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Mendeleev Commun., 2018, **28**, 648–650

Mendeleev Communications

DFT modeling of active particles with one and two Mg atoms in post-titanocene catalytic systems for ethylene polymerization

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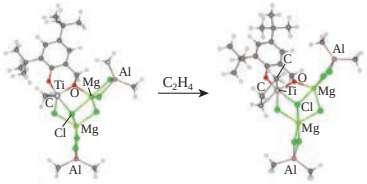
DOI: 10.1016/j.mencom.2018.11.029

The DFT modeling of active particles in post-titanocene catalytic systems for ethylene polymerization suggests that catalytic centers with two magnesium atoms are more stable and more reactive with respect to ethylene as compared to the centers with one magnesium atom; this is in agreement with experimental data.



Magnesium compounds increase the catalytic activity of Zr and Ti complexes in alkene polymerization reactions. Previously an activation effect of Bu_2Mg on the catalytic activity of post-titanocene complexes $LTiCl_2$ (L is a bidentate ligand, which forms two ≡C–O–Ti bonds, Scheme 1) was observed.[1–4] Bu_2Mg was introduced as a binary cocatalyst (Bu_2Mg/Et_2AlCl) or at the stage of the synthesis of $LTiCl_2$. In the latter case,[1] the activator AlR_3 (R is an alkyl) and C_2H_4 were added to the reaction mixture immediately after the $LTiCl_2$ synthesis without the preliminary separation of Mg-containing compounds from the Ti complex. The catalytic activity of the system with the Ti : Mg ratio of 1 : 2 was much higher than that of the system with the Ti : Mg ratio of 1 : 1.[1] Thus, the catalytic particles may contain not only one but also two Mg atoms. High molecular weight linear polyethylene was formed in the system. This fact indicates that Ti^{IV} compounds participate in the catalysis.

Previously,[5–9] the density functional theory (DFT) method was used for modeling active particles in the $LTiCl_2 + Bu_2Mg/Et_2AlCl$ system. The mechanism of $LTiCl_2$ activation by the binary co-catalyst Bu_2Mg/Et_2AlCl was proposed.[9] The participation of $RMg(\mu\text{-}Cl)_2AlR'_2$ binuclear heterocomplexes (R, R′ are alkyl groups) or $RMg(\mu\text{-}Cl)_2MgR$ dimers formed by reactions (1) and (2) was suggested.

$$R_2Mg + R'_2Al(\mu\text{-}Cl)_2AlR'_2 \rightarrow RMg(\mu\text{-}Cl)_2AlR'_2 + Al(R)R'_2 \quad (1)$$

$$R_2Mg + RMg(\mu\text{-}Cl)_2AlR'_2 \rightarrow RMg(\mu\text{-}Cl)_2MgR + Al(R)R'_2 \quad (2)$$

Both compounds react with $LTiCl_2$ to form the trinuclear compounds (L)(Cl)(R)Ti(μ-O)(μ-Cl)M [structures **1** and **2** in Scheme 1, M = $Mg(\mu\text{-}Cl)_2AlR'_2$ and $Mg(\mu\text{-}Cl)_2MgR$, respectively]. Particles of types **1** and **2** coordinate the ethylene molecule. When it binds to **1** or **2**, the terminal chlorine atom shifts to the Mg atom next to the Ti atom, forming the Ti–Cl–Mg bridge bond and releasing room for the ethylene molecule in the coordination sphere of the Ti atom. The exchange of the second chlorine atom with the alkyl group R was found thermodynamically unfavorable.[8]

The influence of Mg-containing compounds on the catalytic activity of the post-titanocene complexes $LTiCl_2$ was explained[6–9] by higher thermodynamic stability and greater reactivity towards alkenes of the catalytic particles [in particular, (L)(Cl)(R)Ti(μ-O)-$(\mu\text{-}Cl)Mg(\mu\text{-}Cl)_2AlR'_2$ **1**] formed in the Mg-containing systems, as compared to Mg-free structural analogs [in particular, (L)(Cl)(R)-$Ti(\mu\text{-}O)(\mu\text{-}Cl)AlR'_2$]. In this work, the possible transformations of compounds **1** and **2** leading to either inactive compounds or catalytic centers with higher activity than that of **1** and **2** are considered.

More than two active particles with similar catalytic activities are involved in alkene polymerization catalyzed by the $LTiCl_2$ + + Bu_2Mg/Et_2AlCl system; a relatively fast catalyst inactivation has been observed.[1] Which catalytic particles other than **1** and **2** could participate in ethylene polymerization? Another unexplained result was that the Ti : Mg ratio of 1 : 2 was better for the catalytic activity than 1 : 1. This work was aimed at getting answers to these questions.[†]

Scheme 1 shows three stable particles (**1**, **3** and **4**) which contain one Mg atom, and seven stable structures (**2**, **5**–**10**) which contain two Mg atoms. These structures correspond to energy minima on the potential energy surface of the system. To evaluate the influence of alkyl group on the results of the calculations, two fragments R = Me and Et were considered. Both groups are presented in Al-containing compounds used as activators, for instance, in $AlMe_3$ and Et_2AlCl.[1–4]

The mechanism of the formation of particles **1** and **2** was considered in detail.[9] A terminal chlorine atom in **1** at the titanium atom can bind the R_2AlCl molecule to form compound **3**. The latter isomerizes into compound **4** as a result of the concerted process of the rupture of one Al–Cl bond and the formation of another Al–Cl bond. Compound **4** dissociates to two thermodynamically stable products LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2$. This reaction leads to the reversible inactivation of the Mg-containing catalytic particles.

There is the three-coordinated Mg atom in particle **2**. The >Mg–R fragment can react with the R_2AlCl dimer to form more stable compounds **5** and **6**. Particle **5** is a structural analog of **1**, and **6** is a structural analog of **3**. As the result of the monomolecular reactions **6** → **7** → **8** → **9**, **10**, compound **6** isomerizes into **9** or

[†] Calculations were carried out using the PRIRODA program,[10] functional PBE,[11] and TZ2P Gaussian-type basis sets. The contraction schemes for orbital basis sets used in this work were reported elsewhere.[5–9] Complete geometry optimization was performed for all stable and transition states without imposing symmetry or other restrictions and followed by vibrational frequency analysis. Free energies G_{298} were calculated at T = 298.15 K using ideal gas, rigid rotator and harmonic oscillator approximations.

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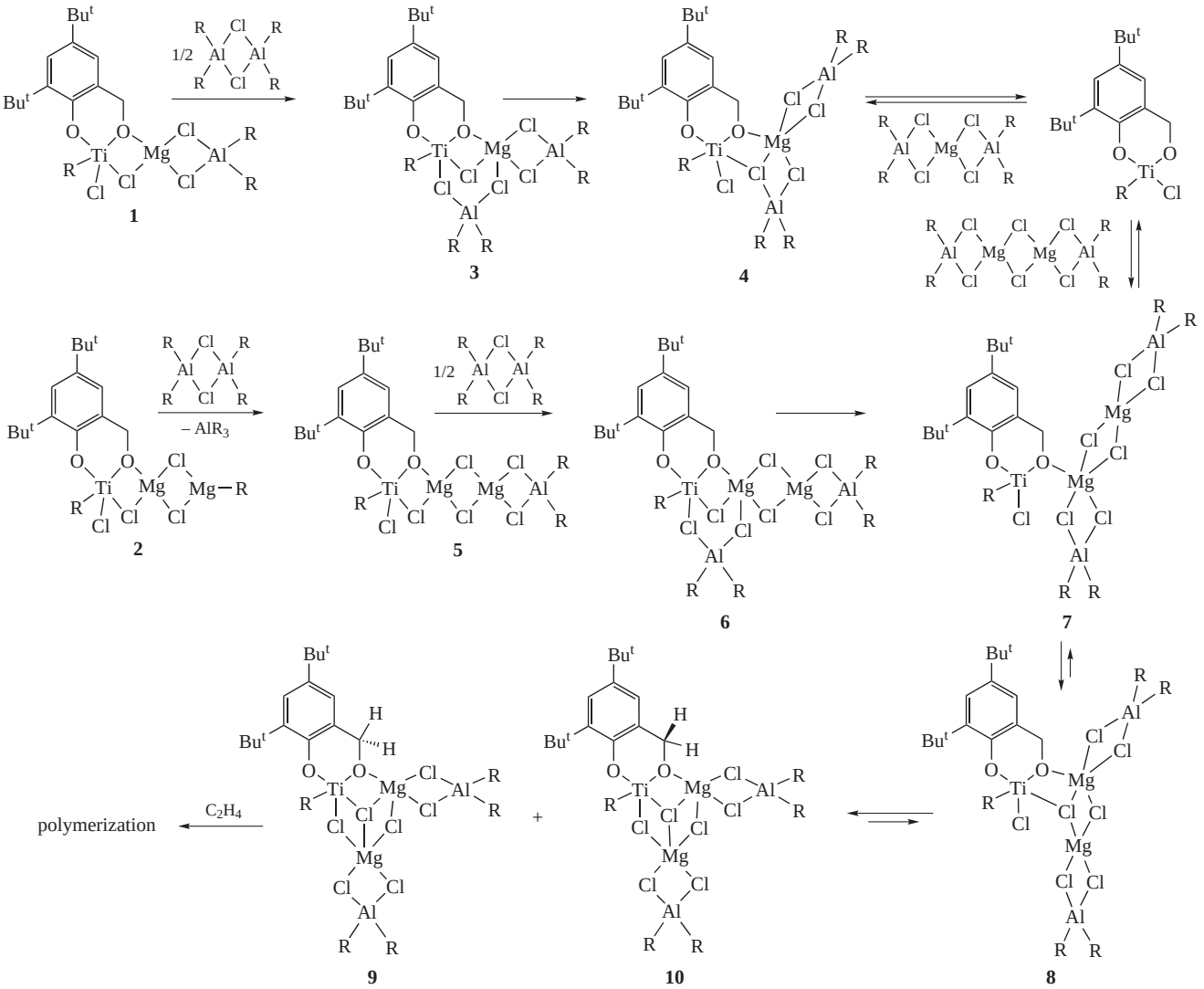

Scheme 1

its conformer **10** (Scheme 1, Figure 1). Structures **7**–**10** can be considered as the products of $R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2\text{-}AlR_2$ addition to LTi(R)Cl. The reversible dissociation of **7**–**10** is a possible mechanism of catalyst deactivation.

Table 1 lists total (ΔE) and free (ΔG_{298}) energies of structures **1**–**10** shown in Scheme 1. Among the structures with one Mg atom, the most thermodynamically stable are **1** and **4**, but they easily dissociate into more stable compounds LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2$. Among the structures with two Mg atoms, the most stable are **9** and **10**; their transformations to LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2$ are thermodynamically unfavorable processes. The interconversion of conformers **9** and **10** proceeds through the transition state **TS**(**9**–**10**). The corresponding energy barrier does not exceed 3 kcal mol^{-1} (see Table 1). Therefore, one can expect a rapid establishment of equilibrium between **9** and **10**. Thus, the most thermodynamically stable particles **9** and **10** (with respect to dissociation products) contain two Mg atoms.

Particles **1**–**10** can react with ethylene. The formation of a new C–C bond in the coordination sphere of Ti atom is the rate-limiting step of the reaction. The height of the corresponding energy barrier (**TS1**–**TS10**) can serve as a measure of the particle reactivity with respect to ethylene. In this work, the energies of all stable and transition states were calculated with respect to LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2\{Mg(\mu\text{-}Cl)_2\}_nAlR_2$ (n = 1,2). This allowed to compare the energies of the structures with one and two Mg atoms. For the structures with one Mg atom, Table 1 presents the total and free energies of the transition states **TS1**, **TS3** and **TS4** of C–C bond formation in the reactions of particles **1**, **3** and **4**, respectively, with ethylene. For the particles with two Mg atoms,

Table 1 Total energies ΔE and free energies ΔG_{298} of stable compounds **1**–**10** and the transition states of their reactions calculated relatively to LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2\{Mg(\mu\text{-}Cl)_2\}_nAlR_2$ (n = 1, 2).

Structure	ΔE/kcal mol^{-1}		ΔG_{298}/kcal mol^{-1}	
	R = Me	R = Et	R = Me	R = Et
1 + 1/2 $(R_2AlCl)_2$	–6.3	–6.8	1.2	1.8
TS1–C_2H_4	5.1	3.8	28.8	27.8
2 + 3/2 $(R_2AlCl)_2$ – AlR_3	5.7	6.1	12.2	13.8
2 + 3/2 $(R_2AlCl)_2$ – 1/2 $(AlR_3)_2$	13.7	12.8	13.3	12.1
3	–9.1	–9.8	6.0	6.4
TS3–C_2H_4	–3.0	–4.5	27.4	26.1
4	–13.4	–13.0	1.1	2.7
TS4–C_2H_4	3.2	3.5	32.6	32.8
5 +1/2 $(R_2AlCl)_2$	–6.3	–6.5	2.3	1.2
6	–9.0	–9.6	5.5	6.1
7	–13.3	–13.0	0.6	2.1
8	–13.6	–14.1	0.2	1.2
9	–15.4	–16.3	–0.7	–1.5
TS9–C_2H_4	–7.6	–9.5	22.0	20.4
10	–16.9	–17.2	–2.6	–1.9
TS10–C_2H_4	–5.3	–8.1	23.6	22.0
TS(9–10)	–14.3	–15.1	0.5	0.8

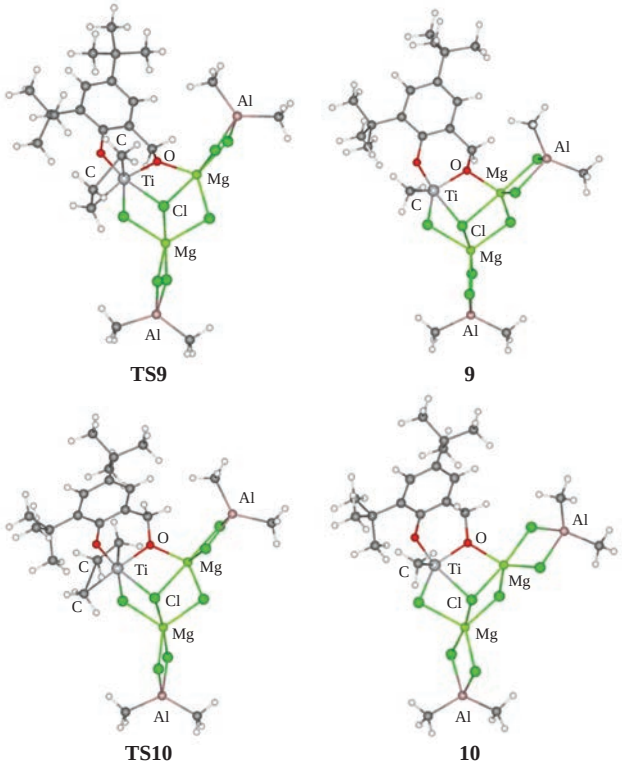

Figure 1 Structures of conformers **9** and **10** and transition states **TS9** and **TS10** (R = Me).

only the lowest by energy transition states **TS9** and **TS10** (see Figure 1) characteristics are given in Table 1 for brevity. The energy barriers for the particles with two Mg atoms are lower than those for the particles with one Mg atom. On the other hand, the catalytic particles with two Mg atoms are also more thermodynamically stable with respect to dissociation than the catalytic particles with one Mg atom.

Conformer **9** has a higher free energy than **10**, but the corresponding energy barrier **TS9** is approximately by 1.5 kcal mol^{-1} lower than **TS10**. Since the energy barrier **TS**(**9**–**10**) of conformers **9** and **10** interconversion never exceeds 3 kcal mol^{-1} (which is much lower than the energies of **TS9** and **TS10**), the main channel for the polymerization reaction corresponds to the formation of the lowest by energy **TS9**.

Thus, the particles of type **1**, **3**, and **4** formed at the first stage of $LTiCl_2$ activation by the binary cocatalyst Bu_2Mg/Et_2AlCl, are low reactive with respect to ethylene. They can transform to much more active particles **9** and **10** as a result of the sequence of transformations shown in Scheme 1. The probable mechanism of catalyst deactivation is the reversible dissociation of the active particles into LTi(R)Cl and $R_2Al(\mu\text{-}Cl)_2\{Mg(\mu\text{-}Cl)_2\}_nAlR_2$ (n = 1, 2). The equilibrium is shifted towards the inactive products in the case of the particles with one Mg atom or to the active particles (**9** and **10**) in the case of compounds containing two Mg atoms. The irreversible processes of LTi(R)Cl transformations to dialkyl compounds $LTiR_2$ and (or) Ti^{III} compounds can complete the catalyst deactivation.

The results of DFT modeling also lead to the conclusion that the alternative mechanism of the formation of catalytic particles of type **9** and **10** is also possible. This mechanism does not imply the formation of **2** as an intermediate. The alkyl chloride complex LTi(R)Cl is formed as a result of $LTiCl_2$ alkylation by AlR_3 [reaction (3)]:

$$LTiCl_2 + 1/2\,(AlR_3)_2 \rightarrow LTi(R)Cl + 1/2\,(R_2AlCl)_2 \qquad (3)$$

Similarly to metallocene complexes of Ti and Zr, the exchange of the first Cl atom for the alkyl group is thermodynamically more favorable than the exchange of the second Cl atom.[5–9] Thus, the reaction can be stopped at the first stage. Simultaneously, $R_2Al(\mu\text{-}Cl)_2\{Mg(\mu\text{-}Cl)_2\}_nAlR_2$ linear compounds with $n \geqslant 2$ can be formed as a result of the reaction between the cocatalyst components, for instance, if n = 2 [reaction (4)]:

$$2\,R_2Mg + 3\,(R_2AlCl)_2 \rightarrow$$
$$\rightarrow R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2 + 2\,(AlR_3)_2 \qquad (4)$$

Then, the products of reactions (3) and (4) interact with the formation of conformers **9** and **10**. Reaction (5) is thermodynamically favorable process. Recent experimental data are in agreement with this mechanism.‡

$$LTi(R)Cl + R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2 \rightleftarrows \mathbf{9} + \mathbf{10} \qquad (5)$$

The results of this work predict the optimum Mg : Al ratio of 2 : 7, which corresponds to the formation of compounds **9** and **10**. Approximately the same ratio (1 : 3) was used in the previous experimental studies.[1–4] It is different from the optimum Mg : Al ratios for the formation of particles **1** (1 : 2), **3** and **4** (2 : 5). According to Kurmaev,‡ the catalyst is inactive at Mg : Al = 1 : 2. Another question concerns the high Ti : Mg(Al) ratios, which are necessary for catalyst activation. These ratios are probably needed to form an excess of compounds like $R_2Al(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2Mg(\mu\text{-}Cl)_2AlR_2$ with respect to Ti and to shift equilibrium (5) to the formation of compounds **9** and **10**.

In conclusion, it was observed experimentally[1] that three or more types of catalytic centers were involved in the polymerization. In this work, their possible structures, thermodynamic stability, and reactivity toward ethylene have been scrutinized. The results of DFT calculations are in agreement with experimentally observed regularities of the post-metallocene type catalytic systems under study: the catalyst inactivation mechanism and the role of the second Mg atom in the catalytic particle formation.

This work was supported in part by the Russian Foundation for Basic Research (project no. 14-03-00603a). The author is grateful to D. A. Kurmaev and B. M. Bulychev for helpful discussions and information about their experimental studies of the catalytic systems modeled in this work.

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Received: 5th June 2018; Com. 18/5601

‡ D. A. Kurmaev, unpublished results.