

SIMULATION MODELING ON THE COORDINATION MECHANISM OF ETHYLENE MONOMER ON VARIOUS PREREDUCED $\text{Cr(II)O}_x/\text{SiO}_2$ PHILLIPS POLYETHYLENE MODEL CATALYSTS*

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Abstract As one of the most important catalysts in polyethylene industry, Phillips catalyst ($\text{CrO}_x/\text{SiO}_2$) was quite unique for its activation by ethylene monomer without using any activator like alkyl-aluminium or MAO. In this work, the density functional theory (DFT) calculation combined with paired interacting orbitals (PIO) method was applied for the theoretical studies on coordination reaction mechanism between ethylene monomer and two model catalysts namely Cr(II)(OH)_2 (M1) and silsesquioxane-supported Cr(II) (M2) as surface Cr(II) active site precursors on Phillips catalyst at the early stage of ethylene polymerization. Unexpected multiplicity of the coordination states of ethylene monomer on both M1 and M2 model catalysts had been first reported on a molecular level. In general, increasing the coordination numbers of ethylene, the corresponding binding energy per ethylene for all the complexes was decreased. The supporting effect of chromium oxide onto silica gel surface was found to be destabilizing the corresponding complexes and decreasing the multiplicity of the coordination states as well due to both electronic and steric effect. Moreover, tri- and tetra- or higher ethylene coordination states could not be possibly formed on the supported catalyst as on the Cr(II)(OH)_2 . The optimized complex geometries were adopted for determining the intermolecular orbital interactions. In-phase overlap orbital interaction for all the molecular complexes indicated favorable coordination between ethylene and Cr(II) sites. The molecular orbital origin of the π -bonded Cr(II) , and mono- and di- C_2H_4 M1 complexes had been elucidated by PIO method showing high possibility of the formation of metallacyclopentane or metallacyclopentane active sites in the subsequent initiation of polymerization stage.

Keywords: Phillips catalyst ($\text{CrO}_x/\text{SiO}_2$); Polyethylene; Model catalysts; Density functional theory (DFT); Paired interacting orbitals (PIO).

INTRODUCTION

Phillips catalysts ($\text{CrO}_x/\text{SiO}_2$) have been used for ethylene polymerization since 1950s, and nowadays account for the commercial production of more than one-third of all the polyethylene (PE) sold worldwide, especially for commercial production of high density polyethylene (HDPE)^[1, 2]. Due to its quite unique product properties deriving from the unique microstructure of polymer chains with very broad molecular weight distribution, short chain branches and long chain branches, Phillips catalysts is still quite competitive against other commercial catalysts especially in the application area of blow molding products^[2]. More importantly, it does not require the intervention of any activators, and ethylene monomer itself can act as an activator to reduce the hexavalent chromate species ($\text{Cr(VI)O}_{x,\text{surf}}$) into surface-stabilized divalent chromium species ($\text{Cr(II)O}_{x,\text{surf}}$) within a short induction period, followed by alkylation of the $\text{Cr(II)O}_{x,\text{surf}}$ before the initiation of ethylene polymerization.

However, in spite of the intensive research, the catalyst is still one of the most debated systems, concerning both the molecular structure of the active sites and the related initiation mechanism, for which a unifying picture

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is still missing^[2, 3]. The main reasons why these two strictly connected questions are not properly addressed are the high intrinsic heterogeneity of the Cr sites formed at the surface of amorphous silica gel and the high Cr dilution (typically less than 1 wt% Cr).

Many efforts have been made to explore the early stages in the polymerization of ethylene over Phillips catalysts by experimental and theoretical methods. A model^[4] was probed by Fourier transform infrared spectroscopy using C₂D₄ and C₂H₄ as reactant, in which the IR bands of methylene group was clear. The formation of di-ethylene π -bonded complexes, accompanied by evolving in mono-ethylene complexes when the C₂H₄ pressure decreases, was also observed by FTIR technique^[5].

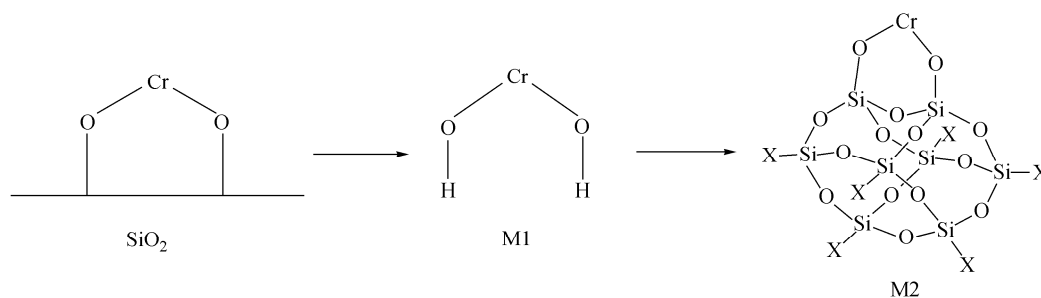
At the same time, different mechanisms of polymerization initiation by ethylene have been proposed. Groppo *et al.* reviewed seven initiation mechanisms appeared in the literature, which involved carbene, metallacyclic intermediates, Cossee-type, allylic mechanisms and so on^[3]. All the mechanisms were on the base of the coordinatively unsaturated Cr(II) site initially adsorbs one, two, or three ethylene molecules *via* a coordinative d- π bond, which were considered as a viable starting structure for polymerization.

Theoretical chemistry has emerged as an important technique to provide insights in the atomic scale phenomena governing heterogeneous catalysis. The *ab initio* calculations performed by Espelid and Børve showed that both one and two ethylene molecules may coordinate to the reduced Cr(II) cluster, without activation and with considerable binding energy in two different ways, either as a molecular complex or covalently bound to chromium atom^[6].

Fujimoto *et al.*^[7] proposed a method of determining unequivocally the orbitals which should play dominant roles in interactions between two molecular systems. Then, interactions were represented compactly in terms of a few pairs of localized orbitals ‘paired interacting orbitals’ (PIO). It has been developed and should give theoretical evidence especially in-between the intermolecular frontier area either in favor of or contrary to the potential electron delocalization for the formation of the new bonding of the intermediate in the proposed mechanism, which has been useful in gaining insight into the role of complicated catalytic systems^[8].

Recently, we have proposed a novel Cr-carbene species mechanism of metathesis initiation in the ethylene polymerization over the Phillips catalyst based on temperature programmed desorption-mass spectrometry (TPD-MS) and X-ray photoelectron spectroscopy (XPS) evidence^[9, 10]. In the induction period, the reduction of surface Cr(VI) species into Cr(III) and Cr(II) species occurred in the presence of ethylene monomer at room temperature. Formaldehyde and unsaturated hydrocarbons, such as propylene, butene, and pentene were also found. Thus, reduction and alkylation of Cr species as well as initiation of ethylene insertion occurred even in the induction period. Later, though the combination of density functional theory (DFT) calculations and PIO method, it was shown that the ethylene monomer preferentially approached to the surface monochromate Cr(VI) species in a symmetric orientation relative to the two carbon atoms of ethylene from the upper site between the two double-bonded oxo-atoms of surface monochromate species.

As a successive part of our previous studies, in this work, two kinds of Cr(II) model catalysts including Cr(II)(OH)₂ (defined as M1) and silsesquioxane-supported Cr(II) (defined as M2) as shown in Scheme 1, avoiding the complexity of the Cr(II) species supported on the amorphous silica gel surface, were utilized to study the initiation of the reaction by investigation the interaction of the Cr(II) active site precursor and the ethylene monomer in terms of intermolecular orbital origin of the most preferential intermolecular coordination configuration. For the silsesquioxane-supported Cr(II) model catalyst, the ligand X was tuned as X = —OH corresponding to fully hydroxylated silica gel surface. From M1 to M2, the supporting effect of chromium oxide on silica gel surface could be investigated.



Scheme 1 Cr(II)(OH)_2 (M1) and silsesquioxane-supported Cr(II) (ligand $\text{X} = -\text{OH}$) (M2) as molecular models of prerduced Phillips catalyst $\text{Cr(II)O}_x/\text{SiO}_2$

COMPUTATIONAL METHOD

The equilibrium structure of ethylene monomer and molecular models of prerduced monochromate species (M1 and M2) in ground state were calculated by DFT method (B3LYP, basis set: 6-31G*, spin multiplicity: 5) using SPARTAN'04 Windows developed by Wavefunction, Inc. The mono-, di- and multiple ethylene binding on Cr(II) sites through coordination was calculated by DFT method. These optimized molecular structures of various molecular complexes between ethylene and Cr(II) site were used for the subsequent PIO calculations. LUMMOX software for Windows PC computer, which was developed by Sumitomo Chem. Corp. based on the PIO theory established by Fujimoto *et al.* was used for calculation of intermolecular orbital interaction by PIO method. More detail of the computational method was shown elsewhere^[11–13]. The states of the interaction of Cr(II) model catalyst with one, two or more ethylene monomers were considered, respectively. The extended Hückel calculations were used to obtain the canonical molecular orbitals. The interaction between Cr(II) active models and ethylene monomer in the system could be well represented by 12 pairs of localized orbitals. In each orbital pair, one orbital belongs to fragment Cr(II) model and the other to fragment ethylene monomer. PIO-1 and PIO-2 are found to be the main contribution in this molecular orbital interaction compared with the other 10 PIO orbital pairs (PIO-3 to PIO-12) for each complex. The contour maps of the PIO-1 and PIO-2 for each molecular complex were obtained.

RESULTS AND DISCUSSION

The polymerization reaction may formally be divided into three phases, denoted by initiation, propagation, and termination, respectively. For Cr(VI)/SiO_2 catalyst, ethylene polymerization can be carried out at room temperature by contacting ethylene gas with an induction time. The absence of using cocatalyst like Al alkyl or methylaluminoxane (MAO) made it quite unique among all the polyolefin catalysts. Meanwhile, it is important to notice that the prerduced $\text{Cr(II)O}_x/\text{SiO}_2$ form of the Phillips catalyst can be considered as “active”, as it initiates the polymerization of ethylene without an induction period. The subsequent coordination reaction between ethylene monomer and the Cr(II) sites is the first step of active site formation *i.e.* initiation of ethylene polymerization, which will be investigated theoretically in this work.

Based on DFT calculations, the interaction geometries of ethylene and M1 model catalyst (Cr(II)(OH)_2) were optimized. The initial intermolecular distance of 0.3 nm was selected according to the literature^[8]. Too small intermolecular distance must be avoided in order to omit the calculation deviation from the internucleic interaction; meanwhile, stable coordination states may not be obtained if the initial intermolecular distance was too far away.

Firstly, the interaction of Cr(II)(OH)_2 M1 model with one ethylene monomer was investigated. As shown in Fig. 1, three typical intermolecular complexes between Cr(II)(OH)_2 model and one ethylene monomer, namely M1-1, M1-2, M1-3, were presented from side or top view, respectively. The corresponding bond lengths of $\text{C}=\text{C}$ for ethylene and average $\text{Cr}-\text{C}$ distance, as well as the values of total binding energy of all the ethylene molecules in each complex, ΔE , were shown in Table 1. The original bond length of the ethylene with

equilibrium geometry is C=C: 0.1330 nm. The C=C bond length of ethylene monomer in the coordination complexes systems were all extended due to the d- π complexing reaction. The corresponding values for the three mono-ethylene complexes were 0.1363, 0.1379, and 0.1369 nm, respectively. The value of binding energy ΔE was the difference between after and before the coordination interaction of ethylene and Cr(II)(OH)₂ M1 model. As can be seen from Table 1, the system energies were lower for M1-1 and M1-2 than that for M1-3. It was suggested that the molecular orientation was favored if the ethylene monomer was located between the Cr—O bond, or roughly in the plane of O—Cr—O. The repulsive interaction was larger if the ethylene monomer approached to the Cr(II) perpendicularly to the O—Cr—O plane. This is the first report that one ethylene monomer can coordinate on Cr(II) site with multiple orientations.

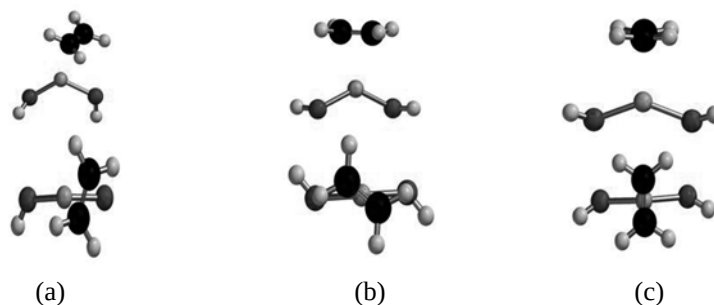


Fig. 1 Mono-ethylene coordination molecular complexes formed from M1 model catalyst and one ethylene monomer

a) M1-1; b) M1-2; c) M1-3. Upper: side-view; lower: top-view

Table 1. Equilibrium geometries of various mono-, di- and multiple ethylene coordinated molecular complexes formed between M1 and M2 model catalysts and ethylene monomer and total binding energies ΔE of ethylene monomers on Cr(II) sites obtained by DFT method

d- π Complex ^a	Ratio of ethylene/Cr(II)	Bond length (nm)		ΔE (kJ/mol)
		C=C	Cr—C ^b	
M1-1	1	0.1363	0.2354	-144.81
M1-2	1	0.1379	0.2251	-141.96
M1-3	1	0.1369	0.2277	-129.41
M1-4	2	0.1356	0.2435	-196.06
M1-5	2	0.1357	0.2394	-183.47
M1-6	2	0.1352	0.2429	-180.00
M1-7	2	0.1355	0.2587	-169.49
M1-8	2	0.1358	0.2453	-160.33
M1-9	2	0.1350	0.2497	-148.49
M1-10	2	0.1350	0.2447	-126.61
M1-11	3	0.1351	0.2471	-211.63
M1-12	3	0.1351	0.2471	-209.91
M1-13	3	0.1349	0.2499	-150.08
M1-14	3	0.1340	0.2755	-118.37
M1-15	4	0.1336	0.2798	-106.36
M1-16	4	0.1338	0.2990	-98.28
M2-1	1	0.1358	0.2347	-101.63
M2-2	1	0.1358	0.2375	-96.11
M2-3	2	0.1352	0.2463	-163.30
M2-4	2	0.1354	0.2442	-136.31
M2-5	2	0.1356	0.2461	-129.37
M2-6	2	0.1354	0.2482	-128.03

^a Ethylene Cr(II) d- π complexes: M1-1–3: in Fig. 1; M1-4–10: in Fig. 2; M1-11–16: in Fig. 3; M2-1 and M2-2: in Fig. 4; M2-3–6: in Fig. 5;

^b Average Cr—C distance between Cr atom and all the C atoms in ethylene molecules

Furthermore, the cases of the formation of di-ethylene complex with Cr(II)(OH)_2 M1 model catalyst were also investigated according the coordination structures. Seven di-ethylene-complexes were found depending on the different orientation of the ethylene molecule and the hydroxyl groups of M1, and the structures were shown in Fig. 2. In Table 1, from M1-4 to M1-10, the values of the binding energy ΔE were gradually decreasing, suggesting the stability of the coordination molecular complexes was also decreasing in the same order. For M1-4, as the two ethylene monomers just symmetrically located above Cr(II) active site, the ΔE was maximum and up to -196.06 kJ/mol. Concerning about the ratio of ethylene to Cr(II) , the ΔE for di-ethylene-complexes were not the twice as that for mono-ethylene-complex. In general, the stabilized energy value per ethylene for all di-ethylene M1 complexes is lower than that for all mono-ethylene M1 complexes. At the same time, the length of the $\text{C}=\text{C}$ band in all the complexes was all similarly extended from the original $\text{C}=\text{C}$ value 0.1330 nm of ethylene monomer before complexing, but less extended than the $\text{C}=\text{C}$ bond length of those mono-ethylene M1 complexes as shown in Table 1. Concerning the average $\text{Cr}-\text{O}$ distance, it can be found that the average $\text{Cr}-\text{O}$ distance for mono-ethylene M1 complexes is generally shorter than that for di-ethylene M1 complexes. It was likely due to the interaction and/or the steric effect from the two ethylene monomers. All these facts indicate that the di-ethylene M1 complexes are less likely to be formed and less stable as well compared with the mono-ethylene M1 complexes.

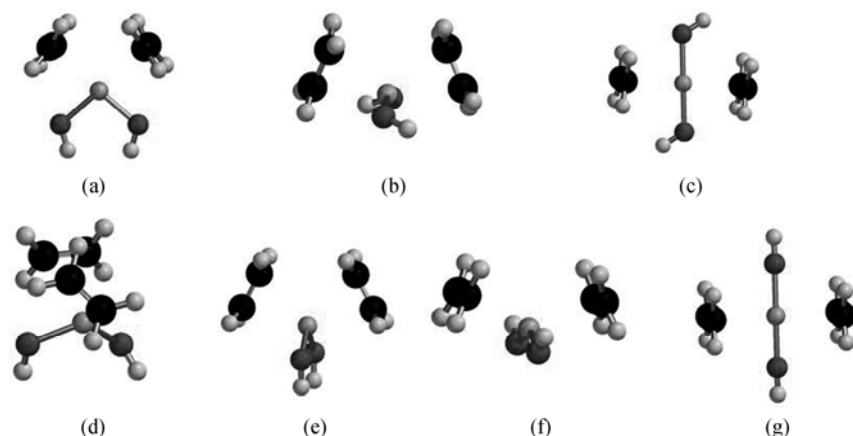


Fig. 2 Di-ethylene coordination molecular complexes formed from Cr(II) model catalysts and two ethylene monomers
a) M1-4; b) M1-5; c) M1-6; d) M1-7; e) M1-8; f) M1-9; g) M1-10

Further DFT calculations disclosed that it is even possible to form tri- and tetra-ethylene M1 complexes as shown in Fig. 3. M1-11–M1-14 are tri-ethylene M1 complexes, while M1-15 and M1-16 are tetra-ethylene M1 complexes. The $\text{O}-\text{Cr}-\text{O}$ bond angles are stretched to near 180° . According to Table 1, as the number of ethylene molecule in the complexes increases, the stabilization energy per ethylene for all ethylene M1 complexes becomes lower. At the same time, the length of the $\text{C}=\text{C}$ band in all the complexes are all similarly extended longer. Moreover, the average $\text{Cr}-\text{O}$ distance for ethylene M1 complexes generally become longer. This was likely due to the interaction and/or the steric effect from the multiple coordinated ethylene monomers. All these facts indicate that the M1 complexes with the higher number of ethylene molecules are less likely to be formed and less stable as well.

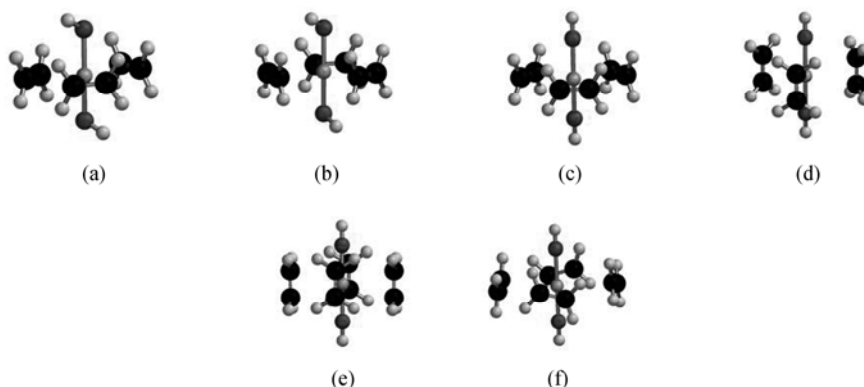


Fig. 3 Tri- or tetra-ethylene coordination molecular complexes formed from Cr(II) model catalysts and three or four ethylene monomers
a) M1-11; b) M1-12; c) M1-13; d) M1-14; e) M1-15; f) M1-16

In order to investigate the supporting effect of chromium oxide on silica gel surface, DFT calculations were performed for the coordination reaction of ethylene on silsesquioxane-supported Cr(II) M2 model catalyst. The results are shown in Fig. 4 and Fig. 5. The corresponding bond lengths of C=C for ethylene and average Cr—C distance, as well as the values of total binding energy of all the ethylene molecules in each M2 complex, ΔE , were shown in Table 1. Figure 4 shows two typical intermolecular complexes between M2 model catalyst and one ethylene monomer, namely M2-1 and M2-2, from both side and top view, respectively. Compared with M1-1–M1-3 complexes, bond lengths of C=C for ethylene within M2-1 and M2-2 complexes became shorter and the binding energy per ethylene decreased significantly. Four di-ethylene-complexes were found depending on the different orientation of the ethylene molecule on the Cr(II) center of M2, and the complexes structures were shown in Fig. 5. Compared with M1-4–M1-10 complexes, the bond lengths of C=C for ethylene and average Cr—C distance within M2-3–M2-6 complexes are similar, however the binding energy per ethylene decreased obviously. Therefore, after supporting the chromium acid on the surface of silica gel, it seemed the stability of ethylene Cr(II) complexes decreased mostly probably due to the steric and electronic effects from silica gel surface. The multiplicity of the coordination states for mono- and di-ethylene complexes also decreased. We also found that it is impossible to form stable tri- and tetra-ethylene M2 complexes.



Fig. 4 Mono-ethylene coordination molecular complexes formed from M2 model catalyst and one ethylene monomer
a) M2-1 (side-view); b) M2-1 (top-view); c) M2-2 (side-view); d) M2-2 (top-view)

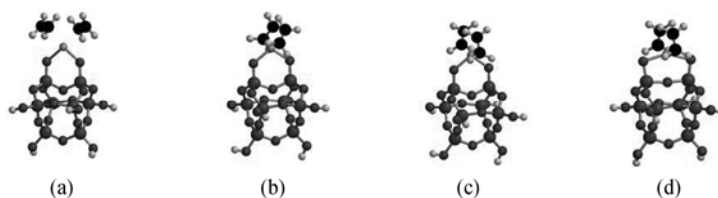


Fig. 5 Di-ethylene coordination molecular complexes formed from M2 model catalysts and two ethylene monomers
a) M2-3; b) M2-4; c) M2-5; d) M2-6

The PIO orbitals for the combined interacting coordination system may provide crucial information regarding favorable or unfavorable electron delocalization in-between the frontier area between the Cr(II) center and ethylene monomers. The extended Hückel calculations were used to obtain the canonical molecular orbitals for the mono-ethylene M1 complexes as shown in Fig. 1. Twelve pairs of localized orbitals were obtained for each complex. In each orbital pair, one orbital belonged to ethylene monomer and the other to Cr(II)(OH)_2 model. PIO-1 and PIO-2 were found to make the main contribution in the interaction for each M1 complex. The analysis of the other 10 pairs of PIO orbitals (from PIO-3 to PIO-12) for each complex could be neglected due to their too small contribution in each interaction system. The contour maps of PIO-1 and PIO-2 of the coordinating complexes M1-1, M1-2, and M1-3 are shown in Fig. 6, respectively. The overlapping of molecular orbital with the same type (positive or negative sign corresponding to the dark or light gray lines) showed that the presence of in-phase overlap molecular orbital interaction at all mono-ethylene M1 complexes, M1-1, M1-2, and M1-3 indicating the favorable intermolecular coordination. Moreover, the PIO-1 for all three mono-ethylene complexes all showed an in-phase overlap orbital interaction between the anti-bonding π^* orbital of ethylene and occupied d orbitals of Cr. The electron delocalization from the occupied d orbitals of Cr into the anti-bonding π^* orbital of ethylene will lead to the breaking of the $\text{C}=\text{C}$ double bond in ethylene favoring the formation of the metallacyclopropane as suggested by Groppo *et al.*^[14, 15].

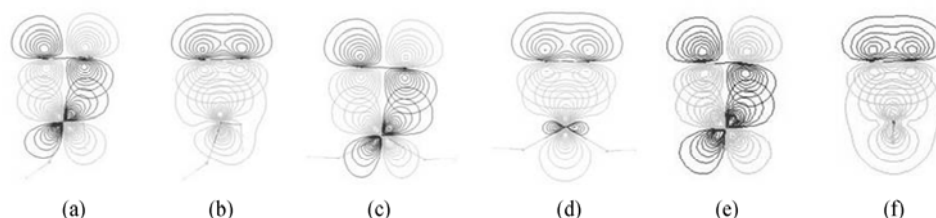


Fig. 6 Contour maps of PIO orbitals of the mono-ethylene coordination complexes formed from Cr(II) model catalyst and one ethylene monomer
a) PIO-1(M1-1); b) PIO-2(M1-1); c) PIO-1(M1-2); d) PIO-2(M1-2); e) PIO-1(M1-3); f) PIO-2(M1-3)

The extended Hückel calculations were also used to obtain the canonical molecular orbitals for the di-ethylene M1 complexes. Twelve pairs of localized orbitals were obtained for each M1 complex. In each orbital pair, one orbital belonged to ethylene monomer and the other to Cr(II)(OH)_2 model. PIO-1 and PIO-2 were found to make the main contribution in the interaction for each complex. The analysis of the other 10 pairs of PIO orbitals (from PIO-3 to PIO-12) could be neglected due to their too small contribution in each interaction system. The contour maps of PIO-1 and PIO-2 of the interacting system at the intermolecular complexes M1-4–M1-10 are shown in Fig. 7, respectively. The overlapping of the intermolecular orbitals with the same type (positive or negative sign) showed that the presence of in-phase overlap molecular orbital interaction at all interaction systems, M1-4–M1-10 indicating the favorable intermolecular coordination. This is the first report that two ethylene monomers can coordinate on Cr(II) site with multiple orientations. Moreover, the two di-ethylene molecular complexes namely M1-5 and M1-8 are in consistent with those previously proposed in the literature based experimental approaches. Moreover, the PIO-1 for M1-5 and M1-8 di-ethylene complexes all showed an in-phase overlap orbital interaction between the anti-bonding π^* orbital of ethylene and the occupied d orbitals of Cr(II) center. The electron delocalization from the occupied d orbitals of Cr(II) center into the anti-bonding π^* orbital of ethylene will lead to the breaking of the $\text{C}=\text{C}$ double bond in ethylene favoring the formation of the metallacyclopentane as suggested by Liu *et al.*^[16] and Groppo *et al.*^[14, 15]. Similar PIO analytical results for mono- and di-ethylene M2 complexes had also been obtained and would not be discussed in detail herein. Further DFT investigations are still in progress in order to elucidate the second step of active sites formation in term of Cr and C bonding formation and subsequent chain propagation on Phillips Cr-based polyethylene catalysts.

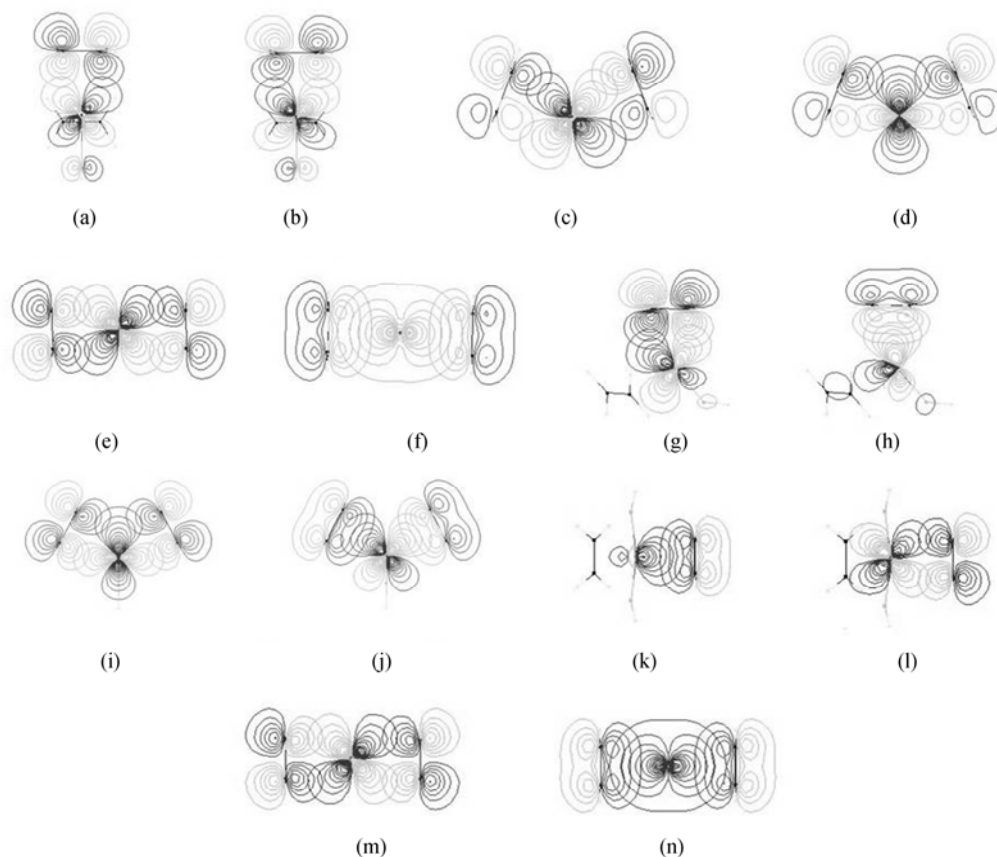


Fig. 7 Contour maps of PIO orbitals of the di-ethylene coordination complexes formed from Cr(II) model catalyst and two ethylene monomers

a) PIO-1(M1-4); b) PIO-2(M1-4); c) PIO-1(M1-5); d) PIO-2(M1-5); e) PIO-1(M1-6); f) PIO-2(M1-6); g) PIO-1(M1-7); h) PIO-2(M1-7); i) PIO-1(M1-8); j) PIO-2(M1-8); k) PIO-1(M1-9); l) PIO-2(M1-9); m) PIO-1(M1-10); n) PIO-2(M1-10)

CONCLUSIONS

Various mono-, di- and multiple C_2H_4 coordination reactions on prereduced Phillips $Cr(II)O_x/SiO_2$ model catalysts namely $Cr(II)(OH)_2$ (M1) and silsesquioxane-supported $Cr(II)$ (M2) were first made clear through the combination of DFT calculations and PIO method. Unexpected multiplicity of the coordination states of ethylene monomer on both M1 and M2 model catalysts had been first reported on a molecular level. In general, increasing the coordination numbers of ethylene, the corresponding binding energy per ethylene for all the complexes was decreased. The supporting effect of chromium oxide onto silica gel surface was found to be destabilizing the corresponding complexes and decreasing the multiplicity of the coordination states as well due to both electronic and steric effect. Moreover, tri- and tetra- or higher ethylene coordination states could not be possibly formed on the supported catalyst as on the $Cr(II)(OH)_2$. The optimized complex geometries were adopted for determining the intermolecular orbital interactions. In-phase overlap orbital interaction for all the molecular complexes indicated favorable coordination between ethylene and $Cr(II)$ sites. The molecular orbital origin of the π -bonded $Cr(II)$ and mono- and di- C_2H_4 M1 complexes had been elucidated by PIO method showing high possibility of the formation of metallacyclopropane or metallacyclopentane active sites in the subsequent initiation of polymerization stage.

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