

Activation of Ziegler-Natta Catalysts by Organohalide Promoters: A Combined Experimental and Density Functional Theory Study

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Received 22 December 2010; accepted 13 March 2011

DOI 10.1002/app.34589

Published online 30 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Several organohalide (HC) compounds were tested as promoters for a Ti-based Ziegler-Natta (Z-N) catalyst at different polymerization conditions. Results show that the intensity of the promoting effect depends on the nature and amount of the promoters. A proper amount, especially optimum amount, of aliphatic type organohalides leads to a strong productivity, and aromatic ones leads to a weak productivity improvement; however, 3-chloro-1-propene poison the catalyst even at lower HC/Ti molar ratios. Among studied compounds, chlorocyclohexane has the best activity promotion effect at HC/Ti molar ratio of 128, and with this as a promoter, the activity increases over 85%. To understand more details about this phenomenon, the rate of polymerization during time

and the effect of polymerization conditions (the temperature and hydrogen partial pressure) on the performance of chlorocyclohexane as the most effective promoter were studied. Finally, to explore the mechanism of reactivation of catalyst species by organohalides, molecular modeling was employed and a new oxidation-addition mechanism was proposed, which basically consisting of homolytic breaking of C–Cl bond in organohalides. It was found that reoxidation of the catalyst, restoring active center, by Cl rich organohalides is energetically more favored. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2526–2533, 2012

Key words: organohalide; Ziegler-Natta catalyst; promoter; ethylene polymerization; DFT studies

INTRODUCTION

Polyethylene is the largest synthetic commodity polymer in terms of annual production and is widely used throughout the world because of its versatile physical and chemical properties. Industry is constantly seeking catalyst systems, which fulfill various needs in the production of polyethylene. Heterogeneous Z-N catalysts are the main systems among polyolefin catalysts, and they are responsible for the production over tens of millions tones of polyethylene per year. One of the disadvantages with the use of Z-N catalyst, however, is that a relatively high concentration of the catalyst is required because the yield of the polymer per unit amount of the catalyst used is relatively low.

It is known that polymerization yield can be increased if halogenated organic compounds are

added during the polymerization reaction.^{1,2} These halogenated compounds are so called promoters or reactivators. Organohalides have been commonly used as the activity promoters for the vanadium based catalysts,^{3–6} but the reports for the organohalides used as the activity promoters for the Ti-based catalysts are very few.^{7,8}

By investigating the promotion effect of organohalides on vanadium based catalysts, the researchers from Union Carbide Corp. found out that only CH₂Cl₂ could promote the activity of the Ti center, and most of these compounds such as CFC₃, CHCl₃, and CCl₄ largely inhibit the Ti center and substantially decrease the catalytic activity.⁹ However, this is not always the case. At a suitable molar ratio of the organohalide to titanium, the catalyst activity of conventional Ti-centered Z-N catalysts can be improved by 50%–100%.¹⁰

The most important role of organohalides is related to the oxidizing ability of these compounds. It was shown that they change the oxidation state of transition metal and facilitate the active centers to contribute more in a polymerization process.^{5,6} In this regard, it was reported that Ti^{III} and Ti^{II} are active centers in ethylene polymerization, but Ti^{III} is more active and productive. In the activation of Ti^{IV}

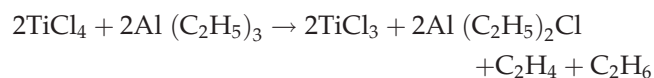
Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: Maroon Petrochemical Company; contract grant number: 38-106-2/375.

Journal of Applied Polymer Science, Vol. 123, 2526–2533 (2012)
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by TEAL, it changes to a Ti^{III} center by this mechanism¹¹:



At higher Al/Ti molar ratio relative to the optimum amount, Ti^{IV} undergoes extensive reduction to Ti^{II} by:



Organohalides reoxidize the Ti^{II} centers, that are produced from over reduction of Ti^{IV} by TEAL, and therefore increase the catalyst activity.^{12,13}

Despite the important role of organohalides in the activation of Z-N catalysts, there is no systematic study of the activity dependency on the concentration and nature of the organohalides under different polymerization conditions. Furthermore, aside from the practical developments, the understanding at molecular level of the restoring/improving catalyst efficiency by organohalide promoters is still not achieved.

In this contribution, we try to fill this gap. In the previous study, the effect of organohalides on different polymer properties was published.¹⁴ In this study, we try to get better understanding about the effect of polymerization conditions on the promoter performance and explore the possible mechanism for the reactivation of the catalyst centers by these compounds. To do the experimental part, like previous study, we focused on the $MgCl_2$ (Ethoxide type)/ $TiCl_4/AlEt_3$ catalyst system and examined the effect of concentration and nature (alicyclic, aliphatic and aromatic) of organohalides on the catalyst productivity. In the next step, effect of temperature and hydrogen partial pressure on the performance of chlorocyclohexane, as the mostly effective promoter, was studied.

Finally, we used DFT molecular modeling study in an attempt to explore the possible mechanism for the reactivation/restoring of catalyst center by organohalides.

EXPERIMENTAL

Materials

Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical (Tehran, Iran) and used without further purification. Nitrogen gas (purity 99.99%) was supplied by Roham Co. (Tehran, Iran) and was purified by passing through columns of activated 13X and 4 Å molecular sieves. $Mg(OEt)_2$, $TiCl_4$, and all halogenated compounds were purchased from Merck chemical (Darmstadt, Germany) and used as received. *n*-Heptane was sup-

plied by Arak Petrochemical and distilled over calcium hydride and stored over sodium wire and 13X and 4 Å activated molecular sieves. Triethylaluminum (TEAL) was acquired from Schering Co., Ltd. (Bergkman, Germany) and was diluted using *n*-heptane prior to use.

Instruments

The porosity (surface area and average pore size) of the catalyst was measured with the BET method with nitrogen physisorption by Quantachrome Corp. Nova2200, Version 7.11. Average pore diameter was determined as pore diameter at 50% of cumulative pore volume. For determination of Ti amount, after sample digestion in H_2SO_4 , Ti was oxidized with H_2O_2 and analyzed by visible spectrophotometer ($\lambda = 410$ nm) in a Shimadzu spectrophotometer model 6800. The Cl amount was determined by the classic method of precipitation of AgCl with $AgNO_3$ (Volhard's method). Mg was determined by titrimetry of the catalyst acidic solution with EDTA.

Synthesis of catalyst precursor

Catalyst preparation was carried out in accordance with procedure in Ref. 15, where 114.3 g of magnesium ethylate were dispersed under a blanket of N_2 in 1.5 L of a diesel oil fraction in a 3-L four-necked flask equipped with a dropping funnel, a stirrer, a reflux condenser, and a thermometer. Then 332 g of titanium tetrachloride were added dropwise at 90°C to this dispersion in the course of 2 h. The reaction product was then washed with the diesel oil fraction until the supernatant solution no longer contained any titanium and then dried.

Elemental analysis of the catalyst was: Ti = 3.43%, Mg = 21.29%, and Cl = 55.63%.

Polymerization experiments

The tests of ethylene polymerizations were carried out under slurry conditions at a constant pressure and temperature in a 1-L Buchi stainless steel reactor equipped with a mechanical stirrer (Buchi bmd 300, Switzerland). Before each polymerization experiment, reactor was purged with nitrogen gas at 100°C for about 1.5 h to ensure the absence of moisture and oxygen. After cooling the reactor to 83°C, it was fed with 500 mL of dry heptane, and then, with stirring, a given Al/Ti molar ratio of TEAL, organohalide and catalyst were added by means of syringe in an atmosphere of purified nitrogen. Polymerization started when ethylene was fed to the reactor. All experiments were carried out at an absolute pressure of 8.5 bar by supplying ethylene to the reactor. Residence time was kept constant at 1 h and stirrer

speed was 500 rpm to minimize ethylene transport limitations. At the end, the reactor was discharged, and the powder polymer was dried in air. Catalyst activity or productivity was defined as the kg of the polymer per gram of the catalyst at time 1 h (KgPE/gcat.h). Relative increase in the activity is the productivity enhancement as a result of organohalide addition (increase in activity) divided by the activity of the original catalytic system (without promoter). This index is expressed by Formula 1:

$$\text{Increase in activity (\%)} = \frac{A_P - A}{A} \times 100 \quad (1)$$

A_P and A are catalyst activity with and without promoter, respectively.

COMPUTATIONAL DETAILS

A $(\text{MgCl}_2)_3$ cluster was used in all the simulations to support the monometallic Ti-species. The MgCl_2 bulk was assumed to be in the α crystalline phase, and the surface was modeled as a (110) monolayer. The DFT calculations were performed with the Gaussian09 package,¹⁶ using the B3LYP hybrid GGA functional of Becke-Lee, Parr, and Yang.^{17,18} The electronic configuration of the atoms was described by a triple- ζ basis set augmented with one polarization functions of Ahlrichs and coworkers (TZVP keyword in Gaussian).¹⁹ In case of Ti^{IV} species the singlet electronic state is favored and thus closed shell calculations were performed, unless it was mentioned. Differently, for Ti^{III} and Ti^{II} unrestricted calculations were performed, since Ti^{III} has one unpaired electron, while for Ti^{II} we found that a triplet electronic state with two unpaired electrons is favored relative to the singlet electronic state. Unrestricted calculations were performed for all the radical species involving main group atoms. Characterization of the located stationary points as minima or transition state was performed by frequency calculations. Total energies and geometries are provided in the Supporting Information.

RESULTS AND DISCUSSION

Effect of organohalide concentration and structure

To study the promoting effect of organohalides on Z-N catalysts, a model active catalyst was synthesized based on magnesiummethoxide ($\text{Mg}(\text{OEt})_2$) support. During treatment with TiCl_4 , $\text{Mg}(\text{OEt})_2$ was mainly converted to MgCl_2 .²⁰ For this reason, catalytic system was shown by MgCl_2 (Ethoxide type)/ $\text{TiCl}_4/\text{AlEt}_3$ formula. The surface area and the average pore diameter of the catalyst were $234 \text{ m}^2/\text{g}$ and 59 \AA , respectively.

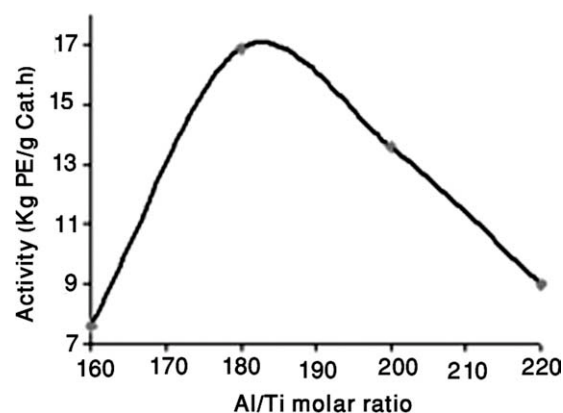


Figure 1 Effect of Al/Ti molar ratio on the catalyst activity. Polymerization conditions are: P : 8.5 bar, T : 83°C , t : 1 h.

It is known that the catalyst activity depends significantly on reaction conditions.²¹ To consider such effects, in the next step the influence of TEAL concentration on the catalyst activity was studied (Fig. 1). The variation of the Al/Ti molar ratio, considerably affected the activity of the catalyst. The highest catalyst productivity was observed when Al/Ti molar ratio equaled 180, therefore, all polymerization experiments were done on Al/Ti = 180. The effect of TEAL on the catalyst activity can be explained as follows. At lower concentration of TEAL relative to the optimum value, it is probable that a small amount of contamination present in the system has affected the polymerization behavior and decreased the catalyst activity. At a higher concentration than the optimum value, over reduction of Ti^{IV} to Ti^{II} may have occurred, which decreases the catalyst activity because of the lesser activity of the Ti^{II} center in compare with Ti^{III} one.²¹

To understand better the role of organohalide structure and concentration in improving the catalyst activity, synthesized catalyst was examined in the presence of different Cl containing compounds including chlorocyclohexane, and chlorocyclopentane as alicyclic; chloromethane, dichloromethane, and chloroform as aliphatic; chlorobenzene, and trichlorobenzene as aromatic; and trichloro-1-propene as alkenic type organohalides at different HC/Ti molar ratios. The catalyst activity and increase in the catalyst activity relative to the blank system (without promoter) are reported in Table I.

The results show that the efficiency of organohalides depends significantly on their nature and decreases in the order alicyclic > saturated aliphatic > aromatic. A lower productivity of aromatic compounds can be related to their reaction with TEAL cocatalyst that makes them unavailable for the reaction as a promoter.^{3,22} It has been reported that aromatic organohalides aid in the reaction of trialkylaluminum compounds and ethyl chloride.²² Considering

TABLE I
Promotion Effect of Different Amount of Organohalides on MgCl₂ (Ethoxide Type)/TiCl₄/AlEt₃ Catalyst System in Ethylene Polymerization^a

Organohalide type	HC/Ti (molar ratio)	Activity (kg PE/g Cat.h)	Increase in activity (%)
Without promoter	0	16.9	–
Chlorocyclohexane	80	26.5	57
	128	31.2	85
	160	25.2	49
Chlorocyclopentane	80	27.9	65
	110	30.5	80
	140	29.6	75
	160	27.9	65
Chloromethane	10	23.0	36
	20	27.9	65
	30	21.4	27
Dichloromethane	0.27	18.6	10
	0.54	28.7	70
	1	23.9	41
Chloroform	0.015	21.5	27
	0.033	30.0	78
	0.044	23.9	41
	0.088	18.5	9
Chlorobenzene	80	18.5	9
	120	19.6	16
	160	19.0	12
Trichlorobenzene	0.05	19.5	15
	0.1	20.4	21
	0.2	16.5	–2
	0.4	13.2	–22
3-Chloro-1-propene	0.01	7.0	–59
	0.05	0	–100
	0.2	0	–100

^a Polymerization conditions are: *P*: 8.5 bar, *H*₂ = 0, *T*: 83°C, *t*: 1 h, Al/Ti = 180.

this reaction, aromatic organohalides can perform two different roles.

They may act as both aromatic hydrocarbons (which make complexes with TEAL) and organohalide promoters (which react with active centers and promote polymerization reaction). A lower efficiency of the aromatic organohalides is mostly because of their first role.

Among studied organohalides, chlorocyclohexane and chlorocyclopentane have the best catalyst reactivation effect, and with these as promoter the catalyst activity is increased over 85% and 80%, respectively. On the other hand, 3-chloro-1-propene poisons the catalyst system, probably, because of the formation of a stable complex between this compound and Ti active center, so that the complexation of ethylene and propagation of the polymer chain is inhibited.

Activity results in the case of the same organohalide with different concentrations in Table I show that with increasing the ratio of HC/Ti activity has a maximum value and this value changes greatly for different promoters. The occurrence of this peak can be explained by the strong interaction of organohalides with TEAL that was published by Yang et al.²³ They showed that the specific interaction mode between dimeric TEAL and geminal chloro groups

accelerate dissociation of dimeric TEAL into the monomeric form and therefore accelerate catalyst activation process. However, with increasing concentration of organohalides, it seems that they can form complexes with TEAL and make it unavailable for the catalyst activation process. Further, the value of the maximum activity decreases with increasing the number of Cl atoms on the organohalide structure. For example, the optimum amounts of chloromethane, dichloromethane, and chloroform are seen in HC/Ti = 20, 0.54 and 0.015, respectively, (relation between the organohalide structure and reactivity will be discussed later). When the molar ratio of a promoter to Ti is higher or lower than optimum amount, the activity of the catalyst is not appreciably modified in polymerization process.

Effect of polymerization condition

To study the effect of H₂ concentration on the efficiency of chlorocyclohexane, polymerization experiment was done at three different H₂ partial pressures (3, 5, and 6.5 bar) and the catalyst productivity results are collected in Table II. It is clear from the data in Table II that with increasing H₂ pressure, the catalyst activity decreases significantly. It is in accordance with the results that were published before by other authors.²⁴ Activity depression of Z-N catalyst in ethylene polymerization by H₂ molecule is because of the more frequent formation of unusually stable Ti–C₂H₅ center by insertion of ethylene into Ti–H bond that was reported by Kissin et al.^{25,26} With increasing the H₂ pressure, the promoting effect of chlorocyclohexane increases from 90% to 95% and 98% for the H₂ pressure of 3, 5, and 6.5 bar, respectively.

To study the effect of temperature on the catalyst activity, polymerization experiments were performed in 65°C, 83°C, and 90°C and the results are shown on Table III. From this Table it is concluded that with increasing temperature from 65°C to 83°C,

TABLE II
Effect of H₂ Pressure on the Promoting Ability of Chlorocyclohexane^a

HC/Ti molar ratio	Hydrogen pressure (bar)	Catalyst activity (KgPE/grCat.hr)	Relative increase in activity (%)
0	0	16.9	–
0	3	13.1	–
0	5	10.5	–
0	6.5	5.2	–
128	3	24.9	90
128	5	20.4	95
128	6.5	10.3	98

^a Polymerization conditions are: *P*: 8.5 bar, *T*: 83 °C, *t*: 1 h, Al/Ti = 180, CHC/Ti = 128.

TABLE III
Effect of Temperatures on the Promoting Ability of Chlorocyclohexane^a

HC/Ti molar ratio	Temperature (°C)	Catalyst activity (KgPE/grCat.hr)	Relative increase in activity (%)
0	65	12.8	–
128	65	23.3	82
0	83	16.9	–
128	83	31.2	85
0	90	15.4	–
128	90	29.0	88

^a Polymerization conditions are: *P*: 8.5 bar, *H*₂:0, *t*: 1 h, Al/Ti = 180, HC/Ti = 128.

the activity of the catalyst increases which is related to the increase of propagation rate constant.^{27,28} On the other hand, the decrease in the activity with increasing temperature from 83°C to 90°C can be related to the irreversible deactivation of active sites.^{27,28} Furthermore, as shown in Table III, with increasing the temperature, the promoter performance is increased. This effect is explained by increasing oxidizing ability of organohalides with temperature that can restore the active centers more easily.⁶

Polymerization kinetics with and without promoters

The rate of polymerization (*R_p*) is defined as the instantaneous rate of polymer production at a given polymerization time calculated per gram of the catalyst and per hour (kgPE/g cat.h).

To study and compare the effect of organohalide promoters on *R_p* trend, two more efficient promoters, i.e., chlorocyclohexane and chlorocyclopentane were selected. The effect of these organohalides on the *R_p* during polymerization is illustrated in Figures 2 and 3, respectively. The following can be deduced from the figures:

1. The activity profile with chlorocyclohexane addition is almost identical to that with chlorocyclopentane addition. This indicates that the addition of different organohalides changes the absolute activities, but does not change the activation and deactivation trend.
2. In both cases (with and without organohalide), after 3–4 min the catalyst activity reaches the maximum value and then decreases with time. Nevertheless, in the presence of the promoters, the area under the kinetic curve and the maximum rate are increased similarly to those in the blank system. It can be deduced that the presence of the promoters does not change the location of the time of the maximum activity as well as the overall form of the catalyst kinetic behavior.

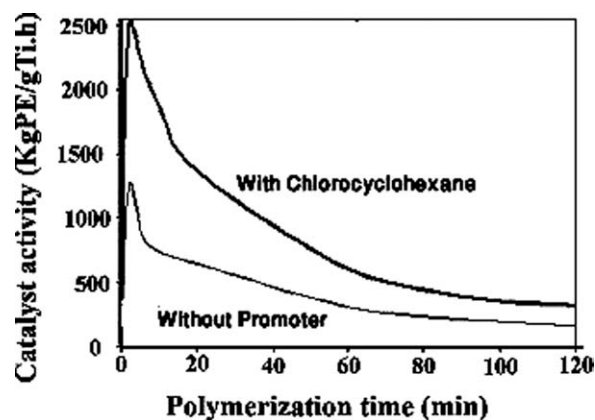


Figure 2 Effect of chlorocyclohexane on the *R_p* (catalyst activity) during polymerization. Polymerization conditions are: HC/Ti: 0 (without halogenated hydrocarbon) and 128, *P*: 8.5 bar, *T*: 83°C, Al/Ti = 180, *t*: 2 h.

3. With the addition of chlorocyclohexane and chlorocyclopentane, a slower decrease in the catalyst activity is only observed from about 3–19 min (i.e., the maximum in the activity profiles) of polymerization. After 19 min, a more rapid decrease in the catalyst activity is observed with the addition of organohalides, but still the activity of the catalysts containing promoters is higher than those without promoters. After 2 h, the catalyst activity with and without organohalides decreases to a different degree. This indicates that the addition of these reagents has a strong effect on the catalyst deactivation mechanism.

Concluding this section, *R_p* plots show that activation and deactivation mechanisms are affected by organohalides. To know better about these effects,

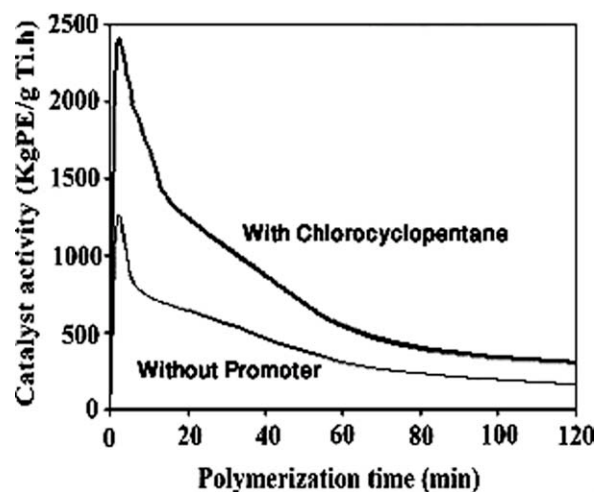


Figure 3 Effect of chlorocyclopentane on the *R_p* (catalyst activity) during polymerization. Polymerization conditions are: HC/Ti: 0 (without halogenated hydrocarbon) and 110, *P*: 8.5 bar, *T*: 83°C, Al/Ti = 180, *t*: 2 h.

TABLE IV
 ΔE , in kcal mol⁻¹, for the Different Steps of Oxidative Addition of CH_nCl_{4-n} ($n = 0-3$) to a [Mg]/TiCl₂ Species

	Reaction	ΔE_{Coord}	ΔE_{OxAdd}	$\Delta E_{\text{Products}}$
1	[Mg]/TiCl ₂ + CH ₃ Cl → [Mg]/TiCl ₃ CH ₃	-15.9	-16.2	-32.1
2	[Mg]/TiCl ₂ + CH ₂ Cl ₂ → [Mg]/TiCl ₃ CH ₂ Cl	-15.6	-18.6	-34.2
3	[Mg]/TiCl ₂ + CHCl ₃ → [Mg]/TiCl ₃ CHCl ₂	-13.7	-20.9	-34.6
4	[Mg]/TiCl ₂ + CCl ₄ → [Mg]/TiCl ₃ CCl ₃	-11.8	-25.2	-37.0

some other experiments together with computational methods should be employed.

Mechanism of reactivation by organohalides

In the second part of our study, to explore the mechanism of organohalides reactivation, DFT studies were employed. As mentioned before, Ti^{III} centers are supposed to be more active than Ti^{II} centers in ethylene polymerization. Thus, the decreased performances during polymerization could be associated to the reduction of Ti^{III} to less active Ti^{II} centers. In this framework, the reactivation role of organohalide is rather simple. They reactivate the catalyst center by oxidizing the poorly active Ti^{II} center, reintroducing it into the active cycle.^{6,29} To eliminate the effect of different conformations of the promoters containing more than one carbon atom, we considered only chloromethanes CH_{4-n}Cl_n ($n = 1-4$) as the promoters. For the oxidation of Ti^{II} by n -chloromethanes, two oxidation-addition pathways were considered which basically consisting of the homolytic breaking of C-Cl bond in organohalides: (1) oxidation of Ti^{II} to Ti^{IV} by the addition of both Cl atom and organic section into the Ti^{II} center. The restored Ti^{IV} centers can be activated again, which increases the overall activity³⁰; and (2) oxidation of Ti^{II} to Ti^{III} by the addition of only Cl atom of the organohalides to the Ti^{II} center.

Here we discuss about the first mechanism. Preliminary calculations indicate that the favored electronic state in the uncoordinated [Mg]/TiCl₂ species, as well as after organohalide coordination, is a triplet with both unpaired electrons substantially localized on the Ti^{II} center, with the singlet at least 20 kcal mol⁻¹ higher in energy. Differently, after oxidative addition of the organohalide the favored electronic state of the resulting [Mg]/TiCl₃CH_nCl_{3-n} (n

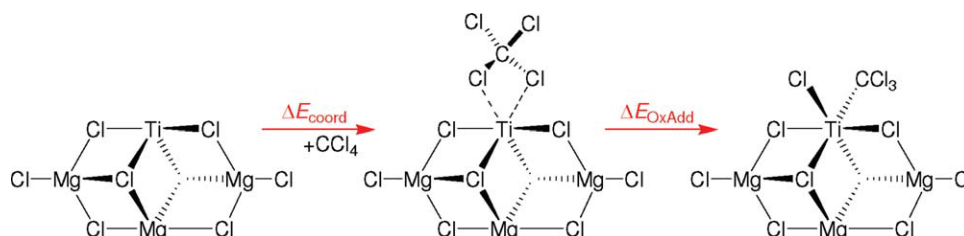
= 0-3) species is singlet, with the triplet at least 15 kcal mol⁻¹ higher in energy. This implies that during the oxidative addition there will be a change in the electronic state of the system from triplet to singlet.

The calculated energies for the oxidation of Ti^{II} to Ti^{IV} are reported in Table IV. Each reaction is split between the organohalide coordination to the [Mg]/TiCl₂ species and the oxidative addition of the coordinate organohalide to the Ti center.

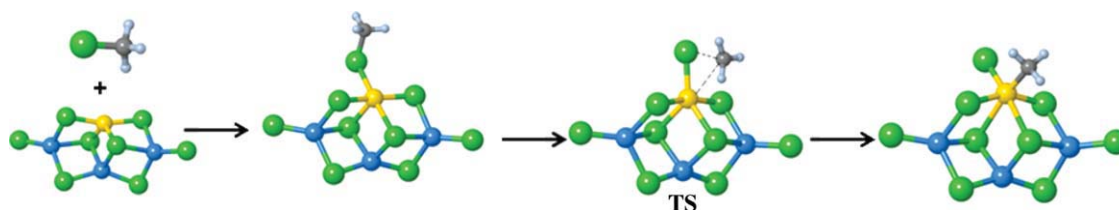
The reaction starts with the remarkable exothermic coordination (ΔE_{Coord} around 11-16 kcal mol⁻¹) of the organohalides to the Ti^{II} center. There is a regular decreasing trend of the coordination energy with the amount of Cl atoms in the organohalide and coordination of CCl₄ is less favored. Natural population analysis (NPA)³¹ of the free organohalides indicates that the NPA charge on the Cl atoms is -0.08e, -0.03e, 0.02e and 0.05e on going from CH₃Cl to CCl₄, which suggests that the decrease in the coordination energy with increasing the number of Cl atoms in the organohalide could be related to a decreased donor ability of the more halides rich molecules.

Coordination of organohalides having more than one Cl occurs with two Cl atoms inducing a roughly octahedral coordination around the Ti^{II} center, see Scheme 1.

Therefore, for these systems next step is the oxidative addition of the coordinated organohalide. In this case, the more Cl rich the organohalide the more favored is the oxidative addition step, see the ΔE_{OxAdd} in Table IV, with oxidative addition of CCl₄, with a ΔE_{OxAdd} of -25.2 kcal mol⁻¹, favored by 9.0 kcal mol⁻¹ over oxidative addition of CH₃Cl, with a ΔE_{OxAdd} of -16.2 kcal mol⁻¹. The trend in the ΔE_{OxAdd} correlates with the trend in the homolytic dissociation energy of the C-Cl bond in the



Scheme 1 [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2 [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

organohalides considered, 80.6, 74.3, 67.1, and 58.6 kcal mol⁻¹ on going from CH₃Cl to CCl₄. In other words, the higher energy gain associated with the oxidative addition of CCl₄ relative to CH₃Cl can be related to the weaker C—Cl bond in CCl₄ relative to CH₃Cl. The final energy gain, $\Delta E_{\text{Tot}} = \Delta E_{\text{Coord}} + \Delta E_{\text{OxAdd}}$, reflects the trend of ΔE_{OxAdd} , although the differences between the various organohalides are reduced in magnitude.

On the other hand, in the case of chloromethane (containing one Cl atom) a TS structure would be found which connects reagents to the products. In this structure Cl—C bond is partially broken and new C—Ti bond is partially formed, see Scheme 2.

Considering spin state of the structure in TS, two electronic states, which are related to the open shell and close shell calculation, can be taken in to account. The triplet state is clearly favored over the singlet state by nearly 18 kcal mol⁻¹. To pass this TS, activation energy of 8.0 kcal mol⁻¹ should be overcome. After this step, reaction reaches to the final product that is 32.1 kcal mol⁻¹ below the energy of the starting stage.

Second mechanism is related to the coordination of *n*-chloromethanes to Ti^{II} center, only by its Cl atom, results in the formation of Ti^{III} center by moving away of organic section as a radical. We investigated thermodynamics of these reactions and results are reported in Table V.

Coordination energies for this mechanism are like the ones discussed for the first mechanism. Here we assumed that after coordination C—Cl bond elongates in an amount that makes possible the removal of organic section as a radical species. Energy difference between reagents and products reveals that with increasing the number of Cl atom, this mechanism becomes more favored. This can be related to the lower C—Cl binding energy in the Cl rich molecules that was discussed before. Furthermore, comparing total energies of two mechanisms, which is reported in Tables IV and V, indicates the preferential oxidation of Ti^{II} to Ti^{IV} rather than Ti^{III}.

Concluding simulation section, our results suggest that organohalides reproduce catalyst center by preferential oxidation of Ti^{II} to Ti^{IV} rather than Ti^{III} species. This can be understood from the more stability of the products which are produced from this mechanism (compare $\Delta E_{\text{Products}}$ in Tables IV and V). Fur-

thermore, with increasing the number of Cl atoms, the oxidation (reactivation) of a Ti^{II} center becomes thermodynamically more favored. A higher catalyst productivity and a lower maximum activity which was resulted from the presence of the chlorine-rich organohalides (see experimental section) can be because of a higher probability of the oxidation reaction in the presence of these promoters. Therefore, the results of the DFT calculations suggest a higher potential of chlorine-rich organohalides as the promoters.

CONCLUSIONS

To increase the activity of MgCl₂ (ethoxide type)/TiCl₄/AlEt₃ catalyst system, eight Cl containing compounds with different alicyclic, aliphatic, aromatic, and alkenic structures were employed in the slurry phase ethylene polymerization.

The results show that:

1. Promoting effect of the organohalides depends on the nature of them and increases in the following order: alicyclic > aliphatic > aromatic. On the studied catalyst, only alkene type organohalide poison the catalyst. It seems that alkenic organohalide cage the active sites like polar monomers and inhibit the polymerization process.
2. In the *n*-chloromethane (*n* = 1–3) promoters with increasing *n*, the optimum amount of HC/Ti decreases and the promoter efficiency in restoring catalyst active center increases.
3. With the increasing polymerization temperature and hydrogen partial pressure, the activity promotion effect of chlorocyclohexane increases.
4. The catalyst activity profile shows that in the presence of chlorocyclohexane and chlorocyclopentane rate of ethylene consumption increases, whereas

TABLE V
Thermodynamics, in kcal mol⁻¹, Associated with the Oxidation of [Mg]/TiCl₂ to [Mg]/TiCl₃• by CH_{*n*}Cl_{4-*n*} (*n* = 0–3)

Reaction	$\Delta E_{\text{Products}}$
[Mg]/TiCl ₂ + CH ₃ Cl → [Mg]/TiCl ₃ • + CH ₃ •	2.2
[Mg]/TiCl ₂ + CH ₂ Cl ₂ → [Mg]/TiCl ₃ • + CH ₂ Cl•	-4.3
[Mg]/TiCl ₂ + CHCl ₃ → [Mg]/TiCl ₃ • + CHCl ₂ •	-11.4
[Mg]/TiCl ₂ + CCl ₄ → [Mg]/TiCl ₃ • + CCl ₃ •	-19.8

decrease of the catalyst activity versus time is slowed, supporting both the activating and stabilizing effects of halogenated hydrocarbons.

- Using DFT studies, it is revealed that restoring catalyst activity is mainly because of the oxidative-addition of organohalides to the less active Ti^{II} center and turning it into Ti^{IV} rather than Ti^{III} center. Furthermore, for Cl rich promoters oxidation (reactivation) of a Ti^{II} center becomes thermodynamically more favored.

The authors would like to express their appreciation to Prof. Luigi Cavallo (University of Salerno, Italy) for useful discussions and MOLNAK (www.molnac.unisa.it) for its computer facility.

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