Polymerization Mechanisms

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Polymerization of Ethylene by Silica-Supported Dinuclear Cr^{III} Sites through an Initiation Step Involving C–H Bond Activation

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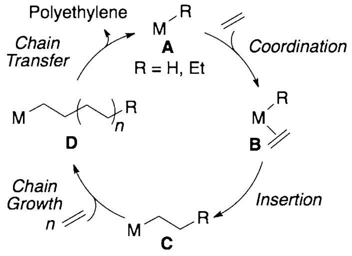
***Abstract:** The insertion of an olefin into a preformed metal–carbon bond is a common mechanism for transition-metal-catalyzed olefin polymerization. However, in one important industrial catalyst, the Phillips catalyst, a metal–carbon bond is not present in the precatalyst. The Phillips catalyst, CrO_3 dispersed on silica, polymerizes ethylene without an activator. Despite 60 years of intensive research, the active sites and the way the first Cr–C bond is formed remain unknown. We synthesized well-defined dinuclear Cr^{II} and Cr^{III} sites on silica. Whereas the Cr^{II} material was a poor polymerization catalyst, the Cr^{III} material was active. Poisoning studies showed that about 65 % of the Cr^{III} sites were active, a far higher proportion than typically observed for the Phillips catalyst. Examination of the spent catalyst and isotope labeling experiments showed the formation of a Si–(μ-OH)–Cr^{III} species, consistent with an initiation mechanism involving the heterolytic activation of ethylene at Cr^{III}–O bonds.*

Olefin-insertion polymerization catalysts contain a metal–carbon (or a metal–hydride) bond and an open coordination site to accommodate incoming molecules of ethylene (Scheme 1, **A**). Coordination of ethylene forms the alkyl–ethylene complex **B**, which undergoes olefin insertion to give **C**. Growth of the polymer chain is a repetition of this step until chain transfer occurs. Chain transfer depends on the conditions and chosen catalyst, but generally takes place through β-hydride elimination, transmetalation to an alkyl aluminum species, hydrogenolysis, or through a direct β-proton transfer to a coordinated ethylene molecule.[1] The metal product then reenters the catalytic cycle.

Generation of the catalytically active polymerization species containing the necessary metal–carbon bond, whether Ziegler–Natta catalysts or more well defined systems, requires the treatment of the precatalyst, typically a supported or ligated metal chloride, with alkyl aluminum reagents, such as methylaluminoxane (MAO) or triethylaluminum.[2] Alternatively, metal–alkyl derivatives are treated with a Lewis acid to abstract one of the alkyl groups to generate the active species.[3]



Scheme 1. Generally accepted mechanism for ethylene polymerization by metal–alkyl complexes.

Exploitation of this general mechanism has led to a large family of catalysts that can polymerize olefins with control of the polymer molecular-weight distribution,[4] incorporate long-chain branches,[5] and stereoselectively polymerize α-olefins.[6] This mechanism applies to "chain-shuttling" catalysis,[7] surface-supported organometallic species,[8] and cationic/neutral nickel[9] and palladium[10] complexes that can tolerate polar functionalities.[11]

The chromium-based Phillips catalyst seemingly defies this mechanism. This catalyst, discovered in 1951, currently accounts for 40–50 % of global linear high-density polyethylene (PE).[12] The catalyst precursor is prepared by dispersing CrO_3 on silica; exposure to ethylene forms a "reduced" chromium active site that polymerizes ethylene without a cocatalyst. The absence of a preformed Cr–C bond in this composition separates this class of catalysts from the family of olefin-insertion catalysts mentioned above.

Spectroscopic analysis of the Phillips catalyst involves multiple techniques (IR, UV/Vis, EPR, XAS, etc.) to obtain data about the surface Cr species.[13] Since only about 10 % of the chromium present is active in polymerization,[14] the spectroscopic information relates mostly to inactive sites. Due to this obstacle, even fundamental information about the Phillips catalyst, such as the active-site structure and the functional oxidation state, remain controversial. From spectroscopic studies, the major species observed in the reduced Phillips catalyst are isolated Cr^{II} sites, which are often interpreted as active species.[15] Related empirical studies have shown that silica-supported Cr^{III} salts are ethylene-polymerization catalysts.[16] These complications limit the understanding of this catalyst. The grafting of inorganic chromium compounds[17] or organometallic chromium complexes onto silica[18] has also been investigated, although in each case access to isolated Cr^{II} or Cr^{III} silicates was not

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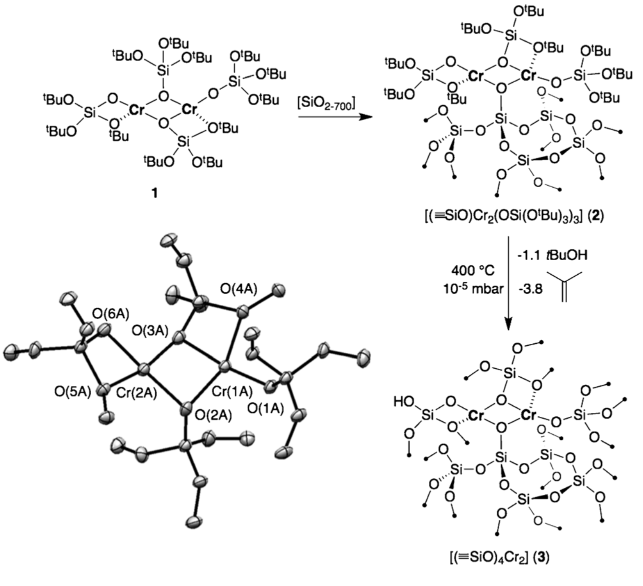
possible owing to the incorporation of ligands around the metal center. Herein, we describe the formation and detailed characterization of silica-supported dinuclear Cr^{II} and Cr^{III} sites. We found that the Cr^{III} silicates are highly active, in contrast to the Cr^{II} analogues, and we propose that ethylene polymerization initiates through the heterolytic C–H bond activation of ethylene on a Cr–O bond.

The ligand environment around the chromium center is critical for metal-silicate formation. We chose tri-*tert*-butoxysiloxy ($-OSi(OtBu)_3$) as a ligand for the coordination of chromium because these complexes are known to decompose at relatively low temperatures (ca. 200 °C) into silica materials through the loss of isobutene, *tert*-butanol, and water.[19] We envisioned that the grafting of a hypothetical Cr^{II} complex containing only $-OSi(OtBu)_3$ ligands on silica dehydroxylated at 700 °C (ca. 0.8 SiOH nm^{-1}), followed by thermal treatment, would yield well-defined Cr^{II} sites on the silica surface without additional ligands.

$Cr\{N(SiMe_3)_2\}_2 \cdot 2THF$[20] was treated with two equivalents of $HOSi(OtBu)_3$ to give the blue crystalline Cr^{II} dimer $[\{Cr(OSi(OtBu)_3)_2\}_2]$ (**1**) in 60 % yield. The ^1H NMR spectrum of **1** in C_6D_6 contained a broad signal at $\delta = 1.77$ ppm ($\nu_{1/2}$=530 Hz, $\mu_{eff} = 5.99\ \mu_B$). Compound **1** crystallized as two independent molecules in the unit cell with similar bond lengths and angles; one of the molecules is shown in Scheme 2. Compound **1** contains two chromium atoms in distorted square-planar geometries, typical for high-spin Cr^{II} species. The Cr–Cr distance in **1** is 2.884(2) Å, which is outside the range for significant metal–metal bonding. The terminal Cr(2A)–O(1A) and Cr(1A)–O(4A) bonds have a length of 1.934(4) and 1.984(4) Å, respectively, similar to other chromium siloxide complexes.[21] The bridging Cr–O(2A) and Cr–O(3A) distances are slightly longer than the terminal Cr–O bonds. Besides the terminal and bridging chromium–oxygen bonds in **1**, two $-OSi(OtBu)_3$ ligands coordinate through a O*t*Bu fragment to satisfy the distorted square-planar geometry; these distances are longer (2.109(4) and 2.167(4) Å, respectively).

When a blue solution of **1** in benzene was brought in contact with silica (Aerosil-200) partially dehydroxylated at 700 °C (0.26 mmol SiOH g^{-1}), immediate blue coloration of the solid resulted. A combination of mass-balance (0.16 mmol SiOH g^{-1}) and elemental analysis (0.31 mmol Cr g^{-1}; 18 C atoms per Cr atom) was consistent with the presence of chromium dimers on the silica surface and indicated that $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**; Scheme 2) had formed. Thermal treatment of $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**) under high vacuum (10^{-5} mbar) yielded the blue solid $[(\equiv SiO)_4Cr_2]$ (**3**; Scheme 2). Analysis of the volatile products gave 3.6 equivalents of isobutene and 1.1 equivalents of *t*BuOH per Cr atom, which is close to the expected value of 4.5 C_4 products per Cr atom. The infrared spectrum of this material lacked ν_{CH} bands but did contain new silanol vibrations. Exposure of $[(\equiv SiO)_4Cr_2]$ (**3**) to excess CO resulted in one ν_{CO} band at 2189 cm^{-1}, thus indicating a rather narrow distribution of surface species. This particular vibration has been observed for the reduced Cr/SiO_2 Phillips catalyst upon exposure to CO, although multiple other vibrations are also observed because many Cr sites are present in the Phillips catalyst.[22]

We performed XAS experiments at the Cr K-edge to gain deeper insight into the structure and oxidation state of the grafted species. X-ray absorption near-edge (XANES) spectra for the molecular precursor **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), and $[(\equiv SiO)_4Cr_2]$ (**3**) are shown in Figure 1. The XANES spectrum of the molecular species **1** is nearly identical to those of $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**) and $[(\equiv SiO)_4Cr_2]$ (**3**), thus indicating that the oxidation state and the local geometric



Scheme 2. Grafting of **1** on SiO_{2-700} to form $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**) and thermal decomposition under high vacuum to yield $[(\equiv SiO)_4Cr_2]$ (**3**). The solid-state structure obtained by X-ray diffraction for an independent molecule of **1** is shown at 50 % probability. Methyl groups of $-OSi(OtBu)_3$ ligands and H atoms have been removed for clarity.

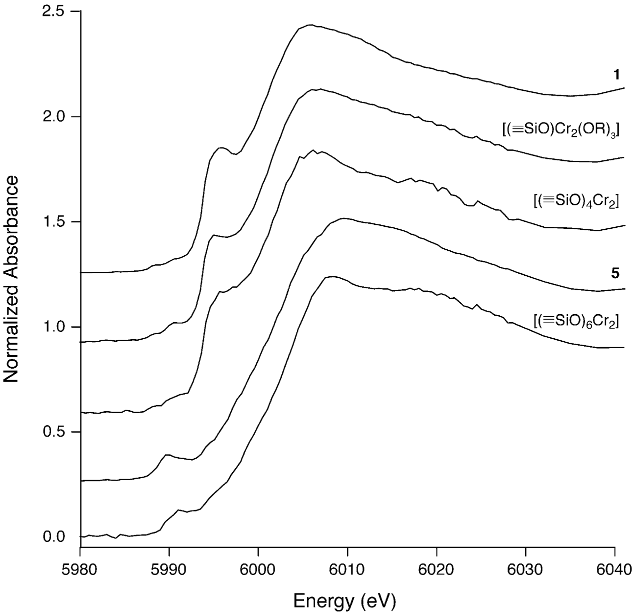


Figure 1. XANES spectra (collected in the transmission mode) of **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), $[(\equiv SiO)_4Cr_2]$ (**3**), $[(\equiv SiO)_6Cr_2]$ (**4**), and **5**.

structure of chromium in these materials is very similar to those in molecular precursor **1**.

The results of the extended X-ray absorption fine structure (EXAFS) analysis of **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), and $[(\equiv SiO)_4Cr_2]$ (**3**) are summarized in Table 1. The Cr–O, Cr–Si, and Cr–Cr scattering paths used in our model correspond to the nearest neighbors present in **1**. To reduce the number of variables, we used oxygen scattering paths corresponding to the average Cr–O distance in each species (Table 1). For **1**, we compared the average Cr–O fit with a fit based on four independent oxygen scattering paths corresponding to the Cr–O distances in the crystal structure of **1**. The quality of both fits (see the Supporting Information) was statistically similar. We used this approach for all structures, which explains the higher effective Debye–Waller factors for the O coordination shell (Table 1).

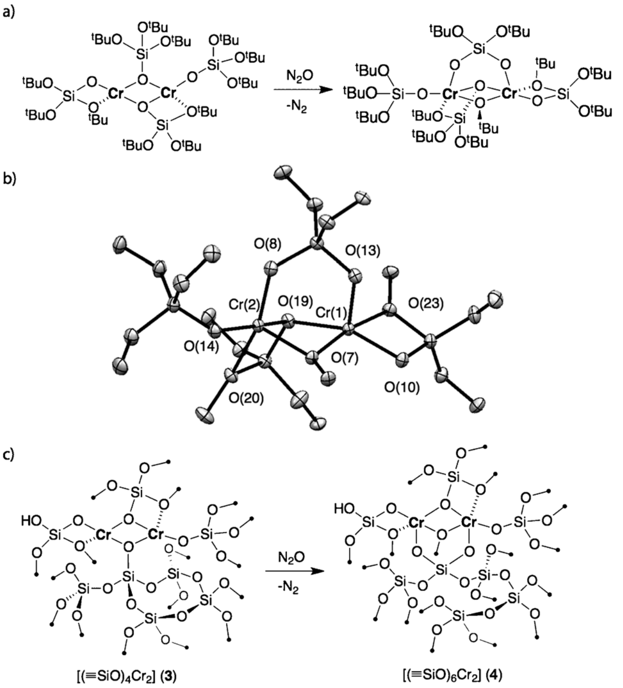
Table 1: EXAFS fit parameters for **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), $[(\equiv SiO)_4Cr_2]$ (**3**), $[(\equiv SiO)_6Cr_2]$ (**4**), and **5**.[a]

Sample	Neighbor	N[b]	r [Å][c]	σ^2 [Å^2][d]
1[e]	O	4	2.03	0.013(1)
	Si	1	2.77	0.0058(23)
	Cr	1	2.89	0.0045(12)
2[e]	O	4	1.98(1)	0.0093(11)
	Si	1	2.73(3)	0.0058
	Cr	1	2.93(2)	0.0045
3[e]	O	4	2.00(1)	0.0072(8)
	Si	1	2.66(2)	0.0056(29)
	Cr	1	2.98(2)	0.0045(19)
4[e]	O	5	2.00(1)	0.012(1)
	Si	1	2.69(1)	0.0098(43)
	Cr	1	3.01(1)	0.0052(19)
5[f]	O	5	1.96(1)	0.016(1)
	Si	1	2.59(1)	0.0071(18)
	Cr	1	2.96	0.0042(10)

[a] Values without errors were fixed. [b] Number of neighbors. [c] Distance between Cr and the neighbor(s). [d] Debye–Waller factor. [e] The measurement was made at 100 K in the fluorescence mode. [f] The measurement was made at 298 K in the fluorescence mode.

We anticipated that $[(\equiv SiO)_4Cr_2]$ (**3**) would initiate ethylene polymerization because this material contains Cr^{II} sites on silica. The polymerization activity of $[(\equiv SiO)_4Cr_2]$ was monitored at a low ethylene pressure (ca. 300 mbar) in a glass reactor equipped with an IR cell. To accurately determine the polymerization activities, we used Sylopol-948, an amorphous silica support composed of particles that fragment when polymer is formed, to avoid mass-transfer limitations. $[(\equiv SiO)_4Cr_2]$ has a low initial polymerization activity of 1.6 kg PE (mol Cr)$^{-1}$ h^{-1}. The addition of 4-methylpyridine (20 mol %) to this material resulted in negligible polymerization activity. Furthermore, the EPR spectrum of $[(\equiv SiO)_4Cr_2]$ at 100 K contained a weak EPR signal that is characteristic Cr^{III}, suggesting that the active sites on $[(\equiv SiO)_4Cr_2]$ could arise from small amounts of Cr^{III}. This result was surprising owing to the wealth of literature that has implicated Cr^{II} as the active site during polymerization catalysis.[12,15b,23]

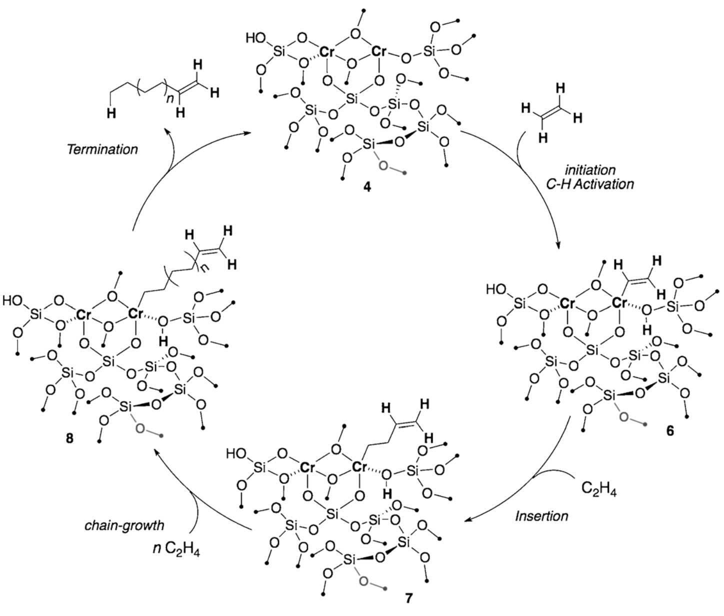
The treatment of $[(\equiv SiO)_4Cr_2]$ with N_2O, as inspired by a recent report showing that N_2O increases the ethylene-polymerization activity of the reduced Phillips catalyst,[24] led to the formation of the Cr^{III} dimer $[(\equiv SiO)_6Cr_2]$ (**4**; Scheme 3c). The Cr K-edge XANES spectrum of $[(\equiv SiO)_6Cr_2]$ (Figure 1) was shifted relative to those of **1**, $[(\equiv SiO)Cr_2(OSi(OtBu)_3)_3]$ (**2**), and $[(\equiv SiO)_4Cr_2]$ (**3**). Also, a pre-edge feature at 5990–5992 eV appeared. Exposure of $[(\equiv SiO)_6Cr_2]$ (**4**) to ethylene at 25 °C resulted in the rapid saturation of the ν_{CH} region in the IR spectrum and the formation of a white film on the pellet, thus indicating ethylene polymerization.



Scheme 3. a) Reaction of **1** with N_2O to give **5**. b) Solid-state structure of **5** as obtained by X-ray diffraction. Methyl groups of $-OSi(OtBu)_3$ ligands and H atoms have been removed for clarity. c) Surface rearrangement of $[(\equiv SiO)_4Cr_2]$ (**3**) to form $[(\equiv SiO)_6Cr_2]$ (**4**).

Although the XANES spectrum is consistent with the oxidation of $[(\equiv SiO)_4Cr_2]$ (**3**) by N_2O to give $[(\equiv SiO)_6Cr_2]$ (**4**), we confirmed this proposal by preparing the corresponding molecular analogue. Exposure of the Cr^{II} dimer **1** to N_2O resulted in purple single crystals of **5** (Scheme 3 a,b). X-ray crystallographic analysis revealed that the two five-coordinate Cr^{III} centers had different geometries: Cr(1) adopted a distorted trigonal-bipyramidal geometry, whereas the Cr(2) center had a square-pyramidal geometry typical of five-coordinate metal species. The Cr–Cr distance in **5** was 2.966(1) Å and thus slightly longer than in **1**. Importantly, the Cr K-edge XANES spectrum of **5** contained similar edge and pre-edge features to those of $[(\equiv SiO)_6Cr_2]$ (**4**). This result confirms that the chromium centers in $[(\equiv SiO)_6Cr_2]$ are in the +3 oxidation state and have a similar coordination geometry to those in **5**. The results of the EXAFS analysis of **5** and $[(\equiv SiO)_6Cr_2]$ are given in Table 1 and show similar environments between the molecular and the surface species.

The $[(\equiv SiO)_6Cr_2]$ surface species displayed an initial ethylene-polymerization activity of 19 kg PE (mol Cr)$^{-1}$ h^{-1},



Scheme 4. Proposed mechanism for ethylene polymerization by $[(\equiv SiO)_6Cr_2]$.

roughly one order of magnitude higher than that found for $[(\equiv SiO)_4Cr_2]$. The higher activity of Cr^{III} is not surprising in view of what has been shown in homogeneous catalysis.[25] In a fixed-bed reactor at 70 °C under gas-phase polymerization conditions, the activity increased to 107 kg PE (mol Cr)$^{-1}$ h^{-1} at an ethylene pressure of 6 bar. The polymer obtained under high-pressure conditions had a number-average molecular weight of $M_n = 5500\ g\,mol^{-1}$, a weight-average molecular weight of $M_w = 52\,000\ g\,mol^{-1}$, and a dispersity $Đ = M_w/M_n = 9.4$. The ^1H and ^{13}C NMR spectra of the polymer were consistent with linear polyethylene containing 1.5 branches per 1000 C atoms as well as olefin and methyl end groups. The broad polymer dispersity indicates multisite behavior. Despite the well-defined first coordination sphere in $[(\equiv SiO)_6Cr_2]$ as established by XAS, there are probably small variations in the chromium environment as a result of the amorphous silica surface; these variations would impact the rate of polymerization and/or chain transfer.[26]

We also evaluated the number of active sites in $[(\equiv SiO)_6Cr_2]$ by carrying out poisoning experiments with 4-methylpyridine (see the Supporting Information for details). The ethylene-polymerization activity, monitored by IR spectroscopy under a low ethylene pressure, decreased linearly with increasing amounts of catalyst poison. The estimated number of active sites present in $[(\equiv SiO)_6Cr_2]$ on the basis of this method is at least 65 %. This result indicates that the surface chromium(III) sites in $[(\equiv SiO)_6Cr_2]$, characterized by XANES and EXAFS, are related to the active sites.

$[(\equiv SiO)_6Cr_2]$ exposed to ethylene contains some intriguing features. The XANES spectrum of $[(\equiv SiO)_6Cr_2]$ exposed to ethylene is identical to that of pristine $[(\equiv SiO)_6Cr_2]$. The IR spectrum of this material contains the expected ν_{CH} and δ_{CH} vibrations associated with the polymer chain, and a vibration observed at 3692 cm^{-1} for surface silanols interacting with the polymer chain.[27] Two new OH bands are also present: a major vibration at approximately 3605 cm^{-1} and a minor vibration at 3640 cm^{-1}. These vibrations, which we assign to Si–(μ-OH)–Cr^{III} interactions, are typical of SiOH groups interacting with an adjacent Lewis acidic metal center and are often observed for crystalline zeolitic materials.[28] The formation of Si–(μ-OH)–Cr^{III} interactions would arise from the C–H activation of ethylene across a Cr–OSi bond. Consistent with this proposal, when $[(\equiv SiO)_6Cr_2]$ was brought into contact with C_2D_4, an isotopically shifted Si–(μ-OD)–Cr^{III} band was observed at 2580 cm^{-1} (expected at 2575 cm^{-1}; see the Supporting Information).

From these results, we propose the following polymerization mechanism (Scheme 4): Polymerization is initiated through C–H bond activation of ethylene across one of the Cr–O bonds in $[(\equiv SiO)_6Cr_2]$ (**4**). This reaction results in the formation of a surface chromium(III) species **6** that contains a chromium–vinyl group, two anionic siloxides, and one SiOH group. The intermediate **6** can insert ethylene, and chain growth continues through a classical Cossee–Arlman insertion mechanism. Chain termination could be the microreverse of the initiation step, proton transfer from the coordinated silanol to the carbon atom bound to Cr, or through direct β-proton transfer to a coordinated ethylene to liberate a polymer chain containing olefinic and methyl end groups with regeneration of the neutral Cr^{III} site.

The key step in this mechanism is the heterolytic C–H activation of ethylene, a process that conserves the oxidation state of chromium and is consistent with the XANES spectrum of $[(\equiv SiO)_6Cr_2]$ exposed to ethylene. On metal-oxide surfaces, the activation of C–H bonds often occurs heterolytically by σ-bond-metathesis-type mechanisms.[29] Trivalent Lewis acid sites are particularly prone to activate C–H bonds; for example, tricoordinate Al sites of highly dehydroxylated γ-Al_2O_3 activate methane and other hydrocarbons at low temperatures.[30] Alkane dehydrogenation over Cr/Al_2O_3 or Ga/Zn-zeolite were also proposed to occur through C–H activation and the formation of metal–alkyl surface species as key intermediates.[29,31]

We have described the formation of isolated Cr^{II} and Cr^{III} dinuclear surface species by a molecular approach. The well-defined Cr^{II} sites are not efficient olefin-polymerization catalysts, but Cr^{III} sites do polymerize ethylene. Like the Phillips catalyst, these materials polymerize ethylene in the absence of alkyl aluminum cocatalysts or preformed Cr–C bonds. The formation of the first Cr–C bond, key to ethylene polymerization, occurs through heterolytic C–H bond activation of ethylene on the Cr^{III} silicates in $[(\equiv SiO)_6Cr_2]$. This mechanistic insight clearly distinguishes chromium-based catalysts from other olefin-insertion polymerization catalysts and opens new avenues for the manipulation of these materials to produce a wider range of polymer properties.

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