A surface science model for the Phillips ethylene polymerization catalyst has been prepared, by impregnating aqueous CrO$_3$ on a flat silicium (100) substrate covered by amorphous silica. Impregnating in a spin-coating technique offers control over the chromium loading, which was varied between 0.4 and 4.0 Cr/nm$^2$. After impregnation chromium is dispersed molecularly at loadings smaller than 2 Cr/nm$^2$. Upon calcination chromium is anchored to the support over Cr$\rightarrow$O$\rightarrow$Si ester bonds, although a fraction is lost from the surface due to volatilization, as could be established with X-ray photoelectron spectroscopy. The model catalyst polymerizes ethylene at 160 °C and atmospheric pressure after being activated in 80/20 He/O$_2$ at 650 °C, confirming its validity as a model for the industrial catalyst.

Introduction

Highly dispersed chromium oxide supported on silica or silica/alumina is an industrially important catalyst for ethylene polymerization. The well-known Phillips catalyst consists of less than 1 wt % Cr, impregnated commonly as aqueous CrO$_3$ on high surface area silica ($\pm$300 m$^2$/g), which corresponds to about 0.4 Cr/nm$^2$ only. The raw catalyst is activated at at least 550 °C in dry air, yielding anchored Cr[VI]-oxide (along with some inactive Cr$_2$O$_3$) on a dehydroxylized support. Upon polymerization with ethylene the chromium is reduced, probably to a Cr[II] state. Despite continuous and extensive research for more than 40 years now, there is little understanding of the chemical state of the supported chromium. Furthermore, characterization techniques have their limitations, in particular when applied on catalysts with mixed contents as low as that of the Phillips catalyst. Consequently, results obtained by different groups are difficult to compare, and there is still controversy about the state of the supported chromium species. For example, after calcination the anchored Cr[VI] may be present as mono-, di-, or even polychromate, McDaniel (investigating the CrO$_3$ saturation loading) and Hierl and Kraus (using a gravimetric method) concluded that CrO$_3$ binds to the silica support mainly as a monochromate species upon calcination. However, Zecchina et al. inferred from hydroxyl population measurements that anchored CrO$_3$ is almost exclusively present as dichromate on silica supports. Applying diffuse reflectance ultraviolet spectroscopy, Weckhuysen et al. found mainly dichromate (chromate/dichromate ratio = 0.62) present on calcined silica even at extremely low loadings (0.2 wt % Cr on 735 m$^2$/g silica gel).

Ultrahigh-vacuum spectroscopic techniques are potentially very powerful for the desired microscopic characterization of catalysts in general, as they provide direct information originating from the atoms and molecules on the surface. However, with industrial catalysts the active phase is usually hidden inside a porous, spongelike, high surface area support, e.g. silica, and most of the active phase is hidden inside the pores, out of reach for the surface spectroscopist. Moreover, these supports are nonconductive, and thus the sample will charge when applying electron- or ion-releasing techniques such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), or ion scattering. To avoid these complications, model catalysts have been prepared on flat, conducting substrates. (For a review of surface science model catalysts see ref 8.)

Magni and Somarjai recently prepared a surface science model for the TiCl$_4$/MgCl$_2$ Ziegler–Natta catalyst in ultrahigh vacuum by gas phase deposition using polycrystalline gold foil as the conducting substrate.

We have now embarked to explore the Cr/SiO$_2$ system using two model supports and surface science techniques. The first one is prepared on flat Si(100) wafers, which are covered with a thin (~4 nm) layer of amorphous silica. This support is impregnated with aqueous CrO$_3$ using the spin-coating technique, which gives control over Cr loading and mimics the conventional pore-volume impregnation used in industry for high surface area silica gels. This approach has already successfully been applied to create a working surface science model of the MoS$_2$ and CoMoS hydrodesulfurization catalyst.

To complement the flat model support, we use silica spheres, often referred to as Stöber spheres, which also yield catalysts with exposed active sites. This model allows the use of infrared spectroscopy (DRIFT) to characterize the surface silanols of the support as well as the produced polymer.

While anticipating that our model catalyst approach will eventually contribute to the understanding of the challenging Cr/o silica system on a molecular level, in this first paper we want to show that our models exhibit essential features of their “real” counterparts, such as anchoring of a Cr-oxo species to...
then cleaned in a mixture of H$_2$O$_2$ and NH$_4$OH (3/2 v/v) at 65 °C under vacuum until the pressure at the 5 mbar. Polymerization tests were done with ethylene (99.99% O$_2$, 99.995% O$_2$, 99.99% He) in a vacuum chamber operating at 510 W with a background pressure of 2 × 10$^{-9}$ mbar. Spectra are recorded using the VG S5000 data system within 2 h, to obtain a good signal to noise ratio. However, since Cr[VI]-oxide is known to decompose rapidly when exposed to X-rays, some spectra were limited to 10 min to obtain the Cr[VI] binding energy. All binding energies are referred to the Si 2p at 103.3 eV on the flat system. Intensities are normalized to the total Si 2p area ($I_{Si(total)}$) according to

$$I_{Si(total)} = I_{SiO_2} + \frac{\lambda_{SiO_2} n_{SiO_2}}{\lambda_{Si} n_{Si}} I_{Si}$$

Here $\lambda$ is the mean inelastic free path of the Si 2p emission ($\lambda_{SiO_2}$ = 3.92 nm, $\lambda_{Si}$ = 3.09 nm$^2$), $n$ is the atomic density ($n_{SiO_2}$ = 3.63 × 10$^{-2}$ mol/cm$^3$, $n_{Si}$ = 8.29 × 10$^{-2}$ mol/cm$^3$), and $I$ is the integrated area of the Si 2p peak.

**Results and Discussion**

**Control over Chromium Loading during Spin-Coating Impregnation.** First we describe the preparation of the flat model system made by impregnating Cr on a thin SiO$_2$ layer on a silicon wafer. According to a model proposed by van Hardeveld et al.,$^{13}$ the amount of deposited solute during spin-coating can be predicted quantitatively, with high accuracy. Evaporation of the solvent and radial liquid flow (due to centrifugal forces) of the solution determine the amount of solute, which precipitates on the wafer. Solving the resulting differential equation for a spin-coating experiment with an angular velocity $\omega = 293.2$ s$^{-1}$ (2800 rpm) at room temperature yields

$$L_{Cr} = 2.76 (t_{evap})^{-0.5} C_0$$
Figure 2. Survey XPS spectrum of a CrOx/SiO2/Si(100) model catalyst after spin-coating impregnation. Loading is 1 Cr/nm². The inset shows an enlargement of the O 1s energy loss region of the spectrum where the Cr 2p emission is observed.

Figure 3. Cr 2p XPS spectra of CrOx/SiO2/Si(100) model catalyst after spin-coating impregnation as a function of Cr loading. Spectra on the left side are as acquired (within 2 h), while on the right side the blanco (0.0 Cr/nm²) has been subtracted.

Figure 4. Integrated Cr 2p intensities of CrOx/SiO2/Si(100) model catalysts after spin-coating impregnation as a function of Cr loading.

This finding can tentatively be explained as follows: After wet impregnation the impregnated CrOx species are coadsorbed on the silica surface together with ~1 monolayer of water. As the isoelectric point of silica is rather low (~2), this thin water film is acidic and the impregnated chromium is essentially a mixture of mono- and dichromate at relatively low loadings. With increasing loadings tri- and tetrachromate species become important. This picture of hydrated chromium on silica has been proposed by Weckhuysen et al. This authors found tri- and tetrachromates between 4 and 8 wt % Cr on a 735 m²/g silica, which corresponds to a loading of ~1 Cr/nm². Thus it is reasonable to expect some clustering at loadings of 4 Cr/nm², resulting in a decreased dispersion of the impregnated chromium and therefore in a slightly reduced visibility in XPS.

**Anchoring of Chromium to the Support.** It is generally accepted that upon calcination in dry air or oxygen chromium-[VI] is anchored to the silica substrate in the form of chromate esters, regardless of which precursor has been used for impregnation. However, the calcination of the Phillips catalyst is a complicated process, that, depending on loading and calcination temperature, may yield mixtures of molecular surface monochromate and dichromate species sometimes along with bulk (inactive) Cr(III)oxide. Although we cannot contribute to the elucidation of the molecular structure of anchored Cr on silica yet, we can prove that our flat SiO2/Si(100) model system is indeed capable of anchoring chromium to the surface and that this process can be followed by XPS.

The X-ray photoelectron spectra in Figure 5 show the Cr 2p emission of CrOx/SiO2/Si(100) models and of two Cr(VI) references. After spin-coat impregnation of 1 CrO3/nm² the Cr 2p maximum appears at 580.0 eV, the same binding energy that we measured for bulk CrO3 (Figure 5). Upon calcination at 450 °C the binding energy increases to 581.3 eV. This binding energy is in excellent agreement with the 581.6 eV (with Si 2p = 103.5 eV) measured by Merryfield et al. for a 1.1 wt % Cr/SiO2 (0.42 Cr/nm²) catalyst calcined in dry air at 650 °C. Moreover we measured a siloxane ester of chromic acid ([(CrO2(OSi(C6H5)2)2OSi(C6H5)2O)]2; see Figure 5) as a reference for surface chromium(VI) esters, which turned out to have the same Cr 2p/2 binding energy (Figure 5) as the anchored chromium[VI] on silica. Thus we conclude that the shift in Cr 2p/2 binding energy proves the anchoring of Cr to our SiO2/Si(100) model support upon calcination.

Although all of the detectable chromium on the calcined wafer is anchored to the support by ester bonds, it is interesting to note that the intensity of the Cr 2p emission has decreased by about 20%. Such a decrease of intensity upon calcination was only observed on the flat CrOx/SiO2/Si[110] system and not on...
the calcined Cr/silica spheres. We believe that some of the impregnated chromium on the flat support was lost due to evaporation.\textsuperscript{23} To check this, SiO\textsubscript{2}/Si(100) wafers impregnated with more than one monolayer of CrO\textsubscript{3} were covered with an unloaded Si wafer and calcined in oxygen at temperatures between 400 and 875 °C. After calcination, chromium was detected on the initially clean silica wafer. Although preliminary, these results indicate that impregnated chromium can redistribute on the silica support (inside the pores) via the gas phase upon calcination.\textsuperscript{24}

**Polymerization of Ethylene.** To polymerize ethylene on the flat Cr ox /SiO\textsubscript{2}/Si(100) model catalyst, we need to consider that the latter exposes an active surface of about 1 cm\textsuperscript{2} only, which makes the model extremely sensitive to irreversible deactivation by impurities. Thus we chose to protect the surface by embedding the Cr ox /SiO\textsubscript{2}/Si(100) wafer in a batch of Cr-impregnated silica spheres. In this experiment the Cr ox /SiO\textsubscript{2}/Si(100) wafer was placed in the quartz tube reactor with the active surface facing downward to prevent the silica spheres, which also produced polyethylene, from coming into contact with the active surface of the Cr ox /SiO\textsubscript{2}/Si(100) catalyst. Figure 6 shows XPS spectra of a Cr ox /SiO\textsubscript{2}/Si(100) catalyst with a loading of 1 Cr/cm\textsuperscript{2} after polymerization at 160 °C following calcination at 650 °C, and the same wafer before reaction. The latter shows some impurity carbon only. After polymerization, the C 1s/Si 2p intensity ratio has increased drastically and the maximum of the C 1s emission has shifted by 0.5 eV to lower binding energies. In addition the peak width at half-height has decreased from 1.96 to 1.54 eV and the peak has become more symmetrical. These findings indicate that only one carbon species is observed after polymerization in ethylene, the CH\textsubscript{2}-carbon from polyethylene. The same trends in the C 1s emission are observed when comparing Cr/SiO\textsubscript{2} spheres after impregnation and after polymerization (not shown). The formation of polyethylene on the Cr/SiO\textsubscript{2} spheres is confirmed by DRIFT, which shows the development of the CH\textsubscript{2} stretching bands (ν\textsubscript{as}(CH\textsubscript{2}), Figure 7, left), the symmetric CH\textsubscript{2} bending band (δ\textsubscript{s}(CH\textsubscript{2}), Figure 7, middle), and the CH\textsubscript{2} rocking band (δ′(CH\textsubscript{2}), Figure 7, right) upon polymerization. Note that CH\textsubscript{3} bands such as ν\textsubscript{as}(CH\textsubscript{3}) = 2975 and δ\textsubscript{s}(CH\textsubscript{3}) = 1368 cm\textsuperscript{-1} are not detectable. The CH\textsubscript{2} symmetric bending and rocking bands appear as doublets (δ\textsubscript{s}(CH\textsubscript{2}) = 1463 and 1471 cm\textsuperscript{-1}, δ′(CH\textsubscript{2}) = 720 and 792 cm\textsuperscript{-1}), characteristic of crystalline polyethylene, while the broad shoulder at ~1443 cm\textsuperscript{-1} is associated with amorphous polyethylene.\textsuperscript{25}

**Conclusions**

A surface science model for the Phillips ethylene polymerization catalyst has been prepared by spin-coating impregnation of aqueous CrO\textsubscript{3} on a SiO\textsubscript{2}/Si(100) support. Characterization with X-ray photoelectron spectroscopy reveals that the impregnated Cr(VI)-oxide is dispersed molecularly up to a loading of 2 Cr/nm\textsuperscript{2}. Upon calcination chromium binds to the silica surface, forming Cr–O–Si ester bonds; however, some chromium is lost, probably due to evaporation. The model catalyst
polymerizes ethylene at 160 °C and atmospheric pressure after being calcined at 650 °C. From these findings we conclude that the Crox/SiO2/Si(100) system is a realistic model that may contribute to a better understanding of the industrial Phillips catalyst in forthcoming experiments.

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References and Notes
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