are responsible for the catalytic activity, while the overwhelming majority of surface sites play the role of spectator under normal reaction conditions. In the second part of the review the proposed initiation/polymn. mechanisms are fully reported. A peculiarity of the Cr/SiO<sub>2</sub> system, which makes it unique among the polymn. catalysts (Ziegler-Natta, metallocenes, etc.), lies in the fact that it does not requires any activator (such as aluminum alkyls etc.) because ethylene itself is able to create the catalytic center from the surface chromate precursor. The aim of this review is to illustrate, on one side, how much progress has been made recently in the understanding of the site's structure and, on the other side, the strategies and the techniques which can be adopted to study the **catalyst** under working conditions.

~14 Citings

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### 106. Tuning the structure, distribution and reactivity of polymerization centers of Cr(II)/SiO<sub>2</sub> **Phillips** catalyst by controlled annealing

By Groppo, Elena; Lamberti, Carlo; Spoto, Giuseppe; Bordiga, Silvia; Magnacca, Giuliana; Zecchina, Adriano

From [Journal of Catalysis \(2005\)](#), 236(2), 233-244. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2005.09.013

The catalytic activity of two Cr(II)/SiO<sub>2</sub> samples obtained after two different controlled annealing procedures are discussed and compared. The combined application of FTIR spectroscopy and micro-gravimetric detns. demonstrated that the two Cr(II)/SiO<sub>2</sub> samples are characterized by a different relative population of the families of Cr(II) sites present on the silica surface and by a different catalytic activity toward ethylene polymn. The different polymn. activity of the two catalysts is explained by supposing the presence of a distribution of Cr sites, all active but characterized by different turnover frequencies in ethylene insertion, which is related to the ability of Cr sites to insert up to three ligands into their coordination spheres. It is thus clear that the activation procedure plays an important role in detg. the catalytic activity and the local structure of the active sites in the **Phillips** catalyst, which are strictly related. In this sense, the obtained results are of general validity, because identification of the structure-activity relation is a challenge common to many catalytic systems.

~35 Citings

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### 107. Ethylene and 1-hexene copolymerization with CO-prerduced **Phillips** CrOx/SiO<sub>2</sub> catalyst in the presence of Al-Alkyl cocatalyst

By Fang, Yuwei; Liu, Boping; Hasebe, Kouichi; Terano, Minoru

From [Journal of Polymer Science, Part A: Polymer Chemistry \(2005\)](#), 43(19), 4632-4641. Language: English, Database: CAPLUS, DOI:10.1002/pola.20935

In this work, ethylene and 1-hexene copolymn. with **Phillips** catalyst prerduced by CO was carried out in the presence of tri-Et aluminum (TEA) cocatalyst. The microstructures of polymers were investigated by <sup>13</sup>C NMR and gel permeation chromatog. (GPC) methods. A hybrid-type kinetics was found for both homo- and copolymn. kinetics, which indicated that there existed two types of active sites namely site A and site B. Site A with instant activation, high activity, and fast decay was transformed from a metathesis site, namely Cr(II) site, coordinated with CO or CO<sub>2</sub> through desorption of CO or CO<sub>2</sub> by TEA, which contributed to the formation of short chain branches, esp. Me branches. Site B with slow activation, low activity, and slow decay was generated from redn. of residual chromate (VI) by TEA. Both 1-hexene and TEA can decrease the mol. wt. of polyethylene as well as enhance short chain branching.

~24 Citings

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**108. Organochromium chemistry supported by Nacnac ligands**

By Theopold, Klaus H.

From [Abstracts of Papers, 230th ACS National Meeting, Washington, DC, United States, Aug. 28-Sept. 1, 2005 \(2005\)](#), [INOR-213](#). Language: English, Database: CAPLUS

We have a long-standing interest in building functional homogeneous models for com. used heterogeneous olefin polymn. catalysts contg. chromium. The desire to mimic the proposed bidentate coordination of chromium with hard O-donors on the surface of silica, and yet maintaining steric protection of a coordinatively unsatd. chromium active site, led us to investigate sterically hindered  $\beta$ -diketiminato (i. E. 'nacnac') complexes of chromium. We have prepd. a variety of nacnacCr compds. ranging from +I to +V in formal oxidn. states. Low-coordinate cationic Cr(III) alkyls catalyze the homopolymn. of ethylene and copolymn. of ethylene with  $\alpha$ -olefins; thus they constitute functional models of the **Phillips catalyst**. Syntheses, mol. structures, and mechanistic details of the reactions of these and related compds. will be described.

~0 Citings

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**109. FTIR Investigation of the H<sub>2</sub>, N<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> Molecular Complexes Formed on the Cr(II) Sites in the **Phillips Catalyst**: a Preliminary Step in the understanding of a Complex System**

By Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Damin, A.; Zecchina, A.

From [Journal of Physical Chemistry B \(2005\)](#), [109\(31\)](#), [15024-15031](#). Language: English, Database: CAPLUS, DOI:10.1021/jp051826w

This work reports the first complete FTIR characterization of H<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> mol. complexes formed on the Cr(II) sites in the **Phillips catalyst**. The use of a silica aerogel as support for Cr(II) sites, substituting the conventional aerosil material, allowed us to obtain a remarkable increase in the signal-to-noise ratio of the IR spectra of adsorbed species. The improvement is directly related to an increase of the surface area of the support (~700 m<sup>2</sup>g<sup>-1</sup>) and to an almost complete absence of scattering [Groppo et al., Chem. Mater. 2005, 17, 2019-2027]. The use of this support and the adoption of suitable exptl. conditions results, for the first time, in the clear observation of H<sub>2</sub> and N<sub>2</sub> adducts formed on two different types of Cr(II) sites, thus yielding important information on the coordinative state of the Cr(II) ions, which well agrees with the evidences provided in the past by other probe mols. Furthermore, we report the first complete characterization of the C<sub>2</sub>H<sub>4</sub>  $\pi$ -complexes formed on Cr(II) sites. These results are particularly important in the view of the understanding of the polymn. mechanism, since the C<sub>2</sub>H<sub>4</sub> coordination and the formation of  $\pi$ -bonded complexes are the first steps of the reaction.

~32 Citings

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**110. Polymerization of Ethylene Molecules Chemisorbed on CrOH<sup>+</sup> as a Model System of Chromium-Containing Catalyst**

By Hanmura, Tetsu; Ichihashi, Masahiko; Monoi, Takashi; Matsuura, Kazuo; Kondow, Tamotsu

From [Journal of Physical Chemistry A \(2005\)](#), [109\(29\)](#), [6465-6470](#). Language: English, Database: CAPLUS, DOI:10.1021/jp040723v

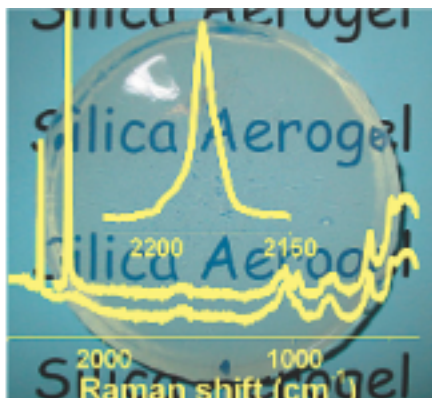
The reaction process of the prodn. of CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> was studied in connection with the ethylene polymn. on a silica-supported chromium oxide **catalyst** (the **Phillips catalyst**). Cluster ions CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> and CrOH(C<sub>4</sub>H<sub>8</sub>)<sup>+</sup> were produced by the reactions of CrOH<sup>+</sup> with C<sub>2</sub>H<sub>4</sub> (ethylene) and C<sub>4</sub>H<sub>8</sub> (1-butene), resp., and were allowed to collide with a Xe atom under single collision conditions. The cross section for dissocn. of each parent cluster ion was measured as a function of the collision energy (collision-induced dissocn., or CID). It was found that (i) the CID cross section for the prodn. of CrOH<sup>+</sup> from CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> increases sharply at the threshold energy of 3.16 ± 0.22 eV and (ii) the CID cross section for the prodn. of CrOH<sup>+</sup> and C<sub>4</sub>H<sub>8</sub> from CrOH(C<sub>4</sub>H<sub>8</sub>)<sup>+</sup> also increases sharply at the threshold energy of 3.26 ± 0.21 eV. In comparison with the calcs. based on a B3LYP hybrid d. functional method, it is concluded that two ethylene mols. in CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> are polymd. to become 1-butene. The calcn. also shows that the dimerization proceeds via CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> (ethylene complex) and CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> (ethylene complex), in which the ethylene mols. bind with CrOH<sup>+</sup> through a  $\pi$ -bonding.

~4 Citings

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### 111. New Strategies in the Raman Study of the Cr/SiO<sub>2</sub> Phillips Catalyst: Observation of Molecular Adducts on Cr(II) Sites

By Groppo, Elena; Damin, Alessandro; Bonino, Francesca; Zecchina, Adriano; Bordiga, Silvia; Lamberti, Carlo  
 From *Chemistry of Materials* (2005), 17(8), 2019-2027. Language: English, Database: CAPLUS,  
 DOI:10.1021/cm050043k



We report the first Raman spectra of mol. adducts (CO and N<sub>2</sub>) formed on Cr(II) sites dispersed on silica surface (Phillips catalyst for ethylene polymn.), thus obtaining indirect information about the metal anchored species. These results have been achieved using an ad hoc selected laser line (able to excite a ligand to Cr charge-transfer transition that does not relax in a radiative channel), and adopting as a support a silica aerogel behaving as an optically uniform medium in the region of work. These two combined strategies, never simultaneously applied before, allowed us to obtain great quality Raman spectra of surface species, demonstrating that Raman spectroscopy can have great sensitivity toward surface species present in small concn. Raman spectroscopy thus becomes a powerful tool complementary to IR and UV-vis DRS spectroscopies for surface investigation. The improvement can be quantified by comparing published spectra of the oxidized Cr(VI)/SiO<sub>2</sub> system (the only available in the literature) with the more intense and much richer one obtained under the present exptl. conditions, where new spectroscopic features (never obsd. before) are clearly obsd.

~48 Citings

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### 112. In situ, Cr K-edge XAS study on the Phillips catalyst: activation and ethylene polymerization

By Groppo, E.; Prestipino, C.; Cesano, F.; Bonino, F.; Bordiga, S.; Lamberti, C.; Thuene, P. C.; Niemantsverdriet, J. W.; Zecchina, A.  
 From *Journal of Catalysis* (2005), 230(1), 98-108. Language: English, Database: CAPLUS,  
 DOI:10.1016/j.jcat.2004.11.017

In an in-situ EXAFS and XANES study on the Phillips ethylene-polymn. Cr/SiO<sub>2</sub> catalyst, two polymn. routes are investigated and compared. The first mimics that adopted in industrial plants, where ethylene is dosed directly on the oxidized catalyst, while in the second the oxidized catalyst is first reduced by CO at 623 K. On this reduced catalyst C<sub>2</sub>H<sub>4</sub> polymn. has been investigated at room temp. and at 373 K. To allow expts. in transmission mode, a Cr loading of 4 wt% has been adopted. At this loading a fraction of clustered Cr<sub>2</sub>O<sub>3</sub> particles has been obsd. and quantified. The use of a third-generation synchrotron radiation source has allowed us to improve the energy resoln. and signal-to-noise ratio of the XANES data, allowing us to det. the fraction of Cr sites involved in the polymn. reaction. This no. represents an upper limit of the active sites. Preliminary RefEXAFS expts. have been performed on a model catalyst prepd. by impregnation of Cr on a flat Si(100) substrate covered by a thin layer of amorphous silica. Expts. have been performed ex situ on the grafted catalyst (i.e., after impregnation and thermal activation) and at the end of the polymn. stage.

~65 Citings

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### 113. Photo-stability of surface chromate species on Phillips CrOx/SiO<sub>2</sub> catalysts isothermally calcined at various temperatures, probed by high resolution X-ray photoelectron spectroscopy

By Fang, Yuwei; Liu, Boping; Terano, Minoru  
 From *Applied Catalysis, A: General* (2005), 279(1-2), 131-138. Language: English, Database: CAPLUS,  
 DOI:10.1016/j.apcata.2004.10.023



**Phillips**  $\text{CrO}_x/\text{SiO}_2$  **catalyst** is still an important industrial **catalyst** for ethylene polymn. Poor understanding of the electronic states of surface chromate species has hindered further mechanistic exploration and improvement of this **catalyst** system. The objective of this work is to systematically study the photo-stability of **Phillips catalyst** by XPS method, since such photo-stability has not been well documented yet in the literature. Five catalysts: namely, PC200, PC300, PC400, PC600 and PC800 with 1.0 wt.% of Cr loading were prep'd. from the industrial **Phillips catalyst** precursor PCP120 at 200, 300, 400, 600 and 800°, resp. The photo-stability in terms of electronic stability for the surface chromate species ( $\text{Cr(VI)O}_{x,\text{surf}}$ ) on these catalysts was investigated by a high resoln. XPS method. The resistance to photo-redn. into supported  $\text{Cr(III)O}_{x,\text{surf}}$  species induced by X-ray irradiation during XPS measurement was studied. The photo-stability of surface chromate species on **Phillips catalyst** was significantly dependent on the calcination temp. for prep'n. of the catalysts. A correlation between the photo-stability of surface chromate species and the calcination temps. for **catalyst** prep'n. has been established. Deeper insight on the electronic states of surface chromate species on **Phillips** type catalysts has been achieved by high resoln. XPS methods.

~20 Citings

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#### 114. The Structure of Active Centers and the Ethylene Polymerization Mechanism on the $\text{Cr/SiO}_2$ **Catalyst**: A Frontier for the Characterization Methods

By Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A.

From *Chemical Reviews* (Washington, DC, United States) (2005), 105(1), 115-183. Language: English, Database: CAPLUS, DOI:10.1021/cr040083s

A review on progress in the understanding of structures active sites and strategies and techniques of study of the **catalyst** under working conditions. Methods adopted for studying  $\text{Cr/SiO}_2$  **catalyst** can be extended to other catalytic systems. Surface chem. of silica support was discussed. Literature on **Phillips catalyst** until 1985 was reviewed.

~258 Citings

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#### 115. A Chromium **Catalyst** for the Polymerization of Ethylene as a Homogeneous Model for the **Phillips Catalyst**

By MacAdams, Leonard A.; Buffone, Gerald P.; Incarvito, Christopher D.; Rheingold, Arnold L.; Theopold, Klaus H.

From *Journal of the American Chemical Society* (2005), 127(4), 1082-1083. Language: English, Database: CAPLUS, DOI:10.1021/ja043877x



A structurally characterized cationic chromium(III) alkyl featuring a bulky nacnac ligand catalyzes the polymn. of ethylene as well as the copolymn. of ethylene with  $\alpha$ -olefins. This well-characterized homogeneous **catalyst** constitutes a structural as well as functional model of the widely used heterogeneous **Phillips** olefin polymn. **catalyst**.

~98 Citings

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#### 116. Active sites transformations of Ziegler-Natta and **Phillips** catalysts

By Nakatani, Hisayuki; Boping, Liu; Terano, Minoru

From *Shokubai* (2004), 46(8), 622-627. Language: Japanese, Database: CAPLUS

A review. Two unique approaches were carried out in order to get better mechanistic understanding of Ziegler-Natta and **phillips** catalysts. At first, the deactivation phenomenon of Ziegler-Natta catalysts for propylene polymn. induced by the interaction with Al-alkyl cocatalyst was investigated. It was demonstrated that hydrogen dissocn. sites for chain transfer reaction was produced by the transformation of polymn. sites. The second attention was paid to the induction period of **Phillips catalyst**. It was found that ethylene metathesis sites were formed during the induction period followed by a transformation into polymn. sites with desorption of formaldehyde. Novel mechanisms in terms of active sites transformation were proposed for the better understanding of heterogeneous olefin polymn. catalysis.

~0 Citings

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#### 117. High resolution X-ray photoelectron spectroscopic analysis of transformation of surface chromium species on **Phillips** $\text{CrO}_x/\text{SiO}_2$ catalysts isothermally calcined at various temperatures

By Liu, Boping; Fang, Yuwei; Terano, Minoru

From [Journal of Molecular Catalysis A: Chemical](#) (2004), 219(1), 165-173. Language: English, Database: CAPLUS, DOI:10.1016/j.molcata.2004.05.001

High resolu. XPS surface anal. methods were used to study the transformation of chromium(III) acetate into supported chromate species ( $\text{Cr(VI)O}_{x,\text{surf}}$ ) of **Phillips**  $\text{CrO}_x/\text{SiO}_2$  catalysts isothermally calcined at various temps. The **Phillips** catalysts are used in industrial polyolefin prodn., esp. polyethylene. The specific transformation process of chromium(III) acetate into bulky  $\text{CrO}_3$  and subsequently into  $\text{Cr(VI)O}_{x,\text{surf}}$  as a function of calcination temp. at 120 - 800° was elucidated. The sp. surface components in various **catalyst** samples vs. calcination temp. were identified. Chromium(III) acetate was easily oxidized and decompd. into bulky  $\text{CrO}_3$  during 120° isothermal drying process. The bulky  $\text{CrO}_3$  started to be transformed into supported chromate species at 200° and could be completely stabilized on silica gel surface as chromate species at 400°. Significant amt. of bulky pentavalent Cr oxide ( $\text{Cr}_2\text{O}_5$  or  $(\text{Cr}_2\text{O}_7)^{4-}$ ) due to partial thermal decompn. of bulky  $\text{CrO}_3$  was only obsd. in a 200°-calcined sample due to the incomplete stabilization of bulky  $\text{CrO}_3$  into chromate species at 200°. As the precursor of active sites on calcined **Phillips catalyst**, the chromate species ( $\text{Cr(VI)O}_{x,\text{surf}}$ ) gradually became more and more electron-deficient with increasing calcination temp. of the **catalyst** from 200 to 800°. Only a slight thermal-induced partial redn. of chromate species into  $\text{Cr(III)O}_{x,\text{surf}}$  was obsd. at high temp. (600-800°).

~44 Citings

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### 118. Characterization of a model **Phillips catalyst** by mass spectrometry

By Di Croce, Pascal Gabriel; Aubriet, Frederic; Chety-Gimondo, Rachel; Muller, Jean-Francois; Grange, Paul

From [Rapid Communications in Mass Spectrometry](#) (2004), 18(6), 601-608. Language: English, Database: CAPLUS, DOI:10.1002/rcm.1375

A model **Phillips catalyst** for ethylene polymn., prepd. by spin coating a  $\text{Cr(III)}$  ( $\text{Cr(acac)}_3$ ) precursor on a silicon wafer, was submitted to an oxidative activation. Laser ablation Fourier transform mass spectrometry provided direct information on mol. species at the silicon wafer surface during activation. At 350°C the chromium precursor was degraded, while chromium oxide species were formed. The chromium concn. decreased with temp. The activated model **catalyst** was active for ethylene polymn. Using complementary techniques (Fourier transform IR spectroscopy, laser desorption/ionization mass spectrometry), the polymer was identified as cryst. polyethylene. After 1-h of polymn. at 160°C, dome-like structures were obsd. by at. force microscopy. Their morphologies were constituted of regions of parallel aligned lamellae of polymer.

~8 Citings

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### 119. A surface science model for the **Phillips ethylene polymerization catalyst**: thermal activation and polymerization activity

By van Kimmenade, E. M. E.; Kuiper, A. E. T.; Tamminga, Y.; Thune, P. C.; Niemantsverdriet, J. W.

From [Journal of Catalysis](#) (2004), 223(1), 134-141. Language: English, Database: CAPLUS, DOI:10.1016/j.jcat.2003.12.019

A series of  $\text{CrO}_x/\text{SiO}_2/\text{Si(100)}$  model catalysts were tested for ethylene polymn. activity, varying chromium loading, and calcination temp. Chromium coverage of the model **catalyst**, quantified by Rutherford backscattering spectrometry, decreases with increasing calcination temp. as some chromium desorbs from the silica support. The polymn. activity of the model catalysts is correlated to calcination temp. and chromium coverage. Based on the evidence presented, we propose that high local Cr coverage-short Cr-Cr distances is detrimental to polymn. activity, possibly because it facilitates dimerization leading to inactive chromium sites. Calcination at high temps. not only causes depletion of surface silanol groups, but may also facilitate the formation of isolated chromium sites, which can evolve into active polymn. centers. AFM images of nascent polymer films after short polymn. times offer a means to visualize the distribution of polymn. activity on the silica surface. The catalytically active chromium forms islands on the silica surface.

~37 Citings

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### 120. Procedure and apparatus for selection of polymerization catalysts

By Rhode, Wolfgang; Kristen, Marc Oliver; Lilge, Dieter

From [PCT Int. Appl.](#) (2004), WO 2004026919 A1 20040401, Language: English, Database: CAPLUS

In a method of selecting polymn. catalysts, in particular **Phillips** catalysts for the polymn. of olefins, from a multiplicity of catalysts on the basis of their catalytic properties, a multiplicity of **catalyst** precursors or **catalyst** supports are converted in parallel into polymn. catalysts in a pretreatment step in an array of reactors, where the pretreatment comprises at least one thermal treatment step at 250-1200°C. Furthermore, at least one starting material is converted with the aid of the resp. polymn. catalysts under prescribed polymn. conditions into at least one polymer product in a polymn. step and, finally, anal. of the polymer product or products is carried out to det. its compn. and/or chosen properties. This makes it possible to carry out a thermal pretreatment of polymn. catalysts quickly under defined conditions which can be varied. In the 1st step a heat treatment of **catalyst** precursors or **catalyst** supports is carried out at 250-1200°, in the 2nd step  $\geq 1$  monomer (ethylene, propylene, 1-butene) is (co)polymd. under predetd. polymn. conditions by use of the catalysts obtained in the 1st step, and in the 3d step the compns. of the polymers obtained in the previous step and their properties selected from d., mol. wt. distribution, intrinsic viscosity in soln., melt flow index and comonomer proportion, are analyzed (no examples).

#### ~0 Citings

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### 121. Procedure and apparatus for selection of polymerization catalysts

By Rohde, Wolfgang; Kristen, Marc Oliver; Lilge, Dieter

From [Ger. Offen. \(2004\)](#), [DE 10243239 A1 20040325](#), Language: German, Database: CAPLUS

In a rapid procedure for selection of a **catalyst** from a multiplicity of catalysts based on their catalytic properties, esp. **Phillips** catalysts for the polymn. of polyolefins, a variety of **catalyst** precursors or **catalyst** supports is converted into polymn. catalysts in a series of polymn. reactors. In the 1st step a heat treatment of **catalyst** precursors or **catalyst** supports is carried out at 250-1200°, in the 2nd step  $\geq 1$  monomer (ethylene, propylene, 1-butene) is (co)polymd. under predetd. polymn. conditions by use of the catalysts obtained in the 1st step, and in the 3d step the compns. of the polymers obtained in the previous step and their properties selected from d., mol. wt. distribution, intrinsic viscosity in soln., melt flow index and comonomer proportion, are analyzed (no examples).

#### ~0 Citings

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### 122. 1,3,5-Triazacyclohexane complexes of chromium as homogeneous model systems for the **Phillips catalyst**

By Koehn, Randolf D.; Smith, D.; Lilge, D.; Mihan, S.; Molnar, F.; Prinz, M.

From [ACS Symposium Series \(2003\)](#), [857\(Beyond Metallocenes\)](#), [88-100](#). Language: English, Database: CAPLUS, DOI:10.1021/bk-2003-0857.ch007

Complexes of N-substituted 1,3,5-triazacyclohexanes with  $\text{CrCl}_3$  can be activated by MAO or  $\text{PhNMe}_2\text{H}(\text{B}(\text{C}_6\text{F}_5)_4)/\text{AlR}_3$  to give solns. that can polymerize and/or trimerize ethylene depending on the N-substituents R with activities and polymer products similar to those of the heterogeneous **Phillips** catalysts.  $\alpha$ -Olefins are selectively trimerized or co-polymd. with ethylene. Variation of these substituents R showed a large dependence of the trimerization/polymn. ratio on branching in the N-substituent. Spectroscopic studies show that the triazacyclohexane stays coordinated during the catalysis and that mono-nuclear metallacyclic complexes with a weakly coordinating anion in one coordination site are likely involved.

#### ~1 Citing

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### 123. Long chain branching in polyethylene from the **Phillips catalyst**

By McDaniel, Max

From [Abstracts, 59th Southwest Regional Meeting of the American Chemical Society, Oklahoma City, OK, United States, October 25-28 \(2003\)](#), [167](#). Language: English, Database: CAPLUS

The Phillips chromium oxide catalyst has been used com. for nearly half a century to produce perhaps 50% of the world's high d. polyethylene. One of the key attributes that det. the acceptability of these polymers for com. applications is the level of long chain branching (LCB) imparted by the catalyst, because LCB influences the flow behavior of molten polymer, its melt strength, die swell, melt fracture, orientation, pipe slumping, and film bubble stability. Consequently Phillips and other PE manufacturers have developed proprietary catalysts to exploit or limit these LCB-related characteristics. Macromonomer incorporation has long been postulated as the mechanistic origin for LCB from the Phillips catalyst (and more recently from metallocenes as well). Chain transfer occurs through beta-H elimination, which leaves a terminal vinyl on the end of polymer chains. These vinyls are then thought to randomly copolymerize with ethylene in another growing chain, creating a long chain branch. The event occurs very infrequently, leading to one branch in say 10<sup>6</sup> or 10<sup>5</sup> carbons, but this is enough to have profound rheol. consequences. Although commonly accepted, this simple view still leaves many questions concerning LCB prodn. A macromonomer reactant is conceivable in a soln. process, but in slurry or gas phase processes, where the chains become immobilized as they are formed, it is a bit more difficult to understand. Another problem with the mechanism is the ability of some catalysts to produce more LCB than others. One might expect catalysts that most efficiently incorporate large comonomers (1-hexene or 1-octene) to also produce the highest levels of LCB, but this is not always the case. Actually, for chromium oxide catalysts, the variables that seem to have the strongest influence on LCB-related character in the polymer, such as Cr loading, activation temp., and porosity, have no obvious explanation by the simple macromonomer incorporation mechanism. Likewise other expected LCB variables, like ethylene concn., do not always provide the predicted LCB response. The major variables considered to affect LCB are cataloged in this talk and each response is discussed. LCB from soln. and slurry processes are also compared. These and other problems with the simple macromer insertion view suggest that, at a min., a more complex picture of the mechanism of LCB formation is required.

#### ~0 Citings

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### 124. Supported chromium catalysts for ethylene polymerization

By Katzen, Stanley J.; Lin, Zerong; Specia, Anthony N.; Kendrick, James A.; Roger, Scott T.

From [U.S. Pat. Appl. Publ. \(2003\), US 20030232715 A1 20031218](#), Language: English, Database: CAPLUS

A method of forming a catalyst system in a polymn. reactor comprises (a) providing a supported chromium catalyst, (b) providing a trialkylaluminum cocatalyst of the formula AlR<sub>3</sub>, where each R group is independently a linear or branched C<sub>4</sub>-C<sub>12</sub>-alkyl group, and (c) contacting the catalyst and cocatalyst by (i) cofeeding the catalyst and cocatalyst to the reactor, or (ii) feeding the catalyst and cocatalyst sep. to the reactor, the catalyst and cocatalyst being not contacted prior to the feeding step. The catalysts can be contacted with ethylene and optional  $\alpha$ -olefin comonomers to produce ethylene homopolymers or copolymers. Polyethylene produced in the presence of the invention catalysts has improved properties, such as environmental stress crack resistance. Thus, a silica-supported chromium catalyst (HA 30W) activated with triisobutylaluminum (Al:Cr mol ratio of 4.5) showed activity of 2,138 g/(g h) in slurry polymn. of ethylene, the process being carried out in isobutane at 107° with ethylene pressure of 180 psi and total pressure of 460-500 psig.

#### ~6 Citings

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### 125. Temperature resolved FTIR spectroscopy of Cr<sup>2+</sup>/SiO<sub>2</sub> catalysts: acetylene and methylacetylene oligomerization

By Zecchina, A.; Bertarione, S.; Damin, A.; Scarano, D.; Lamberti, C.; Prestipino, C.; Spoto, G.; Bordiga, S.

From [Physical Chemistry Chemical Physics \(2003\), 5\(20\), 4414-4417](#). Language: English, Database: CAPLUS, DOI:10.1039/B305805K

As is well known, the Cr<sup>2+</sup>/SiO<sub>2</sub> system is an efficient catalyst for ethylene polymn. already at RT (even if in the industrial process the running temp. is ~380 K). For this reason it is the ideal system for in situ spectroscopic investigations on a genuinely working catalyst (Adv. Catal., 2001, 46, 265). Many questions are still uncertain as to the initiation, propagation and termination steps of the polymn. mechanism. On a pre-reduced sample polymn. commences very quickly and there is no way to record initial stages. When the expts. are performed at RT the phenomenon is too fast and IR spectroscopy, even in the time-resolved mode, failed up to now in the identification of the species formed during the initiation of the ethylene polymn. step on the Cr<sup>2+</sup>/SiO<sub>2</sub> Phillips catalyst. We present results related to time-resolved FTIR spectroscopy at variable temp. of acetylene and methylacetylene oligomerization on a model Phillips catalyst. These expts. have been highly informative on the nature of the active sites because we have obsd. that acetylene and methylacetylene result in the immediate formation of benzene and 1,3,5-trimethylbenzene, resp., without the evidence of any measurable intermediate product. This implies that the active Cr sites are able to coordinate simultaneously three monomers and thus must exhibit a high un-satn. coordination. The results of these expts. could be an insight of chromium species active in the Phillips catalyst.

#### ~14 Citings

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**126. Theoretical models of active sites: general considerations and application to the study of Phillips-type Cr/silica catalysts for ethylene polymerization**

By Borge, Knut J.; Espelid, Oystein

Edited By: Scott, Susannah L.; Crudden, Cathleen M.; Jones, Christopher W

From *Nanostructured Catalysts* (2003), 85-111. Language: English, Database: CAPLUS, DOI:10.1007/978-0-387-30641-4\_4

A review. Quantum chem. cluster-model approxns. are briefly reviewed as tools for studying local properties of solid surfaces. In its mol.-cluster version, this technique is applied to Phillips-type Cr/silica catalysts for ethylene polymn. and used to discuss spectroscopic and catalytic properties of low-valent chromium sites. The characterization part includes d-d electronic transitions as well as IR vibrational spectra of adsorbed carbonyl species. Comparison to exptl. spectra facilitates identification of surface species. Next, cluster models are used to investigate if and how polymn. may be initiated and sustained at the most topical of the proposed active sites. Two of the chromium sites studied here show promising activity for ethylene polymn.

~2 Citings

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**127. On the first stages of the ethylene polymerization on Cr<sup>2+</sup>/SiO<sub>2</sub> Phillips catalyst: time and temperature resolved IR studies**

By Bordiga, S.; Bertarione, S.; Damin, A.; Prestipino, C.; Spoto, G.; Lamberti, C.; Zecchina, A.

From *Journal of Molecular Catalysis A: Chemical* (2003), 204-205, 527-534. Language: English, Database: CAPLUS, DOI:10.1016/S1381-1169(03)00335-2

IR spectroscopy, even in the time resolved mode, failed up to now in the identification of the species formed during the initiation of the ethylene polymn. step on the Cr<sup>2+</sup>/SiO<sub>2</sub> Phillips catalyst. To overcome this problem in this investigation we have designed and performed new expts. allowing to collect IR spectra at lower T or/and in presence of a poison (CO), which are both exptl. conditions where the polymn. rate is so highly depressed to hopefully allow the detection of the species formed in the initiation stage. Time, pressure and temp. dependent IR spectra collected in the 173-300 K range on the Cr<sup>2+</sup>/SiO<sub>2</sub> catalyst in CO/C<sub>2</sub>H<sub>4</sub> atmosphere show, at the lowest temps., the formation of mixed Cr<sup>2+</sup>... (CO)(C<sub>2</sub>H<sub>4</sub>) physisorbed complexes and, upon increasing the temp. the switching on of the C<sub>2</sub>H<sub>4</sub> polymn. A 5-10% fraction of Cr<sup>2+</sup> sites forming the mixed Cr<sup>2+</sup>... (CO)(C<sub>2</sub>H<sub>4</sub>) is sufficient to greatly inhibit the polymn. activity. This suggest that the Cr<sup>2+</sup> sites active at 300 K represent a small fraction of the total no. of Cr<sup>2+</sup> sites present on the surface of the catalyst.

~15 Citings

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**128. New proposal on the branching mechanism of Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst for ethylene homo-polymerization**

By Terano, Minoru; Liu, Boping; Fang, Yuwei

From *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* (2003), 44(2), 22-23. Language: English, Database: CAPLUS

To study mechanism of Phillips catalyst-mediated polymn. of ethylene, industrial calcined catalyst (Cr(VI)O<sub>x</sub>/SiO<sub>2</sub>) was treated with ethylene gas at different conditions and the reaction was followed by XPS and TPD measurements. The formation of Cr-alkylidene species during induction period was confirmed. The transformation of ethylene metathesis site into polymn. site was also obsd. Based on these findings, plausible mechanisms concerning the formation of short and long chain branches through metathesis during ethylene homopolymn. were proposed.

~4 Citings

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**129. New proposal on the branching mechanism of Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst for ethylene homo-polymerization**

By Terano, Minoru; Liu, Boping; Fang, Yuwei

From *Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003* (2003), POLY-181. Language: English, Database: CAPLUS

As one of the most important industrial polyolefin catalysts, **Phillips catalyst** is still producing ca. 40% of world HDPE per yr. It is most interesting to note that **Phillips catalysts** always produce PE with both short and long chain branches (SCB and LCB) as well as broad mol. wt. distribution, which contribute to its unique properties regarding processing and final applications. However, the polymn. mechanism still remains mysterious in spite of half century of great efforts. Recently, the first evidence indicating an ethylene metathesis initiation before polymn. on **Phillips catalyst** has been obtained. In this work, the first direct XPS evidence of the Cr-alkylidene species was successfully obtained. The transformation of ethylene metathesis site into polymn. site was obsd. Based on these evidences, the formation mechanisms of SCB and LCB during ethylene homo-polymn. were considered to be different from traditional Ziegler-Natta catalysts, which will be discussed in detail.

~0 Citings

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### 130. Flame-retardant ethylene- $\alpha$ -olefin copolymer compositions with good high-speed processability, electric cables jacketed with them, and their manufacture

By Tachikawa, Takeshi; Oki, Yumi

From [Jpn. Kokai Tokkyo Koho \(2003\)](#), [JP 2003183456 A 20030703](#), Language: Japanese, Database: CAPLUS

Title compns. contain 100 parts a (5-95):(5-95) mixt. of linear ethylene (l)- $\alpha$ -olefin copolymers with  $M_w/M_n$  7-20, MFR 0.2-5 g/10 min, and d. 0.90-0.96 g/cm<sup>3</sup>, and linear l- $\alpha$ -olefin copolymers with  $M_w/M_n$  2 to <7, MFR 0.2-10 g/10 min, and d. 0.86-0.96 g/cm<sup>3</sup>, and 30-180 parts metal hydroxides. Title cables are manufd. by extruding the compns. onto metal conductors at  $\geq 200$  m/min to form an insulating layer and/or sheath layer. Thus, a compn. contg. linear l-butene-1 copolymer ( $M_w/M_n$  15.1, MFR 0.7 g/10 min, d. 0.920 g/cm<sup>3</sup>, manufd. with **Phillips catalyst**) 50, linear l-octene-1-copolymer ( $M_w/M_n$  5.1, MFR 3 g/10 min, d. 0.901 g/cm<sup>3</sup>, manufd. with Ziegler catalyst) 50, and Magseeds N 4 [surface-treated Mg(OH)<sub>2</sub>] 100 parts showed tensile stress 11 MPa, low-temp. brittleness -25°, and O index 26%.

~0 Citings

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### 131. Mechanistic implications of the unprecedented transformations of ethene into propene and butene over **Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst** during induction period

By Liu, Boping; Nakatani, Hisayuki; Terano, Minoru

From [Journal of Molecular Catalysis A: Chemical \(2003\)](#), [201\(1-2\)](#), 189-197. Language: English, Database: CAPLUS, DOI:10.1016/S1381-1169(03)00151-1

In this work, an industrial calcined **Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst** engaged in the induction period through interaction with ethene at ambient conditions was characterized by temp.-programmed desorption (TPD) equipped with a quadrupole mass spectrometer (MS). It was unprecedented to find that the first hydrocarbon species had already been formed and was obsd. to be propene instead of the expected butene. In fact, butene is the second hydrocarbon species formed after propene during the induction period. This evidence strongly implied that the initiation in terms of Cr-carbon bond formation on the **Phillips catalyst** occurs through an ethene metathesis mechanism during the induction period. Three most possible routes regarding the ethene metathesis initiation and formation of the first hydrocarbon species propene during the induction period on the **Phillips catalyst** were proposed.

~41 Citings

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### 132. Ethylene polymer-propylene polymer multilayer blow-molded containers for liquid dairy products

By Kurumi, Jiro

From [Jpn. Kokai Tokkyo Koho \(2003\)](#), [JP 2003053915 A 20030226](#), Language: Japanese, Database: CAPLUS

The containers, having volatile C<sub>6-10</sub> hydrocarbon content of  $\leq 300$  ppm and C<sub>11-30</sub> oligomer fraction of  $\leq 600$  ppm, comprise  $\geq 2$  layers having outermost layers contg. propylene polymers, neutralizing agents, and phenolic antioxidants and/or hindered amine stabilizers and innermost layers contg. ethylene polymers. Thus, a container comprised an outer layer comprising a compn. contg. 100 parts ethylene-propylene copolymer manufd. using Ziegler-Natta catalyst, 0.1 part Irganox 1010 (phenolic antioxidant), 0.1 part Irgaphos 168 (P-based antioxidant), and 0.05 part Ca stearate, an intermediate layer comprising 1:1 blend of the compn. and ethylene-1-butene copolymer manufd. by using **Phillips catalyst**, and an inner layer comprising the copolymer. Milk coffee packaged in the container was stored at 80° for 2 h, showing no flavor change.

~0 Citings

**133. Performance of the  $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{SiO}_2$  catalyst for ethylene polymerization compared with the performance of the Phillips catalyst**

By Ikeda, Haruhiko; Monoi, Takashi; Sasaki, Yasuaki

From *Journal of Polymer Science, Part A: Polymer Chemistry* (2003), 41(3), 413-419. Language: English, Database: CAPLUS, DOI:10.1002/pola.10590

The activity of a silica-supported chromium system  $[\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{SiO}_2]$  was compared with a silica-supported chromium oxide catalyst, the Phillips catalyst ( $\text{CrO}_3/\text{SiO}_2$ ) for HDPE prodn. In slurry-phase polymn., this catalyst promoted the polymn. of ethylene at a high activity without organoaluminum compds. as cocatalysts or scavengers. The activity per Cr was about 6-7 times higher than that of the Phillips catalyst. Upon the introduction of hydrogen to the system, the mol. wt. of the HDPE did not change with the Phillips catalyst, but it decreased with the  $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3/\text{SiO}_2$  catalyst.

~18 Citings

**134. Elaboration and characterization of a model Phillips catalyst for ethylene polymerization**

By Di Croce, P. G.; Aubriet, F.; Bertrand, P.; Rouxhet, P.; Grange, P.

From *Studies in Surface Science and Catalysis* (2002), 143(Scientific Bases for the Preparation of Heterogeneous Catalysts), 823-835. Language: English, Database: CAPLUS

A model Phillips catalyst for ethylene polymn. has been prepd. by spin coating of a Cr(III) precursor ( $\text{Cr}(\text{acac})_3$ ) on a flat silicon wafer (100) covered by amorphous silica. The spin coating parameters were chosen in order to obtain a homogeneous film. The model catalyst was submitted to an activation process. The surface concn. of Cr decreased from about 0.8 to 0.4 Cr atom/nm<sup>2</sup> as the temp. increased from 150 to 550°C. Direct information concerning the surface mol. species and the environment of Cr was provided by ToF-SIMS and XPS. At 350°C, the catalyst precursor was decompd.; Cr species were in the form oxide and surface-anchored chromates. Upon final activation at 650°C for 6 h, Cr species were below the XPS detection limit; however the model catalyst was active for ethylene polymn. at 160°C and 2 bar pressure.

~3 Citings

**135. Additive interactions in the stabilization of film grade high-density polyethylene. Part II: stabilization during long-term service**

By Parrondo, Aitor; Allen, Norman S.; Edge, Michele; Liauw, Christopher M.; Fontan, Eusebio

From *Journal of Vinyl & Additive Technology* (2002), 8(2), 90-102. Language: English, Database: CAPLUS, DOI:10.1002/vnl.10350

The performance of phenol/phosphite/Zn stearate packages and the contribution of each additive to the long-term thermal stabilization and photostabilization of HDPE film were evaluated using Phillips catalyst technol. IR, UV and yellowness index measurements were used to establish the performance of the additive combinations. HPLC anal. of dichloromethane exts. of the polymer was carried out after melt processing to det. the amt. of phenolic antioxidant remaining in the samples. The long-term thermal stabilization was dependent only on the phenolic antioxidant concn., whereas both phenolic antioxidants and phosphites contributed directly to photostabilization. Zn stearate did not show any significant influence on the stabilization under either thermooxidative or photooxidative conditions.

~3 Citings

**136. Additive interactions in the stabilization of film grade high-density polyethylene. Part I: stabilization and influence of zinc stearate during melt processing**

By Parrondo, Aitor; Allen, Norman S.; Edge, Michele; Liauw, Christopher M.; Fontan, Eusebio; Corrales, Teresa

From *Journal of Vinyl & Additive Technology* (2002), 8(2), 75-89. Language: English, Database: CAPLUS, DOI:10.1002/vnl.10349

The melt stabilization activity of com. phenolic antioxidants and phosphites (alone and in combination), with and without Zn stearate, was studied in HDPE produced by **Phillips catalyst** technol. Multiple pass extrusion expts. were used to progressively degrade the polymer melt. The effect of stabilizers was assessed via melt flow rate and yellowness index measurements conducted as a function of the no. of passes. The level of the phenolic antioxidant remaining after each extrusion was detd. by HPLC. Phenolic antioxidants and phosphites both improve the melt stability of the polymer in terms of melt viscosity retention; the influence of Zn stearate is almost insignificant. However, the phosphites and Zn stearate decrease the discoloration caused by the phenolic antioxidants. A correlation was found between the melt stabilization performance of phosphites and their hydroperoxide decompn. efficiency detd. via a model hydroperoxide compd. Steric and electronic effects assocd. with P influence the reactivity towards hydroperoxides. Furthermore, high hydrolytic stability did not automatically result in lower efficiency. Besides the phosphite mol. structure, stabilization activity also was influenced by the structure of the primary phenolic antioxidant and the presence of Zn stearate.

~11 Citings

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### 137. New aspects of the induction period of ethene polymerization using **Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst** probed by XPS, TPD and EPMA

By Liu, Boping; Nakatani, Hisayuki; Terano, Minoru

From *Journal of Molecular Catalysis A: Chemical* (2002), 184(1-2), 387-398. Language: English, Database: CAPLUS, DOI:10.1016/S1381-1169(02)00019-5

In this work, an industrial **Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst** engaged in the induction period through interaction with ethene at room temp. (RT) was studied by the combination of surface anal. methods: XPS, temp. programmed desorption (TPD) and electron probe microanal. (EPMA). XPS method disclosed the redn. of surface chromate species (expressed as Cr(VI)O<sub>x,surf</sub>) into surface-stabilized Cr<sup>3+</sup> and Cr<sup>2+</sup> species (expressed as Cr(III)O<sub>x,surf</sub> and Cr(II)O<sub>x,surf</sub>, resp.) by monomer during the induction period and the simultaneous formation of two kinds of surface carbon species, namely, formaldehyde and unsatd. hydrocarbons. The hydrocarbon species were supposed to be composed of not only coordinated ethene, but also adsorbed longer olefin chains. TPD measurement confirmed the formation of formaldehyde. EPMA characterization revealed that the surface Cr aggregation occurred in a low extent during the induction period resulting in a few Cr islands in sizes of several microns on **catalyst** surface. It was demonstrated that redn. and alkylation of Cr species as well as initiation of ethene insertion had already occurred even in the induction period. A mechanism concerning the reactions occurred during the induction period on the **Phillips catalyst** was proposed. The Cr(II)O<sub>x,surf</sub> species coordinated with one formaldehyde and one ethene is postulated to be the active sites precursor for the alkylation as well as initiation of the ethene insertion. The coordinatively-adsorbed formaldehyde mols. on the **catalyst** are supposed to be the very reason for the hindered ethene oligomerization rather than normal polymn., as well as for the induction of the surface Cr aggregation.

~53 Citings

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### 138. 1,3,5-Triazacyclohexane complexes of chromium as homogeneous model for the **Phillips Catalyst CrO<sub>3</sub>/SiO<sub>2</sub>**

By Koehn, Randolph D.; Smith, David; Schichtel, Bjoern; Kociok-Koehn, Gabriele; Lilge, Dieter; Mihan, Shahram; Molnar, Ferenc; Maas, Heiko

From *PMSE Preprints* (2002), 86, 313. Language: English, Database: CAPLUS

1,3,5-Triazacyclohexane complexes of chromium was prepd. by one-pot synthesis from 4-phenyl-1-butylamine, paraformaldehyde, and CrCl<sub>3</sub> was used as **catalyst** for polymn. of ethylene using methylaluminoxane as activators.

~0 Citings

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### 139. Molecular-level insight into Cr/silica **Phillips-type catalysts**: polymerization-active dinuclear chromium sites

By Espelid, Oystein; Borge, Knut J.

From *Journal of Catalysis* (2002), 206(2), 331-338. Language: English, Database: CAPLUS, DOI:10.1006/jcat.2001.3499



Prospects of ethylene polymn. over dinuclear Cr(II) sites of the reduced Cr/SiO<sub>2</sub>-based **Phillips catalyst** have been investigated by means of cluster models and gradient-cor. d. functional theory. The starting structure for polymn. is considered to arise through reactions between ethylene and the dichromium site. A feasible route is found to a structure with a butane moiety suspended between the two chromium centers. The bridging alkane ligand may grow by facile insertion of ethylene into either of the chromium-carbon bonds. The relative rates of monomer insertion and termination through  $\beta$ -hydrogen transfer, as a function of the length of the bridging org. ligand, agrees with the prodn. of 1-hexene obsd. during early stages of polymn.

~35 Citings

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#### 140. 1,3,5-Triazacyclohexane complexes of chromium as homogeneous model for the **Phillips catalyst** CrO<sub>3</sub>/SiO<sub>2</sub>

By Kohn, Randolph D.; Smith, David; Schichtel, Bijjoern; Kociok-Kohn, Gabriele; Lilge, Dieter; Mihan, Shahram; Molnar, Ferenc; Maas, Heiko

From [Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002 \(2002\)](#), PMSE-031. Language: English, Database: CAPLUS

Chromium based heterogeneous catalysts are being used com. for over forty years. However, there are only few chromium complexes that act as single site catalysts with sufficient polymn. activity. New highly active chromium pre-catalysts react sensitively upon changing the substitution pattern, producing a range of products from liq. olefins to ultra high mol. wt. polyethylene. In combination with methylaluminoxane, these catalysts are among few homogeneous model systems, which allow investigation of the reaction mechanism and unique characteristics of conventional chromium catalysts. A simple one-pot synthesis, mechanistic and product control aspects of these new **catalyst** families will be described.

~0 Citings

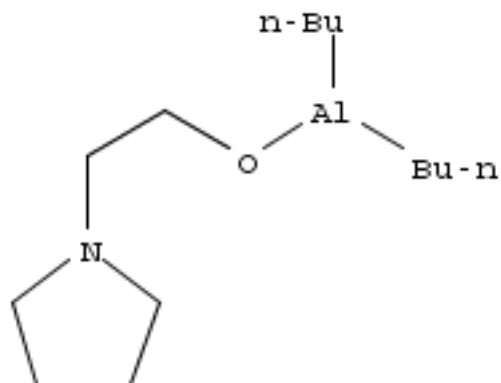
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#### 141. Hexavalent Chromium-based **Phillips** polymerization catalysts and manufacture of ethylene polymers using them and hydrogen for blow moldings

By Monoi, Hisashi; Tori, Hidenobu

From [Jpn. Kokai Tokkyo Koho \(2002\)](#), JP 2002020412 A 20020123, Language: Japanese, Database: CAPLUS

The catalysts, useful for manufg. gasoline tanks and drums, contain inorg. oxide-supported Cr<sup>6+</sup>-contg. solid components (A) prepd. by sintering under nonreducing conditions, dialkylaluminum functional group-contg. alkoxides (B), and trialkylaluminum (C). Thus, liq.-phase polymn. of ethylene (I) and 1-hexene in the presence of H and a **catalyst** [prepd. from CariAct P 6 (SiO<sub>2</sub>)-supported CrO<sub>3</sub>, dibutylaluminum methoxyethoxide, and tributylaluminum] at the wt. ratio of H/I 8.4 × 10<sup>-4</sup> resulted in a polymer with M<sub>n</sub> 2.1 × 10<sup>4</sup>, M<sub>w</sub> 35.2 × 10<sup>4</sup>, and good creep and environmental stress cracking resistance.



~0 Citings

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#### 142. Effects of **catalyst** activity profiles on polyethylene reactor dynamics

By Wells, Gary J.; Ray, W. Harmon; Kosek, Juraj

From [AIChE Journal \(2001\)](#), 47(12), 2768-2780. Language: English, Database: CAPLUS, DOI:10.1002/aic.690471215

The dynamics and stability characteristics of slurry loop and tank reactors were studied using continuation anal. to examine the effects of **catalyst** activity profiles on reactor dynamics. The prodn. of high-d. polyethylene through the copolymn. of ethylene with hexene was studied using catalysts of the decay type (for example,  $\text{TiCl}_4$  on silica, or other Ziegler-Natta catalysts) and the buildup-type (for example, chromium oxide catalysts on silica of the **Phillips** type). Sustained oscillations were found to exist for decay-type catalysts in loop reactors. For both tank and loop reactors, the buildup-type **catalyst** exhibited isolated soln. branches (isola) and multiplicity phenomena in addn. to sustained oscillations. The sigmoidal shape of the buildup-type **catalyst** rate curve is postulated as the reason for the addnl. multiplicity and isola phenomena. The implications for industrial operating conditions are discussed.

~4 Citings

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#### 143. Theoretical Analysis of CO Adsorption on the Reduced Cr/Silica System

By Espelid, Oystein; Borge, Knut J.

From [Journal of Catalysis](#) (2002), 205(1), 177-190. Language: English, Database: CAPLUS, DOI:10.1006/jcat.2001.3416

Cluster models are constructed for mononuclear Cr(II) and Cr(III) sites as well as dinuclear Cr(II) sites of the reduced Cr/SiO<sub>2</sub>-based **Phillips catalyst**. The binding energies and structures of oligocarbonyl complexes formed at these cluster models have been computed using d. functional theory. Furthermore, harmonic frequencies and IR intensities are calcd. for the carbonyl stretching modes of these complexes. The resulting parameters are compared to literature spectra of CO-exposed **Phillips** catalysts and related model systems. A reassignment is proposed for the IR spectrum of carbon monoxide on the reduced Cr/silica system. (c) 2002 Academic Press.

~24 Citings

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#### 144. Manufacture process for bimodal ethylene-based polymers by a **catalyst** system containing both Ziegler-Natta **catalyst** and chromium **catalyst**

By Hernandez-Vaquero Alvarez, Jose Luis; Del Amo Fernandez, Bernardo; Fernandez Sibon, Francisco Jose; Rodriguez Sinoga, Jesus; Madueno Casado, Manuel

From [Eur. Pat. Appl.](#) (2001), EP 1153943 A1 20011114, Language: English, Database: CAPLUS

The **catalyst** system, for producing ethylene homopolymer or copolymers with broad mol. wt. distribution, comprises two active catalysts: a chromium-contg. (**Phillips**) **catalyst** and a titanium-contg. (Ziegler) **catalyst**., wherein both catalysts are supported on silica. The catalysts are pre-mixed for joint addn. and introduced into the olefin polymn. reactor through individual dosing.

~3 Citings

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#### 145. Theoretical analysis of d-d transitions for the reduced Cr/silica system

By Espelid, Oystein; Borge, Knut J.

From [Catalysis Letters](#) (2001), 75(1-2), 49-54. Language: English, Database: CAPLUS

Cluster models are constructed for mono- and dinuclear Cr(II) sites and mononuclear Cr(III) sites on the Cr/SiO<sub>2</sub> **Phillips catalyst** and used to compute d-d transition energies and intensities. Mononuclear pseudo-tetrahedral Cr(II) gives rise to 2 bands of elec.-dipole-allowed d-d transitions, at 8,400 and 12,300 cm<sup>-1</sup>. This doublet is lowered in energy and intensity as the bond angle about Cr, OCrO, opens up. The dinuclear site gives rise to bands at 5,200 and 10,300 cm<sup>-1</sup>, consistent with calcns. for a mononuclear cluster of comparable value for OCrO. A tricoordinated Cr(III) cluster shows bands of comparable oscillator strengths at energies of 11,000, 16,000, 18,000-20,000 and 33,000 cm<sup>-1</sup>. The predicted bands correspond well with d-d bands in exptl. diffuse reflectance spectra.

~24 Citings

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#### 146. Polyolefin blends containing polyolefins prepared using late transition metal catalysts

By Christie, Susan Katherine; Samson, John Norman Reid; Reed, Warren

From [Eur. Pat. Appl.](#) (2001), EP 1125979 A1 20010822, Language: English, Database: CAPLUS

The polymer blend comprises  $\geq 1$  polymer made using a late transition metal catalyst, and  $\geq 1$  polyolefins made using a free radical process or polymd. using a Phillips type (chromium oxide) catalyst, a metallocene catalyst, or a Ziegler-Natta catalyst. Thus, 70% polyethylene prepd. by polymn. using EP 30 (silica supported Phillips catalyst) as catalyst was mixed with 30% polyethylene prepd. by polymn. using 2,6-diacetylpyridinebis(2,4,6 trimethylanil)FeCl<sub>2</sub> supported on silica as catalyst and other additives, and pelletized, showing melt flow rate (2.16 kg) 0.30 g/10 min and annealed d. 954.0 kg/m<sup>3</sup>.

#### ~1 Citing

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### 147. Containers for hydrogen peroxide-containing liquid.

By Kodama, Hiroto; Kawai, Keiji

From *Jpn. Kokai Tokkyo Koho* (2001), JP 2001206334 A 20010731, Language: Japanese, Database: CAPLUS

The title containers are formed from polyethylene or ethylene- $\alpha$ -olefin copolymer having d. 0.940-0.970 g/cm<sup>3</sup> and polymd. in the presence of activity-improved Phillips catalyst or metallocene catalyst, having gel permeation chromatog.-measured wt. av. mol. wt. (12-35)  $\times 10^4$ , and contg. 0.01-5 wt.% polymers having mol. wt.  $\leq 1 \times 10^3$ .

#### ~0 Citings

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### 148. Investigation of the physico-chemical state and aggregation mechanism of surface Cr species on a Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst by XPS and EPMA

By Liu, B.; Terano, M.

From *Journal of Molecular Catalysis A: Chemical* (2001), 172(1-2), 227-240. Language: English, Database: CAPLUS, DOI:10.1016/S1381-1169(01)00121-2

XPS and electron probe microanal. (EPMA) were jointly applied to achieve some basic understandings of the physico-chem. state and aggregation mechanism of surface Cr species on an industrial Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalyst calcined in dry air at 800°C for 20 h with 0.4 Cr/nm<sup>2</sup>. The XPS results showed the coexistence of surface-stabilized hexavalent chromate species (70.4% expressed as Cr(VI)O<sub>x, surf</sub>) and trivalent chromium oxide (29.6%) on the catalyst. The latter derived from calcination-induced redn. of the Cr(VI)O<sub>x, surf</sub> species is mostly chem.-bonded to the silica surface (expressed as Cr(III)O<sub>x, surf</sub>). The EPMA map and line curves of the Cr distribution state on the catalyst revealed a small amt. of the trivalent chromium oxide existed as a few aggregates in sizes of 200-300 nm on the surface of each particle, which were supposed to be crystd. aggregates of Cr<sub>2</sub>O<sub>3</sub>. Consequently, the calcination-induced redn. of Cr(VI)O<sub>x, surf</sub> to Cr(III)O<sub>x, surf</sub> species and the formation of Cr<sub>2</sub>O<sub>3</sub> microcrystals on the Phillips catalyst with relatively low Cr loading were specifically confirmed. The variation of distribution and oxidn. states of surface Cr species for the catalyst after being further calcined at 800°C for 2 h in the presence of moisture had also been studied in terms of the role of moisture and effect of atm. (pure air or N<sub>2</sub>). It was found that the purposely introduced moisture induced the transformation of all the Cr(III)O<sub>x, surf</sub> and one-seventh of Cr(VI)O<sub>x, surf</sub> species into aggregates of Cr<sub>2</sub>O<sub>3</sub> at high temp., whereas oxidizing and inert atmospheres made no obvious difference. Finally, the formation mechanism of aggregates of Cr<sub>2</sub>O<sub>3</sub> induced by moisture through cleavage of Cr(III)O<sub>x, surf</sub> species during the calcination had been speculated considering of the indispensable evolution of traces of moisture from the simultaneous dehydroxylation of residual hydroxyl groups on silica surface. The advantages of the combination of XPS and EPMA techniques for the basic investigation of Phillips catalysts were substantiated by the results obtained in this study.

#### ~69 Citings

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### 149. Surface analytical approaches for the Phillips catalyst by EPMA and XPS

By Liu, Boping; Shimizu, Takami; Terano, Minoru

Edited By: Blom, Richard

From *Organometallic Catalysts and Olefin Polymerization* (2001), 206-216. Language: English, Database: CAPLUS, DOI:10.1007/978-3-642-59465-6\_17

Electron probe microanal. (EPMA) and XPS were jointly applied to study the distribution state of Cr species on a Phillips catalyst with 1 wt.-% Cr loading. The EPMA images revealed the existence of aggregates of Cr species in sizes of 200-300 nm on the surface of the catalyst, which were supposed to be crystd. aggregates of chromia (Cr<sub>2</sub>O<sub>3</sub>). The variation of distribution state of Cr for the catalyst after being treated in various moisture-contg. atmospheres was also studied. Aggregation of Cr species occurred in all treatments. Correspondingly, the variation of binding energy and full width of half max. intensity of the Cr2p (3/2) spectrum from the XPS anal. gave further evidence for identification of all Cr species formed after the treatments. The formation mechanism of crystd. aggregates of chromia during the calcination of the Phillips catalyst was postulated to be related with a surface-stabilized trivalent Cr species.

## ~5 Citings

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**150. 1,3,5-triazacyclohexane complexes of chromium as homogeneous model systems for the Phillips catalyst**

By Kohn, Randolph D.; Seifert, Guido; Kociok-Kohn, Gabriele; Mihan, Shahram; Lilge, Dieter; Maas, Heiko

Edited By: Blom, Richard

From [Organometallic Catalysts and Olefin Polymerization \(2001\)](#), 147-155. Language: English, Database: CAPLUS, DOI:10.1007/978-3-642-59465-6\_13

1,3,5-Triazacyclohexane complexes prep'd. from N-substituted triazacyclohexanes and  $\text{CrCl}_3$  can be activated by MAO or trialkylaluminum/dimethylanilinium tetrakis(pentafluorophenyl)borate to give solns. that have unprecedented high activities in the polymn. and/or trimerization of ethylene, depending on the N-substituent.  $\alpha$ -Olefins are selectively trimerized or co-polym'd. with ethylene. The N-substituents in sym.- and asym.-substituted triazacyclohexanes, including some with different functional groups, are varied in order to obtain a better understanding of their effect on catalysis. A detailed study of the activities and the polymer structures shows that these systems are very good models for the Phillips catalyst. The homogeneous reactions can be studied by several spectroscopic methods esp. for the  $\alpha$ -olefin trimerization. The triazacyclohexane stays coordinated during the catalysis and that mono-nuclear metallocyclic complexes are likely involved.

## ~5 Citings

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**151. Bonding of Supported Chromium during Thermal Activation of the  $\text{CrOx/SiO}_2$  (Phillips) Ethylene Polymerization Catalyst**

By Thuene, P. C.; Linke, R.; van Gennip, W. J. H.; de Jong, A. M.; Niemantsverdriet, J. W.

From [Journal of Physical Chemistry B \(2001\)](#), 105(15), 3073-3078. Language: English, Database: CAPLUS, DOI:10.1021/jp0039417

An active surface science model for the Phillips ethylene polymn. catalyst was prep'd. by impregnating aq.  $\text{CrO}_3$  on a flat Si(100) substrate covered by amorphous silica. Using a combination of XPS, secondary ion mass spectrometry, and Rutherford backscattering spectrometry, we studied the effect of calcination on the state of the supported chromium. Depending on the calcination temp. and the initial Cr loading of the catalyst, two processes are obs'd. The impregnated chromate anchors to the silica surface in an esterification reaction with the surface silanol groups of the support. The satn. coverage of these surface chromates is  $2.4 \text{ Cr/nm}^2$  for a calcination temp. of  $450^\circ\text{C}$ . Superficial, not anchored, chromate slowly desorbs from the flat silica surface. Under crowded conditions a portion of the surface chromates also desorb if the calcination temp. is increased, while low Cr loadings ( $>1 \text{ Cr/nm}^2$ ) are stable up to the highest calcination temp. in our expts. ( $730^\circ\text{C}$ ). The silica-bound surface chromates are monochromates exclusively, independent of the initial loading or calcination temp.

## ~5 Citings

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**152. 1,3,5-Triazacyclohexane complexes of chromium as homogeneous model systems for the Phillips catalyst**

By Mihan, Shahram; Lilge, Dieter; Kohn, Randolph; Seifert, Guido; Kociok-Kohn, Gabriele

From [Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 \(2001\)](#), INOR-222. Language: English, Database: CAPLUS

Chromium based heterogeneous catalysts are important ethylene polymn. catalysts (Phillips, Union Carbide). Several homogeneous model systems have been investigated (e.g. Jolly, Theopold). However, the mechanism of this important process is still largely unknown. MAO activated 1,3,5-triazacyclohexane complexes of chromium(III) are highly active ethene polymn. catalysts that resemble the Phillips catalyst in many important properties and may represent the first good homogeneous model system. A detailed study of the activities and the polymer structures of these systems in comparison to that of Phillips catalyst will be presented. A mechanism via metalla-cyclopentanes and -heptanes is used to explain the results.

## ~0 Citings

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**153. Manufacture of Phillips catalysts for the polymerization of olefins with improved productivity, and their use**



By Evertz, Kaspar; Funk, Guido; De Lange, Paulus; Koelle, Peter; Deckers, Andreas  
From [Ger. Offen. \(2001\)](#), [DE 19943206 A1 20010315](#), Language: German, Database: CAPLUS

An oxide support in suspension is treated with a Cr salt soln. and then, after solvent removal, calcined in an O-contg. atm. at  $>300^{\circ}$ . The oxide support before calcination and/or the **catalyst** after calcination is ground to av. particle size  $<100\text{ }\mu\text{m}$  ( $\geq 30\%$   $<50\text{ }\mu\text{m}$ ). Homo- or copolymers (with  $\text{C}_{3-12}$  comonomer) contg.  $\geq 90\%$  ethylene are manufd. in the presence of the **catalyst** at  $30-150^{\circ}$  and 0.2-15 MPa, preferably by pptn. polymn. in a loop reactor.

~3 Citings

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#### 154. Ethylene- $\alpha$ -olefin copolymer compositions containing paraffin waxes and method for manufacturing pipes with smooth surface by extrusion molding of the compositions

By Kobayashi, Katsuoki; Watanabe, Ichigen; Mori, Hironori  
From [Jpn. Kokai Tokkyo Koho \(2001\)](#), [JP 2001059045 A 20010306](#), Language: Japanese, Database: CAPLUS

The compns. contain **Phillips**-type linear ethylene- $\alpha$ -olefin copolymers with d. 0.910-0.930 g/cm<sup>3</sup>, melt mass flow rate 0.05-5 g/10 min, and melt tension  $\geq 3\text{ g}$  at  $190^{\circ}$ , 75-1000 ppm phosphites and/or phosphonites, and 300-5000 ppm paraffin waxes. Thus, GS 650 (LLDPE) contg. P-EPQ (phosphonite) 140, Paraflint H 1 (paraffin wax) 2000, Irganox 1010 (antioxidant) 800, and Zn stearate 50 ppm were extruded through a sizing die to give a pipe showing no wrinkles and no blooming.

~0 Citings

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#### 155. Process for intermittent thermal treatment of catalysts

By De Lange, Paulus; Kaemmerer, Michael; Brauch, Thomas; Feindt, Hans-Jacob; Letzelter, Thomas; Koelle, Peter; Evertz, Kaspar  
From [Ger. Offen. \(2000\)](#), [DE 19914752 A1 20001005](#), Language: German, Database: CAPLUS

In the title process, which does not cause strong fatigueing of the reactor material and is esp. useful with catalysts for olefin polymn., the **catalyst** is placed in a reactor, heated, tempered at the reactor temp., poured out of the reactor, and cooled, the reactor temp. being held const. during these steps. Use of the process to heat a **Phillips catalyst** in a fluidized bed is exemplified.

~0 Citings

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#### 156. Triazacyclohexane complexes of chromium as highly active homogeneous model systems for the **Phillips catalyst**

By Kohn, Randolph D.; Haufe, Matthias; Mihan, Shahram; Lilge, Dieter  
From [Chemical Communications \(Cambridge\) \(2000\)](#), (19), 1927-1928. Language: English, Database: CAPLUS, DOI:10.1039/b005842o

MAO-activated 1,3,5-trialkyl-1,3,5-triazacyclohexane complexes of  $\text{CrCl}_3$  are highly active ethene polymn. catalysts that resemble the **Phillips catalyst** in many important properties and may represent the first good homogeneous model system.

~114 Citings

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#### 157. Theoretical Models of Ethylene Polymerization over a Mononuclear Chromium(II)/Silica Site

By Espelid, Oystein; Borge, Knut J.  
From [Journal of Catalysis \(2000\)](#), 195(1), 125-139. Language: English, Database: CAPLUS, DOI:10.1006/jcat.2000.2986

Cluster models are constructed for mononuclear Cr(II) sites of the Cr/SiO<sub>2</sub> **Phillips catalyst** for ethylene polymn., displaying chromium covalently bound to two oxygen ligands. Based on these models, gradient-cor. d. functional theory was used to compare different routes of initiation and chain propagation with respect to structure, thermodynamical, and kinetic properties. It is shown that, for these sites, propagation mechanisms that involve four-coordinated chromium lead to activation energies that are incompatible with high catalytic activity. In the case of a chromacycloalkane intermediate, the relative rates of  $\beta$ -hydrogen transfer and monomer insertion are in agreement with the obsd. prodn. of 1-hexene during early stages of polymn. However, the anchoring site needs to be fairly strained before the activation energies drop significantly below 100 kJ/mol. On the other hand, a monoalkylchromium site supports insertion of ethylene into the Cr-alkyl bond according to the Cossee mechanism, with an activation energy of 56 kJ/mol relative to the ethylene-chromium precursor complex. (c) 2000 Academic Press.

~54 Citings

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#### 158. Effect of **catalyst** residues on the chain structure and properties of a **phillips** type polyethylene

By Epacher, Edina; Krohnke, Christoph; Pukanszky, Bela

From **Polymer Engineering and Science** (2000), 40(6), 1458-1468. Language: English, Database: CAPLUS, DOI:10.1002/pen.11275

A large no. of high-d. polyethylene (HDPE) powder samples produced by **Phillips** technol. were taken from an industrial polymn. reactor and their **catalyst** residue content was detd. by x-ray fluorescence spectroscopy. The chem. structure of the powder was characterized by diffuse reflectance IR spectroscopy (DRIFT), while the functional group content of samples processed in the presence and absence of a phenolic antioxidant was detd. by Fourier transform IR spectroscopy (FTIR). The melt flow index (MFI) of all processed samples was measured. Oxygen induction time (OIT) measurements were carried out to characterize the oxidative stability of 15 selected stabilized samples. The results indicate that the distribution of both the amt. of chromium-based **catalyst** residues and their compn. are very heterogeneous in the produced polymer. With increasing **catalyst** residue content, the concn. of double bonds increases in the samples extruded with or without stabilizer. Viscosity was not influenced by **catalyst** residues, while discoloration increased slightly with increasing **catalyst** residue content. The stability of the processed polymer also depends on the concn. of double bonds and on other factors. Since other components of the **catalyst**, including the SiO<sub>2</sub> support, also take part in the reactions occurring during processing, chromium content is not the sole, and perhaps not even the decisive, factor detg. the properties and esp. the stability of HDPE produced by a **Phillips catalyst**.

~14 Citings

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#### 159. Stretched ethylene polymer pipes with excellent environmental stress crack resistance

By Tanaka, Tomohiko; Nakamaru, Masashi; Urash, Ibrahim

From **Jpn. Kokai Tokkyo Koho** (2000), JP 2000185349 A 20000704, Language: Japanese, Database: CAPLUS

The pipes are obtained from ethylene polymers prepd. by using **Phillips** catalysts (contg. Cr compds. and inorg. supports) and satisfy  $\lambda_a, \lambda_h \geq 1.1$  and  $\lambda_a/\lambda_h$  0.7-2.5 ( $\lambda_a, \lambda_h$  = stretch ratio in the axial, and circumferential direction, resp.). Thus, a polyethylene pipe showing  $\lambda_a$  4.6,  $\lambda_h$  3.1, and wall thickness 1.7% (based on initial wall thickness) was manufd.

~0 Citings

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#### 160. Application of transition metal **catalyst** to polymerization of ethylene

By Chen, Mingliang

From **Suliao** (1999), 28(6), 33-38. Language: Chinese, Database: CAPLUS

A review with 32 refs. on structures and catalytic properties of Ziegler-Natta **catalyst**, **Phillips catalyst**, and metallocene **catalyst** for polymn.. The applications of these catalysts for ethylene polymn. and the structures and properties of polyethylene prepd. with these catalysts were discussed.

~0 Citings

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#### 161. $\beta$ -Diketiminato chromium catalysts for olefin polymerization.

By MacAdams, Leonard; Theopold, K. H.

From [Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 \(2000\)](#), INOR-418.

Language: English, Database: CAPLUS

In an effort to create a homogeneous model for the -**Phillips catalyst**' (i.e.  $\text{CrO}_3/\text{SiO}_2$ ) we have prepd. paramagnetic chromium complexes bearing  $\beta$ -diketiminate ligands, e.g.  $(\text{Ph})_2\text{nacnacCr}(\text{THF})_2\text{Cl}_2$  ( $(\text{Ph})_2\text{nacnac}=\text{CH}_3(\text{NPh})\text{CHC}(\text{NPh})\text{CH}_3$ ). When activated with methylalumoxane (MAO) these complexes catalyzed the polymn. of small olefins (e.g. ethylene, propylene). Alkylation of the dichloride species yielded novel organometallic chromium derivs. The structures and reactivities of various cationic chromium alkyls will be discussed. We have also probed how variations in the ligand and in the chromium oxidn. state effect catalytic activity.

~0 Citings

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## 162. Flame retardant linear ethylene-olefin copolymer compositions and electric wires insulated therewith

By Tachikawa, Takeshi; Ishihara, Koji; Hotta, Katsuhiro; Okazawa, Makoto

From [Jpn. Kokai Tokkyo Koho \(2000\)](#), JP 2000095901 A 20000404, Language: Japanese, Database: CAPLUS

The compns. contain 100 parts linear ethylene- $\alpha$ -olefin copolymers (d. 0.900-0.955 g/cm<sup>3</sup>, melt index 0.2-5.0 g/10 min,  $M_w/M_n$  6-20) prepd. by using chromium oxide **Phillips** catalysts, 10-100 parts metal hydroxides, and 0.1-10 parts organopolysiloxanes (dynamic viscosity 0.001-15 m<sup>2</sup>/s). Thus, a compn. contg. ethylene-1-hexene copolymer (d. 0.920 g/cm<sup>3</sup>) 100,  $\text{Mg}(\text{OH})_2$  100, and dimethylpolysiloxane 4 parts was extruded onto a Cu wire at a linear speed 500 m/min to give a test piece showing surface resistivity  $1 \times 10^{14}$  k $\Omega$ , and good fire, abrasion, and oil resistance.

~0 Citings

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## 163. Surface treatment of hollow plastic articles

By Tinant, Anne

From [Belg. \(1998\)](#), BE 1010622 A3 19981103, Language: French, Database: CAPLUS

The treatment is performed on at least a portion of the surface of a hollow plastic article (esp. a polyethylene fuel tank) contg. an acid acceptor. Thus, a HDPE fuel tank was formed from polyethylene made with a **Phillips catalyst** to which 0.3 wt.% hydrotalcite was added, and the internal surface was sulfonated with  $\text{SO}_3$  (15% in  $\text{N}_2$ ) and neutralized with 10% aq.  $\text{NH}_4\text{OH}$ , resulting in a permeability to leadfree gasoline contg. 10% EtOH of 10.7 g-mm/m<sup>2</sup>-day, compared with 21.4 g-mm/m<sup>2</sup>-day when the hydrotalcite was not present.

~0 Citings

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## 164. Diketimate-chromium alkyls: Toward a homogeneous model system for the **Phillips catalyst**.

By Theopold, Klaus H.; MacAdams, Leonard A.; Rheingold, Arnold L.

From [Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22-26 \(1999\)](#), INOR-230. Language: English, Database: CAPLUS

Having previously constructed a homogeneous model system for the Union Carbide **Catalyst** (i.e.  $\text{Cp}_2\text{Cr}/\text{SiO}_2$ ), we are now turning our attention to the **Phillips** catalysts (i.e. inorg.  $\text{Cr}/\text{SiO}_2$ ). To mimic the coordinatively unsatd. chromium on a hard oxide support, we have chosen N,N'-disubstituted diketimate ligands (abbr. "(R)<sub>2</sub>nacnac"), i.e. bidentate nitrogen ligands that confer variable steric protection upon the chromium. We have prepd. a series of neutral and cationic chromium alkyls supported by one or two (R)<sub>2</sub>nacnac ligands per metal atom. These complexes feature chromium in the formal oxidn. states +II and +III. Their syntheses, structures and reactivities (esp. with ethylene) will be described. Many of the complexes catalyze the polymn. of ethylene in the presence of an excess of MAO, and some are activated by  $\text{B}(\text{C}_6\text{F}_5)_3$ . Our goal is the prepn. of compds. that polymerize ethylene without any cocatalysts, one of the attractive features of the **Phillips catalyst**.

~0 Citings

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## 165. Polyethylene compositions containing fluoropolymers for high-speed blow molding

By Shimizu, Nobuyuki

From [Jpn. Kokai Tokkyo Koho \(1999\), JP 11181171 A 19990706](#), Language: Japanese, Database: CAPLUS

Title compns. contain HDPE prep'd. by Cr-based **Phillips** catalysts and 0.01-1% fluoropolymers. Thus, HB 332R (HDPE; MFR 0.3) was kneaded with 0.1% Dynamar FX 9613 (fluorovinylidene-hexafluoropropylene copolymer) to give a compn. showing low die swell and output rate 20.5 kg/h at resin temp. 183°.

~0 Citings

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#### 166. Polyethylene-based compositions with good moldability, stiffness, toughness and environmental stress crack resistance

By Yasukawa, Yuichirou; Sasaki, Yoshihito; Nagaoka, Takashi; Toneaki, Nobuhiro

From [Jpn. Kokai Tokkyo Koho \(1999\), JP 11166083 A 19990622](#), Language: Japanese, Database: CAPLUS

The compns. have characteristics of: (A) high-load melt flow rate (HLMFR) 50-200 g/10-min, (B) strand-extrusion time on capilog. at 290° of >24 s, (C) die swell during the measurement of HLMFR >90%, (D) environmental stress crack resistance rating (ESCR) such that  $(\text{HLMFR}) \times (\text{ESCR}) / 0.83^{(d-0.95) \times 1000} \geq 2500$  ( $d = d_1$ ; during bottle formation under a const. pressure), and (E) no. of fish-eye with diam. >0.5 mm and 0.1-0.5 mm of 0 and <100/0.1 m<sup>2</sup>, resp., when forming a film with thickness of 20 µm. The compns. are obtained from a blend of a Mg compd.-contg. Ziegler **catalyst**-type polyethylene resin having high-mol.-wt. component and low-mol.-wt. component, and **Phillips catalyst**-type polyethylene resin. Thus, an ethylene-1-hexene copolymer (I) was prep'd. by a 2-step polymn. using supported Ziegler **catalyst**, and had a high-mol.-wt. component (P1) with HLMFR 1.0 g/10-min and  $d_1$  0.925 g/cm<sup>3</sup>, a low-mol.-wt. component (P2) with MFR 150 g/10-min and  $d_1$  0.957 g/cm<sup>3</sup> at P1/P2 ratio of 15/85, and overall HLMFR 390 g/10-min and  $d_1$  0.958 g/cm<sup>3</sup>. Mixing 70 parts of the I with 30 parts an ethylene-1-hexene copolymer prep'd. by using **Phillips catalyst** (HLMFR 6.2 g/10-min,  $d_1$  0.938 g/cm<sup>3</sup>, long branching degree 0.2/1000 C), and additives, pelletizing and blow molding gave bottles at a rate of 6.8 s/bottle with good impact, stiffness and ESCR properties.

~0 Citings

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#### 167. Blow-molded ethylene polymer articles having good balance of rigidity, environmental stress cracking resistance, and impact resistance

By Miyamoto, Akira

From [Jpn. Kokai Tokkyo Koho \(1999\), JP 11138618 A 19990525](#), Language: Japanese, Database: CAPLUS

Title articles such as bottles, are obtained from compns. contg. (A) 30-90 parts resin mixts. of (A1) ethylene (I) homopolymer or I-C<sub>3-20</sub> α-olefin copolymers [ $d_1$  0.950-0.985 g/cm<sup>3</sup>;  $M_w$  measured by GPC 5000-100,000;  $1.25 \times \log(M_w) - 2.5 \leq M_w/M_n \leq 3.0 \times \log(M_w) - 8.0$  (formula Q)] and (A2) I-C<sub>3-20</sub> α-olefin copolymers ( $d_1$  0.910-0.950 g/cm<sup>3</sup>;  $M_w$  measured by GPC 110,000-1,500,000; (A2)'s  $M_w/M_n \geq$  (A1)'s  $M_w/M_n$ ) at A1/A2 ratio of (30-70)/(30-70) and (B) 10-70 parts I polymers ( $d_1$  0.945-0.975 g/cm<sup>3</sup>;  $M_w$  measured by GPC 50,000-500,000;  $M_w/M_n$  10-25; die-swell value 50-90 g/20 cm), which is prep'd. by polymn. in the presence of catalysts comprising organometallic compds. and supported Cr compds. The component A2 further satisfy the above-defined formula Q and specified relation between elution temps. and max. mol. wt. Thus, polyethylene (MFR 340 g/10 min;  $d_1$  0.9788;  $M_w$  18,000;  $M_w/M_n$  3.2) prep'd. by slurry polymn. using a constrained geometry-type single-site **catalyst**, was kneaded with I-1-hexene copolymer (MFR 0.016 g/10 min;  $d_1$  0.9375;  $M_w$  388,000;  $M_w/M_n$  6.1) prep'd. by similar process to give 50:50 resin mixt., 60 parts of which was further kneaded with 40 parts I polymer (MFR 2.5 g/10 min;  $M_w$  83,000;  $M_w/M_n$  22.5;  $d_1$  0.9702) prep'd. by polymn. in the presence of a **Phillips**-type polymn. **catalyst**. Then, the prep'd. compn. was molded to give a test piece showing  $d_1$  0.9630 g/cm<sup>3</sup>, Charpy impact strength (JIS K 7111) 19.3 kg-cm/cm<sup>2</sup>, and environmental stress cracking resistance (JIS K 6760) 220 h.

~0 Citings

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#### 168. Realistic surface science models of supported catalysts: the chromium oxide ethylene polymerization catalyst

By Thune, P. C.; Niemantsverdriet, J. W.

From [Israel Journal of Chemistry \(1998\), 38\(4\), 385-391](#), Language: English, Database: CAPLUS, DOI:10.1002/ijch.199800044



Depositing catalytically active particles onto flat, thin oxide films which have elec. cond. forms an attractive way to make supported catalysts suitable for surface science investigations. Here we describe the development of a model system for the chromium oxide-on-silica catalyst used in industry for the polymn. of ethylene, the so-called Phillips catalyst. The model system, consisting of molecularly dispersed chromium ions, deposited by wet chem. impregnation on a thin silica film and anchored to it by treating it in oxygen, displays a representative activity for polyethylene formation.

### ~9 Citings

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## 169. Surface compounds of transition metals. Part 41. Preparation and properties of organochromium compounds by reaction of Phillips catalysts with ethylene

By Xing, Q.; Milius, W.; Krauss, H. L.; Bluemel, J.; Hilbig, H.; Koehler, F. H.; Strauss, W.; Bayreuther, G.  
From *Zeitschrift fuer Anorganische und Allgemeine Chemie* (1999), 625(3), 521-529. Language: German, Database: CAPLUS

Reaction of reduced Phillips catalysts with  $C_2H_4$  at  $300^\circ$  deactivates the catalyst; supported organochromium compds. are formed. These can be cleaved from the  $SiO_2$  support by HCl and other acids, and transferred into soln. by extn. with MeOH. Chromatog. yields fractions of organochromium compds. which differ by  $CH_2$  moieties. XPS,  $^1H$  NMR, and mass spectra as well as magnetic measurements prove an ensemble of  $(R_nCp)CrCl_2(MeOH)$  ( $R_nCp$  = alkylated cyclopentadienyl) was formed. The  $R_nCp$  ligand results from a Cr-assisted oxidative coupling of the olefin with or without CC-cleavage. According to UV/visible and mass spectroscopy Cl<sup>-</sup> and MeOH can be substituted for other anions and donor mols. Without a donor dinuclear, chloro-bridged mols. were obtained, of which  $[(1,2,3-Me_3Cp)CrCl_2]_2$  was established by crystal structure anal. (monoclinic,  $P2_1/c$ , a 981.2(2), b 1387.8(3), c 1468.2(3) pm,  $\beta$  105.72(3) $^\circ$ ,  $V = 1925.8(7) \times 10^6$  pm<sup>3</sup>,  $\rho_c = 1.587$  g/cm<sup>3</sup>,  $\mu(MoK\alpha) = 1.676$  mm<sup>-1</sup>, 2522 obsd. reflections with  $F_o > 2\sigma(F_o)$ ,  $R = 0.050$ ,  $R_w = 0.029$ ). Reaction with  $O_2$  reversibly leads to Cr(V) compds.  $(R_2Cp)Cr(O)Cl_2$ .

### ~13 Citings

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## 170. Polyethylene Formation on a Planar Surface Science Model of a Chromium Oxide Polymerization Catalyst

By Thune, P. C.; Loos, J.; Lemstra, P. J.; Niemantsverdriet, J. W.  
From *Journal of Catalysis* (1999), 183(1), 1-5. Language: English, Database: CAPLUS, DOI:10.1006/jcat.1999.2448

A planar  $CrO_x/SiO_2/Si(100)$  model for the Phillips ethylene polymn. catalyst was prepd. by spin-coat impregnation from an aq. soln. of  $CrO_3$ . In order to test the model catalyst with its extremely low chromium content, a special reactor was designed with a  $CrO_x/Al_2O_3$  filter to effectively remove impurities. The model catalyst polymerizes ethylene in the gas phase at  $160^\circ$  with const. activity and forms a 350-nm-thick layer of polyethylene in 1 h. At. force microscopy reveals the expected spherulite morphol. of the polyethylene films in different stages of development. The method allows for study of nascent morphol. of catalytically formed polymers. (c) 1999 Academic Press.

### ~38 Citings

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## 171. Mesoporous molecular sieve supports and chromium catalysts for polymerization of olefins

By Rohde, Wolfgang; Mueller, Ulrich  
From *Ger. Offen.* (1998), DE 19636126 A1 19980312, Language: German, Database: CAPLUS

Olefin polymers with increased mol. wt. are manufd. by Cr catalysts contg. also oxides of specified metals, on mesoporous aluminosilicate or silicate supports. Thus, polymn. of ethylene at  $90^\circ/40$  bar in isobutane in the presence of n-BuLi and Cr-contg. Phillips catalyst supported on a mesoporous mol. sieve (support and catalyst prepn. given) gave polyethylene having Staudinger index 953 mL/g, vs. 687 mL/g for polyethylene produced at the same temp. in the presence of a previous art catalyst having the same pore vol. and the activation temp.

### ~2 Citings

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## 172. Water-crosslinkable polyethylene-based compounds having silanol groups and moldings therefrom

By Kawasaki, Yoichi  
From *Jpn. Kokai Tokkyo Koho* (1998), JP 10017625 A 19980120, Language: Japanese, Database: CAPLUS

The compds., comprising (a) granular linear low-d. ethylene- $\alpha$ -olefin copolymers prep'd. by using **Phillips** catalysts which are impregnated with unsat'd. alkoxy silanes and org. peroxides and (b) polyethylene contg. silanol condensation catalysts and antioxidants, are extruded by use of extruders with L/D 20-28 and contacted with H<sub>2</sub>O to give moldings. Thus, ethylene and 1-butene were copolymerized in the presence of CrO<sub>3</sub>, tetra-iso-Pr titanate, and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>, etc., and treated with vinyltrimethoxysilane and dicumyl peroxide to give an impregnated copolymer (A). Then, 95% A and 5% of a compn. contg. low-d. polyethylene, Bu<sub>2</sub>Sn dilaurate, and Irganox 1010 were mixed, extruded from an extruder having L/D 24, applied to a Cu conductor, and dipped in hot H<sub>2</sub>O to give an elec. insulated wire showing tensile strength 1.8 kg/mm<sup>2</sup>, elongation 650%, and good wear resistance.

#### ~1 Citing

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### 173. Nonequilibrium plasma activation of supported Cr(III) **Phillips catalyst** precursors

By Ruddick, V. J.; Badyal, J. P. S.

From *Journal of Physical Chemistry B* (1997), 101(45), 9240-9243. Language: English, Database: CAPLUS, DOI:10.1021/JP962990+

The ethylene polymn. activities of low-temp. plasma-activated CrO<sub>x</sub>/SiO<sub>2</sub> catalysts prep'd. from two different types of precursor are compared. Chromium(III) acetate wet impregnated onto high surface area silica is found to yield polyethylene, while chromium(III) acetylacetonate dry blended with silica does not. This is despite both precursors exhibiting good catalytic activity following conventional thermal activation.

#### ~12 Citings

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### 174. Ethylene polymer compositions for pipes

By Kobayashi, Katsuoki; Ishihara, Koji

From *Jpn. Kokai Tokkyo Koho* (1997), JP 09143314 A 19970603, Language: Japanese, Database: CAPLUS

The compns. for preventing corrosion of metals in extruding machines for pipe manuf., comprise linear-low-d. ethylene- $\alpha$ -olefin copolymers prep'd. by using **Phillips** catalysts 100, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylenediphosphonite (I) 0.01-0.1, and chloride adsorbents 0.0005-0.05 part. The corrosion prevention of the extrusion app. results in discoloration prevention of the pipes. Thus, ethylene-butene-1 copolymer (d. 0.92 g/cm<sup>3</sup>) prep'd. by using the **catalyst** 100, Sandostab P-EPQ (I) 0.05, Zn stearate 0.006, and Irganox 1010 0.05 part were kneaded, pelletized, and extrusion-molded to give pipes to show no rust generation in the extruding machine for 1 mo-operation.

#### ~0 Citings

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### 175. Laminated films having extrusion-coated ethylene polymer layers for food packagings

By Furukawa, Takashi; Komatsu, Tadashi; Sakuma, Yuichiro

From *Jpn. Kokai Tokkyo Koho* (1997), JP 09169087 A 19970630, Language: Japanese, Database: CAPLUS

Title films showing improved low temp. sealability without affecting good coatability in extrusion consist of (A) extrusion-coated layers comprising 100 parts linear-low-d. ethylene (I)- $\alpha$ -olefin copolymers prep'd. by using Ziegler or **Phillips** catalysts, 30-70 parts I- $\alpha$ -olefin copolymers prep'd. by using single-site catalysts, and 50-100 parts high-pressure low-d. polyethylene (HPLDPE) and (B) single or multilayer substrates made of polyamides, polyesters, poly(vinylidene chloride), ethylene-vinyl alc. copolymers, and/or Al. Thus, linear-low-d. I-1-butene copolymer 100, Affinity (I-1-octene copolymer) 50, and HPLDPE 70 parts were kneaded at 180° for 10 min, pelletized, and extruded on a drawn nylon 6 film having isocyanate-type anchor coating to give a laminated film showing 2.0-kg/15 mm heat sealing strength at sealing temp. 107° and good hot tack strength.

#### ~2 Citings

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### 176. **Phillips** catalysts reduced with organic compounds and possessing short induction times, their preparation and use

By Rohde, Wolfgang

From *PCT Int. Appl.* (1997), WO 9719115 A1 19970529, Language: German, Database: CAPLUS

**Catalyst** systems suitable for the polymn. of ethylene and 1-alkenes contain as active components (A) a Cr-contg. component obtainable by redn. of a **Phillips catalyst** with linear C<sub>4</sub>-C<sub>10</sub> or cyclic C<sub>3</sub>-C<sub>10</sub> alkenes with ≥1 internal C-C double bond, 1,3-butadiene, C<sub>2</sub>-C<sub>10</sub> alkynes, or C<sub>1</sub>-C<sub>10</sub> aldehydes and optionally (B) an organometallic compd. of a Group IA, II, IIIA, or IVA element. Thus, a Cr **catalyst** activated at 750° in air and reduced with 1 mol norbornene per g-atom Cr gave 48.2% conversion in 10 min in polymn. of 1-hexene at 90°, compared with 30.4% for the unreduced Cr **catalyst**.

~2 Citings

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### 177. Polymers of ethylene for moldings with a high degree of resistance to stress crack, and a **catalyst** system for the production thereof

By Rohde, Wolfgang; Saive, Roland; Lilge, Dieter; Lux, Martin; Bauer, Peter  
From *PCT Int. Appl.* (1997), [WO 9708213 A1](#) 19970306, Language: German, Database: CAPLUS

Ethylene polymers that give moldings with the title property are manufd. by polymn. or ethylene optionally with other monomers in the presence of a **catalyst** system contg. a **Phillips catalyst**, a solid distinguishable from the **Phillips** catalysts contg. a constituent which is derived from metallocene complexes, and optionally an organometallic compd. constituent selected from the Groups IA, IIA, IIB and IIIA of the periodic system. Thus, 18.1 vol.% ethylene was polymd. with 2.0 vol.% 1-hexene in the presence of an isobutane suspension contg. silica gel impregnated with Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and calcined 2 h at 550°, silica gel impregnated with bis(cyclopentadienyl)chromium, BuLi, and 0.31 vol.% H to give a copolymer with environmental stress crack resistance ≥200 h (DIN 53735).

~9 Citings

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### 178. On surface compounds of transition metals. Part 40. Characterization of chromium-doped silica **catalyst** systems of the **Phillips** type by scanning electron microscopy with energy dispersive analyzing system (SEM/EDS)

By Schmidt, H.; Riederer, W.; Krauss, H. L.  
From *Journal fuer Praktische Chemie/Chemiker-Zeitung* (1996), 338(7), 627-633. Language: German, Database: CAPLUS

The surface of typical supports for the **Phillips catalyst** was studied by SEM. The seemingly smooth surfaces are composed of closely packed, ball-shaped substructures; macro- and micropores can be seen. Adherent particles on the surface ( $\phi \ll 1 \mu\text{m}$ ) show the same substructures as the usual surface. After impregnation and activation/redn. of the catalysts, crystallites were seen at the surface, which were characterized as Cr<sub>2</sub>O<sub>3</sub> by their crystal shape and EDS anal. Polymn. of ethylene occurs at the doped surface, whereas the Cr<sub>2</sub>O<sub>3</sub> particles do not exhibit a special activity. At mech. breaks of the **catalyst** grains, formation of threadlike polyethylene with diams. of 200-300 nm was obsd.

~10 Citings

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### 179. **Phillips catalyst** for polymerization of $\alpha$ -olefins

By Mueller, Hans Joachim; Braun, Hans Georg; Marczinke, Bernd Lothar; Mueller, Ulrich  
From *Ger. Offen.* (1994), [DE 4228883 A1](#) 19940303, Language: German, Database: CAPLUS

The title **catalyst** comprises ≥1 Cr(III) compd. supported on (Si<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>)O<sub>2</sub> (x = 0.05-0.5; y = 0.1-1.0; z = 0.1-1.0) and shows high activity in the homopolymn. and copolymn. of ethylene.

~3 Citings

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### 180. IR study of the interaction of hydroxyl groups of silica gel with chromium species of **Phillips'** type catalysts

By Nishimura, Madoka; Thomas, John Meurig  
From *Catalysis Letters* (1993), 21(1-2), 149-55. Language: English, Database: CAPLUS, DOI:10.1007/BF00767380

Spectroscopic evidence for the interaction of hydroxyl groups and chromium ions was obtained by using a **catalyst** prep'd. from chromyl chloride. A new OH peak, obs'd. at 3705 cm<sup>-1</sup> after pumping away CO gas, is attributed to the direct interaction of OH with the low-valent chromium. This peak shifts to 3590 cm<sup>-1</sup> on contact with O<sub>2</sub> at room temp. and it is assigned to a hydroxyl interacting with the oxidized chromium. New assignments are also proposed for IR bands of CO presorbed on the **catalyst**. The peak due to CO at 2188 cm<sup>-1</sup> decreases as the OH intensity at 3705 cm<sup>-1</sup> increases, suggesting that the former peak arises from adsorption on Cr(II) species to which two oxygen atoms are attached.

~24 Citings

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### 181. **Phillips catalyst** and its use for preparation of ethylene (co)polymers

By Evertz, Kaspar; Saive, Roland; Funk, Guido; Koelle, Peter; Konrad, Rainer; Gropper, Hans  
From *Eur. Pat. Appl.* (1993), EP 555747 A1 19930818, Language: German, Database: CAPLUS

A fluoride-modified Cr **catalyst** supported on a finely divided aluminosilicate contg. 0.5-6% Al oxide and having an Al oxide-enriched surface region is activated by heating in an oxidizing atm. and used for the homo- or copolymn. of ethylene, showing high activity and giving polymers which have high impact strength at low temp. and form films with good swelling resistance when extruded and blow-molded.

~4 Citings

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### 182. **Phillips catalyst** and its use for the copolymerization of ethylene with alpha-olefins

By Mueller, Hans Joachim; Evertz, Kaspar; Weber, Siegfried; Funk, Guido; Konrad, Rainer; Saive, Roland  
From *Eur. Pat. Appl.* (1993), EP 555741 A1 19930818, Language: German, Database: CAPLUS

A finely divided, aluminosilicate-supported, P-contg. Cr **catalyst** [e.g., prep'd. from Cr tris(acetylacetonate) and (EtO)<sub>3</sub>PO] is used to prep. copolymers of ethylene and an  $\alpha$ -olefin (e.g., 1-hexene) in which the  $\alpha$ -olefin is distributed more uniformly than in copolymers prep'd. with a P-free **catalyst**. Moldings prep'd. from the copolymers show good environmental stress cracking resistance and creep resistance.

~1 Citing

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### 183. New aspects on the mechanism of olefin polymerization with reduced **Phillips catalysts**

By Krauss, H. L.; Schmidt, H. A.; Siebenhaar, B.; Wolff, P.; Xing, Q.  
From *Studies in Surface Science and Catalysis* (1993), 75(New Frontiers in Catalysis, Pt. C), 2325-8. Language: English, Database: CAPLUS

The polymn. of olefins with reduced **Phillips** systems is hindered (induction period) or fostered (fast start) by residues of the reducing agents. The catalytic activity is restricted to a small part of the surface Cr centers which are coordinatively unsat'd. and carry Cr-C  $\sigma$ -bonds; both are prerequisites of chain propagation. These active organometallic centers contain probably a sat'd. metallacycle loop which is still reflected in the Cr(IV) end product of the high temp. redox reaction between the surface metal and the olefin.

~4 Citings

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### 184. **Phillips catalyst** suspension for polymerization of ethylene alone or with $\alpha$ -olefins

By Evertz, Kaspar; Saive, Roland; Funk, Guido; Koelle, Peter; Konrad, Rainer  
From *Ger. Offen.* (1993), DE 4139256 A1 19930603, Language: German, Database: CAPLUS

The **catalyst** suspension contains (A)  $\geq 1$  finely divided, supported Cr **catalyst**; (B)  $\geq 1$  organometallic comp'd. of the formula MR or M<sup>1</sup>R<sub>2</sub>, where M = Li, Na, or K; M<sup>1</sup> = Mg, Ca, or Zn; and R = C<sub>1-10</sub> alkyl or C<sub>6-20</sub> aryl; and (C)  $\geq 1$  inert suspension agent. It is prep'd. by applying  $\geq 1$  Cr comp'd. to a finely divided, inorg. hydrogel or xerogel with formation of a finely divided **catalyst** precursor; activating the precursor at elevated temps. in an oxidizing atm., forming the Cr **catalyst**; and suspending the Cr **catalyst** and the organometallic comp'd. in the inert suspension agent.

~0 Citings



A **Phillips catalyst**, for ethylene homo- or copolymn. with  $\alpha$ -olefins, contains as the active components: (A) a finely divided, Al silicate-supported, P-contg. Cr **catalyst** prep'd. by (1) applying  $\geq 1$  org. P(III), P(IV), or P(V) comp'd. and  $\geq 1$  Cr(III) comp'd. (which does not react with the P comp'd.) in any order or simultaneously to a finely divided Al silicate hydrogel or xerogel to form a **catalyst** precursor, and (2) activating the **catalyst** precursor at elevated temps. in an oxidizing atm. to produce the Cr **catalyst**; and (B)  $\geq 1$  comp'd. of the formulas  $MR$ ,  $M^1R^2$ ,  $M^2R^1$ ,  $_{3-n}X_n$ , or  $MM^2RR^1$ , where  $M = Li, Na, \text{ or } K$ ;  $M^1 = Mg \text{ or } Zn$ ;  $M^2 = B \text{ or } Al$ ;  $R = C_{1-20}$  alkyl or  $C_{6-20}$  aryl;  $R^1 = R, C_{1-20}$  alkoxy, or  $C_{6-20}$  aryloxy;  $R^2$  not defined;  $X = F, Cl, Br, \text{ or } I$ ; and  $n = 0-2$ , as a cocatalyst.

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A **catalyst** prep'd. by depositing a Cr comp'd. on finely divided Al phosphate having P/Al molar ratio ~1 and pore vol. >1 mL/g and activating the intermediate and high temp. in an oxidizing atm. is useful with cocatalysts such as Et<sub>3</sub>B and BuLi for the polymn. of ethylene or an ethylene- $\alpha$ -olefin mixt. The **catalyst** gives high productivity and has an long useful life.

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A Cr/silica **Phillips catalyst** with a Cr loading of 1 wt.% was prepd. by impregnating an aq. soln. of Cr(III) acetate onto Davison 952 silica. The characterization of the surface Cr species formed during the activation process was performed using TPO/R (temp.-programmed oxidn./redn.) and FTIR spectroscopy. During activation with dry air, Cr(III) acetate was stabilized on the surface as a Cr<sup>6+</sup> species. The av. oxidn. nos. of surface Cr species after activation at 823, 923, 1023, 1123, and 1223 K are 6.0, 5.4, 5.1, 4.2, and 3.7, resp. The amts. of the Cr(VI) species varied with activation temp. The fraction of Cr(VI) atoms existing in monochromate form increased with increasing activation temp., which was a result of the decrease in the fraction of dichromate and/or polychromate. The OH stretching bands of Cr/silica prepd. by the redn. of Cr(VI)/silica with CO and the stretching bands of CO adsorbed on it indicate the existence of 3 distinct types of Cr(II) whose amts. are strongly dependent on the activation temp.

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The valence of Cr in a Phillips polymn. catalyst was studied by  $^{29}\text{Si}$  CP/MAS NMR and magnetic susceptibility. Data show the presence of Cr(III) and the spectrum of the  $\text{SiO}_2$  support is affected by both the magnetic moment of the paramagnetic species and their distribution over its surface.

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### 189. Modified chromium/silica gel catalysts: an FTIR study of the addition of alkali metal ions

By Rebenstorf, Bernd

From *Acta Chemica Scandinavica* (1991), 45(10), 1012-17. Language: English, Database: CAPLUS,

DOI:10.3891/acta.chem.scand.45-1012

Addn. of alkali metal ions to the **Phillips catalyst** has a strong neg. influence on the amt. of Cr(II) surface ions detectable in low-temp. FTIR spectra of CO adsorbed on various Cr(II) species. However, small addns. of Li and Na (below 0.1 or 0.05 mmol g<sup>-1</sup> silica gel, resp.) have no adverse effect, while such an 'offset' was not obsd. for K, Rb, or Cs. The decrease of the amt. of Cr(II) surface ions shows that Li forms Li<sub>2</sub>CrO<sub>4</sub> during the prepn. of the samples and K, Rb, and Cs alkali metal dichromates. Na forms both compds. Surprisingly, a small shift of 1 to 2 cm<sup>-1</sup> to higher wavenumbers is obsd. for the CO bands at 2047, 2035 and 2027 cm<sup>-1</sup>, indicating a decrease of the electron d. at the Cr(II) ions.

~7 Citings

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### 190. The active species of the chromium (**Phillips type**) catalysts for the polymerization of ethylene: a unifying approach

By Rebenstorf, Bernd

From *Journal of Polymer Science, Part A: Polymer Chemistry* (1991), 29(13), 1949-53. Language: English, Database: CAPLUS, DOI:10.1002/pola.1991.080291315

From literature data it is concluded that the rate of the redn., alkylation, polymer chain growth, and chain transfer reactions of 3 Cr(II) and 1 Cr(III) surface species all increased with decreasing electron d. at the Cr ion. This electron d. was measured by the IR shift of the stretching vibration of 1 CO mol. terminally adsorbed on these Cr ions. The redn. half-time decreased proportionally to the increasing Lewis acidity and the rate of the polymer chain growth reaction increased exponentially for 3 Cr surface species with increasing CO stretching vibration. Due to the large difference of the polymer chain growth rates for 2 Cr(II) species (A<sub>d</sub> and C<sub>d</sub>), common in the normal **Phillips catalyst**, both contribute almost equally to the polymer product, although the A<sub>d</sub> species outnumbered the C<sub>d</sub> species by >3 to 1.

~13 Citings

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### 191. Influence of chromium concentration and addition of fluorine, titanium, or boron on the chromium species of the **Phillips catalyst**: a quantitative evaluation

By Rebenstorf, B.; Sheng, T. C.

From *Langmuir* (1991), 7(10), 2160-5. Language: English, Database: CAPLUS, DOI:10.1021/la00058a031

A new Cr(II) surface species on the reduced **Phillips catalyst** was obsd. at low temp. with a characteristic CO IR band at 2027 cm<sup>-1</sup> (together with 2 more bands at 2120 and 2100 cm<sup>-1</sup>). This species was named Cr(II) D and a structure model was proposed consisting of a dinuclear Cr(II) surface complex in which 1 Cr ion had 3 O ligands and the other one had 2 O ligands. Three Cr(II) surface species (including the D) were detd. quant. by low-temp. IR spectra of adsorbed CO at 2027 (D), 2035 (A) and 2047 cm<sup>-1</sup> (C). Specific trends in the relative amts. of the different Cr surface species were obsd. by varying the Cr concn. and modifying the **catalyst** with F, Ti, or B. The results were compared with **catalyst** performance in the industrial polymn. of ethylene as reported in the literature. Modifying the **catalyst** with F decreased the relative amts. of the C and D species, resulting in a more uniform distribution of catalytically active Cr(II) surface sites [mainly Cr(II) A species] and a narrower mol.-wt. distribution for produced polymer. Modifying the **catalyst** with Ti increased the relative amt. of C species and increased the polymer melt index (lower polymer mol. wt.).

~11 Citings

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### 192. **Phillips-type** polymerization catalysts: kinetic behavior and active center determination

By Wang, Shemin; Tait, Peter J. T.; Marsden, Christine E.

From *Journal of Molecular Catalysis* (1991), 65(1-2), 237-52. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(91)85100-G

The kinetic behavior of chromium oxide **Phillips catalysts** in the presence of alkylaluminum is examd. as a function of ethylene (I) monomer pressure at 1-11 atm. Electron microscope data and kinetic data show the importance of **catalyst** fragmentation; **catalyst** fragmentation yields fragments of 6-11μ and 600-1000Å at pressures of 1 and 10 atm., resp. Values of active propagating centers and rate coeffs. are both a function of I pressure. Only 3.2-7.3% of Cr is involved in the active centers; the percent of active Cr increases with I pressure. Polymn. rate increases with polymn. time and with I pressure beyond 1st-order.

~21 Citings

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### 193. The **Phillips catalyst** (chromium(VI)/silica gel) modified by (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>: its influence on the chromium surface species

By Rebenstorf, Bernd

From [Journal of Molecular Catalysis](#) (1991), 66(1), 59-71. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(91)85021-S

Low-temp. CO IR spectra of the reduced **Phillips catalyst** show that treatment with (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> decreases the amt. of Cr(III) and the dinuclear Cr(II)-C surface species, so that the catalytically active sites consist almost exclusively of the dinuclear Cr(II)-A surface species. The IR band of terminal CO adsorbed on this Cr(II)-A species is shifted by 5 cm<sup>-1</sup> to 2183 cm<sup>-1</sup>, which is interpreted as due to decreasing electron d. at the Cr ion. These results agree with polymn. measurements described in the literature, in which a narrowing of the mol. wt. distribution of the polymer and a better comonomer incorporation were obsd. Treatment of the **Phillips catalyst** with (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> decreases the amt. of surface silanol groups during the activation between 600 and 800° by some 80% but shifts the O-H IR band of the remaining silanol groups only by 1 cm<sup>-1</sup>. F covers almost the entire surface, but is not bonded together with OH at the same Si atom. From a comparison of the IR bands from CO adsorbed on Cr supported on SiO<sub>2</sub> gel or amorphous AlPO<sub>4</sub>, it is concluded that F is bonded to the Si atom that binds to Cr via an O atom. Modification of the (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>-treated **Phillips catalyst** with Ti showed only a small effect.

~17 Citings

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### 194. An infrared study of carbon monoxide/ethylene coadsorption and reaction on silica-supported chromium(II) ions

By Ghiotti, Giovanna; Garrone, Edoardo; Zecchina, Adriano

From [Journal of Molecular Catalysis](#) (1991), 65(1-2), 73-83. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(91)85084-F

Ethylene and CO interact at low pressure on a reduced **Phillips catalyst** to yield CO/C<sub>2</sub>H<sub>4</sub> mixed complexes involving the most exposed type of Cr(II) (A type). Cr centers responsible for ethylene polymn. form the most stable mixed complexes. At high pressure (≥4 torr), Cr<sub>A</sub>(CO)C<sub>2</sub>H<sub>4</sub> complexes react with a second ethylene mol. to yield a metallacyclohexanone species. After reaction, polymn. is prevented and oligomerization of ethylene is only obsd. on less reactive sites. A hierarchy of ions Cr<sub>A</sub> may be established in this way. The implications for the polymn. mechanism are discussed.

~32 Citings

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### 195. Coordination chemistry of silica-supported chromium ions: types of chromium(II) ions on reduced samples

By Garrone, E.; Ghiotti, G.; Zecchina, A.

From [NATO ASI Series, Series C: Mathematical and Physical Sciences](#) (1990), 326(Olefin Metathesis Polym. Catal.), 393-406. Language: English, Database: CAPLUS

Three kinds of Cr(II) ions are present on CO-reduced **Phillips** polymn. catalysts (i.e., CrO<sub>3</sub>/SiO<sub>2</sub>) having 2, 3, and 4 O ligands before chemisorption, resp. Thermal deactivation converts the species having 2 O ligands into the species having 4 O ligands, while the species having 3 O ligands remains unaffected. The behavior of the three kinds of ions was discriminated by IR spectroscopy so that the relative populations, coordinative chem., and polymn. ability could be established. Supported Cr atoms contg. 2 O ligands are the most reactive species and comprise the sites active for ethylene polymn. Numerous IR spectra are presented.

~10 Citings

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### 196. Investigation of polymerization and metathesis reactions. XVIII. Syntheses of heterogeneous, bimetallic metathesis catalysts by reactions of Fischer-type carbene and carbyne complexes with reduced **Phillips catalyst**

By Weiss, Karin; Guthmann, Wilfried; Denzner, Michael; Maisuls, Sergio

From [NATO ASI Series, Series C: Mathematical and Physical Sciences](#) (1990), 326(Olefin Metathesis Polym. Catal.), 517-20. Language: English, Database: CAPLUS

A conference. Fischer type carbene complexes of molybdenum, tungsten and rhenium form in topospecific reactions with the surface chromium(II) atoms of the reduced **Phillips catalyst** heterogeneous, bimetallic metathesis catalysts. The reactions proceed presumably by [2+1] cycloaddns. of the metal carbene double bonds to the surface chromium(II) atoms to give surface bound dimetallacyclopropane derivs. Fischer type carbyne tungsten complexes also react with reduced **Phillips catalyst** in [2+1] cycloaddns. to yield dimetallacycloprenes. These heterogeneous, bimetallic catalysts are very active alkene metathesis catalysts. By reaction with the carbene and carbyne complexes the alkene polymn. activity of the surface chromium atoms vanishes and the alkene metathesis activity of the carbene and carbyne complexes is drastically enhanced. Both types of heterogeneous catalysts oligomerize or polymerize 1-alkynes.

~0 Citings

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### 197. The **Phillips catalyst** site with high catalytic activity

By Rebenstorf, Bernd

From *Journal of Molecular Catalysis* (1989), 56(1-3), 170-82. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(89)80181-6

FTIR spectroscopy was employed to study 2 **catalyst** samples with 0.5% Cr and 0.074% Cr on silica gel in ethylene polymn. at room temp. and in the adsorption of CO. In 1 of the 2 series of expts. studied, samples were reacted with ethylene at 200° prior to further reaction with ethylene at room temp. The previously reported broad band at 2750 cm<sup>-1</sup> arising from the hydrocarbon group connecting the living polymer to the chromium(II) site was split into 2 bands situated at 2768 and 2725 cm<sup>-1</sup>, resp. These bands were assigned to the asym. and sym. stretching vibrations of the methylene group. A model for polymn. initiation and for the mechanism of the polymn. reaction is proposed, which involves dinuclear surface species and explains results obtained with the (reduced) **Phillips catalyst**.

~17 Citings

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### 198. **Phillips** polymerization catalysts for the manufacture of ethylene (co)polymers

By Weber, Siegfried; Funk, Guido

From *Ger. Offen.* (1990), DE 3841436 A1 19900613, Language: German, Database: CAPLUS

**Phillips** olefin polymn. catalysts, comprised primarily of silicate-supported Cr compds., P compds., and Al compds., which produced polyolefins with high **catalyst** activity, are prepd. Thus, a highly porous silicate carrier (particle diam. 50-150 µm, pore vol. 1.75 cm<sup>3</sup>/g, surface area 320 m<sup>2</sup>/g) was dried for 8 h at 140°/20 Torr, 100 parts of the carrier suspended in 400 parts of anhyd. n-heptane under Ar, 1 part Cr(III) acetylacetonate added, 2 parts Al(iso-Bu)<sub>3</sub> added, the resulting suspension treated first with 2 parts triethylphosphate at 20°, the intermediate heated at 80°/20 Torr until dry, contacted with anhyd. N at 200° for 120 min, calcined in anhyd. air for 120 min at 600°, contacted with anhyd. N for 60 min at 250° to 100°, 100 parts of the treated carrier suspended in 700 parts n-heptane, 2 parts Et<sub>3</sub>B in 175 parts n-heptane added at 30° with stirring, after 30 min the suspension heated to 80°/10 Torr and the solvent removed. An autoclave was charged with 2 mL of a 10 g n-BuLi in 1 L n-heptane soln., 500 mL isobutane added, the mixt. heated at 95°, H added to 2 bar, ethylene added to 40 bar, 80 mg of the carrier **catalyst** added, and polymn. conducted at 95° ± 2° to produce polyethylene having melt-flow ratio 21.1 g/10 min, and having **catalyst** activity 1920 g polyethylene/g-**catalyst**.

~0 Citings

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### 199. Ethylene polymerization with **Phillips catalyst** co-catalyzed with tris(iso-butyl)aluminum

By Woo, Tae W.; Woo, Seong I.

From *Journal of Catalysis* (1990), 123(1), 215-27. Language: English, Database: CAPLUS, DOI:10.1016/0021-9517(90)90170-O

The kinetics of ethylene polymn. with CrO<sub>3</sub>/SiO<sub>2</sub>/Al(iso-Bu)<sub>3</sub> was investigated at 323-353 K and 116.7-268.7 psia. The effects of aluminum alkyl on the formation and the deactivation of active sites were discussed. Decay of the polymn. rate, which was independent of the monomer concn., was ascribed to the excess aluminum alkyl that could poison the active sites by the Langmuir-Hinshelwood mechanism. Activation energy obtained from the max. polymn. rates between 323-353 K was 8.8 kcal/mol. An apparent neg. activation energy was obtained above 343 K and was ascribed to the destruction of active sites.

~10 Citings

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**200. On the active site of the Phillips catalyst for ethylene polymerization**

By Rebenstorf, Bernd

From *Journal of Catalysis* (1989), 117(1), 71-7. Language: English, Database: CAPLUS, DOI:10.1016/0021-9517(89)90221-2

The FTIR spectra of CO adsorbed on the Cr(II)-A (A represents species having only two O ions as ligands) surface compd. (the active site of the Phillips catalyst) before and after short polymn. with ethylene were reexamd. No difference in the CO spectra of the room temp. triplet at 2190, 2185, and 2179  $\text{cm}^{-1}$  was found for that part of Cr which reacts with ethylene compared to the CO spectra of the unreacted surface compd. The same result was obsd. with the low temp. CO IR triplet at 2120, 2100, and 2035  $\text{cm}^{-1}$ . After low temp. polymn. with ethylene, a new CO IR band at 2176.82  $\text{cm}^{-1}$  was obsd. After high temp. reaction with ethylene, a sym. and rather sharp CO IR band at 2171.52  $\text{cm}^{-1}$  was noted at room temp. instead. In both cases rather well-structured Cr surface compds. are formed. The CO IR bands of the room temp. triplet shifted from 2190.79, 2184.74 and 2178.69  $\text{cm}^{-1}$  to 2192.28, 2185.03, and 2180.76  $\text{cm}^{-1}$  after seven oxidn. (800°, O)/redn. (350°, CO) cycles. The CO IR bands of the low temp. triplet (-145°C) sepd. into two triplets with higher (2121.12, 2102.06, and 2040.37  $\text{cm}^{-1}$ ) and lower (2117.12, 2098.47 and 2031.34  $\text{cm}^{-1}$ ) positions than the original one. The surface structure of the support has a rather large influence on the electronic d. of the Cr(II) surface ions.

~8 Citings

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**201. Investigations of polymerization and metathesis reactions. XIV. Preparation of heterogeneous bimetallic metathesis catalysts by reactions of Fischer-type tungsten carbyne complexes with reduced Phillips catalyst**

By Weiss, Karin; Denzner, Michael

From *Journal of Organometallic Chemistry* (1988), 355(1-3), 273-80. Language: German, Database: CAPLUS

Reactions of Fischer-type carbyne tungsten complexes  $\text{Cp}(\text{CO})_n\text{W}\equiv\text{CPh}$  ( $\text{X} = \text{Cl}, \text{Br}$ , iodo,  $n = 4$ ;  $\text{Cp} = \eta^5\text{-cyclopentadienyl}$ ,  $n = 2$ ) with reduced Phillips catalyst, a chromium(II) compd. surface-bound to silica, yield heterogeneous bimetallic metathesis catalysts for alkenes. The reactions probably proceed via a [2 + 1] cycloaddn. of the  $\text{W}\equiv\text{C}_{\text{carbyne}}$  bond with the chromium(II) atoms to give dimetallacyclopropene derivs. The bimetallic catalysts formed by reaction with the halo-substituted carbyne complexes are very active alkene metathesis catalysts, as demonstrated by the reaction with 1-octene. The original polymn. activity towards 1-alkenes of the surface-bound chromium(II) atoms disappeared after reaction with carbyne complexes.

~2 Citings

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**202. Investigation of polymerization and metathesis reactions. Part XIII. Heterogeneous bimetallic metathesis catalysts by reactions of differently substituted Fischer-type tungsten carbene complexes with reduced Phillips catalyst**

By Weiss, Karin; Guthmann, Wilfried; Denzner, Michael

From *Journal of Molecular Catalysis* (1988), 46(1-3), 341-9. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(88)85106-X

Reactions of reduced Phillips catalyst, a polymn. catalyst for 1-alkenes, with differently substituted Fischer tungsten carbene complexes  $(\text{CO})_5\text{W}:\text{CR}^1\text{R}^2$  ( $\text{R}^1 = \text{Ph}$ , 4-tolyl, Me;  $\text{R}^2 = \text{Ph}$ , OMe), which are metathesis catalysts with poor activity, give bimetallic heterogeneous compds. via loss of one CO ligand. Diffuse reflectance FTIR spectroscopy of the heterogeneous compds. shows a strong shift of the  $\nu\text{-CO}$  absorptions to higher wavenumbers, probably caused by a chromium-tungsten bond. The catalytic activity of these surface compds. was tested with 1-octene. All were very active metathesis catalysts, and no polymn. of 1-octene was obsd. The surface chromium atoms act as activating species for the metathesis activity of the carbene complex fragments. The influence of the carbene substituents on the metathesis reaction is not significant, with the exception of the Me substituent of  $(\text{CO})_5\text{W}:\text{C}(\text{OMe})\text{Me}$ . The new metathesis catalysts are stable at 20° and can be stored without loss of activity for some months.

~0 Citings

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**203. Monomer transport influences in the nascent polymerization of ethylene by silica-supported chromium oxide catalyst**

By Webb, Steven W.; Conner, W. Curtis; Laurence, Robert L.

From *Macromolecules* (1989), 22(7), 2885-94. Language: English, Database: CAPLUS, DOI:10.1021/ma00197a003



Transport influences during nascent ethylene polymn. over **Phillips catalyst** were evaluated by pulse solid-gas chromatog. The Thiele modulus for ethylene polymn. at 50° and 1 atm monomer pressure and yields <0.1 g polymer/g **catalyst** was ~1.5, and this value increased as polymer formed inside the **catalyst** pores. The rate of adsorption of ethylene over active Cr oxide was very fast relative to the surface reaction.

~11 Citings

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#### 204. Preparation of ethylene-propylene block copolymers by three-stage polymerization

By Buechner, Osakr; Gruber, Wolfgang

From *Ger. Offen.* (1988), DE 3702038 A1 19880804, Language: German, Database: CAPLUS

The title polymers, with a predetd. spectrum of properties, are prepd. by successive gas-phase Ziegler-Natta polymn. in the presence of H, fluidized-bed polymn. in the presence of H, and gas-phase Ziegler or **Phillips** polymn., optionally in the presence of H, under specified conditions. Thus, polymn. of 100:2 C<sub>3</sub>H<sub>6</sub>-H at 70° and 28 bar in the presence of AlCl<sub>3</sub>.2TiCl<sub>3</sub>.2PrOBz, Et<sub>2</sub>AlCl, and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (0.16:1:0.04), adding this product with addnl. 1:4 TiCl<sub>3</sub>-Et<sub>2</sub>AlCl and 100:35:38 C<sub>3</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>4</sub>-H to a fluidized bed at 55° and 15 bar, and adding this stream to a stirred bed of fine polyethylene particles prepd. by polymn. with 2% CrO<sub>3</sub>/SiO<sub>2</sub> (1st stage C<sub>3</sub>H<sub>6</sub>-3rd stage C<sub>2</sub>H<sub>4</sub> ratio 100:17) at 108° and 35 bar gave 26.5 kg/h block polymer with a favorable balance of stiffness, toughness, and resistance to cold impact.

~2 Citings

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#### 205. IR investigation of polymerization centers of the **Phillips catalyst**

By Ghiotti, Giovanna; Garrone, Edoardo; Zecchina, Adriano

From *Journal of Molecular Catalysis* (1988), 46(1-3), 61-77. Language: English, Database: CAPLUS,

DOI:10.1016/0304-5102(88)85083-1

CO-reduced **Phillips catalyst** (Cr<sup>2+</sup> ions supported on silica) was studied with emphasis on the CO/C<sub>2</sub>H<sub>4</sub> interaction, vibrational features of the polymer, its reactivity towards O, and the effect of CO on the spectrum of the polymer and vice versa. The no. of active sites increased during the polymn. and reached some 10% of the total loading. The spectral features of the Cr ions involved in the active sites are consequently visible in IR: before polymn. they chemisorb CO more strongly and form stable CO-ethylene complexes; after polymn. they can still adsorb CO in a distinguishable form (stretching frequency at 2173 cm<sup>-1</sup>). The polymer chain does not show any terminal group such as Me or vinyl; a cyclic structure is proposed. The chain may exist in either alkyl or alkylidenic form, in equil. with each other and differing by a proton reversibly transferred to a nearby O. A model for the polymn. mechanism is advanced involving a metallacyclobutane intermediate and accounting for the obsd. absence of scrambling among H atoms.

~0 Citings

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#### 206. Pretreated **Phillips** catalysts in manufacture of ethylene polymers

By Tomotsu, Norio

From *Jpn. Kokai Tokkyo Koho* (1988), JP 63068606 A 19880328, Language: Japanese, Database: CAPLUS

The ethylene polymers are prepd. with short initiating periods by polymg. C<sub>2</sub>H<sub>4</sub> and/or  $\alpha$ -olefins in the presence of catalysts (dialkyl Mg and baked solids of inorg. oxides and Cr compds.) precontacting with monomers to give  $\leq 500$  g polymers per mol Cr. Thus, 0.25 g CrO<sub>3</sub>, 40 mL H<sub>2</sub>O, and 13 g silica were stirred for 1 h, dried at 120° for 2 h, baked at 800° for 1 h to form a solid, 10 mg of which was mixed with 0.10 mmol BuMgEt, deoxygenated and dewatered, contacted with C<sub>2</sub>H<sub>4</sub> (20 kg/cm<sup>2</sup>-G) at 120° for 3 min, rapidly cooled, further contacted with C<sub>2</sub>H<sub>4</sub> (20 kg/cm<sup>2</sup>-G) at 100° for 1 h to form a polymer showing **catalyst** activity 21.3 kg/g-h-atm with no initiating period; vs. 15.4 kg/g-h-atm and 12 min, resp., without pretreatment.

~0 Citings

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#### 207. An IR study of the polymerization mechanism of the **Phillips catalyst**

By Rebenstorf, Bernd

From *Journal of Molecular Catalysis* (1988), 45(2), 263-74. Language: English, Database: CAPLUS,

DOI:10.1016/0304-5102(88)80016-6

IR investigation of the catalytic center of a Cr(II) surface compd. on silica gel (the active center of a **Phillips catalyst**) showed a broad band at 2750  $\text{cm}^{-1}$ , assigned to the stretching vibrations, and a new IR band at 1448  $\text{cm}^{-1}$ , assigned to the deformation vibration of a methylene group at the Cr(II) surface ion (carbene polymn. mechanism). On adsorption of CO on the Cr(II) surface compd., the CO stretching vibration was shifted to 2176  $\text{cm}^{-1}$  and the above two IR bands were replaced by normal methylene stretching vibrations (2852 and 2919  $\text{cm}^{-1}$ ) and by a methylene deformation vibration at 1466  $\text{cm}^{-1}$ . At higher polymn. temps. ( $>150^\circ$ ), Me groups (bands at 2879, 2962, 1456 and 1379  $\text{cm}^{-1}$ ) were obsd. in the polymer and also after reaction with CO.

~11 Citings

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## 208. Heterogeneous bimetal metathesis catalysts from carbene complexes of the Fischer type and reduced **Phillips catalyst**

By Weiss, Karin; Guthmann, Wilfried; Maisuls, Sergio

From *Angewandte Chemie* (1988), 100(2), 268-70. Language: German, Database: CAPLUS

The title catalysts were prepd. by treating reduced **Phillips catalyst** [Cr(II) on silica gel] with  $(\text{OC})_5\text{M}:\text{CPhOMe}$  (M = Cr, Mo, W) in pentane. The Cr-Cr **catalyst** was not active for polymn. or metathesis of 1-octene (I), but the Cr-Mo **catalyst** gave 7-tetradecene (II) and  $\text{C}_2\text{H}_4$  from I metathesis. The Cr-W **catalyst** gave significant amts. of nonene and tridecene byproducts from isomerization-metathesis, as well as II and  $\text{C}_2\text{H}_4$ .

~2 Citings

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## 209. Polymerization and metathesis reactions. Part X. Polymerization, trimerization and metathesis of allenes and heteroallenes with reduced **Phillips catalyst**

By Weiss, Karin; Hoffmann, Kurt

From *Zeitschrift fuer Naturforschung, B: Chemical Sciences* (1987), 42(6), 769-73. Language: German, Database: CAPLUS, DOI:10.1515/znb-1987-0621

The reduced **Phillips catalyst**, a surface Cr(II) on silica, catalyzes the polymn. of the allene 1,2-butadiene to yield predominantly 1,2-polybutadiene, yields trimerization products with isocyanates, and causes metathesis of 2 differently substituted carbodiimides.

~5 Citings

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## 210. Preparation of ethylene polymers with **Phillips catalysts**

By Konrad, Rainer; Mueller-Mall, Rudolf; Schweier, Guenther

From *Ger. Offen.* (1987), DE 3618259 A1 19871203, Language: German, Database: CAPLUS

$\text{C}_2\text{H}_4$  homopolymers or copolymers with  $\text{C}_{3-12}$   $\alpha$ -olefins are prepd. by polymn. at 30-150°/2-150 bar in the presence of catalysts contg. oxides of Cr, P, and Ti supported on fine, porous silicates heated in dry gases contg.  $>10\%$  O at 300-900° for 10-1000 min. A silicate (particle size 30-100  $\mu$ , pore vol. 1.75 mL/g, sp. surface 320  $\text{m}^2/\text{g}$ ) was stirred (100 parts) with 50 parts  $\text{CrO}_3$  (particle size  $<500 \mu$ ) in  $\text{CH}_2\text{Cl}_2$  and then with  $(\text{EtO})_3\text{PO}$  (Cr-P wt. ratio 1:1) at 20° for 30 min, mixed with 4 parts (as Ti)  $\text{Ti}(\text{OPr-iso})_4$ , stirred 30 min at 20°, dried at 80°/20 mm, and heated 2 h in dry N at 250° and 1 h in dry air at 500° to give a **catalyst**. Stirring 80 mg **catalyst** in 500 mL isobutane contg. BuLi (Cr-Li at. ratio 1:10) with  $\text{C}_2\text{H}_4$  at 93-97° for 1 h gave polyethylene with productivity 3.9 kg/g **catalyst**, melt index (190°, 21.6 kg) 6.0 g/10 min, polydispersity 32.3, and fraction with particle size  $<125 \mu$  0.2%.

~1 Citing

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## 211. Process for manufacture of ethylene (co)polymers using **Phillips catalysts**

By Konrad, Rainer; Warzelhan, Volker; Gropper, Hans; Schweier, Guenther

From *Ger. Offen.* (1987), DE 3609828 A1 19870924, Language: German, Database: CAPLUS

The title supported catalysts are prepd. and used in the (co)polymn. of  $C_2H_4$ . Thus,  $SiO_2$  (surface area  $320\text{ m}^2/\text{g}$ , pore vol.  $1.75\text{ cm}^3/\text{g}$ ) was heated for 8 h at  $140^\circ/20\text{ torr}$ , mixed (100 parts) with 400 parts anhyd. n-heptane, finely powd. ( $500\text{ }\mu\text{m}$  particle size)  $CrO_3$  to a ratio of 1 part  $CrO_3$  to 100 parts  $SiO_2$ , tert-BuOH ( $25^\circ$ ), and 4 parts  $Ti(\text{iso-PrO})_4$  per 100 parts carrier, stirred for 30 min, heated to  $80^\circ/20\text{ torr}$  until dry, heated for 120 min at  $250^\circ$  under anhyd. N, for 60 min at  $500^\circ$  in anhyd. air, then cooled in anhyd. N to  $100^\circ$ , producing a catalyst. An autoclave was charged with BuLi and the catalyst with n-heptane and isobutane, and the Cr-Li at. ratio maintained at 1:10 during the polymn. of  $C_2H_4$  at  $9 \pm 2^\circ/40\text{ bar}$ , producing polyethylene which had melt flow index (DIN 53735;  $190^\circ/21.6\text{ kPa}$ )  $6.1\text{ g}/10\text{ min}$ , and polydispersity 36.1. The catalyst activity was  $4000\text{ g polymer/g catalyst}$ .

~3 Citings

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## 212. High-density ethylene polymers (PE-HD)

By Strobel, Wolfgang K. F.

From *Aufbereit. Polyolefinen* (1984), 21-33. Language: German, Database: CAPLUS

A review with 21 refs. of high-d. ethylene copolymers, their use, relation between structure and properties, and processing, including Ziegler and Phillips catalyst systems and various manufg. methods, are reviewed.

~0 Citings

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## 213. Mechanistic aspects of the olefin polymerization by Phillips catalysts via $C_1$ species

By Hums, Erich

From *Industrial & Engineering Chemistry Product Research and Development* (1985), 24(4), 517-20. Language: English, Database: CAPLUS, DOI:10.1021/i300020a006

There is evidence for involvement of a  $C_1$  species that selectively interacts with the surface Cr(II) when the catalyst is treated with olefins or with  $C_1$  analogs like CO/H or  $CO_2/H$ . The observation that surface Cr(VI), when reacted with ethylene [74-85-1], delivers, among other products, CO,  $CO_2$ , and H provides an explanation for the development of alkanes at a chromium center with a lower valence state via  $C_1$  species. The development of alkanes can be understood as a Fischer-Tropsch reaction that is secondary to the dominant polymn. process. The  $C_1$  species, which seems to be an  $sp^2$ -hybridized C bonded to surface Cr(II), reacts with surface H via alkanes/alkylated metal just as with scavenging cyclohexene or chlorobenzene, which form methylated products.

~3 Citings

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## 214. Surface compounds of transition metals. XXIX. Reaction of surface chromium(VI)/silica gel with aluminum alkyls: "formation" of Phillips catalysts

By Krauss, H. L.; Hanke, B.

From *Zeitschrift fuer Anorganische und Allgemeine Chemie* (1985), 521, 111-21. Language: German, Database: CAPLUS

By the reaction of surface Cr(VI)/silica gel with Al alkyls (leading to the so called Phillips catalysts of the 2nd generation) the metal is reduced in 2 electron steps via a Cr(IV) intermediate to a final Cr product. The extent of the redn. depends on the ratio Al/Cr, the influence of light, the presence of higher olefins, and the temp.

~5 Citings

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## 215. UV/Vis investigation of the polymerization center of the Phillips catalyst

By Rebenstorf, Bernd

From *Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry* (1985), A39(2), 133-41. Language: English, Database: CAPLUS

UV-vis diffuse reflectance spectra were recorded of the Cr(II)/silica gel system with low Cr concn. (0.074%) after polymn. of C<sub>2</sub>H<sub>4</sub> at 373 K. From the decrease of the UV band of the CO (at 10<sup>5</sup> Pa) complex with the Cr(II) surface ion at 34,000 cm<sup>-1</sup>, it was estd. that ~50% of all Cr is polymn. active at this concn. The difference spectra of the polymn.-active Cr show 2 bands at 16,000 and 31,500 cm<sup>-1</sup> with absorbed CO or C<sub>2</sub>H<sub>4</sub>. After removing CO or C<sub>2</sub>H<sub>4</sub> by evacuation, a difference spectrum with 4 bands at 13,500, 27,500, 31,500 and 35,700 cm<sup>-1</sup> was obtained. These bands are interpreted as arising from a Cr(III) surface compd. formed by reaction of Cr(II) with C<sub>2</sub>H<sub>4</sub> and thus creating the Cr-C bond, which is essential for the polymn. active center of the **Phillips catalyst**.

~0 Citings

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## 216. Investigations of polymerization and metathesis reactions. Part I: carbene reactions with polymerization and metathesis catalysts

By Weiss, Karin; Hoffmann, Kurt

From *Journal of Molecular Catalysis* (1985), 28(1-3), 99-105. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(85)87021-8

With a polymn. **catalyst**, a reduced **Phillips catalyst**, and a Dolgoplosk metathesis **catalyst** (WCl<sub>6</sub>/N<sub>2</sub>CHCO<sub>2</sub>Et), well-known carbene ligand reactions such as cyclopropanation with alkenes and a Wittig-like reaction with ketones may be used as model reactions. For all these model reactions, N<sub>2</sub>CHCO<sub>2</sub>Et has been used as the carbene source. Whereas the reduced **Phillips catalyst** produced cyclopropanes as the main products, the metathesis **catalyst** WCl<sub>6</sub>/N<sub>2</sub>CHCO<sub>2</sub>Et gave dimers of the carbene ligand in good yield and only poor yields of cyclopropanes. No carbene complex reaction products could be found with the heterogeneous metathesis catalysts WO<sub>3</sub>/SiO<sub>2</sub> and W(CO)<sub>6</sub>/Al<sub>2</sub>O<sub>3</sub> in both model reactions.

~3 Citings

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## 217. Surface compounds of transition metals. Part XXVII. Redox reactions of reduced **Phillips catalysts** with olefins at higher temperatures: reactions via carbene/metallacyclobutane intermediates

By Krauss, Hans L.; Hagen, Klaus; Hums, Erich

From *Journal of Molecular Catalysis* (1985), 28(1-3), 233-8. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(85)87031-0

While Cr(II)/silica gel catalysts form polyethylene from ethylene at temps. around 100°, at higher temps. other reactions predominate; thus, together with the formation of alkanes (C<sub>1</sub>-C<sub>4</sub>) and even H<sub>2</sub>, surface compds. of Cr(IV) are formed. With higher 1-olefins, a shift of the double bond, branching of the C chain, and CH<sub>2</sub> transfer reactions occur simultaneously. All these reactions, including the initial step of chain propagation, may originate from a common intermediate, i.e. from a carbene complex of the surface Cr in equil. with a metallacyclobutane structure. The analogy to the metathesis mechanism of Herisson and Chauvin (1970) is obvious. The sites are finally killed by the formation of (π-allyl)<sub>2</sub>Cr(IV) surface compds. which are stable with respect to further attack by olefins. These units can be split off from silica gel by H<sup>+</sup> and may be characterized in soln.

~16 Citings

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## 218. The activation of the **Phillips polymerization catalyst**. III. Promotion by titania

By McDaniel, M. P.; Welch, M. B.; Dreiling, M. J.

From *Journal of Catalysis* (1983), 82(1), 118-26. Language: English, Database: CAPLUS, DOI:10.1016/0021-9517(83)90123-9

Cr/silica polymn. catalysts are rendered much more active by the incorporation of a small amt. of titania either in or on the support. The mol. wt. of the resultant polyethylene [9002-88-4] is also affected. In this report the promotional influence of titania has been examd. under different activation conditions. Results varied widely with the type of incorporation and the method of activation. Cr<sub>B</sub> centers were more sensitive to titania than Cr<sub>A</sub> centers.

~37 Citings

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## 219. The activation of the **Phillips polymerization catalyst**. I. Influence of the hydroxyl population

By McDaniel, M. P.; Welch, M. B.

From [Journal of Catalysis](#) (1983), 82(1), 98-109. Language: English, Database: CAPLUS, DOI:10.1016/0021-9517(83)90121-5

Parameters in the thermal activation of Cr/silica and Cr/silica-titania polymn. catalysts were studied. Both the activity and the mol. wt. of the polyethylene [9002-88-4] formed depended on the activation temp., suggesting a connection with the surface hydroxyl population surrounding each active center. Hydroxyls could be removed by chem. as well as by thermal means to take advantage of this dependence, such as by calcining the unpromoted support in carbon monoxide, sulfur, or halogen, and then afterward adding the chromium anhydrously. This two-step process also provided evidence of two types of chromium centers yielding high- and low-mol-wt. polymer. Combining all three influences, i.e. thermal dehydroxylation, chem. dehydroxylation, and the optimum distribution of active centers, yielded catalysts of extremely high activity and melt index potential.

~56 Citings

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## 220. Hydrogen transfer during propagation of the **Phillips catalyst**

By McDaniel, M. P.; Cantor, D. M.

From [Journal of Polymer Science, Polymer Chemistry Edition](#) (1983), 21(4), 1217-21. Language: English, Database: CAPLUS, DOI:10.1002/pol.1983.170210428

The transfer of H occurs during termination and initiation of polymn. of ethylene on **Phillips Cr/SiO<sub>2</sub> catalyst**, but no evidence of transfer was found during propagation to any significant extent. This ruled out the four-center mechanism described by M. M. Johnson and also the modified carbene mechanism of Merryfield, et al. (1982). The origin of the first initiating H was left unresolved.

~19 Citings

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## 221. Olefin-polymerization **catalyst**

By Ikegami, Tadashi; Takaya, Katsuhiko

From [Eur. Pat. Appl.](#) (1982), EP 67598 A2 19821222, Language: English, Database: CAPLUS

Ethylene (co)polymers having good melt flow and environmental stress cracking resistance are prepd. in the presence of a **Phillips catalyst** system comprising a solid component prepd. by calcining a Zr compd. in a Cr compd. supported on an inorg. oxide carrier and an organometallic compd. component. Thus, a 50 mg component (prepd. by stirring 1 kg SiO<sub>2</sub> with a soln. of 20 g CrO<sub>3</sub> in 4 L H<sub>2</sub>O for 1 h at room temp., drying at 100°, mixing with 42.1 g Zr(OBu)<sub>4</sub> [1071-76-7] and 4 L hexane, heating 2 h at 60°, and calcining 4 h at 800°), 0.05 mmol AlMg<sub>6.0</sub>Et<sub>3.0</sub>Bu<sub>12.1</sub>, and 0.15 mmol AlEt<sub>2</sub>OSiHMeEt [24989-85-3] were put in an autoclave contg. 1.6 L hexane. C<sub>2</sub>H<sub>4</sub> and H were added in an amt. to give C<sub>2</sub>H<sub>4</sub> pressure 10 kg/cm<sup>2</sup> and total pressure 14 kg/cm<sup>2</sup> and heated 2 h at 80° to give 365 g polyethylene [9002-88-4] having melt index 0.12 g/10 min and flow rate 270. The **catalyst** efficiency was 3560 g polymer/g **catalyst**/h.

~4 Citings

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## 222. Why do homogeneous analogs of **Phillips (chromium(VI) oxide/silica)** and Union Carbide (chromocene/silica) polyethylene catalysts fail? Some answers from IR investigations

By Rebenstorf, B.; Larsson, R.

From [Journal of Molecular Catalysis](#) (1981), 11(2-3), 247-56. Language: English, Database: CAPLUS, DOI:10.1016/0304-5102(81)87012-5

Both catalysts show strong IR bands after adsorption of CO, assigned to bridging CO mols. These bands are at 2120, 2100, and 2035 cm<sup>-1</sup> at low temps. (-145°) for the CO-reduced **Phillips catalyst** (Zecchina et al., 1975) and at 1920, 1825, and 1620 cm<sup>-1</sup> for the Union Carbide **catalyst**. Singly bonded CO shows IR bands at 2190, 2186, and 2179 cm<sup>-1</sup>, shifted to higher wavenumbers than CO gas (2143 cm<sup>-1</sup>), in contrast to bridging CO, or at 2046 and 1974 cm<sup>-1</sup> (and 2008 cm<sup>-1</sup>), resp. The singly bonded CO is replaced at low temps. (**Phillips catalyst**) or after some days at room temp. (Union Carbide **catalyst**) by bridging CO mols. These findings support not only the presence of binuclear Cr surface complexes, and indicate that such surface complexes account for most of the Cr. The IR studies make it possible to propose detailed models of the surface complexes. The polymn. of ethylene might be initiated by the addn. of an ethylene mol. to a surface complex by forming a M-CH<sub>2</sub>-CH<sub>2</sub>-M bridge. Homogeneous analogs for the catalysts should consist of incompletely coordinated binuclear complexes.

~31 Citings



**223. Modified Phillips catalysts for olefin polymerization**

By Eve, Paul Leslie

From *Brit. UK Pat. Appl.* (1980), GB 2048284 A 19801210, Language: English, Database: CAPLUS

The title catalysts for olefin polymn. comprise a heat-activatable catalyst base of Cr oxide and Ni oxide on a refractory oxide support and an organometallic compd. The polymn. reaction is optionally effected in the presence of a polyene modifier. Thus, to 3.2 g  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in 30 mL  $\text{H}_2\text{O}$  was added 30 g com.  $\text{Cr}_2\text{O}_3$  on silica. The catalyst material was dried at  $150^\circ$  and activated by heating 5 h at  $700^\circ$  in a bed fluidized by 900 mL air/min, giving a catalyst contg. Cr 1.0, Ni 3.1, and Cr(VI) 0.68%. A N-purged stainless steel reactor was baked 2 h at  $110^\circ$ , cooled to  $100^\circ$ , and charged with 417 mg catalyst, 1.7 mg  $\text{Et}_3\text{Al}$  [97-93-8], 2.1 g butadiene [106-99-0], and 1 L isobutane. The reactor was maintained at  $100^\circ$  and ethylene was supplied during 44 min to maintain a pressure of 41.4 bar to give 188 g polyethylene [9002-88-4].

**~1 Citing****224. Process and catalyst for polymerizing olefins**

By Downs, Gordon Wylie; Eve, Paul Leslie; Speakman, John Gabriel

From *Eur. Pat. Appl.* (1980), EP 18108 A1 19801029, Language: English, Database: CAPLUS

Phillips catalysts for the manuf. of polyolefins with high mol. wt. and broad mol. wt. distribution are prepd. by supporting a Cr compd. on a refractory oxide, adding a Ti(IV) compd., heating, and adding a group I A, II A, II B, or III A organometallic compd. Thus, 30 g  $\text{Cr}_2\text{O}_3$  on  $\text{SiO}_2$  is slurried in 30 mL petroleum ether with 4.5 g  $(\text{iso-PrO})_4\text{Ti}$  [546-68-9] and the solvent is distd. The catalyst is activated by heating for 5 h at  $500^\circ$  in a bed fluidized with 900 mL/min air. The catalyst, contg. Cr 1.00, Ti 2.42, and Cr(IV) 0.87%, is used with  $\text{Et}_3\text{Al}$  and optionally butadiene [106-99-0] in polymn. of  $\text{C}_2\text{H}_4$ . The polyethylene [9002-88-4] has a mol. wt. distribution broader than that when prepd. with an unmodified Phillips catalyst.

**~4 Citings****225. Polymerization of ethylene**

By Eve, Paul Leslie

From *Brit. UK Pat. Appl.* (1979), GB 2023153 A 19791228, Language: English, Database: CAPLUS

Ethylene or ethylene mixts. with other 1-olefins or diene monomers are polymd. in a liq. hydrocarbon solvent at  $<112^\circ$  by a modified Phillips catalyst comprising a heat-activated supported  $\text{CrO}_3$  catalyst and an organomagnesium modifier  $\text{MgRR}'$  ( $\text{R}$  = hydrocarbon;  $\text{R}'$  = H, halogen, hydrocarbon,  $\text{SiR}^2_3$ ,  $\text{NR}^2_2$ ,  $\text{PR}^2_2$ ,  $\text{OCR}^2_3$ ,  $\text{OSiR}^2_3$ ,  $\text{OR}^2$ , or  $\text{SR}^2$ ;  $\text{R}^2$  = H or hydrocarbon). Thus, 320 kg of a com.  $\text{Cr}_2\text{O}_3/\text{SiO}_2$  catalyst was activated 5 h at  $732^\circ$  in a 1.07-m-diam. gas-fired activator with a fluidizing air flow of 91 mm/s at  $\sim 1$  atm. The activated catalyst contg. 0.94% Cr was stored and handled under N. A baked-out N-purged 2.3-L stirred autoclave was charged with 396 mg catalyst, 15.0 mg  $\text{Bu}_2\text{Mg}$  [1191-47-5], and 1 L dry  $\text{Me}_3\text{CH}$ . The autoclave was heated to  $100^\circ$  and ethylene was admitted to maintain a total pressure of 41.4 bar during polymn. Polyethylene [9002-88-4] was obtained with productivity 707 kg/kg h having a melt index ( $\text{MI}_{21.6}$  ASTM 1238) 11.7 and a  $K_d$  value (Sabia, R., 1963) 4.6.

**~2 Citings****226. Evidence for alkylidenic configuration of polymethylene chains on a Phillips catalyst**

By Ghiotti, Giovanna; Garrone, Edoardo; Coluccia, Salvatore; Morterra, Claudio; Zecchina, Adriano

From *Journal of the Chemical Society, Chemical Communications* (1979), (22), 1032-3. Language: English, Database: CAPLUS, DOI:10.1039/c39790001032

IR studies of a low-loading (0.5% Cr) Phillips catalyst indicate that the catalyst acts by a similar mechanism to that proposed for the Ziegler-Natta process by K. J. Ivin et al. (1978). In the polymn. of ethylene [74-85-1] in the gas phase, polymethylene chains of  $\sim 20$   $\text{CH}_2$  units are linked to surface  $\text{Cr}^{2+}$  by alkylidene groups.

**~12 Citings**

**227. Supported polymerization catalysts for 1-olefins**

By Eve, Paul Leslie

From [Brit. UK Pat. Appl. \(1979\), GB 2017521 A 19791010](#), Language: English, Database: CAPLUS

Supported **Phillips** polymn. catalysts for 1-alkenes were manufd. by impregnating a support contg. 1.0-90% B phosphate and  $\geq 10\%$   $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , or  $\text{ThO}_2$  with a Cr compd. and heat activating. Thus, 9.4 g boric acid was dissolved in a soln. of 16.4 g  $\text{H}_3\text{PO}_4$  in 80 mL  $\text{H}_2\text{O}$  at  $60^\circ$  and the soln. mixed with a slurry of 64 g  $\text{SiO}_2$  in 200 mL  $\text{H}_2\text{O}$  and heated 1 h at  $60^\circ$ . Excess  $\text{H}_2\text{O}$  was removed under reduced pressure in a rotary evaporator and the solid was dried 4 h at  $120^\circ$ . To 24 mL of a soln. of 1.8 g  $\text{Cr}_2\text{O}_3$  in 2.2 mL tert-BuOH and 80 mL petroleum ether (b.  $40\text{--}60^\circ$ ) was added 25 g support material in 100 mL petroleum ether and the mixt. was stirred 1 h before removing excess solvent in a rotary evaporator, drying 1 h at  $150^\circ$ , and activating 5 h in a dry air-fluidized bed at  $500^\circ$ . The activated **catalyst** (465 mg) was mixed with 1 L isobutane under N at  $104^\circ$  and ethylene was added to maintain a total pressure of 41.4 bar. Polyethylene [9002-88-4] was formed at productivity 969 kg/kg h with melt index ratio 68.4.

**~1 Citing**

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**228. Ethylene-hexene-1 copolymers through modified **Phillips** catalysis**

By Spitz, R.; Florin, B.; Guyot, A.

From [European Polymer Journal \(1979\), 15\(5\), 441-4](#), Language: English, Database: CAPLUS, DOI:10.1016/0014-3057(79)90057-0

The title polymers were prepd. at const.  $\text{CH}_2\text{:CH}_2$  pressure in the absence of solvent using a Cr oxide- $\text{SiO}_2$  **catalyst** modified with small amts. of  $\text{Et}_3\text{Al}$  [97-93-8]. The ethylene-1-hexene copolymer [25213-02-9] samples were highly disperse in mol. wt. and compn. consisting of a solid fraction contg.  $<4\%$  hexene and a waxy fraction contg. most of the hexene units. With increasing  $\text{Et}_3\text{Al}$  concn. the polymn. rate increased to a sharp max. and then decreased and the amt. of waxy polymer formed decreased.

**~18 Citings**

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**229. Study of ethylene-1-hexene copolymers by proton and carbon-13 NMR**

By Florin-Michel, Brigitte; Llauro, Marie France; Spitz, R.; Pham, Q. T.

From [European Polymer Journal \(1979\), 15\(3\), 277-83](#), Language: French, Database: CAPLUS

The compn. and sequence distribution of samples of ethylene-1-hexene copolymer [25213-02-9] prepd. using a **Phillips catalyst** ( $\text{CrO}_3/\text{SiO}_2\text{-AlEt}_3$ ) were detd. by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, resp. Variations in the microstructure of the polymer were related to the polymn. conditions.

**~0 Citings**

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**230. Recent advances on **catalyst** of polyethylene and polypropylene production process**

By Matsuura, Tamotsu

From [Kagaku Sochi \(1979\), 21\(8\), 19-25](#), Language: Japanese, Database: CAPLUS

A review with 19 refs. of **Phillips catalyst** for polyethylene (I) [9002-88-4] manuf. and of Ziegler **catalyst** for I and polypropylene [9003-07-0] manuf.

**~0 Citings**

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**231. Polymerization **catalyst****

By Todd, Michael James

From [Brit. \(1979\), GB 1539375 A 19790131](#), Language: English, Database: CAPLUS

Catalysts for polymn. of alkenes were manufd. by treating  $\text{CrO}_3$ -contg. **Phillips**-type catalysts with  $\text{BCl}_3$  in anhyd. conditions. Polymers prepd. using such catalysts had narrow mol. wt. distributions and broad melt indexes and were useful for injection and rotational molding and other applications where low shear polymers are required. Thus, to 20 g predried Davison MS 969 **catalyst** in  $\text{CH}_2\text{Cl}_2$  was added 2.18 g  $\text{BCl}_3$  at  $0^\circ$  and the mixt. stirred 20 min at room temp. The  $\text{CH}_2\text{Cl}_2$  was evapd. in a N stream and the **catalyst** was activated in a fluidized bed 5 h at  $580^\circ$  in dry air. The **catalyst** (0.12 g) was placed in a stainless steel stirred 1 L reactor at  $120^\circ$ , 425 g cyclohexane was added and the temp. raised to  $130^\circ$ , ethylene was admitted until the pressure rose to 450 psi and polymn. proceeded 1 h at  $138^\circ$  to give polyethylene [9002-88-4] melt index 13.6 (ASTM 1238 method) and melt index ratio 23.6.

~0 Citings

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### 232. The influence of preparation parameters on the reactivity of chromium(II) surface compounds (modified **Phillips** catalysts)

By Krauss, H. L.; Rebenstorf, B.; Westphal, U.; Schneeweiss, D.

Edited By: Delmon, Bernard; Jacobs, P. A.; Poncelet, G

From *Prep. Catal., Proc. Int. Symp.* (1976), 489-95. Language: English, Database: CAPLUS

The properties of nonuniform surface catalysts such as  $\text{Cr}^{2+}$ -silica gel can be described by a reactivity quality profile. Coordinative shielding by neighboring groups is the most important parameter. Spectroscopic data differentiates domains of typical reactivity. **Phillips** Cr catalysts are useful in polymn. of olefins.

~4 Citings

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### 233. **Catalyst** preparation

By Stannard, Ivan C.

From *Brit.* (1977), [GB 1465264 A 19770223](#), Language: English, Database: CAPLUS

A **Phillips catalyst** or **catalyst** precursor, used in the polymn. of  $\text{C}_2\text{H}_4$  [74-85-1], was prepd. by rolling 50 g Davison Grade 952 MS-ID silica gel 30 min with 5 mL  $\text{H}_2\text{O}$  (6% of the total  $\text{H}_2\text{O}$  pore vol. of the gel) to moisten the gel without altering its free flowing properties.  $\text{CrO}_3$  was added, and the mixt. rolled a further 15 min to evenly coat the silica gel. Satisfactory Cr dispersion was detd. by anal. The **catalyst** was activated by heating several h at  $700^\circ$  in a dry air fluidized bed, before being successfully used in  $\text{C}_2\text{H}_4$  polymn.

~0 Citings

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### 234. **Catalyst** for the polymerization of 1-olefins

By Goldie, Brian Peter Forsyth

From *Ger. Offen.* (1977), [DE 2636496 A1 19770224](#), Language: German, Database: CAPLUS

A **Phillips catalyst** was treated with  $\text{TiCl}_4$  and  $\text{Me}_2\text{CHOH}$  [67-63-0], activated at  $400$ - $900^\circ$ , and used to prep. polyethylene (I) [9002-88-4] with a high melt index and a broad mol. wt. distribution. Thus, 30 g Davison MS 969 was dried at  $150^\circ$ , impregnated with 5% Ti as a soln. of  $\text{TiCl}_4$  in cyclohexane, distd. to remove solvent, treated at  $50^\circ$  with 10 mL  $\text{Me}_2\text{CHOH}$  in a stream of  $\text{N}_2$ , heated for 4 h at  $700^\circ$ , and used (0.131 g) in 1 L isobutane to polymerize ethylene at  $104^\circ/42$  atms. for 60 min, giving 378 g I.

~1 Citing

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### 235. Olefin polymerization **catalyst**

By Chalfont, Geoffrey R.; Crump, Ronald A.; Thukral, Prem S.

From *Brit.* (1975), [GB 1415649 A 19751126](#), Language: English, Database: CAPLUS

Polyethylene [9002-88-4] with high melt index was manufd. using an improved **Phillips catalyst** activated by heating at 900° in the presence of a titanium alkoxide or (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> [16962-40-6]. Thus, a conventional **catalyst** pore vol. 2.1-2.3 ml/g contg. 1.3 wt. % chromium oxide [1333-82-0] supported on SiO<sub>2</sub> was predried at 150° and impregnated with a soln. of titanium tetraisopropylate [546-68-9] in petroleum ether giving, after solvent removal and activation ~5 hr at 900° in a dry air stream, a **catalyst** contg. 4.10 wt. % Ti. Ethylene was supplied at 600 psi to a hot autoclave contg. 0.120 g **catalyst** and 500 ml isobutane giving, after 50 min at 108-9°, 240 g polyethylene which, after treatment with antioxidant and homogenization had ASTM 1238 melt index at 2.16 kg load 5.5 g/10 min compared with 1.97 g/10 min when the **catalyst** contained no Ti.

### ~3 Citings

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### 236. **Catalyst** for polymerization of 1-olefins

By Crump, Ronald A.

From **Brit. (1975)**, **GB 1415648 A 19751126**, Language: English, Database: CAPLUS

Polyethylene [9002-88-4] with high melt index was manufd. using an improved **Phillips catalyst** manufd. by impregnating a chromium oxide [1333-82-0] on SiO<sub>2</sub> **catalyst** (MS969), predried at 150°, with a petroleum ether soln. of Et titanate [3087-36-3] to give, after solvent removal and activation by heating ~5 hr at 800° in a dry air stream, a **catalyst** contg. 5.9 wt. % Ti. H<sub>2</sub>C:CH<sub>2</sub> was supplied at 600 psig to a hot autoclave contg. 0.107 g **catalyst** and 500 ml isobutane giving, after 50 min at 108-9°, 230 g polyethylene which, after treatment with antioxidant and homogenization, had ASTM 1238 melt index at 2.16 kg load 2.2 g/10 min.

### ~0 Citings

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### 237. **Catalyst** for polymerizing 1-olefins

By Chalfont, Geoffrey R.; Crump, Ronald A.; Thukral, Prem S.

From **Brit. (1975)**, **GB 1415647 A 19751126**, Language: English, Database: CAPLUS

Polyethylene [9002-88-4] with high melt index was manufd. using an improved **Phillips** polymn. **catalyst** manufd. by adding dropwise com. diisopropoxytitanium acetylacetonate [17927-72-9] to an agitated slurry of a predried chromium oxide [1333-82-0] on SiO<sub>2</sub> **catalyst** (MS969) in petroleum ether until Ti concn. was ~5 wt. %, distg. off solvent, and dry mixing with (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> [16919-19-0] giving a **catalyst** contg. 0.54 wt. % F, which was activated by heating ~4.75 hr in a dry air stream at 700°. H<sub>2</sub>C:CH<sub>2</sub> was supplied at 600 psig to a hot autoclave contg. 0.122 kg **catalyst** and 1000 ml isobutane, and, after 15 min the mixt. was heated 60 min at 110° giving 232 g polyethylene which, after treatment with antioxidant and homogenization, had ASTM 1238 melt index at 2.16 kg load 1.4 g/10 min.

### ~0 Citings

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### 238. Polymerization **catalyst**

By Chalfont, Geoffrey R.; Crump, Ronald A.; Thukral, Prem S.

From **Brit. (1975)**, **GB 1415646 A 19751126**, Language: English, Database: CAPLUS

Polyethylene [9002-88-4] with high crystallinity and melt index was manufd. using an improved **Phillips** polymn. **catalyst** manufd. by ball milling a SiO<sub>2</sub> support pore vol. ~1.6 ml/g, surface area ~280 m<sup>2</sup>/g, and mean pore diam. ~200 Å 1.5-2 hr with 2 wt. % CrO<sub>3</sub> [1333-82-0] and activated by heating ~4.5 hr at 800° in a dry air stream. Ethylene was supplied at 600 psi to a hot autoclave contg. 0.147 g of the **catalyst** and 500 ml isobutane, and, after 5 min the mixt. was heated 90 min at 108-9° giving 310 g polyethylene which, after treatment with antioxidant and homogenization, had crystallinity 84.6% and ASTM 1238 melt index at 2.16 kg load 0.29 g/10 min compared with 0.1 g/10 min for an unmilled but otherwise similar **catalyst**.

### ~0 Citings

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### 239. Polymerization process

By Crump, Ronald A.

From **Brit. (1975)**, **GB 1391772 A 19750423**, Language: English, Database: CAPLUS

Control of the mol. wt. distribution of polyethylene [9002-88-4] produced by C<sub>2</sub>H<sub>4</sub> polymn. over a chromium oxide [11118-57-3] (Phillips) catalyst was improved by pretreating the catalyst with ammonium hexafluorotitanate [16962-40-6] and activating at 600° in the absence of H<sub>2</sub>O. Thus, silica-alumina supported Cr oxide, contg. 2 wt. % of the Cr oxide, was dry mixed with (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> and activated 5 hr at 600° in dry air to give a final catalyst F content 1.1 wt. %. C<sub>2</sub>H<sub>4</sub> at 600 psi was admitted to 0.122 g of the catalyst in 500 ml isobutane. Polymn. 80 min at 109° gave 230 g polymer at productivity 1900 g/g catalyst. After treating with antioxidant and milling 5 min at 150° the polyethylene had ASTM1238 melt index ratio at 2.16 and 21.6 of 72 compared with 130 for a sample prepd. using untreated catalyst.

~1 Citing

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## 240. Polymerization process

By Crump, Ronald A.; Chalfont, Geoffrey R.; Thukral, Prem S.

From *Brit. (1975)*, [GB 1391771 A 19750423](#), Language: English, Database: CAPLUS

Control of the mol. wt. distribution of polyethylene [9002-88-4] produced by C<sub>2</sub>H<sub>4</sub> polymn. over chromium oxide [11118-57-3] (Phillips) catalyst was improved by pretreating the catalyst with a tetraalkyl titanate and an ammonium perfluoroanion salt and activating at 700-50° in the absence of H<sub>2</sub>O. Thus, predried supported Cr oxide was slurried with iso-Pr titanate [546-68-9] in isopentane, the mixt. contg. 4.9 wt. % on the catalyst of Ti, the isopentane was evapd. off, and the catalyst dry mixed with ammonium hexafluorotitanate [16962-40-6] to give a final catalyst contg. 1.1 wt. % F. The catalyst was activated ~5 hr at 750° in dry air. C<sub>2</sub>H<sub>4</sub> at 600 psi was supplied to 0.125 g of the catalyst in 500 ml isobutane preheated to 107-9°. After 90 min 300 g polyethylene was obtained at a productivity of 2400 g polymer/g catalyst. After treatment with antioxidant and milling 5 min at 150° the ASTM 1238 melt index under 2.16 and 21.6 kg loads were 0.30 and 49.0 g/10 min, resp.

~1 Citing

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## 241. Ethylene polymerization with Phillips catalysts

By Crump, Ronald A.; Chalfont, Geoffrey R.; Thukral, Prem S.

From *Ger. Offen. (1974)*, [DE 2240246 A1 19740221](#), Language: German, Database: CAPLUS

Polyethylene (I) [9002-88-4] of controlled mol. wt. distribution was prepd. by org. soln. polymn. in the presence of Phillips catalysts prepd. from 2% Cr oxide-0.2% Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> microspheres, alkyl titanates, and F-compds., e.g. ammonium hexafluorotitanate (II) [16962-40-6], followed by activation at 700-50.deg.. Thus, above microspheres were treated with isopropyl titanate [546-68-9] soln., the solvent evapd., and II added to give a catalyst contg. 4.9% Ti and 1.1% F and which was activated by heating 5 hr at 750.deg. in dry air. Polymn. of ethylene over this catalyst 90 min at 107-9.deg. and 42 kg/cm<sup>2</sup> gave 2400 g l/g catalyst of melt index (ASTM 1238, 2.16 kg) 0.30 g/10 min and melt index ratio (21.6:2.16 kg) 49.0.

~0 Citings

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## 242. Ligand effects on the heterogeneous catalysis of the ethylene polymerization. Modification of the Phillips catalyst

By Henrici-Olive, G.; Olive, S.

From *Angewandte Chemie (1973)*, [85\(18\)](#), 827-8. Language: German, Database: CAPLUS

Polymn. of ethylene over the CO-activated and molybdenum oxide [1313-27-5] modified Phillips catalyst (chromium trioxide [1333-82-0] on silica) at 300.deg., 10-3 g-atom Cr/g catalyst, and 0.65-1.3 mole ethylene/min g-atom Cr led to the formation of ethylene oligomers (mainly butene and hexene), while over the unmodified catalyst polyethylene [9002-88-4] was formed. At lower temp. and (or) lower rate of ethylene addn., the modified catalyst led also to the formation of polymers and cracking products. The active species was characterized by an interaction between Cr(II) and Mo [predominantly as Mo(VI)]. The redn. in electron d. at the Cr center by acid Mo oxide explains the change in mol. wt. distribution in the product and the reduced conversion.

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## 243. Melt viscosity of polyethylene fractions. Polyethylene produced by the slurry method using the Phillips catalyst



By Saeda, Shigeru; Suzuki, Tadao; Ogawa, Masao

From [Zairyo](#) (1972), 21(224), 440-4. Language: Japanese, Database: CAPLUS, DOI:10.2472/jsms.21.440

The fractions of polyethylene (I) [9002-88-4] polymd. by a slurry process using **Phillips catalyst** in a poor solvent showed a considerably higher melt viscosity and stronger extent of non-Newtonian behavior than the usual linear I in the high mol. wt. region, .sim. 5 .tim. 104. No difference was obsd. between the 2 series of fractions in the soln. behavior, such as the relation between the inherent viscosity (or the radius of gyration) and wt. av. mol. wt., and no microgels were obsd. The I fractions (**Phillips**) had smaller terminal vinyl group content (ir) than usual linear I at the same no. av. mol. wt. range and may contain starlike mols. by a few percent having long chain branches centered by the very fine **catalyst** particle.

~0 Citings

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#### 244. Vanadium and chromium catalysts for polymerization of ethylene

By Henrici-Olive, G.; Olive, S.

From [Angewandte Chemie, International Edition in English](#) (1971), 10(11), 776-86. Language: English, Database: CAPLUS, DOI:10.1002/anie.197107761

A combined study of magnetic properties and polymn. activity of heterogeneous **catalyst** systems showed vanadium formed active species as V(II) and V(III), but chromium, only as Cr(II). Ethylene [74-85-1] polymn. models are discussed for systems contg. vanadyl bis(2,4-pentanedionate) [3153-26-2] and chromium tris(2,4-pentanedionate) [21679-31-2]. General principles of **catalyst** activity and polymer properties based on a comparison of the systems with **Phillips catalyst** systems are given.

~9 Citings

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#### 245. Fluidized-bed polymerization

By Andersson, Kent; Sorvik, Erling

From [Kemisk Tidskrift](#) (1969-1993) (1970), 82(2), 32-5. Language: Swedish, Database: CAPLUS

Polymn. of ethylene and propylene using either a Ziegler or a **Phillips catalyst** are discussed.

~0 Citings

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#### 246. Measurement of the susceptibility of antiferromagnetic catalysts at a very low temperature

By Spitz, Roger; Turlier, Pierre

From [Journal de Chimie Physique et de Physico-Chimie Biologique](#) (1969), 66(7-8), 1256-8. Language: Russian, Database: CAPLUS

App. is described for obtaining measurements of magnetic susceptibility with >1% precision at 4-77°K. Thermal equil. is obtained between sample and resistance. The reciprocal of magnetic susceptibility of a **Phillips catalyst**, measured with this device, varied linearly with temp.

~0 Citings

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#### 247. Surface compounds of transition metals. III. Reactions of reduced Philips contact catalysts

By Krauss, Hans L.; Stach, Helmut

From [Zeitschrift fuer Anorganische und Allgemeine Chemie](#) (1969), 366(1-2), 34-42. Language: German, Database: CAPLUS

**Phillips** contact catalysts contg. surface Cr(VI) react with city gas, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, SO<sub>2</sub>, NH<sub>3</sub>, CO, CH<sub>4</sub>, and H forming reduced **Phillips catalyst** contg. surface Cr(II). The reduced **Phillips** catalysts react with various gases under reoxidn. or by coordination; by this reaction O can be removed from other gases to <0.02 ppm. Analogous behavior is observed with contact catalysts doped with Cu, Ti, V, Cr, Mo, Mn, Re, Fe, and Ti.

~26 Citings

**248. Chromium(II) as the active constituent in the Phillips catalyst in ethylene polymerization**

By Krauss, H. L.; Stach, H.

From [Inorganic and Nuclear Chemistry Letters \(1968\)](#), 4(7), 393-7. Language: German, Database: CAPLUS

Under optimum conditions, Cr in the Phillips catalyst reached the oxidn. no. 2. Other observations indicated that the higher the Cr(VI) content the more complete the redn. The obtainable redn. with the reducing agent decreased in the sequence CO, CH<sub>4</sub>, H<sub>2</sub>, higher hydrocarbons; e.g., C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>, CH<sub>4</sub>, and CO gave reduced oxidn. nos. of 2.94, 2.61, 2.57, and 2.10, resp. The polymn. rate of reduced material with oxidn. no. between 2 and 3 increased linearly with the Cr(II) content indicating that the active centers contain Cr(II). It appeared that polymn. required only that the Cr(II) prepd. from surface Cr(VI) remained unsatd. with respect to coordination.

**~13 Citings**

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**249. Recovery of volatile solvent from polymer as it is skimmed from aqueous slurries**

By Bell, Evan W.; Miller, Neil C.

From [No Corporate Source data available \(1966\)](#), US 3257374 19660621, Language: Unavailable, Database: CAPLUS

An improved method is described for recovery of solvent, stripping stream, and inert gas in a polymerization process from solids that have been removed from a slurry by flotation. The solids are treated with steam and inert gas that vaporizes the solvent and carries it along with the steam and inert gas. The gas stream is cooled, condensing the steam and solvent that are sepd. from the inert gas. The inert gas is mixed with steam from an ejector and used for further stripping of the solvent. Thus, polyethylene was prepd. by using a Phillips catalyst and processed through C<sub>2</sub>H<sub>4</sub> removal, catalyst removal, effluent concn., polymer pptn. in H<sub>2</sub>O, and stripping of the slurry to remove the solvent. The slurry is fed to the skim tank where 3500 lb./hr. (dry-polymer basis) polymer and 70 lb./hr. I are removed by an overhead inclined auger. Steam (60 lb./hr.) and 10 lb. N/hr. satd. with 8.8 lb. I vaporizes the I in the auger, which is at 175°F. and a pressure of 1 in. H<sub>2</sub>O. The polymer entering the drier contains 14 lb. I/hr., 56 lb./hr. having been removed. The vapor contains 10 lb. N/hr. and 64.8 lb. I/hr. I is condensed and the vapors are carried through a knockout pot (100°F. and 10 in. H<sub>2</sub>O abs. pressure) to a steam injector that requires 60 lb. II/hr. The vapors from the ejector are recycled to the auger. In previous processes, 130 lb. II/hr. and ~10 lb. N/hr. were required to recover 47.2 lb. I/hr.

**~0 Citings**

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**250. The activation of Phillips catalyst**

By Matsuda, Tsuneo; Ono, Yoshio; Keii, Tominaga

From [Journal of Polymer Science, Part A-1: Polymer Chemistry \(1966\)](#), 4(3), 730-2. Language: English, Database: CAPLUS, DOI:10.1002/pol.1966.150040328

A Cr oxide catalyst is heated at 300° in vacuo for 1 hr. before using it for C<sub>2</sub>H<sub>4</sub> polymerization. This heat treatment markedly improves the activity of the catalyst.

**~1 Citing**

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**251. Polyolefin-containing molding compositions**

No Inventor data available

From [No Corporate Source data available \(1965\)](#), NL 6503522 19650921, Language: Unavailable, Database: CAPLUS

The title compns. are obtained by blending or melting together polyolefins with a mol. wt. >180,000 with salts of bi- or trivalent metals and carboxylic acids with 1 or 2 acid groups with >10 C atoms, alkali metal salts or amides of carboxylic acids with >10 C atoms, the usual fillers or inorg. compds. with a layer structure m. >350° and having a hardness of <2 Mohs along the cleavage surface, and optionally solid foaming agents that form gases at 140-300°. Thus, 100 parts by wt. low-pressure polyethylene (I) (prepd. with a **Phillips catalyst**, mol. wt. 650,000, limiting viscosity no. 8, granulated to 100-2000 $\mu$ ) was blended with 1 part by wt. Na stearate and 4 parts by wt. Zn stearate (first impregnated with 6 parts by wt. montmorillonite on heating at 140°). The mixt. was extruded at 230° at 360 parts by wt./hr. into strings and granulated. The granules are re-extruded at 220° at a rate of 420 parts by wt. per hr. into pipes having a smooth, glossy surface. If no salts are added, I can only be extruded with difficulty at 280° at 100 parts by wt./hr., while the polymer is degraded. The rate increases to 170 parts by wt. per hr. when re-extruded due to a decrease in the mol. wt., but the pipes have no regular cross-section and are subject to melt-break failures.

~0 Citings

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## 252. The polymerization of olefins catalyzed by metallic oxides. II. Effect of impurities on the kinetics of polymerization of propylene by the **Phillips catalytic system**

By Guyot, Alain; Daniel, Jean Claude; Durrieu, Marc; Ptack, Marius

From *Journal of Polymer Science, Part A: General Papers* (1965), 3(5), 1765-73. Language: French, Database: CAPLUS

cf. CA 59, 11667d. The kinetics of polymerizations of  $C_3H_6$  were detd. for the **Phillips catalyst** contg. 2.19% Cr(V) on silica-alumina gel. Polymerizations were made with purified reagents or with reagents contg.  $CH_2:CHCH_2OH$  or  $EtCHO$ . Approx. 50 mg. of these compds. can completely poison several g. of **catalyst**. A plot of the rate const. against the wt. of **catalyst** for the system contg. impurities has an initial curved portion followed by a linear portion. A similar plot for the purified system is completely linear with a higher slope than that shown by the linear portion of the previous plot. Since 3 mg. of impurities can completely inhibit the activity of 1 g. of **catalyst**, if it is assumed that 1 mol. of impurity can poison 1 active site, then the no. of active sites per g. of **catalyst** must be less than  $3 \times 10^{19}$ . The catalysts contained ~2.5% Cr or  $3 \times 10^{20}$  atoms of Cr/g. Hence, only a fraction of Cr atoms are active centers, and these are Cr(V).

~0 Citings

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## 253. Polymerization of olefins catalyzed by metal oxides. I. Experimental methods of the kinetic study; preliminary results of the polymerization of propylene with a **Phillips catalyst**

By Guyot, Alain; Daniel, Jean Claude

From *Journal of Polymer Science* (1963), 1(Pt. A;8), 2989-3008. Language: French, Database: CAPLUS

cf. CA 56, 4129c. The kinetics of the polymerization of  $C_3H_6$  catalyzed by Cr oxide on an aluminosilicate carrier were investigated.  $C_3H_8$  was added as an inert diluent. Samples removed from the fluid medium surrounding the **catalyst** were analyzed with a gas chromatograph. The reaction was 1st order with respect to monomer and **catalyst**. Between 80 to 120°, the activation energy was 16 kcal./mole. When the pressure was low and the temp. high, a 2nd process occurred causing formation of volatile oligomers and retardation of the normal polymerization.

~1 Citing

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## 254. Metallic compounds as catalysts for polymerization

By Tsuruta, Teiji

From *Kagaku (Kyoto, Japan)* (1958), 13, 614-21. Language: Unavailable, Database: CAPLUS

Semicond. and catalytic action indicate the similarity of the **Phillips catalyst** and Standard **catalyst** with the Ziegler **catalyst**. 42 references.

~0 Citings

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## 255. Real-time Analysis of a Working Triethylaluminium-Modified Cr/Ti/SiO<sub>2</sub> Ethylene Polymerization **Catalyst** with In Situ Infrared Spectroscopy

By Cicmil Dimitrije; Weckhuysen Bert M; Meeuwissen Jurjen; Vantomme Aurelien  
From *ChemCatChem* (2016), 8(11), 1937-1944, Language: English, Database: MEDLINE

A diffuse reflectance infrared Fourier-transform (DRIFT) study has been conducted at 373 K and 1 bar on an industrial Cr/Ti/SiO<sub>2</sub> Phillips-type catalyst modified with, and without, triethylaluminium (TEAL) as co-catalyst. The reaction rate of the polymerization of ethylene, as monitored by the increase in the methylene stretching band of the growing polyethylene (PE), has been investigated as a function of the titanium content. After an initial period of mixed kinetics, with the reaction rate significantly higher for the TEAL-modified catalysts compared with the non-modified catalysts, the polymerization proceeded as a pseudo-zero-order reaction with a reaction rate that increased as a function of titanium loading. Furthermore, it was found that the higher Ti loading caused the appearance of more acidic hydroxyl groups and modified the Cr sites by making them more Lewis acidic, ultimately shortening the induction time and increasing the initial polymerization rate.

~0 Citings

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## 256. The Effect of the Electronic Nature of Spectator Ligands in the C-H Bond Activation of Ethylene by Cr(III) Silicates: An ab initio Study

By Nunez-Zarur Francisco; Comas-Vives Aleix  
From *Chimia* (2015), 69(4), 225-9, Language: English, Database: MEDLINE

The Phillips catalyst, chromium oxides supported on silica, is one of the most widely used catalysts for the industrial production of polyethylene (PE). We recently synthesized a well-defined mononuclear Cr(III) silicate as active site model of the Phillips catalyst. The catalytic activity of this well-defined catalyst was similar to the industrial Phillips catalyst. We proposed that C-H bond activation of ethylene over a Cr-O bond initiates polymerization in this Cr(III) catalyst. Our results also showed that the presence of a second ethylene olefin in the coordination sphere of Cr decreases the intrinsic energy barrier of the C-H activation of ethylene. In order to understand the effect of this additional ligand in the C-H activation of ethylene by the Cr(III) catalyst, we evaluated the energetics of this step with different spectator ligands (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>, N<sub>2</sub> and CO) coordinated to the Cr center. The Charge Decomposition Analysis (CDA) of the bonding interactions between the Cr(III) catalyst and the ligands showed that the intrinsic energy barrier for the C-H activation of ethylene decreases with the increasing electron-donor properties of the spectator ligand.

~0 Citings

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## 257. A Molecular Approach to Well-defined Metal Sites Supported on Oxides with Oxidation State and Nuclearity Control

By Delley Murielle F  
From *Chimia* (2015), 69(4), 168-71, Language: English, Database: MEDLINE

A molecular understanding of the catalytically active site is essential to rationally develop metal-containing heterogeneous catalysts. The controlled grafting of molecular precursors on pre-treated supports, often referred to as surface organometallic chemistry, is an approach to prepare well-defined heterogeneous catalysts with complex organic functionalities. However, many heterogeneous catalysts do not contain organic ligands coordinated to their active sites. To model such sites, the principles of surface organometallic chemistry therefore have to be adapted. Here, we describe a method, which provides access to molecularly-defined metal sites supported on oxides, which do not contain organic functionalities and are uniform in oxidation state and nuclearity. By consecutive grafting of suitable molecular precursors and controlled thermal treatment, we prepared and characterized well-defined dinuclear Cr(II) and Cr(III) species and mononuclear Cr(III) species supported on silica. We also investigated the polymerization activity of these materials in view of the well-known ethylene polymerization catalyst based on CrO(x)/SiO<sub>2</sub>, the so-called Phillips catalyst. This study led to new insights on the catalytically active sites in ethylene polymerization, which are based on Cr(III), not Cr(II).

~0 Citings

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## 258. Polyethylene with Reverse Co-monomer Incorporation: From an Industrial Serendipitous Discovery to Fundamental Understanding

By Cicmil Dimitrije; van Ravenhorst Ilse K; van der Bij Hendrik E; Munoz-Murillo Ara; Weckhuysen Bert M; Meeuwissen Jurjen; Vantomme Aurelien; Wang Jian

From *Angewandte Chemie (International ed. in English)* (2015), 54(44), 13073-9, Language: English, Database: MEDLINE

A triethylaluminium(TEAL)-modified Phillips ethylene polymerisation Cr/Ti/SiO<sub>2</sub> catalyst has been developed with two distinct active regions positioned respectively in the inner core and outer shell of the catalyst particle. DRIFTS, EPR, UV-Vis-NIR DRS, STXM, SEM-EDX and GPC-IR studies revealed that the catalyst produces simultaneously two different polymers, i.e., low molecular weight linear-chain polyethylene in the Ti-abundant catalyst particle shell and high molecular weight short-chain branched polyethylene in the Ti-scarce catalyst particle core. Co-monomers for the short-chain branched polymer were generated in situ within the TEAL-impregnated confined space of the Ti-scarce catalyst particle core in close proximity to the active sites that produced the high molecular weight polymer. These results demonstrate that the catalyst particle architecture directly affects polymer composition, offering the perspective of making high-performance polyethylene from a single reactor system using this modified Phillips catalyst.

~0 Citings

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### 259. Corrigendum: Polymerization of Ethylene by Silica-Supported Dinuclear Cr(III) Sites through an Initiation Step Involving C-H Bond Activation

By Conley Matthew P; Delley Murielle F; Siddiqi Georges; Lapadula Giuseppe; Norsic Sebastien; Monteil Vincent; Safonova Olga V; Coperet Christophe

From *Angewandte Chemie (International ed. in English)* (2015), 54(23), 6670, Language: English, Database: MEDLINE

~0 Citings

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### 260. Heterolytic Activation of C-H Bonds on Cr(III)-O Surface Sites Is a Key Step in Catalytic Polymerization of Ethylene and Dehydrogenation of Propane

By Conley Matthew P; Delley Murielle F; Nunez-Zarur Francisco; Comas-Vives Aleix; Coperet Christophe

From *Inorganic chemistry* (2015), 54(11), 5065-78, Language: English, Database: MEDLINE

We describe the reactivity of well-defined chromium silicates toward ethylene and propane. The initial motivation for this study was to obtain a molecular understanding of the Phillips polymerization catalyst. The Phillips catalyst contains reduced chromium sites on silica and catalyzes the polymerization of ethylene without activators or a preformed Cr-C bond. Cr(II) sites are commonly proposed active sites in this catalyst. We synthesized and characterized well-defined chromium(II) silicates and found that these materials, slightly contaminated with a minor amount of Cr(III) sites, have poor polymerization activity and few active sites. In contrast, chromium(III) silicates have 1 order of magnitude higher activity. The chromium(III) silicates initiate polymerization by the activation of a C-H bond of ethylene. Density functional theory analysis of this process showed that the C-H bond activation step is heterolytic and corresponds to a  $\sigma$ -bond metathesis type process. The same well-defined chromium(III) silicate catalyzes the dehydrogenation of propane at elevated temperatures with activities similar to those of a related industrial chromium-based catalyst. This reaction also involves a key heterolytic C-H bond activation step similar to that described for ethylene but with a significantly higher energy barrier. The higher energy barrier is consistent with the higher pK<sub>a</sub> of the C-H bond in propane compared to the C-H bond in ethylene. In both cases, the rate-determining step is the heterolytic C-H bond activation.

~0 Citings

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### 261. Proton transfers are key elementary steps in ethylene polymerization on isolated chromium(III) silicates

By Delley Murielle F; Nunez-Zarur Francisco; Conley Matthew P; Comas-Vives Aleix; Siddiqi Georges; Coperet Christophe; Norsic Sebastien; Monteil Vincent; Safonova Olga V

From *Proceedings of the National Academy of Sciences of the United States of America* (2014), 111(32), 11624-9, Language: English, Database: MEDLINE



Mononuclear Cr(III) surface sites were synthesized from grafting [Cr(OSi(O(t)Bu)<sub>3</sub>)<sub>3</sub>(tetrahydrofurano)<sub>2</sub>] on silica partially dehydroxylated at 700 °C, followed by a thermal treatment under vacuum, and characterized by infrared, ultraviolet-visible, electron paramagnetic resonance (EPR), and X-ray absorption spectroscopy (XAS). These sites are highly active in ethylene polymerization to yield polyethylene with a broad molecular weight distribution, similar to that typically obtained from the **Phillips catalyst**. CO binding, EPR spectroscopy, and poisoning studies indicate that two different types of Cr(III) sites are present on the surface, one of which is active in polymerization. Density functional theory (DFT) calculations using cluster models show that active sites are tricoordinated Cr(III) centers and that the presence of an additional siloxane bridge coordinated to Cr leads to inactive species. From IR spectroscopy and DFT calculations, these tricoordinated Cr(III) sites initiate and regulate the polymer chain length via unique proton transfer steps in polymerization catalysis.

~0 Citings

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## 262. Polymerization of ethylene by silica-supported dinuclear Cr(III) sites through an initiation step involving C-H bond activation

By Conley Matthew P; Delley Murielle F; Siddiqi Georges; Lapadula Giuseppe; Norsic Sebastien; Monteil Vincent; Safonova Olga V; Coperet Christophe  
From *Angewandte Chemie (International ed. in English)* (2014), 53(7), 1872-6, Language: English, Database: MEDLINE

The insertion of an olefin into a preformed metal-carbon bond is a common mechanism for transition-metal-catalyzed olefin polymerization. However, in one important industrial **catalyst**, the **Phillips catalyst**, a metal-carbon bond is not present in the precatalyst. The **Phillips catalyst**, CrO<sub>3</sub> dispersed on silica, polymerizes ethylene without an activator. Despite 60 years of intensive research, the active sites and the way the first Cr C bond is formed remain unknown. We synthesized well-defined dinuclear Cr(II) and Cr(III) sites on silica. Whereas the Cr(II) material was a poor polymerization **catalyst**, the Cr(III) material was active. Poisoning studies showed that about 65 % of the Cr(III) sites were active, a far higher proportion than typically observed for the **Phillips catalyst**. Examination of the spent **catalyst** and isotope labeling experiments showed the formation of a Si-(μ-OH)-Cr(III) species, consistent with an initiation mechanism involving the heterolytic activation of ethylene at Cr(III) O bonds.

~0 Citings

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## 263. The effect of hydrosilanes on the active sites of the **Phillips catalyst**: the secret for in situ α-olefin generation

By Barzan Caterina; Gianolio Diego; Groppo Elena; Lamberti Carlo; Monteil Vincent; Quadrelli Elsje Alessandra; Bordiga Silvia  
From *Chemistry (Weinheim an der Bergstrasse, Germany)* (2013), 19(51), 17277-82, Language: English, Database: MEDLINE

~0 Citings

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## 264. Low temperature activation and reactivity of CO<sub>2</sub> over a Cr(II)-based heterogeneous **catalyst**: a spectroscopic study

By Groppo Elena; Zecchina Adriano; Barzan Caterina; Vitillo Jenny G  
From *Physical chemistry chemical physics : PCCP* (2012), 14(18), 6538-43, Language: English, Database: MEDLINE

A new heterogeneous **catalyst** for CO<sub>2</sub> activation was identified in the Cr(II)/SiO<sub>2</sub> **Phillips catalyst**, one of the most important catalysts used industrially for olefin polymerization. Interestingly, it was found that Cr(II)/SiO<sub>2</sub> strongly activates CO<sub>2</sub> already at room temperature, making it available for chemicals synthesis. A preliminary attempt in this direction was done by following the reaction of CO<sub>2</sub> with ethylene oxide at room temperature by means of FT-IR spectroscopy, which showed the formation of ethylene carbonate. Besides non-reductive CO<sub>2</sub> activation, Cr(II)/SiO<sub>2</sub> showed good performances in catalytic reduction of CO<sub>2</sub> to CO, when heated under mild conditions or irradiated with UV-Vis light. Both, in situ FT-IR and UV-Vis spectroscopy, were applied to highlight the redox process occurring at the Cr centres. These results open interesting perspectives to be developed in the field of CO<sub>2</sub> chemical fixation.

## ~0 Citings

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**265. Ethylene polymerization on a SiH<sub>4</sub>-modified Phillips catalyst: detection of in situ produced  $\alpha$ -olefins by operando FT-IR spectroscopy**

By Barzan Caterina; Groppo Elena; Quadrelli Elsie Alessandra; Monteil Vincent; Bordiga Silvia

From *Physical chemistry chemical physics : PCCP* (2012), 14(7), 2239-45, Language: English, Database: MEDLINE

Ethylene polymerization on a model Cr(II)/SiO<sub>2</sub> Phillips catalyst modified with gas phase SiH<sub>4</sub> leads to a waxy product containing a bimodal MW distribution of  $\alpha$ -olefins ( $M(w) < 3000 \text{ g mol}^{-1}$ ) and a highly branched polyethylene, LLDPE ( $M(w) \approx 10(5) \text{ g mol}^{-1}$ ,  $T(m) = 123 \text{ }^\circ\text{C}$ ), contrary to the unmodified catalyst which gives a linear and more dense PE, HDPE ( $M(w) = 86,000 \text{ g mol}^{-1}$  ( $PDI = 7$ ),  $T(m) = 134 \text{ }^\circ\text{C}$ ). Pressure and temperature resolved FT-IR spectroscopy under operando conditions ( $T = 130\text{-}230 \text{ K}$ ) allows us to detect  $\alpha$ -olefins, and in particular 1-hexene and 1-butene (characteristic IR absorption bands at 3581-3574, 1638 and 1598  $\text{cm}^{-1}$ ) as intermediate species before their incorporation in the polymer chains. The polymerization rate is estimated, using time resolved FT-IR spectroscopy, to be 7 times higher on the SiH<sub>4</sub>-modified Phillips catalyst with respect to the unmodified one.

## ~0 Citings

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**266. Enhancing the initial rate of polymerisation of the reduced Phillips catalyst by one order of magnitude**

By Groppo Elena; Damin Alessandro; Otero Arean Carlos; Zecchina Adriano

From *Chemistry (Weinheim an der Bergstrasse, Germany)* (2011), 17(40), 11110-4, Language: English, Database: MEDLINE

## ~0 Citings

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**267. Modeling CO and N<sub>2</sub> adsorption at Cr surface species of Phillips catalyst by hybrid density functionals: effect of Hartree-Fock exchange percentage**

By Damin Alessandro; Vitillo Jenny G; Ricchiardi Gabriele; Bordiga Silvia; Lamberti Carlo; Groppo Elena; Zecchina Adriano

From *The journal of physical chemistry. A* (2009), 113(52), 14261-9, Language: English, Database: MEDLINE

In this article, we present a computational study of the structure and vibrational properties of the species formed by the interaction between Cr sites of Phillips catalyst and probe molecules (CO, N<sub>2</sub>). The vibrational properties of these surface species, intensively investigated in the past, form a very rich and ideal set of experimental data to test computational approaches. By adopting the X<sub>4</sub>Si<sub>2</sub>O<sub>3</sub>Cr (X = H, OH, F) cluster as a simplified model of the ([triple bond]SiO)<sub>2</sub>Cr(II) species present at the surface of the real catalyst, we found that the B3LYP hybrid functional (containing 20% of Hartree-Fock exchange), when applied to this model, is unable to reproduce with reasonable accuracy the currently available experimental data (principally coming from IR spectroscopy). Better agreement is obtained when the percentage of Hartree-Fock exchange is increased (up to 35-40%).

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**268. FTIR investigation of the H<sub>2</sub>, N<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> molecular complexes formed on the Cr(II) sites in the Phillips catalyst: a preliminary step in the understanding of a complex system**

By Groppo E; Lamberti C; Bordiga S; Spoto G; Damin A; Zecchina A

From *The journal of physical chemistry. B* (2005), 109(31), 15024-31, Language: English, Database: MEDLINE

This work reports the first complete FTIR characterization of H<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> molecular complexes formed on the Cr(II) sites in the **Phillips catalyst**. The use of a silica aerogel as support for Cr(II) sites, substituting the conventional aerosil material, allowed us to obtain a remarkable increase in the signal-to-noise ratio of the IR spectra of adsorbed species. The improvement is directly related to an increase of the surface area of the support (approximately 700 m<sup>2</sup> g<sup>-1</sup>) and to an almost complete absence of scattering [Groppo et al., Chem. Mater. 2005, 17, 2019-2027]. The use of this support and the adoption of suitable experimental conditions results, for the first time, in the clear observation of H<sub>2</sub> and N<sub>2</sub> adducts formed on two different types of Cr(II) sites, thus yielding important information on the coordinative state of the Cr(II) ions, which well agrees with the evidences provided in the past by other probe molecules. Furthermore, we report the first complete characterization of the C<sub>2</sub>H<sub>4</sub> pi-complexes formed on Cr(II) sites. These results are particularly important in the view of the understanding of the polymerization mechanism, since the C<sub>2</sub>H<sub>4</sub> coordination and the formation of pi-bonded complexes are the first steps of the reaction.

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### 269. Polymerization of ethylene molecules chemisorbed on CrOH<sup>+</sup> as a model system of chromium-containing catalyst

By Hanmura Tetsu; Ichihashi Masahiko; Monoi Takashi; Matsuura Kazuo; Kondow Tamotsu  
From *The journal of physical chemistry. A* (2005), 109(29), 6465-70, Language: English, Database: MEDLINE

The reaction process of the production of CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> was studied in connection with the ethylene polymerization on a silica-supported chromium oxide catalyst (the **Phillips catalyst**). Cluster ions CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> and CrOH(C<sub>4</sub>H<sub>8</sub>)<sup>+</sup> were produced by the reactions of CrOH<sup>+</sup> with C<sub>2</sub>H<sub>4</sub> (ethylene) and C<sub>4</sub>H<sub>8</sub> (1-butene), respectively, and were allowed to collide with a Xe atom under single collision conditions. The cross section for dissociation of each parent cluster ion was measured as a function of the collision energy (collision-induced dissociation, or CID). It was found that (i) the CID cross section for the production of CrOH<sup>+</sup> from CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> increases sharply at the threshold energy of 3.16 +/- 0.22 eV and (ii) the CID cross section for the production of CrOH<sup>+</sup> and C<sub>4</sub>H<sub>8</sub> from CrOH(C<sub>4</sub>H<sub>8</sub>)<sup>+</sup> also increases sharply at the threshold energy of 3.26 +/- 0.21 eV. In comparison with the calculations based on a B3LYP hybrid density functional method, it is concluded that two ethylene molecules in CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> are polymerized to become 1-butene. The calculation also shows that the dimerization proceeds via CrOH(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup> (ethylene complex) and CrOH(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>+</sup> (ethylene complex), in which the ethylene molecules bind with CrOH<sup>+</sup> through a pi-bonding.

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### 270. On the fraction of Cr(II) sites involved in the C<sub>2</sub>H<sub>4</sub> polymerization on the Cr/SiO<sub>2</sub> **Phillips catalyst**: a quantification by FTIR spectroscopy

By Groppo E; Lamberti C; Cesano F; Zecchina A  
From *Physical chemistry chemical physics : PCCP* (2006), 8(21), 2453-6, Language: English, Database: MEDLINE

An estimation of the fraction of Cr(II) sites involved in the C(2)H(4) polymerization on a Cr(II)/SiO(2) **Phillips catalyst** has been obtained by means of in situ alternated CO adsorption and C(2)H(4) polymerization FTIR experiments: about 28% of the total surface sites react fast with C(2)H(4), while a lower fraction, which depends upon the temperature reaction conditions, is more slowly involved, in agreement with XANES results.

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### 271. Activation processes and polyethylene formation on a **phillips model catalyst** studied by laser ablation, laser desorption, and static secondary ion mass spectrometry

By Aubriet Frederic; Muller Jean-Francois; Poleunis Claude; Bertrand Patrick; Di Croce Pascal G; Grange Paul  
From *Journal of the American Society for Mass Spectrometry* (2006), 17(3), 406-14, Language: English, Database: MEDLINE

Since the discovery of the **Phillips catalysts**, there still is much uncertainty concerning their activation, their molecular structure, the nature of the active chromium sites, and the polymerization mechanisms. Surface techniques are not easy to be used for such study according to the nonconductive behavior of the support. Therefore, model **Phillips catalyst** is elaborated by spin coating a trivalent chromium precursor on a silicon wafer. The surface characterization of this model **catalyst** is conducted by laser ablation mass spectrometry (LA-MS), laser desorption/ionization mass spectrometry (LDI-MS), and static secondary ion mass spectrometry (s-SIMS), at different steps of its preparation. To validate our approach, a comparison is also made between the model and the real **Phillips catalyst**. Moreover, the model **catalyst** efficiency for polyethylene synthesis is evaluated and allows us to discuss the validity of the mechanisms previously proposed to explain the catalytic process. The characterization of **Phillips model catalyst** by mass spectrometry allows us to better understand the activation processes of such **catalyst**. Depending on the activation temperature, chromium oxide species are formed and anchored at the support surface. They consist mainly in mono-chromium sites at high temperature. The chromium valence is hexavalent. This model **catalyst** is active for the polymerization of ethylene. A pseudo-oligomer molecular weight distribution is observed by LA-MS, whereas s-SIMS allows us to elucidate the anchorage of the polymer at activate chromium surface sites.

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#### 272. A chromium **catalyst** for the polymerization of ethylene as a homogeneous model for the **phillips catalyst**

By MacAdams Leonard A; Buffone Gerald P; Incarvito Christopher D; Rheingold Arnold L; Theopold Klaus H  
From *Journal of the American Chemical Society* (2005), 127(4), 1082-3, Language: English, Database: MEDLINE

A structurally characterized cationic chromium(III) alkyl featuring a bulky nacnac ligand catalyzes the polymerization of ethylene as well as the copolymerization of ethylene with alpha-olefins. This well-characterized homogeneous **catalyst** constitutes a structural as well as functional model of the widely used heterogeneous **Phillips olefin polymerization catalyst**.

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#### 273. Characterization of a model **Phillips catalyst** by mass spectrometry

By Di Croce Pascal Gabriel; Aubriet Frederic; Chety-Gimondo Rachel; Muller Jean-Francois; Grange Paul  
From *Rapid communications in mass spectrometry : RCM* (2004), 18(6), 601-8, Language: English, Database: MEDLINE

A model **Phillips catalyst** for ethylene polymerization, prepared by spin coating a Cr(III)(Cr(acac)<sub>3</sub>) precursor on a silicon wafer, was submitted to an oxidative activation. Laser ablation Fourier transform mass spectrometry provided direct information on molecular species at the silicon wafer surface during activation. At 350 degrees C the chromium precursor was degraded, while chromium oxide species were formed. The chromium concentration decreased with temperature. The activated model **catalyst** was active for ethylene polymerization. Using complementary techniques (Fourier transform infrared spectroscopy, laser desorption/ionization mass spectrometry), the polymer was identified as crystalline polyethylene. After 1 h of polymerization at 160 degrees C, dome-like structures were observed by atomic force microscopy. Their morphologies were constituted of regions of parallel aligned lamellae of polymer.

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