Graphical abstract

Reduction of the Phillips Catalyst by Various Olefins: Stoichiometry, Thermochemistry, Reaction Products and Polymerization Activity

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Abstract:

The adsorption, reaction and desorption of ethylene or hexenes on Cr(VI)/SiO₂ containing 1 or 3 weight% chromium was monitored by thermogravimetry, differential scanning calorimetry and mass spectrometry. Reaction of Cr(VI)/SiO₂ with ethylene at a temperature of 200 °C always included some oligomerization, making it impossible to identify the stoichiometry of the initial redox reaction. Reaction of Cr(VI)/SiO₂ with 1-hexene or cyclohexene at 150 °C indicated an adsorption stoichiometry of one olefin per chromium. Heats of reaction were consistent with oxidation of the olefin to an aldehyde or ketone, or even to a carboxylic acid or ester. Oxidation products were retained on the surface. Thermal desorption of surface products resulted in CO₂ evolution at temperatures of 265-285 and 390-415 °C; with the co-products indicating decomposition of formate and acetate species, respectively. Reduction of Cr(VI) with ethylene led to sites active for ethylene polymerization after thermal desorption of the redox products, whereas reduction with hexenes did not generate active sites irrespective of thermal desorption of products.

Keywords: silica, CrO₃, reduction, reaction enthalpy, adsorbate, ligand, temperature-programmed desorption, polyethylene

1 Introduction

Approximately 40–50% of the worldwide production of high density polyethylene is obtained with the help of the Phillips catalyst, which is also used to generate some linear low density polyethylene and specialty oils.¹ While the catalyst was commercialized more than 50 years ago, the exact structure of the site that is active for polymerization is still being debated,²⁻⁴ although the ingredients in the simplest form of the catalyst are only a silica support and chromium ions. There are several reasons for the lack of knowledge of the active site. One is that only a fraction of the chromium appears to be active, and there is substantial disagreement on the size of this fraction. Reported percentages of active chromium range from 0.1 to 98 % with most values below 50 %.¹ This data implies that the relevant structure must be identified among inactive structures. Site heterogeneity may, in part, be caused by the nature of the support.⁵ Another reason is that the calcined catalyst contains only a precursor of the active chromium form, and not even this precursor structure is completely established. Reports agree that in calcined Cr/SiO₂ materials, chromate is covalently bound to the silica surface and, typically, several structures can co-exist including monochromate, dichromate, and polychromate. In addition to Cr(VI), Cr(III) may be present, in the form of Cr₂O₃. Some authors found dichromate species to dominate in the range of 0 to 5 wt.% chromium content.⁶ Weckhuysen et al.⁷ reported increasing fractions of polychromate and Cr₂O₃ with increasing chromium loading. Recently, it was proposed that all chromium is present as monochromate, some of which is in the often reported bidentate form and some of which is tetradentate with a single Cr=O unit (“mono-oxo”).⁸⁻¹⁰

In commercial operations, the chromium precursor is usually converted to the active structure upon contact with the olefin, or, in some cases, through reaction with another reagent such as CO and subsequent contact with the olefin.¹ CO-reduced catalysts do not show an induction period and exhibit a slightly different polymerization behavior from olefin-reduced catalysts, for

example with respect to the rate at which a second olefin is incorporated.¹ Consistent with these activation procedures, there is consensus that the active chromium has a valence lower than +VI,^{1,11} but there is dissent on the exact oxidation state. Cr(II) was proposed as active species¹² and has been investigated for many years;¹³ however, recent reports have advocated Cr(III),²⁻⁴ possibly formed through oxidation of Cr(II) by ethylene.

The multitude of structures present in a typical catalyst and the uncertainty about the reduction step complicate identification of the active site. Not all of the precursor structures may react in the same way during these reduction steps, possibly creating a variety of reduced species. Only a few investigations address the reduction of the calcined Phillips catalyst by olefins. Baker and Carrick¹⁴ used a test reagent to determine reaction products and concluded that ethylene is cleaved into two molecules of formaldehyde with concomitant reduction of Cr(VI) to Cr(II). The molecules were proposed to be released from the site, generating a bare Cr(II). However, the maximum formaldehyde yield was 18%. The formation of formaldehyde as reaction product of ethylene was also inferred by Liu et al.¹⁵ on the basis of a temperature-programmed desorption (TPD) experiment. Groppo et al.¹⁶ recorded X-ray absorption spectra and confirmed reduction of chromium by ethylene. Chakrabati et al.¹⁷ acquired mass spectra during temperature-programmed reduction in ethylene and observed two reduction steps, which were associated with different monochromate structures. Carbon dioxide was the only detected gas phase product at temperatures of 280 and 410 °C, with water presumed to have condensed in unheated lines. Cyclohexene was recently applied as a reductant by Barzan et al.¹⁸ and reacted at room temperature, yielding divalent chromium sites and aldehydes, which rapidly underwent secondary reactions to esters. These oxygenates remained “in strong interaction” with the

chromium, thus forming a ligand sphere. The cyclohexene-reduced catalyst was active for ethylene polymerization.

Results to date are contradictory with respect to the nature and the fate of the olefin oxidation products – while HCHO and CO₂ are assumed to be released, heavier products may remain coordinated.¹⁸

In the present work, a novel approach was taken. The stoichiometry and thermochemistry of the reaction between Cr(VI)/SiO₂ and olefins were investigated by applying thermogravimetry (TG) and differential scanning calorimetry (DSC). Previously, the stoichiometry of the reaction has been inferred but not observed, and knowledge thereof would help reconcile principal products and chromium valence. To prevent results from being obscured by polymerization products, the olefins were applied in the form of short pulses, and the temperature and pressure conditions were chosen to minimize polymerization. Two chromium loadings were investigated to probe for chromium species of different reactivity, assuming the fractions of chromate, dichromate, and Cr₂O₃ are a function of loading. Ethylene, 1-hexene, or cyclohexene were used for the reaction. 1-Hexene was interesting because it is often co-polymerized with ethylene, whereas cyclohexene can be seen as representing internal olefins (without the possibility to isomerize into a terminal olefin). To investigate whether the olefin oxidation products are part of the active site or need to be removed to obtain an active catalyst, the organic products were completely or partially decomposed by temperature-programmed desorption and the polymerization activity was determined.

2 Experimental Section

2.1 Catalyst preparation

Catalysts were made by impregnation of silica with an aqueous solution of chromium (VI) trioxide to incipient wetness. Commercial grade HA30W silica, often used in HDPE

manufacturing, was obtained from W.R. Grace Corporation, having a surface area of about 500 m²/g, a pore volume of about 1.6 mL/g, and an average particle size of 100 microns. Catalysts contained either 1.0 or 3.0 wt.% chromium and are designated as 1Cr/SiO₂ and 3Cr/SiO₂ in the following.

These catalysts were initially calcined by fluidization in dry air (2.1 cm/s). The temperature of the fluidized bed was ramped up to 700°C over a period of 1.7 hours and then held for three hours. Afterward, the calcined catalysts were stored in flasks under dry N₂ atmosphere. Both catalysts were orange, indicating high conversion to Cr(VI).¹

2.2 Thermogravimetry with on-line mass spectrometry and differential scanning calorimetry

2.2.1 Olefins

Ethylene for the TG experiments was used as received from Matheson, specified as research purity (99.999%). 1-Hexene was received from Sigma with a specified purity of > 99.8%; cyclohexene was Product # 125431 from Sigma-Aldrich, designated as inhibitor-free, ReagentPlus®, 99%; and 2-pentene was a mixture of cis and trans from Sigma-Aldrich with 99% purity. The liquid olefins were dried over 3A molecular sieve prior to the thermogravimetry experiments. GC-MS analysis of the dried cyclohexene did not reveal any impurities.

2.2.2 Instrumentation

The thermogravimetry and differential scanning calorimetry experiments with evolved gas analysis (TG-EVA) were performed using a NETZSCH STA 449 F1 Jupiter with on-line mass spectrometer QMS 403 C Aëolos. Two different sample holders were used, a TG or a DSC sample holder. The alumina crucibles designed for these holders were charged with about 400 or about 25 mg of sample, respectively. The mass spectrometer was operated at an ionization energy of 70 eV, and a secondary electron multiplier was used for detection.

2.2.3 Protocol

Catalyst powders were transferred into alumina crucibles inside a N₂-filled glove bag and then exposed to air for less than 2 min while the crucible was placed in the sample holder and the instrument was closed and purged. All parts of the experiment were conducted at atmospheric pressure, with a total gas flow rate of 50 ml/min. The materials were first heated in an 80 % air and 20 % argon mixture to a temperature of 600 °C at a rate of 10 K/min, held at this temperature for 1 h, and then cooled to the reaction temperature, whereby the gas was switched to argon at about 300 °C.

Conditions for Cr/SiO₂ reduction depended on the olefin. The reaction temperature for ethylene was 200 °C to ensure reaction within a short time while minimizing subsequent polymerization (which progresses rapidly at lower temperatures). Ethylene was mixed with argon and admitted at a concentration of 40 mol% as a sequence of 1-min pulses (typically 6 pulses). 1-Hexene, cyclohexene, and 2-pentene were injected as liquid into argon flow. Typical pulse sizes were a few microliters. These pulses vaporized and traveled to the sample in the gas stream. The reaction temperature was 150 °C.

After exposure to olefins, a temperature-programmed desorption (TPD) experiment was optionally conducted. The sample was heated to a temperature of 300 or 500 °C at a rate of 10 K/min in a flow of argon.

After reduction and optional TPD, the activity of the sample for polymerization was tested by flowing a 40 mol % ethylene-in-argon mixture at a temperature of 150 °C for a duration of 10 min.

2.2.4 Data analysis

DSC signals were integrated using the Netzsch Software package and an S-shaped background or Origin and a linear background. An average rate of polymerization was calculated

from the catalyst mass before and after the 10 min exposure to ethylene. Steady state rates were obtained from flat sections in the first derivative of the mass with respect to time.

2.3 Reduction followed by polymerization under commercially relevant conditions

2.3.1 Olefins

Polymerization-grade ethylene from Airgas Co. was used in these experiments after purification through activated alumina and 13X molecular sieve. 1-Hexene was obtained from ChevronPhillips Chemical Company and similarly purified. The isobutane diluent, also polymerization grade, was purchased from Enterprise Co. It was first degassed by distillation followed by purification through an alumina and 13X molecular sieve bed.

2.3.2 Reactor

Polymerization runs were made in a 2.2 liter stainless steel reactor equipped with a marine stirrer rotating at 500 rpm. The reactor was surrounded by a steel jacket through which water was circulated for precise temperature control (± 0.5 K) using an instrumented control loop.

2.3.3 Pre-reduction with 1-hexene (moved from results)

In these experiments, Cr/silica-titania (1wt.% Cr) was initially calcined by fluidization in dry air at 850°C. Then the temperature was lowered to 100°C, the gas stream was changed to dry N₂, and small amounts of 1-hexene were vaporized into gas stream. These catalysts were then transferred into the reactor and tested for polymerization activity.

2.3.4 Protocol

Typically, a small amount (0.01 to 0.10 g) of the solid catalyst was first charged under N₂ to the dry reactor. Next, 1.2 liter of isobutane liquid was charged and the reactor heated to the specified temperature, usually 105°C. Finally ethylene was added to the reactor to equal a fixed pressure, normally 3.89 MPa, which was maintained during the experiment. The stirring was

allowed to continue for about one hour, 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 slowly 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 was then removed and weighed. Activity was specified as grams of polymer produced per gram of solid catalyst charged per hour.

3 Results

3.1 Reaction of Cr(VI)/SiO₂ with Olefins

3.1.1 Ethylene uptake during pulses and gas phase products

The catalyst was exposed to a sequence of one-minute ethylene pulses (40% in argon) at a temperature of 200 °C. Control experiments showed that there is no adsorption of ethylene on the silica support under these conditions; hence, any mass gain is associated with reactions of the chromium. Figure 1a shows the evolution of the sample mass during the pulse sequence. The number of ethylene molecules in each pulse was at least 50 times the number of chromium atoms in the sample. The mass change during the pulse always had a step-shape, indicating exclusively irreversible adsorption, even though a large excess of ethylene was offered. Generally, there was only a small mass gain in the first pulse followed by a much larger mass gain in the second pulse (3 wt.% Cr, Figure 1a) or in later pulses (1 wt.% Cr, Figure 1c). The mass gain per pulse passed through a maximum and then became smaller during subsequent pulses. For samples containing 3 wt.% chromium, it was nearly zero in the last pulse, consistent with saturation or a self-terminating reaction. A plot of the uptake vs the exposure shows an S-shaped profile for samples with 1 or 3 wt.% chromium (Figure 2). For samples containing 1 wt.% chromium, the uptake exceeded three molecules per chromium without a distinct saturation level emerging, whereas for

samples containing 3 wt.%, the ratio was well defined and reproducible at two ethylene molecules per chromium.

(a)

(b)

(c)

Figure 1: TG, DSC and MS data recorded during six one-minute pulses of ethylene administered at 200 °C. (a) 3/CrSiO₂, TG and DSC (b) 3/CrSiO₂, corresponding mass spectra for selected m/z ratios; inset: the second pulse; and (c) 1/CrSiO₂, TG and DSC.

The highest concentrations of gas phase products were observed during the pulse that created the largest mass gain. The mass-to-charge ratio (m/z) with the highest intensity was 41, followed by 56, 55, 42 and by 43, 50, 51, 53, and 54. In addition, there were very weak signals at m/z of 49, 69, 52 and 57. The same fragments were obtained during later pulses, with gradually declining intensity (Figure 1b). The mass spectra can be explained with dimerization and trimerization products. The main fragments of 1-butene that do not overlap with peaks from ethylene or argon are at $m/z = 41, 56,$ and 55 , according to NIST. The fragments at 42, 43 and 69 suggest that a molecule with a longer alkyl chain was also formed. MS spectra of 1-hexene were collected and the main fragments (in order of descending contribution) were at $m/z = 41, 42, 55, 43, 56, 84, 69$. All observed peaks are attributable to fragments of butene, hexenes, or both types of molecule. The intensity of the signals at $m/z = 55$ and 56 was close to equal, with one or the other occasionally being slightly larger. 1-Butene and 1-hexene are characterized by a larger signal at $m/z = 56$ than at $m/z = 55$, whereas 2-butenes, 2-hexenes, and 3-hexenes are characterized by a larger signal at $m/z = 55$ than at $m/z = 56$. Hence, the volatile oligomers contained both, terminal and internal double bonds.

Figure 2: Uptake curves for ethylene during reaction with 3Cr/SiO_2 and 1Cr/SiO_2 . Ethylene was administered at a temperature of $200\text{ }^\circ\text{C}$ in the form of pulses of 1 min duration (40 kPa ethylene diluted in inert gas, at atmospheric pressure). Units on both axes are mol/mol.

The main peaks of formaldehyde at 29, 30, and 28, overlap with those of ethylene and ^{13}C -ethylene (from natural ^{13}C abundance), and, consequently, this molecule is difficult to detect by MS.

3.1.2 1-Hexene and cyclohexene uptake during pulses and gas phase products

The typical behavior of the Cr/SiO₂ catalysts during exposure to hexenes at a temperature of 150 °C is illustrated in Figure 3. The mass gain during the first hexene pulses was generally irreversible, whereas during later pulses, the initial mass increase was followed by a decrease, indicating partially reversible adsorption. The DSC curves mirrored the behavior of the mass during a pulse, with a distinct exothermic signal followed by a shallow endothermic signal when adsorption was partially reversible.

Figure 3: TG and DSC traces recorded during 13 pulses of 1-hexene administered at a temperature of 150 °C to 3/CrSiO₂. Pulse size 3 or 5 μl liquid, evaporated into an argon stream. Partially reversible adsorption is first visible in the 7th pulse.

Analysis of the TG data produced the adsorption isotherms seen in Figure 4. The curves for 1Cr/SiO₂ could be fit with a Langmuir-type equation, and the monolayer coverage was found to be around one olefin per chromium for 1-hexene and slightly lower for cyclohexene. The curves

for 3Cr/SiO₂ were steep until a hexene/chromium ratio of about 0.5 was reached, then the slope became shallower. Past this point, the curves for a chromium content of 1 wt.% were slightly above those for a content of 3 wt.%. The form of the curve prevented high fidelity in the determination of the monolayer coverages for hexenes on 3Cr/SiO₂; values between 0.7 and 0.85 were estimated. No gas phase products were identifiable in the mass spectra; however, detection of hydrocarbons was hampered because of the extensive number of 1-hexene fragments.

Figure 4: Uptake curves for 1-hexene (a) and cyclohexene (b) during reaction with 3Cr/SiO₂ or 1Cr/SiO₂. Pulses of olefin vapor (typically corresponding to 3 μ l of liquid) were administered at a temperature of 150 $^{\circ}$ C in a stream of inert gas.

3.1.3 Heat evolution during reaction of Cr/SiO₂ with olefins

The DSC signals recorded during ethylene pulses are shown in Figure 1a. Because of the increasing baseline level, the peak area depended significantly on the method of background subtraction. It was assumed that the mass change of the sample corresponds to the moles of ethylene reacted, which is justified by the absence of significant amounts of gas phase products for most pulses. Using a straight two point baseline, the heat evolved during the first pulse varied between 300 and 465 kJ/mol. Subsequent pulses resulted in smaller heats, as shown in Figure 5, which were close to the heat of oligomerization. At 200 $^{\circ}$ C, polyethylene (PE) would be liquid; further the uptake per chromium suggests chain lengths might be short, even if only a fraction of

the chromium is active. The heat of formation of PE from gaseous ethylene ranges from 40 to 80 kJ/mol ethylene, for chain lengths up to 10 ethylene units and a temperature of 223 °C.¹⁹ Heats of oligomerization of gaseous ethylene to gaseous butene or hexene are also around 100 kJ/mol ethylene. No distinct effect of the chromium loading on the heats was recognizable.

Figure 5: Heats of reaction during pulsing of gaseous olefins. Catalyst: 3Cr/SiO₂ or 1Cr/SiO₂ as indicated. Reaction temperature: 200 °C for ethylene, 150 °C for all other olefins.

DSC signals measured during the first pulses of 1-hexene, cyclohexene, or 2-pentene dosed onto Cr(VI)/SiO₂ were associated with a similar step-like increase in the baseline as those observed during ethylene pulses; thus the uncertainty in the heats of reaction is significant for the initial pulses and estimated to be ± 50 kJ/mol. The heats measured for the C5 and C6 olefins are included in Figure 5. It is evident that all olefins undergo a highly exothermic reaction with Cr(VI)/SiO₂. In general, the heats decline with increasing mass uptake of the sample. Even though uptakes larger than 0.5 molecules per chromium were achieved, the corresponding heat signals were difficult to analyze as a fraction of the olefin desorbed very slowly, thus generating a broad endothermic signal at the tail end of the exotherm.

3.2 Temperature-programmed desorption of redox products

Since oxygenates were not detectable during reduction by olefins while high heats of reaction indicated a redox reaction, products must have been retained on the surface. To learn more about the nature of the redox products, they were thermally decomposed in an inert gas stream, and the evolving gas phase products were monitored by mass spectrometry.

Figure 6: Mass spectroscopic traces recorded during temperature-programmed desorption in argon at a heating rate of 10 K/min. Catalysts and olefin uptake as specified: (a) 1Cr/SiO₂ with 2.24 mol ethylene/mol Cr ; (b) 3Cr/SiO₂ with 2.01 mol ethylene/mol Cr ; (c) 3Cr/SiO₂ with 0.61 mol 1-hexene/mol Cr ; (d) 3Cr/SiO₂ with 0.46 mol cyclohexene/mol Cr .

All TPD profiles were characterized by two main events, which had their maximum gas evolution at 260 to 285 °C, and at 390 to 435 °C, respectively (Figure 6). The first event was associated with a smaller mass loss – it accounted for roughly 40% of the entire loss during TPD,

and the second event accounted for the remaining 60 %. The weight at the end of the TPD was slightly above that of the fresh catalyst except for cases with very low olefin coverage (≤ 0.16 hexene/Cr). Accounting only for oxygen loss, reduction of Cr(VI) would be associated with a weight loss in the range of 0.46 wt.% (1% Cr reduced from Cr(VI) to Cr(III)) to 1.85 wt.% (3% Cr to Cr(II)). Hence, the weight gain indicates residual hydrocarbon moieties on the surface.

The observed mass/charge ratios (m/z) are summarized in Table 1. All curves showed broad signals of water ($m/z = 18, 17$), the maxima of which did not necessarily coincide with the main two events. Carbon dioxide ($m/z = 44$) desorbed, in about equal quantities, during both events for ethylene, and in relatively higher quantities during the second event for the hexenes. Carbon monoxide or ethylene ($m/z = 28$) were produced during the second event, because a higher intensity at $m/z = 28$ was detected than would be expected from CO_2 fragmentation (NIST: 10% of $m/z = 44$; this MS, 20%). H_2 ($m/z = 2$) evolved during both events for ethylene, and during the high temperature event for 1-hexene, and not at all for cyclohexene. In assessing intensities, different ionization cross sections have to be considered; for example, the ionization cross section of CO_2 is 3.5 times as large as that of H_2 .

Table 1: Overview of m/z ratios observed during TPD in argon

Temperature Range	Ethylene	1-Hexene	Cyclohexene	Assignment
<i>From 200 -500 °C</i>	17, 18	17, 18	17, 18	H_2O
<i>Maximum at 260-285 °C</i>	2 (27) ^b (41) ^b 44	(2) ^a 44	44	H_2 - C_2H_3 - C_3H_5 CO_2
<i>Maximum at 390-435 °C</i>	2 15 26, 27 28 29 41, 42 44	2 15 26, 27 28 41, 42 44	15 28 44	H_2 - CH_3 - C_2H_2 , - C_2H_3 CO , C_2H_4 - C_2H_5 - C_3H_5 , - C_3H_6 CO_2

^aNot always observed

^bTraces observed once

Alkyl fragments ($m/z=15$) occurred with the high temperature event in all cases. Weak signals of unsaturated hydrocarbon fragments were observed, which included $m/z=26$, 27 , and 41 . More such fragments were observed for ethylene-reduced samples than for 1-hexene or cyclohexene-reduced samples.

For ethylene- or 1-hexene-treated samples, the maxima for the various m/z ratios during the high-temperature event appeared at slightly different temperatures. The signals at $m/z=44$ and 15 coincided and had their maxima at a slightly lower temperature than the other signals.

Formaldehyde, a product reported in the literature,^{14,15} would produce three signals at mass-charge ratios of 29 , 30 , and 28 (in order of decreasing intensity). Signals at $m/z=29$ were weak (ethylene) or absent (hexenes), suggesting that formaldehyde release is not a major pathway during TPD. Ethylene oxide also has its strongest signal at $m/z=29$ (followed by $m/z=44$) and can equally be excluded as a major product.

3.3 Polymerization activity of olefin-reduced catalyst before and after selective TPD

To determine whether the exposure to olefins produced an active catalyst and whether the redox products are part of the active site, polymerization tests were performed with or without these products present. The two-step decomposition process identified in Figure 6 provides a unique opportunity for partial removal of redox products. Polymerization was conducted at a temperature of $150\text{ }^{\circ}\text{C}$, either immediately after reduction, or after a temperature-programmed desorption step with a final temperature of either 300 or $500\text{ }^{\circ}\text{C}$.

Three different mass gain profiles could be discerned: accelerating rate, constant rate, or decelerating rate (Figure 7 a-c). The DSC signals reflected these profiles with either increasing, constant, or decreasing power.

Accelerating profiles were observed for samples charged with small amounts of hexenes (i.e., low hexene/chromium ratios) and immediate exposure to ethylene, that is, without thermal

decomposition of surface species. Close to linear increases in mass were observed for samples that had been reduced with ethylene at 200 °C and had not been subject to TPD. Decelerating rate profiles were observed after temperature-programmed desorption to 500 °C, independent of the olefin used. The variations in rate within the 10-min polymerization time prevented exact correlations; however, several trends could be identified.

Figure 7: Examples of catalyst mass changes and DSC signals recorded during polymerization of ethylene at a temperature of 150 °C. Catalyst 3Cr/SiO₂, previously reacted with (a) cyclohexene, no TPD, showing accelerating rate and increasing power; (b) ethylene, no TPD, constant rate and power; (c) cyclohexene, TPD to 500 °C, decelerating rate and decreasing power.

Samples reduced with ethylene fell into three groups (Figure 8). The catalysts were active without any TPD, as would be anticipated for ethylene-reduced catalysts. After TPD to a temperature of 300 °C, the materials were nearly inactive. After TPD to a temperature of 500 °C, the materials were the most active; the ethylene polymerization rate was about one order of magnitude larger than for catalysts used directly after reduction in ethylene.

Figure 8: Ethylene polymerization rates with and without thermal decomposition of initial surface redox products. Catalyst: 3Cr/SiO_2 , reduction temperature: 200 °C. Optional temperature programmed-desorption to 300 or 500 °C. Polymerization at a temperature of 150 °C and an ethylene pressure of 40 kPa.

When analyzing ethylene polymerization activity after initial reduction with hexenes, it has to be considered that unreacted chromium sites will be reduced by ethylene and become active. Indeed, towards lower hexene loadings, a slow start of the polymerization, reminiscent of the induction period typical of reduction by ethylene, was observed. For the lowest loading of 0.16 1-hexene molecules per chromium, a steady state was not achieved within the ten-minute long ethylene exposure.

The effect of hexene uptake on the polymerization rate should reveal whether active sites can be generated by reaction with hexenes. Experiments conducted using a variety of conditions consistently showed the same trend of decreasing ethylene polymerization rates with increasing hexene uptake or exposure. Figure 9 shows polymerization rates as a function of hexene uptake per chromium as measured by TG. Steady state rates were used for this plot, but the same trend

with hexene loading emerged also when average rates were used. The plot includes samples that were subject to TPD, with the olefin-to-chromium ratio prior to TPD used. Initial rates observed after TPD samples were significantly higher than the shown steady-state rates. Catalysts containing only 1 wt.% chromium (circled in Figure 9) displayed the same activity as catalysts with 3 wt.% chromium that had been charged with less hexene.

Figure 9: Ethylene polymerization steady state rates vs hexene/chromium ratio as adjusted during initial reduction. Catalysts: 3Cr/SiO₂ or 1Cr/SiO₂, reduction temperature: 150 °C. Optional temperature programmed-desorption to 500 °C. Polymerization at a temperature of 150 °C and an ethylene pressure of 40 kPa.

The general trend of a decreasing polymerization rate after reduction by increasing amounts of 1-hexene also held for commercially relevant polymerization conditions, as shown in Figure 10. In Figure 9, the molar ratio of hexene to chromium represents the amount of hexene that actually adhered to the catalyst; in contrast, the ratio in Figure 10 represents the applied amount

of 1-hexene. Figure 9 demonstrates that uptakes of less than one olefin per chromium can significantly affect the rate, suggesting that only a fraction of the molecules offered in Figure 10 have actually reacted. This result is consistent with Figure 4, which indicates a fraction of reacting 1-hexene of roughly 5% (at the conditions in the thermobalance).

Figure 10: Ethylene polymerization activity at commercially relevant conditions after treatments with various amounts of 1-hexene. Catalyst: 1Cr/SiO₂-TiO₂; exposure to 1-hexene at a temperature of 100 °C.

4 Discussion

4.1 Initial Reaction of Cr(VI)/SiO₂ with Olefins

4.1.1 Gas phase products during olefin pulses

During the pulses of ethylene or hexenes, no oxidation products could be discerned. In some cases, significant amounts would be needed for detection because of coinciding signals. Ethylene produces a signal at a mass-charge ratio of 28, which obscures CO, and a signal at $m/z=29$ as a result of the natural ¹³C abundance (and imperfect resolution of the quadrupole), which coincides with the main signal of both formaldehyde and ethylene oxide. Similarly, 1-hexene produces a

propyl fragment and an according ^{13}C -related signal at $m/z=44$, which obscures the main signal of CO_2 .

Moreover, oxidation products, for example aldehydes, are likely to be more reactive reductants than ethylene, and may react with residual Cr(VI) sites. In sum, the data suggest that olefin oxidation products do not evolve in major amounts under the applied conditions, which is consistent with the literature. After exposing Cr/SiO_2 to ethylene, Baker and Carrick¹⁴ hydrolyzed their reaction mixture and then discovered aldehydes or ketones. In a temperature-programmed experiment, Chakrabati et al.¹⁷ saw CO_2 evolution from oxidation of ethylene only at $280\text{ }^\circ\text{C}$, thus at much higher temperatures than those used here for the pulse experiments. The lack of volatile oxidation products is consistent with the observed increase in weight during the pulses.

Oligomers of ethylene were seen in the gas phase, indicating that the conditions are principally suitable to generate active sites and that short oligomers can desorb at a temperature of $200\text{ }^\circ\text{C}$. Oligomers of hexenes, if formed, would probably be too heavy to be detected.

4.1.2 *Mass gain and reaction stoichiometry during reduction by ethylene*

All uptake curves for ethylene showed an S-shaped form (

Figure 2). The following explanations were considered: chromium sites formed upon first contact were more reactive towards ethylene than the original Cr(VI) sites as would be expected for sites active for polymerization, or more reactive reductants were formed from ethylene during the pulse. The first scenario is supported by the heats of reaction, which are indicative of oligomerization rather than reduction during those pulses that resulted in substantial weight gain. However, several observations speak for the second scenario. During the pulse with the largest weight gain, the catalyst produced volatile oligomers, namely butene and some hexene. These

longer chain olefins are expected to be more reactive than ethylene based on the observations with hexenes and may react with residual Cr(VI) sites. Reduction of Cr(VI) sites by hexenes, according to Figure 9 and Figure 10, would not produce active sites, and the same may be true for reduction by butene. The fact that subsequent pulses do not lead to a more rapid weight gain or more release of oligomers indeed suggests that no or at least not many additional active sites were generated.

The weight gain ceased finally, indicating that the active sites changed – possibilities are a rearrangement of ligands or a coordinated chain, or their reaction with a residual Cr(VI) in a dichromate site, or poisoning by internal olefins (desorbing oligomers). No temporary mass increase was observed during the late pulses, demonstrating that ethylene did not reversibly coordinate under the applied conditions. However, further polymerization (at a low rate) was observed after the temperature was lowered to 150 °C, without an obvious induction period, indicating that active sites were principally available.

The uptake stoichiometry provides limited insight as to whether the overall weight gain is mainly the result of ethylene oligomerization without elimination and desorption, or mainly the result of reduction of Cr(VI) by the more reactive and longer olefins that are released at the chosen temperatures. At a chromium content of 3 wt.%, the ethylene uptake ended at a fixed stoichiometry of two olefins per chromium whereas at a chromium content of 1 wt.%, the uptake stoichiometry approached a value around three. Possibly, the lower site density reduces self-poisoning through desorbing and re-adsorbing oligomers, or the longer olefins are less effective poisons at lower chromium contents because only one chromium is poisoned in monochromate whereas both chromium sites in dichromate may be poisoned at once. That such effect exists is

suggested by the data in Figure 9, which shows that catalysts with a lower chromium content can tolerate more hexenes on their surface, as further discussed in Section 4.1.3.

4.1.3 *Mass gain and reaction stoichiometry during reduction by hexenes*

Hexenes were found to be more reactive reducing agents than ethylene; the fraction of offered hexene molecules that was retained by the sample at a reaction temperature of 150 °C was higher than the fraction of ethylene molecules retained at 200 °C (cf.

Figure 2 and Figure 4). The conditions are also milder than those used for reduction of Cr(VI) by H₂ or CO.^{10,20,21}

The Langmuir shape of the adsorption-reaction isotherms for hexenes suggests that the majority of sites on 1Cr/SiO₂ are similar in nature. This interpretation is consistent with observation of predominantly chromate species at this loading level on silica.¹ The fact that a monolayer corresponds to an olefin-to-chromium ratio of 1 implies that all chromate species are reactive and that the reaction stoichiometry is 1:1, consistent with the scheme shown by Baker and Carrick.¹⁴ In contrast, the sharp bend in the isotherm for 3Cr/SiO₂ and much smaller heats past an uptake of ≈ 0.5 olefin/chromium indicate at least two types of site. The sites could be the first and second chromium atom of dichromate species. The reduction of the second atom could be more difficult due to steric hindrance by the already attached hexene or the electronic effect of the Cr-O-Cr linkage, which distinguishes this site from monochromate.

4.1.4 *Interpretation of the heats of reaction*

The initial heats represent the redox reaction between Cr(VI) and the olefin and are potentially useful to identify the reaction chemistry. The heats of reaction at higher coverages of ethylene approached values expected for polymerization;¹⁹ for the other olefins, the heats of reaction could not be determined because of concomitant reversible adsorption. The reversible adsorption demonstrates that sites capable of coordinating an olefin were formed.

Of the olefins reacted, cyclohexene is the least likely to undergo oligomerization or polymerization, and the measured values can be considered to stem from the redox reaction alone. The observed trend seems to indicate a sharp decline in heat at or slightly below a coverage of 0.5 molecules per chromium, consistent with the bend in the isotherms around this coverage. This observation supports the hypothesis of different types of chromium sites.

To interpret the heats, the transformations of both the organic and the inorganic reactants must be considered. Given that the products do not appear to desorb, the measured heats reflect adsorption of the olefin and subsequent reaction. Heats of adsorption can only be estimated since experimental values exist only for surfaces with non-reactive interactions and not for supported chromate species. As an example, adsorption of ethylene on silica produces 20 kJ/mol;²² adsorption of 1-hexene produces 50 to 55 kJ/mol.²³ For lack of suitable thermochemical data, bulk chromium oxides substitute for supported chromium species on SiO₂. Thus these energies are also an estimate only. In Table S1, a number of possible oxidation and hydration reactions of olefins are listed, and a number of possible redox reactions between olefins and chromium oxides. Considering only the oxidation reactions of olefins to gaseous or liquid aldehydes, ketones, or acids (and not the chromate reduction), the oxidation to aldehydes or ketones produces lower heats than experimentally observed and the oxidation to acids produces higher heats than experimentally observed. From the enthalpies of formation of the chromium oxides, it can be seen that the formation of Cr(III) would be most favorable and only in this case do the redox reactions become strongly exothermic. This result is consistent with recent calculations by Gierada et al.,²⁴ who found the reduction to Cr(IV) highly exergonic and the deep reduction to Cr(II) less thermodynamically favored. In conclusion, the heats suggest formation of at least an aldehyde or ketone, if not a carboxylic acid, upon reaction of Cr(VI) with an olefin.

4.2 Volatiles formed during thermal decomposition of redox products

The well-defined isotherms and TPD profiles consistently indicate a reaction chemistry characterized by only a few dominant paths. Volatile products of the reduction of Cr/SiO₂ by ethylene have been reported by two groups. Terano and co-workers^{15,25} reacted Cr/SiO₂ with ethylene at ambient temperature and did not see distinct peaks during subsequent TPD, but associated a continued increase in intensity at m/z=30 with the evolution of formaldehyde. The result in Figure 6 clearly differs from that of Terano and co-workers; two discrete events were seen, and formaldehyde was not a major product. Chakrabati et al.¹⁷ sent a 1% C₂H₄-stream through a packed bed of 3%CrO₃/SiO₂ and conducted a temperature-programmed reaction experiment. The authors observed the evolution of CO₂, with two distinct maxima at 280 °C and 410 °C, respectively. While the data shown in Figure 6 a and b were collected following a slightly different protocol than that of Chakrabati et al.,¹⁷ CO₂ evolution was observed at similar temperatures (Table 1), suggesting that similar chemical reactions may have occurred. Chakrabati et al.¹⁷ presumed that water was also formed. Their mechanism for ethylene oxidation, leading to CO₂ and H₂O as sole oxidation products requires many redox equivalents. The proposed oxidation of ethylene on exclusively monochromate sites to Cr³⁺ as the final oxidation state implies release of intermediates and their further oxidation on another chromate site, or formation of a carbonaceous surface byproduct. Additional products reported in Figure 6 that were not seen by Chakrabati et al.¹⁷ provide more information on the stoichiometry of ethylene oxidation, and experiments with hexenes allow identification of reactions unique to terminal olefins.

One of the major gas phase products during the TPD experiments was water, but the evolution occurred over a broad range and was observed for all three reactants, limiting its diagnostic value for the analysis of the surface chemistry. Desorption from silica rather than from chromium sites

may explain the broad peaks and indicates that water was released and readsorbed, making it difficult to backtrack to its formation. Oxidative dehydrogenation of hydrocarbons would be an obvious route to water, and more highly unsaturated species than monoolefins would be expected in turn. There was no clear evidence of such molecules, but they may not desorb or may be too few to be detected by MS among other species.

Carbon dioxide evolution in two steps was observed independently of the nature of the olefin. The low temperature event included formation of H_2 ($m/z=2$) after reduction with ethylene, also typically after reduction with 1-hexene, but not after reduction with cyclohexene. This reactivity pattern suggests that a terminal olefin is the precursor for the surface species decomposing between 260 and 285 °C. Isomerization of 1-hexene to 2-hexene and 3-hexene, which was observed, may reduce the fraction of terminal olefin and lead to low intensity H_2 signals during TPD after 1-hexene adsorption. The surface species that are decomposing could include a methylene group and a carboxylate on the same carbon, or at least parts thereof such as a methyne group. Dioxymethylene ($-O-CH_2-O-$) is a surface species that forms on many oxides after adsorption of formaldehyde and could also be formed through oxidative cleavage of ethylene, but it is relatively labile and typically disproportionates into methoxy groups and formate at or above room temperature.²⁶ Decomposition of metal formates can produce H_2 ; there are two general decomposition pathways of metal formates, to CO_2 and H_2 , or to CO and H_2O .²⁷ Cr(III) formate is known to decompose according to the first pathway, at a temperature of about 350 °C.²⁸ Other authors report that the decomposition of $Cr(OH)_x(HCO_2)_{3-x} \cdot yH_2O$ is complete at 410 °C.²⁹ These temperatures are much higher than that of the first event, but apply for bulk formates. Hence, decomposition of surface formate species is the most likely scenario to explain the simultaneous evolution of CO_2 and H_2 at 260 to 285 °C. The evolution of CO_2 without

concomitant formation of H₂ evolution as observed for cyclohexene can be explained with the decomposition of carbonates, or non-C1 carboxylates or esters. Indeed, Barzan et al.¹⁸ have recently reported the formation of surface esters after reaction of Cr(VI)/SiO₂ with cyclohexene.

Whether the species decomposing at a temperature of 260 to 285 °C are formed upon initial olefin adsorption or upon heating during TPD is not obvious from the data. The heats of reaction indicate that oxidation occurs upon initial contact, which, however, does not preclude further rearrangement. The C-C bond cleavage is consistent with the observations by Baker and Carrick,¹⁴ only the oxidation eventually progresses further than formaldehyde. This difference could be ascribed to the higher reaction temperature compared to the 125 °C applied by Baker and Carrick and to the elimination of H₂. Formation of H₂ implies that fewer electrons need to be accommodated by chromium, thus allowing the formation of CO₂ from olefinic carbon on a single chromium site assuming reduction of Cr(VI) to Cr(II). This mechanism still leaves open the fate of the second olefin carbon, which would either require a dichromate to follow the same pathway if ethylene is the reactant, or would have to form another moiety.

The second CO₂ (m/z=44) evolution coincides with a signal at m/z=15 (methyl) and no other large signals, and not even small signals of longer alkyl chains (m/z=29, ethyl). Additional carbon-containing fragments are observed only at slightly higher temperature. Assuming no species have escaped detection, a species containing two carbons appears to decompose into CH₄ and CO₂. Candidates could be surface acetate or methylformate species, or chromium complexes bearing, for example, one formate and one methyl ligand. Methyl formate is a neutral and highly volatile molecule that reportedly desorbs from chromium supported on ordered mesoporous silica below 200 °C,³⁰ and transition metal alkyl complexes are generally not stable to such high temperatures.³¹ The thermal decomposition of silica-supported chromium (III) acetate has been

investigated, because the Phillips catalyst can be synthesized using this precursor. In inert gas, the supported acetate decomposes into methane and carbon dioxide, with the maximum gas evolution observed at a temperature of 425 °C.³² The products and the decomposition temperature are in excellent agreement with the second TPD peak in Figure 6, which is consequently assigned to the decomposition of a surface acetate species. Formation of acetate through oxidation of one carbon in an ethylene molecule is a possible scenario; however, oxidative cleavage of longer, internal olefins formed through oligomerization of ethylene may be the preferred route. Acetate decomposition peaks after contact of Cr(VI)/SiO₂ with 1-hexene support this interpretation; in this case, facile double bond shifts produces 2-hexene which is oxidatively cleaved to acetate.

It was also considered that the two TPD events are associated with different chromium species. The applied chromium loadings should result in either predominantly monochromate (1 wt.%) or predominantly dichromate (3 wt.%)¹. Hence, there should be a discernable effect of the loading if the two events represent these different chromate structures, but the TPD profiles in Figure 6 a and b are remarkably similar. The hypothesis of exclusively monochromate species was also examined. Chakrabati et al.¹⁷ ascribed the low-temperature event to the reaction of ethylene with more stable and thus more abundant dioxo monochromate species, and the high-temperature event to the reaction of mono-oxo monochromate species. The TPD profile in Figure 6 b, which represents a catalyst of equal chromium content as that in Ref. 17, is characterized by two equally sized peaks, inconsistent with the idea of chromium species of different stability and abundance. An association of the two events with different chromium species could thus be excluded.

The relative intensities of the TPD events at 260-285 °C and 390-415 °C are mainly a function of the nature of the olefin. In TPD profiles after reduction of Cr/SiO₂ with ethylene, the size of the two signals was always almost equal, whereas after reduction with 1-hexene, the second (higher temperature) signal was always larger. This pattern is explained with the lower fraction of terminal olefinic carbons in 1-hexene as compared to ethylene and its oligomers. The total amount of CO₂ formed scaled with the sample mass, the chromium content, and the surface olefin-to-chromium ratio (at low coverages), as one would expect.

Immediately after the second CO₂ evolution, that is, at a slightly higher temperature, intense signals at $m/z=2$ and $m/z=28$ are observed for ethylene- and 1-hexene reduced samples. These signals are attributed to the evolution of H₂ and ethylene. The temperature is typical of the decomposition of polyethylene, which commences at 400 °C³³ and yields alkanes and alkenes.³⁴ Ethylene can result from decomposition of alkyl chains, which either stem from oligomerization of ethylene or from 1-hexene depending on the olefin reactant. The evolution of H₂ is not typical for PE decomposition, but obviously, the alkyl chains are very short, implying a significant number of methyl groups.

4.3 Polymerization behavior

When the catalyst was reduced with ethylene, there was some ethylene polymerization activity without thermal decomposition of the surface products, after the temperature was lowered to 150 °C. Since there was no pronounced induction period, it appears that activity was associated with pre-reduced sites rather than pristine Cr(VI) sites, which always require an induction time.

After TPD to a temperature of 300 °C following contact with ethylene, the 3Cr/SiO₂ catalyst was completely inactive. This behavior implies that all Cr(VI) sites must have reacted in some manner. Otherwise, they could become active during the 10 min ethylene exposure, as was

observed for all catalysts with remaining Cr(VI) sites (*i.e.*, with low olefin coverages). Because the polymerization activity without TPD also indicated the absence of Cr(VI) sites, the surface reactions occurring during TPD to 300 °C must alter previously reduced, active sites. This result suggests that active sites with redox products as ligands exist. The decomposition products observed during the low temperature TPD event, which are CO₂ and H₂, indicate a C1 species as one ligand.

After TPD to a temperature of 500 °C following contact with ethylene, a very active catalyst is obtained, more active than after TPD to 300 °C or after reduction with ethylene. The decomposition occurring at higher temperature produces active sites. If all carbon-containing species were removed and chromium was reduced through loss of oxygen, the mass of the catalyst should be below its initial mass, but it was not. It is thus not possible to conclude on the nature of the active sites generated by this treatment; they may be bare chromium sites, or they may have ligands.

After partial reduction with hexenes, chromium sites that had not yet reacted became active as evidenced by an induction period. A higher rate correlated with a lower uptake, that is, a higher number of unreacted sites (Figure 9). Even after thermal decomposition of the 1-hexene redox products, the rate roughly scaled with the number of unreacted sites. Also when polymerization was conducted under commercially relevant conditions, prior exposure to 1-hexene resulted in a lower rate of ethylene polymerization and the decline scaled with the amount of 1-hexene applied (Figure 10). This trend, manifest in many experiments, is in contradiction with some literature that infers that reduction by hexenes leads to an active Phillips catalyst.^{18,35} The difference in conditions has to be considered, in particular the reacted amount of hexene per chromium or, accordingly, the residual amount of unreduced chromium. Lynch and Reinking³⁵

reported preferable olefin concentrations of 10 to 30 ppm, and Barzan et al.¹⁸ offered cyclohexene at its vapor pressure for 1 h. Without knowing the reacted amount of olefin (or residual Cr(VI)), results may not be compared. Knowing the offered amount is not sufficient, since the fraction of reacting hexene was found to be small (Figure 4 and Figure 10), and probably depends on the conditions. It has to be emphasized that the conditions in the experiments here are characterized by very low olefin partial pressures and have periods without olefin present. The sites created by reduction with hexenes are capable of coordinating olefins as the temporary mass gains in Figure 3 demonstrate. It is thus possible that active sites form but rearrange into an inactive form, which may be prevented at high olefin partial pressures when olefins coordinate and stabilize the active site. In conclusion, Cr(VI) is easily reduced by hexenes, but active sites are either not produced or are not stable in the absence of a coordinating olefin.

Scheme 1: Observed reaction pathways for the reduction of Cr(VI)/SiO₂ by ethylene or 1-hexene.

5 Conclusions

Thermogravimetric and calorimetric measurements of the reaction between olefins and Cr(VI)/SiO₂ indicated a reactive adsorption mode characterizing the stoichiometry of the initial redox reaction, and a polymerization mode. While the reaction with ethylene at 200 °C was self-limiting in some cases, the obtained uptake of two to three olefins per chromium and the observed heats implied some oligomerization, limiting information on the stoichiometry of the initial redox reaction. At 200 °C, oligomerization products, specifically butenes and hexenes, were released and reacted with unreduced chromium sites (Scheme 1) . Adsorption and reaction of 1-hexene or cyclohexene at 150 °C proceeded towards a monolayer coverage with near 1:1 stoichiometry. The obtained uptake values suggest that the vast majority of chromium sites initially react with olefins. Principal non-reactivity of some Cr(VI) sites towards olefins is thus not the reason for the frequently reported observation that only a fraction of the chromium sites become active.

At low olefin-to-chromium stoichiometries, oxidation progresses at least to ketones or aldehydes if not to carboxylates or esters, as indicated by the heats of reaction and the thermal decomposition products. Oxidation products do not desorb into the gas phase at temperatures below 250 °C, suggesting that under commercial polymerization conditions, oxygenates may remain attached to the chromium sites. Simultaneous evolution of CO₂ and H₂, and subsequently of CO₂ and CH₄ suggested that formate and acetate species may be formed on both ethylene- and 1-hexene treated samples. Formate formation is associated with terminal olefins, and acetate formation with internal olefins (obtained through double bond shift).

Reduction by exposure to small amounts of hexenes did not yield sites active for ethylene polymerization. This result implies that oligomers formed from ethylene during the induction

period may poison not previously reduced chromium sites provided the temperature is high enough to stimulate oligomer desorption.

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