Chromium Allyls on Silica: A Study of Structure and Reactivity

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Received October 22, 1997

The reactions of Cr(2-Me-allyl)$_3$ with the surface of silica dehydrated at temperatures in the range 200−800 °C have been studied by quantitative gas chromatography measurements and diffuse reflectance infrared spectroscopy and as catalysts for polymerization of ethylene. While relatively high molecular weight polyethylene with a negligible amount of side chain branches was produced with Cr(2-Me-allyl)$_3$ on silica dehydrated at 200 °C, the catalyst based on silica dehydrated at 800 °C produced polymer with a high concentration of short-chain branches as well as a broad distribution of oligomers. During preparation, Cr(2-Me-allyl)$_3$ reacts primarily with hydroxyl groups with release of the allyl ligands as isobutene to form supported chromium complexes; the reaction stoichiometry depends on the density of surface hydroxyl groups. Diffuse reflectance infrared spectroscopy shows the presence of π-bonded allyl ligands only on samples prepared with highly dehydrated silica. All catalysts give bands typical for vinyl groups, indicating the presence of σ-bonded allyl ligands. CO adsorption is more extensive on Cr(2-Me-allyl)$_3$ reacted on highly dehydrated silica compared with samples prepared on silica dehydrated at lower temperatures, reflecting different levels of coordinative unsaturation of chromium for the catalysts. The diffuse reflectance infrared spectra recorded in the presence of ethylene at ambient temperature reflect the results from the slurry polymerization experiments performed under realistic conditions.

Introduction

Tris(allyl)chromium, Cr(allyl)$_3$, reacts on the surface of calcined silica to form an active catalyst for ethylene polymerization.[1,2] The properties of the catalyst formed are strongly dependent on the pretreatment of the silica used. Typically, when ethylene is polymerized on a Cr(allyl)$_3$/SiO$_2$ catalyst where the silica has been dehydrated at a temperature between 200 and 400 °C, high-molecular-weight polyethylene with a relatively low number of short-chain branches is formed. However, if the silica used is dehydroxylated at higher temperatures, typically 700−800 °C, the product consists of waxy oligomers.[3] The activity of the catalyst is also strongly dependent on the calcination temperature, and maximum activity is obtained when the silica is dehydrated at around 400 °C.[4,5] Previous investigation of the reaction between Cr(allyl)$_3$ and silica show that propene is released during the reaction, indicating that the allyl complex reacts with the silanol groups on the silica surface.[2] The stoichiometry of this reaction depends on the density of silanol groups on the surface. Higher calcination temperature leads to a lower number of silanol groups and thus a higher number of intact chromium−allyl fragments present.

The aim of the present work is to investigate the structures of surface complexes and the behavior during polymerization of ethylene for the catalysts formed when reacting Cr(2-Me-allyl)$_3$ with silica calcined at temperatures in the range 200−800 °C. Slurry polymerizations have been carried out, and the solid products have been characterized by infrared spectroscopy. GC analyses of the liquid phase in the reactor after the polymerizations have been performed to study the oligomers present. DRIFT spectra of both Cr(2-Me-allyl)$_3$ and Cr(allyl)$_3$ on silica have also been recorded.

The two complexes Cr(2-Me-allyl)$_3$ and Cr(allyl)$_3$ are assumed to react in a similar fashion; hence, studies of the former are expected to reveal information relevant to the latter. The reaction between Cr(2-Me-allyl)$_3$ and silanol groups on the silica surface will yield isobutene, while reactions with Cr(allyl)$_3$ yield propene. Isobutene will remain in the pentane solution if the reaction is carried out at −25 °C and is easier to collect and measure (by GC) than propene. But most important, isobutene is much less likely to polymerize or oligomerize than propene. On the other hand, the Cr(allyl)$_3$/SiO$_2$ catalyst is easier to study with DRIFTS than is Cr(2-Me-allyl)$_3$/SiO$_2$, as a consequence of the simpler spectra obtained in the absence of methyl groups.

Experimental Section

All solvents used throughout this study were dried, degassed, and purified according to standard techniques. All

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[1] Union Carbide Corp. U.S. Patent 4,054,538.

[2] Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263.

[3] Karol, F. J.; Johnsen, R. N. *J. Polym. Sci.* **1975**, *13*, 1607.

[4] Yermakov, Yu. I. *Catal. Rev.-Sci. Eng.* **1976**, *13* (1), 77.

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S0276-7333(97)00921-7 CCC: $15.00

handling and storage of metal complexes and catalysts were carried out either on a Schlenk line or in a glovebox under an argon atmosphere. Cr(allyl)$_3$ and Cr(2-Me-allyl)$_3$ were prepared as described by O'Brien and co-workers.[6]

The concentrations of chromium in the organochromium/pentane solutions were measured by ICP analyses. In addition, a sample of the Cr(2-Me-allyl)$_3$ solution was reacted with excess amounts of 1-butanol at −50 °C; the released isobutene was then remaining in solution and could be measured by gas chromatography.

Silica (EP10 from Crosfiled Chemicals) was dehydrated in dry air in a fluidized bed reactor for 16 h at the desired temperature. The silicas dehydrated at 200, 400, and 800 °C are hereafter referred to as SiO$_2$(200), SiO$_2$(400), and SiO$_2$(800), respectively. The procedure was as follows: first, the silica sample was suspended in a certain amount of purified pentane. Then, a certain amount of a pentane solution of either Cr(allyl)$_3$ or Cr(2-Me-allyl)$_3$ was added at −25 °C in order to obtain 1.0 wt % Cr in the final catalyst. After a few minutes of stirring at −25 °C, the supernatant solution became colorless and clear. To measure the isobutene released during the reaction, samples of the pentane solution were collected for GC characterization. After the catalyst sample was heated to ambient temperature, the pentane solution was filtered off. The catalyst was washed twice with purified pentane and finally dried under reduced pressure at ambient temperature for about 1 h. The samples were stored in a glovebox.

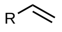
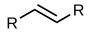
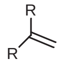
To determine the amount of allyl/2-Me-allyl ligands still attached to the chromium, excess purified 1-butanol was added to 40 mL bottles containing 0.3 g of catalyst under argon at ambient temperature. The gas composition in the bottle was analyzed chromatographically in order to determine the amount of released propene/isobutene.

Polymerization with ethylene was performed in a 1 L stirred autoclave where 0.5 L of isobutane was used as diluent. The polymerization temperature was 90 ± 1 °C, and the total pressure was kept constant at 30 bar by continuously adding ethylene. The polymer product will be completely insoluble under these conditions, while low-molecular-weight oligomers will stay in solution. At the end of each run, the liquid content in the reactor was analyzed by an on-line HP 5890 GC. To get representative analyses, the sample was taken at the same pressure as used in the reactor. Tentative assignments of peaks in the chromatograms are based on calibration runs with known compositions. The solid polymer and/or wax were analyzed by IR spectroscopy, as described by Bade and Blom.[7]

DRIFTS experiments were performed by using a high-temperature vacuum chamber (HVC) and diffuse reflectance attachment (DRA-3C5) from Harrick Scientific Corp. The sample chamber was filled with catalyst in granular form in a glovebox under argon, and an argon line was connected to the cell in the IR instrument. A 50 mL/min flow of argon was passed through the cell continuously, and CO and ethylene could be admitted into this argon flow with a syringe during the experiments. Argon (99.999% from AGA), ethylene (polymerization grade from Borealis AS), and CO (99.7% from AGA) were used without further purification.

The spectra are recorded with a resolution of 4 cm^{-1} on a Perkin-Elmer FTIR 2000 equipped with an MCT detector. When DRIFT spectra of silica are recorded, a steep fall in reflectance energy is observed below 2000 cm^{-1} due to overtones and combination bands of silica. However, if the silica are diluted with KBr or CaF$_2$, the reflectance energies in the region 1300−2000 cm^{-1} are increased by an order of magnitude, and a better signal-to-noise ratio is obtained. Due to this, the spectra recorded of the catalyst in the present work are recorded on catalyst samples diluted with equal amounts (by weight) of CaF$_2$ powder. The CaF$_2$ from Merck was dried over 48 h at 400 °C and stored under argon in the glovebox. All spectra were recorded under an atmospheric pressure of argon and at ambient temperature if not otherwise stated.

Table 1. Activities and Results from IR analyses[7] of Polymers Produced with the Cr(2-Me-allyl)$_3$/SiO$_2$ Catalysts[a]

		no. of fragments/1000 C			
support	activity[b]	CH$_3$			
SiO$_2$(200)	64	1.0	1.7	<0.1	<0.1
SiO$_2$(400)	166	9.6	3.4	0.2	0.4
SiO$_2$(800)	38	59	18	3.2	2.7

[a] Conditions: slurry polymerization at 90 °C and 30 bar total pressure in a stirred autoclave with isobutane diluent; ethylene homopolymerization without hydrogen. [b] Activity = (g of solid product)/(g of catalyst)(bar of ethylene)(h).

Results and Discussion.

Polymerization in a Slurry Reactor. Homopolymerizations of ethylene were performed with Cr(2-Me-allyl)$_3$ anchored on silica samples dehydrated at 200, 400 and 800 °C. Polymerization activity with the Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst was substantially better than the activities found for the catalysts based on silica dehydrated at 200 and 800 °C, in accordance with earlier findings.[4] The specific activities, together with the results of polymer microstructure analyses, are illustrated in Table 1.

Because no hydrogen was used in the experiments, it is reasonable to assume that each polymer chain contains one unsaturated group. The ratio between methyl groups and the total concentration of unsaturated groups is then indicative of the branching content in the polymer. No simple methyl branches were detected by the infrared spectroscopy analyses,[8] which indicates that isomerization of the growing polymer chain is not extensive at the polymerization temperatures used here. Chain branches are therefore most probably formed by generation and subsequent copolymerization of α-olefins into growing polymer chains.

To explain the relatively high amount of *trans*-vinylene in the polymer produced with the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst, isomerization of the double bond has to be considered. Produced oligomers may recoordinate through the C=C bond and undergo isomerization, which results in displacement of the double bond. In addition, rearrangement of a σ-*n*-alkyl growing chain to a σ-bonded isoalkyl chain (by a 1,2 chromium−hydride shift) with subsequent chain termination may also result in a *trans*-vinylene group.

The catalyst made with SiO$_2$(200) apparently produces long linear chains, each with one methyl and one vinyl end group and with a negligible amount of side branches. The measurement of the methyl concentration must be considered somewhat uncertain at these low contents, which may explain the difference in methyl and vinyl amounts.

Table 2 shows the results from the GC analyses of the liquid phase, obtained at the end of the polymerizations. No oligomers were obtained after polymerization

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(6) O'Brien, S.; Fishwick, M.; McDermott, B.; Wallbridge, M. G. H.; Wright, G. A. *Inorg. Synth.* **1972**, *13*, 73

(7) Bade, O. M.; Blom, R. *Appl. Catal., A* **1997**, *161*, 249.

(8) Methyl side groups give a specific band at 1150 cm^{-1} determined from ethylene/propylene copolymers: Blom, R., unpublished results.

Table 2. Analysis of the Liquid Content (wt %) in the Reactor at the End of Ethylene Polymerizations with the Cr(2-Me-allyl)$_3$−silica Catalysts[a]

support	isobutane	1-butene	1-hexene	1-octene	other C_8 olefins	1-decene	other C_{10} olefins
SiO_2(200)	100	0	0	0	0	0	0
SiO_2(400)	97.0	0.4	1.6	0.3	<0.1	0.1	0.6
SiO_2(800)	84.6	3.5	7.1	1.2	0.4	0.5	2.7

[a] The concentration of ethylene is about 7 wt % but is not included in the table.

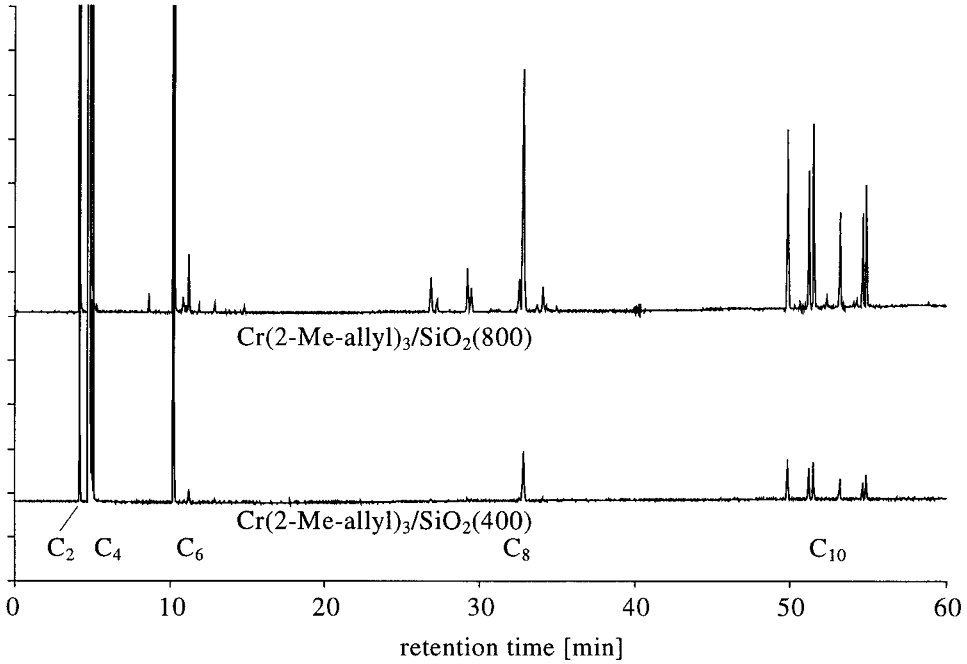

Figure 1. GC chromatograms obtained from the liquid phase after ethylene polymerization with Cr(2-Me-allyl)$_3$/SiO$_2$-(400) and Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalysts.

with the Cr(2-Me-allyl)$_3$/SiO$_2$(200) catalyst. The chromatograms from the runs with Cr(2-Me-allyl)$_3$/SiO$_2$(400) and Cr(2-Me-allyl)$_3$/SiO$_2$(800) are presented in Figure 1. Except for a large difference in total amounts, the distributions of detected species are similar for the two catalysts.

The main C_4 (except form the isobutane), C_6, and C_8 peaks in both chromatograms are assigned to 1-butene, 1-hexene, and 1-octene, respectively. Only traces of *cis*- and *trans*-2-butene are detected, while several isomers of C_6, C_8, and C_{10} were observed. The concentration of isomers relative to that of the linear 1-alkenes increases strongly with increasing chain length. With regard to the C_{10} components, the 1-alkene is no longer dominating. Only traces of C_{12} components (not shown in Figure 1) are observed. Generally, the peaks in front of the main 1-alkene peak are assigned to olefins with branches, while the peaks behind the main peak are ascribed to linear olefins with the double bond in an internal position. 1-Hexene is the major oligomeric product, while the reason for the high concentration of C_{10} isomers relative to C_8 and C_{12} fragments is not clear. Copolymerization of ethylene, 1-butene, and 1-hexene with preferably formation of C_{10} species seems to occur. Olefins with an internal double bond are assumed to be only slightly reactive toward further polymerization and will accumulate in the reactor during the reaction.

The solid product obtained with the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst was suspended in CS_2, and the filtered solution was analyzed by gas chromatography. Oligomers from C_8 even up to C_{40} were detected, with a maximum concentration (29 wt %) of C_{10} isomers. The relative amounts of C_{12}, C_{14}, C_{16}, and C_{18} oligomers constitute about 14, 17, 10 and 7 wt %, respectively. Only minor amounts of oligomers above C_{20} are detected.

Reaction between Chromium Allyl and Silica: Analyses of Reaction Products. If 1-butanol is added directly to a pentane solution of Cr(2-Me-allyl)$_3$ at −50 °C, the solution slowly turns green and a precipitate is formed. GC analyses on this solution show the presence of isobutene and a C_8 olefin (probably diolefin) in addition to pentane and the excess 1-butanol. Compared with the chromium content measured by ICP analysis, approximately 2.9 mol of and 2.3 mol of C_8 (di)-olefin were found per mole of chromium. The C_8 fragments are assumed to be decomposition products from the synthesis and coexist with Cr(2-Me-allyl)$_3$ in the solution. NMR analysis of Cr(2-Me-allyl)$_3$ showed paramagnetic chromium together with the C_8 diolefin, 2.5-dimethyl-1,5-hexadiene. No diamagnetic chromium-(II) dimers were observed.[9]

The main reactions between Cr(allyl)$_3$ and silica are believed to be those shown in Schemes 1 and 2, where the latter reaction is expected to be increasingly important at higher dehydration temperatures, because the distance between the silanol groups becomes larger. It has previously been reported that silica calcined at 200,

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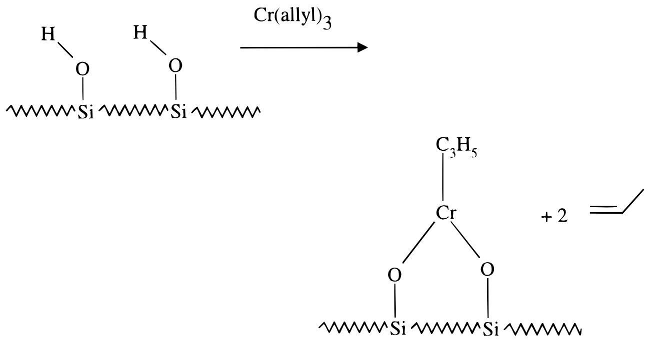
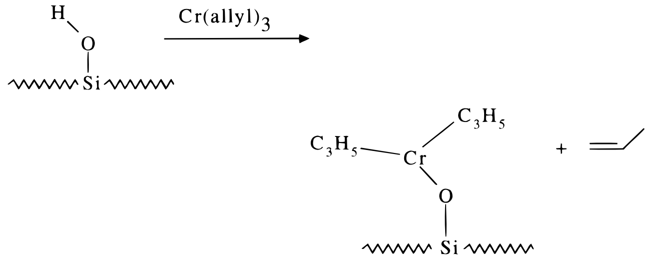
[9] Benn, R.; Rufinska, A.; Schroth, G. *J. Organomet. Chem.* **1981**, *217*, 91.

Scheme 1



Scheme 2



400, and 800 °C has approximately 4.5, 2.3, and 1.0 OH groups per square naonometer, respectively.[10,11]

The results from the GC analyses of the pentane phase after reacting Cr(2-Me-allyl)$_3$ with the different silicas are summarized in Table 3. The releases of isobutene after the dry catalyst samples are quenched with 1-butanol have also been included in Table 3.

The release of 1.3 mol of isobutene/mol of chromium on the SiO$_2$(400) sample is in good agreement with results by Denim et al.[12] and Markova et al.,[13] who reported releases of 1.2 and 1.1−1.3 mol of propene/mol of chromium when reacting Cr(allyl)$_3$ with silica and aluminosilicate (both activated at 400 °C), respectively. This result indicates that the reactions both in Scheme 1 and Scheme 2 are occurring. However, the release of only 0.78 mol of isobutene when Cr(2-Me-allyl)$_3$ is reacted with SiO$_2$(800) indicates that reactions other than those proposed in Schemes 1 and 2 above also have to be considered. Oligomerization of released isobutene is not expected due to its steric hindrance, and in accordance with this we observe no polymerization activity when adding isobutene to the resulting catalyst systems at room temperature. However, the possibility of a reaction between Cr(allyl)$_3$ and siloxane bridges must be considered when the silica has been calcined at high temperatures, since reactive Si−O−Si bridges are formed during dehydroxylation. The resulting Si−R groups, as indicated on the right-hand side in Scheme 3, is relatively stable and can be detected by DRIFT spectroscopy on hydrolyzed samples. Similar reactions have been observed on highly dehydrated silica with AlMe$_3$,[14] Ni(η^3-allyl)$_3$,[15] and *t*-BuLi.[16]

By summation of the amount of isobutene released during preparation and after quenching the final catalyst with 1-butanol, total amounts of 1.87, 1.82, and 1.61 mol of isobutene/mol of chromium are found for the SiO$_2$(200), SiO$_2$(400), and SiO$_2$(800) samples, respectively. The reaction with siloxane bridges cannot explain the low content of released isobutene for the SiO$_2$(200) and SiO$_2$(400) samples, since the amount of siloxane bridges formed at temperatures below 400 °C is low. The most likely explanation for the missing organic species for these catalysts is that chromium−allyl species attached to the silica surface gradually decompose at room temperature and that a part of these are lost in the period between the catalyst preparation and the quenching experiments. The quenching experiments reported in Table 1 were carried out with fresh samples, prepared the same day. However, when the experiment with 1-butanol is repeated with the Cr(2-Me-allyl)$_3$/SiO$_2$(800) sample after 2 weeks of storage in the glovebox, the release of isobutene is less than 30% of the amount reported in Table 1.

For similar catalysts prepared with Cr(allyl)$_3$, the release of propene after the samples were quenched with 1-butanol were 0.25, 0.23, and 0.56 mol/mol of chromium for the SiO$_2$(200), SiO$_2$(400), and SiO$_2$(800) samples, respectively. The lower amounts of propene released, compared to the isobutene release presented in Table 1, indicates that the chromium−allyl species are less stable than the 2-methylallyl analogue. It should be noted that Cr(allyl)$_3$ decomposes at room temperature and even at −17 °C gradually to the bis(allyl)chromium dimer.[3] Some Cr$_2$(allyl)$_4$ may therefore be formed before or during the reaction with the silica. Cr$_2$(allyl)$_4$ itself has a structure with a direct Cr(II)−Cr(II) bond,[17] which may be preserved after reaction with silica activated at 400 °C[18,19] (Scheme 4).

Karol and Johnsen[3] have reported similarity in polymerization behavior of catalysts formed from tris(allyl)chromium and bis(allyl)chromium dimer reacted on silica. According to this, they suggested that tris(allyl)chromium was converted to bis(allyl)chromium prior to or during deposition on silica to form the active catalyst.

DRIFT Spectroscopy of the Catalysts. DRIFT spectra recorded of the three silica samples reacted with Cr(2-Me-allyl)$_3$ and Cr(allyl)$_3$ are shown in Figures 2 and 3, respectively. All spectra are presented as difference spectra, with unreacted silica as reference. A strong negative band at 3748 cm^{-1} in all spectra (outside the ranges in Figures 2 and 3) indicates that O−H groups on the silica surface are consumed in the reaction. Residues of pentane and/or diethyl ether from the synthesis might be present, but none of these could be identified in the spectra.

Unsaturated species are usually observed by bands in the C−H stretching region above 3000 cm^{-1} and in the C=C stretching region around 1600 cm^{-1}. Infrared study of homogeneous π-allyl complexes has concluded

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(10) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47.

(11) Little, L. H. *Infrared Spectra of Adsorbed Species*; Academic Press: New York, 1966; p 275.

(12) Demin, E. A.; Zakarov, V. A.; Yermakov, Yu. I.; Derbeneva, S. S. *Izv. VUZOV, Stroit. Arkhit.* **1975**, *18*, 1283.

(13) Markova, T. A.; Smirnov, S. A.; Oreshkin, I. A.; Dolgoplosk, B. A. *Kinet. Catal. (Transl. of Kinet. Katal.)* **1986**, *28*, 1229.

(14) Yates, D. J. C.; Dembinski, G. W.; Kroll, W. R.; Elliott, J. J. *J. Phys. Chem.* **1969**, *73*, 911.

(15) Yermakov, Y. I.; Kuznetsov, B. N.; Karakchiev, L. G.; Derbeneva, S. S. *Kinet. Catal. (Transl. of Kinet. Katal.)* **1973**, *14*, 611.

(16) Bade, O. M.; Blom, R.; Ystenes, M. *J. Mol. Catal.*, in press.

(17) Aoki, T.; Furusaki, A.; Tomiie, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 545.

(18) Iwasawa, Y.; Sasaki, Y.; Ogasawara, S. *J. Mol. Catal.* **1982**, *16*, 27.

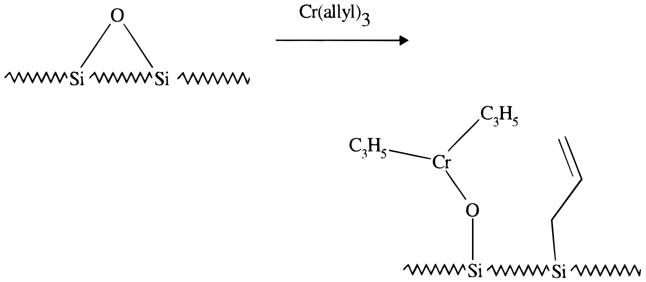
(19) Iwasawa, Y.; Chiba, T.; Ito, N. *J. Catal.* **1986**, *99*, 95.

Table 3. Results From the GC Analysis: Reaction between $Cr(2\text{-}Me\text{-}allyl)_3$ and 1 g of Silica and Termination of Resulting Catalysts with 1-Butanol[a]

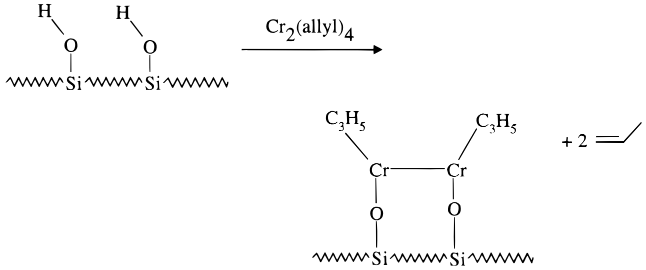
support	amt of Cr added (mmol)	amt of isobutene in prepn soln (mmol)	amt of C_8 olefin in prepn soln (mmol)	amt of isobutene released after adding 1-butano (mmol)
SiO_2(200)	0.192	0.294 (1.53)	0.403 (2.01)	0.065 (0.34)
SiO_2(400)	0.192	0.253 (1.32)	0.422 (2.20)	0.096 (0.50)
SiO_2(800)	0.192	0.149 (0.78)	0.445 (2.32)	0.160 (0.83)

[a] Values in parentheses are the moles released per mole of chromium.

Scheme 3



Scheme 4



that negligible interaction occurs between two or more allyls in the same complex,[20] and a local symmetry of C_s is therefore assumed for the allyl groups. Each allyl group may then give five fundamental bands in the C−H stretching region: four from the CH_2 groups (symmetric and asymmetric, in phase and out of phase) and one from the central C−H. The 2-methyl-substituted analogue will not have the latter band, but instead bands in the aliphatic C−H stretch-region and in the deformation region, stemming from the methyl group.

All samples contain bands in the regions 1450−1460 and 1380−1390 cm^{-1} and several bands in the aliphatic C−H stretching region, which are ascribed to the presence of methyl and methylene groups. The $Cr(allyl)_3/SiO_2$ samples should not contain methyl groups unless they are due to further reactions, i.e., decomposition of allyl fragments and further reactions of the decomposition products.

The samples made from SiO_2(800) have bands at around 1500 cm^{-1} and in the region between 3000 and 3074 cm^{-1}. These bands are assigned to η^3-bonded allyl. $\nu_{as}(CH_2)$ bands of allylic species are expected to lie at a lower frequency than the corresponding $\nu_{as}(CH_2)$ in an olefin group,[21] and $\nu_{as}(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C})$ of η^3-coordinated allyls is expected at considerably lower frequency than that of free olefins, which typically is found around 1650 cm^{-1}. Demin *et al.*[12] has assigned a band at 1520 cm^{-1} to a η^3-coordinated allyl on a chromium/silica surface; Dent and Kokes[22] studied the interaction of propylene on zinc oxide and found evidence for formation of η^3-coordinated allyl by a band at 1545 cm^{-1}, assigned to $\nu_{as}(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C})$.

The spectra of the samples with silica calcined at low temperatures do not show these bands, which indicate the absence of η^3-coordinated allyl ligands. Instead, these spectra exhibit bands at approximately 3074 cm^{-1} and in the region 1640−1650 cm^{-1}, which can be assigned to $\nu_{as}(CH_2)$ and $\nu(C{=}C)$ of vinyl or vinylidene groups. The most obvious interpretation is that these unsaturated groups are unsaturated ends of σ-bonded allyls. However, we cannot rule out that the C=C bond is due to species formed through decomposition of allyls. In solution both $Cr(allyl)_3$ and $Cr(2\text{-}Me\text{-}allyl)_3$ decompose by coupling of allyl ligands with formation of 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene, respectively. Similar reactions can take place on the silica surface.

The GC experiments showed that isobutene is released when the $Cr(2\text{-}Me\text{-}allyl)_3/SiO_2$ samples are quenched with 1-butanol, which indicates that 2-Me-allyl or isobutene species are attached to chromium. Formation of isobutene on the surface would need an additional hydrogen atom, and the comparatively high concentration of silanol groups on silica dehydrated at moderate temperatures could represent such a hydrogen source. The reaction is illustrated in Scheme 5.

The chromium sites remain as Cr(III) after this rearrangement, and it could be noted that similar Cr(III) sites by some authors have been suggested to constitute the active centers of the Phillips catalyst.[23−26]

Isobutene is nondissociatively π-coordinated to Cr(II) sites, and this coordination can be observed from strong bands at 1605, 1464, 1444 and 1381 cm^{-1} in the spectrum of the reduced Phillips catalyst.[27] The first band is assigned as the C=C stretching mode; the other three are ascribed to CH_3 deformation vibrations. In the spectra recorded of the $Cr(2\text{-}Me\text{-}allyl)_3/SiO_2$(200) and $Cr(2\text{-}Me\text{-}allyl)_3/SiO_2$(400) samples, very weak bands around 1600 cm^{-1} are observed that can be assigned to coordinated carbon−carbon double bonds. Exposure to isobutene did not, however, lead to formation of additional bands. However, Cr(III)-ions may not form stable π-complexes with olefins.

Thermal decomposition of the surface allyl complexes was observed by the DRIFTS experiments. By recording spectra of the $Cr(2\text{-}Me\text{-}allyl)_3/SiO_2$(800) sample stored in the glovebox for some days, the bands at 1493 and 3058 cm^{-1} assigned to allylic species were signifi-

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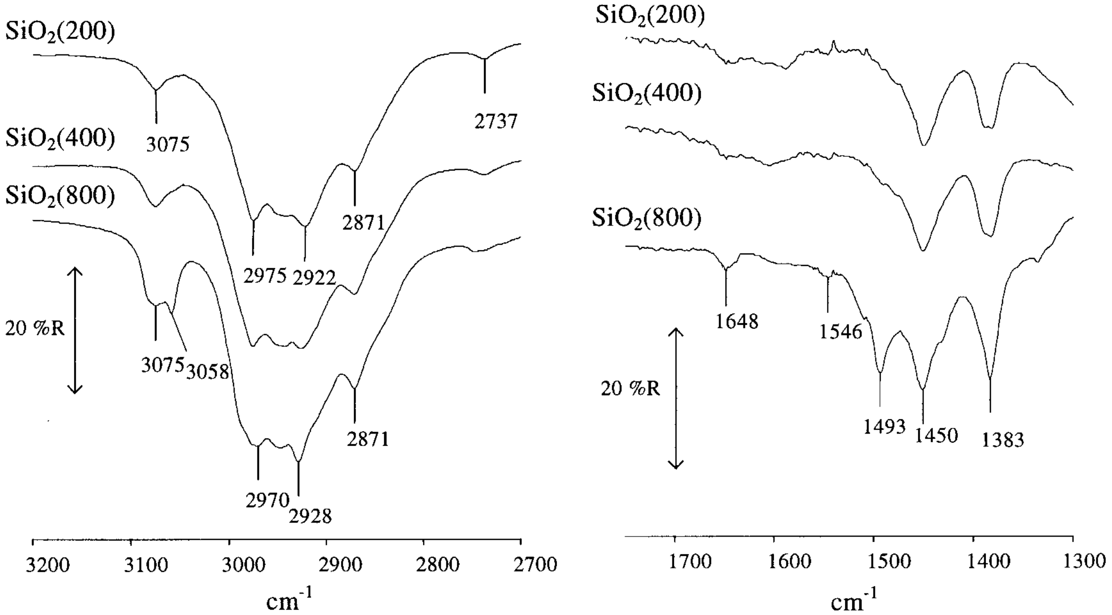


Figure 2. DRIFT spectra of the catalyst samples after reaction with Cr(2-Me-allyl)$_3$ to obtain 1.0 wt % chromium. The spectra are referenced against spectra of pure silica dehydrated at 200, 400, and 800 °C, respectively. The base lines of the spectra in the sequence have been shifted vertically for clarity.

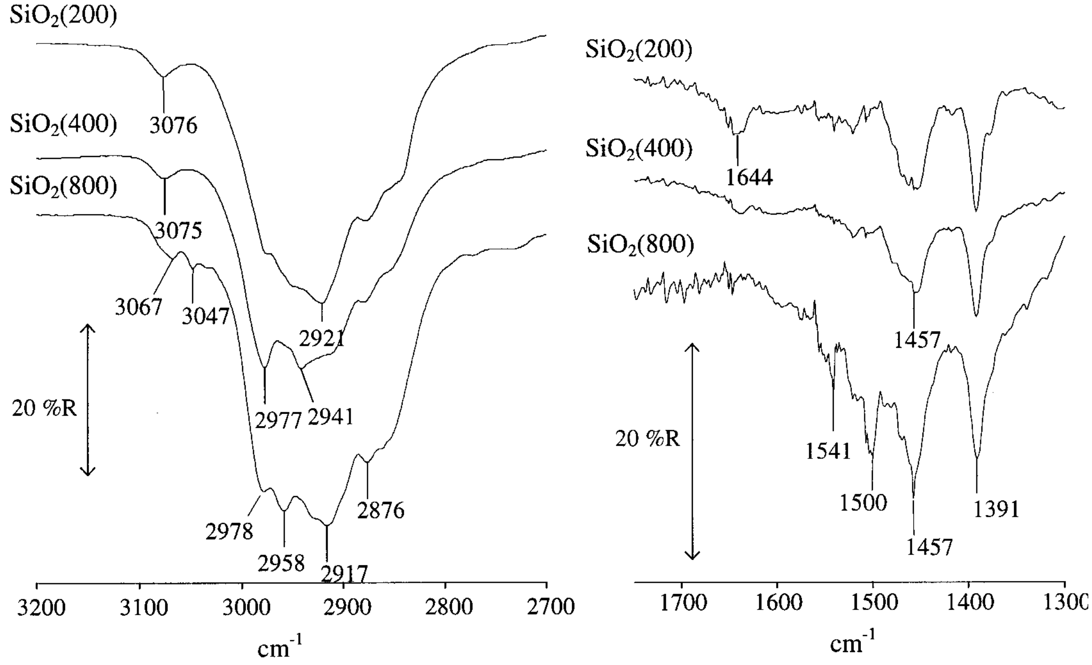


Figure 3. DRIFT spectra of the catalyst samples after reaction with Cr(allyl)$_3$ to obtain 1.0 wt % chromium. The spectra are referenced against spectra of pure silica dehydrated at 200, 400, and 800 °C, respectively. The base lines of the spectra in the sequence have been shifted vertically for clarity.

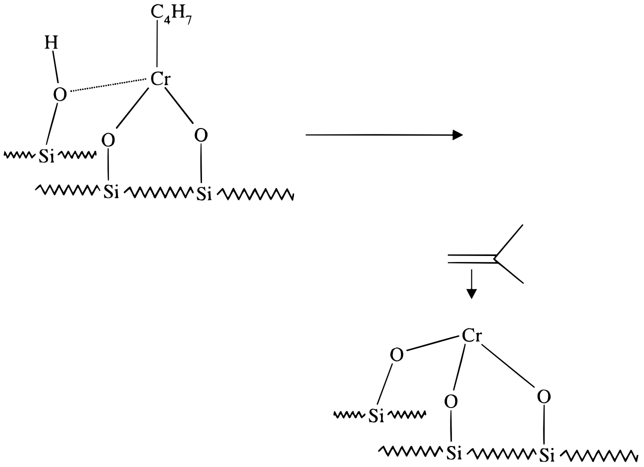
cantly weakened. No oxygenated compounds were observed, which excludes the possibility of decomposition due to traces of oxygen in the glovebox.

Reaction with O$_2$. When the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst is oxidized with excess O$_2$ at ambient temperature, strong bands grow up in the region between 1570 and 1670 cm^{-1} (spectrum not shown) which are typical for carbonyl groups, while the bands at 3058 and 1494 cm^{-1} disappear. Also, spectra recorded of the SiO$_2$(200) and SiO$_2$(400) samples show bands in the region 1580−1670 cm^{-1} after exposure to oxygen, while the band at 3074 cm^{-1} is much weakened.

After oxidation, the Cr(2-Me-allyl)$_3$/SiO$_2$(400) sample was heated in the DRIFT cell to 400 °C for several hours under an argon flow to remove all organic species. For this catalyst no CH bands were observed after the thermal treatment. When the same procedure was carried out with the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst, bands were observed at 2957, 2933, and 2875 cm^{-1}. This shows that organic species bonded to the silica are present which most probably have been formed after the reaction shown in Scheme 3.

Reaction with Ethylene. All catalysts were able to polymerize ethylene in the DRIFT cell. Figures 4 and 5 show the C−H stretching region of spectra recorded of Cr(2-Me-allyl)$_3$/SiO$_2$(400) and Cr(2-Me-allyl)$_3$/SiO$_2$(800) after sequential injections of ethylene. The spectra shown are relative to the spectra of the

Scheme 5



catalysts before polymerization. The polymerization rate was significantly faster for Cr(2-Me-allyl)$_3$/SiO$_2$(400) than for the others; hence, smaller injections were used.

The spectra obtained from the SiO$_2$(200)- and SiO$_2$(400)-supported catalysts were similar, and rapidly methylene groups were detected, assigned to the bands at 2920 cm^{-1} (ν_{as}(CH$_2$)) and 2852 cm^{-1} (ν_s(CH$_2$)). At later stages of polymerization, CH$_2$ deformations were observed at 1463 and 1471 cm^{-1} (not shown in Figure 4). The band at 1471 cm^{-1} is unique to crystalline polyethylene.[28]

No traces of methyl or vinyl end groups are observed. This is in agreement with what is observed in early stages of polymerization with CrCp$_2$/SiO$_2$[29,30] and prereduced Cr^{II}/SiO$_2$.[27,31−34] This may indicate that the growth of the polymer chains follows a metallacyclic structure, as suggested by Zecchina *et al.*[29] and Ghiotti *et al.*[33] for CrCp$_2$/SiO$_2$ and Cr^{II}/SiO$_2$, respectively. Others have proposed that long polymer chains are formed at only a few centers, so that the concentrations of possible end groups are below the detectable limit of the experiments.[27] Fu et al. estimated that only 0.32% of the chromium is active in polymerization with chromocene supported on silica,[30] and a similarly low number of active sites has been proposed for supported catalysts based on chromium allyls.[35]

Formation of weak negative bands above 2920 cm^{-1} may indicate that 2-methylallyl groups are removed or altered during the polymerization. However, a possible low number of propagating sites means that the observed changes may be dominated by changes on the inactive centers. It is therefore not possible to settle whether allyl ligands remain at the site during initiation or become a part of the growing polymer chain.

When ethylene was polymerized with the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst, strong methyl bands at 2967 and 2880 cm^{-1} were observed in addition to those arising from CH$_2$ groups. The methyl groups are probably due to a significant number of short-chain branches on the polymer chains. Most likely, α-olefins formed on sites with high termination rate are copolymerized with ethylene on other sites. The DRIFTS results clearly show the differences in polymerization/oligomerization behavior for the two catalysts.

Reaction with CO. The interaction of CO with supported chromium catalysts has been widely used to characterize the surface Cr sites, both for the Phillips type catalysts[25,32,36−38] and for organochromium catalysts such as CrCp$_2$/SiO$_2$.[29,39,40]

Addition of CO to the Cr(2-Me-allyl)$_3$/SiO$_2$(200) catalyst yielded no detectable amount of coordinated CO. When ethylene was admitted after the exposure to CO, the catalyst was immediately active for ethylene polymerization. This observation was quite surprising, as to our knowledge no other heterogeneous chromium catalyst for ethylene polymerization is unable to coordinate CO at ambient temperature. The degree of coordinative unsaturation was found to be strongly dependent on the dehydration temperature. We generally found that the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst has a higher capacity for CO adsorption than Cr(2-Me-allyl)$_3$/SiO$_2$(400).

Figure 6 shows the DRIFT spectra of Cr(2-Me-allyl)$_3$/SiO$_2$(400) at different CO coverages. The sample became quickly saturated after sequential injections of CO; that is, the intensities of the carbonyl bands did not increase with further injections. Carbonyl bands were observed at 2183, 2092, 2043, 1976, 1952, and 1884 cm^{-1}. The 2183 cm^{-1} band disappeared almost completely after 2−3 min upon flushing with argon, while the 2043 cm^{-1} band decreased in intensity. The other bands remained at their original intensities after more than 15 min of flushing.

The very weak band at 2183 cm^{-1} has a frequency typical for CO on Cr^{II}/SiO$_2$,[32] but on this catalyst the bands are much more intense and they are not completely removed by vacuum treatment or argon flushing.

After the Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst is treated with CO, the catalyst is still active for ethylene polymerization, indicated by rapidly growing methylene bands at 2920 and 2852 cm^{-1} after ethylene exposure. The CO bands are not affected by the presence of ethylene and remained at unshifted frequencies and constant intensities. However, when ethylene and CO were added simultaneously, the catalyst did not polymerize. CO coordination to the active sites is therefore not strong enough to withstand prolonged vacuum or purging, but active sites are blocked if CO is continuously present. The fact that some sites are active and others not may be due to their ability to coordinate donors such

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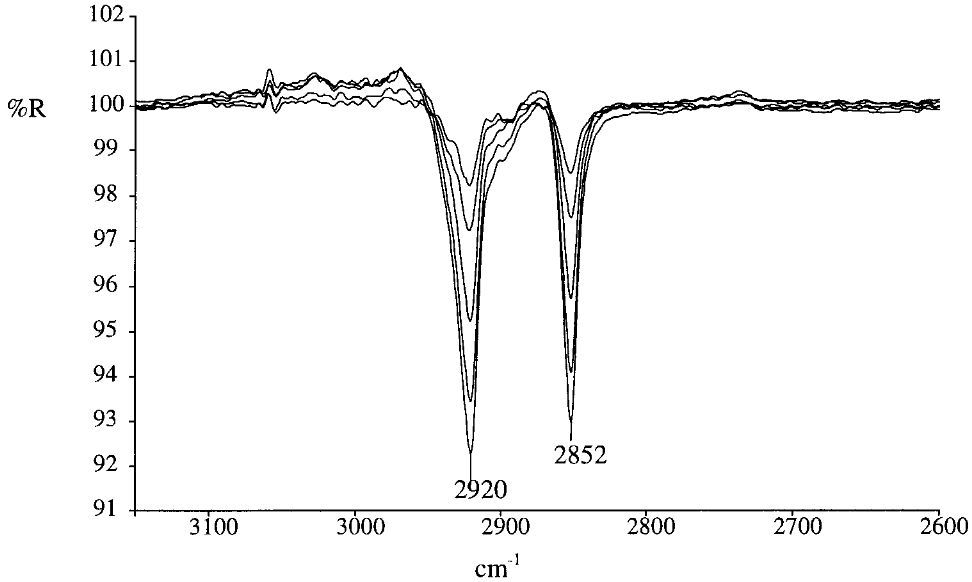


Figure 4. Early stages of polymerization on Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst. The IR spectra were recorded after sequential injections of ethylene onto the catalyst. All spectra are relative to a spectrum of the catalyst before polymerization.

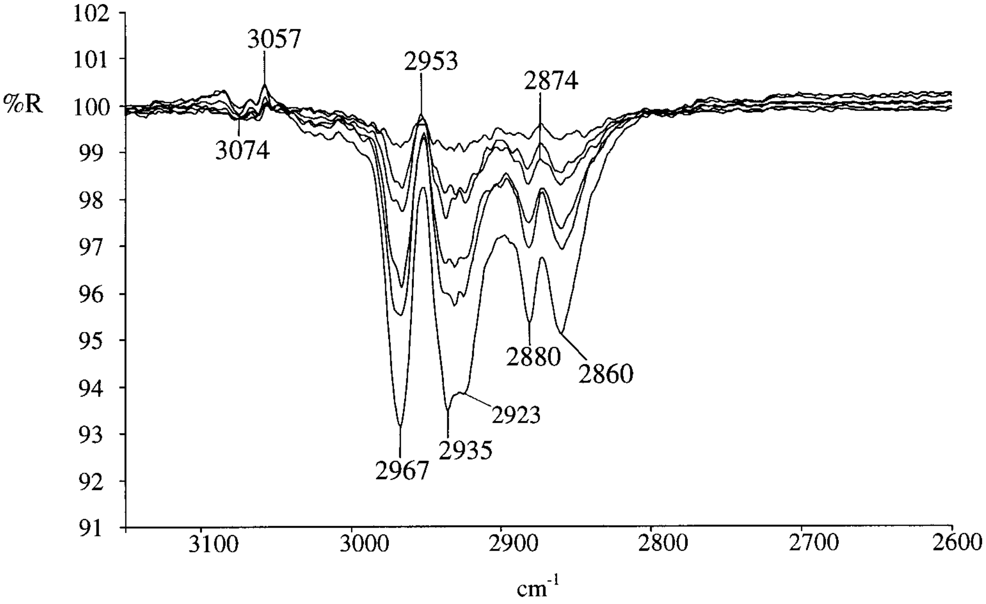


Figure 5. IR spectra showing the early stages of polymerization on Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst.

as CO and ethylene. The active sites may only be those that coordinate CO and ethylene weakly.

Figure 7 shows difference spectra of the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst with low CO coverage and after completely saturating the catalyst. The spectra are recorded only a few minutes after exposure; hence, traces of CO gas may be present. When the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst is exposed to CO, the spectrum becomes more complex than for the SiO$_2$(400) case. From the number of CO injections that had to be admitted to reach saturation, and the intensities of the carbonyl bands, this catalyst apparently forms complexes with a larger amount of CO. In addition, there is a shift in the relative intensities of the carbonyl bands as a function of time after exposure. The spectrum also shows negative bands at frequencies assigned to π-allyls, which suggests that insertion of CO into the Cr–allyl group occurs. New bands in the 1600–1700 cm^{-1} region are also observed, which may be assigned to organic carbonyls. The latter bands are also observed for Cr(2-Me-allyl)$_3$/SiO$_2$(400) in Figure 6, but to a much lesser extent.

As seen in Figure 8, the relative intensities of the carbonyl bands change with time after CO exposure and the changes are ascribed to a rearrangement of adsorbed CO. The sharp high-frequency bands first formed are after converted a few minutes to broad bands of lower frequencies. Similar changes have been observed for the interaction of CO on heterogeneous chromocene-based catalysts,[39] but was not observed for the Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst, except that the intensity of the bands at 2183 and 2143 cm^{-1} were reduced as a function of time.

If the catalyst saturated with CO was exposed to ethylene, polymerization occurred, but the rate was much lower than without the CO preexposure. The band at 2130 cm^{-1} disappears upon exposure to ethylene, and the bands at 2040 and 1993 cm^{-1} are much

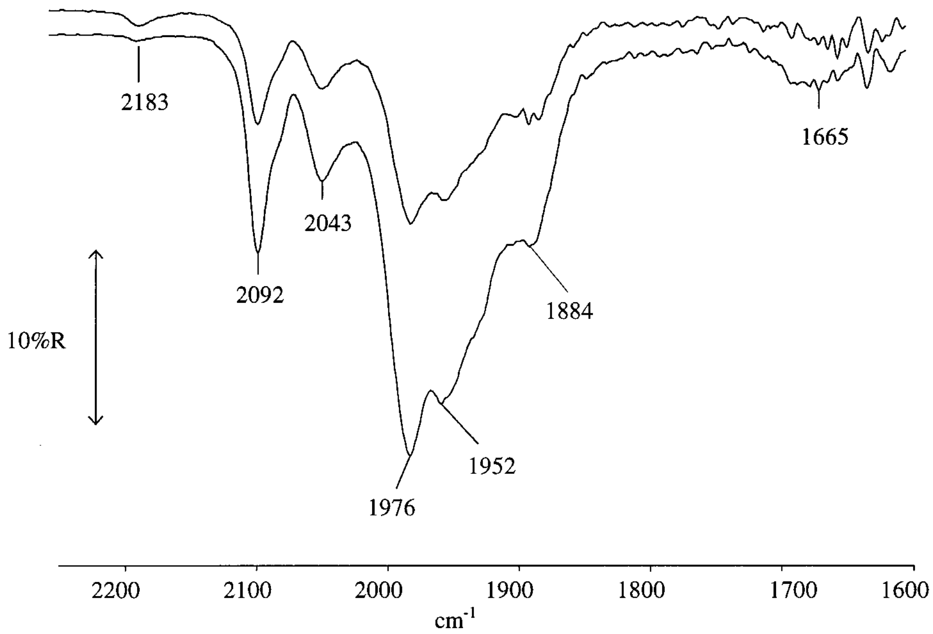


Figure 6. DRIFT difference spectra of the Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst with low CO coverage (above) and after saturating the sample with CO (below). The spectra are relative to a spectrum of the sample before CO exposure.

Figure 7. DRIFT difference spectra of the Cr(2-Me-allyl)$_3$/SiO$_2$(800) catalyst with low CO coverage (above) and after saturating the sample with CO (below). The spectra are relative to the spectrum before CO exposure.

weakened. The reduced polymerization activity may be caused by the proposed reaction between CO and Cr allyls.

Conclusions

In homopolymerization of ethylene with the Cr(2-Me-C_3H_5)$_3$/SiO$_2$(800) catalyst, oligomers and polymers with high concentrations of side-chain branches were found in the reactor after reaction. The major liquid product was 1-hexene. Polyethylene with some side-chain branches was also obtained with the Cr(2-Me-C_3H_5)$_3$/SiO$_2$(400) catalyst; however, the amount of branches and the concentration of oligomers in the reactor were much less than what was observed with the Cr(2-Me-C_3H_5)$_3$/SiO$_2$(800) catalyst. A negligible amount of side branches was found in the polymer produced with catalyst based on silica dehydrated at 200 °C. Polymerization activity with the Cr(2-Me-allyl)$_3$/SiO$_2$(400) catalyst was substantially higher than the activities found for the catalysts based on silica dehydrated at 200 and 800 °C.

Quantitative measurements of the reaction products formed during the reaction of Cr(allyl)$_3$ or Cr(2-Me-allyl)$_3$ with silica calcined at 200, 400, and 800 °C have been carried out. Also, the amounts of organic species released during hydrolysis of the catalysts have been measured. The sum of these two measurements does not account for the total amount of allyl ligands added. The allyl not measured is most probably lost between the two measurements, either as the corresponding

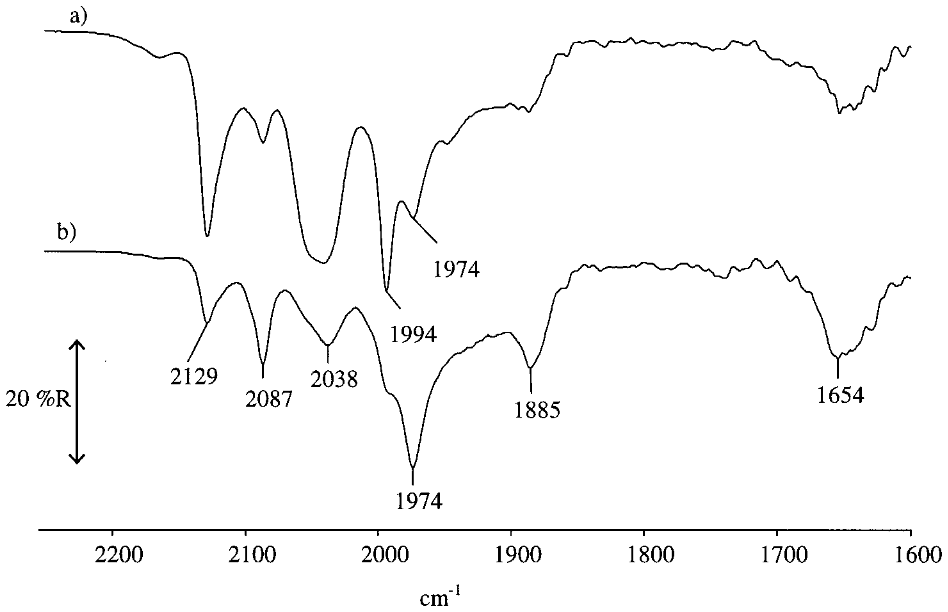
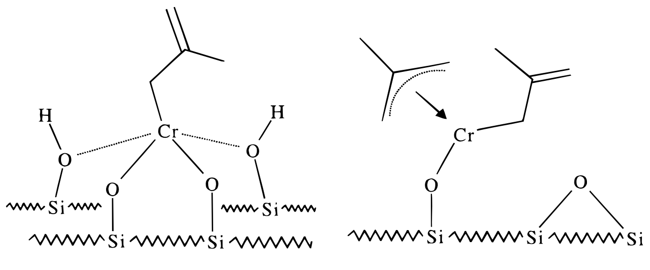


Figure 8. DRIFT spectra of a partially CO covered Cr(2-Me-allyl)$_3$/SiO$_2$(800) sample: (a) 1 min after injection of CO; (b) after subsequent 15 min of purging with argon.

olefin (i.e. propene or isobutene) or as the diene (i.e. 1,5-hexadiene or 2,5-dimethyl-1,5-hexadiene). In addition, some of the allyl–chromium species reacts with siloxane species to form Si–allyl fragments, which are stable toward hydrolysis.

DRIFT spectra of the catalysts show different bands, depending on the calcination temperature of the silica used. Only the catalysts using SiO$_2$(800) show bands typical for η^3-bonded allyl fragments. All catalysts show weak bands consistent with σ-bonded allyl ligands. However, we cannot rule out that the unsaturated bonds observed partly are partially due to small amounts of diene, which may be formed by coupling of two allyl ligands. Also, isobutene–chromium π-complexes can be present. When CO is added to the catalysts, the amount of CO that is able to coordinate is very different: the catalyst prepared with SiO$_2$(200) adsorbs no CO and that SiO$_2$(400) gives a number of bands in the region from 1665 to 2183 cm^{-1}, while the catalyst obtained with SiO$_2$(800) gives the strongest bands. This clearly indicates the different degrees of coordinative unsaturation of the chromium ions for the different catalysts. Our data are consistent with the surface species shown in Chart 1.

Chart 1



SiO$_2$(200), SiO$_2$(400)

SiO$_2$(800)

All three catalysts are unstable at ambient temperatures. We suggest that the decomposition of the SiO$_2$(800) sample on the right-hand side of Chart 1 proceeds either through a coupling of the two allyl ligands to form a diene or through reaction with neighboring siloxane bridges. For the samples prepared with SiO$_2$(400) and SiO$_2$(200), we suggest that the decomposition occurs through a reaction between the allyl ligand and hydroxyl groups at a certain distance. The rate of this reaction will be dependent on the distance to the hydroxyl group.

DRIFT spectra in the presence of ethylene reflect the behavior of the catalysts under realistic polymerization/oligomerization conditions: the catalysts prepared with SiO$_2$(200) and SiO$_2$(400) only show bands corresponding to $-CH_2-$ fragments. This indicates the formation of linear polyethylene chains with a low number of side branches, as observed for the polymer produced under realistic conditions. On the other hand, the catalyst prepared with SiO$_2$(800) also gives significant bands from methyl groups, consistent with the formation of oligomers and polyethylene with a high concentration of short-chain branches observed for this catalyst.

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