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Semi-empirical Molecular Orbital Computations for Polymerization of Ethylene on a Chromium Silicate Catalyst

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Abstract
Semi-empirical molecular orbital computations were conducted, employing the MOPAC program, for polymerization of ethylene on a model two-layer dichromium silicate catalyst of 40 atoms displaying D_{2h} point group symmetry. Application of the basic concepts of a theoretical catalyst effort demonstrated chromium(II) with π-bonded ethylene catalyzes conversion to a chromium(III) with a σ-bonded alkyl group as the first five steps of polymerization occur. A proposed molecular mechanism is presented.

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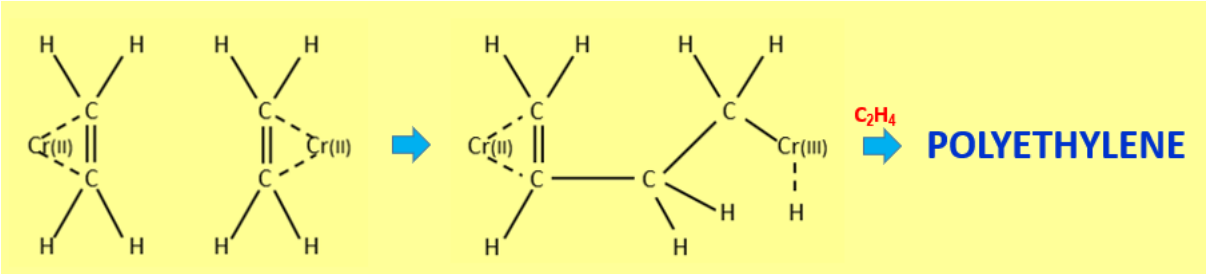


I. Introduction

Polyethylene has been produced employing a number of first row transition metal catalysts[1] including titanium, chromium, iron, cobalt and nickel. Experimental investigators studying polymerization of ethylene on a chromium silicate catalysthave observed the presence of Cr(II) and Cr(III) states but a detailed molecular mechanism has yet to be presented. The goal of this work is to apply the basic concepts of a theoretical catalysis effort and demonstrate how theirapplication facilitates the chemistry of polymer formation.

A molecular model dichromium silicate, two-layer, catalyst of 40 atoms was assembled that displayed D_{2h} point group symmetry. Molecular point group symmetry centered at the transition metal atoms results in degenerate molecular energy levels for the catalyst. This is a fundamental requirement for catalysis to occur. Semi-empirical molecular orbital computations were conducted for polymerization of ethylene on this model chromium silicate catalyst. A MOPAC computational program was employed to determine the energy levels, molecular orbitals and electronic charges for the molecular system at each step as the polymer chain grew. As a result of this work, a detailed molecular mechanism has been proposed for polymerization of ethylene on a chromium silicate catalyst.

II. Computational Results

PM7 type computations employing the MOPAC computer program[2]were conducted. Chemical bond distances were selected from the literature and/or calculated to be compatible with the catalyst structure. Both hydrogen-carbon and hydrogen-oxygen bond distances were set to 109.4 pm[4] (1.094 Å) and carbon=carbon double bond distances were set to 133 pm. Silicon-oxygen single bond distances were set to 158.6 pm, the silicon-oxygen double bond distances were set to 153 pm and the O-Si-O bond angles were set to 90°. The chromium(II)-silicon π-bond distances were set to 290.97 pm, chromium(II)-oxygen σ-bond distances were set to 169.7 pm and chromium(II)-oxygen π-bond distances were set to 300.87 pm[5]. The chromium-chromium π-bond distance was set to 290 pm[6].

When aliphatic carbon-carbon bonds were formed they were set to 154 pm with both C-C-C bond angles and H-C-C bond angles set to 102°. The chromium(II)-carbon (ethylene) π-bond distances were set to 222.0 pm[7] and the chromium(III)-carbon (alkyl) σ-bond distances were set to 199.3 pm[8].

Structure 1.

A molecular orbital computation was conducted for a chromium(II) silicate catalyst with no ethylene molecules present – 40 atoms having an empirical formula of$(H_6O_{10}Si_3Cr)_2$, molecular weight

604.59 amu. A PM7 calculation was conducted using MOPAC 2016 (Version: 19.179W) computer program[6] as generously provided by J. J. P. Stewart. Each of the 40 atom positions was determined prior to MO computation through iterative optimization of sets of three system spherical coordinates (r, θ and φ) available for each atom, until the Cartesian coordinate (x, y and z) values matched correct geometric values to within 4 units in the fourth place past the decimal (Ångstrom) or 2 units past the decimal (picometer) depending the units preferred. This same iterative adjustment was conducted for each atom position in each of the computed structures.

MOPAC computational atom positions are presented for structure 1, refer to tables 1a and 1b that follow. The covalently bonded silica, SiO_2 groups, were set at Cr(II)-Si π-bond distances of 290.97 pm[3] and Cr(II)-O π-bond distances of 300.87 pm[2] as stated above.

Table 1a. Lower Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.00	0.00	0.00
O2	108.40	0.00	0.00
Si3	187.70	137.35	0.00
O4	325.05	58.05	0.00
H5	433.45	58.05	0.00
O6	50.35	216.65	0.00
H7	-58.05	216.65	0.00
O8	267.00	274.70	0.00
Cr9	351.85	421.66	0.00
O10	351.85	591.36	0.00
Si11	351.85	749.96	0.00
O12	510.45	749.96	0.00
H13	604.33	695.76	0.00
O14	193.25	749.96	0.00
H15	99.37	804.16	0.00
O16	351.85	908.56	0.00
H17	445.73	962.76	0.00
O18	60.88	423.03	0.00
Si19	112.78	485.72	0.00
O20	99.18	565.96	0.00

Table 1b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
Cr21	351.85	421.66	290.00
O22	267.00	274.70	290.00
Si23	187.70	137.35	290.00
O24	108.40	0.00	290.00
H25	0.00	0.00	290.00
O26	325.05	58.05	290.00
H27	433.45	58.05	290.00
O28	50.35	216.65	290.00
H29	-58.05	216.65	290.00
O30	351.85	591.36	290.00
Si31	351.85	749.96	290.00
O32	510.45	749.96	290.00
H33	604.33	695.76	290.00
O34	193.25	749.96	290.00
H35	99.37	804.16	290.00
O36	351.85	908.56	290.00
H37	445.73	962.76	290.00
O38	60.88	423.03	290.00
Si39	112.78	485.72	290.00
O40	99.18	565.96	290.00

The 40 atom catalyst molecular structure was arrayed in two parallel x-y planes separated by 290 pm (2.900 Angstroms) in the z-direction. Each identical 20 atom molecular segment contains one Cr(II) metal atom with one π-bonded SiO_2 group lying in the same molecular plane. This positions the two Cr(II) silicate groups arrayed as one set above the other separated by 290 pm in the z-direction.

The MO computation produced results showing 84 doubly occupied energy levels. The gap between the highest occupied energy level (ionization potential) and lowest unoccupied energy level is -5.321 to -0.572 eV or -4.749 eV = -109.51 kcal/mol. The two highest filled levels, Root 83 energy level E = -5.378 eV and Root 84 energy level E = -5.321 eV, are separated by 0.057 eV = 1.31 kcal/mol. Thus, there are two essentially degenerate energy levels. This molecular structure is described as belonging to a D_{2h} point group symmetry. It is believed that the degeneracy may have been lifted as a result of a

1.3 kcal/mol vibronic distortion.

Table 2. Computed Net Atomic Charges for a Dichromium Silicate Catalyst.

Atom No.	Type	Charge	No. of Electronss	-Popp	-Popd	-Pop
1	H	0.343131	0.6569	0.65687		
2	O	-0.467112	6.4671	1.75315	4.71397	
3	Si	0.856348	3.1437	0.58961	2.08224	0.47180
4	O	-0.616868	6.6169	1.67390	4.94297	
5	H	0.403356	0.5966	0.59664		
6	O	-0.549317	6.5493	1.69710	4.85222	
7	H	0.370935	0.6291	0.62906		
8	O	-0.718498	6.7185	1.66720	5.05130	
9	Cr	0.746154	5.2538	0.21466	0.02621	5.01297
10	O	-0.721940	6.7219	1.66716	5.05478	
11	Si	0.824235	3.1758	0.59611	2.10680	0.47285
12	O	-0.667023	6.6670	1.69327	4.97375	
13	H	0.385559	0.6144	0.61444		
14	O	-0.474416	6.4744	1.70395	4.77046	
15	H	0.382330	0.6177	0.61767		
16	O	-0.457172	6.4572	1.76721	4.68996	
17	H	0.344233	0.6558	0.65577		
18	O	-0.313807	6.3138	1.44203	4.87178	
19	Si	0.644789	3.3552	0.44977	2.34902	0.55642
20	O	-0.314767	6.3148	1.44257	4.87220	
21	Cr	0.746199	5.2538	0.21464	0.02620	5.01295
22	O	-0.718635	6.7186	1.66716	5.05147	
23	Si	0.856270	3.1437	0.58962	2.08227	0.47184
24	O	-0.467102	6.4671	1.75312	4.71399	
25	H	0.343137	0.6569	0.65686		
26	O	-0.616823	6.6168	1.67365	4.94317	
27	H	0.403400	0.5966	0.59660		
28	O	-0.549751	6.5498	1.69740	4.85235	
29	H	0.370747	0.6293	0.62925		
30	O	-0.721621	6.7216	1.66709	5.05453	
31	Si	0.824221	3.1758	0.59602	2.10681	0.47295
32	O	-0.666922	6.6669	1.69337	4.97355	
33	H	0.385504	0.6145	0.61450		
34	O	-0.474692	6.4747	1.70383	4.77087	
35	H	0.382453	0.6175	0.61755		
36	O	-0.456878	6.4569	1.76689	4.68999	
37	H	0.344299	0.6557	0.65570		
38	O	-0.313702	6.3137	1.44200	4.87170	
39	Si	0.645087	3.3549	0.44984	2.34873	0.55634
40	O	-0.315343	6.3153	1.44266	4.87268	

The net atomic charges have been computed for each atom, refer to Table 2. The number of electrons and total orbital populations are in reasonable agreement for the two chromium atoms and silicon atoms number 3, 11, 23 and 31. The two π-bonded SiO_2 groups, silicon atoms 19 and 39 are also in reasonable agreement with each other but differ from the other siliconatoms, refer to figures 1a and 1b. The p-orbital populations of the oxygen atoms bonded to the chromium atoms, atoms number 8, 10, 22 and 30, are in close agreement but higher than the other oxygen atoms. This indicates probable charge contribution from the bonded chromium atoms indicating the chromium atoms to be more electro-positive than the bonded oxygen atoms. The charge differential for chromium atom 9 (0.746154) and bonded oxygen atoms 8 (0.718498) and 10 (0.721940) is 2.2 correlating with a formal charge of +2. The charge differential for the upper O-Cr-O bonds was similarly 2.2.

The relative symmetries of the molecular orbital wave functions were examined for energy levels 83 and 84. Energy level 83 was anti-symmetric as orbital d_{xy} of chromium atom 9 was populated as were the p_x and p_y orbitals of oxygen atoms 18 and 20. It was also anti-symmetric as orbital d_{xy} of chromium atom 21 was populated as were the p_x and p_y orbitals of oxygen atoms 38 and 40. The same observations were made for energy level 84 except the function was of opposite sign.

The d_{x2}, d_{xz}, d_{z2} and d_{xy} orbitals of chromium atoms 9 and 21, for energy level 82, were highly populated.

Structure 2.

A molecular orbital computation was conducted for the chromium(II) silicate catalyst plus two ethylene molecules, one π-bonded to each Cr(II) atom – 52 atoms as a $H_{20}C_4O_{20}Si_6Cr_2$ structure, refer to figures 1a and 1b. The C=C portion of each ethylene group was positioned in the same plane as the catalyst layer to which it was π-bonded. The hydrogen atoms were, thus, extended above and below those planes at H-C-H bond angles of 120°.

Figure 1a – Atom Positions for Lower Layer of Structure 2.

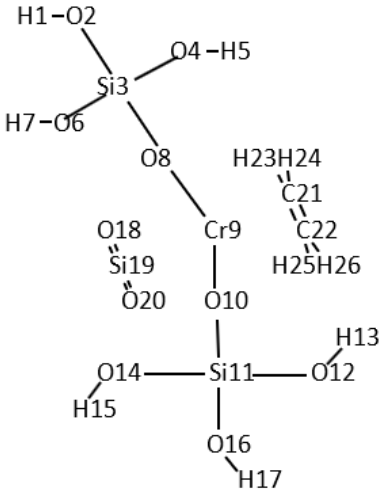
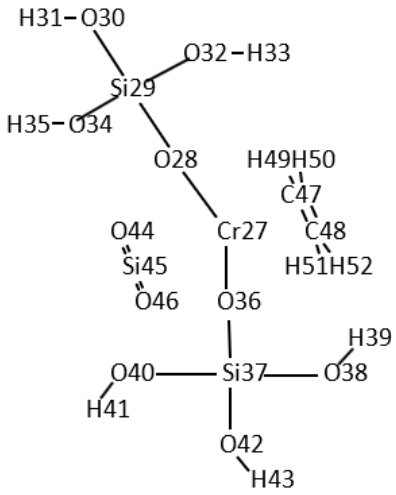


Figure 1b – Atom Positions for Upper Layer of Structure 2.



Atom positions are presented for the structure 2 computation, refer to tables 3a and 3b that follow. A MOPAC computation was conducted for this structure.

Table 3a. Lower Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.00	0.00	0.00
O2	108.40	0.00	0.00
Si3	187.70	137.35	0.00
O4	325.05	58.05	0.00
H5	433.45	58.05	0.00
O6	050.35	216.65	0.00
H7	-58.05	216.65	0.00
O8	267.00	274.70	0.00
Cr9	351.85	421.66	0.00
O10	351.85	591.36	0.00
Si11	351.85	749.96	0.00
O12	510.45	749.96	0.00
H13	604.33	695.76	0.00
O14	193.25	749.96	0.00
H15	99.37	804.16	0.00
O16	351.85	908.56	0.00
H17	445.73	962.76	0.00
O18	60.88	423.03	0.00
Si19	112.78	485.72	0.00
O20	99.18	565.96	0.00
C21	537.81	300.40	0.00
C22	573.52	433.70	0.00
H23	513.51	209.72	93.88
H24	513.51	209.72	- 93.88
H25	597.82	524.38	93.88
H26	597.82	524.38	- 93.88

Table 3b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
Cr27	351.85	421.66	290.00
O28	267.00	274.70	290.00
Si29	187.70	137.35	290.00
O30	108.40	0.00	290.00
H31	0.00	0.00	290.00
O32	325.05	58.05	290.00
H33	433.45	58.05	290.00
O34	50.35	216.65	290.00
H35	-58.05	216.65	290.00
O36	351.85	591.36	290.00
Si37	351.85	749.96	290.00
O38	510.45	749.96	290.00
H39	604.33	695.76	290.00
O40	193.25	749.96	290.00
H41	99.37	804.16	290.00
O42	351.85	908.56	290.00
H43	445.73	962.76	290.00
O44	60.88	423.03	290.00
Si45	112.78	485.72	290.00
O46	99.18	565.96	290.00
C47	537.81	300.40	290.00
C48	573.52	433.70	290.00
H49	513.51	209.72	383.88
H50	513.51	209.72	196.12
H51	597.82	524.38	383.88
H52	597.82	524.38	196.12

The MO computation for the 52 atom Cr-Cr catalyst plus ethylenes produced results showing 96 doubly occupied energy levels. The gap between the highest occupied energy level and lowest unoccupied energy level is -5.286 to -0.448 eV or -4.838 eV = -111.56 kcal/mol. The three highest filled levels, Root 94 energy level E = -5.464 eV, Root 95 energy level E = -5.376 eV and Root 96 energy level E = -5.286 eV, are separated by 0.088 eV = 2.03 kcal/mol and 0.090 eV = 2.07 kcal/mol respectively. Thus, there are three essentially degenerate energy levels. This molecular structure is described as belonging to a D_{2h}point group symmetry. It is believed that the apparent near degeneracy may have been lifted as a result of vibronic distortion.

Net atomic charges have been computed for each atom, refer to Table 4. The number of electrons and total orbital populations are in reasonable agreement for the two chromium atoms and silicon atoms number 3, 11, 29 and 37. The two π-bonded SiO_2 groups, silicon atoms 19 and 45 are also in reasonable agreement with each other but differ from the other silicon atoms. The p-orbital populations of the oxygen atoms bonded to the chromium atoms, atoms number 8, 10, 28 and 36, are in close agreement but higher than the other oxygen atoms. This indicates probable charge contribution from the bonded chromium atoms indicating the chromium atoms to be more electro-positive than the bonded oxygen atoms. The charge differential for chromium atom 9 (0.699961), bonded oxygen atoms 8 (0.691353) and 10 (0.704235) is 2.1 correlating with a formal charge of +2. The charge differential for the upper
O-Cr-O bonds was similarly 2.1.

Table 4. Computed Net Atomic Charges for a Dichromium Silicate Catalyst plus Two Ethylene Molecules.

Atom No.	Type	Charge	No. of Electronss-Popp-Popd-Pop			
1	H	0.342441	0.6576	0.65756		
2	O	-0.470698	6.4707	1.75293	4.71777	
3	Si	0.847167	3.1528	0.59361	2.08696	0.47226
4	O	-0.631513	6.6315	1.67557	4.95594	
5	H	0.389167	0.6108	0.61083		
6	O	-0.549482	6.5495	1.69701	4.85247	
7	H	0.368749	0.6313	0.63125		
8	O	-0.691353	6.6914	1.67140	5.01996	
9	Cr	0.699961	5.3000	0.30010	0.03258	4.96736
10	O	-0.704235	6.7042	1.66342	5.04081	
11	Si	0.814873	3.1851	0.59768	2.11425	0.47320
12	O	-0.674315	6.6743	1.69462	4.97970	
13	H	0.369438	0.6306	0.63056		
14	O	-0.482394	6.4824	1.70271	4.77968	
15	H	0.383800	0.6162	0.61620		
16	O	-0.454576	6.4546	1.76737	4.68720	
17	H	0.341709	0.6583	0.65829		
18	O	-0.303642	6.3036	1.43999	4.86366	
19	Si	0.625963	3.3740	0.45517	2.35931	0.55955
20	O	-0.309682	6.3097	1.44289	4.86680	
21	C	-0.429513	4.4295	1.12247	3.30704	
22	C	-0.103077	4.1031	1.16209	2.94099	
23	H	0.178925	0.8211	0.82108		
24	H	0.163411	0.8366	0.83659		
25	H	0.170454	0.8295	0.82955		
26	H	0.138765	0.8612	0.86124		
27	Cr	0.715709	5.2843	0.29917	0.03286	4.95226
28	O	-0.699540	6.6995	1.66254	5.03700	
29	Si	0.844894	3.1551	0.59180	2.09137	0.47194
30	O	-0.471507	6.4715	1.75271	4.71879	
31	H	0.342971	0.6570	0.65703		
32	O	-0.628056	6.6281	1.67473	4.95333	
33	H	0.388005	0.6120	0.61200		
34	O	-0.556486	6.5565	1.69699	4.85950	
35	H	0.370652	0.6293	0.62935		
36	O	-0.687503	6.6875	1.67158	5.01592	
37	Si	0.811743	3.1883	0.60066	2.11399	0.47361
38	O	-0.680936	6.6809	1.69561	4.98533	
39	H	0.372212	0.6278	0.62779		
40	O	-0.475403	6.4754	1.70392	4.77148	
41	H	0.378155	0.6218	0.62184		
42	O	-0.460849	6.4608	1.76712	4.69373	
43	H	0.340783	0.6592	0.65922		
44	O	-0.311424	6.3114	1.44262	4.86880	
45	Si	0.625637	3.3744	0.45571	2.35939	0.55926
46	O	-0.303480	6.3035	1.43987	4.86361	
47	C	-0.072228	4.0722	1.15634	2.91589	
48	C	-0.490136	4.4901	1.10638	3.38376	
49	H	0.136190	0.8638	0.86381		
50	H	0.150653	0.8493	0.84935		
51	H	0.164902	0.8351	0.83510		
52	H	0.164698	0.8353	0.83530		

Ethylene carbon atoms are negatively charged compared to the bonded hydrogen atoms as expected, however Table 4 shows carbon atoms number 21 and 48 display charges of
-0.429 and -0.490 while carbon atoms 22 and 47 with charges of -0.103 and -0.072. This is also reflected in the p-orbital populations as well as reduced charges of hydrogen atoms number 26 and 49 indicating preferential orbital overlap with chromium and possibly other adjacent atoms.

The relative symmetries of the molecular orbital wave functions were examined for energy levels 94, 95 and 96. Energy level 94 was anti-symmetric as orbital d_{x2} and orbital d_{z2} of chromium atom 9 were populated as were the same orbitals of chromium atom 27. The same orbitals were populated for energy level 96 but it was asymmetric while these orbitals were not well populated for energy level 95.

Energy level 94 was symmetric as orbitals p_x and p_y of oxygen atoms 18, 20, 44 and 46 were well populated. Energy level 95 was anti-symmetric for these same orbitals. For energy level 96 orbitals p_x and p_y of oxygen atoms 18 and 20 were well populated as were the p_x and p_y orbitals for oxygen atoms 44 and 46. Energy level 96 was symmetric for these same orbitals.

Structure 3.

A computation was conducted for the 52 atom chromium silicate catalyst structure $H_{20}C_4O_{20}Si_6Cr_2$ where the two ethylene molecules have reacted to form a 1-butylene group for which a terminal carbon becomes σ-bonded to chromium(III) at atom 27. The lower C=C group, C_{21} and C_{22}, remained positioned in the same plane as the catalyst layer to which it was originally π-bonded. Three hydrogen atoms were, thus, extended above and below that plane. The fourth bond of C_{22} was σ-bonded with carbon atom C_{48}. Hydrogen H_{25} has been repositioned 156 pm[7] above Cr_{27} as a coordinately covalent bonded metal hydrogen. The second or upper C-C group, C_{47} and C_{48}, formed the saturated alkyl group for which C_{47} becomes σ-bonded to chromium atom 27. A chromium-carbon-carbon bond angle of 102° allowed for a carbon-carbon bond distance of 154 pm.

Bond lengths of Cr(II)-C(ring) π-bond of 222.0 pm, a Cr(III)-C(alkyl) σ-bond of 199.3 pm and a Cr(II)-O π-bond of 202.0 pm were employed as stated previously. The covalently bonded silica, SiO_2 groups, were set at Cr(II)-Si π-bond distances of 290.97 pm and Cr(II)-O π-bond distances of 300.87 pm as for the previous computation.

Tables 5a and 5b of bond positions of the atoms follow.

Table 5a. Lower Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.00	0.00	0.00
O2	108.40	0.00	0.00
Si3	187.70	137.35	0.00
O4	325.05	58.05	0.00
H5	433.45	58.05	0.00
O6	50.35	216.65	0.00
H7	-58.05	216.65	0.00
O8	267.00	274.70	0.00
Cr9	351.85	421.66	0.00
O10	351.85	591.36	0.00
Si11	351.85	749.96	0.00
O12	510.45	749.96	0.00
H13	604.33	695.76	0.00
O14	193.25	749.96	0.00
H15	99.37	804.16	0.00
O16	351.85	908.56	0.00
H17	445.73	962.76	0.00
O18	60.88	423.03	0.00
Si19	112.78	485.72	0.00
O20	99.18	565.96	0.00
C21	537.81	300.40	0.00
C22	573.52	433.70	0.00
H23	513.51	209.72	93.88
H24	513.51	209.72	- 93.88
H25	351.85	421.66	446.00
H26	597.82	524.38	- 93.88

Table 5b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
Cr27	351.85	421.66	290.00
O28	267.00	274.70	290.00
Si29	187.70	137.35	290.00
O30	108.40	0.00	290.00
H31	0.00	0.00	290.00
O32	325.05	58.05	290.00
H33	433.45	58.05	290.00
O34	50.35	216.65	290.00
H35	-58.05	216.65	290.00
O36	351.85	591.36	290.00
Si37	351.85	749.96	290.00
O38	510.45	749.96	290.00
H39	604.33	695.76	290.00
O40	193.25	749.96	290.00
H41	99.37	804.16	290.00
O42	351.85	908.56	290.00
H43	445.73	962.76	290.00
O44	60.88	423.03	290.00
Si45	112.78	485.72	290.00
O46	99.18	565.96	290.00
C47	555.67	367.05	181.45
C48	613.12	463.99	76.50
H49	366.72	463.32	272.36
H50	716.56	511.92	272.36
H51	424.17	560.26	-17.38
H52	774.01	608.86	-17.38

A molecular orbital computation was conducted for the 52 atom Cr-Cr catalyst whereon a

1-butylene group formed from the previously π-bonded ethylene molecules. This produced a result showing 96 doubly occupied energy levels as before. The gap between the highest occupied and lowest unoccupied energy levels is -5.110 (E_{96}) to -1.152 eV (E_{97}) or -3.958 eV = -91.27 kcal/mol. The highest filled energy levels of the catalytic system are no longer degenerate. The gap between Root 93 and Root 94 is -6.746 eV to -6.251 eV = 0.495 eV = 11.41kcal/mol, the gap between Root 94 and Root 95 -6.251 eV to -5.789 eV = 0.462 eV = 10.65kcal/mol and the gap between Root 95 and Root 96 is -5.789 eV to
-5.110 eV = 0.679 eV = 15.66kcal/mol. Thus, the original point group symmetry of D_{2h} has degraded to C_1.

The net atomic charges are listed for each atom, refer to Table 6. The charge is no longer in agreement for the two chromium atoms since chromium atom 27 (0.496506) has become σ-bonded to carbon atom 47 while chromium atom 9 (0.563920) remains π-bonded to carbon atoms 21 and 22.

Table 6. Computed Net Atomic Charges for a Dichromium Silicate Catalyst plus a 1-Butylene Group.

Atom No.	Type	Charge	No. of Electrons	s-Pop	p-Pop	d-Pop
1	H	0.339055	0.6609	0.66094		
2	O	-0.459901	6.4599	1.75343	4.70647	
3	Si	0.835790	3.1642	0.58761	2.10234	0.47426
4	O	-0.622592	6.6226	1.67496	4.94763	
5	H	0.401347	0.5987	0.59865		
6	O	-0.579107	6.5791	1.69220	4.88691	
7	H	0.375365	0.6246	0.62463		
8	O	-0.631620	6.6316	1.66542	4.96620	
9	Cr	0.563920	5.4361	0.31792	0.03196	5.08620
10	O	-0.478412	6.4784	1.57632	4.90209	
11	Si	0.781575	3.2184	0.59510	2.14567	0.47765
12	O	-0.674227	6.6742	1.70332	4.97091	
13	H	0.418929	0.5811	0.58107		
14	O	-0.510652	6.5107	1.69540	4.81525	
15	H	0.416460	0.5835	0.58354		
16	O	-0.437581	6.4376	1.76408	4.67350	
17	H	0.357457	0.6425	0.64254		
18	O	-0.266754	6.2668	1.44090	4.82586	
19	Si	0.603417	3.3966	0.46015	2.36971	0.56672
20	O	-0.309597	6.3096	1.44734	4.86225	
21	C	-0.842975	4.8430	1.06373	3.77925	
22	C	-0.002198	4.0022	0.95346	3.04874	
23	H	0.217860	0.7821	0.78214		
24	H	0.203230	0.7968	0.79677		
25	H	0.228277	0.7717	0.77172		
26	H	0.146131	0.8539	0.85387		
27	Cr	0.496506	5.5035	0.61955	0.03151	4.85244
28	O	-0.592781	6.5928	1.66989	4.92289	
29	Si	0.833106	3.1669	0.59919	2.09501	0.47270
30	O	-0.473578	6.4736	1.75303	4.72055	
31	H	0.342067	0.6579	0.65793		
32	O	-0.624168	6.6242	1.67379	4.95038	
33	H	0.401864	0.5981	0.59814		
34	O	-0.573296	6.5733	1.69623	4.87707	
35	H	0.373188	0.6268	0.62681		
36	O	-0.515863	6.5159	1.68101	4.83485	
37	Si	0.755342	3.2447	0.62251	2.14791	0.47424
38	O	-0.680165	6.6802	1.69583	4.98433	
39	H	0.402018	0.5980	0.59798		
40	O	-0.513084	6.5131	1.70596	4.80712	
41	H	0.384354	0.6156	0.61565		
42	O	-0.481105	6.4811	1.76390	4.71721	
43	H	0.350567	0.6494	0.64943		
44	O	-0.314980	6.3150	1.44265	4.87233	
45	Si	0.626287	3.3737	0.45309	2.35692	0.56370
46	O	-0.324285	6.3243	1.44444	4.87984	
47	C	0.608025	3.3920	1.75031	1.64166	
48	C	-0.786395	4.7864	1.13052	3.65588	
49	H	-0.122052	1.1221	1.12205		
50	H	0.039224	0.9608	0.96078		
51	H	0.356553	0.6434	0.64345		
52	H	-0.040549	1.0405	1.04055		

π-Bonded chromium 9 has an s-orbital population of 0.31792 and a d-orbital population of 5.08620 compared to σ-bonded chromium 27 that reflects a higher s-orbital population of 0.61955 and a d-orbital population of 4.85244.

Even the two π-bonded SiO_2 groups display slightly different electronic charges (silicon atom 19, electronic charge 0.603417, and silicon atom 45, electronic charge 0.626287) as a result of formation of 1-butylene. The charge differential for chromium atom 9 (0.563920), bonded oxygen atoms 8 (-0.631620) and 10 (-0.478412)is 1.7while the charge differential for the upper O-Cr-O bonds plus the C-C bonds was 3.0, compared to 1.7 for the lower O-Cr-O group, indicating partial electron contribution from the growing polymer chain.

Ethylene carbon atoms 21 and 22 are negatively charged compared to the bonded hydrogen atoms as expected for the π-bonded unsaturated group. Carbon 47, which has become σ-bonded to chromium atom 27, displays a positive charge of 0.608025 compared to carbon atom 48 that displays a negative charge of -0.786395. A total net charge for two carbon and four hydrogen atoms number 21 through 26 is -0.0497 compared to a net charge for atoms 47 through 52 of +0.0548 indicating electron bonding contribution of chromium atom 27.

The relative symmetries of the molecular orbital wave functions, in particular at the two chromium atoms, were examined for energy levels 94, 95 and 96. The symmetries were all different for chromium atom 9 and for chromium atom 27.

Structure 4.

Another computation was conducted for the 52 atom chromium silicate catalyst complex with the bonded 1-butylene group system plus an additional ethylene molecule π-bonded to chromium atom 9. This ethylene was positionedin a vertical orientation, parallel to the z-direction, in the open space

π-bonded to the lower chromium atom opposite the growing hydrocarbon chain. Two of its hydrogen atoms were oriented above and below, and hydrogen bonded with, an adjacent catalyst oxygen atom. This becomes a 58 atom chromium silicate catalyst system $H_{24}C_6O_{20}Si_6Cr_2$ where the 1-butylene group remains σ-bonded to chromium(III) at atom 27. All bond lengths remain the same as for the previous computation.

Tables 7a and 7b of bond positions of the atoms for the catalyst with 1-butylene + one ethylenefollow.

Table 7a. Lower Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.00	0.00	0.00
O2	108.40	0.00	0.00
Si3	187.70	137.35	0.00
O4	325.05	58.05	0.00
H5	433.45	58.05	0.00
O6	50.35	216.65	0.00
H7	-58.05	216.65	0.00
O8	267.00	274.70	0.00
Cr9	351.85	421.66	0.00
O10	351.85	591.36	0.00
Si11	351.85	749.96	0.00
O12	510.45	749.96	0.00
H13	604.33	695.76	0.00
O14	193.25	749.96	0.00
H15	099.37	804.16	0.00
O16	351.85	908.56	0.00
H17	445.73	962.76	0.00
O18	60.88	423.03	0.00
Si19	112.78	485.72	0.00
O20	99.18	565.96	0.00
C21	537.81	300.40	0.00
C22	573.52	433.70	0.00
H23	513.51	209.72	93.88
H24	513.51	209.72	- 93.88
H25	351.85	421.66	446.00
H26	59782	524.38	- 93.88
Cr27	351.85	421.66	290.00
O28	267.00	274.70	290.00
Si29	187.70	137.35	290.00

Table 7b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
O30	108.40	0.00	290.00
H31	0.00	0.00	290.00
O32	325.05	58.05	290.00
H33	433.45	58.05	290.00
O34	50.35	216.65	290.00
H35	-58.05	216.65	290.00
O36	351.85	591.36	290.00
Si37	351.85	749.96	290.00
O38	510.45	749.96	290.00
H39	604.33	695.76	290.00
O40	193.25	749.96	290.00
H41	99.37	804.16	290.00
O42	351.85	908.56	290.00
H43	445.73	962.76	290.00
O44	60.88	423.03	290.00
Si45	112.78	485.72	290.00
O46	99.18	565.96	290.00
C47	555.67	367.05	181.45
C48	613.12	463.99	76.50
H49	366.72	463.32	272.36
H50	716.56	511.92	272.36
H51	424.17	560.26	-17.38
H52	774.01	608.86	-17.38
C53	515.80	554.54	69.00
C54	515.80	554.54	-69.00
H55	421.90	554.54	123.20
H56	609.68	554.54	123.20
H57	421.90	554.54	-123.20
H58	609.68	554.54	-123.20

The MO computation for the 58 atom Cr-Cr reactant catalyst system produced results showing 102 doubly occupied energy levels. The gap between the highest occupied energy level, Root 102, and lowest unoccupied energy level, Root 103, is -5.613 to -0.981 eV or -4.632 eV = -106.81 kcal/mol. The gap between Root 99 and Root 100 is -6.464 eV to -6.007 eV = 0.457 eV = 10.54kcal/mol, the gap between Root 100 and Root 101 -6.007 eV to -5.686 eV = 0.321 eV = 7.40kcal/mol and the gap between Root 101 and Root 102 is essentially degenerate as -5.686 eV to -5.613 eV = 0.073 eV = 1.68kcal/mol. The point group symmetry is C_1.

The net atomic charges are listed for each atom, refer to Table 8.

Table 8. Computed Net Atomic Charges for a Dichromium Silicate Catalyst, a 1-Butylene Group + an Ethylene.

Atom No.	Type	Charge	No. of Electronss-Popp-Popd-Pop			
1	H	0.342012	0.6580	0.65799		
2	O	-0.456805	6.4568	1.75363	4.70317	
3	Si	0.852382	3.1476	0.59062	2.08390	0.47310
4	O	-0.618810	6.6188	1.67510	4.94371	
5	H	0.399874	0.6001	0.60013		
6	O	-0.564575	6.5646	1.69463	4.86994	
7	H	0.376691	0.6233	0.62331		
8	O	-0.697368	6.6974	1.67042	5.02695	
9	Cr	0.628819	5.3712	0.30843	0.03613	5.02662
10	O	-0.732165	6.7322	1.62062	5.11154	
11	Si	0.780828	3.2192	0.58332	2.16176	0.47408
12	O	-0.657056	6.6571	1.70095	4.95611	
13	H	0.428661	0.5713	0.57134		
14	O	-0.502009	6.5020	1.69631	4.80570	
15	H	0.400532	0.5995	0.59947		
16	O	-0.444902	6.4449	1.76487	4.68003	
17	H	0.352044	0.6480	0.64796		
18	O	-0.290133	6.2901	1.44240	4.84774	
19	Si	0.606440	3.3936	0.45538	2.37409	0.56409
20	O	-0.298779	6.2988	1.44331	4.85547	
21	C	-0.663447	4.6634	1.02360	3.63985	

The electronic charge is different for the two chromium atoms since chromium atom 27 (0.494042) is σ-bonded to carbon atom 47 while chromium atom 9 (0.628819) is

π-bonded to carbon atoms 21, 22 53 and 54.

π-Bonded chromium 9 has an s-orbital population of 0.30843 and a d-orbital population of 5.02662 compared to σ-bonded chromium 27 that reflects a higher s-orbital population of 0.62098 and a reduced d-orbital population of 4.85276.

One π-bonded SiO_2 group displays similar electronic charges as before (silicon atom 19, electronic charge 0.606440and silicon atom 45, electronic charge 0.625346). The charge differential for chromium atom 9 (0.628819), bonded oxygen atoms 8 (0.697368) and 10 (0.732165) is 2.0, the formal charge is +2, but the

charge differential for the upper chromium 27, including oxygen 28, oxygen 36 and carbon 47was 2.3, compared to a formal charge of +3.

Carbon 47, which has become σ-bonded to chromium atom 27, displays a positive charge of 0.635870 compared to carbon atom 48 that displays a negative charge of -0.324889. A total net charge for two carbon and four hydrogen atoms number 21 through 26, the π-bonded end of butylene bonded to chromium atom 9, is -0.0259 compared to a net charge for atoms 47 through 52, σ-bonded to chromium atom 27, is +0.2974. The net charge for π-bonded two carbon and four hydrogen atoms number 53 through 58 is -0.0610.

22	C	-0.370982	4.3710	0.87817	3.49281	
23	H	0.208316	0.7917	0.79168		
24	H	0.217161	0.7828	0.78284		
25	H	0.215129	0.7849	0.78487		
26	H	0.367889	0.6321	0.63211		
27	Cr	0.494042	5.5060	0.62098	0.03222	4.85276
28	O	-0.598793	6.5988	1.66917	4.92963	
29	Si	0.834667	3.1653	0.59936	2.09313	0.47284
30	O	-0.475930	6.4759	1.75300	4.72293	
31	H	0.343825	0.6562	0.65618		
32	O	-0.624473	6.6245	1.67413	4.95034	
33	H	0.401498	0.5985	0.59850		
34	O	-0.566665	6.5667	1.69727	4.86939	
35	H	0.373942	0.6261	0.62606		
36	O	-0.539512	6.5395	1.67273	4.86679	
37	Si	0.763496	3.2365	0.61543	2.14615	0.47493
38	O	-0.671054	6.6711	1.69508	4.97598	
39	H	0.396279	0.6037	0.60372		
40	O	-0.507077	6.5071	1.70338	4.80370	
41	H	0.384311	0.6157	0.61569		
42	O	-0.467904	6.4679	1.76404	4.70387	
43	H	0.349710	0.6503	0.65029		
44	O	-0.317388	6.3174	1.44279	4.87460	
45	Si	0.625346	3.3747	0.45176	2.35837	0.56452
46	O	-0.314400	6.3144	1.44308	4.87132	
47	C	0.635870	3.3641	1.79517	1.56896	
48	C	-0.324889	4.3249	0.94243	3.38245	
49	H	-0.116114	1.1161	1.11611		
50	H	-0.190556	1.1906	1.19056		
51	H	0.460358	0.5396	0.53964		
52	H	-0.167289	1.1673	1.16729		
53	C	-0.751676	4.7517	0.90885	3.84283	
54	C	-0.637448	4.6374	0.89796	3.73949	
55	H	0.316427	0.6836	0.68357		
56	H	0.373826	0.6262	0.62617		
57	H	0.319926	0.6801	0.68007		
58	H	0.317896	0.6821	0.68210		

The relative symmetries of the molecular orbital wave functions, in particular at the two chromium atoms, were examined for energy levels 100, 101 and 102. The symmetries were all different for both chromium atom 9 and chromium atom 27.

Structure 5.

Another computation was conducted for the 58 atom chromium silicate catalyst complex with the bonded 1-hexylene group system. This 58 atom chromium silicate catalyst system $H_{24}C_6O_{20}Si_6Cr_2$was computed for the 1-hexylene group σ-bonded to chromium(III) at atom 9 and π-bonded to chromium(II) at atom 27. Carbon atoms 21, 22, 47, 48, 53 and 54 were repositioned to account for C=C shift to chromium atom 27 and formation of C-C bond at chromium atom 9. The hydrogen atoms were also repositioned to accommodate this new structure. All other bond lengths remained the same as for the previous computation.

Tables of bond positions of the atoms forthe catalyst with 1-hexylenefollow.

Table 7a. Lower Layer Atom Positions (pm)Table 7b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.00	0.00	0.00
O2	108.40	0.00	0.00
Si3	187.70	137.35	0.00
O4	325.05	58.05	0.00
H5	433.45	58.05	0.00
O6	50.35	216.65	0.00
H7	-58.05	216.65	0.00
O8	267.00	274.70	0.00
Cr9	351.85	421.66	0.00
O10	351.85	591.36	0.00
Si11	351.85	749.96	0.00
O12	510.45	749.96	0.00
H13	604.33	695.76	0.00
O14	193.25	749.96	0.00
H15	99.37	804.16	0.00
O16	351.85	908.56	0.00

Atom	x-position	y-position	z-position
O30	108.40	0.00	290.00
H31	0.00	0.00	290.00
O32	325.05	58.05	290.00
H33	433.45	58.05	290.00
O34	50.35	216.65	290.00
H35	-58.05	216.65	290.00
O36	351.85	591.36	290.00
Si37	351.85	749.96	290.00
O38	510.45	749.96	290.00
H39	604.33	695.76	290.00
O40	193.25	749.96	290.00
H41	99.37	804.16	290.00
O42	351.85	908.56	290.00
H43	445.73	962.76	290.00
O44	60.88	423.03	290.00
Si45	112.78	485.72	290.00

H17	445.73	962.76	0.00
O18	60.88	423.03	0.00
Si19	112.78	485.72	0.00
O20	99.18	565.96	0.00
C21	547.70	282.00	0.00
C22	573.52	433.70	0.00
H23	569.50	253.94	68.22
H24	525.90	253.94	68.22
H25	351.85	421.66	-156.00
H26	551.72	461.76	- 68.22
Cr27	351.85	421.66	290.00
O28	267.00	274.70	290.00
Si29	187.70	137.35	290.00

O46	99.18	565.96	290.00
C47	555.67	367.05	181.45
C48	445.00	395.00	76.50
H49	595.32	365.48	-68.22
H50	654.97	449.54	252.28
H51	345.70	289.73	5.69
H52	345.70	477.49	61.79
C53	420.00	222.30	69.00
C54	420.00	222.30	-69.00
H55	398.20	204.64	113.06
H56	441.80	204.64	113.06
H57	402.00	204.64	-97.06
H58	445.60	204.64	-97.06

The MO computation for the 58 atom Cr-Cr reactant catalyst system produced results showing 102 doubly occupied energy levels. The gap between the highest occupied energy level, Root 102, and lowest unoccupied energy level, Root 103, is -5.419 to +0.622 eV or -4.797 eV = -110.62 kcal/mol. The highest filled energy levels of the catalytic system are not degenerate. The gap between Root 99 and Root 100 is -7.981 eV to -7.609 eV = -0.372 eV = -8.58kcal/mol, the gap between Root 100 and Root 101 -7.609 eV to -5.910 eV = -1.699 eV = -39.18kcal/mol and the gap between Root 101 and Root 102 is -5.910 eV to -5.419 eV = -0.491 eV = -11.32kcal/mol. The point group symmetry is C_1.

The net atomic charges are listed for each atom, refer to Table 8.

Table 8. Computed Net Atomic Charges for a Dichromium Silicate Catalyst, a 1-Butylene Group + an Ethylene.

The atomic chargesaredifferent for the two chromium atoms since chromium atom 27 (0.764376) is π-bonded to carbon atoms 47 and 48 while chromium atom 9 (0.487099) is σ-bonded to carbon atom 54.

σ-Bonded chromium 9 has an s-orbital population of 0.55932 and a d-orbital population of 4.90541 compared to π-bonded chromium 27 that reflects a lower s-orbital population of 0.23071 and an increased d-orbital population of 4.97370.

The π-bonded SiO_2 groups display similar electronic charges as before (silicon atom 19, electronic charge 0.594484 while silicon atom 45, electronic charge 0.635104). The charge differential for chromium atom 9 (0.487099) and bonded oxygen atoms 8 (0.525708), 10 (0.654885), carbon atom 54 (0.734872) and hydrogen atom 25 (0.010925) is 2.4, the formal charge is +3, while the charge differential for the upper chromium 27, including oxygen 28 and oxygen 36was 2.2, compared to a formal charge of +2.

Carbon 54, which has become σ-bonded to chromium atom 9, displays a negative charge of -0.734872 compared to carbon atom 53 that displays a negative charge of -1.344495. A total net charge for two carbon and four hydrogen atoms number 47 through 52, the π-bonded end of hexylene bonded to chromium atom 27, is +1.0181 compared to a net charge for atoms 53 through 58, σ-bonded to chromium atom 9, is -0.8703.

Atom No.	Type	Charge	No. of Elctronss	Popp	Popd	Pop
1	H	0.332735	0.6673	0.66727		
2	O	-0.446909	6.4469	1.75570	4.69121	
3	Si	0.811801	3.1882	0.57944	2.13608	0.47268
4	O	-0.654097	6.6541	1.68306	4.97103	
5	H	0.452744	0.5473	0.54726		
6	O	-0.570459	6.5705	1.69228	4.87818	
7	H	0.383542	0.6165	0.61646		
8	O	-0.525708	6.5257	1.57885	4.94686	
9	Cr	0.487099	5.5129	0.55932	0.04817	4.90541
10	O	-0.654885	6.6549	1.64252	5.01236	
11	Si	0.788157	3.2118	0.60452	2.13474	0.47258
12	O	-0.672357	6.6724	1.69343	4.97893	
13	H	0.398858	0.6011	0.60114		
14	O	-0.507641	6.5076	1.69894	4.80870	
15	H	0.390073	0.6099	0.60993		
16	O	-0.460127	6.4601	1.76523	4.69489	
17	H	0.346011	0.6540	0.65399		
18	O	-0.291713	6.2917	1.44225	4.84947	
19	Si	0.594484	3.4055	0.45271	2.38071	0.57211
20	O	-0.289620	6.2896	1.44209	4.84753	
21	C	-0.368057	4.3681	0.89091	3.47715	
22	C	-0.651312	4.6513	1.07079	3.58052	
23	H	0.318920	0.6811	0.68108		
24	H	0.458508	0.5415	0.54149		
25	H	0.010925	0.9891	0.98907		
26	H	0.177481	0.8225	0.82252		
27	Cr	0.764376	5.2356	0.23071	0.03121	4.97370
28	O	-0.729260	6.7293	1.66463	5.06463	
29	Si	0.850556	3.1494	0.58707	2.09032	0.47206
30	O	-0.459068	6.4591	1.75375	4.70532	
31	H	0.342885	0.6571	0.65711		
32	O	-0.620024	6.6200	1.67417	4.94585	
33	H	0.403361	0.5966	0.59664		
34	O	-0.543243	6.5432	1.69651	4.84673	
35	H	0.373378	0.6266	0.62662		
36	O	-0.732087	6.7321	1.66430	5.06779	
37	Si	0.820499	3.1795	0.59545	2.11112	0.47292
38	O	-0.664640	6.6646	1.69361	4.97103	
39	H	0.388629	0.6114	0.61137		
40	O	-0.474902	6.4749	1.70211	4.77279	
41	H	0.387400	0.6126	0.61260		
42	O	-0.448341	6.4483	1.76711	4.68123	

43	H	0.344893	0.6551	0.65511	
44	O	-0.322721	6.3227	1.44297	4.87975
45	Si	0.635104	3.3649	0.44790	2.35943 0.55756
46	O	-0.322972	6.3230	1.44307	4.87991
47	C	-0.119670	4.1197	1.55282	2.56685
48	C	0.019261	3.9807	1.12840	2.85234
49	H	0.395236	0.6048	0.60476	
50	H	0.075107	0.9249	0.92489	
51	H	0.447821	0.5522	0.55218	
52	H	0.200299	0.7997	0.79970	
53	C	-1.344495	5.3445	0.78249	4.56200
54	C	-0.734872	4.7349	0.76698	3.96790
55	H	0.313385	0.6866	0.68662	
56	H	0.328713	0.6713	0.67129	
57	H	0.268342	0.7317	0.73166	
58	H	0.298595	0.7014	0.70140	

The relative symmetries of the molecular orbital wave functions, in particular at the two chromium atoms, were examined for energy levels 100, 101 and 102. The symmetries were all different for both chromium atom 9 and chromium atom 27.

Structure 6.

Another computation was conducted for the 52 atom chromium silicate catalyst system $H_{20}C_4O_{20}Si_6Cr_2$ where 1-butylene was moved away from chromium(II) atom 9 and chromium(II) atom 27 by 1,000 pm. Hydrogen atom number 25 was repositioned at carbon atom 47 to complete the methyl end of the 1-butylene molecule. Thus, polymerization has been terminated leaving the 40 atom catalyst with two chromium(II) atoms resulting in formation of the separated 1-butylene.

Tables 11a and 11b of bond positions of the atoms of the catalyst + 1-butylene displaced by 1,000 pm in the x-direction.

Table 11a. Lower Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
H1	0.0000	0.0000	0.0000
O2	1.0840	0.0000	0.0000
Si3	1.8770	1.3735	0.0000
O4	3.2505	0.5805	0.0000
H5	4.3345	0.5805	0.0000
O6	0.5036	2.1661	0.0000
H7	-0.5803	2.1667	0.0000
O8	2.6702	2.7474	0.0000
Cr9	3.5186	4.2164	0.0000
O10	3.5187	5.9133	0.0000
Si11	3.5182	7.4993	0.0000
O12	5.1042	7.4994	0.0000
H13	6.0432	6.9578	0.0000
O14	1.9325	7.4993	0.0000
H15	0.9938	8.0414	0.0000
O16	3.5183	9.0858	0.0000
H17	4.4573	9.6274	0.0000
O18	0.6087	4.2300	0.0000
Si19	1.1276	4.8574	0.0000
O20	0.9918	5.6595	0.0000
C21	15.3783	3.0042	0.0000
C22	15.7351	4.3370	0.0000
H23	15.1352	2.0974	0.9391
H24	15.1352	2.0972	- 0.9387
H25	15.9781	5.2438	0.9389
H26	15.9779	5.2437	- 0.9391

Table 11b. Upper Layer Atom Positions (pm)

Atom	x-position	y-position	z-position
Cr27	3.5185	4.2167	2.9002
O28	2.6702	2.7470	2.9000
Si29	1.8770	1.3737	2.8999
O30	1.0838	0.0000	2.9000
H31	0.0000	0.0000	2.9000
O32	3.2505	0.5807	2.9000
H33	4.3345	0.5807	2.9001
O34	0.5034	2.1665	2.9000
H35	-0.5806	2.1664	2.9001
O36	3.5184	5.9133	2.9001
Si37	3.5187	7.4993	2.9000
O38	5.1047	7.4993	2.9001
H39	6.0435	6.9573	2.9000
O40	1.9325	7.4997	2.9000
H41	0.9937	8.0417	2.9002
O42	3.5185	9.0853	2.8999
H43	4.4573	9.6273	2.9000
O44	0.6085	4.2301	2.9000
Si45	1.1278	4.8569	2.9001
O46	0.9918	5.6594	2.9000
C47	15.3778	3.0040	2.9000
C48	15.7351	4.3370	2.9000
H49	15.1352	2.0973	3.8390
H50	15.1351	2.0969	1.9610
H51	15.9782	5.2340	3.8387
H52	15.9781	5.2438	1.9612

The MO computation for the 52 atom Cr-Cr catalyst plus the terminated 1-butylene molecule produced results showing 96 doubly occupied energy levels as before.

The gap between the highest occupied and lowest unoccupied energy levels is -5.472 (E_{96}) to -1.397 eV (E_{97}) or -4.075 eV = -93.97 kcal/mol. Degeneracy is not observed but the energy levels are relatively close together. The gap between Root 93 and Root 94 is -7.856 eV to -7.508 eV = 0.348 eV = 8.02kcal/mol, the gap between Root 94 and Root 95 -7.508 eV to -5.743 eV = 1.765 eV = 40.70kcal/mol and the gap between Root 95 and Root 96 is -5.743 eV to -5.472 eV = 0.271 eV = 6.25kcal/mol. The point group symmetry is close to but not D_{2h} where the alkyl hydrogen atoms are reflective but not a mirror image.

The net atomic charges are listed for each atom, refer to Table 12. The number of electrons is in closer agreement for the two chromium atoms - for chromium atom 27 (0.791266) and chromium atom 9 (0.743252). π-Bonded chromium 9 has an s-orbital population of 0.20996 and a d-orbital population of 5.02075 compared to chromium 27 that reflects an s-orbital population of 0.17889 and a d-orbital population of 5.00516.

The charge differential for chromium atom 9 (0.743252) and bonded oxygen atoms 8 (0.719238) and 10 (0.725262) is 2.2 and the charge differential for the upper O-Cr-O bonds is similarly 2.2. The net atomic charges are listed for each atom, refer to Table 12.

Table 12. Computed Net Atomic Charges for a Dichromium Silicate Catalyst and a Terminated 1-Butylene Molecule.

Atom No.	Type	Charge	No. of Electrons	s-Pop	p-Pop	d-Pop
1	H	0.343142	0.6569	0.65686		
2	O	-0.467364	6.4674	1.75312	4.71424	
3	Si	0.856426	3.1436	0.58967	2.08212	0.47178
4	O	-0.616882	6.6169	1.67392	4.94296	
5	H	0.403377	0.5966	0.59662		
6	O	-0.549365	6.5494	1.69708	4.85229	
7	H	0.370905	0.6291	0.62910		
8	O	-0.718487	6.7185	1.66723	5.05125	
9	Cr	0.746302	5.2537	0.21464	0.02621	5.01285
10	O	-0.721695	6.7217	1.66714	5.05455	
11	Si	0.824482	3.1755	0.59600	2.10665	0.47286
12	O	-0.666972	6.6670	1.69320	4.97377	
13	H	0.385955	0.6140	0.61404		
14	O	-0.474887	6.4749	1.70377	4.77112	
15	H	0.382450	0.6175	0.61755		
16	O	-0.457525	6.4575	1.76713	4.69040	
17	H	0.344346	0.6557	0.65565		
18	O	-0.314220	6.3142	1.44205	4.87217	
19	Si	0.644858	3.3551	0.44979	2.34898	0.55637
20	O	-0.314660	6.3147	1.44255	4.87211	
21	C	-0.307834	4.3078	1.17218	3.13565	
22	C	-0.307277	4.3073	1.17253	3.13475	
23	H	0.167863	0.8321	0.83214		
24	H	0.139866	0.8601	0.86013		
25	H	0.167450	0.8326	0.83255		
26	H	0.139933	0.8601	0.86007		
27	Cr	0.746254	5.2537	0.21468	0.02621	5.01285
28	O	-0.718558	6.7186	1.66716	5.05140	
29	Si	0.856283	3.1437	0.58978	2.08219	0.47175
30	O	-0.467560	6.4676	1.75315	4.71441	
31	H	0.343062	0.6569	0.65694		
32	O	-0.617065	6.6171	1.67390	4.94316	
33	H	0.403360	0.5966	0.59664		
34	O	-0.549233	6.5492	1.69743	4.85180	
35	H	0.370623	0.6294	0.62938		
36	O	-0.721324	6.7213	1.66707	5.05425	
37	Si	0.824668	3.1753	0.59594	2.10654	0.47285
38	O	-0.666813	6.6668	1.69328	4.97353	
39	H	0.385954	0.6140	0.61405		
40	O	-0.475603	6.4756	1.70381	4.77180	
41	H	0.382605	0.6174	0.61740		
42	O	-0.457074	6.4571	1.76699	4.69009	
43	H	0.344333	0.6557	0.65567		
44	O	-0.314189	6.3142	1.44204	4.87215	
45	Si	0.645128	3.3549	0.44986	2.34870	0.55632
46	O	-0.315036	6.3150	1.44263	4.87241	
47	C	-0.307150	4.3072	1.17269	3.13446	
48	C	-0.307916	4.3079	1.17180	3.13612	
49	H	0.140006	0.8600	0.85999		
50	H	0.167497	0.8325	0.83250		
51	H	0.139561	0.8604	0.86044		
52	H	0.168002	0.8320	0.83200		

There was no contribution to the molecular orbital wave functions at the two chromium atoms for energy levels 94, 95 and 96. Thus, the symmetries of the wave functions were not considered for chromium atom 9 and for chromium atom 27.

III. Discussion

A. Background

Laboratory measurements demonstrated specific chemical reactions proceeded to products at accelerated rates in the presence of catalytic substances, most often transition metals and/or their compounds. Certain non-transition metal, free radical compounds, electrochemical processes or high voltage discharge processes may also catalyze organic reactions but at the expense of applying excess energy producing multiple products.

Karl Ziegler discovered that hydrocarbon solutions of titanium tetrachloride in the presence of triethylaluminum produced heterogeneous suspensions that polymerize ethylene at only one atmosphere pressure[10]. This opened a window of discovery wherein numerous novel, extremely diverse, chemical polymerization mechanisms for unsaturated compounds were reported. Phillips Petroleum Company reported specially activated chromium oxides on alumina supported polymerization of ethylene[11]. A more effective process for polymerization of ethylene was reported by Union Carbide that used alumina treated with bis(cyclopentadienyl)chromium(II). These materials catalyzed olefin polymerization processes that produced linear, high density polyethylene as compared to low density, branched polymer produced by the high-pressure gas process.

Later improvements to the Ziegler-Natta catalytic process were reported by several companies including the Montedison Company that facilitated production of $2.5x10^5$ grams of polypropylene per gram of titanium[12]. This was a great improvement over the previous $3x10^3$ grams of polymer per gram of titanium.

While these production processes have been well documented for more than sixty years the molecular mechanism of polymer formation remains an open question. The focus of this work is to demonstrate application of fundamental concepts of catalysis during formation of polymer products that lead to a proposed molecular mechanism.

B. Catalysis Concepts

A theoretical work[13] was conducted previously to understand the physical chemical properties of catalysis. Catalytic action can occur during simultaneous presence of a reactant and an embryonic product, both at the same energy, for which electron bonding shifts from reactant to product. An embryonic product is observed as new product for which chemical bonds form but the atoms have not yet moved (vibrated) from their original positions. This electron shift occurs between degenerate molecular energy levels while the atoms remain in their original positions. This requires the catalyst atoms and their immediately bonded neighbors to be of a symmetric form that supports degenerate energy levels. It can be shown that this requires a catalyst to be at least two-fold degenerate belonging to the C_{4v}, D_{4h} or D_{2h} point group symmetry. This symmetry, involving the transition metals and their nearest neighbor atoms, may be attained with a M - M metal to metal bond at the heart of the catalyst. For chromium metal, a Cr - Cr bond at catalyst center is observed to be degenerate in the 2+ valence state.

Catalysis requires that the highest occupied energy levels of the reactant-catalyst system (just prior to initial reaction steps) be doubly or triply degenerate (same energy) such that the reactant and the embryonic product may exist simultaneously. Such degenerate species typically lie in the 0 to

-60 kcal/mol (0.0 to -2.6 eV) thermodynamic free energy range since catalysis must always comply with thermodynamic limitations. Catalysis was redefined as *catalysis is a barrier free transformation of one electronic configuration to another*, changing reactants to products.

A catalytic backbone may be formed by transition metals of (first, second and/or third row transition metal series) of the form M-N, M-N-M (for which metals M must be the same or greater electronegativity than N). Results of the theoretical[13] work led to numerous novel catalysts designed for Fischer-Tropsch transformations and air oxidative destruction of aliphatic hydrocarbons, both conducted at ambient temperature. This laid the groundwork for a deeper understanding of the molecular mechanism of formation of polyethylene on a chromium silicate catalyst.

C. Catalytic Polymerization of Ethylene

Catalysis literature is replete with articles both claiming and disclaiming chromium(II), chromium(III) and in some cases chromium(IV) as active polymerization sites. One experimental investigation has clearly identified chromium(II) as the initiating site and chromium(III) as the sustaining polymerization site. This research team confirmed the presence of chromium(II) sites, employing high-frequency/high-field EPR spectroscopy[14], that facilitated polymerization of ethylene under dry, oxygen free, conditions. Chromium(II) sites reacted quantitatively with ethylene, producing chromium(III) active sites as measured using X-ray absorption and UV-vis spectroscopy, facilitating polymerization. This and other works established a basis for modeling a chromium-silicate catalyst for this work.

A chromium silicate catalytic compound was modeled for the purposes of molecular orbital computations. The essential elements of the model are (1) each chromium(II) is bonded to a silicate group, (2) an SiO_2 group is coordinate covalently bonded to each chromium(II) site and (3) two chromium(II) silicate groups are coordinate covalently bonded to each other. Thus, a two-layer dichromium silicate model catalyst, containing 20 atoms per layer, possessing D_{2h} point group symmetry as required, was assembled. This generates a 40 atom chromium silicate model, refer to figure 1a for one layer of the two layer catalyst.

This same model catalyst was employed in each of six molecular orbital computations. They are identified as (1) the bare 40 atom catalyst; (2) the catalyst plus two ethylene molecules coordinate covalently bonded to each chromium atom (52 atoms); (3) same as (2) except the two ethylene molecules become bonded to each other to form a 1-buteneyl chromium silicate complex; (4) the 1-buteneyl chromium silicate complex plus an additional ethylene (58 atoms); (5) formation of a 1-hexeneyl chromium silicate complex. Finally, (6) a computation was conducted for 1-butylene terminated and separated from the catalyst by 1,000 pm. Refer to section II, Computational Results, for details of atom positions, bond lengths, doubly occupied molecular energy levels and other information for each structure.

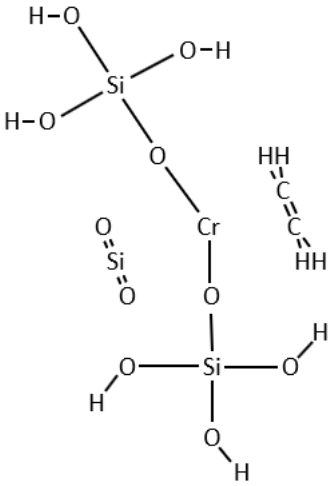


Figure 1a – One Layer of the Two Layer Catalyst with aπ-Bonded Ethylene Molecule.

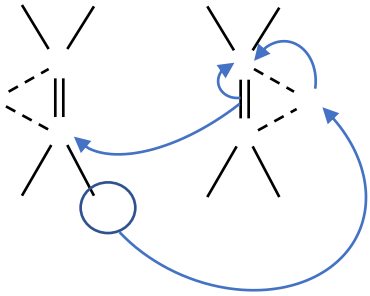


Figure 1b – Two Ethylene Molecules π-Bonded to Chromium(II) Centers of the Catalyst.

Structure 1 – Chromium Silicate Catalyst

The MO computation for the 40 atom Cr-Cr silicate catalyst, having D_{2h} point group symmetry, produced results showing 84 doubly occupied energy levels. The two highest filled energy levels were separated by 0.057 eV or 1.31 kcal/mol where the degeneracy may have been lifted slightly as a result of molecular vibronic distortion, often observed for catalytic structures. Thus, this demonstrated that the model catalyst was in compliance with the concepts of catalysis presented previously in section IIIB.

Structure 2. Chromium Silicate Catalyst Plus Two Ethylene Molecules

A 52 atom catalyst complex plus two ethylene molecules, arrayed as in part 1, placed the ethylene molecules in the x,y-layers, π-bonded to the chromium atoms, opposite the SiO_2 groups. Thus, one ethylene molecule was added to each catalyst layer occupying the fifth and sixth bonds for each chromium atom. Refer to figure 1b for a representation of ethylene on the chromium(II) catalyst centers.

The molecular orbital computation for the 52 atom Cr-Cr silicate catalyst complex, containing two ethylene molecules, produced results showing 96 doubly occupied energy levels. This molecular structure is also described as belonging to a D_{2h} point group symmetry. The three highest filled levels,

E = -5.464 eV, E = -5.376 eV and E = -5.286 eV, were separated by 0.088 eV = 2.03 kcal/mol and 0.090 eV = 2.07 kcal/mol respectively. Thus, there are three essentially degenerate energy levels. It is believed that the degeneracy may have been lifted by 2 kcal/mol as a result of vibronic distortion. Since these three highest energy levels lie close in energy it is possible for level switching to occur as the catalytic reaction proceeds from π-bonding to σ-bonding when the ethylene groups bond together. This was observed in the Ni(I) catalyzed ethylene polymerization reaction[15].

Structure 3. Chromium Silicate Catalyst With 1-Butylene Group

Another 52 atom catalyst complex plus two ethylene molecules was configured for which the lower ethylene molecule remained π-bonded as before while the upper ethylene molecule became σ-bonded to it forming a 1-buteneyl chromium silicate complex. The MO computation for this 52 atom Cr-Cr catalytic complex produced results showing 96 doubly occupied energy levels as before. The highest filled energy levels of the catalytic system were no longer degenerate. The gap between Root 93 and Root 94 was

-6.746 eV to -6.251 eV = 0.495 eV or 11.41kcal/mol, the gap between Root 94 and Root 95 -6.251 eV to -5.789 eV = 0.462 eV or 10.65kcal/mol and the gap between Root 95 and Root 96 is -5.789 eV to -5.110 eV = 0.679 eV or 15.66kcal/mol. Thus, the original point group symmetry of D_{2h} had degraded to C_1 symmetry. Polymerization may continue in the presence of excess ethylene gas as long as one chromium(II)-carbon bond exists in the catalytic system.

The highest filled energy level was -5.110 eV or -117.8 kcal/mol. This indicates a negative free energy for formation of the 1-butene catalyst complex. Furthermore, the energy difference between the highest filled levels of structure 2 (-5.286 eV) and structure 3 (-5.110 eV) was 0.176 eV or 4 kcal/mol of energy,most likely available from modest operating conditions.

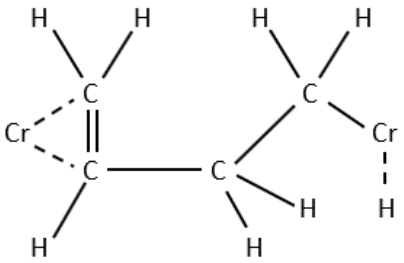


Figure 2a – 1-Butylene Bonded to Chromium(II) and Chromium(III).

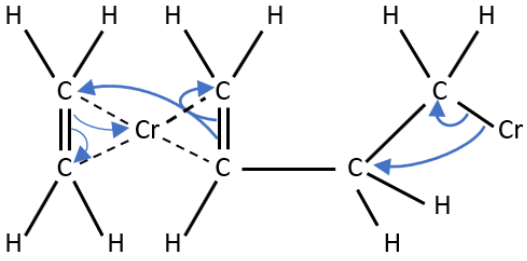


Figure 2b – 1-Butylene Plus Additional π-Bonded Ethylene.

Figure 1b transitioning to 2a demonstrates the electron shifts required for two ethylene molecules to react on the catalyst to produce the 1-butyleneyl group. The curved blue arrows each represent a single electron shift. As chromium(II) transitions to chromium(III) one electron is donated to a carbon atom, a double bond donates its electrons and a hydrogen atom migrates to Cr(III) transferring its electron.

Structure 4. Chromium Silicate Catalyst with 1-Butylene Group Plus an Ethylene Molecule

The 1-buteneyl chromium silicate complex of structure 3 plus an additional ethylene molecule (58 atoms) π-bonded to the lower chromium atom formed this structure. This placed another ethylene molecule adjacent to the lower chromium(II) atom in an open area, oriented vertically, parallel with the z-axis, ready for a carbon-carbon insertion into the growing polymer chain. Refer to figure 2b. This becomes a 58 atom chromium silicate catalyst system $H_{24}C_6O_{20}Si_6Cr_2$ where the 1-butylene group remains σ-bonded to the upper chromium(III) atom. All bond lengths remain the same as for the previous computation.

The MO computation produced results showing 102 doubly occupied energy levels. The highest filled energy levels of the polymer-catalytic complex were not degenerate. The energy of the highest filled level was -4.833 eV or 111.4kcal/mol. The point group symmetry remained C_1.

Structure 5. Chromium Silicate Catalyst with 1-Hexylene Group

Formation of a 1-hexeneyl chromium silicate complex was completed. The π-bonded ethylene molecule was inserted into the bond between the lower chromium atom, π-bonded to the butylene group, producing a σ-bonded alkyl group forcing the upper chromium atom to become π-bonded to the opposite end of butylene. Thus, the lower chromium atom became Cr(III) while the upper chromium atom became Cr(II). All of the carbon and hydrogen atom positions were adjusted slightly to accommodate this new structure. All other bond lengths remained the same as for the previous computation. Refer to figure 3.

Figure 2b demonstrates the electron shifts that occur as the 1-hexeneyl group is formed. Should the following step be termination of the growing polymer chain, then 1-hexene and the original catalyst would be produced. Thus, each polyethylene chain is anticipated to be terminated with one terminal unsaturated group. This has been observed for polymers produced using several alternate transition metal based catalysts[16].

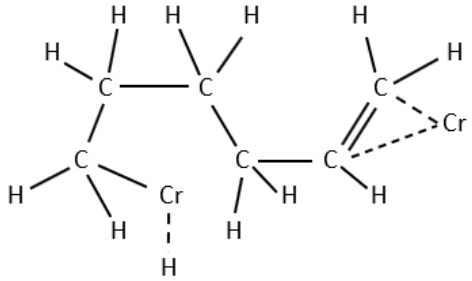


Figure 3 – 1-Hexylene Bonded to Chromium(II) and Chromium(III).

The MO computation produced results showing 102 doubly occupied energy levels. The highest filled energy levels of the polymer-catalytic complex were not degenerate. The energy of the highest filled level was -4.470 eV or 103.0kcal/mol. Should the polymerization reaction be terminated at this point then
1-hexylene and chromium(II) silicate would be the resulting products. The net result is polymerization of three ethylene monomers to form a 1-hexylene product and the original catalyst, the 40 atom dichromium(II) silicate double layer complex, would be returned to its starting molecular state.

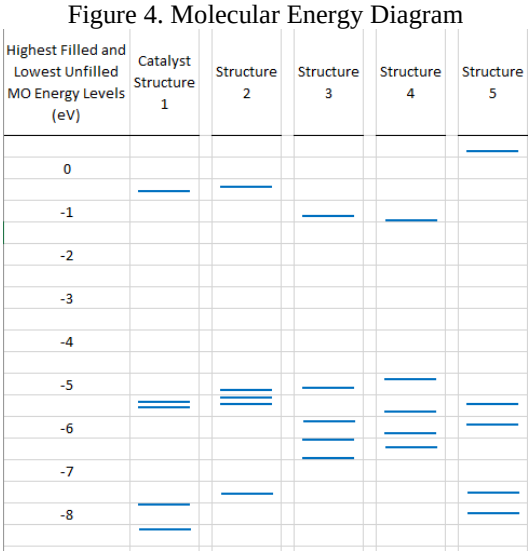
Structure 6. Chromium Silicate Catalyst Plus 1-Butylene Molecule
A computation was also conducted for 1-butene separated from the catalyst by 1,000 pm. This was equivalent to structure 3 except it was assumed that polymer chain growth had terminated producing
1-butene separated from the catalyst by a 1,000 pm distance. The energy difference between the highest filled energy levels of structures 3 and 6 was -0.203 eV or 4.68kcal/mol. This was an indication of the energy required for formation of the 1-buteneyl chromium silicate complex. Thermal energy available at room temperature is estimated to be 0.023 eV or about 0.5kcal/mol. Thus, another 4.2kcal/mol would be required to be supplied by the process conditions. This might be supplied as reactant gas pressure or warming of the reactants or both.

A molecular energy diagram is presented in Figure 4. The highest filled energy levels range from -5 eV to -4 eV as the polymer chain grows. These are thermodynamically allowed bonding energies and are anticipated to remain negative as high molecular weight polyethylene is produced.

In previous works, C_1 monomer insertion[17] and C_2 monomer insertion[18] mechanismshave demonstrated that polymer chain growth most likely occurs by monomer insertion into the existing metal-carbon bond. Existence of a chromium(II)-carbon bond in the presence of reactant monomers can sustain continuing growth of a polymer chain. The most probable primary chain growth mechanism,demonstrated in this work, is ethylene monomer insertion between a Cr(II) and its π-bonded ethylene or the alkene end of an existing polymer chain. Once monomer insertion occurs then the Cr(II) is promoted to a Cr(III)-alkyl bond. The next monomer insertion occurs at the other Cr(II) π-bonded to the alkene end of the growing polymer chain. This becomes active end switching for which first one chromium-carbon bond adds a monomer then the other chromium-carbon bond adds a monomer and so on ad infinitum.

Other possible chain growth mechanismshave been proposed but not demonstrated.
Catalytic chemistry occurs as a result of an electron transfer from the catalytic site, chromium(II), to one carbon of a π-bonded ethylene. The result is the bonding transition metal becomes promoted to chromium(III) while the excited carbon becomes σ-bonded to it. This electron shift occurs in symmetry determined degenerate energy levels while the atoms remain in their original positions. Thus, the transition barrier is close to zero energy.The transition metal atom, chromium for this polymerization example, rests in the 2+ valence state.

Figure 4. Molecular Energy Diagram



Upon activation, it donates one electron to chemically bond to an ethylene to begin the polymerization process. The excited ethylene opens its double bond, donates one electron to form a Cr(III) - C bond while the other end of the opened ethylene bonds to the adjacent ethylene forming a 1-buteneyl group.

Once the electron shifting has been completed (this may occur in a time the order of 10^{-14} second) then the effected atoms can vibrate (10^{-12} second) into their new positions. This leaves one hydrogen atom with its electron to find a new bonding site. Since Cr(III) is in a d^3 or triplet electronic state it can form a spin paired or coordinate covalent bond with the hydrogen atom. Thus, the lone hydrogen finds a new home residing on the Cr(III) atom. This is neither a hydride nor an ionized atom bond. While this work showed the Cr(III) – hydrogen bond shifting from one chromium to the other, the lowest energymolecular configuration is to position this hydrogen atom between the two chromium atoms residing at 145 pm to 146 pm from each such that no movement occurs during polymerization.

IV. Conclusions

Semi-empirical molecular orbital computations were conducted for polymerization of ethylene, in several process steps, on a model double layer chromium silicate catalyst possessing D_{2h} point group symmetry. This computational polymerization effort demonstrated how requirements of symmetry drove catalytic formation of the polymer. A previous theoretical effort taught that catalytic symmetry at a transition metal site is required for the occurrence of catalysis. Resulting degeneracy provided an opportunity for an electron shift to occur between simultaneous presence of a reactant structure and an embryonic product structure before atoms could vibrate to their new positions. As a result, activation energies approaching zero, but less than 60 kcal/mol, promoted catalysis. A proposed molecular mechanism was presented.

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