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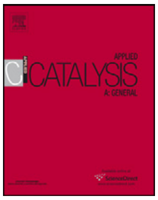

Reduction of Cr(VI) polymerization catalysts by non-olefinic hydrocarbons

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ABSTRACT

The Phillips Cr(VI)/silica catalyst, which is widely used for commercial ethylene polymerization, is usually considered to be reduced to a lower-valent active Cr species in the reactor upon contact with ethylene or other α-olefin monomers. In this paper, however, the case is presented that Cr(VI) is actually quite reactive with other hydrocarbons to which it is also often exposed, including alkanes and aromatics. Redox products from these reactions are identified, and the effect on catalyst polymerization activity and polymer character is described.

1. Introduction

Polyethylene is the world's most commonly used polymer, and a significant portion of it (HDPE in particular) is made with the Phillips Cr/silica catalyst. Discovered in 1951 at Phillips Petroleum Company [1,2], this catalyst is made by impregnating a chromium compound onto a high-porosity silica carrier to a loading of about 1 wt% Cr, followed by calcination at >500 °C. During this high temperature "activation" step the chromium is oxidized and reacts with surface hydroxyl groups to become anchored to the support as hexavalent chromate or dichromate species such as illustrated in Scheme 1A.

This is the catalyst precursor. The active sites responsible for ethylene polymerization are formed when this surface-anchored Cr(VI) is then reduced to a lower-valent isolated species [2,3]. This is usually thought to occur in the polymerization reactor with ethylene as the reducing agent, such as shown in Scheme 1B. Surface Cr(II) and formaldehyde have most often been suggested as the by-products of this redox reaction [4–7], although other possible products have also been proposed [8,9], and some recent data from this laboratory (to be presented elsewhere) likewise argues for a more complicated reduction pathway. As the chromium is reduced, from tetrahedral Cr(VI) to a probably octahedral lower-valent species, the potential coordination sphere is expanded, and in the absence of other ligands, coordinative unsaturation is created that initiates polymerization.

In commercial practice, the hexavalent catalyst precursor usually also comes into contact with other hydrocarbons, such as the reaction solvent or diluent. These commonly include paraffins, such as isobutane, n-butane, cyclohexane, hexanes, isopentane, and even mineral oil. Ethylene comprises only a small part of the typical reaction mixture, e.g. only 3–5 wt% in isobutane (slurry at 80–110 °C) or in cyclohexane (solution at 125–150 °C). Typically, the hexavalent catalyst is charged into a storage vessel, sometimes while still quite hot (100–250 °C) after calcination, into which one of these non-olefinic hydrocarbons is immediately introduced. Afterward the catalyst is then stored under one of these hydrocarbons at ambient temperature for hours, days, and sometimes weeks, prior to introduction into the reactor where it can contact ethylene.

Although the reactivity of the Phillips Cr/silica catalyst with alkanes has not been investigated to our knowledge, some hexavalent chromium compounds have been reported to oxidize many organics, including olefins, alcohols, carbonyls, and even alkanes [10]. Thus, there is reason to suspect that in some commercial usage the Cr(VI) could be reduced even before contact with ethylene. In this paper we explore this possibility. The reactivity of the hexavalent catalyst with various paraffins and aromatics has been investigated, and the resultant implications for the formation of the active species and the polymerization mechanism is discussed.

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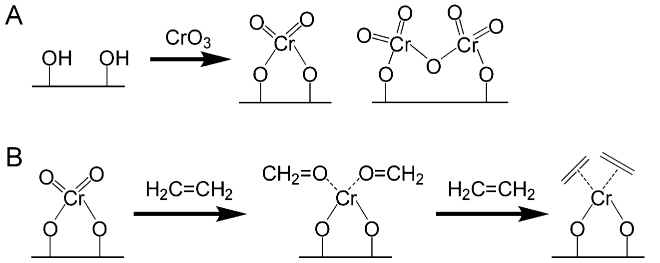


Scheme 1. (A) Formation of Cr(VI)/silica catalyst precursor; (B) reduction of Cr(VI) by ethylene to lower valent active species, as suggested by Ref. [4] and others.

2. Experimental

2.1. Catalyst preparation

An attempt was made to select a range of catalysts (Cr/silica and Cr/silica-titania), activation temperatures (600 °C to 850 °C), Cr loadings (1% to 5%), and Ti loadings (0%, 2.5%, 4.5%) that are still representative of commercial operations. Detection of products was enhanced by higher Cr loadings and lower activation temperatures, which produce higher conversion to Cr(VI).

Cr/silica catalysts were prepared from grade 951 silica, obtained from W.R. Grace Co., which was impregnated to incipient wetness with an aqueous solution of chromic trioxide, followed by drying overnight in a vacuum oven at 110 °C. The final catalyst contained either 1 or 3 wt% chromium, and had a surface area of approximately 600 m^2/g and a pore volume of approximately 1.0 mL/g. Cr/silica-titania catalysts were made by ter-gelation of silica, titania, and chromium (III) hydroxide (from a solution of Cr nitrate) according to Dietz [11]. This yields a catalyst containing either 2.5 or 4.5 wt% Ti, 1.0 or 3.0 wt% Cr, a surface area of 480 m^2/g and a pore volume of 2.5 mL/g. Like the impregnation technique, this method leaves the Cr on the surface.

The next step, activation or calcination, anchors the chromium to the surface and converts trivalent chromium on the catalyst into the hexavalent form [3]. All of the catalysts used in this study, whether Cr/silica or Cr/silica-titania, were found to contain 90–100% of the chromium as Cr(VI). To activate these catalysts, about 10 g was placed in a 4.75 cm quartz tube fitted with a sintered quartz disk at the bottom. While the catalyst was supported on the disk, dry air was blown up through the disk at the linear rate of about 1.6–1.8 standard cubic feet per hour. An electric furnace around the quartz tube was then turned on and the temperature was raised at the rate of 400 °C/h to the indicated temperature, such as 600 °C or 800 °C. At that temperature the catalyst was allowed to fluidize for 3 h in the dry air. Afterward the catalyst was collected and stored under dry nitrogen, where it was protected from the atmosphere.

2.2. Reduction of the catalyst

Activated catalyst containing Cr(VI) was then exposed to various non-olefinic hydrocarbons in one of two ways. In the first method, the catalyst was contained in a glass vessel sealed with Teflon-seated valves. Enough of the hydrocarbon liquid was added to just submerge the catalyst. Then the sealed vessel was allowed to stand for hours or perhaps days as desired. Sometimes it was shielded from light in a foil wrap. Other times it was exposed to ambient fluorescent light. After the specified time had passed the liquid was sampled and injected into a GC–MS instrument for analysis of products.

As a second step the vessel was then drained of as much of the hydrocarbon as possible, and the remainder was removed by evaporation in a nitrogen flow at 25 °C. A solution of methanol or ethanol and 5–10% water, as indicated in each experiment, was then added to again just submerge the catalyst. The solution also often contained 0.3% HCl to encourage hydrolysis of ligands on the chromium. After the ethanol solution was allowed to contact the catalyst for the specified time, usually about 1 day, it was sampled and analyzed by GC–MS.

In the second method of reduction the catalyst was left in the fluidized bed where it was activated, as described. Dry nitrogen was used to fluidize the catalyst, and the temperature was set as described (usually at 100 °C). About 5 mL of non-olefinic hydrocarbon was then injected into the nitrogen stream, where it evaporated over a period of about half an hour. The vapor was carried up through the catalyst bed where it reduced Cr(VI). After passing through the catalyst bed, the nitrogen was directed through a cold trap where the oxidized hydrocarbon was collected and later analyzed by GC–MS.

As a second step in this second method of contact, the catalyst bed was then exposed to water vapor at 100 °C in order to hydrolyze any remaining ligands left on the chromium. About 5 mL of water was injected into the nitrogen stream where it evaporated over about half an hour and passed up through the catalyst bed. After exiting the catalyst bed, the nitrogen was then directed through another cold trap, where the water and hydrocarbon oxidation products were collected and later analyzed by GC–MS.

2.3. Analysis by GC–MS

Gas chromatography was performed using a Varian 3800 GC analyzer equipped with two separate all-purpose capillary columns (30 m × 0.25 mm × 0.25 μm) and flame ionization (FI) detector. In a typical injection, a 5 μL aliquot was removed by syringe from the sample vial and injected into a GC port held at 250 °C using a split ratio of 20:1. The carrier gas used was ultra-high purity helium and was electronically controlled throughout the run to a constant flow rate of 1.0 mL/min. In a typical run, the initial column temperature was held at 70 °C for 2 min, then ramped at 20 °C/min to 250 °C and then held at 250 °C for 9 min. In cases where FI detection was used, the FI detector on the GC was maintained at 300 °C.

Mass spectral analysis was performed in conjunction with a Varian 320 MS instrument connected to the GC unit using electron ionization at 70 eV. The nominal mass range scanned was 50–900 m/z using a scan time of 0.5 s. Nominal detector voltage used was 1200 V.

2.4. Polymerization

Polymerization runs were made in a 2.5 L steel reactor equipped with a marine stirrer rotating at 400–500 rpm. The reactor was surrounded by a steel jacket through which a coolant was circulated. The temperature of the coolant was precisely controlled through instrumentation so that the temperature in the reactor could be controlled to within 0.5 °C.

Unless otherwise stated, a small amount (0.01–0.10 g normally) of the solid catalyst was first charged under nitrogen to the dry reactor. Next 1.2 L of isobutane liquid was charged and the reactor heated up to 105 °C. Finally ethylene was added to the reactor to equal 3.8 MPa (550 psig), which was maintained during the experiment. The stirring was allowed to continue for the specified time, usually about 1 h, and the activity was noted by recording the flow of ethylene into the reactor to maintain the set pressure.

After the allotted time, the ethylene flow was stopped and the reactor depressurized and opened to recover a granular polymer powder. In all cases the reactor was clean with no indication of any wall scale, coating or other forms of fouling. The polymer powder

Table 1
Activity change at −30°C resulting from brief exposure to hydrocarbons at elevated temperatures.

Reducing treatment	Reductant/Cr ratio	Activity[a] ($\times 10^{-4}$ min^{-1} g^{-1})
None	NA	0
Ethylene, 140 °C	7	27
Propylene, 100 °C	3	25
1-Butene, 100 °C	3	19
2-Butenes, 100 °C	1	28
Isobutene, 100 °C	3	26
Cyclohexane, 150 °C	0.13	13
Cyclohexane, 150 °C	0.25	14
Cyclohexane, 150 °C	1	23
Cyclohexane, 150 °C	4	22
Cyclohexane, 150 °C	15	25
Acetone, 150 °C	3	0.1
Benzene, 150 °C	2	5.2

[a] First order rate constant measured at −30 °C.

was then removed and weighed. Activity was specified as grams of polymer produced per gram of solid catalyst charged per hour.

3. Results and discussion

3.1. Polymerization at −30 °C

Cr(VI)/silica catalysts are not active for ethylene polymerization at low temperatures. When contacted with ethylene at 25 °C or below, Cr(VI)/silica catalysts display little or no activity. This is because reduction of Cr(VI) by ethylene is slow at low temperatures. As the temperature is raised the catalyst gradually develops activity after an initial dormant period. This interval is called the “induction time”, during which reduction of Cr(VI) occurs to form a lower-valent active species. At 25 °C the induction time is so long that activity is usually regarded as being near zero. At higher temperatures the induction time decreases, and by about 100 °C, where commercial slurry and gas phase polymerization occurs, only a short induction time is observed, from approximately 5 to 15 min. At temperatures higher than 125 °C, where the solution process operates, there is no induction time. Polymerization begins immediately when the catalyst contacts ethylene.

As an example of this behavior, the ethylene uptake of a Cr(VI)/silica catalyst was measured at −30 °C. At this low temperature no activity was observed. However, in a second experiment the Cr(VI)/silica was first exposed to a small amount of ethylene (7 per Cr) at 140 °C, then it was tested for polymerization activity at −30 °C. This time it exhibited strong activity. Thus, it is clear that ethylene performs more than one function. First it reduces Cr(VI) to a lower valent active form [4], and second it acts as a monomer. As might be expected, the optimum temperature for reduction by ethylene was found to be about 130–140 °C. At lower temperatures the reduction is perhaps incomplete, and at higher temperatures some instability in the reduced form must lower the polymerization activity.

In similar experiments, other olefins were also effective at reducing the Cr(VI)/silica to create a catalyst that would polymerize ethylene at −30 °C. This includes propylene, 1-butene, 2-butene, and isobutene. Such activity developed at lower temperatures when the catalyst was first exposed to propylene compared to ethylene. This suggests that propylene was more easily oxidized than ethylene. 1-Butene was also tested as the reducing agent, and it developed activity at perhaps even lower temperatures. These results, and others, are summarized in Table 1.

Thus, it is clear that olefins reduce Cr(VI) easily and that olefins with alkyl substituents are even more effective. As noted in Scheme 1, aldehydes have been proposed as the by-product by some researchers [4]. However, it is not entirely clear in these experiments whether it is the reduction of Cr(VI) that is the slowest step in the production of activity, or a later desorption of by-products, or even a rearrangement of ligands that leads to alkylation.

In high pressure polymerization runs conducted in laboratory autoclaves, it is common for the catalyst to contact the reaction solvent or diluent, even at elevated temperature, before ethylene is introduced. This exposure can last for several minutes. In the commercial reactors the catalyst is first stored in the hydrocarbon at ambient temperature for hours, days, and sometimes even weeks, before being introduced into the reaction zone, where the solvent concentration is still 20–30 times higher than that of ethylene. Thus, under these circumstances, it is reasonable to ask whether alkanes could also reduce the Cr(VI) and whether the resulting site would still be active.

Therefore, the above experiment was repeated, but the catalyst was exposed to small amounts of cyclohexane (used as solvent in the solution process) instead of ethylene. A color change from orange to green indicated Cr(VI) was reduced by cyclohexane. Then the reduced catalyst was tested at −30 °C as before. The results are again listed in Table 1. It is clear that cyclohexane was indeed an effective reducing agent at 150 °C and that it produced a catalyst that was active for ethylene polymerization at −30 °C. Acetylene, benzene, and acetone were effective as reducing agents, although they produced considerably weaker polymerization activity at -30 °C.

3.2. Storage in alkanes or aromatics at 25 °C

n-Heptane: Since commercial catalysts are typically stored under non-olefinic hydrocarbons for prolonged periods before use, it was of interest to determine whether reduction by alkane can occur over time at 25 °C. Therefore, a Cr/silica-titania catalyst was calcined at 800 °C to produce one of the most active Phillips catalysts used commercially. It had a bright orange color, indicating near quantitative conversion to Cr(VI), as would be expected. Protected under a nitrogen blanket, the catalyst was immersed in n-heptane (industrial grade, dried twice over 13× molecular sieve). The bright orange powder immediately started to darken to a blackish orange color, which indicates a reduction of the hexavalent chromium. Within an hour the color turned green-black. The catalyst was allowed to stand under n-heptane for six days with no further color change.

Therefore, far from being the inert diluent that is usually imagined, this industrial grade of n-heptane was found to be surprisingly reactive with the catalyst, reducing Cr(VI) almost immediately. This means that the mechanism of reduction shown in Scheme 1B may not always represent catalyst formation in a commercial process, and the oxidation products could be different.

A similar result was obtained using a Cr/silica catalyst, although the color change occurred a little more slowly.

Although this industrial grade of n-heptane is sometimes used commercially, we wondered if the observed reduction could have been due to traces of olefinic impurities rather than to the alkane itself, since olefins are more reactive with Cr(VI)/silica-titania. Therefore, the experiment was repeated with research grade n-heptane, again after it was dried over molecular sieve two times. This grade, which assayed at 98.6% n-heptane, contained no trace of olefins. The remaining 1.4% was a mixture of branched heptane isomers, dimethylcyclopentane, methylcyclohexane, and isooctane. When the catalyst was immersed in this grade it exhibited very similar behavior, although the color changes, which are shown in Fig. 1, occurred a little more slowly. Within an hour the bright orange color darkened to orange-black. After three days the catalyst was dark green. The catalyst was allowed to stand under the n-heptane for six days without further color change. It was then dried under nitrogen in order to be tested for polymerization activity (experiment A2).

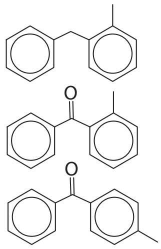
No redox by-products were found in the n-heptane by GC–MS analysis. This suggests that these products were still attached to the chromium as ligands. However, wet methanol was added to the catalyst to hydrolyze or displace whatever ligands remained on the catalyst. The methanol solvent was then analyzed by GC–MS, and a C_7 ketone was then found.

In a variation of the experiment, n-heptane vapor was applied to the Cr(VI)/silica-titania catalyst as a vapor at 100 °C. At this temperature it took only a small amount of n-heptane to obtain the green-black color previously observed. Again nothing was observed in the n-heptane off-gas, but as before, a C_7 ketone was observed when the catalyst was treated with wet methanol. Table 2 summarizes the results of this and similar experiments. This catalyst was then tested for polymerization activity (experiment A3).

n-Hexane: The experiment was repeated using n-hexane instead of n-heptane. A silica having a surface area of 600 m^2/g was impregnated with 3 wt% Cr and then calcined in dry air at 650 °C, which converts most of the chromium into the hexavalent state. One sample of this catalyst was soaked in n-hexane liquid for 18 h, which caused the same darkening of the orange Cr(VI) catalyst to a black-green color. No oxygenate redox by-products were found in the n-hexane liquid when it was subjected to GC–MS analysis. After the n-hexane had been decanted off, the catalyst was dried by passing dry nitrogen over it for several hours. It was then slurried at 80 °C in several mL of a solution of ethanol containing 5% H_2O and 0.3% HCl in an attempt to hydrolyze or displace the redox products from the chromium. After several hours of soaking, this liquid was then analyzed by GC–MS. The major redox products found were 2-hexanone and 3-hexanone, and also 2-hexanol and 3-hexanol.

In a second experiment, this same Cr(VI)/silica catalyst was exposed to n-hexane vapor in nitrogen at 100 °C for a few minutes. Again a darkening of the color, from orange to green, was observed. The n-hexane off-gas was condensed and analyzed by GC–MS, but no redox by-products were observed. Then the catalyst was exposed at 100 °C to a few mL of vaporized aqueous solution containing 0.3% concentrated HCl. This off-gas was condensed and analyzed. It was found to contain 2-hexanone and 3-hexanone, and also 2-hexanol and 3-hexanol.

Table 2
Oxidation products detected from reaction of Cr(VI) catalysts with alkanes or aromatics followed by hydrolysis.

Hydrocarbon	Main products	Minor products
n-Pentane	2-Pentanone 3-Pentanone	Pentanedione
n-Hexane	2-Hexanone 3-Hexanone 2-Hexanol 3-Hexanol	Dimer, hexanedione
n-Heptane	C_7 Ketone	
Isobutane	t-Butanol	
Cyclohexane	Cyclohexanone	Cyclohexanedione
Cyclopentane	Dimers	
Toluene	Benzaldehyde	
Benzene	Not detected	

n-Pentane: The experiment was repeated, but using another common solvent, n-pentane (purity 99.0%, dried over 13× molecular sieve). The 800 °C Cr(VI)/silica-titania catalyst was sealed in a

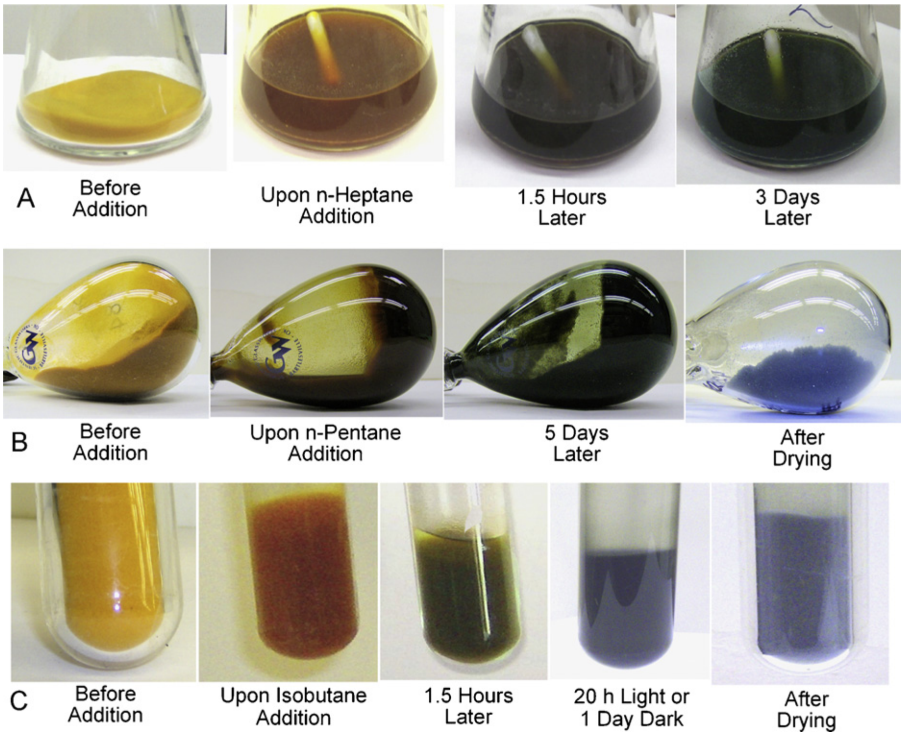


Fig. 1. Cr(VI)/silica-titania catalysts reduced at 25 °C in the presence of (A) n-heptane, (B) n-pentane, and (C) isobutane.

glass vessel, then wetted and covered with the n-pentane. Once again the orange color of the catalyst darkened to brown after 1–2 h, indicating reduction. It darkened further over the next few days, quickly reaching a green-black color. The color transition is shown in Fig. 1. After 4.5 days the n-pentane was sampled for analysis, and the remainder was evaporated off under nitrogen at 25 °C. The resulting dry catalyst had a sky-blue color, as shown in Fig. 1. This catalyst was then tested for ethylene polymerization activity (experiment A4).

In another experiment, a catalyst containing 5% Cr on silica was calcined at 600 °C and immersed in n-pentane. After about 3 h it too turned from orange to an orange-black color, indicating the start of reduction. It was then allowed to stand for 18 days, after which it was entirely black. The n-pentane was again sampled and analyzed.

GC–MS analysis of the n-pentane solutions from both experiments revealed no oxidation products. This again suggests that the products were still held on the catalyst by the chromium, either through bonding or simple coordination. Therefore, these catalysts were then washed in a solution of 10% water in methanol, or in the second experiment of 0.3% HCl in methanol, to liberate the oxidation products by hydrolysis or displacement. GC–MS analysis of the decanted methanol detected the presence of C_5 carbonyls. Two peaks were observed which were identified from the fragmentation pattern as 2-pentanone (∼65%) and 3-pentanone (∼35%). Hydrogen on primary carbons (methyl) is thought to be less reactive with chromate than those on secondary carbons (methylene), and those in turn much less reactive than tertiary carbon hydrogens (methine) [10]. This would explain why pentanal was not found. The preference for formation of 2-pentanone over 3-pentanone probably reflects the relative abundance of the 2 position in n-pentane (two possible carbons) over the 3 position (only one carbon). A small amount of what may have been pentanedione was also found, possibly from the double oxidation of n-pentane.

The influence of titania: The presence of titania on the catalyst is known to create new Cr(VI) species that are more easily reduced [3,12,13], thus improving the activity. This is thought to be due to the creation of strong Bronsted acid sites that, when bonded to Cr(VI), pull electron density from the chromium. Therefore, for comparison, the experiments above used two catalysts, one Cr(VI)/silica-titania and the other Cr(VI)/silica. Both were calcined at 800 °C to yield an orange powder, and then submerged in research-grade n-pentane. Both catalysts turned a dark green, however, the change seemed to occur a little more slowly when the catalyst was Cr(VI)/silica, indicating that titania does make the catalyst more reactive with these hydrocarbons.

A similar result was observed with n-heptane when the catalysts (700 °C Cr(VI)/silica and 700 °C Cr(VI)/silica-titania) were submerged in the liquid for up to two weeks. They also turned dark green, indicating reduction of Cr(VI). However, the change occurred more slowly on Cr(VI)/silica, indicating that Cr(VI)/silica-titania was more reactive.

Cylclohexane: The preferred solvent in the Phillips solution HDPE process, used around the world with chromium catalysts since the 1950s by various polyethylene producers, was cyclohexane, which contains only methylene C—H bonds. A catalyst containing 5% Cr on silica was calcined at 650 °C to produce an orange powder, indicating Cr(VI). It was then immersed in dry cyclohexane and within minutes it turned to a darker orange-brown, indicating the beginning of reduction. After about 3 h it was a full brown, and within 5 h it became green-brown. It was allowed to set at room temperature for 29 days, during which time it turned completely black. The solvent was then sampled for analysis, and the remainder evaporated off under flowing nitrogen at 25 °C, leaving a dry green-brown catalyst.

GC–MS analysis of the cyclohexane solvent detected no oxidation products, which again indicates that they were attached to the chromium. Therefore the catalyst was wet with a dilute solution of dilute solution of water in methanol. After stirring for an hour the methanol solution was also sampled for GC–MS analysis. Cyclohexanone was found, and a small amount of cyclohexanedione as well.

Cyclopentane: The experiment above was repeated, using 650 °C Cr(VI)/silica and cyclopentane. While the catalyst was fluidizing at 100 °C in dry nitrogen, a large amount (32 mL) of cyclopentane was evaporated into the nitrogen stream and up through the catalyst bed. A color change marked the reduction of the catalyst, but no redox by-products could be found in the condensed cyclopentane off-gas. The temperature of the bed was then lowered to 80 °C and an aqueous solution of 0.7% HCl was then evaporated into the nitrogen stream that moved up through the bed. Analysis of the condensed vapor detected only dimers of cyclopentane as the redox by-products.

Isobutane: In the Phillips loop-slurry polymerization process, which accounts for most of the world's PE produced using chromium catalysts, the calcined catalyst is usually stored in isobutane for days or sometimes even weeks before being introduced into the reactor. Therefore a sample of Cr(VI)/silica-titania (800 °C), calcined at 800 °C, was immersed in liquid isobutane at 25 °C. After 10 min the color began to darken, turning brown, and in 1–4 h it had turned green-black, which is an indication of a rapid reduction. Cr/silica catalyst (800 °C) also went through the same color progression when exposed to isobutane, although a bit more slowly.

In one experiment the catalyst was allowed to soak in isobutane for 10 days. It appeared to be green-black. The flask was then vented, allowing the isobutane liquid to vaporize, leaving a dry blue-gray powder. In another experiment the flask was pressurized with about 3 atm of isobutane gas. The catalyst changed colors quickly in the same way. After a week the pressure was vented, leaving a gray-green powder.

In one case the dry catalyst was then slurried in a dilute solution of water in methanol. After being stirred for about 1 h the methanol solution was analyzed by GC–MS. The oxidation/hydrolysis product was found to be t-butanol.

In another experiment the calcined Cr/silica-titania catalyst was treated with isobutane vapor at 250 °C for about 5 min to simulate the charging of a still hot catalyst immediately after calcination. This catalyst was a dark green, indicating that Cr(VI) had been mostly reduced. It was then tested for ethylene polymerization activity (experiment A9).

Toluene: Occasionally in commercial operations catalysts can also be exposed to small amounts of aromatics. Therefore two samples of Cr(VI)/silica-titania (3.2% Cr, 2.5% Ti, and 1% Cr, 4.5% Ti) both calcined at 850 °C, were immersed in dry toluene. Both immediately turned green-black indicating a rapid reduction. They were allowed to stand for two weeks, and then the toluene was sampled and analyzed by GC–MS. In both experiments, the toluene was found to contain a dimer of toluene, which had been produced during the reduction. The toluene was then evaporated off under flowing nitrogen at 25 °C, leaving a dry gray-brown powder which was later tested for polymerization activity (experiment C2).

A dilute solution of water in methanol was then added and the mixture was stirred for 1 h. GC–MS analysis of the methanol solution indicated that the primary oxidation product was benzaldehyde in both experiments. The toluene dimer was also found in smaller amounts, as well as small amounts of two isomers of a dimer composed of toluene and benzaldehyde. These structures are summarized in Table 2.

Benzene: In still another test, Cr(VI)/silica-titania catalyst, calcined at 850 °C, was submerged in benzene. The catalyst darkened immediately, indicating a rapid reduction. It was allowed to set for two weeks, during which time it turned green-black. After three weeks the benzene was sampled and then evaporated off

Table 3
Summary of polymerization results using Cr(VI) catalysts reduced by alkanes or aromatics.

Experiment/condition	Hydrocarbon reductant	Reduction treatment	Activity (gPE/g/h)	Melt index (g/10 min)
A1	None	Non-reduced control	4526	3.49
A2	n-Heptane	6 days in C7 liquid at 25 °C in light	50	NA
A3	n-Heptane	10 min in C7 vapor at 100 °C in dark	3019	2.93
A4	n-Pentane	5 days in C5 liquid at 25 °C in light	2398	2.57
A5	Isobutane	3 days in iC4 liquid at 25 °C in dark	3558	2.84
A6	Isobutane	10 days in iC4 liquid at 25 °C in light	1810	1.76
A7	Isobutane	10 days in iC4 liquid at 25 °C in dark	1749	1.17
A8	Isobutane	10 min in iC4 vapor at 90 °C in dark	3128	2.67
A9	Isobutane	10 min in iC4 vapor at 250 °C in dark	1911	0.53
A10	Isobutane	1 h in iC4 liquid at 105 °C in dark	3880	NA
B1	None	Non-reduced control	6173	1.42
B2	Isobutane	1h in iC4 liquid at 105 °C in dark	5232	1.25
B3	Isobutane	3h in iC4 liquid at 120 °C in dark	5627	0.51
C1	None	Non-reduced control	4416	5.32
C2	Toluene	13 days in toluene liquid at 25 °C in light	855	2.75

Catalyst: 1% Cr(VI) on silica-titania, reaction at 105 °C, 1.45 molar ethylene.
A: 2.5% Ti, calcination at 800 °C, yield to ~2500 g/g.
B: 2.5% Ti, calcination at 800 °C, yield to ~3500 g/g.
C: 4.5% Ti, calcination at 850 °C, yield to ~3600 g/g.

in a nitrogen stream at 25 °C leaving a green powder. Although the color change indicates a reduction of Cr(VI), we were unable to determine what the oxidation products were, either in the benzene solution or in subsequent treatment with wet methanol.

3.3. Acceleration by light

While these tests were being conducted, a suspicion developed that the reduction of Cr(VI) was being accelerated by light. Therefore two tests were made in which the reaction mixture was stored in the dark, protected from ambient lighting. In one test, Cr(VI)/silica calcined at 700 °C was submerged in n-heptane and stored in the dark. It was only uncovered on occasion for less than a minute for observation. The catalyst darkened and after a week was found to be black, indicating that the Cr(VI) was reduced even in the dark. However, the reduction occurred somewhat more slowly than had occurred in the presence of ambient lighting.

In the second test, a portion of Cr(VI)/silica-titania catalyst, calcined at 800 °C, was sealed in a glass tube, then wetted and covered with isobutane liquid. The tube was then shielded with aluminum foil to prevent exposure to light. The sample was examined 21.5 h later, and compared to a similar experiment conducted in the presence of ambient lighting. Although the covered catalyst had darkened slightly, it was clear that the reduction occurred more slowly in the absence of light. Even after 21.5 h the catalyst still had a dark orange color, in contrast to the un-covered sample which was considerably darker even after an hour, and turned green-black after 21 h.

This sample was then monitored for the next 10 days, always protected from light. It continued to darken, reaching an orange-black color after five days. At the end of the experiment the isobutane was vented and the dry catalyst had a blue-gray color, which was just like the catalyst exposed to light.

Thus, light did accelerate the reduction process, although the final reduced state appeared to be similar. The presence of titania did not seem to be necessary for light to accelerate the reduction. However, it is not clear whether titania may have been more efficient at harnessing the power of light than simple Cr(VI)/silica catalysts.

3.4. Chemiluminescence

Cr(VI)/silica can be cleanly reduced to Cr(II)/silica by carbon monoxide at 350 °C [3]. The oxidation product is carbon dioxide, and at 350 °C it does not remain coordinated by the chromium but instead it is flushed away by the CO stream. A final flush in nitrogen at 350 °C removes even residual CO, which can be strongly adsorbed at 25 °C if the catalyst is cooled in CO. But the nitrogen flush at 350 °C results in a clean divalent catalyst containing no adsorbed oxidation products. The chromium tends to be highly coordinatively unsaturated. Such Cr(II)/silica catalysts are blue (green if cooled in a vacuum because the Cr weakly coordinates nitrogen to yield the blue color), and quite active for ethylene polymerization. And, because the chromium is already reduced and vacant upon contact with ethylene, it develops activity more quickly than Cr(VI)/silica.

When exposed to oxygen such CO-reduced catalysts display a brilliant yellow chemiluminescence that resembles a flash of fire. Cr(II) is cleanly converted back to Cr(VI) and the energy is released as light. This is probably an indication that the oxidation occurs easily with little or no molecular rearrangement. However, if the chromium coordinates a ligand, such as CO or ethylene, there is no chemiluminescence, even though the oxidation does proceed.

The catalysts of this study, that were reduced with alkanes or aromatics, displayed no such chemiluminescence upon exposure to oxygen. For example, one Cr(VI)/silica-titania catalyst was allowed to soak in isobutane for a total of 10 days before the isobutane was vented. The dry catalyst had a blue-gray color. It turned a yellowish green when exposed to dry air, signifying partial restoration of Cr(VI), but it did not chemiluminesce like a CO reduced catalyst. In another experiment the same Cr(VI)/silica-titania catalyst was reduced with n-pentane to yield a beautiful blue catalyst after drying, identical in color to the CO-reduced catalysts. Upon exposure to air it also turned a yellow-green color, but again it did not chemiluminesce.

The lack of chemiluminescence is probably an indication that these catalysts still retain ligands coordinated from the oxidation of the hydrocarbon. As noted above, these oxidation products were usually not detected in the hydrocarbon solvent after reduction, which also indicates that they remained coordinated. Only the addition of water/methanol solution liberated them.

3.5. Polymerization activity of alkane- or aromatic-reduced catalysts

Some of the catalysts described above (i.e. reduced by exposure to non-olefinic hydrocarbon in various ways) were then dried and tested for polymerization activity in a laboratory reactor at 105 °C. Most of these alkane- or aromatic-reduced catalysts were active when placed in a reactor containing ethylene and isobutane

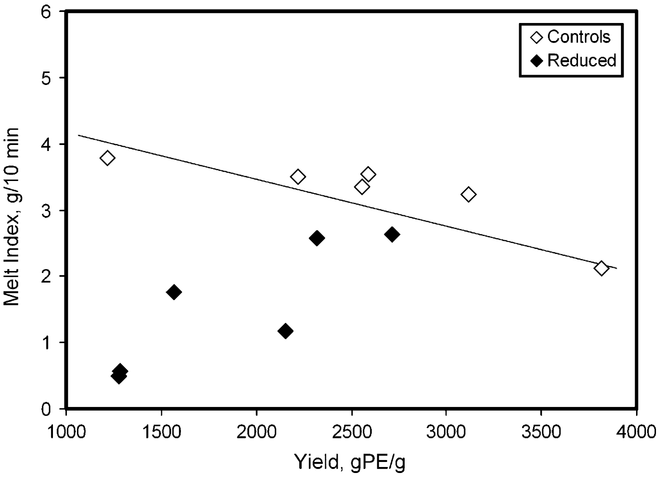


Fig. 2. Catalysts reduced in isobutane tended to produce PE of higher MW (lower melt index) for a given polymer yield.

Table 4
Polymerization results from Cr(VI)/silica-titania (850 °C) before and after reduction by alkane. (Each entry is an average of 5–7 runs.).

Treatment	Activity (gPE/g/h)	Melt index (g/10 min)
Untreated	5203	3.12
Isobutane	4535	2.48
Isobutane, Air	1349	1.95
n-Hexane	3054	1.63

diluent at 105 °C. However, they often tended to exhibit diminished activity. The results of these tests are listed in Table 3, where they are compared to non-reduced catalyst control runs.

Some of the experiments in Table 3 show the loss in activity that resulted from prolonged or intense exposure to various alkanes or aromatics. For example, in experiments A2 and A4, storage at 25 °C in simple alkanes (n-heptane or n-pentane) caused a significant loss of activity. Similarly, in experiment C2 one can see that storage in toluene also lowered the activity significantly.

Other catalysts were treated with isobutane, which is of special interest because it is widely used for catalyst storage in many commercial operations. Catalysts were treated with isobutane in various ways in Table 3, and the results were somewhat variable. Nevertheless, it is clear that the catalyst activity is lowered when Cr(VI) has the opportunity to be reduced by isobutane rather than by the more reactive ethylene. For example, in experiments A5, A6 and A7, Cr(VI) catalyst was stored at 25 °C under liquid isobutane for varying lengths of time. This would be similar to its treatment in a manufacturing plant. Then each catalyst was charged to the reactor where it simultaneously contacted isobutane and ethylene at 105 °C. Reduction in isobutane again seems to cause a loss in activity.

This caused some concern that the observed loss in activity might be caused by contamination from the storage vessel. Therefore, to avoid using a storage vessel, some catalysts were treated with isobutane vapor at the end of the calcination step, at 90 °C (A8, which produced a dull yellow color) and then at 250 °C (A9, which resulted in a green color). These catalysts also lost activity, especially the latter.

In other experiments in Table 3 (A10, B2, B3), the catalyst was treated with isobutane in the reactor itself. That is, the catalyst was charged to the reactor with isobutane, and allowed to stir for 1–3 h at reaction temperature or higher in the absence of ethylene. Then ethylene was added and the polymerization activity was recorded. Even this treatment produced a loss in activity.

Also shown in Table 3 is the melt index of the polymer obtained, which is an indication of the ease of flow of the molten polymer. Melt index usually varies inversely with the molecular weight, and is often used to monitor the character of the polymer. In the experiments of Table 3, melt index tends to parallel the activity. That is, reduction by alkanes tended to lower the melt index produced.

Melt index is also known to decrease as the amount of polymer produced rises. That is, melt index is a function of reaction time, more commonly expressed as the yield of polymer (g of PE produced per g of catalyst). This happens because some active sites come on stream more rapidly (producing lower MW polymer) than others [3]. In Fig. 2 the melt index obtained from various control runs using non-reduced catalyst is plotted against polymer yield, and one can see the gentle decline in melt index. The melt indices from various alkane- or aromatic-reduced catalysts are also plotted in Fig. 2, and it is immediately obvious that these are generally below the non-reduced control curve. This means that the melt index potential of the catalyst has been diminished. The most severe example of this is the catalyst exposed to isobutane vapor at 250 °C, which would be equivalent to the immediate charging of a hot catalyst into the storage vessel, which is then quickly filled with isobutane.

Fig. 3 shows the effect of this reduction treatment on the molecular weight distribution. In another experiment, a Cr(VI)/silica-titania catalyst (800 °C) was allowed to polymerize ethylene and then stored under isobutane in the light for about 10 days. Then it was tested again. As expected, it had lost activity during this time, and the melt index of the resultant polymer had also dropped. The size exclusion chromatograms of the polymers are shown in Fig. 3. Also shown is the polymer from experiment A9, in which the catalyst was briefly treated with isobutane vapor at 250 °C. Each curve has been normalized according to the activity of the catalyst, so that one may see which part of the distribution was most affected. The change observed was significant. Isobutane treatment caused a narrowing of the MW distribution from a loss on the low-MW side. This would correspond to a loss of some of the most reactive Cr(VI) sites, which suggests that they were preferentially inhibited by the reduction treatment. On this particular catalyst, it is the titania-associated sites that are known to be more reactive, and to contribute to this low-MW region [3,12,13].

3.6. *Oxygen sensitivity after reduction*

Cr(VI) catalysts are not reactive with oxygen at 25 °C. If exposed to dry air the catalyst remains active, provided that the air is first purged with nitrogen before the catalyst is introduced into the reactor. However, alkane-reduced catalysts seemed to be quite

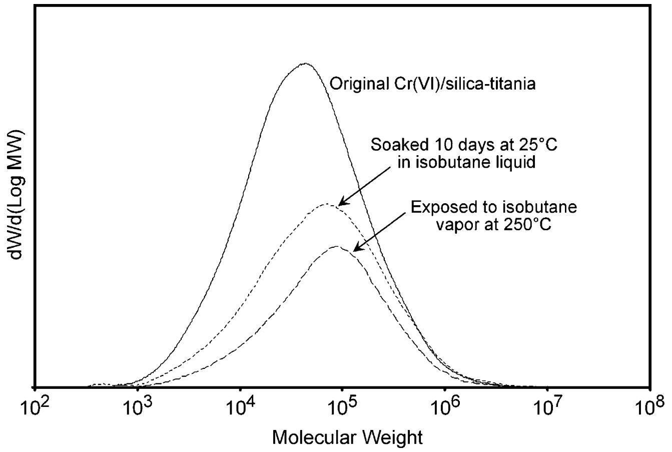
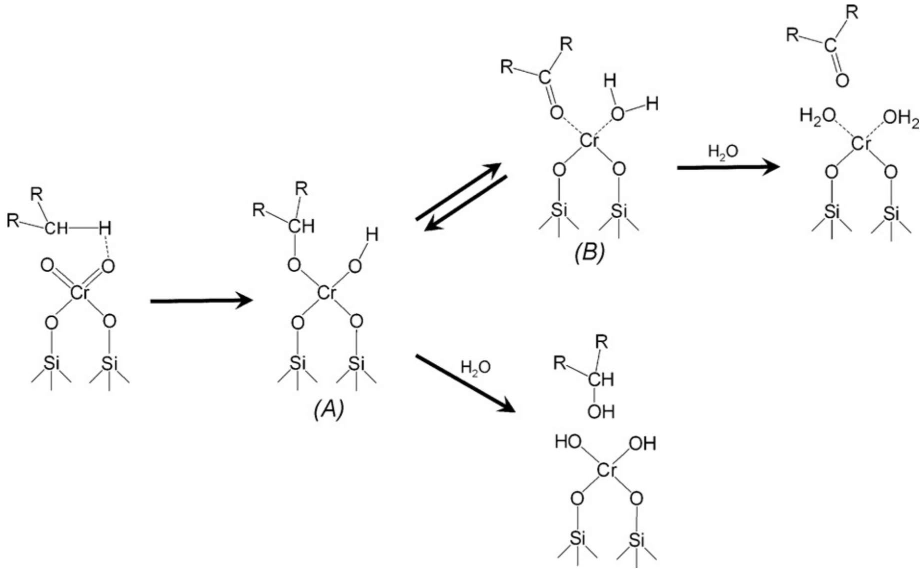


Fig. 3. MW distribution of polymer made with Cr/silica-titania, before and after two different treatments with isobutane.



Scheme 2. Possible oxidation of alkanes by Cr(VI)/silica catalysts.

sensitive to oxygen. During the course of this study, it was noted that such exposure to oxygen resulted in a strong loss of activity – beyond that caused solely by the reduction in alkane. This is shown in Table 4, where alkane-reduced catalysts were tested and then exposed to dry air briefly before being tested again. The melt index potential of the catalyst seemed to parallel the activity. Exposure of the alkane-reduced catalyst to air greatly lowered the melt index produced, even below that of the alkane-reduced catalyst itself.

3.7. Adsorption/desorption of ketones

Finally, several experiments were done to better understand the nature of ketones generated by reduction of Cr(VI) with alkanes. A Cr(VI)/silica-titania catalyst was calcined at 800 °C, then it was treated with carbon monoxide at 350 °C for half an hour to convert the chromium into the divalent state [3]. A final 30 min flushing in dry nitrogen at 350 °C removed traces of residual CO, and then the catalyst was cooled in nitrogen to 25 °C. This Cr(II) catalyst is well known as a very active catalyst exhibiting a shortened induction time, in comparison to its Cr(VI) counterpart. A sample of this catalyst was then exposed to 2-hexanone vapor at 25 °C in the amount of 2.5/Cr and then another sample was exposed to 1.0 2-hexanone/Cr. The addition of the ketone changed the color of both catalysts from sky-blue to a bluish grey. Both catalysts were tested for polymerization activity, and both were found to be inactive, indicating that the ketone had adsorbed onto the Cr and blocked polymerization. This is not surprising.

Then, in order to drive off the adsorbed ketone and regenerate the active site, both of these catalysts were heated in flowing nitrogen to 300 °C for 1 h. Both were then cooled in nitrogen and retested for polymerization activity. They were still inactive. And, unlike the original Cr(II) catalyst, they did not chemiluminescence upon exposure to oxygen.

This result can only mean that the ketone did not reversibly coordinate to the coodinatively unsaturated Cr(II) and then desorb upon further heating. This indicates that the ketone behaved differently from CO, which adsorbs and desorbs reversibly with heating and cooling. It suggests that the ketone oxidized the Cr(II) sites to form a different species, probably containing an oxy-hexane group, that permanently destroyed the active site. It will become evident later that this observation is important in the interpretation of reduction to form active sites.

4. Conclusions

Cr(VI)-containing catalysts were found to be reduced, not only by 1-alkenes during the course of their polymerization, but also by alkanes, which are frequently used as solvents and diluents for reaction and for catalyst storage. The reaction with alkanes, which have long been considered inert, is indeed quite slow in comparison to reaction with 1-alkenes.

The −30 °C data indicates that reduction by alkanes can sometimes help activate the catalyst (i.e. generate active sites) in comparison with the original Cr(VI) catalyst at −30°C. However, it is also clear from the 105 °C polymerization data that reduction by alkanes can diminish the activity and melt index potential, in comparison to the the olefin-reduced catalysts. That is, catalysts reduced by olefins at 105 °C tended to produce higher overall activity (at 105 °C) than catalyst reduced by alkanes. Changes in the MW distribution suggest that it is the more reactive sites, those that normally produce low-MW polymer, that are most affected by reduction with alkanes. Possibly the by-products from alkane oxidation inhibit the development of activity on those sites, compared to reduction by olefins. Thus, the effect of prolonged contact with alkanes can sometimes be seen in diminished activity and higher PE molecular weight.

The methine hydrogen (R_3CH) on isobutane, and the methylene hydrogens ($—CH_2—$) on other alkanes, were found to be more reactive than the methyl ($—CH_3$) hydrogens, resulting after hydrolysis in the corresponding secondary ketone or alcohol, or the tertiary alcohol. Scheme 2 shows one possible pathway in which a methylene C—H is attacked by Cr(VI) to form a Cr(IV) species. Adding water at this point could result in hydrolysis to the corresponding alcohol. Alternatively, a second hydrogen shift could result in the ketone coordinated to a Cr(II) species. This species could further react with water to desorb the ketone, or even to oxidize the Cr(II) to Cr(IV) or Cr(III) hydroxide and hydrogen gas.

The exception to this view is isobutane, which has only the one hydrogen on the reactive carbon. Thus, adding water to a catalyst reduced by isobutane released only t-butanol.

Although the activation temperatures and the Cr and Ti loadings were varied over a wide range in this study, similar results were usually obtained. Only the rate of reduction seemed to vary, especially with titania content.

Finally it is interesting to note that species B in Scheme 2 is comparable to the catalyst prepared above by exposing coordinatively unsaturated Cr(II) to 2-hexanone vapor (last section above). The ketone could not be removed by heat to regenerate the original Cr(II) site. This indicates that the ketone probably oxidizes the initial Cr(II) site, probably back to Cr(IV) as in species A of Scheme 2.

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References

[1] J.P. Hogan, R.L. Banks, U.S. Patent 2,825,721 to Phillips Petroleum Company, filed August 1954, Issued March 1958, and Belgian Patent 530,617, filed January, 1955, filed in the U.S. Jan 1953, S.N. 333,576, also Austrian Patent App. 864/54, filed August 6, 1954.
[2] J.P. Hogan, J. Polym. Sci.: Part A-1 8 (1970) 2637–2652.
[3] M.P. McDaniel, Adv. Catal. 33 (1985) 47–98;
M.P. McDaniel, Adv. Catal. 53 (2010) 123–606 (Chapter 3).
[4] L.M. Baker, W.L. Carrick, J. Org. Chem. 33 (2) (1968) 616–618.
[5] L.M. Baker, W.L. Carrick, J. Org. Chem. 35 (3) (1969) 774–776.
[6] B. Liu, Y. Fang, M. Terano, Mol. Simul. 30 (15) (2004) 963–971.
[7] B. Lui, H. Nakatani, M. Terano, J. Mol. Catal. A: Chem 184 (2002) 387–398.
[8] H.L. Krauss, H. Schmidt, Z. Anorg. Allg. Chem. 392 (1972) 258–270.
[9] R.E. Cunningham, B.H., Ashe, A. Clark, G.C. Bailey, Phillips Petroleum Co. Research Report 2613 from 1960.
[10] G. Cainelli, G. Cardillo, in: K. Hafner, C.W. Rees, B.M. Trost, J.M. Lehn, P. von Rague Schleyer, R. Zahradnik (Eds.), Reactor and Structure Concepts in Organic Chemistry, vol. 19, Springer-Verlag, Berlin, 1984.
[11] R.E. Dietz, U.S. Patent 3,887,494, issued June 3, 1975 to Phillips Petroleum Co.
[12] C.E. Marsden, in: V.E.G. Poncelet, P.A. Jacobs, P. Grange, D. Delmon (Eds.), Studies in Surface Science and Catalysis (Preparation of Catalysts V), vol. 63, Elsevier Science Publishers B.V., Amsterdam, 1991, pp. 215–227.
[13] M.P. McDaniel, M.B. Welch, M.J. Dreiling, J. Catal. 82 (1983) 118–126.