Strain Effect and Dual Initiation Pathway in Cr^{III}/SiO₂ Polymerization Catalysts from Amorphous Periodic Models

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Abstract

Heterolytic C-H bond activation of ethylene on Cr^{III}-O has been proposed as the initial step in olefin polymerization on (≡SiO)₃Cr^{III} active sites of molecularly-defined analogues of the Philips catalyst. Here, by using realistic amorphous periodic models that account for structural complexity, strain, and active site heterogeneity of well-defined silica-supported Cr^{III}-based polymerization catalysts, we show that this activation step is significantly favored due to the strain present on highly dehydroxylated silica. Furthermore, we find that initiation by insertion of ethylene into the Cr-O bond is even more favorable, especially for more strained sites, while both mechanisms can compete for less strained and thereby less active sites. Our results suggest a competing dual pathway for ethylene polymerization on Cr^{III} sites and are consistent with a distribution of active sites, the experimentally observed broad distribution of polymer molecular weight, and the increased polymerization activity upon high-temperature calcination in Phillips catalysts.

Keywords

Cr^{III} Sites, Silica, Olefin Polymerization, Amorphous Model, C-H Activation, Ethylene Insertion

The Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst,^[1] which accounts for 40-50% of the world's annual production of high-density polyethylene (HDPE), has caused a large research effort and many controversies regarding the nature of the active site and the polymerization mechanism^[2] since its invention by J.P. Hogan and R.L. Banks at Phillips Petroleum Company in the early 1950s. The preparation of the catalyst involves impregnation of porous silica with a Cr source and a subsequent calcination step that leads to morphological changes of the silica support:^[3] the density of surface silanol groups gradually decreases, which is accompanied by the formation of siloxane bridges and rings on the surface. Worthy of note, increasing calcination temperature has a beneficial influence on the performance of the final Phillips catalyst when Cr(VI) is reduced with ethylene^[1, 4] while the contrary has been observed for CO-reduced Cr-catalysts for ethylene polymerization by *in situ* IR spectroscopy.^[5] Calcination temperatures above 400 °C are essential for activity, and enhanced catalytic activity is found when very high temperatures, *i.e.* above 800 °C, are used. This has been attributed to the formation of the highly strained siloxane rings formed at elevated temperatures, which are expected to be more reactive.^[4-5] Upon contact with ethylene, the Philips catalyst precursor undergoes a step-wise reduction of Cr^{VI} to mainly Cr^{II} but also Cr^{III} based on spectroscopic studies^[2c] and the introduction of a co-monomer increases the catalytic activity.^[6] Hence, several mechanisms have been proposed based on isolated Cr^{II} sites, most of them involving two-electron redox processes leading to Cr^{IV} organometallic intermediates that could then allow for olefin insertion and chain growth.^[2g, 7] More recently, one-electron processes from Cr^{II} to Cr^{III} have been also proposed.^[2f, 8] However, only a fraction of the Cr sites are active in ethylene polymerization, ranging from 12 to 61 % depending on the poison used,^[1, 9] which severely complicates the spectroscopic characterization^[2c] of the active sites.^[8]

In order to overcome this limitation, the formation of silica-supported Cr sites with well-defined oxidation states and nuclearity was carried out by Surface Organometallic Chemistry approach.^[7f, 10] Recently, well-defined Cr^{II} and Cr^{III} silicates were synthesized by grafting molecular chromium siloxide on silica partially dehydroxylated at 700 °C followed by a post-thermolysis step.^[10a] The catalytic activity towards ethylene polymerization was much higher for the Cr^{III} sites than for the Cr^{II} sites, the latter having from little to no activity.^[10a, 11] Polymerization initiation was proposed to occur via heterolytic C-H bond activation of ethylene on one of three Cr^{III} -O bonds of the $(=\text{SiO})_3\text{Cr}$ active site (Scheme 1a), resulting in the formation of a

($\equiv\text{SiO}$)₃Cr-vinyl site (Cr^{III} -vinyl), which subsequently undergoes multiple ethylene insertion and polymer chain growth via a Cossee-Arlman mechanism.

Previous density functional theory calculations on cluster models of this well-defined $\text{Cr}^{\text{III}}/\text{SiO}_2$ catalytic system, found the initiation C-H bond activation step to be rather energy-demanding and endothermic, while termination by proton transfer (microreverse of the initiation step) could compete with classical termination pathways such as β -H and chain transfer.^[10a] However, cluster models give a rather simplistic view of surface sites present on amorphous silica materials since they do not account for the structural complexity, strain, and active site heterogeneity of real catalytic systems. Amorphous models have been developed earlier to understand the possible structures of silica^[12] and chromium oxides supported on silica.^[13]

Scheme 1. Proposed ethylene polymerization mechanisms: a) C-H Activation and b) Insertion into the Cr-O bond.

Coordination of ethylene. a) Initiation by formation of a Cr-vinyl site via heterolytic C-H splitting of ethylene on a Cr^{III} -O bond and successive propagation. b) Initiation by formation of an oxachromacycle species via insertion into the Cr-O bond and successive propagation.

In addition to the effect of the strain on the reactivity towards C-H bond activation of ethylene, alternative pathways could come into play for the initiation step of ethylene polymerization, in particular initiation by insertion of ethylene into the Cr-O bond, forming an oxachromacycle as proposed by Wachs *et al.*,^{2e} which may subsequently undergo propagation via repeated ethylene insertion (Scheme 1b).

Herein, we develop amorphous silica-supported Cr^{III} models based on periodic DFT calculations in order to study the olefin polymerization mechanism of the previously synthesized well-defined Cr^{III} sites on SiO_2 ,^[10a] since the oxidation state of Cr was only +3 based on XAS experiments.^[10a] We evaluated both the C-H activation of

ethylene on the Cr-O bond and the insertion of ethylene into the Cr-O bond as initiation steps of olefin polymerization. We show how local strain critically affects polymerization initiation, a structure-activity relationship that explains the broad polymer size distribution and the effect of high-temperature activation observed experimentally. Furthermore, based on a comparison of the two initiation mechanisms and their corresponding successive propagation steps, we propose either a dual reaction pathway or solely the ethylene insertion mechanism, depending on the evaluated site.

Cr^{III}/SiO₂ models were constructed using a recently developed amorphous silica model,^[12d] which corresponds to a slab of dimensions 21.4 Å × 21.4 Å × 34.2 Å and contains 372 atoms. The silica model exposes five isolated silanol groups (SiOH) and has a surface silanol density (1.1 OH nm⁻²) close to the density found for silica partially dehydroxylated under vacuum at 700 °C (SiO₂₋₇₀₀, 0.8 OH nm⁻²), the support used to prepare the well-defined Cr^{III} sites.^[10a] It was obtained from a fully hydroxylated amorphous silica model by direct condensation of adjacent silanol groups and by surface reconstruction steps involving SiO₂ migrations. The amorphous silica model has a high degree of heterogeneity as evidenced by the large variability in the energetics associated with the dehydroxylation steps. The average Si-O distances of the siloxane bridges formed upon surface dehydroxylation serve as descriptors of the strain present on the silica surface.^[12d]

Cr sites were introduced into the silica model by substituting SiOH groups by Cr, *i.e.* turning (≡SiO)₃SiOH sites into (≡SiO)₃Cr sites. The five SiOH groups of the 1.1 OH nm⁻² silica model were in turn substituted with Cr, yielding five individual Cr^{III}/SiO₂ models (models I-V, see Figure 1 for the labeling of the silanols, Table S1a for the resulting structural properties of the Cr sites, and Figure S1 for a close view of the five sites). The procedure for the construction of the Cr^{III}/SiO₂ models is exemplified in Figure 1 for model I. Experimentally, the adsorption of CO on the Cr^{III}/SiO₂ catalyst gives two IR signals at 2188 and 2202 cm⁻¹, which are blue-shifted with respect to the free CO molecule (2143 cm⁻¹).^[10a] In order to test the validity of the constructed Cr^{III}/SiO₂ models, the IR stretching frequencies upon coordination of three CO molecules on models I-V were calculated. Upon adsorption, the calculated CO stretching frequencies are blue-shifted, with IR shifts with respect to the CO molecule in good agreement with the experimental findings (Table S1b).

The models I-V were first used to probe the reactivity of various Cr-O sites towards C-H bond activation of ethylene. The results are shown in Figure 2a1. Cr^{III} was always found to be more stable in its spin quartet ($S = 3/2$) configuration (*i.e.* high-spin d^3). Coordination of ethylene to Cr^{III} appears favorable in all cases. The energies associated with the products after the C-H bond activation of ethylene show a large degree of heterogeneity. They range from -54.3 to $+10.8$ kcal mol⁻¹. Even Cr-O bonds belonging to the same Cr^{III} site do in some cases yield largely different reaction energies. For instance, splitting on Cr-O(1) of model III is disfavored by 4.7 kcal mol⁻¹, while the splittings on Cr-O(2) and Cr-O(3) are favored by respectively -10.9 kcal mol⁻¹ and -12.7 kcal mol⁻¹. By comparison, using the cluster model represented in Figure S2 and previously developed in our group,^[10a, 11b] C-H bond activation was calculated to be endoenergetic by 14.6 kcal mol⁻¹ at the same level of theory (Table S2).

Figure 1. Top-view of unit cell showing the five initial silanol groups (I-V). Construction of the Cr^{III}/SiO₂ model corresponding to model I by substitution of one of the five SiOH groups of the silica model with Cr.

Figure 2. a1) Energy profiles for C-H splitting of ethylene (kcal mol⁻¹) as obtained with models I-V (1.1 OH nm⁻²). The energies are normalized with respect to the free system (bare model + ethylene). a2) Zoom-in of the Cr^{III} active site of model V. Transition state for C-H activation of ethylene on the Cr-O(3) bond. O-H-C_{vinyl} angle = 158.6°. Bond lengths (Å) are indicated. b1) Energy profiles for insertion of ethylene into the Cr-O bond (kcal mol⁻¹) as obtained with models I-V (1.1 OH nm⁻²). The energies are normalized with respect to the free system (bare model + ethylene). b2) Zoom-in of the Cr^{III} active site of model V. Transition state of the ethylene insertion into the Cr-O(3) bond.

Table 1 contains an overview of the Cr···OH distances of the resulting Cr-vinyl sites. Comparing these to the reaction energies for C-H bond activation (Figure 2a1) suggests the following trend: exoenergetic C-H bond activations generally lead to Cr-vinyl sites with longer Cr···OH distances than endoenergetic C-H splittings. For instance, the highly favored reaction energies of -27.0 kcal mol⁻¹ and -54.3 kcal mol⁻¹ are associated with Cr···OH distances of respectively 3.22 Å and 4.71 Å in model V. The exoenergetic reaction energies and large distance increments are indicative of a significant strain release upon C-H bond activation of ethylene on the Cr-O bond. Conversely, for the endoenergetic C-H splittings occurring on Cr-O(2) of model I (8.7

kcal mol⁻¹) or Cr-O(3) of model IV (10.8 kcal mol⁻¹), comparatively small Cr···OH distances of respectively 2.11 Å and 2.07 Å are observed, similarly to what is found for the cluster model for which the endoenergetic reaction energy of 14.6 kcal mol⁻¹ (Table S2) is associated with a Cr···OH distance of 2.44 Å. Table 1 summarizes the activation energies associated with C-H bond activation, which takes values between 27.0 and 41.3 kcal mol⁻¹.

Table 1. Cr···OH distances (Å) and Cr···OC distances (Å) in the products resulting from the C-H activation on the Cr-O bond or ethylene insertion into the Cr-O bond respectively for models I-V. The initial Cr-O distances are given in parenthesis (Å). Energy barriers ($\Delta E^\ddagger$, in kcal mol⁻¹) for the C-H activation of ethylene and ethylene insertion are referenced with respect to the corresponding Cr-ethylene adducts.

C-H activation	I	II	III	IV	V
Cr···O(1)	2.42	3.07	3.07	2.42	2.21
H	(1.85)	(1.85)	(1.84)	(1.83)	(1.81)
$\Delta E^\ddagger$	34.4	29.8	32.2	40.6	30.4
Cr···O(2)	2.11	3.64	3.78	2.18	4.71
H	(1.81)	(1.88)	(1.84)	(1.79)	(1.90)
$\Delta E^\ddagger$	35.9	28.4	27.0	36.7	- ^b
Cr···O(3)	2.86	2.10	4.07	2.07	3.22
H	(1.84)	(1.80)	(1.85)	(1.79)	(1.88)
$\Delta E^\ddagger$	31.8	27.5	27.0	41.3	25.5

Ethylene Insertion	I	II	III	IV	V
Cr···O(1)C	2.09	2.22	2.67	2.12	2.09
	(1.85)	(1.85)	(1.84)	(1.83)	(1.81)
$\Delta E^\ddagger$	18.5	8.9	15.6	22.3	20.0
Cr···O(2)C	2.01	2.33	3.61	2.07	3.93
	(1.81)	(1.88)	(1.84)	(1.79)	(1.90)
$\Delta E^\ddagger$	18.4	8.5	11.1	16.1	- ^b
Cr···O(3)C	2.19	2.05	3.23	2.00	3.12
	(1.84)	(1.80)	(1.85)	(1.79)	(1.88)
$\Delta E^\ddagger$	14.9	9.8	12.8	17.5	9.2

^bThe transition states corresponding to C-H splitting

on Cr-O(2) and ethylene insertion into Cr-O(2) of model V could not be localized.

The related transition state structures have geometries corresponding to a σ -bond metathesis mechanism (see for instance Figure 2a2). For further details, Table S3 summarizes the geometric characteristics of all the transition states corresponding to the C-H bond activation. The observed energetic heterogeneity for initiation on the active sites of models I-V is consistent with the experimental findings that about 60% of mononuclear Cr^{III} sites supported on SiO₂₋₇₀₀ are active in ethylene polymerization, and that they are a range of sites as evidenced by the broad molecular weight polymer distribution.^[10a] The energetics reported could still deviate from experiment due to specific catalytic sites, geometry and shapes not accounted by the model as well as limitations inherent from the methodology used. It should be thus compared to experiment in order to fully test its accuracy.

One can draw a linear relation between the activation barrier and the reaction energy associated with C-H bond activation (Brønsted-Evans-Polanyi relation) (Figure S3a), that is, the more favored C-H bond activations generally exhibit lower activation barriers, however the correlation is relatively scattered ($R^2=0.60$). Figure S3b shows the relation between the activation energy and the change in the Cr-O distance from reactants to products. For comparison, the cluster model yields an activation barrier of 45.2 kcal mol⁻¹ with a reaction endoenergetic by 14.6 kcal mol⁻¹ (Table S2). The higher Cr-O distances in the Cr sites of the amorphous model, with distances ranging 1.79 and 1.90 Å can partially explain the higher reactivity in comparison to the cluster model, which has Cr-O distances equal to 1.80 Å (see Figure S2). This suggests that strain, evidenced by the longer Cr-O distances, is a key factor to explain the higher reactivity of the Cr sites in the amorphous SiO₂ surface in comparison to the Cr sites modeled as a cluster.

In addition, ethylene assisted C-H splitting was investigated (see Table S4 for calculations on the cluster model and Table S5 for calculations on models I-V). The results suggest (see comment to Table S5) that ethylene-assisted C-H bond activation is less favored on these systems, and therefore that coordination of a second ethylene molecule to Cr will not happen before formation of the Cr-vinyl site upon C-H bond activation.

We then evaluated insertion of ethylene into the Cr-O bond, leading to the formation of an oxachromacycle, as an alternative initiation step of ethylene polymerization. The corresponding reaction energies are summarized in Figure 2b1 and, as for C-H bond activation, they show a large degree of heterogeneity with values ranging from –55.4 to +2.8 kcal.mol⁻¹. Initiation by ethylene insertion appears to generally be more thermodynamically favored than initiation by C-H bond activation. In comparison, using the cluster model represented in Figure S2,^[10a, 11b] this step was found to be endothermic by 12.2 kcal mol⁻¹ at the same level of theory (Table S6).

Table 1 contains an overview of the Cr···OC distances of the resulting oxachromacycle sites. Comparing these to the corresponding reaction energies (Figure 2b1) suggests the following trend: initiation by ethylene insertions that are more favored generally leads to oxachromacycle sites with longer Cr···OC distances. This trend is similar to the one observed for initiation by C-H bond activation, and indeed those Cr-O sites presenting more favorable reaction energetics in C-H bond activation of ethylene are also the ones being more favorable towards insertion of ethylene. The activation energies associated with ethylene insertion into the Cr-O bond take values between 8.5 and 22.3 kcal mol⁻¹ (see Table 1). In comparison, the cluster model yields a relatively high energy barrier for ethylene insertion into the Cr-O bond, namely 29.6 kcal mol⁻¹ (see Table S6).

Analogously to the case of the C-H bond activation, the energy barriers associated with initiation by ethylene insertion are also dependent on the evaluated site. However, for this alternative activation mechanism step the energy barriers are significantly lower than in the case of the C-H bond activation, which took values ranging 27.0-41.3 kcal.mol⁻¹. These results show that while the C-H activation of ethylene presents more affordable activation energies on amorphous models than on simpler cluster models, the insertion of the ethylene into the Cr-O bonds forming an oxachromacycle is even more preferred. For further information on structural details and energetics of initiation by ethylene insertion on models I-V see Table S7. The transition state for initiation by ethylene insertion into Cr-O is exemplified in Figure 2b2 for site Cr-O(3) of model V.

Propagation was then evaluated for the Cr-vinyl site resulting from initiation at Cr-O(3) of model V and then for the oxachromacycle site resulting from initiation at Cr-O(3) of model V. This is the most active site for C-H bond activation and it is among the most active sites for ethylene insertion, having activation energies of 25.5 and 9.2

kcal mol⁻¹, respectively. Furthermore, it is the site that yields the second most favorable initiation reaction energetics (for the site yielding the most favorable initiation reaction energetics, Cr-O(2) of model V, the corresponding transition states could not be localized).

Coordination of ethylene to the Cr-vinyl site is highly favored, as is the subsequent insertion of ethylene into the Cr-vinyl bond via a Cossee-Arlman mechanism. The insertion propagation step on the selected Cr-O(3) site of model V has a very low activation energy of only 0.9 kcal.mol⁻¹, significantly lower than the one obtained with the cluster model (Table S8). For other sites, propagation is also associated with a rather low activation barrier of only 2.1-5.5 kcal mol⁻¹ (see Table S9). Based on previous cluster model calculations, proton back-transfer was found to be a low-energy termination pathway,^[10a] which even competed with chain-propagation.^[14] On the periodic model, the significantly more favorable C-H bond activation for the Cr-O(3) site of model V (as well as for several other of the active sites of models I-V (Table 1)) makes the termination by proton back-transfer significantly more energy-demanding. For instance, for the Cr-butenyl site resulting from insertion and chain-propagation at the Cr-O(3) site of model V, proton back-transfer is endothermic by 39.6 kcal mol⁻¹ (see Table S10). On the same site, β -H elimination is also relatively energy-demanding, being endothermic by 18.5 kcal.mol⁻¹ (see Table S11). Chain transfer is the only termination pathway favored thermodynamically but has an energy barrier of 21.4 kcal.mol⁻¹ (Table S12). Overall, none of the above three termination pathways compete with propagation, allowing for long polymer chains to be generated. Coordination of ethylene to the oxachromacycle site formed upon initiation by ethylene insertion into Cr-O(3) of model V is exoenergetic, as was the case for the C-H bond activation route. The subsequent insertion of the coordinated ethylene into the Cr-C bond of the oxachromacycle is associated with an energy barrier of 13.2 kcal mol⁻¹ and is exoenergetic by 13.2 kcal mol⁻¹, with the product located at -60.2 kcal.mol⁻¹ with respect to initial reactants. For other oxachromacycle sites evaluated, propagation is associated with relative energy barriers in the range 12.0-16.9 kcal mol⁻¹, and the corresponding insertion products have energies of -41.1 to -27.4 kcal mol⁻¹ with respect to the free reactants (see Table S13). Concerning termination, β -H elimination from an oxachromacycle site, forming a Cr-H site and an O-alkenyl group, is quite demanding thermodynamically, this termination pathway being

endoenergetic by 21.0 kcal.mol⁻¹ in the case of the Cr-O(3) of model V. Termination by chain transfer exhibits an energy barrier of 28.7 kcal.mol⁻¹, and thus is also significantly more energy-demanding than propagation (see Tables S14-S15).

We then evaluated the Gibbs free energy profiles for the first two steps of the two evaluated reaction mechanisms for some selected sites in order to determine which route is the preferred one (see Figure 3a-d and Tables S16-S19). For all the sites, initiation via the ethylene insertion is favored over C-H activation. Concerning propagation, the opposite trend is found: the relative energy barrier is always lower for the C-H activation route than for the ethylene insertion pathway. Overall, for the C-H activation pathway the initiation is the rate-limiting step in all cases. For the ethylene insertion we see differences among the sites instead. In this case, it is the reaction energy of initiation that determines the energy of the transition-state corresponding to the propagation step. For instance, for the sites where the initiation step is endothermic, such as sites Cr-O(3) (model II) and Cr-O(1) (model III) the propagation step becomes more demanding than the initiation for the ethylene insertion pathway. On these sites, the rate-determining steps of the C-H activation pathway and the ethylene insertion route have very similar energies, and hence, both mechanisms might be operative, although in this case such sites would be less active or even inactive due to the endothermicity of the initiation step. Conversely, for the sites where initiation is exothermic, sites Cr-O(2) (model III) and Cr-O(3) (model V), the propagation step is no longer rate-determining in the ethylene insertion route. For such sites the ethylene insertion pathway will therefore be preferred, and most importantly such sites will be the most active ones, cf. exothermicity of the initiation step. Overall, our results suggest that both routes might be operating for less strained sites while for the most strained ones and thus the most active sites, the preferred pathway would be the ethylene insertion route. It is also important to note that the reported Gibbs energy barriers for all the sites shown in Figure 3 are very low (lower than 25 kcal.mol⁻¹), except for site Cr-O(1) of model III, consistent with the activity of Cr^{III}/SiO₂ catalyst at low temperatures (70°C).^[10a] Finally, we calculated the effect of increasing the size of the oxachromacycle ring after the successive insertion of up to five ethylene molecules for sites Cr-O(2) of model III and site Cr(O(3) of model V. The successive ring growth of the oxachromacycle is thermodynamically favorable for both sites (see Table S20) and more favored than chain termination (Scheme S1).

It is possible that the Cr-vinyl site becomes more stable than the ring oxachromacycle for very large ring sizes. The energy barrier for the interconversion between the oxachromacycle and the proton activated product is however very energy demanding. For instance, it is equal to 53 kcal.mol⁻¹ on site Cr(O)3 of model V after the insertion of two ethylene molecules (pathway from **5b** to **5a**). The proton-transfer from coordinated ethylene to the inserted ethylene group, forming a Cr-vinyl and an O-alkyl group as proposed by Wachs *et. al.*^{2e} (see Scheme S2) is more feasible, however, it still has an energy barrier equal to 22.9 kcal.mol⁻¹ and it is endothermic by 5.9 kcal.mol⁻¹ for site O3 of model V (in electronic energy). Since the second ethylene insertion into the oxachromacycle is exothermic by 13.2 kcal.mol⁻¹ and has an energy barrier equal to 13.2 kcal.mol⁻¹ on the same site, it is more favored than the reorganization of the oxachromacycle to a Cr-vinyl site. Nevertheless, it cannot be fully discarded that for very large ring sizes both mechanisms can compete.

Figure 3. Comparison between the Gibbs free energy profiles (G , in kcal.mol⁻¹) for the initiation and propagation steps in the C-H activation and the ethylene insertion pathways for some selected sites: a) Cr-O(3) of model II, b) Cr-O(1) of model III, c) Cr-O(2) of model III and d) Cr-O(3) of model V. The labels (1, 2, 3a, 3b, 4a, 4b, 5a, 5b) refer to the structures shown in Scheme 1. Transition-state structures are indicated with a double dagger symbol ($\ddagger$).

In conclusion, the existence of a distribution of Cr^{III} sites on the amorphous silica surface, whose structures depend on the pre-treatment (activation temperature) of the catalyst/support and on the local environment of each site, can affect initiation and growth (propagation/termination) of polyethylene, as shown experimentally.^[1] The presence of highly strained $\text{Cr}^{\text{III}}\text{-O}$ sites resulting from thermal treatment of the support significantly facilitates both C-H bond activation of ethylene as well as the insertion of ethylene into the Cr-O bond, leading to highly active sites and formation of long chain polymers (easy propagation vs. higher energy termination pathways). Such sites will preferably favor ethylene polymerization via insertion into the Cr-O bond. Less strained sites, favored at lower activation temperatures, but present at all temperatures, can participate as well in polymerization. These, however, will initiate either by C-H bond activation or ethylene insertion into the Cr-O bond more slowly and generate different active site structures, which will likely affect the structure of the final polymer. Indeed, polymerization on the less strained sites will be more difficult to initiate, very likely perturbed by the chain growth on adjacent sites and involved in additional termination processes, possibly leading to shorter polymer chains. The distribution of active sites with different local environments would account for the broad distribution of polymer chains observed. While cluster models have been very effective in distinguishing the possible from the impossible, this study illustrates the advantage of using amorphous silica models to describe surface sites^[12a, 12c, 13a, 13b, 15]: it is a crucial step in understanding at a molecular level the role of the activation temperature and the difference in reactivity of silica-supported catalysts.

COMPUTATIONAL METHODS

DFT calculations based on the Gaussian and plane waves (GPW) formalism^[16] were carried out using the Quickstep (QS) module^[17] of the CP2K program package^[18]. The functional chosen was PBE^[19] with short range Gaussian double- ζ basis sets^[20] optimized from molecular calculations. For the CO adsorption and the related frequency calculations, the PBE0 hybrid functional was used instead.^[21] The energy cutoff of the auxiliary plane wave basis set was set to 500 Ry. Goedecker-Teter-Hutter pseudopotentials^[22] were used. Chromium was treated in its quartet configuration, unless otherwise stated. Spin-polarization was requested. The orbital transformation method was applied.^[23] A tetragonal simulation box of base area $21.4 \text{ \AA} \times 21.4 \text{ \AA}$ and thickness $34.2 \text{ \AA}$ (*ca.* $24 \text{ \AA}$ of which correspond to a vacuum slab added in order to

avoid interactions between images in the *z* direction) was used.^[12d] Ground state structures were obtained by energy minimization with the BFGS algorithm.^[24] Initial transition state guesses were generally obtained from CI-NEB^[25] band calculations. Transition state structure optimizations were performed using the dimer method^[26] with the conjugate gradient optimizer and the two point based line search. In a few cases, in addition to the correct imaginary frequency along the reaction coordinate, minor imaginary components were obtained that could not be avoided. However, they are expected to have a minimal impact on the reported energies. When used, DFT-D3^[27] was the dispersion correction applied.

ASSOCIATED CONTENT

Supporting Information

Structural data

Reaction and activation energies

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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