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A surface science model for the Phillips ethylene polymerization catalyst: thermal activation and polymerization activity

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Abstract

A series of $CrO_x/SiO_2/Si(100)$ model catalysts were tested for ethylene polymerization activity, varying chromium loading, and calcination temperature. Chromium coverage of the model catalyst, quantified by Rutherford backscattering spectrometry, decreases with increasing calcination temperature as some chromium desorbs from the silica support. The polymerization activity of the model catalysts is correlated to calcination temperature and chromium coverage. Based on the evidence presented, we propose that high local Cr coverage—short Cr–Cr distances—is detrimental to polymerization activity, possibly because it facilitates dimerization leading to inactive chromium sites. Calcination at high temperatures not only causes depletion of surface silanol groups, but may also facilitate the formation of isolated chromium sites, which can evolve into active polymerization centers. AFM images of nascent polymer films after short polymerization times offer a means to visualize the distribution of polymerization activity on the silica surface. They indicate that the catalytically active chromium forms islands on the silica surface.

Keywords: Phillips catalyst; Ethylene polymerization; Chromium oxide; Silica; Thermal activation; Rutherford backscattering spectrometry; X-ray photoelectron spectroscopy; Atomic force microscopy

1. Introduction

Next to the much more famous Ziegler–Natta-type catalysts, thermally activated chromium on silica [1–3] (Phillips catalyst) today is the second most important ethylene polymerization catalyst; it is responsible for roughly one-third of the world market in polyethylene. The Phillips catalyst owes much of its commercial success to the fact that its polymerization properties respond very sensitively variations in catalyst preparation (e.g., choice of silica, Cr loading, addition of promoters) and pretreatment (calcination in dry air, prereduction), which provides ample opportunities for fine tuning the properties of the produced polymer resin. A typical Phillips catalyst features about 1 wt% Cr on a wide-pore silica gel with roughly 300 m^2/g surface area, which corresponds to a loading of about 0.4 Cr/nm^2. After thermal activation (calcination in dry air or oxygen) these catalysts polymerize ethylene at rates between 1 and 10 kg/g per hour (e.g., slurry phase in n-butane, 110 °C, ∼ 14 bar ethylene pressure). Despite its commercial success and almost 50 years of industrial and academic research, there is still a great deal of uncertainty about the molecular fundamentals of this catalytic system. The small commercial loadings in combination with the rich coordinative and redox chemistry of chromium and the diversity of the amorphous silica surface make it difficult to combine different experimental findings from different groups into one unifying picture. Consequently, fundamental aspects of the Phillips catalyst, like the formation and molecular structure of the active site and the polymerization mechanism, especially of the initiation step (formation of the first growing polymer chain), remain unclear.

Two properties of the Cr/SiO_2 catalyst set this system apart from most other olefin polymerization catalysts:

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(1) chromium is not active on its own but must be anchored to the silica (or other oxide) support to be active, and (2) the Phillips catalyst does not need to be activated with an alkylating agent (e.g., AlR_3) prior to polymerization. Within the past decade the Cr/SiO_2 system has been investigated with a multitude of spectroscopic techniques [3–13] in an attempt to unravel the molecular structure of oxide-supported chromium, the interaction between chromium and probe molecules, and the early stages of polymer chain formation. Unfortunately these efforts were not accompanied by sufficient catalytic testing and for all the reasons discussed above these efforts have not converged into a generally accepted molecular-level model of the working Phillips polymerization catalyst. Also, an increasing amount of well-defined organometallic model compounds that polymerize ethylene have been reported in the literature [14,15], allowing a detailed look into the coordination chemistry of chromium. However, to our knowledge all of these chromium complexes either have preformed chromium carbon bonds or require alkylating agents to be turned into an active polymerization catalyst, which raises questions about the validity of these complexes as a model for industrial Phillips catalysts. Very recently Espelid and Børve [16–19] published a series of papers introducing density functional theory calculations into the field of Phillips olefin polymerization catalysis, evaluating the potential catalytic activity of monomeric and dimeric chromium species on the silica surface.

We have developed a flat model catalyst based on a silicon wafer covered with about 20 nm of thermal silicon oxide. With this model we eventually aim to arrive at creating a complete molecular-level picture of the Cr/silica ethylene polymerization catalyst by correlating catalyst preparation, characterization of the active surface, and polymerization activity. The model support allows wet chemical impregnation of the active phase (e.g., CrO_3 in water) and further treatment just as for its industrial complement. Flat model catalysts are especially suited for applying surface spectroscopic (XPS, SIMS) and high-resolution microscopic (SEM, AFM) techniques [20–24]. In a previous publication we concentrated on the effect of calcination on the state of the supported chromium. Applying X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) we reached the following conclusions [23]: On calcination at temperatures above 450 °C all model catalysts feature exclusively surface monochromates, which are formed in an esterification reaction with the surface silanol groups. Fig. 1 illustrates the different surface species present on the flat $CrO_x/SiO_2/Si(100)$ catalyst after calcination. In contrast to conventional, porous catalysts where chromium that cannot be stabilized as a surface chromate forms chromium(III) oxide clusters, this superficial chromium desorbs from the flat silica surface. Up to now these findings have not been properly connected to trends in catalytic activity. Hence in this article we discuss the results of our ethylene polymerization test, which has been determined as a function of initial chromium loading and calcination temperature.

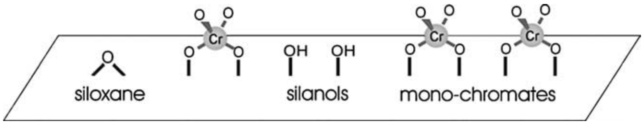

Fig. 1. Surface species present on $CrO_x/SiO_2/Si(100)$ model catalyst after thermal activation. On calcination surface silanols condense to form surface siloxanes; in addition, surface chromates also desorb from the silica surface, especially at high initial chromium loading and at high calcination temperatures.

2. Experimental procedure

2.1. Preparation of the $CrO_x/SiO_2/Si(100)$ model catalyst

Si(100) silicon wafers (Topsil) were calcined at 750 °C for 24 h to obtain a flat, amorphous silica layer approximately 20 nm thick. The silicon wafer was then cleaned in a mixture of concentrated hydrogen peroxide (Merck, 35 vol%, medical extra pure) and ammonia (Merck, 25 vol%, GR for analysis) until the temperature reached approximately 45 °C, which is after about 20 min. After further cleaning and rehydroxylation in boiling water the wafers were covered with the impregnation solution, chromic acid in water (Merck, $Cr(VI)O_3$, GR for analysis), and mounted on the spin-coating device under a nitrogen atmosphere. On spinning most of the solution is ejected from the wafer leaving behind a thin layer, which evaporates. As the thickness of this layer can be calculated for any given rotation speed (2800 rpm), temperature (20 °C), and solvent (water), the loading of the model catalyst can be controlled simply by varying the concentration of the (dilute) spin-coating solution [25]. The polymerization studies reported here were done with an initial loading varying from 0.01 to 4 Cr/nm^2. To achieve these loadings the impregnation solution had to be varied from 0.01 to 4 mmol Cr/l for a rotation speed of 2800 rpm.

2.2. Ethylene polymerization reactor

The reactor used is a medium-throughput version of that described previously [22]. Four parallel tubes separated by glass filters can contain four model catalysts. The advantage of this design is that four samples can be processed within one calcination/polymerization cycle because chromate desorbed from one sample cannot contaminate the other samples. This contamination is observed if a single tube reactor is used to process more than one sample.

Before the reactor is loaded with the model catalyst, it is dried and baked out at 750 °C in flowing O_2/Ar (Hoekloos 20% O_2, grade 5.0, dried with molsieves 4 Å), to remove water, sodium, and carbon from the reactor walls and the chromate-loaded γ-alumina extrudates, which serve as the final cleaning stage of the gas feed inside the quartz reactor. Next the model catalyst is inserted. After drying at 200 °C in vacuum, the catalyst is calcined in flowing O_2/Ar at a maximum temperature of 450, 550, or 650 °C for 30 min (heating rate 20 K/min, plateaus at 350, 450, and 550 °C for 15 min). Polymerization takes place in flowing ethylene at 160 °C and atmospheric pressure. Pumping away the ethylene and changing to argon atmosphere stop the reaction. The polyethylene formed on the catalyst surface is initially present as a molten film and will crystallize on cooling to room temperature.

For polymerizations at low temperature (at 25–80 °C) an extra reduction step is needed. After calcination in O_2/Ar the reactor is cooled to 350 °C and the O_2/Ar mixture is evacuated by pumping and rinsing with argon. The argon is exchanged for a CO flow (Messer Griesheim, grade 4.7, purified over Cu-Cat and molsieves 4 Å) for 15 min, after which the CO is evacuated by pumping and the reactor is allowed to cool under flowing argon. Changing to ethylene atmosphere starts the polymerization.

2.3. Catalyst characterization

The Cr coverage of the samples is determined quantitatively with Rutherford backscattering spectrometry (RBS), using 2-MeV He^+ ions. Nonstandard conditions are required to reliably measure Cr contents as low as 0.01 at./nm^2. The He beam is at normal incidence to the sample surface, so that the beam is aligned with the (100) channel direction of the Si substrate. The applied scattering angle is 95° (hence an exit angle of 5° with the sample surface). The total ion dose per measurement is 300–1200 µC, depending on the Cr coverage: a lower content requires a higher dose to achieve sufficient statistical accuracy. With the chosen glancing exit angle, the Cr signal is spread over about 30 channels (FWHM of about 10 channels). The low overall count rate due to the channeling and glancing exit conditions allows for a beam current of 300 nA, while pileup (coinciding pulses) remains negligible. This results in practical measuring times on the order of 1 h for this type of specimen.

X-Ray photoelectron spectroscopy measurements are made in a VG Escalab 200 using a standard aluminum anode (Al-K_α1486.3 eV) operating at 510 W. Spectra are taken at normal emission at background pressure of 5×10^{-10} mbar. Chromium coverage is determined from the X-ray photoelectron spectra as described in [23].

Polyethylene layer thickness is determined using the height difference between the Si substrate and the polyethylene surface after scratching the layer with a scalpel. For layers in the range of a few nanometers to 2 µm in thickness, atomic force microscopy (AFM) is used. Measurements are performed with a Digital Instruments Dimension 3100 scanning microscope under ambient conditions. Thicker layers are measured using a Tencor P-10 Profilometer.

3. Results and interpretation

3.1. Chromium coverage

During thermal activation (calcination) chromium anchors to the flat silica support to form monomeric surface chromate species. In addition, chromium partially desorbs from the silica surface, especially in the case of high initial chromium loadings and high calcination temperatures. Therefore, using RBS (Fig. 2) and XPS, we have quantified the amount of chromium that is on the catalyst both after impregnation and after calcination at temperatures between 450 and 650 °C (Fig. 3). RBS gives us a full quantification of the total amount of chromium on the model catalyst for loadings of 0.01 Cr/nm^2 and above, while XPS gives a reliable quantification between 0.4 and 2.0 Cr/nm^2 [20,23]. On all catalysts and on a blank reference, RBS in combination with TOF-SIMS detected trace amounts of molybdenum (0.01 ± 0.01 at./nm^2) and iron (0.03 ± 0.01 at./nm^2). These impurities probably originate from traces of these elements in the ammonia solution that is used for rehydroxylation of the thermal oxide layer of the model support. The iron peak partially overlaps with the chromium peak due to limited mass resolution of RBS.

After correction for the small iron contribution in the RBS spectra we find a linear correlation between the concentration of the spin-coating solution and the chromium loading in our entire experimental window between 0.01 and 4 Cr/nm^2 (Fig. 3). This is the behavior expected for chromic

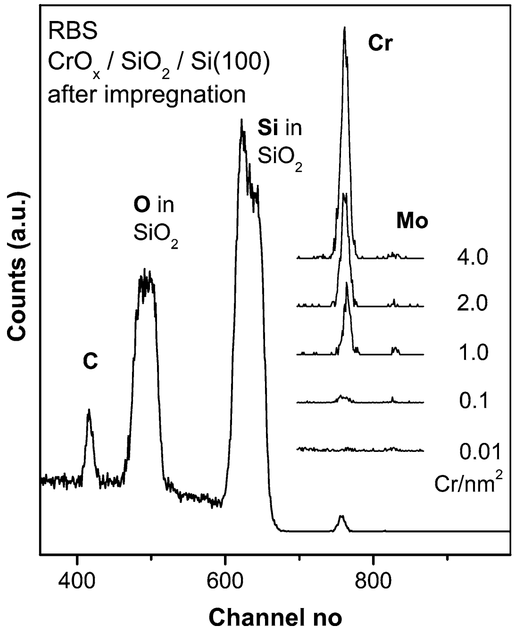

Fig. 2. Typical RBS spectrum of chromium-loaded model catalysts. Inset: Chromium peaks for catalysts with different loadings after spincoating impregnation. The area of the chromium peak is used to validate the theoretical loading and to determine the coverage of the calcined samples. Spectra are normalized to the Si (SiO_2) edge.

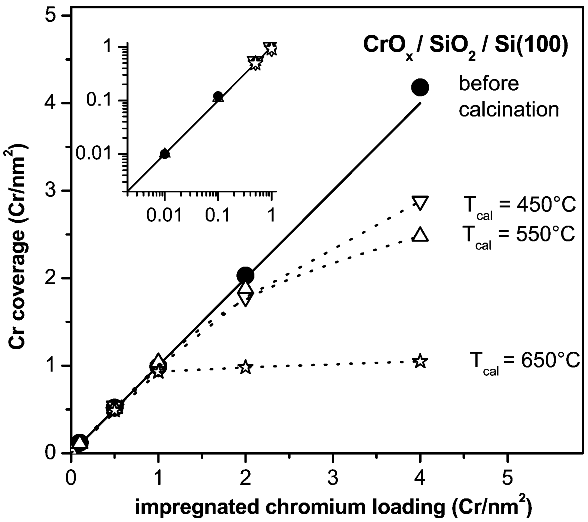

Fig. 3. Chromium coverage after impregnation and calcination at 450, 550, and 650 °C as determined with RBS and XPS. Desorption of chromium is pronounced for high calcination temperatures and high initial loadings. Loadings below 1 Cr/nm^2 remain constant for temperatures below 650 °C.

acid in water, which does not react with the surface silanol groups of the silica support during impregnation.

The model catalysts are activated for ethylene polymerization by calcination in dry O_2/Ar (20/80). During this thermal activation the chromium coverage decreases due to desorption of chromium, an effect that is most pronounced at high initial loadings and high calcination temperatures. Initial loadings below 1 Cr/nm^2 remain stable on the silica surface up to 650 °C [26]. XPS and RBS quantification give basically the same results (between 0.4 and 2.0 Cr/nm^2) indicating that all chromium is present at the very surface of the model catalyst, meaning that no chromium diffuses into the silica layer nor are any chromium particles formed during spin coating or calcination.

3.2. *Catalytic testing*

After thermal activation the catalysts are tested for gas-phase ethylene polymerization at 160 °C and atmospheric pressure. Fig. 4 shows an AFM image (height contrast) of $CrO_x/SiO_2/Si(100)$ model catalyst after polymerization at 160 °C and 1 bar ethylene for 30 min. The polymer film that has formed is 750 nm thick and features a surface roughness of 15 nm. After each polymerization run the polymer yield (the layer thickness of the polymer film that has grown on the model catalyst) is determined by AFM or nano-indentation.

Fig. 5 shows the results of such polymerization tests for a series of model catalysts with chromium loadings between 0.01 and 4 Cr/nm^2, all of which have been activated at 550 °C. For each chromium loading we find a clear linear correlation between polymer thickness and polymerization time. The slope of these lines represents the constant activity of the model catalysts. The catalytic activity per unit surface area reaches a maximum at 0.5 Cr/nm^2, which corresponds to about 1.2 wt% Cr for a 300 m^2/g silica gel catalyst.

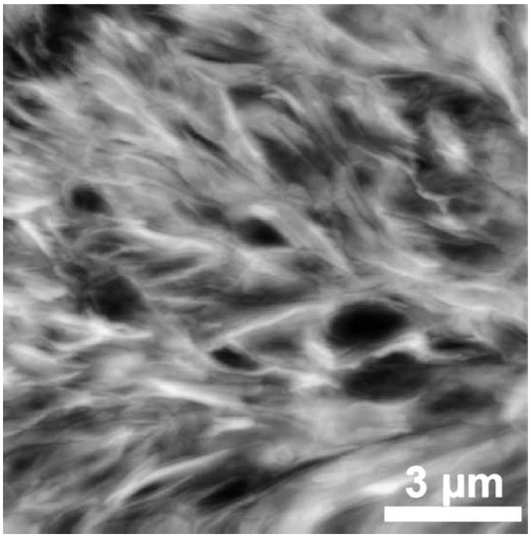

Fig. 4. AFM height image of a 750-nm polyethylene film grown on a $CrO_x/SiO_2/Si(100)$ model catalyst at 1 bar C_2H_4 and 160 °C within 30 min. The model catalyst features 0.5 Cr/nm^2 and was calcined at 550 °C. On cooling, polyethylene crystallizes to form lamellae in random orientation.

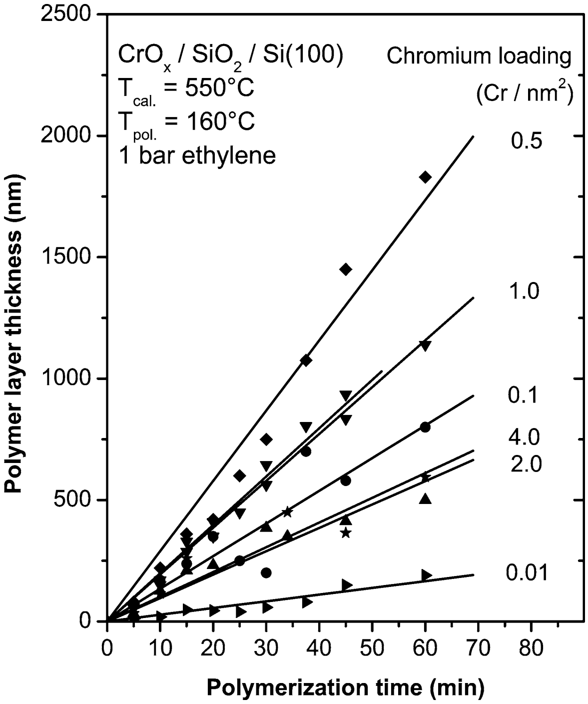

Fig. 5. Polymer yield (polymer film thickness) plotted against polymerization time for a series of model catalysts calcined at 550 °C with chromium loadings varying from 0.01 to 4.0 Cr/nm^2. Ethylene polymerization was performed at 160 °C and atmospheric pressure. The slope of the linear curves (the rate of film growth) is a measure of the constant polymerization activity.

Fig. 6 summarizes the polymerization activity of the model catalysts as a function of initial chromium loading and thermal activation. As with its industrial counterparts, the polymerization activity of the model catalysts increases

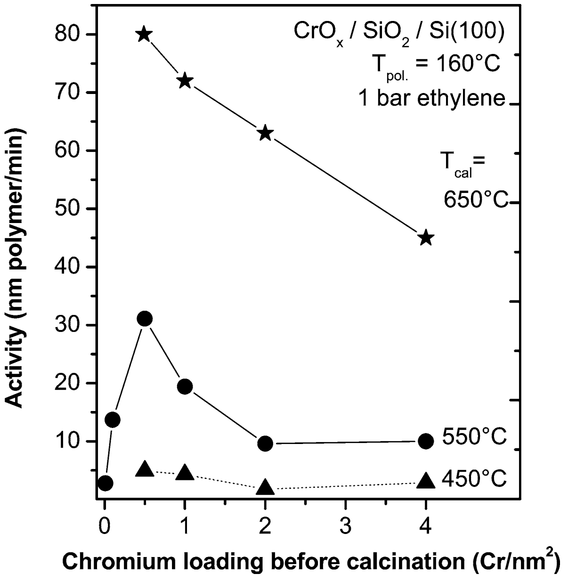

Fig. 6. Rate of film growth (polymerization activity) versus catalyst loading and calcination temperature.

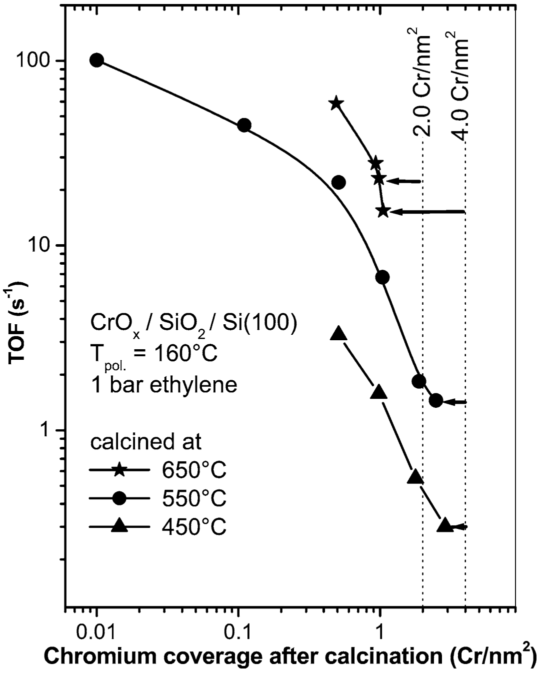

Fig. 7. The nominal turn over frequency of the CrO$_x$/SiO$_2$/Si(100) model catalysts is increasing with increasing calcination temperature and decreasing chromium coverage. The arrows indicate the amount of chromium that as desorbed from the flat silica support during thermal activation.

with increasing calcination temperature. The most active catalyst in our series with a chromium loading of 0.5 Cr/nm^2 and activated at 650 °C grows a polyethylene film at the rate of 80 nm/min, which, again for a 300 m^2/g catalyst, scales to 1500 $g_{PE}/(g_{cat}\,h\,bar)$.

Combining the activity data with the chromium quantification from RBS, we can determine the (pseudo) turnover frequencies of our catalysts, which are depicted in Fig. 7 as a function of chromium coverage and calcination temperature. For all calcination temperatures we observe a monotonous increase in turnover frequency with decreasing chromium coverage. In addition, we again find a strong increase in turnover frequency (TOF) with increasing calcination temperature. This increase ranges from a factor of 18 at 0.5 Cr/nm^2 to a factor of 51 at 4.0 Cr/nm^2. It is interesting to note that the main improvement in catalyst activity is observed at different temperatures for different catalyst loadings. For 0.5 Cr/nm^2, TOF increases by a factor of 6.5 between 450 and 550 °C, whereas between 550 and 650 °C, by only a factor of 2.6. The (relatively) strong increase in catalytic activity coincides with the temperature regime where most of the surface silanol groups on a blank silica support are depleted [27]. Conversely, at 2.0 Cr/nm^2 loading, TOF increases by factors of 3.3 and 12.5, respectively. At 2.0 Cr/nm^2 catalyst loading, most of the surface hydroxyls are already depleted by the anchoring reaction of supported chromate. The main improvement in activity now coincides with the temperature regime, within which most of the chromium desorption takes place.

3.3. Early stages of polymer film growth

In an attempt to visualize the distribution of polymerization activity on the model catalyst in early stages using AFM, we performed polymerization experiments at 80 °C with very short polymerization times. Fig. 8 shows the polyethylene islands formed on the model catalysts that were calcined at 550 °C and reacted with ethylene for 45 s at 80 °C following an additional reduction step with carbon monoxide at 350 °C. Using CO to prereduce the calcined catalyst (instead of using ethylene in the initial stage of the polymerization reaction) is a well-established method to activate the catalyst for ethylene polymerization at low temperatures [28]. At 0.01 Cr/nm^2 chromium loading we observe fractal-shaped (branched and elongated) polyethylene islands ranging between 10 and 15 nm in height. The polyethylene islands cover about 20% of the catalyst surface, while the rest of the catalyst surface (dark regions in the height image, top-left) remains empty (roughness below 0.3 nm). At 0.5 Cr/nm^2 most of the catalyst surface is covered with a somewhat thicker (20 and 50 nm) polyethylene film, leaving less than 20% of the catalyst surface open. At 4 Cr/nm^2 we observe again polymer morphology that somewhat resembles the 0.01 Cr/nm^2 case: roughly 30% of the catalyst surface is covered with a 10 to 15-nm polyethylene film. At this high chromium coverage the remaining silica surface (dark regions in the height image top right) is not completely empty. The phase image reveals a large number of spherical polyethylene islands no more than 1–2 nm in height and with a diameter of about 20 nm. These polymer islands represent only a minor fraction of the overall polymerization activity of the catalyst

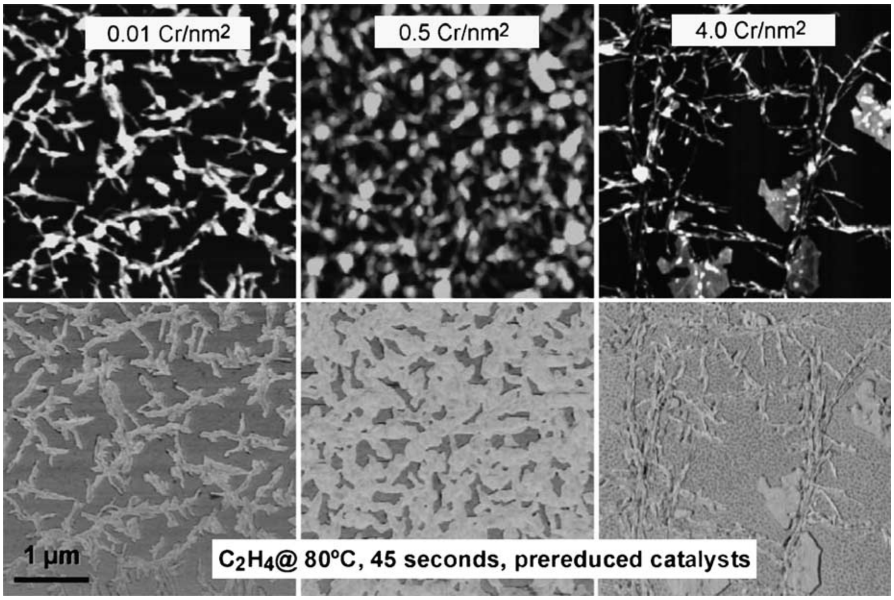

Fig. 8. AFM images ($5 \times 5\ \mu m^2$) of model catalysts (Cr loading as indicated) after treatment with ethylene for 45 s at 80 °C. The bright fractal-shaped features in the height-contrast (top) and phase-contrast images (bottom) are polyethylene islands (10–25 nm high) resembling the parts on the catalyst with high polymerization activity. Dark regions (height images) are bare silica surface with (almost) no catalytic activity in the time frame of the experiment. The phase images reveal very small polymer islands on the catalyst with $4\ Cr/nm^2$; however, these islands do not contribute significantly to the total polymer yield.

4. Discussion

The $CrO_x/SiO_2/Si(100)$ model catalysts feature a realistic polymerization activity. This activity follows the same trends as in the industrial counterpart: An increase in calcination temperature yields a more active catalyst based on the silica surface area, while changing the Cr loading reveals an optimum at about $0.5\ Cr/nm^2$. The activity per chromium atom (turn over frequency), however, shows a monotonous increase with decreasing loading. It is interesting to note that catalysts with high and low loading respond differently to an increase in activation temperature: With low catalyst loading the activity increase is more pronounced between 450 and 550 °C, while at high chromium loadings we observe the strongest improvement between 550 and 650 °C.

The increase in activity with calcination temperature is usually attributed to the depletion of surface silanols on the silica support, which condense to form surface siloxanes on heating [29]. The surface silanol groups are believed to deactivate chromium possibly by blocking their coordination sites. Conversely, surface silanols are also regarded necessary for the initiation step of the ethylene polymerization, more exactly the formation of the first growing polymer chain on the active site [18].

At this stage we can only qualitatively discuss the hydroxyl population on our chromium-loaded catalysts. However, based on the saturation coverage of surface chromate on the flat silica support we estimate that the surface silanol population of the flat silica surface prior to calcination is at least $5\ SiOH/nm^2$ [20,23,27]. Two surface silanol groups are titrated by each chromium atom that anchors to the silica surface by self-condensation to form siloxane bridges. Thus, the surface silanol concentration on the model catalyst decreases with increasing calcination temperature and chromium loading.

At initial chromium loadings of $1\ Cr/nm^2$ and lower, where the loading remains constant on calcination up to 650 °C, the depletion of silanol groups might explain the activity increase for these catalysts. Conversely, at initial chromium loadings of 2 and $4\ Cr/nm^2$, we observe an even stronger increase in turnover frequency. At this high chromium loading almost all surface silanol groups have reacted with chromium to form surface monochromate species already far below 450 °C. On further heating the excess chromium desorbs from the surface, decreasing the chromium coverage while increasing the catalytic activity. This correlation strongly indicates that chromium can be deactivated by neighboring chromium atoms, possibly by simple site blocking or clustering. This form of deactivation is lifted as chromium becomes more isolated on the silica surface, either due to desorption at high calcination temperatures or due to decreasing initial chromium loading. This supposition does not contradict our earlier observation that chromium anchors to the silica surface exclusively as monomeric surface chromate: dimerization or clustering simply takes place as the surface chromate becomes coordinatively unsaturated during the final reduction step.

The monotonous increase in turnover frequency extends to very low chromium coverages as seen in the series with 550 °C activation temperatures, which is in good agreement with findings reported by McDaniel et al. [1]. We estimate the hydroxyl population to increase from nearly none at the highest chromium loadings to about $2/nm^2$ at the lowest Cr loadings [27]. Obviously this activity trend again cannot be explained by poisoning with surface hydroxyls; instead it seems to be a generally accepted assumption that chromium somehow preferentially adsorbs at special sites on the silica surface that offer chromium just the right environment to develop into a very active site. To our knowledge chromium–chromium interactions have not been considered, presumably because the distances between chromium atoms become too large, e.g., about 3 nm for 0.1 $\mathrm{Cr/nm^2}$, assuming chromium is dispersed randomly over the entire silica surface and on all length scales.

While we reserve a more detailed discussion of the early stages of polymer film growth to a future publication, we believe that the AFM data presented here basically represent the lateral distribution of polymerization activity on the catalyst surface, indicating that (very) active polymerization sites are not homogeneously distributed on a submicrometer scale. Thus, the AFM data suggest that polymerization activity can be concentrated in patches that represent only a small portion of the entire silica surface rather then being homogeneously distributed over the silica surface. Consequently, local chromium–chromium distances may be much smaller and Cr–Cr interaction might influence polymerization activity, even at very small nominal loadings.

5. Concluding remarks

A flat $\mathrm{CrO}_x/\mathrm{SiO}_2/\mathrm{Si}(100)$ model catalyst exhibits realistic activity for ethylene polymerization and reproduces the expected trends in catalytic activity: increasing the calcination temperature yields more active catalysts while there seems to be an optimum chromium loading near 0.5 $\mathrm{Cr/nm^2}$.

RBS in combination with XPS has been used to quantify the amount of chromium that remains anchored to the silica surface after calcination, proving that some chromium is lost due to evaporation. This chromium loss is especially strong with high chromium loadings and high calcination temperatures. Combining RBS and activity data allows us to determine the nominal turnover frequency: this increases with decreasing chromium loading and increasing calcination temperature. Even though all chromium on our model support forms silica-bound monochromates during calcination, the chance that they will form (highly) active polymerization sites depends on how far away they are from neighboring surface chromates, presumably because neighboring surface chromates tend to form inactive dimers or clusters.

Atomic force microscopy provides detailed insight into the lateral distribution of the polymerization activity of $\mathrm{CrO}_x/\mathrm{SiO}_2/\mathrm{Si}(100)$ model catalysts. It reveals that the catalytically active centers are not homogeneously distributed over the silica surface but form islands. The shape and size of these islands are dependent on the exact catalyst pretreatment.

Due to a lack of a proper quantification, the role of surface silanols in the activation of the $\mathrm{CrO}_x/\mathrm{SiO}_2/\mathrm{Si}(100)$ model catalyst remains unclear at this point. Moreover, at this stage we have only indirect evidence for chromium clustering. We plan to use time-of-flight secondary ion mass spectrometry in an attempt to determine the surface silanol population on our model catalyst and to detect Cr dimerization on reduction of the calcined catalyst.

In combination with the information about the lateral distribution of catalytic activity this will provide complete insight into the genesis, structure, and dispersion of the active chromium site(s) of the Phillips catalyst on a molecular scale.

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