

The Effect of the Electronic Nature of Spectator Ligands in the C–H Bond Activation of Ethylene by Cr(III) Silicates: An *ab initio* Study

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Abstract: The Phillips catalyst, chromium oxides supported on silica, is one of the most widely used catalysts for the industrial production of polyethylene (PE). We recently synthesized a well-defined mononuclear Cr(III) silicate as active site model of the Phillips catalyst. The catalytic activity of this well-defined catalyst was similar to the industrial Phillips catalyst. We proposed that C–H bond activation of ethylene over a Cr–O bond initiates polymerization in this Cr(III) catalyst. Our results also showed that the presence of a second ethylene olefin in the coordination sphere of Cr decreases the intrinsic energy barrier of the C–H activation of ethylene. In order to understand the effect of this additional ligand in the C–H activation of ethylene by the Cr(III) catalyst, we evaluated the energetics of this step with different spectator ligands (C₂H₄, C₂F₄, N₂ and CO) coordinated to the Cr center. The Charge Decomposition Analysis (CDA) of the bonding interactions between the Cr(III) catalyst and the ligands showed that the intrinsic energy barrier for the C–H activation of ethylene decreases with the increasing electron-donor properties of the spectator ligand.

Keywords: C–H activation · Charge decomposition analysis · Density functional theory · Ethylene polymerization · Phillips catalyst

Introduction

Polyethylene (PE) is one of the most widely used plastics worldwide.^[1] There are three classes of catalysts for the polymerization of ethylene:^[2] the Phillips catalyst containing chromium oxide supported on silica (CrO_x/SiO₂), the Ziegler-Natta catalyst containing TiCl₃ activated with AlR₃ (R = alkyl) supported on MgCl₂, and homogeneous metallocene catalysts of early and late transition metals. In contrast to the Ziegler-Natta and the homogeneous catalysts, the Phillips catalyst does not require an activator or co-catalyst. The catalyst is prepared by impregnating a chromium precursor on a silica support followed by calcination at high temperatures in dry air or oxygen, typically above 400 °C.^[1–3] At low Cr loadings this approach produces mostly monochromates with Cr in the +6 oxidation state.^[4] The reaction of

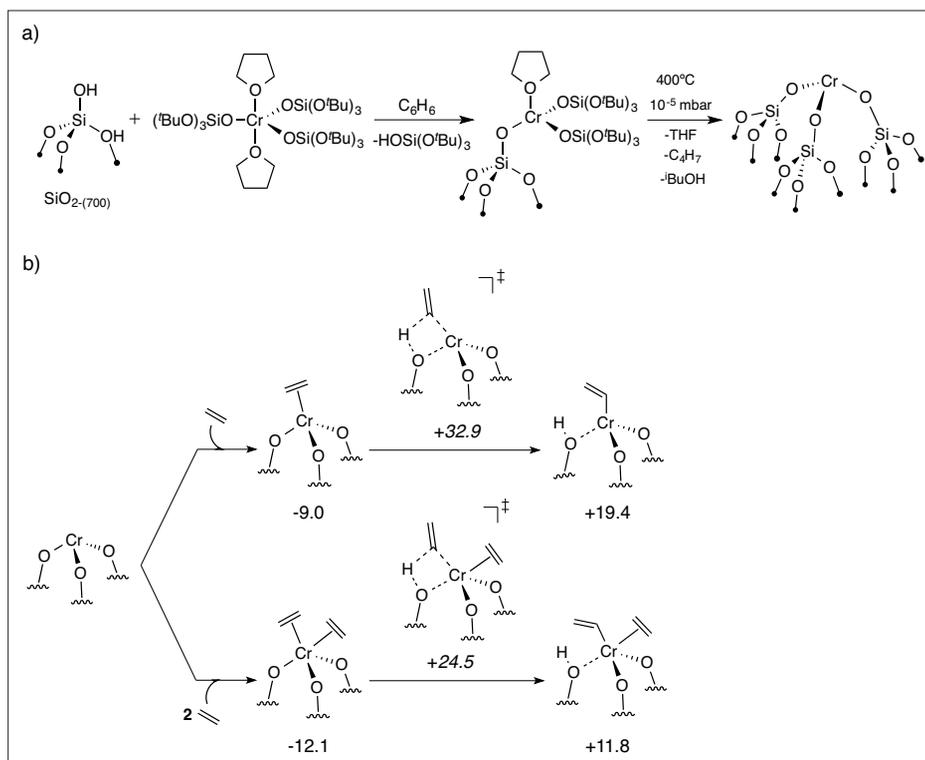
this material with ethylene produces polyethylene with a pronounced induction period. During this period the Cr surface sites undergo complex redox chemistry to form the active species. Several studies showed that Cr(II) is present in pre-reduced catalysts,^[5] though Cr(III) was also shown to be active in model catalysts.^[6] However, the structure of the active site in Phillips catalyst remains unknown.^[2,3] One of the major challenges in determining the active site is the very small fraction (*ca.* 10%) of the surface sites that are active in polymerization, making any structural assignment a daunting task at the current stage.^[7]

The need for better-defined Cr-based systems for the study of ethylene polymerization led our group to synthesize a well-defined Cr(III) catalyst supported on silica^[8] *via* the thermolytic molecular precursor (TMP)^[9] approach, as shown in Scheme 1a. We found this approach allows the construction of well-defined Cr sites of a predetermined oxidation state and nuclearity, and results in an active catalyst that forms high-density PE.^[8a] Experimental and computational evidence suggested that this well-defined Cr(III) catalyst initiates polymerization by C–H bond activation of one ethylene molecule across a Cr–O bond of tri-coordinated Cr(III) site. This reaction forms a Cr-vinyl species containing one in-

teracting silanol in the catalyst, as shown in Scheme 1b. This process corresponds to a concerted σ -bond metathesis mechanism with a four-center transition state, consistent with a proton transfer from carbon to oxygen. Concerted σ -bond metathesis reactions are common on oxide surfaces^[10] and are key steps in a large number of important reactions.^[11] Computational studies on other initiation pathways involving oxidative addition/reductive elimination or oxidative coupling did not lead to stable intermediates.

Importantly, the presence of a second olefin molecule coordinated to Cr decreases the energetic cost of the C–H bond activation step. The intrinsic energy barrier (the barrier with respect to the most stable olefin coordinated species) is decreased by 5.3 kcal·mol⁻¹ (about 12%). These results suggest that the additional ethylene molecule assists the proton transfer and ultimately accelerates the initial step of the ethylene polymerization process. It is therefore critical to understand the stereo-electronic effects associated with the second ligand on the C–H bond activation process. Hence, we investigated the effect of various spectator ligands (CO, N₂ and C₂F₄ and C₂H₄) on the energetic cost of the C–H activation step and evaluated the bonding situation in greater detail.

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Scheme 1. a) Synthesis of mononuclear Cr(III) sites supported on silica prepared by the thermolytic molecular precursor (TMP) approach; b) Initiation mechanisms for the C–H activation of ethylene by the Cr(III) catalyst. The numbers denote Gibbs energies that are given in kcal·mol⁻¹. Detailed methods for calculation of the final energies can be found in ref. [8a].

Density Functional Theory (DFT) is a powerful method to study the interactions between transition metals and organic ligands.^[12] Several bonding models have been developed for the study of transition metal-based compounds, the most widely used being the Ligand Field Theory.^[13] This method considers the interaction between *d* orbitals of the metal and the valence orbitals of the ligands. The Dewar-Chatt-Duncanson^[14] model considers the interactions between the metal (M) and the ligands (L) in terms of electron donation L → M and back-donation M → L. Also, in recent years new methods to quantitatively study the chemical bond that can be applied to transition metal compounds have been developed. The most widely used methods are the Natural Bond Orbital (NBO) method,^[15] the Charge Decomposition Analysis (CDA),^[16] the Atoms-in-Molecules (AIM) model,^[17] and the Energy Decomposition Analysis (EDA).^[18] Among these methods, we decided to adopt the CDA scheme in order to study the electron interactions between the Cr catalyst and the spectator ligands.

Theory and Computational Details

All geometries were optimized at DFT level by means of the B3LYP hybrid density functional^[19] in the unrestricted formalism using the Gaussian 09 code.^[20] We

considered only the high spin configuration of the Cr(III) *d*³ ion (quartet, *S* = 3/2) because the doublet was much higher in energy. Moreover, spin crossing was not encountered during the exploration of the potential energy surfaces. The LanL2DZ Effective Core Potential (ECP) of Hay and Wadt^[21] for Cr and the 6-311G(*d,p*)^[22] basis sets for main group elements were used. The nature of all the stationary points was confirmed by computing the Hessian matrix. No imaginary frequencies were found for minima whereas only one imaginary frequency was found for the transition-state structures. Intrinsic reaction coordinate (IRC) calculations confirmed that the computed transition states were actually connecting the corresponding reactants and products. The final electronic energies reported in the manuscript were calculated at the UB3LYP/TZVP level.

The CDA scheme was carried out as described by Dapprich and Frenking.^[16] In this method, the interaction between the two fragments A and B is partitioned into three terms: the electron donation from A to B, the electron donation from B to A, and the reorganization due to electron–electron repulsion in the bonding region. Here, we will only show the basic formulation as proposed by the authors in order to study bonding interaction between the two fragments. A more detailed description of the formalism can be found elsewhere.^[16]

The charge donation d_i from A to B,

the back-donation b_i from B to A and the repulsion r_i between the two fragments are defined as follows:

$$d_i = \sum_k^{occ,A} \sum_n^{vac,B} m_i c_{ki} c_{ni} \langle \Phi_k | \Phi_n \rangle \quad (1)$$

$$b_i = \sum_l^{occ,B} \sum_m^{vac,A} m_i c_{li} c_{mi} \langle \Phi_l | \Phi_m \rangle \quad (2)$$

$$r_i = \sum_k^{occ,A} \sum_m^{occ,B} m_i c_{ki} c_{mi} \langle \Phi_k | \Phi_m \rangle \quad (3)$$

In Eqns (1)–(3), *i* and *m* are the index and the occupation number of the molecular orbitals of the molecule, respectively. The integrals $\langle \Phi | \Phi \rangle$ are the overlap integrals between the fragment molecular orbitals. The summation of d_i over all molecular orbitals leads to the overall charge donation from A to B. Analogous analysis can be made about b_i . The term r_i is usually interpreted as a closed-shell interaction between two different fragment orbitals in different fragments. Positive values of r_i mean that the electrons of the two fragments are accumulated in their overlap region showing bonding character, while negative values indicate that the electrons are depleted from the overlap region and thus reflect electron repulsive effects. The sum of all r_i terms is in general negative because the overall interaction between filled orbitals are generally repulsive.

The CDA was performed using the B3LYP functional and the all-electron TZVP basis set with the MULTIWFN software,^[23] which uses a generalized version of the original formulation to make it applicable to open-shell systems, such as those studied here.

Results

Geometries of the Ethylene Adducts and Transition States for the C–H Activation

In order to model the catalyst we adopted a cluster approach, in which the active site of the well-defined Cr(III) catalyst is represented by the cluster model **1** shown in Fig. 1a. The active site is a tri-coordinated Cr center where the terminating Si atoms are saturated with F atoms, a common approach when modeling silica-supported catalysts.^[24] All the studied structures are shown in Fig. 1b.

Table 1 shows the main geometrical parameters of the catalyst and olefin adducts with coordinated C₂H₄ (**3**), CO (**4**), N₂ (**5**) and C₂F₄ (**6**), and Fig. 2 shows the corresponding optimized structures. Cluster **2**, which does not contain a spec-

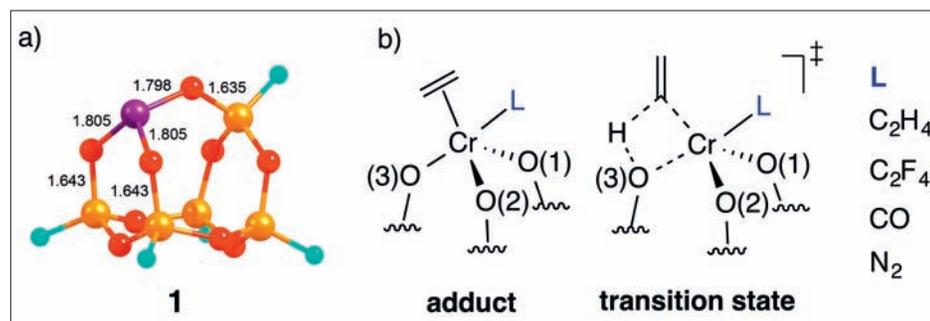


Fig. 1. a) Cluster model used to represent the active site of the silica-supported Cr(III) catalyst; b) Structures of the investigated systems and the ligands used to study the effect of the spectator ligand on the energy barrier of the C–H activation of ethylene.

also affected by the presence of the spectator ligands, with the least pronounced effect corresponding again to C_2F_4 . It is interesting to note that the Cr–L bonds in the transition states are shorter than the same distances in the ethylene adducts (compare the Cr–L columns in Tables 1 and 2), indicating a stronger interaction between the Cr ion and the spectator ligand in the transition state. Unlike the changes in bond distances, the C–H–O angle barely changes to 145–148°, indicating that all transition states correspond to a 4-center σ -bond metathesis reaction.

tator ligand, is used as reference. In **2** the ethylene ligand coordinates almost *trans* to the Cr–O(1) bond, which agrees with the shape of the lowest unoccupied molecular orbital (LUMO) of the bare catalyst.^[24e] The Cr–O distances in the ethylene adduct **2** are 1.823, 1.818 and 1.822 Å (Table 1). The coordination of a spectator ligand in general increases these distances by at least 0.08 Å (Cr–O(3) for structure **5**), except for **6**. **6** contains Cr–O distances practically unchanged with respect to **2**, indicating that the C_2F_4 ligand does not significantly modify the coordination sphere of the Cr center. The distances between Cr and the coordinated ethylene molecule vary from 2.489 to 2.718 Å, while the distance between Cr and the spectator ligand L vary from 2.293 to 3.688 Å. As shown in Fig. 2, the spectator ligands coordinate *trans* to the other Cr–O bond of the 6-member ring system, also in agreement with the distribution of the LUMO of the catalyst.^[24e]

The transition state structures for the C–H bond activation of ethylene are also shown in Fig. 2 and the main geometrical parameters are compiled in Table 2. All transition states for the activation of the C–H bond in ethylene formally correspond to a concerted σ -bond metathesis step, in which the C–H bond of ethylene and a Cr–O bond of the catalyst are broken while new Cr–C and O–H bonds are formed. The transition state **TS-2** (structure without any additional ligand) is characterized by Cr–C, C–H and O–H distances of 2.145, 1.529 and 1.146 Å, respectively. Note that the distance Cr–O(3) in **TS-2** is 1.936 Å, since this is the bond that is broken during the C–H activation step. The C–H–O angle is equal to 144°, a typical value for σ -bond metathesis transition states.^[11b,c,25] As in the case of the ethylene adducts the presence of any of the spectator ligands further increases the Cr–O bonds, with **TS-6** being the least affected. For the C_2F_4 ligand, the Cr–O bond distances only increase by 0.08–0.09 Å while for the rest of the ligands the Cr–O bond increases from 0.012 to 0.031 Å. The bond distances of the 4-center ring in the transition states are

Table 1. Main geometrical parameters of the ethylene coordinated adducts. All distances are given in Å.

Structure	Cr–O(1)	Cr–O(2)	Cr–O(3)	Cr–C(ethylene)	Cr–L
2	1.823	1.818	1.822	2.676/2.489	
3	1.840	1.837	1.840	2.710/2.718	2.694/2.722
4	1.840	1.840	1.837	2.632/2.690	2.293
5	1.833	1.832	1.830	2.624/2.692	2.392
6	1.823	1.819	1.820	2.512/2.679	3.509/3.688

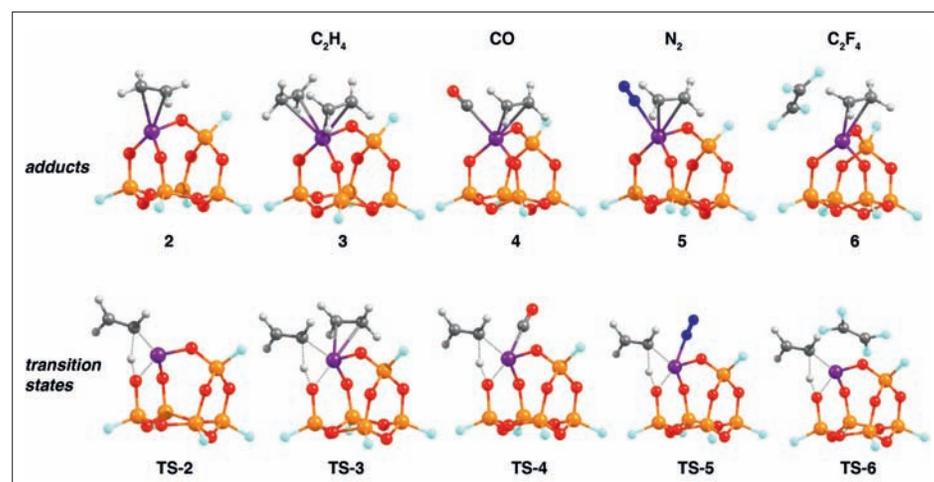


Fig. 2. Structures of the investigated ethylene adducts and the transition states for the C–H bond activation of ethylene by the Cr(III) catalyst.

Table 2. Main geometrical parameters of the transition states (TS) for the ethylene C–H bond activation step. All distances are given in Å and angles in degrees.

TS	Cr–O(1)	Cr–O(2)	Cr–O(3) ^a	Cr–C	C–H	O–H	Cr–L	C–H–O
TS-2	1.863	1.828	1.936	2.145	1.529	1.146		144
TS-3	1.886	1.851	1.967	2.183	1.480	1.160	2.529/2.585	148
TS-4	1.877	1.849	1.962	2.170	1.484	1.164	2.190	148
TS-5	1.875	1.844	1.953	2.166	1.495	1.158	2.239	147
TS-6	1.871	1.837	1.945	2.151	1.509	1.151	2.783/3.013	145

^aCr–O bond that is broken during the C–H activation of ethylene.

Energies of Investigated Systems and Charge Decomposition Analysis

Table 3 shows the reaction energies for the formation of the ethylene adducts and the intrinsic energy barriers for the C–H bond activation of ethylene by **1** with different spectator ligands. The formation of the ethylene adduct **2** is exoenergetic by 12.2 kcal·mol⁻¹. The presence of spectator ligands at the Cr center causes, in general, further stabilization by 2.5–7.0 kcal·mol⁻¹. The formation of the ethylene adduct for **6** (C₂F₄ ligand) is almost isoenergetic with respect to the separate reactants, in agreement with the small geometrical changes previously described.

The energy barrier for C–H activation in the ethylene adduct **2** (TS-2) is 45.2 kcal·mol⁻¹ (Table 3). The presence of the spectator ligands decreases the energy of the transition states by 5.1–7.1 kcal·mol⁻¹ for the CO, N₂ and C₂H₄ ligands, while for C₂F₄ the intrinsic barrier remains practically the same as that of TS-2. Therefore, the stabilization of the transition state for the activation of the C–H bond of ethylene in function of the studied L ligands follows the order: C₂H₄ ≈ CO > N₂ > C₂F₄.

In order to understand this trend in stabilization of the C–H activation transition state the interaction between the spectator ligands and the Cr catalyst was evaluated. The CDA scheme is an excellent tool that has been applied to the study of bonding interactions in organometallic complexes^[26] and to the interaction between small molecules (like CO and NH₃) and metallic surfaces.^[27] At this point it is important to emphasize that the absolute values of the donor–acceptor interactions given by the CDA method have no physical meaning. Instead, it is the *relative* values or *trends* between electron donation and back donation to different ligands that are important for the study of bonding interaction.^[16]

The CDA results for the clusters in this study are shown in Table 3 (electron donation (*d*), the back-donation (*b*) and the repulsion (*r*) terms). Focusing on the electron donation term, *d*, in general the electron-donor ability increase in the order C₂F₄ < N₂ < C₂H₄ < ≈ CO. According to these results, CO is the best electron-donor ligand, with C₂H₄ presenting similar donor ability. C₂F₄ is the poorest electron-donor while the donor ability of N₂ is in between C₂F₄ and C₂H₄/CO. A similar trend of the N₂ and CO electron-donation strength has been found in some metal–carbonyl complexes.^[26b,c] This order in electron donation agrees very well with the assignment of the partial charges calculated with the NBO method. As shown in Table 3, the charges of the L ligand fragment in the transition state decrease in the same order as the electron donor term of CDA, indicating

Table 3. Energies of the ethylene coordinated adducts and the transition states for ethylene C–H bond activation, the CDA results for the studied systems and the NBO charges (*q*) of fragments at the transition state. Energies are given in kcal·mol⁻¹, CDA and partial charges in atomic units.

Structure	ΔE (adduct) ^a	ΔE [‡] (TS) ^a	<i>d</i> ^b	<i>b</i> ^b	<i>r</i> ^b	<i>q</i> Cr	<i>q</i> ethylene ^c	<i>q</i> L
2	-12.2	45.2				1.094	0.265	
3	-17.0	38.3	0.197	-0.004	-0.135	0.822	0.293	0.245
4	-19.2	38.1	0.211	-0.009	-0.143	0.590	0.317	0.399
5	-14.7	40.1	0.104	-0.058	-0.150	0.791	0.307	0.221
6	-11.6	44.6	0.082	-0.022	-0.084	0.888	0.292	0.165

^aReported energies are SCF electronic energies calculated at UB3LYP/TZVP level; ^bdonation (*d*), back-donation (*b*) and repulsion (*r*) in CDA were calculated *via* Eqns (1), (2) and (3); ^cthe ethylene ligand is the ligand which is activated.

that when considering only pure electronic charges the trend in the electron-donor ability is maintained.

The electron donor order of the studied ligands described above agrees with the variation of the intrinsic energy barrier for all studied ligands, as shown in Fig. 3. This finding indicates that the stronger the electron-donating ability of the spectator ligand, the lower the energy barrier for the activation of the C–H bond in ethylene. The same effect has been rationalized for the reaction rate acceleration of C–H bond activation in benzene by cationic Pt(II) complexes.^[28]

It is worth mentioning that the back-donation term from CDA in all studied systems is negative. While having no physical meaning, these negative values indicate that the back-donation from the metal to the ligands is virtually zero. This result is consistent with the observed blue shift in the CO stretch in the CO-adsorbed adducts of the same catalyst.^[8a] The NBO analysis at the transition states revealed the same results, where very low back bonding was

found between the Cr metal and the spectator ligands.

Conclusions

The effect of several spectator ligands with different electron donating abilities (CO, N₂, C₂H₄ and C₂F₄) on the energy barrier of the C–H activation of ethylene by a silica-supported Cr(III) catalyst was investigated using the Charge Decomposition Analysis. The results from this analysis indicate that the strength of electron donation of the spectator ligand is related to the energy barriers for the activation of the ethylene C–H bond. Accordingly, the electron donating ability of the ligands follows the order C₂F₄ < N₂ < C₂H₄ < ≈ CO. These results are also in agreement with the NBO analysis of the fragment charges at the transition state structures.

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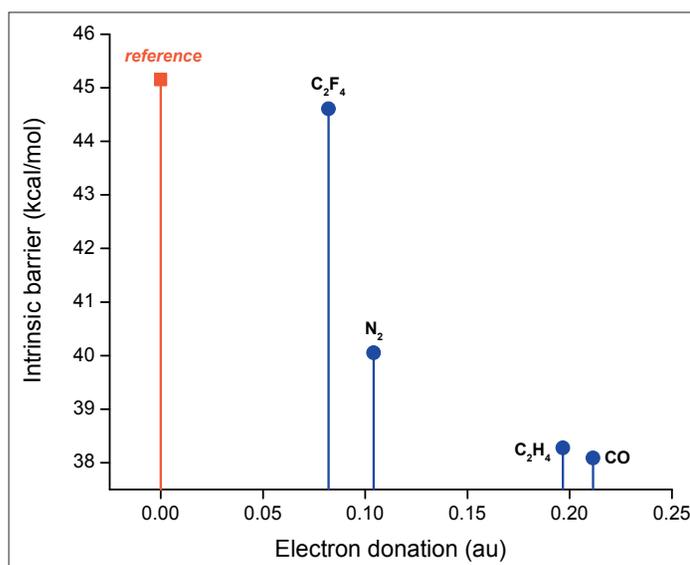


Fig. 3. Relationship between the intrinsic energy barrier for C–H activation of ethylene and the electron donation of the spectator ligand. The reference system (in red) corresponds to TS-2 (Fig. 2, Table 3).

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- [1] M. P. McDaniel, 'A Review of the Phillips Supported Chromium Catalyst and Its Commercial Use for Ethylene Polymerization', in 'Advances in Catalysis', Eds. C. G. Bruce, K. Helmut, Academic Press, **2010**, Vol. 53, pp 123–606.
- [2] B. M. Weckhuysen, R. A. Schoonheydt, *Catal. Today* **1999**, *51*, 215.
- [3] E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, *Chem. Rev.* **2005**, *105*, 115.
- [4] M. P. McDaniel, K. S. Collins, E. A. Benham, *J. Catal.* **2007**, *252*, 281.
- [5] a) B. M. Weckhuysen, I. E. Wachs, R. A. Schoonheydt, *Chem. Rev.* **1996**, *96*, 3327; b) S. Bordiga, E. Groppo, G. Agostini, J. A. van Bokhoven, C. Lamberti, *Chem. Rev.* **2013**, *113*, 1736; c) L. M. Baker, W. L. Carrick, *J. Org. Chem.* **1968**, *33*, 616.
- [6] a) D. L. Myers, J. H. Lunsford, *J. Catal.* **1986**, *99*, 140; b) L. K. Przhivalskaya, V. A. Shvets, V. B. Kazansky, *J. Catal.* **1975**, *39*, 363.
- [7] M. P. McDaniel, S. J. Martin, *J. Phys. Chem.* **1991**, *95*, 3289.
- [8] a) M. F. Delley, F. Nunez-Zarur, M. P. Conley, A. Comas-Vives, G. Siddiqi, S. Norsic, V. Monteil, O. V. Safonova, C. Coperet, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 11624; b) M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova, C. Coperet, *Angew. Chem. Int. Ed.* **2014**, *53*, 1872.
- [9] K. L. Furdala, T. D. Tilley, *J. Catal.* **2003**, *216*, 265.
- [10] C. Coperet, *Chem. Rev.* **2010**, *110*, 656.
- [11] a) S. Q. Niu, M. B. Hall, *Chem. Rev.* **2000**, *100*, 353; b) R. Waterman, *Organometallics* **2013**, *32*, 7249; c) Z. Y. Lin, *Coord. Chem. Rev.* **2007**, *251*, 2280; d) B. A. Vastine, M. B. Hall, *Coord. Chem. Rev.* **2009**, *253*, 1202.
- [12] a) G. Frenking, N. Frohlich, *Chem. Rev.* **2000**, *100*, 717; b) F. Maseras, A. Lledós, 'Computational Modeling of Homogeneous catalysis', Kluwer Academic Publishers: New York, **2002**; c) M. Reiher, *Chimia* **2009**, *63*, 140.
- [13] a) C. L. Ballhausen, 'Introduction to Ligand Field Theory', McGraw-Hill: New York, **1962**; b) C. K. Jørgensen, 'Modern Aspects of Ligand Field Theory', Elsevier: New York, **1971**; c) H. L. G. Schläfer, 'Basic Principles of Ligand Field Theory', Wiley: New York, **1969**.
- [14] a) J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C71; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.
- [15] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899; b) E. D. Glendening, C. R. Landis, F. Weinhold, *Wires Comput. Mol. Sci.* **2012**, *2*, 1.
- [16] S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995**, *99*, 9352.
- [17] a) R. F. W. Bader, 'Atoms in Molecules', Oxford University Press: Oxford, **1990**; b) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893.
- [18] a) K. Morokuma, *J. Chem. Phys.* **1971**, *55*, 1236; b) K. Morokuma, *Acc. Chem. Res.* **1977**, *10*, 294.
- [19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623; d) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo,
- R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, F. J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01. Wallingford CT, **2009**.
- [21] a) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.
- [22] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.
- [23] T. Lu, F. W. Chen, *J. Comput. Chem.* **2012**, *33*, 580.
- [24] a) A. Damin, J. G. Vitillo, G. Ricchiardi, S. Bordiga, C. Lamberti, E. Groppo, A. Zecchina, *J. Phys. Chem. A* **2009**, *113*, 14261; b) O. Espelid, K. J. Borve, *J. Catal.* **2000**, *195*, 125; c) O. Espelid, K. J. Borve, *Catal. Lett.* **2001**, *75*, 49; d) O. Espelid, K. J. Borve, *J. Catal.* **2002**, *205*, 366; e) O. Espelid, K. J. Borve, *J. Catal.* **2002**, *205*, 177.
- [25] S. Lillehaug, K. J. Borve, M. Sierka, J. A. Sauer, *J. Phys. Org. Chem.* **2004**, *17*, 990.
- [26] a) G. Frenking, K. Wichmann, N. Frohlich, C. Loschen, M. Lein, J. Frunzke, V. M. Rayon, *Coord. Chem. Rev.* **2003**, *238*, 55; b) R. K. Szilagy, G. Frenking, *Organometallics* **1997**, *16*, 4807; c) A. W. Ehlers, S. Dapprich, S. F. Vyboishchikov, G. Frenking, *Organometallics* **1996**, *15*, 105.
- [27] M. G. Hernandez, A. Beste, G. Frenking, F. Illas, *Chem. Phys. Lett.* **2000**, *320*, 222.
- [28] H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378.