

Planar model system of the Phillips (Cr/SiO₂) catalyst based on a well-defined thin silicate film

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Abstract: The Phillips catalyst (Cr/SiO₂) is successfully used in the large-scale production of polyethylene and has attracted a great interest in catalytic community over the last sixty years. However, the atomic structure(s) of the active site(s) and the reaction mechanism remain controversial, in particular due to the structural complexity and surface heterogeneity of the amorphous silica. In this work, we used a well-defined, atomically flat silicate bilayer film grown on Ru(0001) as a support offering the opportunity to investigate mechanistic aspects at the atomic scale. To fabricate a planar Cr/SiO₂ model system suitable for surface science studies, chromium was deposited using physical vapor deposition onto the hydroxylated silica film surface. Structural characterization and adsorption studies were performed by infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD). Hydroxyls groups seem to serve as anchoring sites to Cr ad-atoms. As monitored by IRAS, hydroxyls consumption correlated with the appearance of the new band at $\sim 1007\text{ cm}^{-1}$ typical for Cr=O vibrations. In addition, CO titration experiments suggested also the presence of “naked” Cr, which transforms into mono- and di-oxo chromyl species and their aggregation upon oxidation treatments. TPD experiments of ethylene adsorption at low temperatures under UHV conditions showed the formation of butane as one of the main products. The resultant surfaces are thermally stable, at least, up to 400 K which allows to investigate ethylene polymerization further under more realistic conditions.

Keywords: Phillips catalyst; model catalysts; surface structures; thin films; infrared spectroscopy; ethylene adsorption.

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1. Introduction

The Phillips catalyst (Cr/SiO_2) is commercially used in the large-scale production of polyethylene and accounts for more than one-third of the annual production worldwide. [1, 2] The catalyst is commonly prepared by impregnation of an amorphous silica support with an aqueous solution of a chromium compound (e.g. CrO_3) and subsequent calcination at elevated temperatures in oxygen or dry air, thus forming CrO_3 oxide. The latter reacts with hydroxyl groups of the silica gel which behave as anchors to hexavalent Cr(VI) species.[3-5] Although there are ongoing debates about how many types of chromate species may be present in the catalyst, it is believed that polymerization involves monochromate species since model catalysts only possessing monochromate species showed very similar catalytic performance. [4, 6-8] On the other hand, the Phillips catalysts produce polymers with a broad molecular weight distribution, which is possibly due to the large diversity of the active sites. [4, 9-11] The ethylene polymerization exhibits an induction period, in which Cr(VI) species are thought to transform into Cr(II) and/or Cr(III) species. The oxidation state of the active chromium sites and the initiation mechanism on the Phillips catalyst remain controversial even after sixty years since its invention.

To elucidate the reaction mechanism, in particular the initial stages of polymerization, CO is commonly used as a reducing agent. The reduced catalyst contains mainly Cr(II) species and produces very similar polymer as its hexavalent counterpart. Although Cr(II) species is considered as an active precursor, the question of whether Cr remains divalent during polymerization is still open [2, 4, 12-14]. Zecchina and co-workers [14] presented the first spectroscopic evidence of the occurrence of metallocycle intermediate species during ethylene polymerization using infrared spectroscopy. In addition, this group found that the initial rate of polymerization of the reduced Phillips catalyst could be enhanced by order of magnitude after thermal treatment of Cr(II)/SiO_2 with N_2O which, as proposed, results in Cr(IV)-oxo precursor.[15] Scott and co-workers [12, 13] reported results showing that the Cr(III) sites, which are formed upon ethylene coordination with Cr(II) sites, are the initiating sites for the reaction. The structure of the organoCr(III) sites and a two-step initiation mechanism, in which

ethylene oxidative addition leads to various (organo)Cr(IV) sites, and subsequent Cr–C bond homolysis results in (organo)Cr(III) site that is capable of polymerizing ethylene, is proposed through theory calculations. The calculations also revealed that the initiation reaction strongly depends on the Cr coordination number. It is suggested that the siloxanes at self-initiating sites should be coordinated just strong enough to be hemilabile, allowing access to both lower and higher coordination states. However, there is so far no experimental information available about the structure of organoCr(III) sites and also the proposed mechanism.

Monoi's group has compared the performance of the $\text{Cr}[\text{CH}(\text{SiMe}_2)_3]/\text{SiO}_2$ catalyst and Phillips catalysts towards ethylene polymerization. It is found that the activity per Cr on the former one is about 6-7 times higher than the latter one, which indicates that organoCr(III) is more active than traditional Phillips catalysts towards ethylene polymerization.[16]

Activation of the Cr/SiO₂ catalysts by ethylene in the induction period was studied by Wachs and coworkers using operando spectroscopies.[17, 18] They found that in the initial stage Cr(VI) is reduced to Cr(III) with a formation of Cr(III)-(CH₂)₂CH=CH₂ and Cr(III)-CH=CH₂ intermediates, with the latter representing the catalytic active site. However, this active organo Cr(III) site develops through ethylene coordination with hydroxylated Cr(III)-OH, instead of Cr(II) site as suggested by Scott's group. The proposed initiation mechanism involves ethylene bonding to chromium and formation of water. DFT calculations by Handzlik and coworkers also showed that the hydroxylated Cr(III)-OH species, further transforming into Cr(III)-CH=CH₂ complex, is effective for ethylene polymerization. However, the results predict that the oxochromacycle ring expansion mechanism is more probable than the routes involving Cr(III)-CH=CH₂ complexes.[11] It is also found that defect sites in the amorphous silica framework can play a certain role in low-temperature transformation of Cr(II) species into the active Cr(III) sites.

Copéret and coworkers employed a molecular approach by anchoring dinuclear Cr(II), dinuclear Cr(III) and mononuclear Cr(III) species on silica surface.[19-21] The dinuclear Cr(III) species were found highly active towards ethylene in contrast to the Cr(II) ones. Mononuclear Cr(III) sites on silica were also active to yield polyethylene with a broad molecular weight distribution, similar to that typically obtained from the Phillips catalyst. A dual initiation pathway is proposed through the heterolytic C-H bond activation of ethylene on a Cr-O bond

and insertion of ethylene into the Cr-O bond. It is found that the highly strained sites facilities both path way, especially the latter one, which leads to highly active sites and formation of long chain polymers. However less strained sites will initiate more slowly on both path way and generate different active site structures, which will likely affect the structure of the final polymer. The distribution of active sites in different environments would account for broad distribution of polymer chains observed on the sample.[22] The coordination sphere of the Cr(III) site also effects formation of oligomers (e.g. butene, hexene) and branching. [23]

In addition to model studies employing high surface area silicas, planar models suited for “surface science” studies have also been suggested, most notably by Niemantsverdriet and coworkers.[24-27] Thermally oxidized silica films grown on Si(100) wafers were used as supports for chromia deposited from chromate solution using spin coating impregnation. Structural characterization by x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy, and atomic force microscopy led the authors to conclude that isolated chromium sites are the most active, although direct visualization of the active Cr sites was impossible. [7, 26]

In all these model studies, the structural complexity and surface heterogeneity of the amorphous silica render the characterization of chromium species on an atomic level very difficult. In order to circumvent such issue, here we make use of a thin metal-supported silicate film representing a two-dimensional analogue of amorphous silica. [28-30] The so-called “bilayer” film consists of two silicate layers, each being formed by corner sharing of SiO_4 tetrahedra like in sheet silicates, and the film is weakly bonded to the metal surface.[31] Figure 1a displays high-resolution microscopy images of the film surface, obtained in our own laboratories, which are superimposed with a network of N-member silica rings. Being terminated by fully saturated siloxane bonds and hence essentially hydrophobic, the silicate surface could, however, be hydroxylated with a help of low energy electron radiation.[32] It is thought that surface hydroxyls will behave as anchors for chromium species deposited from certain precursors, ultimately resulting in a well-defined planar model system, schematically shown in Fig. 1b, which could, in principle, be characterized with atomic resolution using scanning tunneling microscopy (STM) in combination with other spectroscopic techniques

employed in surface science. In the present study, we only employed Cr physical vapor deposition. The structure of resultant Cr species and its reaction with CO, O₂ and ethylene were studied by infrared reflection-absorption spectroscopy (IRAS) and temperature programmed desorption (TPD).

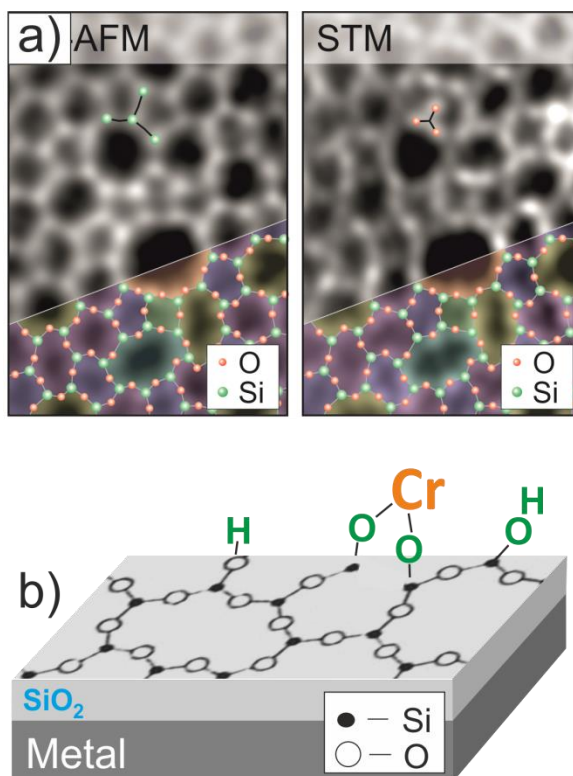


Figure 1. a) Atomic force microscopy (AFM, on the left) and STM (on the right) images of amorphous bilayer silica film grown on Ru(0001) which are superimposed with a silica network. (Reprinted with permission from ref. [33]. Copyright (2012) American Chemical Society.) b) Schematic view of a planar model system for the Phillips catalyst, where Cr species are anchored onto an atomically flat hydroxylated silicate film.

2. Experimental

The experiments were primarily performed in an UHV chamber (base pressure below 5×10^{-10} mbar) equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), IRAS (Bruker 66 ivs) and quadrupole mass-spectrometer (QMS) for TPD measurements. The Ru(0001) single crystal (from MaTeck) was spot-welded to thin Ta wires for resistive heating as well as cooling via filling the manipulator rod with liquid N₂. The

temperature was measured by a K-type thermocouple spot-welded to the backside of the crystal.

The Ru(0001) surface was cleaned using repeated cycles of Ar⁺ bombardment and annealing in UHV at ~1350 K. Cleanliness of the crystal was checked by LEED, AES and well-known TPD spectra of CO. Bilayer silicate films were grown on Ru(0001) as described in detail elsewhere.[28] Briefly, Si was vapor deposited onto oxygen precovered 3O(2×2)-Ru(0001) surface at ~ 100 K, followed by oxidation at ~ 1200 K in 10⁻⁶ mbar O₂.

To hydroxylate the silica film, we make use of a low energy (200 eV) electron bombardment of the surface covered by a thin “ice” film formed by water adsorption at 100 K as described in detail elsewhere.[32] The sample was then flashed to 300 K to ensure molecular water desorption. The amount of hydroxyls ultimately formed may vary from sample to sample as it depends on many parameters such as the electron energy, current, exposure time, and ice film thickness. Nonetheless, all samples were inspected by IRAS prior to the Cr deposition. Chromium was deposited from a Cr rod of 2 mm in diameter using a commercial electron-beam assisted evaporator (Focus EMT3).

The IRA-spectra were recorded using p-polarized light at an 84° grazing angle of incidence (resolution 4 cm⁻¹). TPD spectra were recorded by placing the sample ~ 1 mm away from the aperture of the gold plated cone shielding a differentially pumped QMS.

Ethylene (from Messer, 99.95 %, hydrocarbons impurity below 100 vpm) was further purified using a cold trap. Prior to the ethylene exposure, the samples were flashed to 400 K to get rid of any adsorbate that may adsorb from the residual gases in UHV.

3. Results and discussion

Preparation of Cr/SiO₂ model catalysts

Electron bombardment of a double-layer silicate film covered by “ice” (amorphous solid water) greatly enhances the degree of hydroxylation without destroying the principal structure of the bilayer film as judged by IRAS and also by STM, although atomic resolution had not been

achieved.[32] Upon hydroxylation with deuterated water (D_2O), two additional bands appear in IRA spectra at 2762 and 965 cm^{-1} , as shown in Fig. 2a (black line), which are assigned to $\nu(OD)$ and $\nu(SiO)$ stretching vibrations, respectively, in terminal silanols ($Si-OD$).[32] Apparently, the hydroxylation occurs through siloxane bond breaking in the silica network.[32] The density of hydroxyls was higher than 0.4 nm^{-2} , on average, as calibrated versus the $\nu(OD)$ signal obtained on hydroxylated monolayer silicate films where OH species were directly imaged by STM.[34] These hydroxylated films were then used as a support for Cr species. It is well-documented in the literature, that metal atoms deposited by physical vapor deposition may penetrate the silicate film (as well as other ultrathin films) and thus adsorb at the metal-oxide film interface.[35] This effect depends on metal deposited as well as deposition conditions, and can hardly be predicted *a priori*. Therefore, we first examined Cr deposition at low temperatures to minimize the effect.

IRA-spectra of Cr vapor deposited on a silica film at $\sim 85\text{ K}$ and subsequently heated to 200 K revealed attenuation of the silanols related bands with increasing Cr coverage until their full disappearance. Therefore, Cr deposition is accompanied by hydroxyls consumption thus suggesting the formation of the Cr-O bond(s). The released hydrogen most likely diffuses into the interface and ultimately adsorbs on the $Ru(0001)$ surface. Indeed, heating the sample after Cr deposition revealed D_2 desorption, with the TPD profile being very similar to that of observed on $D_2/Ru(0001)$. Concomitantly, a new band appears at around 1007 cm^{-1} (Fig. 2a, red line), albeit the baseline in this region suffers from instrumental instability. This band falls in the range characteristic for the metal-oxygen double bond stretching vibrations,[36] and thus suggests the formation of chromyl ($Cr=O$) species on the silica surface. Indeed, experimental studies of Cr/SiO_2 catalysts, corroborated by calculations, assigned those IR bands at $980 - 1030\text{ cm}^{-1}$ to $\nu(Cr=O)$ vibrations, and to vibrations of corresponding Cr-O-Si linkages at $900 - 910\text{ cm}^{-1}$. [17, 37-43] In principle, monoxo ($Cr=O$) species shows only one vibrational band, whereas di-oxo $Cr(=O)_2$ structures would exhibit both symmetric and asymmetric vibrational bands which are separated by $10-30\text{ cm}^{-1}$. [17, 44] Since only one band is observed in our experiments, one could tentatively assign the band at 1007 cm^{-1} to monoxo $Cr=O$ species. One has to bear in mind, however, the surface selection rules applied to IRAS on metal supported systems, which

state that only vibrations with net dipole changes normal to the surface are detected. Following this, asymmetric vibrations in di-oxo Cr(=O)₂ groups standing upright (normal to the surface) may hardly be visible.

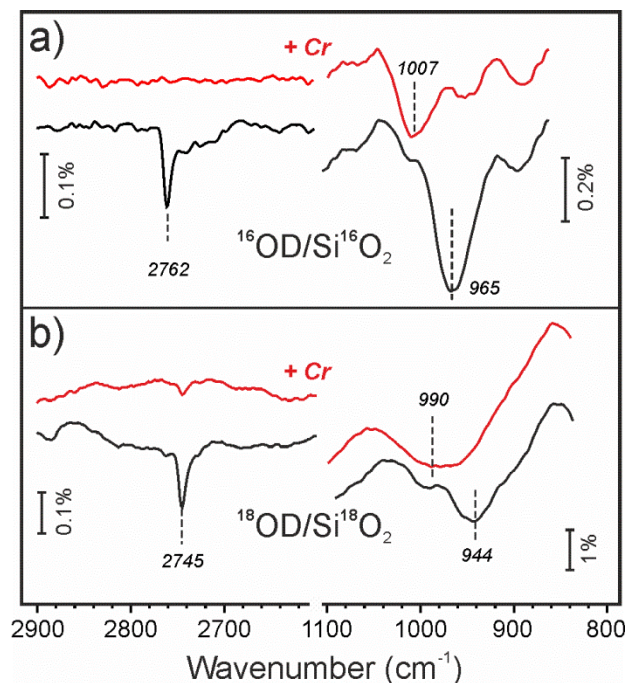


Figure 2. (a) IRA-spectra of a hydroxylated silicate film before (black) and after Cr deposition (red). (b) IRA-spectra of a hydroxylated Si¹⁸O₂ film with D₂¹⁸O before (black) and after Cr deposition (red). Cr was deposited on a hydroxylated surface at 85 K in UHV and then heated to 200 K. All spectra were taken at 200 K and referenced to the spectrum taken on the clean Ru(0001) surface.

To shed more light on our chromium species, we performed isotopic labeling experiments that can be easily carried out on the thin film based model system introduced here. The silicate film was grown using ¹⁸O₂ and then hydroxylated with D₂¹⁸O. IRA spectrum in Fig. 2b (black line) shows silanol bands (2745 cm⁻¹ for ν(OD), and 944 cm⁻¹ for ν(SiO)) which are red-shifted by 17-21 cm⁻¹ when compared to those in the film grown with ¹⁶O₂ (Fig. 2a) in full agreement with predictions based on the reduced mass analysis. Subsequent Cr deposition leads to strong attenuation of the silanols (Si-¹⁸OD) bands and the formation of the broad band at 990 cm⁻¹. Although in this case precise deconvolution of the spectrum is rather difficult, “the center of gravity” of the broad band around 990 cm⁻¹ is consistent with the formation of Cr=¹⁸O species due to the isotopic shift by ~ 17 cm⁻¹.

Thermal stability of deposited Cr species was examined by measuring IRA spectra after the sample was flashed in UHV to the temperatures increased stepwise. The results presented in Fig. S1 in Electronic Supplementary Information (ESI) show that the considerable changes only appear at temperatures as high as 500 K, thus suggesting that the system is fairly stable, at least, up to 400 K.

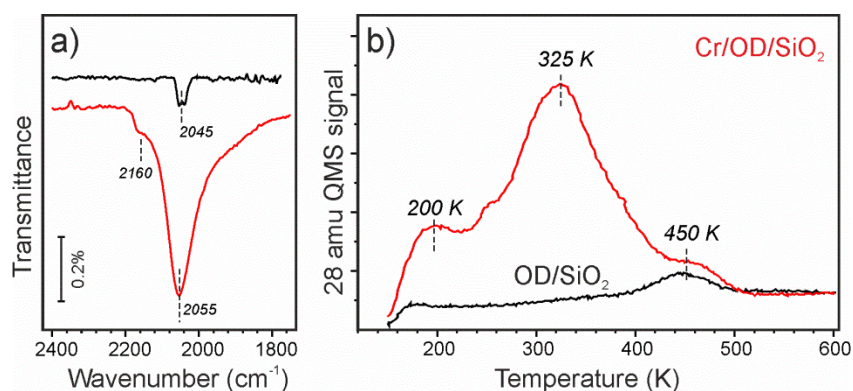


Figure 3. (a) IRA spectra of 60 L CO adsorption on a hydroxylated silicate film before (black line) and after Cr deposition (red line). All spectra were taken at 150 K and referenced to the spectrum taken on clean Ru(0001) single crystal. (b) TPD spectra (28 amu) of CO adsorbed onto a hydroxylated silicate film before (black line) and after Cr deposition (red line) at 150 K and subsequently heated with a rate of 3 K/s.

To determine the oxidation state of the Cr deposited, we measured XP spectra on similarly prepared samples in another chamber. However, at such low Cr loadings, even the intensity of the strongest, Cr 2p core level, signals was insufficient to precisely determine the binding energies. In addition, XP spectra of small clusters and nanoparticles deposited on thin insulating films commonly exhibit particle size as well as charge screening effects that renders determination of the oxidation state in our samples uncertain. Under these circumstances, we made use of adsorption of CO at low temperature whose interaction on solid surfaces and corresponding IRAS and TPD fingerprints are fairly well understood. [2, 20, 38, 45-47]

Figure 3 compares IRA and TPD spectra obtained after dosing ~ 60 L (Langmuirs, $1 \text{ L} = 10^6$ Torr s) to the pristine and Cr-deposited sample. TPD spectrum on the Cr-free sample revealed strongly bound CO species desorbing at ~ 450 K, which is most likely arising from CO adsorption in the “holes” present in small amounts in our silica films. CO adsorbed on the Cr/SiO₂ surface (Fig. 3a, red line) at 150 K showed a broad band peaked at 2055 cm^{-1} with a much higher

intensity. Accordingly, the desorption profile features two states at ~ 200 and 325 K in addition to the above-mentioned signal at 450 K. Clearly, the ability of CO adsorption on Cr sites suggests coordinately unsaturated Cr species.

We also measured IRA spectra of CO adsorbed on “as deposited” Cr at 85 K and after thermal flash to the temperatures increased stepwise up to 400 K. Figure 4 shows that the band at 2065 cm^{-1} gradually attenuates and red-shifts until it disappears at 400 K, in full agreement with the TPD spectrum shown in Fig. 3b. Accordingly, the weak band at $\sim 2160\text{ cm}^{-1}$ appearing at a high frequency side of the main signal, vanishes upon heating to ~ 250 K, which is, again, in nice agreement with the TPD signal at ~ 200 K.

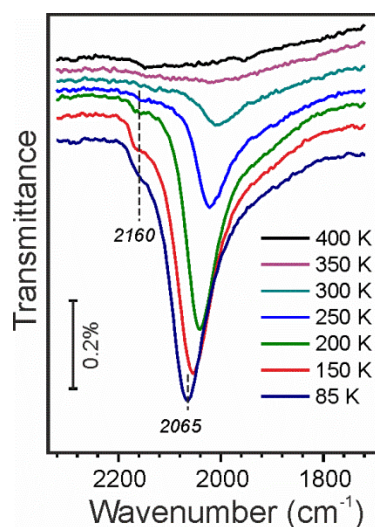


Figure 4. IRA-spectra of CO adsorbed on a chromium surface at 85 K and then heated to the temperatures as indicated. All spectra were taken at 85 K and were offset for clarity.

It is instructive here to survey infrared spectra of CO on the Cr compounds documented in the literature. IR spectra of $\text{Cr}(\text{CO})_6$ carbonyl in the vapor phase show only one intense CO stretching vibration at $\sim 2000\text{ cm}^{-1}$. [48, 49] Physisorbed $\text{Cr}(\text{CO})_6$ on SiO_2 exhibits a strong band at 1990 cm^{-1} and a shoulder at 2015 cm^{-1} . [50] In substituted metal carbonyl complexes of the $\text{X-M}(\text{CO})_5$ (where X is a ligand or a vacancy) composition, at least three CO vibrational bands are IR active: The two A_1 and E modes, although the IR-silent B_1 mode has also been observed. [49-51] The corresponding frequencies of these four modes decrease in the order: $\nu(A_1)_1$ (at $2142\text{--}2075\text{ cm}^{-1}$) $>$ $\nu(B_1)$ ($2090\text{--}2075\text{ cm}^{-1}$) $>$ $\nu(E)$ ($2040\text{--}2000\text{ cm}^{-1}$) $>$ $\nu(A_1)_2$ ($\sim 2000\text{ cm}^{-1}$), with the E

mode having the highest intensity such that the $\nu(A_1)_2$ band only appears as a shoulder to the E signal.

As far as Cr/SiO₂ catalysts are concerned, CO adsorption on Cr(II) at high exposures gives rise to the formation of the so-called “room temperature triplet” in the 2175-2200 cm⁻¹ region.[2, 38, 45, 46] It was suggested that Cr(II) sites exist in two structural configurations, namely: Cr_A having two CO molecules in the coordination sphere and showing bands at 2184 cm⁻¹ and 2179 cm⁻¹ (as a shoulder); and Cr_B coordinated to one CO molecule thus resulting in the band at ~ 2190 cm⁻¹. Finally, IR spectra of CO adsorbed on Cr(III) and Cr(IV) sites show bands at 2188 – 2202 cm⁻¹ and 2206 cm⁻¹, respectively.[20, 46, 47] Not surprisingly, CO does not adsorb on fully coordinated Cr(VI) sites.

Following this literature survey, the principal band at 2055-2065 cm⁻¹(Figs. 3a and 4) can tentatively be assigned to CO adsorbed on “naked” Cr sites, thus resulting in carbonyl-like species, which desorbs at ~ 325 K (see Fig. 3b). Gradual red-shift of this band on heating can be explained by decreasing the number of CO molecules coordinated to Cr and hence reducing dipole-dipole interaction. Accordingly, the 2160 cm⁻¹ band falls in the range characteristic for CO adsorbed on Cr=O species and is more weakly bound (desorption at ~ 200 K). On the basis of TPD results, the amount of chromyl species seems to be relatively low in the samples prepared by Cr physical vapor deposition.

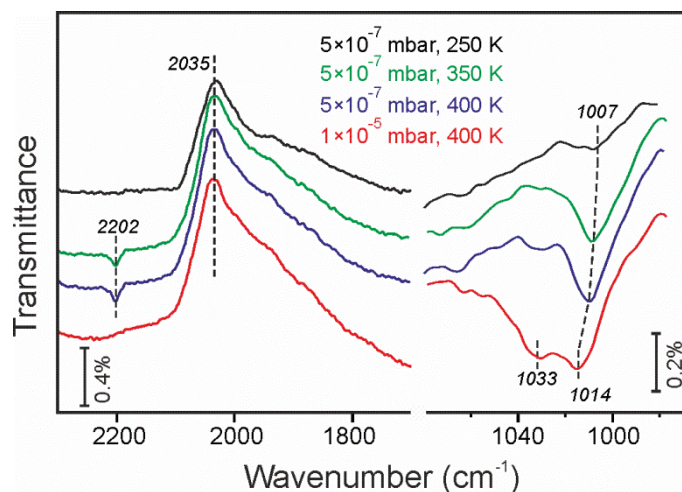


Figure 5. IR spectra of Cr/SiO₂ after sequential oxidation (as indicated). All spectra were recorded at 150 K and referenced to the spectrum of sample exposed to 5×10⁻⁷ mbar O₂ at 150 K.

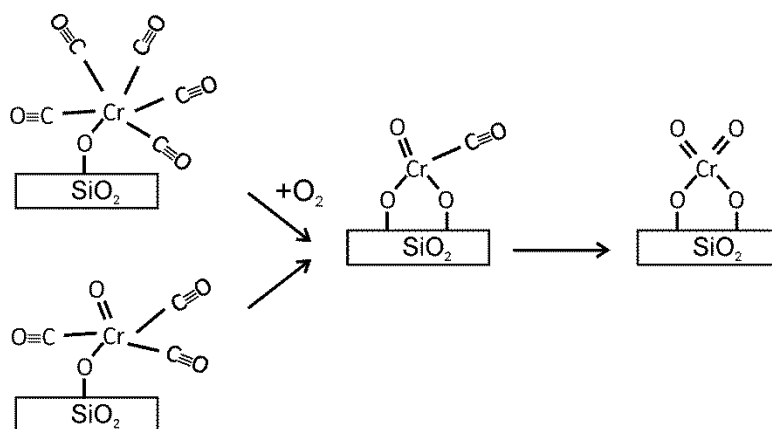
To see whether Cr species can further be oxidized, the “as deposited” sample was exposed to molecular O₂ at increasing pressure and temperature (5×10^{-7} – 10^{-5} mbar; 250 – 400 K) for 2 min each, and monitored by IRAS in UHV at 150 K. For clarity, the spectra presented in Fig. 5 are referenced to the spectrum obtained by exposure to 5×10^{-7} mbar of O₂ at 150 K. Interestingly, a strong positive signal that is clearly observed in the $\nu(\text{CO})$ region at 2035 cm^{-1} indicates the desorption of CO which was initially present in the reference, although CO was not deliberately introduced into the chamber during deposition. It, therefore, appears that CO in the UHV background may readily adsorb on the naked Cr sites.

At low pressures (5×10^{-7} mbar) the original band at 1007 cm^{-1} (see Fig. 2a) gains intensity and slightly shifts to higher frequencies, thus indicating the formation of more chromyl species and probably their clustering that causes the blue-shift to 1014 cm^{-1} .^[52] This correlates well with the CO desorption (as just discussed above) from the naked Cr sites, which become oxidized, and the observation of a new small band at 2202 cm^{-1} , which is characteristic for CO on Cr(IV).^[15] Concomitantly, a new band develops at 1033 cm^{-1} which further grows upon oxidation at 400 K in 1×10^{-5} mbar O₂. Note that the band at 1033 cm^{-1} was not observed upon annealing to 400 K in UHV (Fig. S1). Therefore, its formation includes oxygen from the gas phase. To validate this scenario, we performed isotopic experiments where ¹⁶O₂ was exposed to the films grown with ¹⁸O₂ and hydroxylated with D₂¹⁸O. In essence, the same bands (at ~ 1030 and 1010 cm^{-1}) developed upon oxidation (not shown here), although some oxygen scrambling cannot be excluded.

Subsequent CO exposure to the oxidized samples did not reveal CO-related bands in IRAS, thus suggesting that Cr is fully oxidized by those treatments. As DFT calculations predict dioxo chromyl species to be more stable than the monoxo counterpart,^[41] the IR band at 1033 cm^{-1} is indicative of the formation of dioxo species, with the bands at 1033 and 1014 cm^{-1} being assigned to asymmetric and symmetric vibrations of the O=Cr=O bonds, respectively. Albeit the absolute wavenumbers are higher as compared to those reported in the literature,^[17, 37, 38] the deviation might be related to that our measurements were performed under clean, UHV conditions with no adventitious adsorbates commonly present if measured in low vacuum on powdered samples. In attempt to discriminate monoxo and dioxo species we performed

isotopic experiments with ^{18}O in the film. Due to spectral broadening and overlapping, it was difficult to precisely deconvolute the spectra. However, the $^{16}\text{O}=\text{Cr}=\text{O}$ bands dominated the spectra, suggesting only a minority of $^{18}\text{O}=\text{Cr}=\text{O}$ and $\text{Cr}=\text{O}$ species formed.

On the basis of these results, we propose the following scenario schematically shown below. The “as deposited” Cr/SiO₂ surface exposes “naked” Cr and Cr=O (as minority) species, both of which can adsorb CO as fingerprinted by IRAS and TPD. In oxygen ambient at elevated temperatures, all Cr species become oxidized thus forming more monoxo chromyl species (and possibly their aggregates). Ultimately, a dioxo chromyl species is formed which is not able to coordinate CO.



Scheme 1. Proposed scheme for the formation of Cr species on a silicate film probed by CO adsorption.

3.2 Ethylene adsorption

In the next step, we studied adsorption of ethylene on our model systems under UHV conditions. Prior to the ethylene exposure, the “as deposited” samples were flashed to 400 K to get rid of any adsorbate, particularly of CO that may adsorb from the vacuum background. For comparison, the experiments were performed on a Cr-free hydroxylated silicate film. IRA spectra of the sample exposed to 1×10^{-5} mbar of C₂H₄ at 85 K for 3 min are shown in Fig. 6a. The comparison clearly shows that adsorption and reaction solely occurs on Cr species. Surprising is, however, that the observed IRA bands are not known for ethylene-related species. For comparison, physisorbed ethylene shows vibrations at 943 cm⁻¹, 1623 cm⁻¹ and 1342 cm⁻¹.^[53] Ethylene chemisorption on metal surfaces either through π or di- σ bonding shifts the last

two bands to ~ 1400 and ~ 1000 cm^{-1} , respectively.[54] Ethylene adsorption on oxides, in particular on the $\text{Cr}_2\text{O}_3(0001)$ surface, showed IRA bands at around 1000 and 2980 cm^{-1} . [43] The 2960 and 2865 cm^{-1} bands have also been observed previously during polymerization of ethylene on the Phillips catalysts. They were assigned to $\nu(\text{C-H})$ in Cr(III)-CH=CH_2 and $\nu(\text{Cr-CH}_2)$ in $\text{Cr(III)-(CH}_2)_2\text{CH=CH}_2$ complexes, respectively. Beside these two bands, another band at ~ 1574 cm^{-1} , was observed and assigned to $\nu(\text{C=C})$ vibrations.[18] In our case, two bands at 1462 and 1381 cm^{-1} are only observed in this region which are characteristic for $\delta(\text{C-H})$ vibrations. The absence of the $\nu(\text{C=C})$ band could, in principle, be explained by the surface selection rules assuming that the C=C bond is parallel to the surface. However, the combination of bands at 1462 and 1381 cm^{-1} and 2960 , 2931 , 2862 and 2874 cm^{-1} allows us to assign them to C-H vibrations in $\text{R-CH}_2\text{-R}$ or R-CH_3 . Therefore, the observed bands at 2960 and 2874 cm^{-1} , and 1462 and 1381 cm^{-1} are characteristic for $\nu(\text{C-H})$ and $\delta(\text{C-H})$ vibrations, respectively, in R-CH_3 groups. Accordingly, the bands at 2931 and 2862 cm^{-1} , and 1462 cm^{-1} are assigned to C-H vibrations in $\text{R-CH}_2\text{-R}$. [55] According to the literature database, the observed spectra suggest adsorption of butane/hexane molecules or the formation of butadiyl species. [56, 57]

The TPD spectrum obtained from this sample is depicted in Fig. 6b. For comparison, the desorption traces on the Cr -free sample are shown by dashed lines. Focusing on the formation of alkene and alkane larger than ethylene, we recorded signals up to $m/z^+ = 112$. No desorption of species higher than 84 amu was observed. It is well known that hydrocarbons exhibit rather complex fragmentation patterns in QMS. [58, 59] However, all masses belonging to one species will show identical desorption profiles. Since most of alkene and alkane species will give fragmentations of $m/z^+ = 27, 28, 41, 56$ and 69 , the species can be assigned by comparing the signal intensity ratios of each. For analysis we have chosen $m/z^+ = 25$ (solely of ethylene), $27, 28, 41, 56$ and 69 (of other alkenes and alkanes). [60] The desorption signals at 110 K can be assigned to butene that is formed from butadiyl species as suggested above by IRAS. [56] Accordingly, the signals desorbing at 119 K can be assigned to a mixture of ethylene and butane. Other species are difficult to assign in a definitive manner solely on the basis of desorption profiles. Note that repeated adsorption/desorption IRA/TPD spectra can be repeated and fairly well reproduced, suggesting that the Cr sites are not blocked by these exposures. To minimize

effects of long desorption “tails” caused by weakly adsorbed species at low temperatures, we performed ethylene adsorption (60 L) at 150 K. The TPD spectra (Fig. S2) revealed 41 amu as the main signal, whose intensity is comparable with that observed in this region after ethylene adsorption at 85 K (Fig. 6). Again, the observation of 41 amu further confirms the formation of C₄ molecules as a main product of ethylene adsorption.

Any considerable effect of a Ru(0001) support in observed reactivity can be excluded. First, only tiny amounts of holes in the prepared films exposing Ru were observed by CO titration (e.g., see Figure 3a). Second, if some amounts of ethylene would adsorb on Ru(0001), then ethylene were flat laying parallel to the surface at 120 K and hence will be silent in IRAS due to the above mentioned surface selection rules.[61] Third, the bilayer silicate film is only weakly bound to a metal support and electronically decoupled from the Ru(0001) surface. On the other hand, the formation of C₄ molecules would be consistent with the two-steps initiation mechanism proposed by Scott and co-workers, in which n-butane is formed.[13] It is suggested that butene formation is due to ethylene oligomerization.[23, 62]

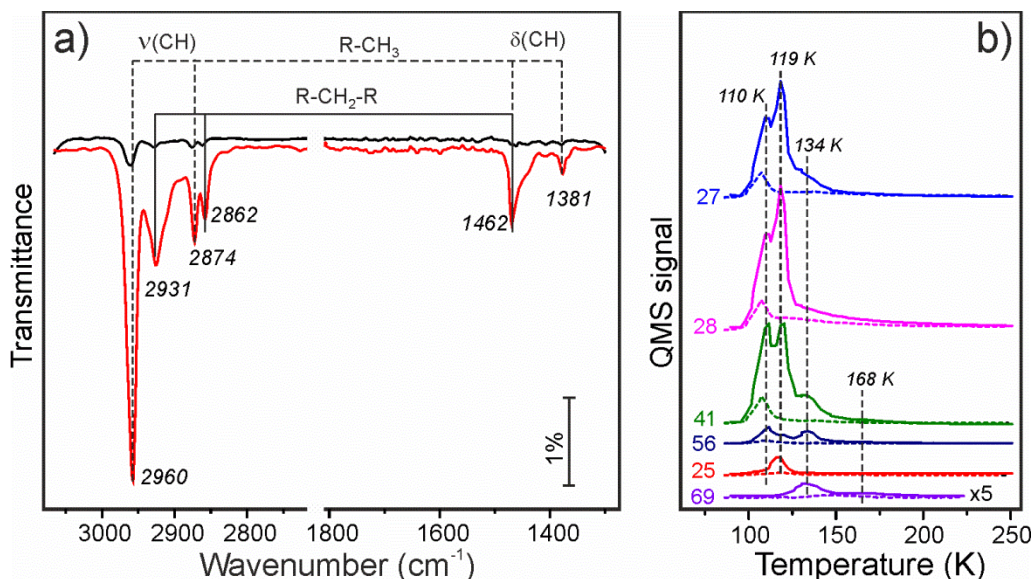


Figure 6. (a) IRA spectra of C₂H₄ adsorbed on “as deposited” Cr/SiO₂ at 85 K (red) and on a pristine hydroxylated silicate film before Cr deposition (black). (b) TPD traces of selected masses of C₂H₄ adsorbed onto a hydroxylated silicate film before (dash lines) and after Cr deposition (solid lines) at 85 K and subsequently heated with a rate of 3 K/s. The spectra are offset for clarity.

4. Conclusions

We studied preparation of a well-defined planar system modeling the Phillips (Cr/SiO₂) polymerization catalysts using Cr physical vapor deposition on a metal-supported atomically flat silicate film. Hydroxyls groups, formed on the silica surface by electron beam assisted hydroxylation, seem to serve as anchoring centers to Cr species. Monitored by IRAS, hydroxyls consumption correlates with the appearance of the new band at $\sim 1007\text{ cm}^{-1}$ assigned to Cr=O vibrations. In addition, CO titration experiments suggested also the presence of “naked” Cr, which transforms into mono and dioxo chromyl species and their aggregation upon oxidation treatment. It appears that mild oxidation allows tuning the oxidation state of surface Cr.

IRAS and TPD experiments of ethylene adsorption at low temperatures under UHV conditions showed the formation of C₄ molecules (butene, butane). This finding would, in principle, be consistent with previously suggested initiation mechanism suggesting butane formation. The resultant surfaces are found thermally stable, at least, up to 400 K which allows to investigate ethylene polymerization further under more realistic conditions. Scanning tunneling microscopy studies of the prepared model systems are also under way.

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