Mechanism of Initiation in the Phillips Ethylene Polymerization Catalyst: Redox Processes Leading to the Active Site

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Supporting Information

ABSTRACT: The detailed mechanism by which ethylene polymerization is initiated by the inorganic Phillips catalyst (Cr/SiO2) without recourse to an alkylating cocatalyst remains one of the great unsolved mysteries of heterogeneous catalysis. Generation of the active catalyst starts with reduction of CrVI ions dispersed on silica. A lower oxidation state, generally accepted to be CrIII, is required to activate ethylene to form an organoCr active site. In this work, a mesoporous, optically transparent monolith of CrV/SiO2 was prepared using sol–gel chemistry in order to monitor the reduction process spectroscopically. Using in situ UV−vis spectroscopy, we observed a very clean, stepwise reduction by CO of CrVI first to CrV, then to CrIV. Both the intermediate and final states show XANES consistent with these oxidation state assignments, and aspects of their coordination environments were deduced from Raman and UV−vis spectroscopies. The intermediate CrV sites are inactive toward ethylene at 80 °C. The CrII sites, which have long been postulated as the end point of CO reduction, were observed directly by high-frequency/high-field EPR spectroscopy. They react quantitatively with ethylene to generate the organoCrII active sites, characterized by X-ray absorption and UV−vis spectroscopy, which initiate polymerization.

KEYWORDS: Phillips catalyst, ethylene polymerization, active site, heterogeneous catalyst, sol−gel, reaction mechanism, redox activation, in situ spectroscopy

INTRODUCTION

The Phillips ethylene polymerization catalyst has been used successfully in the commercial production of high-density polyethylene (HDPE) for over six decades, starting from its serendipitous discovery by Hogan and Banks at Phillips Petroleum in 1951.1 Ever today, it is responsible for producing as much as 50% of the world’s annual HDPE output of 30 million tons.2 Due to its industrial importance, the Phillips catalyst has been studied extensively, and many of the operating parameters that affect its activity and the properties of the polyethylene it produces are well documented.3−4 The catalyst is a supported metal oxide, made by dispersing CrVI ions on an amorphous silica support. It is typically synthesized by wet impregnation of a silica gel with Cr ions, at loadings that are commonly about 1.0 wt % (corresponding to 1.2 mol % Cr). In the original method, CrO3 was used as the Cr source, but its toxicity soon led to its replacement by more benign CrIII compounds.5 After impregnation, the Cr-modified silica is dried and calcined at high temperature (>500 °C), causing complete oxidation to CrVI, which is a precursor of the active oxidation state.

The isolated CrVI sites have been structurally characterized using X-ray absorption fine structure (XAFS) and vibrational spectroscopies, and modeled using DFT methods.5−8 The dominant species is a chromate ester with two anchoring Cr=O−Si bonds and two terminal Cr=O bonds (Scheme 1a). The first step in the activation of the precatalyst is the reduction of the supported CrVI sites. In industrial practice, this is achieved by exposure to either ethylene or CO at slightly elevated temperatures (80−120 °C), and the reduced sites are formed in situ during a prolonged induction period. Catalyst reduction by CO is often preferred in laboratory studies, because it allows the resulting sites to be studied without the complications of ensuing polymerization. Both activation procedures generate highly active catalysts and produce very similar polymers.2,9,10 Regardless of the reduction method, the final oxidation state is accepted to be CrIII.2 Due to the very high reactivity of the fully reduced catalyst, it has generally been characterized only
indirectly, particularly in early studies. The CrII sites are regarded as precursors of the active sites, which form upon reaction of CrII with ethylene. Neither the structure nor the oxidation state of the resulting active sites has been directly characterized, although several organoCrIV species, arising from two-electron oxidation of CrII by ethylene, have been inferred from IR spectra, or otherwise posited. The mechanism of the initial reaction of ethylene with CrII remains elusive. Recently, minor CrIII sites present in the reduced catalyst were proposed to be responsible for forming organoCrIII active sites without a redox reaction, by invoking ethylene deprotonation. This suggestion, which explicitly excludes participation of CrII in the activation process, has been shown to be based on flawed analyses of IR and DFT results and is contrary to a large body of prior results.

In this study, we report a stepwise investigation of the CO reduction pathway leading to the activated CrII precatalyst. The latter was observed directly using high-field/high-frequency EPR spectroscopy. We also provide experimental confirmation that the CrII precatalyst reacts with ethylene in a redox process to form a new species active toward the polymerization of ethylene.

■ RESULTS AND DISCUSSION

Preparation of Cr/SiO2. The Phillips catalyst used in this study was made in the form of sol–gel monoliths, consisting of porous silica containing highly dispersed CrVI ions (see Figure 1). They were synthesized using established multicomponent sol–gel techniques and calcined in air at 500 °C. Once sealed in the spectroscopic cell, the monoliths were calcined yet again at 500 °C under dry oxygen (see Supporting Information). The application of such monoliths in our investigation of the Phillips mechanism builds on our earlier work, in which we pioneered their use in spectroscopic studies of a variety of silica-supported catalysts. In particular, their optical transparency provides significant advantages over powdered catalysts for the spectroscopic characterization of metal oxide active sites, whereas their porosity allows molecular reactants to diffuse to the reactive sites and form intermediates. As fabricated, the monoliths are mesoporous, with an average pore size and pore volume of 2.9 nm and 0.26 cm³/g, respectively (Figure S1). The combined accessibility of high quality UV–vis spectra and reactivity measurements can be exceptionally useful in elucidating reaction mechanisms involving highly dispersed transition metal ions.

Reduction of CrVI to CrIV. It is well-known that active Phillips catalysts can be generated by reducing CrVI/SiO2 with CO at temperatures from 300 to 400 °C. In our experiments, reduction was carried out under flowing CO at atmospheric pressure while monitoring changes in the UV–vis spectrum of the calcined CrVI/SiO2 xerogel. Spectra were monitored in transmission mode as a function of temperature, using a high-temperature/high-pressure spectroscopic cell (Figure S2). In an initial experiment, the temperature of the monolith was increased until the UV–vis spectrum began to change, at ca. 230 °C. In a subsequent experiment, the temperature was held constant at 230 °C under flowing CO, causing the color of the monolith to change from orange to green (Scheme 1a,b). The isothermal UV–vis spectra reveal an extremely clean transformation, with a well-defined isosbestic point at 550 nm and the emergence of a new peak at 720 nm (Figure 2a). After 14 h at this temperature, no further changes were observed.

Reduction of CrVI by CO was reported previously at approximately this temperature, although with no indication...
that the reaction proceeds as cleanly as is apparent in Figure 2a. The oxidation state of the Cr species formed at 230 °C was investigated by X-ray absorption near-edge spectroscopy (XANES). Figure 3 shows the Cr K-edge located at 6004.4 eV, suggesting the presence of CrIV by comparison to a reference material (bus(neopentyl)CrIV/SiO2, 6004.2 eV), and consistent with prior observations made by Krauss et al.25,26 The first step of the process is therefore inferred to be the reduction of CrVII to CrIV, depicted as the transformation of (≡SiO)2CrVIIO3 to (≡SiO)2CrIVO in Scheme 1a,b. When briefly exposed to ca. 1 atm ethylene at 80 °C, the CrIV species proved to be inactive for polymerization, consistent with reports that CO reduction temperatures >300 °C are required to generate an active catalyst.25

Reduction of CrIV to CrII. As the reduction temperature increases further, the UV–vis spectrum remains constant until the temperature reaches 350 °C, when additional changes occur in the spectrum. Over the course of 12 h at 350 °C, the color of the monolith turned from green to blue (Scheme 1b,c). In the UV–vis spectrum, the peak at 465 nm disappeared, whereas the intense, broad peak at 720 nm shifted to 770 nm (Figure 2b). The evolution of the spectra over time shows behavior that is approximately isosbestic, indicating that the second reduction process also occurs very cleanly. The new Cr product is also quite different in its reactivity: when dosed with ca. 1 atm ethylene at 80 °C, the formation of polyethylene was observed by Raman spectroscopy.

High-Frequency/High-Field EPR Spectroscopy. It is generally accepted by Phillips catalyst researchers that CrII is the active catalyst, consistent with high-spin CrII (XANES). Figure 3 shows the Cr K-edge XANES of CrIV/SiO2 prepared by CO reduction of CrVII/SiO2 (0.5 mol % Cr) at 230 °C, with the energy referenced to a Cr foil standard (5989.2 eV).

A CrVII/SiO2 xerogel (3.0 mol % Cr) was reduced under CO to its spectroscopically determined end point at 350 °C and then transferred under scrupulously anaerobic conditions to a quartz ampule and sealed. The complete HF EPR spectrum at 106 GHz is shown in Figure S3; Figure 4 (blue) shows the same spectrum, but with the high-amplitude signal at g = 1.975 (3.82 T) removed (see below). Four features are located far from the g = 2 spectral region, at fields ranging from 1.0 to 5.5 T. Their presence signifies a non-Kramers (integer spin number) species with a sizable zero-field splitting. Indeed, simulation of a quintet (S = 2) spin-state spectrum assuming a true powder distribution reproduces the positions of the features very well (Figure 4, red). Simulation of spectra recorded at 212 and 317 GHz using the same spin Hamiltonian parameters resulted in equally good agreement with experiments (simulation of the 317 GHz spectrum is shown in Figure S4). This observation leaves little doubt that the species responsible for the resonances outside the g ∼ 2 region is indeed CrII (for more details, see the Supporting Information). It represents one of the few direct observations of CrII as the ultimate product of CO reduction, Scheme 1c.

The features at g = 1.975 that were removed from Figure 4 likely originate from a superposition of two Kramers forms of Cr (i.e., with half-integer spin numbers): CrV (3d5) and CrIII (3d4). CrV is a known trace impurity in sol–gel-derived Cr/SiO2 materials, whereas CrIII is an established minor byproduct of CrVI reduction in the Phillips catalyst.27,32 Their large amplitude in the HF EPR spectrum may convey the impression that these resonances represent dominant species. However, this is not the case, for the following reasons. First, CrV has no zero-field splitting (zhf), and CrIII is known to have much smaller zfs than CrII. Consequently, their EPR absorptions converge in a narrow field range around g ∼ 1.98, with correspondingly augmented amplitude. Second, non-Kramers ions typically show much more efficient relaxation than Kramers species, resulting in a significantly weaker EPR absorption.

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response. It is well-known that Kramers ions such as Cr$^{III}$, Mn$^{II}$, and V$^{IV}$ produce high-amplitude HFPEPR resonances that dominate the spectrum even when present only as trace impurities in complexes of the non-Kramers analogues Cr$^{III}$, Mn$^{II}$, and V$^{IV}$, respectively.$^{31,33,34}$

**Structures of the Cr sites in Cr/SiO$_2$.** While XANES and EPR spectroscopies are appropriate for determining the oxidation states of Cr as it is progressively reduced to the catalyst precursor, they do not directly address the structures of the Cr sites in each oxidation state, or their uniformity. Recently, we addressed this in an EXAFS study of fully reduced Cr$^{III}$/SiO$_2$, concluding that two structures are likely present in a ratio that depends on the catalyst calcination temperature. Both involve Cr$^{II}$ embedded in a six-membered chromasiloxane ring, but with different numbers of additional bonds to Cr from Si—O—Si bridges (Scheme 2). The dominant species, based on

![Scheme 2. Proposed Structures for Two Chromate Sites (1, 2), Each Embedded in Six-Membered Chromasiloxane Rings (blue) on Highly Dehydroxylated Amorphous Silica; and the Resulting Cr$^{III}$ Sites (3, 4) Formed upon CO Reduction, as well as the Corresponding Carbonyl Complexes (5, 6)](image).

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Additional siloxane and carbonyl ligands are shown in red. Adapted from and reprinted with permission from ref 35. Copyright 2012 Elsevier.
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the XAFS analysis, is three-coordinate 4, posited as having a trigonal pyramidal geometry. It was proposed to be the more active site in initiating polymerization, based on the change in its relative abundance as the calcination temperature, and catalytic activity, increases. The less abundant, four-coordinate 3, suggested to be square pyramidal, was postulated to be less reactive.

Electronic spectra of Cr$^{III}$ species with coordination numbers of four or fewer are extremely rare, due to the high reactivity of these compounds.$^{37}$ Using the sol—gel matrix, we obtained high-quality transmission UV—vis spectra of the Cr$^{III}$ sites, recorded under rigorously anaerobic conditions. Figure 5 shows the spectrum of a Cr$^{III}$/SiO$_2$ monolith (0.5 mol % Cr), reduced at 350 °C until no further spectral changes were observed. Two bands are observed in the visible and near IR: a relatively intense band at 770 nm ($\varepsilon = 2240$ M$^{-1}$ cm$^{-1}$) and a very broad, weak band centered at 1229 nm ($\varepsilon = 354$ M$^{-1}$ cm$^{-1}$); notably, the magnitudes of the extinction coefficients are consistent with ligand field transitions of low symmetry ions. Similar spectral features for the Cr$^{III}$ were also reported by Budnyk et al., using the same approach of studying the Phillips catalyst with sol—gel materials.$^{38}$

In general, it is problematic to make structural assignments on the basis of electronic spectra, particularly in complex systems containing multiple species and oxidation states. Nevertheless, it is worthwhile to investigate whether the general features of the spectrum are consistent with our expectations for low-coordinate structures of Cr$^{II}$ (e.g., 3 and 4 in Scheme 2). In rigorous tetrahedral symmetry, Cr$^{II}$ has only one spin-allowed ligand field transition, from the $^4T_2$ ground state to the $^4E$ excited state, and it typically occurs in the near-infrared. For example, Cr$^{II}$ exhibits a weak, broad peak at 1020 nm assigned to that $^4T_2 \rightarrow ^4E$ ligand field transition.$^{37}$ Moreover, Cr$^{II}$ substituted into the tetrahedral sites of semiconductors such as CdS and ZnTe (which have weaker ligand fields than oxides) show low-intensity, low-energy ligand field bands at 1786 and 1820 nm, respectively.$^{40,41}$ In fact, emission from these low energy ligand field states has been investigated extensively for near-infrared laser applications.$^{42}$ Thus, the presence of the band at 1229 cm$^{-1}$ in Figure 5 can be viewed as diagnostic of Cr$^{II}$ ions in a low coordination environment.

The assignment of the much more intense, higher-energy transition at 770 nm is less obvious, although Cr$^{III}$-doped CdS and ZnTe exhibit transitions with similar relative intensities at 800 and 1000 nm, respectively.$^{40,41}$ The symmetry of the Cr sites in Cr$^{III}$/SiO$_2$ is lower than tetrahedral, thus the appearance of the second transition in Figure 5 is consistent with this reduction in symmetry. Structure 4 in Scheme 2, which was suggested to be the dominant structure present in the reduced Phillips catalyst, with approximate $C_3v$ symmetry, is closer to pseudotetrahedral than structure 3.$^{35}$ The symmetry reduction splits the triply degenerate $^4T_2$ ground state into $^4A_1$ and $^4E$ states (the higher $^4E$ state is unaltered), giving rise to two $^4A_1 \rightarrow ^4E$ spin-allowed transitions. The actual structure of the three-coordinate site will likely have even lower symmetry, as suggested by the unequal bond lengths found by EXAFS.$^{35}$ Further removing degeneracy. Using multiconfigurational second-order perturbation theory (CASPT2), Espelid and Børve calculated the electronic spectrum for a Cr$^{III}$ site attached to the surface by two Si—O—Cr linkages, (≡SiO)Cr$^{III}$, as a model for the Phillips Cr$^{III}$/SiO$_2$ site.$^{35}$ Its $C_{3v}$ symmetry results in a complete removal of the degeneracy of the T and E states found in $T_d$ symmetry. Their calculations predict a $^3B_1$ ground state with two fully allowed transitions at 1191 and 813 nm, corresponding to the $^3B_1 \rightarrow ^1A_1$ and the $^3B_1 \rightarrow ^2A_1$ ligand field transitions, respectively. These band positions agree well with the observed spectrum of Cr$^{III}$/SiO$_2$ in Figure 5. In contrast, four-coordinate Cr$^{III}$ (Scheme 2, structure 3), derived from octahedral symmetry by tetragonal distortion to square-planar, should have three spin-allowed ligand field bands. Cr$^{III}$ species in tetragonally distorted octahedral fields are well-

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Figure 5. UV−vis spectrum of the CrII site obtained by reduction of a CrVI/SiO2 xerogel (0.5 mol % Cr) with flowing CO at ambient pressure and 350 °C. (Note: sharp features marked * are overtone and combination bands associated with residual surface silanols.)

known, and their lowest energy transitions are typically much higher in energy than those observed for four-coordinate species. Of course, species such as could contribute to the higher energy regions of the spectrum, as could the minor CrIII sites formed during CO reduction. However, the spectrum and, in particular, the broad low energy transition at 1229 cm−1, are consistent with low symmetry CrII.

The transparency of the Cr−SiO2 sol−gel monoliths in the visible region also greatly facilitates the collection of Raman spectra, which can provide complementary structural information about the Cr sites as a function of the degree of reduction. Figure 6 shows Raman spectra in the region below 1300 cm−1, where the Cr−O vibrations are expected. The vibrational spectrum of CrVII/SiO2, shown in Figure 6a, has already been assigned in some detail. The intense band at 982 cm−1 is typically attributed to totally symmetric, predominantly terminal, CrO2 stretching. The origin of the weaker band at 997 cm−1 is complex and includes contributions from antisymmetric CrO2 stretching. The spectrum in Figure 6b was acquired immediately following CO reduction for 1 h at 230 °C to generate the CrIV site. It shows a very intense, sharp band at 988 cm−1 (fwhm 8 cm−1) with a shoulder on the high energy side (ca. 1000 cm−1). As indicated in Scheme 1b, the first reduction by CO is proposed to remove one of the two terminal oxo ligands from the grafted chromate ester. Since the 988 cm−1 band occurs in the spectral region associated with the terminal Cr=O stretches of the bis(oxo)CrVII site, and since the band is similarly sharp and intense, we tentatively assign it to a mode dominated by Cr=O stretching of mono(oxo)CrIV (i.e., chromyl). Consistent with this assignment, the band is strongly polarized, indicating that it is a symmetric stretch. It is unlikely, however, that the CrIV site is as coordinately unsaturated as depicted in Scheme 1b. It likely coordinates to the silica through one or two additional siloxane ligands (resulting in nominal C3v or C4v site symmetry). In fact, the Raman spectrum in Figure 6b is very similar to that of a nominally C3v-symmetry silica-supported vanadyl, (≡SiO)2V=O. Finally, we note that the Raman spectra of the CrIV material was collected using 633 nm excitation, which yielded the highest quality spectrum. However, since excitation at this wavelength impinges on the electronic absorption bands, resonant enhancement of the metal oxo bands can occur.

The Raman spectrum after CO reduction to CrII at 350 °C is shown Figure 6c. Consistent with removal of the last terminal oxo ligand (Scheme 1c), the sharp band at 988 cm−1 is absent. The only band clearly attributable to the CrII site is a weak band at 977 cm−1 (fwhm 25 cm−1). All other bands are modes intrinsic to SiO2, although the spectral region below ~1100 cm−1 is congested and likely contains contributions from Si−O−Si and Si−O−Cr modes.

**Adsorbed CO as a Probe of the CrII Sites.** After CO reduction at 350 °C, the most prominent feature in the Raman spectrum is a sharp, very intense band at 2183 cm−1, Figure 7a. This band, as well as three significantly weaker bands at 2155, 2137, and 2119 cm−1, have been observed previously by IR spectroscopy and represent stretching modes associated with CO coordinated to the CrII sites. Evacuating the system (10−4 Torr) overnight at room temperature caused the low frequency CO modes to disappear, leaving only the attenuated high frequency band (Figure 7b). Heating under vacuum for 2 h at 250 °C (Figure 7c) resulted in almost complete removal of
CO	extsubscript{2} with only a weak remnant of the band at 2183 cm\textsuperscript{−1} still visible. Once the CO is removed, re-exposure of Cr	extsuperscript{II}/SiO\textsubscript{2} to CO at room temperature regenerates the initial spectrum, showing all four bands at the same relative intensities. Excitation into the absorption bands of the Cr	extsuperscript{II} ions makes resonant enhancement of the carbonyl stretches possible. The modes that are enhanced depend on their symmetry, as well as that of the excited state being pumped. An inherently low symmetry system such as this one will likely experience enhancement of the totally symmetric vibrational modes (i.e., A-term enhancement). However, resonant enhancement of carbonyl stretches typically occurs through excitation into LMCT bands involving the carbonyl, which is not the case here.\textsuperscript{49−51} Regardless, we refrain from drawing quantitative conclusions from the relative intensities of the bands.

Carbonyl ligands coordinated to the Cr	extsuperscript{II} sites of the Phillips catalyst have been studied extensively by IR, with the goal of distinguishing Cr	extsuperscript{II} sites having different coordination geometries. In earlier studies of the Phillips catalyst, made through traditional wet impregnation of silica with Cr	extsuperscript{III} compounds, three IR bands at 2191, 2184, and 2179 cm\textsuperscript{−1} were observed at CO pressures roughly corresponding to our experimental conditions (ca. 1 atm CO). These bands were assigned to monocarbonyl (2191 cm\textsuperscript{−1}) and dicarbonyl (2184 and 2179 cm\textsuperscript{−1}) sites.\textsuperscript{3} In a study of a model Phillips catalyst made by anhydrous grafting of CrO\textsubscript{2}Cl\textsubscript{2} onto silica, three carbonyl bands were also observed at similar frequencies: 2191, 2186, and 2179 cm\textsuperscript{−1}.\textsuperscript{35} Based on their correlated changes in intensity as CO was progressively removed from the catalyst, the bands at 2191 and 2179 cm\textsuperscript{−1} were determined to belong to the same site and were assigned to the symmetric and antisymmetric modes of a dicarbonyl species, whereas the band at 2186 cm\textsuperscript{−1}, whose intensity is independent of the other two, was assigned to the stretching of a monocarbonyl species.

The position of the most intense band at 2183 cm\textsuperscript{−1} agrees well with that of the band assigned to the monocarbonyl site by Zhong et al.\textsuperscript{35} In comparison to IR spectra of comparable materials made by wet impregnation or grafting onto silica, the observable bands are spread out over a somewhat larger spectral window, from ca. 2110 to 2200 cm\textsuperscript{−1}. Although we cannot completely rule out the possibility that we are observing carbonyl species not detected in previous IR studies, this seems unlikely given the much lower inherent sensitivity of Raman experiments. Because it is known that metal carbonyl vibrations both broaden and shift in energy due to interactions with metal oxide surfaces,\textsuperscript{52,53} the spreading of the mono- and dicarbonyl stretching frequencies over a wider spectral window likely arises from interactions of the carbonyl groups with walls of the silica xerogel network instead. Although the sol–gel matrix is mesoporous, the pore size distribution is broad, with a significant microporous region. Consequently, Cr sites incorporated into the matrix by co-condensation may experience microenvironments that allow interactions of the carbonyl ligands with the matrix surrounding them.

Raman spectra for CO-reduced Cr	extsuperscript{II}/SiO\textsubscript{2}, collected under both parallel and perpendicular polarization conditions, are shown in Figure 8. The intense band at 2183 cm\textsuperscript{−1} is strongly polarized, as are the two weaker bands at 2155 and 2137 cm\textsuperscript{−1}, indicating that they are all totally symmetric modes. Only one transition, the lowest energy mode at 2119 cm\textsuperscript{−1}, is nonpolarized. It can therefore be assigned with certainty to the antisymmetric stretch of a dicarbonyl species. With this assignment, two of the totally symmetric bands are assignable to the symmetric modes of mono- and dicarbonyl species, while the assignment of the third is unclear.

![Figure 7. Raman spectra of Cr/SiO\textsubscript{2} (1.0 mol % Cr): (a) immediately after reduction with CO at 350 °C for 4 h, (b) after subsequent evacuation overnight (10\textsuperscript{−4} Torr), and (c) after evacuation for 2 h (10\textsuperscript{−4} Torr) at 250 °C. Spectra are normalized to the intensity of the low frequency silica modes that are invariant.](image)

![Figure 8. Parallel- and perpendicularly polarized Raman spectra of the carbonyl stretching region, for Cr\textsuperscript{II}/SiO\textsubscript{2} (1.0 mol % Cr) prepared by reduction with CO at 350 °C for 4 h.](image)
To aid in assigning the totally symmetric bands, a DFT calculation was carried out on an optimized dicarbonyl site, based on structure 5 in Scheme 2 (see Supporting Information). The unscaled values of the predicted frequencies for the antisymmetric and symmetric carbonyl stretches are 2183 and 2212 cm$^{-1}$, respectively (Table 1). Notably, the antisymmetric mode appears at the lower energy, consistent with its assignment in the experimental spectrum. Because its experimental frequency is known, it was used to obtain a frequency-independent multiplicative scaling factor (0.971).45 Using this scaling factor, the calculated frequency of the symmetric stretch is 2152 cm$^{-1}$, in very good agreement with the band observed at 2155 cm$^{-1}$. The difference between the symmetric and antisymmetric stretches is 36 cm$^{-1}$, larger than that observed by Zhong et al.35 However, the energy difference between the symmetric and antisymmetric components depends strongly on the angle between the carbonyls through the cosine dependence of the off-diagonal terms that couple them in the Wilson FG matrix. Our results indicate that the angle is larger in these xerogel materials than for materials made by grafting CrO$_2$Cl$_2$ onto nonporous silica, consistent with interactions imposed by the xerogel pore system.

The totally symmetric stretch at 2183 cm$^{-1}$ is therefore assigned with confidence to a monocarbonyl site, by comparison to the reported IR frequency for that site at 2186 cm$^{-1}$.35 Our DFT calculations for structure 6 predict the unscaled frequency of this band to be 2210 cm$^{-1}$, within 1.2% of the observed value and well within the accepted range for DFT calculations (see Supporting Information). Thus, the only peak that remains to be assigned is the weak, symmetric band at 2137 cm$^{-1}$. It may be, at least in part, the $^{13}$C contribution of the intense monocarbonyl mode. The DFT-calculated frequency for the stretching of Cr($^{13}$CO) is 52 cm$^{-1}$ lower than the Cr($^{12}$CO) mode, or 2131 cm$^{-1}$, in very good agreement with the frequency of the unassigned band, Table 1.

The ratio of integrated intensities for the Cr($^{13}$CO)/Cr($^{12}$CO) modes is approximately 6%, which is higher than the natural abundance of $^{13}$C (ca. 1%). Thus, we cannot rule out a contribution from another monocarbonyl site, possibly derived from structure 5 through loss of a carbonyl. One final point worth noting is that coordination of CO appears to result in little or no perturbation of the metal-oxide region of the Raman spectrum. The lack of coupling is consistent with weak Cr-CO bonding, as expected for Cr$^{III}$ with its relatively poor $\pi$-back-donation properties.

**Table 1. Experimental and Calculated Frequencies for Mono- and Dicarbonyl Cr$^{III}$ Sites**

<table>
<thead>
<tr>
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<th>experimental (cm$^{-1}$)</th>
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<td>2155</td>
<td>2152$^a$</td>
</tr>
<tr>
<td></td>
<td>$\nu_s$</td>
<td>2119</td>
<td>2119$^a$</td>
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<tr>
<td>Cr($^{12}$CO)</td>
<td>$\nu_s$</td>
<td>2183</td>
<td>2183$^b$</td>
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<tr>
<td>Cr($^{12}$CO)</td>
<td>$\nu_s$</td>
<td>2137</td>
<td>2131</td>
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$^a$Scaled by a factor of 0.971. $^b$Scaled by a factor of 0.988, which brings the calculated band into agreement with the $^{12}$CO symmetric stretch so the frequency of the $^{13}$CO band could be predicted.

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**Figure 9.** UV-vis spectra of (a) the Cr$^{III}$ precatalyst, before its reaction with ethylene (1) and after its complete reaction with ethylene (2); and (b) spectroscopic changes recorded for a 0.5 mol % Cr/SiO$_2$ xerogel initially reduced with CO at 350 °C, then titrated with aliquots of ethylene at 80 °C. (Note: the sharp features at ca. 1375 and 1230 nm are overtone and combination bands associated with silanol fundamentals.)39

$^{13}$C under flowing CO, while the progress of the reduction was monitored by UV–vis spectroscopy. Reduction to Cr$^{III}$ was judged to be complete when no further spectral changes were observed. The monolith was then flushed with Ar to remove all CO, both infused and coordinated. The full spectrum of the Cr$^{III}$ site prior to reaction with ethylene is shown in Figure 9a as spectrum 1. After reduction, the temperature was reduced to 80 °C, and the sample was “titrated” with highly dilute aliquots of ethylene; after each injection, a UV–vis spectrum was recorded (Figure 9b).

The spectrum changes slowly but dramatically over the course of the titration, with the peak at 770 nm disappearing and a new peak at 490 nm emerging. Consistent with the spectral changes, the material changes from pale blue to dark green during this process (Scheme 1c,d). The reaction appears to proceed cleanly, albeit with deviation from a true isosbestic point at ca. 700 nm. The final spectrum after titration, when no further spectral changes are observed, is shown in Figure 9a as spectrum 2. Three independent samples were treated in this way until no further spectral changes were observed. Elemental analysis of these materials revealed the presence of carbon, consistent with the product being an organoCr species. (Control samples of Cr/SiO$_2$ xerogels showed, at best, trace amounts of carbon both before and after CO reduction.) Quantitative analysis yielded an average C/Cr ratio of (1.9 ± 0.2) (see Supporting Information), suggesting that at the end point of the titration, when no further changes are observed in the UV–vis spectrum, the material has taken up, on average, one ethylene per Cr site.

The oxidation state of the ethylene-titrated sample was determined from Cr $L_3$-edge XANES, by comparison to the binary oxides of Cr as reference standards (Figure S7). The XANES is consistent with Cr$^{III}$, Figure 10, with no evidence for Cr$^{IV}$ or, as has been postulated for the Phillips initiating site, Cr$^{V}$.$^a$
The UV–vis spectrum is consistent with the oxidation state at the end of the ethylene titration being Cr\textsuperscript{III}. The final spectrum (Figure 9a, spectrum 2) is characterized by two resolved but strongly overlapping bands at 676 nm (1240 M\textsuperscript{-1} cm\textsuperscript{-1}) and 463 nm (1570 M\textsuperscript{-1} cm\textsuperscript{-1}). Notably absent is any intensity above ca. 1100 nm, which would be associated with persistent Cr\textsuperscript{II}. As described above, the Cr\textsuperscript{II} sites in the precatalyst exist in a weak ligand-field environment and most have low coordination numbers (3 or 4). Upon reaction with ethylene, the resulting Cr\textsuperscript{III} sites will likely have higher coordination numbers and, due to the presence of the organic ligand, lower symmetry. Spectroscopic characterization of Cr\textsuperscript{III} ions substituted into the octahedral sites of oxide matrices reveals two spin-allowed ligand field bands, \( \tilde{\text{A}}_{\text{eg}} \rightarrow \tilde{\text{T}}_{\text{eg}} \) and \( \tilde{\text{A}}_{\text{eg}} \rightarrow \tilde{\text{T}}_{\text{lg}} \). For example, they are observed at 580 and 430 nm in Cr-doped MgGa\textsubscript{2}O\textsubscript{4} and at 580 and 410 nm in Cr-doped KZnCl\textsubscript{2}O\textsubscript{4}.\textsuperscript{55,56} Cr\textsuperscript{III} in tetrahedral sites also shows two ligand field transitions, both \( \tilde{T}_{1} \rightarrow \tilde{T}_{1} \), and both observed at much longer wavelengths. For example, bands at 765 and 1490 nm were reported for Cr\textsuperscript{III} substituted into a lithium–gallium spinel.\textsuperscript{57} The transitions observed for the Phillips active sites are clearly more consistent with Cr\textsuperscript{III} in an octahedral ligand field. However, we do not wish to imply that the site is rigorously octahedral. Instead, it likely has a coordination number higher than four. Notably, the magnitude of the extinction coefficients are consistent with Laporte-allowed transitions, which suggests a symmetry lower than octahedral.\textsuperscript{37} It is also significant that transformation of (nominally) distorted tetrahedral Cr\textsuperscript{III} to (nominally) distorted octahedral Cr\textsuperscript{III} would result in a large gain in ligand field stabilization energy, which would help to drive the one-electron oxidation process.

Further evidence for the oxidation state change upon reaction of Cr\textsuperscript{II}/SiO\textsubscript{2} with ethylene is found in the HFEPR spectrum. Resonances associated with Cr\textsuperscript{IV} disappear from the spectrum upon exposure to the olefin (Figure 11). Concomitant with the loss of the non-Kramers Cr\textsuperscript{III} resonances, the intensity of the transitions belonging to the Kramers spin at ca. \( g = 2 \) (3.77 T) increases dramatically, consistent with oxidation of Cr\textsuperscript{II} to Cr\textsuperscript{III}. Notably, no signals are detected for Cr\textsuperscript{IV} which, being a non-Kramers ion, like Cr\textsuperscript{II}, should therefore have resonances that are well separated from the Kramers region of the spectrum.
differing coordination environments.\textsuperscript{35} Thus, the inability of a model Cr\textsuperscript{III} catalyst to polymerize ethylene may merely reflect the poor reactivity of dimeric and oligomeric Cr\textsuperscript{III}. Finally, the modest polymerization activity of a related model supported Cr\textsuperscript{III} complex is not unprecedented in prior literature. The phenomenon has been discussed by McDaniel in his review of the Phillips process,\textsuperscript{7} which notes that, while superlative results have often been claimed for polymerization by Cr\textsuperscript{III}, commercial reactors have never been able to confirm anything but minimal activity. Our own recent computational study of the proposed nonredox-based initiation by ethylene deprotonation revealed it to be implausible for both Cr\textsuperscript{III} and Cr\textsuperscript{IV}.\textsuperscript{39}

In summary, our results show that the generation of the Phillips catalyst active sites occurs through a multistep redox process which converts the supported Cr\textsuperscript{III} sites to Cr\textsuperscript{IV}. This finding is consistent with many other prior studies of the Phillips system. Using CO as the reductant, the Cr\textsuperscript{IV} sites were obtained as intermediates. However, they retain a terminal oxo ligand and are unreactive toward ethylene. Distinct from previous studies, we find that the Cr\textsuperscript{III} sites are oxidized to organoCr\textsuperscript{VI} sites in a stoichiometric reaction with ethylene. The resulting material polymerizes ethylene, suggesting that these organoCr\textsuperscript{VI} species are the initiating sites.

\section*{EXPERIMENTAL METHODS}

\textbf{Fabrication of Cr-SiO\textsubscript{2} Xerogels.} Transparent, porous silica xerogels containing between 0.5 and 3.0 mol % Cr were made by co-condensation of tetramethylorthosilicate (TMOS) with CrO\textsubscript{3} in an aqueous ethanol solution, following published procedures.\textsuperscript{5,16} The solutions were allowed to gel, aged at room temperature over a period of 3–4 months, then slowly dried in air at 100 °C and calcined at 500 °C. This resulted in transparent yellow-orange monoliths (depending on the Cr concentration), containing Cr\textsuperscript{VI} sites well dispersed throughout the silica matrix.

\textbf{CO Reduction and Ethylene Titration of Cr-SiO\textsubscript{2} Xerogels.} In situ monitoring of reduction of the Cr/SiO\textsubscript{2} materials was carried out in a closed, high-temperature/high-pressure UV–vis cell equipped with sapphire windows. In a typical experiment, a Cr\textsuperscript{IV}/SiO\textsubscript{2} xerogel monolith (1.5 × 0.5 × 0.5 mm) was mounted in the cell and calcined in flowing O\textsubscript{2} at 230 °C for approximately 2 h. Reduction was carried out under flowing CO isothermally at either 230 or 350 °C while monitoring the changes in the UV–vis spectrum. Reduction was considered complete when the spectrum ceased to change. Oxidation by ethylene was monitored by delivering small aliquots of ethylene to the Cr\textsuperscript{III}/SiO\textsubscript{2} monolith at 80 °C, while monitoring the spectral changes.

\textbf{X-ray Absorption Near-Edge Spectroscopy.} Hard X-ray absorption near-edge spectroscopy (XANES) data at the Cr K-edge was acquired on beamline BL2–3 (Bend) at the Stanford Synchrotron Radiation Laboratory (SSRL). Soft XANES data were acquired at undulator beamline 8.0.1 at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory. Spectra of binary oxide standards were recorded for samples pressed as powders onto carbon tape.

\textbf{HFEPR Spectroscopy.} HFEPR experiments were performed at the National High Magnetic Field Laboratory, using a home-built instrument described previously.\textsuperscript{50} HFEPR spectra were acquired for Cr\textsuperscript{III}/SiO\textsubscript{2} and Cr\textsuperscript{III}/SiO\textsubscript{2} (3.0 mol % Cr), packed into sealed quartz ampules under rigorously anaerobic and anhydrous conditions, at three frequencies (ca. 106, 212, and 317 GHz).

\textbf{Raman Spectroscopy.} Raman spectra were collected on Cr/SiO\textsubscript{2} xerogel monoliths (1.5 × 0.5 × 0.5 mm\textsuperscript{3}, 1.0 mol % Cr). Samples were placed in a quartz cell equipped with a cylindrical reaction container for in situ high temperature experiments, attached to a side arm equipped with a spectroscopic cell. Raman spectra were obtained using a micro-Raman spectrometer (JY Horiba LabRam HR800), with excitation at 633 nm (HeNe laser) or 785 nm (infrared diode laser).

\section*{COMPUTATIONAL METHODS}

\textbf{Density Functional Calculations.} Structural models used in the computational analysis of vibrational frequencies were built and optimized using Spartan\textsuperscript{10,11} and Spartan\textsuperscript{14} (Wave function, Inc. Irvine, CA; \texttt{www.wavefun.com}) running on a MacBook Pro. Chromasiloxane model structures were built to correspond to surface models 3 and 4 in Scheme 2, as suggested by EXAFS.\textsuperscript{35}

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00927.

Materials, methods, and experimental details of each step in the reaction sequence, as well as product characterization and Cartesian coordinates of calculated structures (PDF).

Structural models as sdf files (ZIP).

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\section*{Notes}

The authors declare no competing financial interest.

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