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Molecular-Level Insight into Cr/Silica Phillips-Type Catalysts: Polymerization-Active Mononuclear Chromium Sites

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Prospects of ethylene polymerization over pseudo-octahedral mononuclear Cr(II) sites as well as tetrahedral mononuclear Cr(II)-B sites with a coordinating silanol moiety have been examined by means of cluster models and gradient-corrected density functional theory. For the octahedral site, candidate active sites are considered to arise through reactions between ethylene and chromium. In the case of a Cr(II)-B site, the added complexity of reactive interactions with the coordinating silanol moiety is taken into account. In the case of propagation, emphasis is put on monomer insertion into a chromium–carbon single bond in four-coordinated Cr(IV) species. The mononuclear Cr(II)-B site is found to afford activation through hydrogen transfer from the coordinating silanol group, given that the silica matrix offers a minimum of strain to prepare the structure for ethylene coordination. © 2002 Elsevier Science

Key Words: **polymerization; ethylene; Phillips catalysis; density functional theory; initiation; propagation; cluster models.**

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1. INTRODUCTION

The last years have witnessed a resurgence in fundamental research aimed at elucidating structural and mechanistic aspects of the Phillips polymerization process (1–3). This catalytic system constitutes the main industrial route to a wide variety of high-density and linear low-density polyethylene polymers (2, 4). At the core of the Phillips process are supported chromium oxide catalysts, prepared by impregnating a chromium salt or oxide onto a wide-pore silica (1, 2). Upon calcination, chromium is anchored and oxidized, and the silica surface is dehydroxylated (1). In the calcined catalyst, monochromate is found to dominate at low Cr loadings on pyrogenic silica, while dichromate and monochromate are identified in ample amounts on sol–gel silica (5). After the catalyst is brought into contact with ethylene, an induction time is observed prior to the onset of polymerization (1). This delay is attributed to a reduction phase and is absent if the catalyst is prereduced in a separate step (1, 6). It is widely accepted that the main chromium surface species after reduction is divalent (1, 5). Furthermore, reoxidation of the catalyst reestablishes the initial monochromate-to-dichromate ratio (7), suggesting a connection between chromium surface species at the reduced and oxidized catalysts. Thus, prior to polymerization, chromium is present as divalent mononuclear and dinuclear surface species, of which both types have been proposed catalytically active for polymerization (see Refs. 8 and 9, respectively). A minor population of Cr(III) species is also found to be present at the reduced catalyst (5, 7, 10). Such trivalent chromium species have been proposed active for polymerization (10–12), and the activity may depend on their nuclearity (10).

Scott *et al.* prepared a working, well-defined model catalyst (13–17) for which magnetic susceptibility measurements indicate that the chromium species are mononuclear and in a triplet spin state, both before and after polymerization (16). The catalyst is prepared by grafting tetra(neopentyl)chromium onto silica. Following liberation of two molecules of neopentane for each chromium, dialkylchromium species are anchored to the silica surface through two ester oxygen bridges (13). Modest heating is required to obtain activity, upon which a third equivalent of neopentane is released (13, 14). Analysis of the volatiles produced upon contact with ethylene indicates that a fraction of the sites are further converted to divalent chromium species (17). Scott *et al.* recently proposed that a second class of dialkylchromium(IV) species are generated in a reaction between ethylene and divalent chromium species (17) and, moreover, that these species are responsible for polymerization. The lack of activity of the analogous, initial di(neopentyl)chromium(IV) structure is rationalized on accounts of steric hindrance presented by the bulky ligands (17).

In previous work (18), we developed theoretical cluster models of mononuclear Cr(II) sites with the ester oxygen ligands positioned *cis* to each other, i.e., what is commonly referred to as (pseudo-)tetrahedral sites. Different mechanisms of chain propagation as well as initiation by ethylene were examined for cluster models covering a range of 90–135° in the $\angle$OCrO angle. In short, all of the investigated

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mechanisms for dialkylchromium(IV) in a tetrahedral configuration gave activation energies incompatible with high catalytic activity (18). It was concluded that factors not included in the model were required to obtain catalytic activity, such as an active participation of the silica substrate during initiation and/or propagation, possibly in connection with structurally strained coordination sites.

In conventionally prepared catalysts, the activity increases as a function of the calcination temperature from 500°C to reach a maximum at 925°C (19). As the formation of surface chromate and dichromate esters is complete below 500°C, it is argued that the activation procedure serves some additional purpose (19). Within the temperature range of increasing activity, gradual dehydroxylation of the surface is observed. The strong inverse correlation between hydroxyl population and activity suggests that surface hydroxyls may inhibit polymerization by detrimental coordination to active sites. However, it is important to realize that even at 925° there is a residual population of isolated hydroxyls (19), which usually are more reactive than vicinal hydroxyl groups (20).

Further insight into the surface composition of silica has been gained by gradually heating silica *in vacuo*, first leading to dehydration and then to progressive dehydroxylation by condensation of pairs of hydroxyl groups into siloxane bridges. Elimination of hydrogen-bonded silanol is facile and proceeds gradually up to 450°C in silica gels, at which stage only isolated silanol groups remain (21). Dehydroxylation above 500°C results in strained siloxane rings, referred to as *defects*. Partial relaxation of some of the highly strained rings is expected, as the dehydroxylation becomes less reversible the higher the applied temperature is (21). These surface defects are reactive and capable of dissociative chemisorption of molecules (21).

The quoted studies of silica topicalize the presence of isolated, yet reactive silanol moieties, as well as highly strained surface sites at Phillips catalysts. If present in sufficient quantities, such sites might be identifiable in spectroscopic studies. Weckhuysen *et al.* analyzed bands in the d–d region of diffuse reflectance spectra of the reduced catalyst in terms of tetrahedral and octahedral Cr(II) sites (22). However, this interpretation was not substantiated in a theoretical cluster-model study (23), as only a single, electric-dipole-forbidden transition was found in this energy region for Cr(II) with two ester linkages in *trans* positions.

An infrared spectroscopic study (24) of the reduced Phillips catalyst revealed a red-shifted hydroxyl peak, assigned to hydroxyls interacting with Cr(II). In the terminology pertaining to Phillips catalysts, sites with one coordinating oxygen donor are classified as type B (8). A cluster-model study of pseudo-tetrahedral mononuclear Cr(II) with a weakly coordinating silanol group was able to account for the observed spectral and adsorbent properties (25). Furthermore, the theoretical models indicated that surface rigidity restricts the hydroxyl group from closer coordination (25).

The present contribution reports on a theoretical study of polymer growth on two classes of mononuclear Cr(II) sites: (i) a highly strained pseudo-octahedral site with *trans*-positioned ester linkages and (ii) a pseudo-tetrahedral Cr(II)-B-type site with a coordinating silanol group. Together with Ref. 18, this work presents a comprehensive examination of the possibilities of mononuclear Cr(II) sites to assist in ethylene polymerization. Both initiation and propagation phases are considered, and whereas for the octahedral site, initiation is assumed to involve reactions between ethylene and chromium, hydrogen transfer from a coordinating silanol moiety is considered in the case of a Cr(II)-B site. Based on the observation of linear α-olefin by-products in the early stages of polymerization (6, 16, 17), emphasis is placed on the insertion of ethylene into a chromium–carbon single bond in four-coordinated Cr(IV) species.

2. COMPUTATIONAL DETAILS

The study was conducted using gradient-corrected density functional theory as implemented in the Amsterdam density functional (ADF) set of programs (26, 27). For the correlation functional, the local potential by Vosko *et al.* (28) and the nonlocal 1986 correction by Perdew (29) were used. The exchange functional consisted of the Slater term augmented by gradient corrections as specified by Becke (30). Extensive studies (31) demonstrate that the resulting energy functional is capable of providing accurate energy profiles for the insertion step during metal-catalyzed olefin polymerization.

Closed- and open-shell systems were described within spin-restricted and -unrestricted formalisms, respectively. Primitive Slater-type basis sets of triple-zeta (O, F, Cr) and double-zeta (H, C, Si) quality were used as supplied with ADF and detailed in Ref. 18, with polarization functions added to all atoms but chromium. Molecular geometries were converged to a gradient below 0.001 $E_H/\text{Å}$ with the accuracy of the numerical integration schemes adjusted accordingly. Transition-state optimization was conducted as described in Ref. 18.

3. CLUSTER MODELS

The dominating mononuclear chromium species of the reduced catalyst are believed to be divalent and bound by two oxygen ester linkages to the surface. Based on the $\angle$OCrO bond angle, these divalent species may be classified as pseudo-tetrahedral ($\angle$OCrO $\sim$ 90–120°) or pseudo-octahedral ($\angle$OCrO $\sim$ 150–180°).

Our model of a pseudo-octahedral site is shown in Fig. 1 and presented in detail in Ref. 23. The use of fluorine atoms as terminating agents makes it a model of a rather acidic

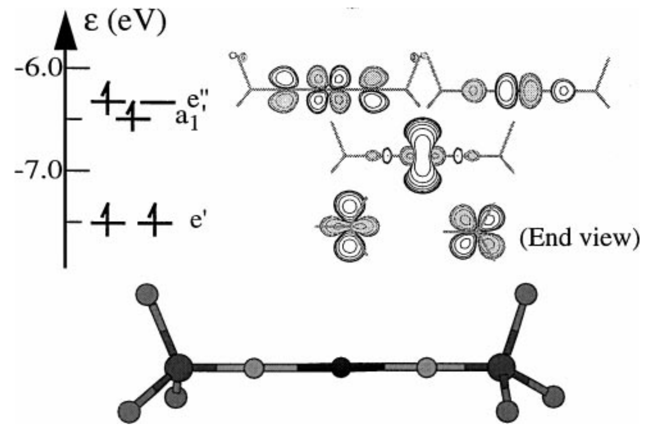

FIG. 1. Energy levels and isosurfaces of the molecular orbitals with mainly Cr 3d character in the pseudo-octahedral cluster model. The elements are coded on a gray scale according to increasing atom number O (light gray) < F < Si < Cr (dark gray).

surface site. To prevent excessive geometric relaxation in the reactivity study, only chromium and ester oxygen ligands were allowed to relax geometrically. In particular, the Si–Si distance was frozen at 6.9 Å. The frontier orbitals of the cluster are shown in Fig. 1 as obtained for the $^5E''$ electronic ground state in D_{3h} symmetry.

The construction of pseudo-tetrahedral Cr(II)-B models was reported in Ref. 25 and is only briefly reviewed here. The surface silanol functionality was represented by a difluorosilanol molecule, which is found to reproduce the gas-phase acidity of larger silasesquioxane clusters (32). The interaction between the silanol and the pseudo-tetrahedral monochromium site was studied by means of the cluster model implied in structure **2a** in Fig. 4, subject to the following geometric constraints: (i) the $O(SiF_2)_2$ part of the cluster was frozen, and (ii) the SiF_2 part of the difluorosilanol molecule was oriented parallel to and at a distance of 5.5 Å from the SiOSi moiety at the bottom of the cluster. These constraints effectively reduce the flexibility of both the silanol molecule and the cluster. It is noteworthy that the resulting model reproduces the observed frequency shift of $-42\ \mathrm{cm}^{-1}$, assigned to hydroxyls coordinating to reduced chromium surface species by Nishimura and Thomas (24). Following hydrogen transfer from the difluorohydridosilanol moiety to the chromium site, geometric relaxation of the site was included as described below.

4. RESULTS AND DISCUSSION

4.1. *Octahedral Cr(II)*

4.1.1. Initiation by ethylene. Ethylene coordinates molecularly to the pseudo-octahedral cluster model, primarily through donation of π electron density into the a_1' cluster orbital shown in Fig. 1. Since this orbital is occupied in the ground state of the cluster, adsorption of the first ethylene induces a single-electron excitation, $e'' \leftarrow a_1'$. Both the first and the subsequent ethylene molecules bind in the equatorial plane of the octahedral cluster at Cr–C distances that increase with the number of adsorbates, from 2.30 to 2.46 Å in the triethylene complex. The binding energy per ethylene drops accordingly from 75 kJ/mol for the first ethylene to 55 and 37 kJ/mol for the second and third, respectively. At room temperature, the enthalpy for coordinating the third ethylene is just enough to make up for the entropy loss.

A second mode of coordination is available at a closer approach of ethylene to the metal, involving spin pairing and back-donation of Cr 3d electrons into the ethylenic π^* orbitals, in addition to the donation bond. The transformation from molecular to covalent coordination modes is found to be moderately endothermic, with a reaction energy increasing with the number of ethylene from 25 to 32 and reaching 50 kJ/mol in the triethylene complex. A schematic overview of the different ethylene–chromium complexes as well as other species derived from them is shown in Fig. 2.

The covalently bound diethylene complex may undergo facile ring fusion to form a chromacyclopentane structure. The energy barrier toward this reaction is a mere 47 kJ/mol, and the reaction is modestly exothermic at −29 kJ/mol. The resulting chromacyclopentane moiety displays only low affinity for further ethylene coordination. A molecular ethylene complex was optimized at an energy of 22 kJ/mol above the asymptote. Starting from this complex, ethylene may be inserted into one of the Cr–C bonds to form the corresponding chromacycloheptane structure. However, the transition state for insertion occurs very late, as is evident from a forming C–C bond distance of 2.06 Å and ethylenic bond lengths of 1.42 Å. The enthalpy of activation is 65 kJ/mol.

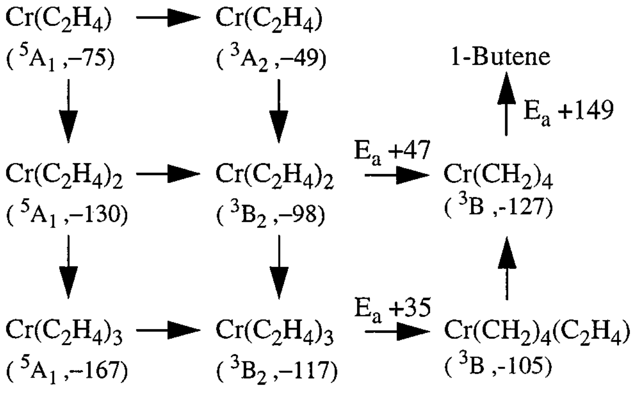

FIG. 2. Schematic overview of initiation reactions between ethylene and the octahedral cluster. Electronic energies relative to separated cluster and ethylene molecules are given within parentheses (kJ/mol). Energy barriers are labeled by E_a. $Cr(CH_2)_4$ denotes a chromacyclopentane ring.

Taking the modest exothermicity of the covalently bound triethylene complex into account, a considerable ethylene pressure is probably required for it to form in appreciable amounts, even at room temperature. This is not a serious obstacle as far as initiation is concerned, since it needs to take place only once at each site. The triplet-coupled triethylene complex may undergo ring-fusion reactions either to form a chromacyclopentane structure with a coordinating ethylene molecule or, alternatively, to form a chromacycloheptane species. The latter route was examined following a path that preserves C_2 symmetry, implying a concerted fusion of two C–C single bonds. While the top point of the resulting energy profile lies a modest 83 kJ/mol above that of the starting triethylene complex, it turns out to represent a point of bifurcating reaction paths rather than a transition state. Relaxation along the symmetry-breaking mode leads to a transition state for formation of chromacyclopentane, and we were thus unable to locate a transition state for the concerted formation of the heptacyclic structure. Our search was not exhaustive though, and a direct route from the triethylene complex to a chromacycloheptane structure can thus not be ruled out completely. The concerted path that was examined leads to a local minimum at the potential energy surface, with chromium adopting a square-planar structure with the organic ligand occupying *trans* positions. However, only a low barrier of 36 kJ/mol separates this structure from the global minimum, in which the hydrocarbon moiety relaxes to provide chromium with the coordination geometry of a flattened tetrahedron.

4.1.2. β-H transfer. Transfer of hydrogen from a β carbon to a δ carbon in chromacyclopentane was examined as a possible route to 1-butene. The transition state displays a strained four-membered pseudo ring consisting of the β hydrogen and the hydrocarbon moiety without the α carbon. The β hydrogen binds simultaneously to chromium and the β and δ carbon atoms. The transition state constitutes a barrier of 149 kJ/mol relative to the chromacyclopentane structure, suggesting that the formation of 1-butene along this path is of little importance.

Starting from a chromacycloheptane structure, the corresponding β-H transfer reaction to form a covalently coordinated 1-hexene is much more facile. The transition state now contains a more flexible six-membered pseudo ring, and the activation energy drops to 58 kJ/mol, reflecting the difference in strain between cyclobutane and cyclohexane (33).

4.1.3. Direct insertion of ethylene. A topical mechanism for chain propagation in a chromacycloalkane structure involves the direct insertion of ethylene into a Cr–C bond. Such a reaction takes place with a negligible barrier at the square-planar conformation described earlier for chromacycloheptane. However, since there does not appear to be any likely mechanisms for stabilizing this reactive conformation, the prospects of chain propagation are tied to the properties of chromacycloalkane in its global minimum structure, i.e., that of a flattened tetrahedron. Rather than considering insertion to a sequence of cyclic structures of increasing length, we note that as the ring size grows, the properties of the chromacycloalkane species approach those of the analogous dialkylchromium structure. For simplicity, we consider ethylene insertion to a dimethylchromium structure, which is interesting also from the perspective of Scott and Ajjou's proposal of a dialkylchromium(IV) starting structure for polymerization (17).

The reactant adopts the shape of a flattened tetrahedron (cf. **1a** in Fig. 3), and ethylene may approach the metal either between the methyl ligands ("front side") or between the ester oxygens ("backside"). In either case the formation of a chromium–ethylene complex is an endothermic process. The front-side complex is 68 kJ/mol above the reactants in energy and adopts a structure with ethylene at the apex of a square pyramid. The ethylenic carbon–carbon bond is stretched to 1.39 Å, and only a negligible energy barrier separates ethylene from being inserted into one of the Cr–C bonds. The methylpropylchromium product resembles the reactant complex as far as the local geometry about chromium is concerned. The back-side dimethylchromium–ethylene complex is 33 kJ/mol more stable than the front-side complex. However, subsequent insertion of ethylene into a Cr–C bond requires an activated inversion about chromium, with an energy requirement exceeding that of the front-side insertion.

4.1.4. Discussion. The pseudo-octahedral chromium (II) cluster is found to provide an accessible route to a

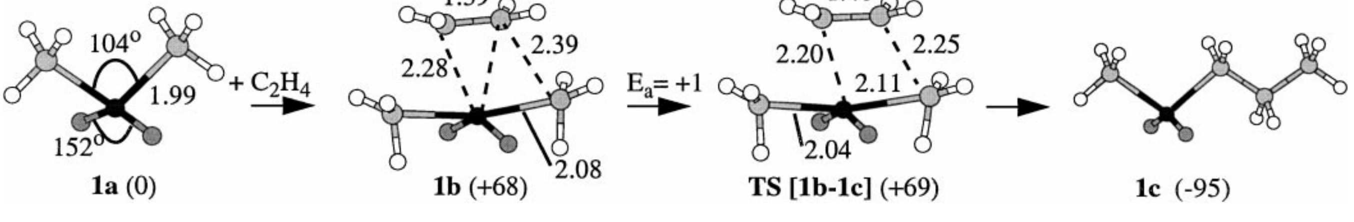

FIG. 3. Stationary points along the reaction path of ethylene insertion into a Cr–methyl bond in a dimethylchromium(IV) species. Electronic energies (kJ/mol) are given within parentheses, relative to the separated cluster and ethylene molecule(s). E_a denotes an energy barrier. Bond lengths are given in Å, and angles are given in degrees. Only the top section of the cluster is shown.

chroma(IV)cyclopentane structure through the adsorption of 2 equiv of ethylene. While the barrier toward formation and release of 1-butene appears prohibitively high, the five-membered ring may insert ethylene into a Cr–C bond and form the analogous chromacycloheptane structure. The activation energy for this transformation is 87 kJ/mol as computed relative to the separated reactants. Formation of 1-hexene proceeds easily, whereas repeated insertion of ethylene is hampered by both an enthalpy of activation of some 70 kJ/mol and an unfavorable entropy factor caused by the lack of a stable ethylene–chromium precursor complex.

The properties of the octahedral site differ from those observed for Phillips catalysts on three accounts. First and foremost, the free energy of the transition state associated with the propagation step is too high to comply with the observed activity toward polymerization. Second, chromium as described here would catalyze the formation of 1-alkenes over polymers. Finally, the initial formation of a chromacycloheptane structure seems to rely on a high partial pressure of ethylene. Although the industrial process uses a high ethylene pressure (2), this does not seem required in order to initiate polymerization without an induction period (16, 17).

It is, however, interesting to note that once the square-pyramidal ethylene–chromium complex **1b** is formed, insertion proceeds essentially without barrier. Thus, given an external steric factor to keep the four-coordinated chromium(IV) species in a square-planar configuration, high activity toward polymerization would probably result. An oxygen donor is a candidate "steric factor," as suggested by Ajjou and Scott (16), given that the donor becomes displaced upon ethylene complexation, only to recoordinate following insertion. Unfortunately, the dialkylchromium (IV) structure displays little susceptibility to nucleophilic attack, be it from ethylene or from a neighboring oxygen donor. Hence, in order to alter the local geometry around chromium, the oxygen donor would have to be nondisplaceable, effectively preventing coordination of etylene.

4.2. *Tetrahedral Cr(II)-B*

4.2.1. Ethylene coordination. The Cr(II)-B cluster model may adsorb 2 equiv of ethylene, with binding energies of 78 and 54 kJ/mol, respectively. In each case, ethylene coordinates *trans* to an ester oxygen ligand (cf. structures **2a** and **2d** in Fig. 4), giving rise to a square planar diethylene complex. Taking into account the change in entropy, it appears that both mono- and diethylene complexes may be present in significant amounts. However, only the monoethylene complex is found to undergo transformation to a covalently bound complex (**2b** in Fig. 4) in which the donation bond is supplemented by back-donation from Cr 3d into the π^* orbital at the olefin. This transformation is endothermic by 24 kJ/mol and formally implies that chromium gets oxidized to Cr(IV), adopting a triplet spin state. Depending on the proximity and orientation of the coordinating silanol group, it may prevent **2b** from adding a second ethylene to form chromacyclopentane.

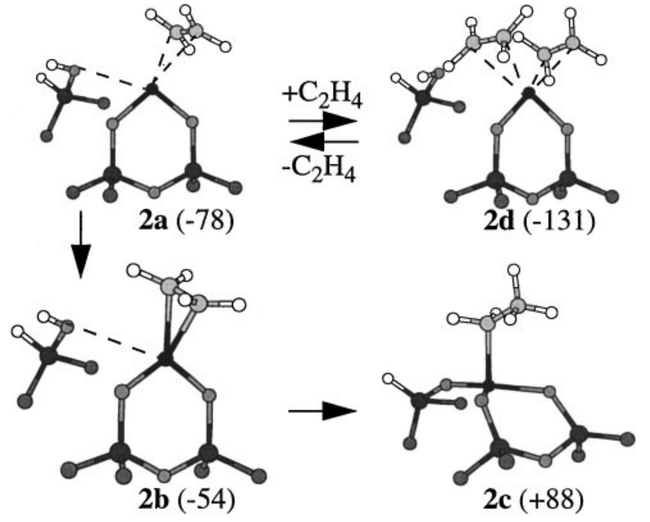

FIG. 4. Initiation reactions at a constrained chromium(II) site. Electronic energies relative to separated cluster and ethylene molecule(s) are given within parentheses (kJ/mol).

4.2.2. Hydrogenation of the chromium site. Deprotonation of a silanol group requires some 1400 kJ/mol (34) to be compared to a proton affinity of 644 kJ/mol computed for a Cr(II)-A cluster model, i.e., without a donor. The feasibility of proton transfer thus depends on mechanisms for stabilizing the cation and anion produced, such as a favorable Madelung potential, polarization of neighboring atoms, and Coulomb attraction between the ions formed. Given the magnitude of the stabilization needed and also the polar-covalent nature of silica, the latter mechanism holds the greater promise for realizing proton transfer. In Fig. 4, **2c** shows the structure resulting from transferral of a silanol proton to the triplet-coupled Cr(IV)(ethylene) complex. The product is highly strained due to geometry constraints imposed on the cluster model, yet displays a four-coordinated chromium. Moreover, the reaction proceeds uphill energetically, by 141 kJ/mol. According to the Mulliken population analysis, the charge on the silanoic base is only 0.37*e* more negative than that of the neutral silanol. This implies that the silanol moiety acts as a hydrogen donor rather than as a Brønsted acid, in agreement with the reported properties of isolated hydroxyl groups at the surface of amorphous silica (35).

To investigate the energetics of hydrogen transfer without relying on predefined geometric constraints, a larger cluster model was constructed (see Fig. 5) and made subject only to C_s symmetry. In this case, the reaction path of hydrogen transfer passes over a modest barrier of 54 kJ/mol, forming a four-coordinated ethylchromium(IV)

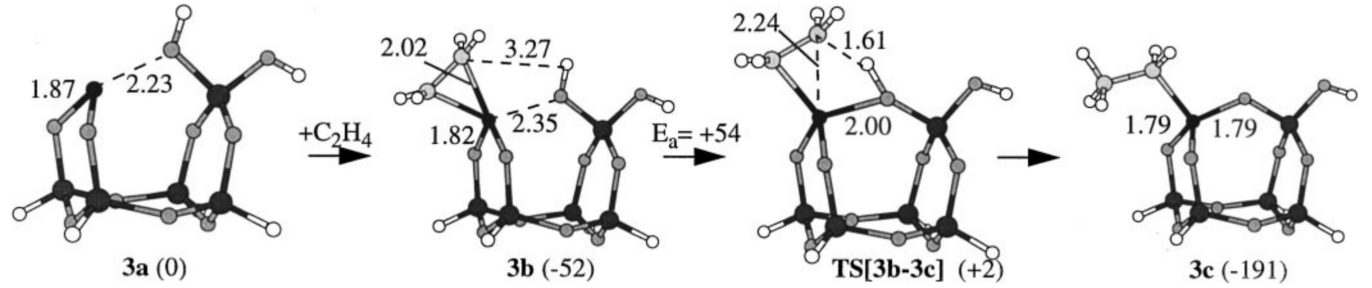

FIG. 5. Fully relaxed reaction path for hydrogen transfer to a chromium(II) site. Electronic energies relative to separated cluster and ethylene molecule(s) are given within parentheses (kJ/mol), and energy barriers are denoted by E_a. Bond lengths are included in Å.

species with an overall exothermicity of 191 kJ/mol. At the transition state, the forming carbon–hydrogen bond distance is 1.61 Å, and the hydroxyl bond is stretched by only 0.15 Å relative to the reactant complex. The chromium–carbon bond to be broken is stretched by 0.22 Å, and the distance between chromium and the silanoic oxygen is down to 2.00 Å.

The preceding two examples show that structural flexibility as well as polarizability of the larger site may change the hydrogen transfer reaction needed to prepare a monoethylchromium(IV) species from being endothermic by more than 140 kJ/mol into being exothermic by about the same amount. When proceeding to study reactivity on the smaller cluster, an element of geometric relaxation following hydrogenation is introduced by decreasing the distance constraint on the silanoic moiety by 0.5 Å, compared to what is described in Section 3. This amount of relaxation suffices to reduce the energy cost of transferring a hydrogen from the silanol moiety to a covalently coordinated ethylene to only 7 kJ/mol, i.e., into an essentially isoenergetic reaction. The resulting ethylchromium(IV) structure displays a slightly distorted trigonal pyramidal geometry in which the oxygen ligands occupy equatorial positions with ∠OCrO angles of 94, 124, and 139°. While this structure does not display affinity for ethylene, such a capacity is introduced by distorting the structure toward a square-pyramidal geometry with a vacant site (cf. values for ∠OCrO listed under **4a** in Table 1). The energy cost of these distortions lies in the range of 15–30 kJ/mol.

Even though we have focused on hydrogen transfer from silanol to an ethylene that is already covalently coordinated to chromium, other routes to a four-coordinated monoalkylchromium(IV) structure are conceivable. For instance, in the model system of Scott and co-workers (13–17), hydrogen transfer to a carbenechromium(IV) species is thermodynamically favored over transfer to a coordinated ethylene. Conversely, we find that the Cr–hydride bond is too weak to facilitate direct hydrogenation of the metal.

4.2.3. Propagation. The insertion of ethylene into the Cr–ethyl bond in ethylchromium(IV) will be described next. The reactant complex is presented in Fig. 6, with selected geometry parameters given in Table 1. As prepared, ethylene coordinates to the vacant position in the equatorial plane of the reactant complex at a Cr–C distance of 2.80 Å. The coordination energy is a modest 20 kJ/mol, and, in accord with this, the ethylenic double bond is barely stretched. The transition state toward insertion of ethylene is found at an energy of 46 kJ/mol above the π-complex. At this point, the forming carbon–carbon bond is still 2.26 Å, and together with values of Cr–C and other C–C bond lengths presented in Table 1, this geometry indicates an early transition state. The insertion is assisted by an α-agostic interaction at the transition state, evident from a C_3–H_α bond that is stretched by 2.7 pm at a Cr–H_α distance of 2.00 Å. Furthermore, along the path of insertion, the weakest bound oxygen ligand (O_1) is temporarily displaced by the incoming ethylene molecule. This is evident from a 0.2 Å elongation of the Cr–O_1 bond in the transition state as compared to either reactants or product (cf. Fig. 6 and Table 1).

The enthalpy of the monomer–chromium bond is too low to render the π-bound complex a realistic resting state in

TABLE 1

Geometry Parameters of Stationary Points along the Reaction Path of Ethylene Insertion into the Cr–Ethyl Bond in Ethylchromium(IV) Species 4a, via an Ethylene–Chromium π-Complex (4b) and the Transition State TS[4b–4c], to the Butylchromium(IV) Product (4c)[a]

	4a	4b	TS[4b–4c]	4c
$r\mathrm{CrC}_1$	—	2.81	2.11	2.00
$r\mathrm{CrC}_2$	—	2.80	2.34	3.01
$r\mathrm{CrC}_3$	2.00	2.02	2.14	4.38
$r\mathrm{C}_1\mathrm{C}_2$	(1.33)[b]	1.34	1.41	1.51
$r\mathrm{C}_2\mathrm{C}_3$	—	3.38	2.26	1.54
$r\mathrm{CrO}_1$	1.99	2.03	2.21	1.98
$r\mathrm{CrO}_2$	1.80	1.82	1.82	1.80
$r\mathrm{CrO}_3$	1.91	1.94	1.91	1.90
$\angle\mathrm{O}_1\mathrm{CrO}_3$	153	161	169	154
$\angle\mathrm{O}_2\mathrm{CrO}_3$	109	105	106	108
$\angle\mathrm{O}_1\mathrm{CrO}_2$	93	91	85	93

[a] Units: bond lengths (r) in Å, angles (∠) in degrees.

[b] Free monomer.

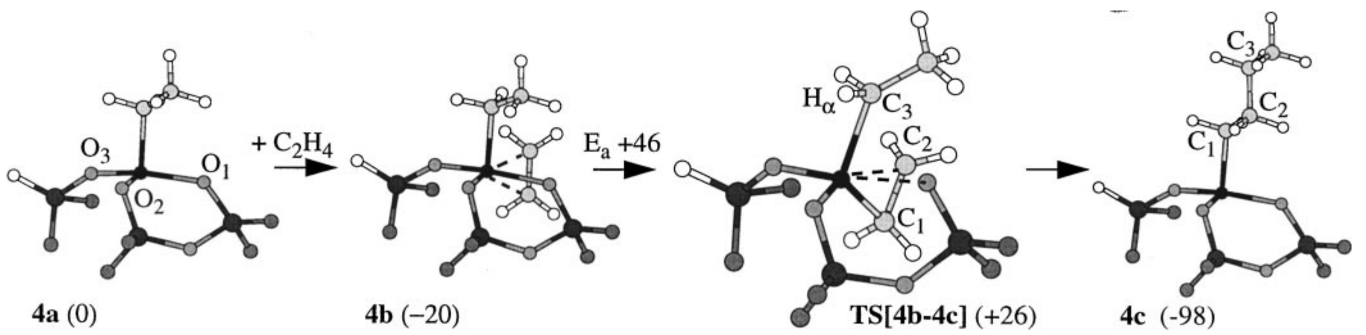

FIG. 6. Stationary points along the reaction path of ethylene insertion into a Cr–ethyl bond in ethylchromium(IV) species. Electronic energies relative to separated cluster and ethylene molecule(s) are given within parentheses (kJ/mol), and energy barriers are denoted by E_a.

this system. The apparent activation energy of chain propagation should thus be calculated relative to free ethylene. In the present model system, this quantity amounts to 26 kJ/mol, which may be decomposed into contributions from coordination and insertion as $\Delta H_\pi = -20$ kJ/mol and $\Delta H^\ddagger = +46$ kJ/mol, respectively.

4.2.4. Local structure vs activity. To determine the optimal surrounding of a Cr(II)-B site with respect to catalytic activity requires a more elaborate model than the one used here, including electrostatic effects from and covalent bonds within a significant part of the embedding silica. However, our study opens for identification two decisive factors in this respect: (i) geometric constraints affecting the orientation of the silanoic group at the hydrogenated site and (ii) the strength of the chromium–oxygen bonds in the same structure.

Concerning the first point, it is probably important that the ethylchromium(IV) structure approaches that of a square pyramid with one position available for complexation. With three equivalent oxygen atoms coordinating to chromium, the affinity for ethylene becomes too low. For example, if the $\angle O_1CrO_3$ angle in **4a** (Fig. 6) is allowed to relax by 15 kJ/mol toward a trigonal structure, the stability of the ethylene–chromium complex drops to 8 kJ/mol, and, at the same time, the apparent enthalpy of activation increases to 57 kJ/mol for the insertion step. The second factor may be demonstrated in a cluster model made subject to constraints that imply lengthened chromium–oxygen bonds. While this gave a vacant site with high affinity toward ethylene complexation and also a low barrier in the subsequent insertion step, the hydrogen transfer reaction required to form the active site turns out to be prohibitively costly.

4.2.5. Discussion. Scott and Ajjou (17) present convincing evidence for the presence of carbenechromium(IV) species during the preparation of their model catalyst. While cycloaddition of ethylene to give chromacyclobutane species is a facile reaction, subsequent hydrogen transfer within the ring is associated with high activation energies, irrespective of the $\angle$OCrO angle characterizing the site (cf. this work and Ref. 18). Hence, initiation mechanisms relying on such reaction steps do not seem topical to systems that show instant activity toward polymerization. Our calculations suggest that, prior to the inlet of ethylene or in competition with cycloaddition of ethylene, the site may get activated through hydrogen transfer from a silanol group to form a tetravalent alkylchromium species with a coordinated silanoic oxygen. Analysis of volatiles during the early stages of polymerization shows a series of odd-numbered alkenes containing a *tert*-butyl end group, originating from the remaining neopentyl ligand. The initiation mechanism proposed here accounts for the structure of these alkenes. The amounts at which they are found indicate that a considerable fraction of the chromium sites at the surface are activated (17). The exothermicity associated with hydrogen transfer from silanol groups to carbenechromium species suggests a higher percentage of activated monochromium sites in Scott and Ajjou's model system than what is the case for conventional Phillips catalysts (1).

Starting from the ethylchromium(IV) conformation **4a** in Fig. 6, the enthalpy of the transition state of monomer insertion is computed to be $\Delta H^\ddagger_{app} = 26$ kJ/mol, relative to free reactants. This number agrees closely with reports for Scott's model system (16, 17), for which the observed enthalpy of activation was $\Delta H^\ddagger_{obs} = (30.2 \pm 0.9)$ kJ/mol, with uncoordinated ethylene found to be the proper reference state. While encouraging, the *ad hoc* construction of our cluster model forbids too much significance to be attached to this agreement. However, the presence of Cr(II)-B sites with weakly coordinating silanol moieties has been observed (24), and cluster models closely related to those presented here are able to account for vibrational frequencies as well as adsorbent properties of these sites (25). Moreover, the model contains mononuclear chromium that maintains an oxidation state of IV during polymerization and supports a propagation mechanism that proceeds by insertion of the monomer *via* an α-agostic transition state. All of these features are shared with properties deduced from the experimental model study (17). Furthermore, a carbonyl IR band (2191 cm^{-1}) assigned to carbonyl species at Cr(II)-B sites (25) is attenuated in IR spectra recorded after short-time polymerization (10). This observation supports the claim that Cr(II)-B sites may be active with respect to polymerization.

Schmid and Ziegler recently reported on a theoretical study of chain propagation in a system related to our Cr(II)-B model, except that chromium was assumed to be protonated, and in oxidation state IV, without any interaction with the corresponding anion (36). Protonation has also been suggested earlier as a mechanism for activation (37, 38). Our results show that the interaction between the metal complex and a proton-donating silanol group will be strong and of covalent character. Combined with the observation that isolated hydroxyl groups at the surface of amorphous silica are only weakly acidic (35), this suggests that formation of isolated, chromium-containing cations is unlikely.

A conventional Phillips catalyst prepared at a calcination temperature below 500°C does not display appreciable activity, most likely due to detrimental coordination of hydroxyl groups to the active sites (1). How can this finding be reconciled with the presently proposed concept of an active site? In light of the rather low complexation energy of ethylene at the activated ethylchromium(IV), the presence of weakly coordinating silanol groups close to the vacant site may be enough to prevent coordination and thus also chain propagation. In this perspective, it is important to reduce the surface hydroxyl population to isolated silanols, as outlined in the Introduction. Indeed, McDaniel and Welch found the polymerization activity to increase as a function of the calcination temperature (19). Dehydroxylation is accompanied by increased surface strain and possibly also by an increase in the acidity of the remaining silanol groups (39). These modifications may be beneficial to the catalytic activity (cf. the preceding comments concerning structure and activity of the active site).

McDaniel and Welch reached the conclusion that the Phillips catalyst possesses two types of active sites producing high- and low-molecular-weight (MW) polymers (19). The complete removal of surface hydroxyls by, e.g., fluorination still allows highly active Phillips-type catalysts to be prepared. However, this patented modification of the catalyst produces a high-MW polymer with a narrow MW distribution (1). Since the Cr(II)-B model investigated here depends on a hydrogen source to become activated, it may be responsible for production of the low-MW polymer. The active sites at catalysts that are dehydroxylated by chemical means are most likely activated in a reaction with ethylene. Rebenstorf suggested that this may take place at dichromium(II) (9) and dichromium(III) (10) sites, leading to μ-ethano(chromium)$_2$ structures. Prospects of ethylene polymerization over dichromium(II) sites are investigated in Ref. 40.

In general, we find hydridochromium(IV) structures to have low stability, and, furthermore, that molecular hydrogen is not able to compete with ethylene as a coordinating ligand. This implies that chain termination is not likely to occur through transfer of hydrogen to the metal, in agreement with the observed lack of influence from ethylene pressure on the chain length of the produced polymer (41). We note that termination by β-hydrogen transfer to monomer leads to linear, even-numbered α-olefins, in agreement with findings for the Phillips catalyst (6) and the model system of Scott and Ajjou, past the initiation phase (17).

Finally, it is interesting to note that Phillips catalysts are unique in their response to H_2 in the feed (1). Contrary to what is seen in Ziegler–Natta systems (1), Phillips catalysts respond by an increase in activity (17), and there is no evidence of hydrogenation (1); i.e., the produced polymers possess vinyl termini and suffer only a minor decrease in chain length (1, 17). The effect of adding hydrogen in the feed may then be understood in terms of dissociative chemisorption of H_2 at strained siloxane defects (42) to give SiOH and SiH and subsequently activation of suitably positioned Cr(II) sites. Alternatively, hydrogen may react with inactive chromacyclobutane and -pentane species to reduce the metal under release of alkanes. This may open for activation through hydrogenation as discussed earlier.

5. CONCLUSION

The pseudo-octahedral site is found to adsorb ethylene readily and to undergo cycloaddition, forming a chroma(IV) cyclopentane species. However, neither this nor the related dialkylchromium structure shows any affinity toward further reactions with ethylene. Drawing on previous work (18), this demonstrates that independent of the $\angle$OCrO realized at the anchoring site, dialkylchromium(IV) structures are not likely to assist polymerization of ethylene.

Ethylene coordinates to chromium(II)-B sites in both molecular and covalent modes. Given the proper balance between surface rigidity and acidity of the coordinating silanol, hydrogen transfer to give a four-coordinated ethylchromium(IV) species is found to be thermodynamically and kinetically feasible. If distorted toward square pyramidal geometry, ethylchromium(IV) displays affinity for ethylene complexation. Furthermore, subsequent insertion of ethylene into the Cr–alkyl bond proceeds with a modest barrier. This reaction step is assisted by an α-agostic interaction in the transition region, and chromium maintains oxidation state IV also after insertion. The resulting active-site model seems to be able to account for a number of properties observed for conventional Phillips catalysts as well as for recently developed model catalysts (17).

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