Modification of Si/Mg Composite Supported Ziegler-Natta Ti-based Catalysts for Propylene Polymerization Using the Third Metal Elements

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ABSTRACT

In this study, several (SiO_2/MgO/ID/MClx/$MgCl_2$)·TiClx *Ziegler-Natta Catalysts are synthesized by a co-impregnation method to study a third metal (Zr, V, Fe, Mn, W) effect on catalytic performance in propylene polymerization. When the metal doping content is 10 wt% (compare to magnesium elements), the activity of W doped catalyst shows 60.0% higher. While the activity of Zr, V, Fe and Mn doped catalyst both decreased. Correlations of the catalyst activities with the iron radius and the electronegativity of the third metal elements are discussed. In the same doping content condition, metals have similar radius with* Mg^{2+} *have higher activity (Fe, Mn and W> V and Zr). The mechanism of Mn and W effects are discussed. The activity of 5 wt% and 3 wt% Mn doped catalyst is higher compared with the catalyst without doping. It means that the doping content also have an influence on the catalyst performance.*

KEYWORDS: *Polypropylene, Ziegler-Natta catalyst, Metal doped, Internal donor, Kinetics (polym.) curves.*

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1. INTRODUCTION

Polypropylene (PP) is the second world widely used polyolefin materials after polyethylene (PE). After Karl Ziegler and Giulio Natta discovered the $TiCl_4$-$AlEt_3$ and $TiCl_3$-$AlEt_2Cl$ catalytic systems in early 1950s. The catalysts of polyolefin had made great improvement during the next few decades.[1-6] The use of supports to improve the activity of Ziegler-Natta (ZN) catalysts has been reported since the early 60s.[7-10] The discovery of activated $MgCl_2$, opened a new era in the field of Ziegler-Natta catalysis both from the industrial and the scientific viewpoints. This is because of its drastic enhancement of catalytic activity. A lot of attention has been focused on the development of various effective supports.

Lots of modifications of Ziegler-Natta catalysts vary in the way of preparing the support. Generally, investigations have shown that doping a suitable amount of lewis acids into $MgCl_2$ support has the ability to change surface properties of $MgCl_2$ crystalline, resulting in the improvement of the catalyst activity or polymer properties. Ziegler-Natta catalysts based on $MgCl_2$ doped with manganese (Mn) was prepared by Garoff and Leinonen [11] . They found that the catalyst had the best activity with 10% mol Mn doping concentration. Zinc (Zn) halides doped Ziegler-Natta catalyst were prepared by Fregonese and Bresadola[12], the activity of the catalyst increased about 60% when the Zn doping content was 0.73wt%. NaCl [13, 14] doped catalysts showed lower catalytic activity and higher isospecificity in catalyzing propylene polymerization. 18 mol% LiCl doped catalyst produce polypropylene (PP) with a much broader MWD and higher isotacticity. Shohjiroh Tanase[15] found that both catalyst and polymer particles have extremely large spherical morphology after the addition of $MnCl_2$ in catalyst carrier. $AlCl_3$ [16] added into the catalyst support could synthesize low isotactic polypropylene. Also, $GaCl_2$[17], $PCl_{3[}$[18] and BCl_3 [17] doped ZN catalysts were synthesized and used for olefin polymerization. However, all these researches are done individually and have not been systematically compared. Therefore, systematic study of the effect of doping metal on the catalyst is important.

Recently, in our group, a series of novel (SiO_2/MgO/$MgCl_2$)·TiClx Ziegler-Natta catalysts for ethylene and propylene polymerization were investigated [19-21]. Also, these catalysts were further studied in ethylene polymerization by doping with certain metals, such as Cr [22] and V [23]. These two doped catalyst showed higher activity, and better 1-hexene incorporation ability. However, the effect of the introduction of the third metal into these novel (SiO_2/MgO/$MgCl_2$)·TiClx Ziegler-Natta on the polymerization of propylene had not been studied yet. Also, novel polypropylene catalyst development is still the hotspot of academic and industry. In this work, a series of bimetallic-type catalysts with different second metal components were prepared based on a co-impregnation method. By comparing the different doped metals, we also tried to find out how these doped metals affect the catalytic properties.

2. EXPERIMENTAL

2.1 Materials

In this work, the magnesium acetate tetrahydrate (AR grade), titanium tetrachloride (AR grade), Zirconium nitrate were (AR grade), vanadate ammonia(AR grade), Ferric chloride(AR grade), Manganese chloride(AR grade) purchased from Ling Feng Chemical Reagent Co., Ltd. Silica gel (Grace Davison 955, surface 261.8 m^2/g, pore volume 1.67 cm^3/g and average pore size 17.4 nm, hydroxyl content value on the silica gel surface is 6.1 $OH{\cdot}nm^{-2}$ and the hydroxyl content decrease to 1.5 $OH{\cdot}nm^{-2}$ after heating under 600) Propylene monomer used for propylene polymerization was purified by subsequently passing through three columns of 4A molecular sieves, Q-5 reactant catalyst (13 wt% of copper (II) oxide on alumina, purchased from Sigma-Aldrich) and 13X molecular sieves (purchased from Sinopharm Chemical Reagent Co., Ltd.) for dehydration and deoxidation. Triisobutylaluminium (TIBA, 1.0 M in n-heptane) as cocatalyst were purchased from Alfa Aesar. 9,9-di(methoxymethyl) fluorine (BMMF), purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Catalyst preparation

The catalyst synthesis process can be simply described in Figure 1. First, about 7 g of silica gel (calcined at 300!) was impregnated with aqueous solution of magnesium acetate and a metal compounds at room temperature by stirring for 4 h and then dried at 120! for 12 h. After impregnation, the products were calcined at 600! under high purity dry air at a flow rate of 600 $mL{\cdot}min^{-1}$ for 4 h in a fluidized-bed quartz reactor with a temperature-programmed heating controller. Then it was cooled down to 400! under the dry air followed by further cooling down to room temperature under N_2 atmosphere. The obtained support sample was transferred into a glovebox for catalyst preparation.

Second, about 2 g support and 30 mL of $TiCl_4$ were charged in a 100 mL 3-neck flask equipped with a magnetic stirrer rotating at 180 rpm under N_2 atmosphere, then the mixture was heated to 140! slowly and kept at this refluxing for 1h. Thereafter, the liquid above was removed and 30 mL toluene and a certain amount of 9,9-di(methoxymethyl)fluorene (BMMF) as the internal electronic donor (ID : Mg = 0.2) were added to the reactor, followed by refluxing at 120! for 2 h. Subsequently, the solid was washed with toluene twice at room temperature and further treated with 30 mL $TiCl_4$ at 120! for 2 h. Finally, the product was washed with n-heptane 7 times to get the final catalyst.

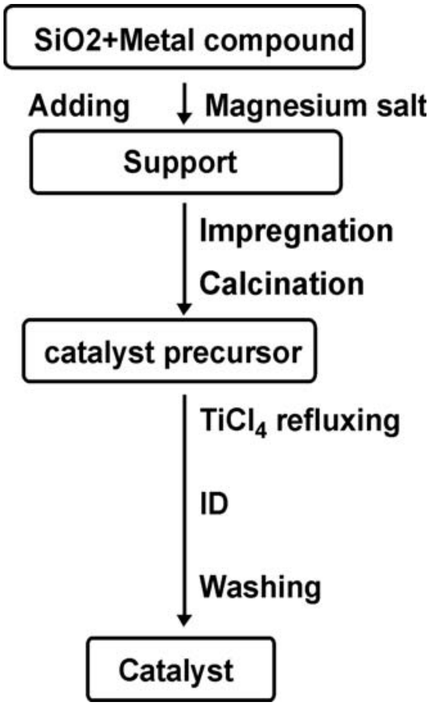


Fig. 1. Novel catalyst preparation method

2.3 Polymerization

Propylene polymerization was performed in a 250mL three-neck flask equipped with a magnetic stirrer rotating at 350 rpm. One small ampoule tube on the top of 250mL three-neck flask was used to contain 100mg catalyst, which was previously weighed and sealed in the glovebox. The reactor was placed at a thermostatic oil bath and purged by nitrogen for at least three times. Then introduce the propylene until the pressure was about 0.12 MPa, and 80 mL of n-heptane, a certain amount of co-catalyst such as TiBA, and a certain amount of DCPMS were introduced into the reactor, the propylene pressure raised to 0.15 MPa at 50!. After the solution was saturated of propylene, 100mg catalyst was fed into the reactor to initiate the polymerization. The polymerization was conducted for 60 min with a continuous supply of propylene gas at 0.15 MPa. The polymer was recovered by pouring the reaction slurry into ethanol with dilute HCl. All the obtained polymers were washed with ethanol, and dried under vacuum at 60! for at least 6 h before weighting.

2.4 Characterization

Inductively coupled plasma (ICP)

ICP spectrometer (varient 710-ES) was used to identify the magnesium loading in catalyst. The flow rates of plasma gas and auxiliary gas are 15.0 L/min and 1.50 L/min, respectively. The pressure of nebulizing gas is 200 KPa and pump speed is 13 rpm.

Ultraviolet-visible spectroscopy (UV-vis)

The titanium content of the synthesized catalysts was determined by UV-vis through hydrogen peroxide colorimetric method. The catalysts were dissolved in an acidic media followed by dilution with double distilled water to 25 mL. The diluted solution was reacted with H_2O_2 to form peroxotitanium complex [$TiO(H_2O_2)$]. UV measurements were carried out in 10 mm quartz glass cells on Mapada UV-3200 spectrophotometer. The intensity of a peak at 409 nm was used to quantify the titanium content. The ID content was determined on gas chromatograph (clarus 580), manufactured by PE in the US.

Nitrogen adsorption/desorption experiments

Nitrogen adsorption/desorption experiments were conducted on automatic physisorption analyzer (Micromeritics ASAP 2020, USA) at 77 K to obtain the value of the specific surface area, SBET, calculated based on the BET method and the pore volume Vp and pore size dm were evaluated using the BJH method.

High Temperature Gel Permeation Chromatography (HT-GPC)

The molecular weight (MW) and molecular weight distribution (MWD) of produced polyethylene was measured by HT-GPC (Agilent PL-220) with two PLgel-Olexis columns at 160! and the flow rate of 1.0 mL/min. 1,2,4-trichlorobenzene (TCB) and polystyrene (PS) were used as solvent and standard sample, respectively.

Differential Scanning Calorimetry (DSC)

DSC analyzer (TA, DSC Q200) was used to record the heating curve and melting temperature (Tm). The enthalpy of fusion (ΔHf) of each sample was calculated by the DSC curve. The isotacticity index of PP was determined by measuring the amount of boiling heptane insoluble fraction percent in the polymer.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was recorded on a Perkine Elmer Model PhI5000 ESCA spectrometer equipped with a hemispherical electron analyzer working in the constant pass energy mode. A monochromatic Al Karadiation (1486.6 eV) operated at 300 W was used as the X-ray source. All binding energies were referenced to the Si $_{2p}$ peak of silica gel at 103.3 eV for the charging effect correction.

NH_3-TPD experiment was carried out on a Micromeritics AutoChem II 2920. For each experiment, 50 mg catalyst sample was loaded. After pretreating at 500 °C with the flow of 30 mL min^{-1} helium for 1 h, the sample was cooled down to 100 °C and fed with surplus of ammonia for 40 min, and it was then purged with helium for 1 h. Afterward, the linear temperature program (10! min^{-1}, from 100 to 600!) was started under the flow of helium at the rate of 50 mL min^{-1}, meanwhile, the ammonia desorption signal was recorded.

3. RESULT AND DISCUSSION

3.1 Characterization of catalysts

The prepared bimetallic catalysts were characterized by ICP, UV-vis and IC. The results are listed in Table 1.

Table 1 shows that the Ti content of the doped catalyst was a little lower than the catalyst without doping. These doped M compounds can be considered as inert filler in the catalyst support, and only $MgCl_2$ is the best support for Ti species [24]. In addition, the Cl content in the Zr, Fe, Mn, and W doped catalysts increase little. In the situation of V, the Cl content decreased as VCl_4 could be easyly washed away from the catalyst by solvent.[25] The pore structure parameters results shows that the surface area, pore volume, and average pore size of the doped catalysts decreased compared with the original SiO_2 raw material (Grace Davison 955 with surface area 261.8 m ^{2}g^{-1}, pore volume1.67 cm ^{3}g^{-1}, and average pore size 17.4 nm), which could be attributed to the supporting of catalytic components on the surface of SiO_2.

TABLE 1. Characterization results of different catalysts.

Catalyst	Mg$^{a)}$ [wt%]	Ti$^{b)}$ [wt%]	Cl$^{c)}$ [wt%]	M$^{a)}$ [wt%]	Pore structure parameters$^{d)}$		
					PV [ml g^{-1}]	SA [cm^3 g^{-1}]	PD [nm]
Cat-No	4.5	3.5	9.8	-	0.97	182.8	21.1
Cat-Zr-10	4.0	3.3	8.2	0.41	1.03	211.9	16.9
Cat-V-10	4.2	3.1	7.8	0.30	0.87	171.3	16.7
Cat-Fe-10	4.2	3.5	8.8	0.40	1.14	209.6	16.7
Cat-Mn-10	4.4	3.2	13.2	0.50	0.84	157.8	16.6
Cat-W-10	4.7	3.1	14.0	0.51	0.89	180.6	16.7

a) Measured by ICP; b) Measured by UV-vis;
c) Measured by IC; d) Measured by Nitrogen adsorption/desorption experiments.

3.2 Propylene polymerization of catalysts

In order to find the relationship between catalyst activity and metal atom properties. These catalysts are used in propylene polymerization. Table 2 summarizes the propylene polymerization results for these bimetallic catalysts.

As is known, the Al-alkyl cocatalyst have an important effect on the performance of Z-N catalyst system. In our previous work, it was found that TIBA as the cocatalyst showed higher activity than TEA for the (SiO_2/MgO/$MgCl_2$) TiClx catalyst.[19, 20, 22, 23] Hence in this work, TIBA is used as the cocatalyst for these prepared M-modified ZN catalysts in the subsequent investigations. The Al/Ti molar ratio varies from 5 to 20 for the series of M-modified catalysts used in propylene homopolymerization. As illustrated in Fig. 2, with the increase of Al/Ti molar ratio, the activities of these catalysts increase firstly and then decrease. However, the optimal Al/Ti molar ratio varies with different catalysts. For the Mg/Ti catalyst, the optimal Al/Ti molar ratio is 5, for the MgZr10%/Ti, MgV10%/Ti, MgFe10%/Ti and MgMn10%/Ti catalysts both are 5, and the MgW10%/Ti catalyst is 10. The function of the cocatalyst was well known to act as activator to reduce and alkylate the transition metal by generating a Ti-C bond. It is responsible for the generation of active sites and essential for monomer insertion.[26] Alkyl aluminum can also scavenge impurities in the polymerization system. However, large amount of cocatalyst may lead to deactivation of the active sites through over-reduction of the active transition

TABLE 2. Propylene homopolymerization activities and the characterization results of the homopolymers[a].

Run No.	Cat.	Metal Precursor	Al/Ti	Activity [b]	T_m [°C][c]	M_w [d] [×10^{5}g/mol]	MWD [e]	II.[f](%)
1	Mg/Ti	-	2.5	1731.7	158.3	2.6	10.5	71.7
2	Mg/Ti	-	5	1792.3	158.3	3.3	14.9	72.4
3	Mg/Ti	-	10	1769.7	159.0	3.9	12.3	72.2
4	Mg/Ti	-	20	1304.3	159.3	3.7	13.8	72.6
5	MgZr10%/Ti	$ZrNO_3$	2.5	291.0	158.1	2.5	10.3	68.8
6	MgZr10%/Ti	$ZrNO_3$	5	512.1	156.3	2.7	10.7	69.1
7	MgZr10%/Ti	$ZrNO_3$	10	378.8	157.5	3.0	11.1	68.4
8	MgZr10%/Ti	$ZrNO_3$	20	306.1	156.9	2.3	10.4	67.3
9	MgV10%/Ti	NH_4VO_3	2.5	393.9	157.7	2.7	10.4	70.1
10	MgV10%/Ti	NH_4VO_3	5	433.3	157.9	3.0	9.8	68.4
11	MgV10%/Ti	NH_4VO_3	10	254.5	156.9	nd	nd	nd
12	MgV10%/Ti	NH_4VO_3	20	190.9	157.0	nd	nd	nd
13	MgFe10%/Ti	$FeCl_2$	2.5	475.8	157.9	2.8	9.9	70.3
14	MgFe10%/Ti	$FeCl_2$	5	836.4	156.7	2.7	10.8	68.5
15	MgFe10%/Ti	$FeCl_2$	10	751.5	157.2	3.0	10.3	67.6
16	MgFe10%/Ti	$FeCl_2$	20	524.2	158.4	2.8	11.1	69.3
17	MgMn10%/Ti	$MnCl_2$	2.5	1239.4	156.6	2.7	11.1	69.0
18	MgMn10%/Ti	$MnCl_2$	5	1487.5	158.6	2.9	10.5	68.2
19	MgMn10%/Ti	$MnCl_2$	10	1368.8	157.1	2.5	10.7	68.5
20	MgMn10%/Ti	$MnCl_2$	20	887.5	156.4	2.6	10.3	70.1
21	MgW10%/Ti	WCl_6	2.5	2174.2	158.2	2.9	11.2	69.5
22	MgW10%/Ti	WCl_6	5	2622.6	157.9	3.1	10.8	69.2
23	MgW10%/Ti	WCl_6	10	2867.7	158.0	3.0	10.9	69.3
24	MgW10%/Ti	WCl_6	20	2100.0	158.1	3.0	11.7	70.3

[a] Polymerization conditions: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TiBA, 50 °C, no ED, 1 h.
[b] The unit of catalyst activity is gPP $(gTi)^{-1}$ h^{-1};
[c] T_m and ÄH_f were measured by DSC thermograms;
[d] M_w was estimated by GPC; [e] MWD (M_w/M_n); [f] Refluxing in boiling n-heptane for 6 hours;

metal and also enhanced the chain transfer reaction to cocatalyst, which might decrease the catalyst activity. From the results of molecular weight distribution of the polymer in Table 2, it can be seen that the doping metal has little effect on the molecular weight distribution of the product. The isotacticity value of PP product is decreased after doped with a third metal, which may ascribe to the coordination of internal electronic donor on the Mg nearby the Ti species is affected by the doped metal.

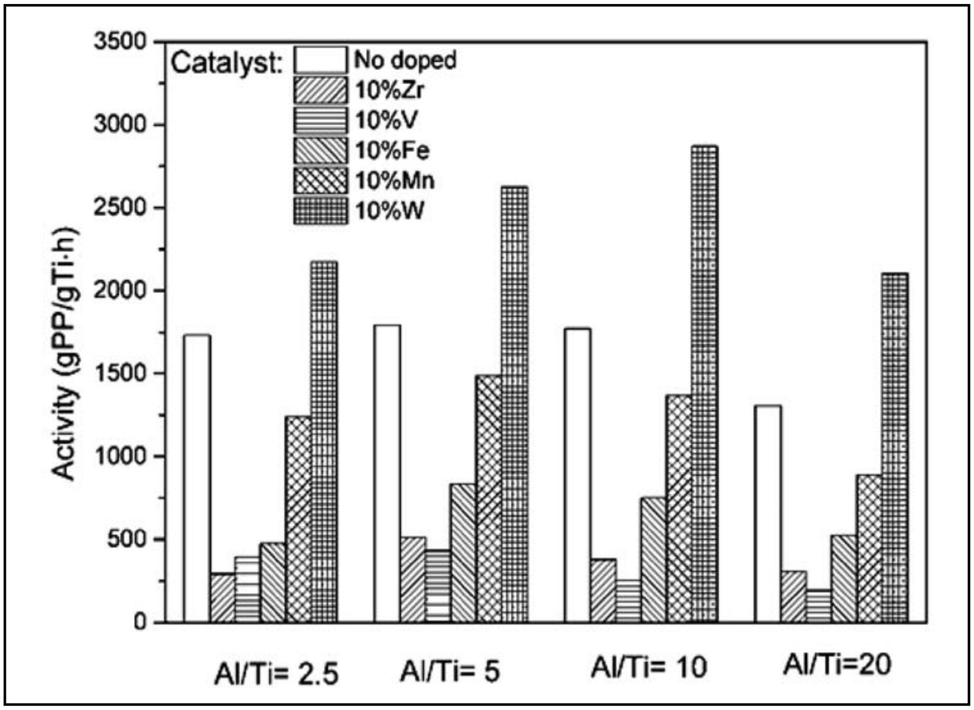


Fig. 2. Catalysts activity with different Al/Ti mole ratio

It has been observed that the introduction of (10 wt%) metal compounds into the catalysts has a big effect on the catalysts performance. In the cases of bimetallic catalyst containing zirconium, vanadium, iron, zirconium and wolfram components as the second metal, the activity of the doped catalysts showed the following order: MgW10%/Ti > MgMn10%/Ti > MgFe10%/Ti > MgZr10%/Ti > MgV10%/Ti. By comparing the activity of the doped catalyst and no doped catalyst, the activity value of W (10 wt%) modified catalyst increased 60% (gPP/gTi·h) and Zr, V, Fe and Mn doped catalyst decreased. The increased activity of the doped catalysts could be ascribed to the formation of structural defects in the supporting materials.[27] However, not all the activity of the doped catalysts are promoted.

The electronegativity of the doped compounds are listed in Table 3 [28-30], and the relationship between the activity and electronegativity and metal radius are shown in Figure 3 and Figure 4, respectively.

Figure 3 shows that the activity seem to have no obvious relationship with the metal electronegativity. However, in Figure 4, ion radius have the similar value (Fe, Mn, W) with magnesium seem to have better activity than bigger one (Zr and V). That is because the similar ion radius have a more possibility to form disorder $MgCl_2$, which is also demonstrated by other works [11, 31-33].

In order to further study the effect of the doped metal on the catalyst active sites, an XPS survey scan was performed on the supported catalysts to investigate the states of the titanium species of catalysts, the values of the binding energies in the supported catalysts are listed in Table 4.

TABLE 3. Effects of second metal on the propylene polymerization

Catalyst	Radius[a)]	M[b)][wt%]	Electronegativity[a)]	activity
			M	(g/gTi·h)
-	0.65	-	1.54	1792.3
Zr	0.80	0.61	1.33	512.1
V	0.74	0.50	1.63	433.3
Fe	0.64	0.40	1.64	836.4
Mn	0.67	0.68	1.55	1487.5
W	0.62	0.39	2.36	2867.7

[a)]Ref[28-30] [b)]Measured by ICP

The XPS results clearly indicate that the third metal has an effect on the $Ti_{2p3/2}$ binding energy. In the case of Zr, V and Fe the binding energy value of $Ti_{2p3/2}$ are almost no change compared with no doped catalyst. When it comes to Mn and W, the binding energy value decreased a little. That means the electron densities of $Ti_{2p3/2}$ for Mn and W modified catalyst are richer to some extent in comparison to Zr, V, Fe doped and no doped catalyst. However, the effect is faint. One possible reason is that this effect caused by a non-bonded manner [34]. The possible model of metal effect could be described in Figure 6. The metal chlorides are involved in the active species and influence the electronic structure of the active titanium. Since the Mn and W have a potential to form MClx compounds with higher valence state, the two elements could coordinate with more Cl atomics and more likely to affect the Ti Species. This is also consistent with the higher Cl content in Mn and W doped catalyst in Table 1.

NH_3-TPD is applied to characterize the acid properties of all the catalysts[35]. The ammonia

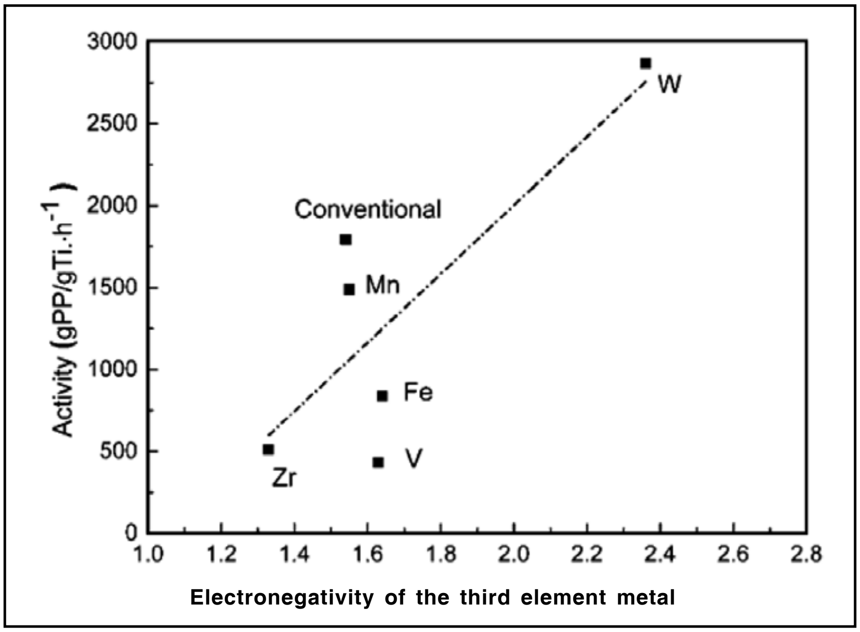


Fig. 3. Relationship between the activity and metal electronegativity

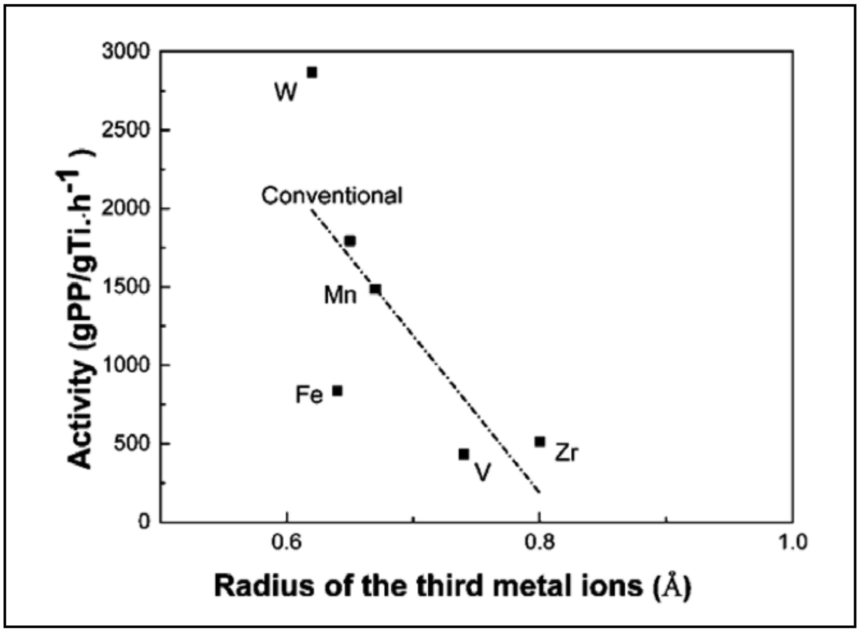


Fig. 4. Relationship between the activity and metal radius

TABLE 4. XPS datas of the $Ti_{2p3/2}$ level in the supported catalysts.

Run No.	Catalyst	Binding Energy^{a} (eV)
1	Mg/Ti	458.9
2	MgZr10%/Ti	458.9
3	MgV10%/Ti	458.9
4	MgFe10%/Ti	458.9
5	MgMn10%/Ti	458.7
6	MgW10%/Ti	458.8

^{a}Reference: Si $_{2p}$ 103.3 eV

desorption profiles of the modified and unmodified catalysts are shown in Figure 7. The results cleanly show the effect of the doped support on the acid properties of the catalysts. A desorption peak located around 160! appeared for Mg/Ti catalyst. After modified by different metal compound, the peak at 160! can still be seen in Mn and W modified catalyst and the intensity is increased. For the V, Zr and Fe the desorption peak is shift. This implies Mn and W could maintain the structure of the catalyst and slightly increase the acid properties of the catalysts, thus affecting the nature of the catalysts. On the other hand, V, Zr and Fe shows a negative effect. The results increase in basic-acidic property of active site being able to react with co-catalyst. However, the relationship between the acid properties and the activity still need to be further investigated.

It is found that the Mn could decrease the binding energy value of Ti $_{2p3/2}$ from the above results. However, the catalyst does not show higher activity when compared with no doped catalyst. In order to investigate the influence of doping content of Mn, different content of Mn

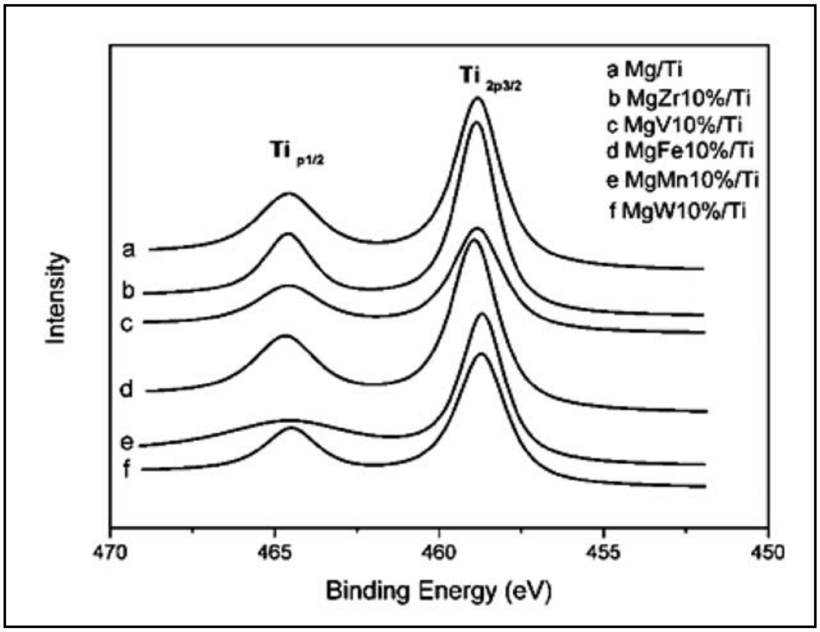


Fig. 5. XPS curves of Ti species for different catalysts

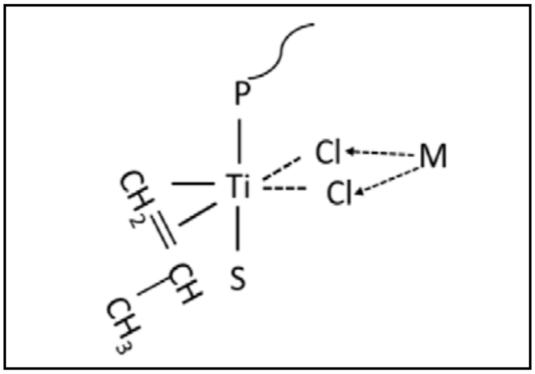


Fig. 6. Possible model of metal effect of Ti^{3+}

doped catalysts are prepared and the polymerization results are listed in Table 5.

From Table 5, it can be seen that when the dosage of $MnCl_2$ was 5 wt%, the activity of the bimetal catalyst increased 47.3% compared with the catalyst with no $MnCl_2$ doped. When the content of the $MnCl_2$ is decreased to 3wt%, the activity of the catalyst increase to 2009. 4 gPP $(gTi)^{-1}$ h^{-1}. However, the activity is also 12.2% higher than the catalyst without $MnCl_2$ doped. This suggests 3 wt% doped and 5 wt% doped catalyst both have a positive effect on the activity of the catalyst. When the $MnCl_2$ content is 1 wt%, the activity decreases to 834.4 gPP $(gTi)^{-1}$ h^{-1}. Moreover, the doped catalyst with different $MnCl_2$ content shows best activity at different Al/Ti mole ratio. The optimal Al/Ti mole ratio for 10%Mn, 5%Mn, 3%Mn and 1%Mn doped catalyst is 5, 20, 2.5 and 10, respectively.

A possible explanation is that, in MgMn5%Ti catalyst, the $MnCl_2$ molecules are uniformly dispersed in the support, resulting in the $MgCl_2$ surface structure more disordered. So, more unsaturated Mg coordination centers suitable

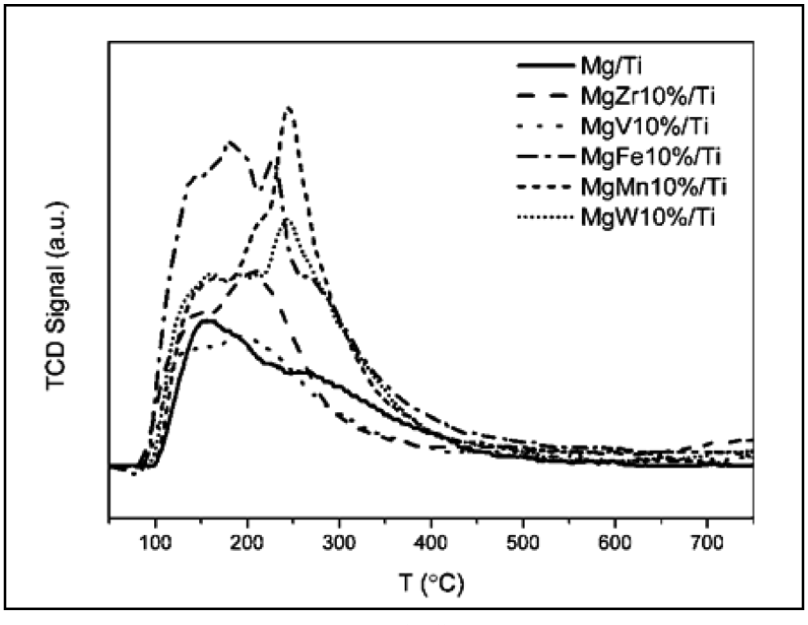


Fig. 7. NH_3-TPD curves of different doped catalysts

TABLE 5. Polymerization results of different dosage of $MnCl_2$.

Run No. [a)]	Cat.	Al/Ti	Activity [b)]	T_m [°C][c)]	M_w [d)] [×10^5g/mol]	MWD [e)]
1	MgMn5%Ti	5	1962.5	158.4	2.7	10.1
2	MgMn5%Ti	10	2490.6	159.3	2.6	10.4
3	MgMn5%Ti	20	2640.6	159.5	3.0	11.3
4	MgMn5%Ti	30	1940.6	159.5	2.7	10.9
5	MgMn3%Ti	1	956.25	157.1	2.5	9.5
6	MgMn3%Ti	2.5	2009.4	156.3	2.7	10.9
7	MgMn3%Ti	5	1787.5	157.9	2.7	10.4
8	MgMn3%Ti	10	1356.3	156.1	2.3	11.1
9	MgMn1%Ti	2.5	618.8	156.4	2.5	10.0
10	MgMn1%Ti	5	818.8	157.0	2.3	9.9
11	MgMn1%Ti	10	834.4	157.8	2.2	10.0
12	MgMn1%Ti	20	715.6	157.0	2.6	10.5

[a)] Polymerization conditions: catalyst 100 mg, propylene 0.15 MPa, *n*-heptane 80 mL, TiBA, 50°C, no ED, 1 h.
[b)] The unit of catalyst activity is gPP $(gTi)^{-1}$ h^{-1};
[c)] T_m and ΔH_f were measured by DSC thermograms;
[d)] M_w was estimated by GPC; [e)] MWD (M_w/M_n);

for absorbing $TiCl_4$ and forming the active sites. On the other hand, in the doped catalysts with higher $MnCl_2$ dosages, these $MnCl_2$ crystallites may absorb on the $MgCl_2$ surfaces and block some of the active sites, which could decrease the activity. In the situation of lower $MnCl_2$ dosages, the $MnCl_2$ may only plays the role of inert support. This leads to less suitable coordination centers forming the Ti species active sites, resulting in the decrease of catalyst activity.

The kinetic curves of propylene homopolymerization with different metal doped catalysts under different Al/Ti molar ratio are shown in Figure 8. It can be seen that the active centers of W, Mn and, Fe modified catalysts shows the same polymerization behavior with Mg/Ti catalyst. However, the Fe may act as a shelter which can hide some active sites. The kinetic behavior of Zr, V doped catalyst shows totally different means that the changes of active site in Mg/Ti catalyst, which is consistent with the results of the NH_3-TPD test.

4. CONCLUSIONS

Several (SiO_2/MgO/MClx/$MgCl_2$)·TiClx Ziegler-Natta Catalysts are synthesized by a co-impregnation method to study a third metal (Zr, V, Fe, Mn, W) effect on catalytic performance in propylene polymerizations. When the doped content of the third metal is 10 wt%, the activity in propylene polymerization follows the sequence of MgW10%/Ti >Mg/Ti >MgMn10%/Ti > MgFe10%/Ti > MgZr10%/Ti > MgV10%/Ti. Moreover, it is found that metals have similar radius with Mg^{2+} have higher activity (Fe, Mn and W >V and Zr). However, the influence of the metal electronegativity is not obvious.

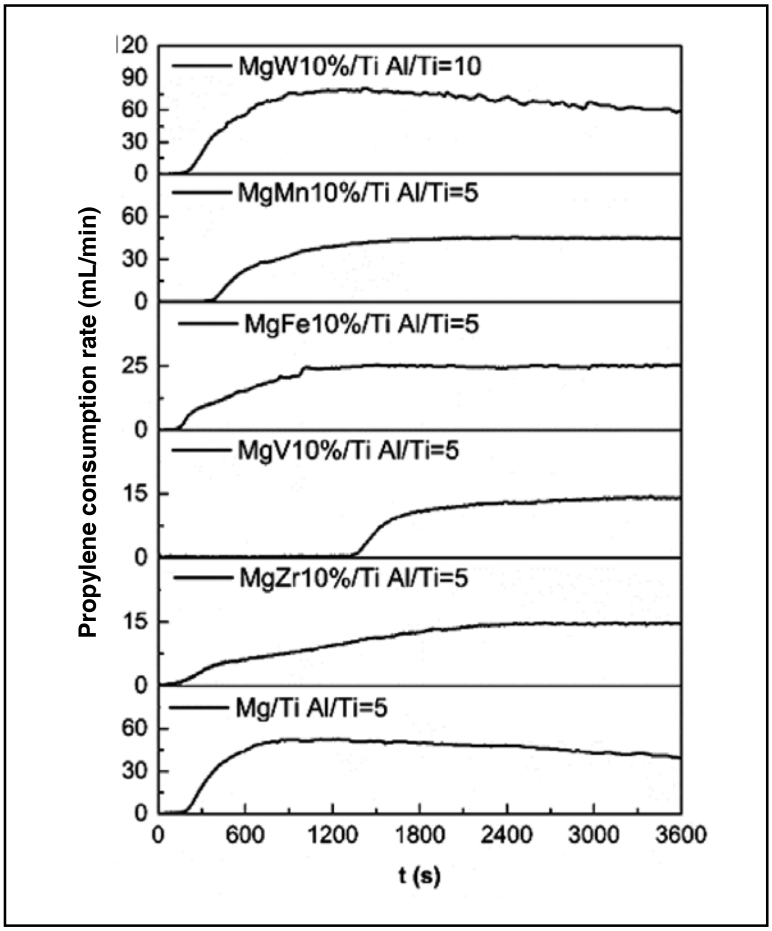
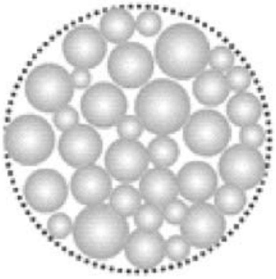


Fig. 8. Polymerization kinetic curves of different catalysts

Doping metals have little effect on the molecular weight distribution of the product but the isotacticity value decreased after dope with a third metal. The Mn and W atom can coordinate with more Cl atomics and more likely to effect the Ti Species. The NH_3-TPD results shows that W and Mn can maintain the structure of active site in the catalyst and slightly increase the acid properties of the catalyst. The V, and Zr showed the negative effect of the active sites and the Fe might hide some of the active sites. The activity of 5 wt% and 3wt% Mn doped catalyst is higher than the catalyst without doping.

Introduction of a metal species
into the (SiO_2/MgO/ID/$MgCl_2$) $TiCl_x$ Ziegler-Natta catalyst

↓



Catalyst particles

Metal-modified (SiO_2/MgO/ID/$MgCl_2$). $TiCl_x$ Ziegler-Natta catalyst

↓

60% higher activity for 10 wt% W doped catalyst

Activity : 5 wt% and 3wt% Mn doped catalyst > no doped catalyst

Metals have similar radius with mg^{2+} have higher activity

The influence of the metal electronegativity is not obvious

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REFERENCES

1. E. Groppo, K. Seenivasan, C. Barzan, *Catal. Sci. & Technol.* 3 (2013) 858.
2. E. S. Gnanakumar, R. R. Gowda, S. Kunjir, T. Ajithkumar, P. Rajamohanan, D. Chakraborty, C. S. Gopinath, *ACS Catal.* 3 (2013) 303.
3. R. Credendino, D. Liguori, Z. Fan, G. Morini, L. Cavallo, *ACS Catal.* 5 (2015) 5431.
4. V. Busico, R. Cipullo, A. Mingione, L. Rongo, *Ind.& Eng. Chem. Res.* 55 (2016) 2686.
5. Z. Y. Ye, L. Wang, H. J. Yu, S. Jiang, *J. Polym. Mater.* 22 (2005) 115.
6. X. Liu, Z. Fan, Z. Fu, *J. Polym. Mater.* 24 (2007) 233.
7. G. C. P.C. Barbe, L. Noristi, *Adv. Polym. Sci.* 1 (1987) 81.
8. H. F. N. Kashiwa, Y. Tokuzumi (Mitsui Chemicals Co.), JP Patent (1968) 1031698.
9. J. F. Wang, L. Wang, L. F. Feng, X. P. Gu, H. J. Yu, *J. Polym. Mater.* 21 (2004) 401.
10. W. Q. Wang, L. Wang, *J. Polym. Mater.* 1 (2003) 20.

11. T. Garoff, T. Leinonen, *J. Mol. Catal. A: Chem*. 104 (1996) 205.
12. D. Fregonese, S. Bresadola, *J. Mol. Catal. A: Chem.* 145 (1999) 265.
13. X. Jiang, Y.-p. Chen, Z.-q. Fan, Q. Wang, Z.-s. Fu, J.-t. Xu, *J. Mol. Catal. A: Chem.* 235 (2005) 209.
14. X. Jiang, X. Tian, Z. Fan, *Mater. Res. Bull.* 43 (2008) 343.
15. S. Tanase, K. Katayama, S. Inasawa, F. Okada, Y. Yamaguchi, T. Sadashima, N. Yabunouchi, T. Konakazawa, T. Junke, N. Ishihara, *Macromol. Rea. Eng*. 2 (2008) 233.
16. A. Xiao, L. Wang, Q. Liu, H. Yu, X. Dong, *Des. Monomers Polym.* 11 (2008) 139.
17. P. Kaivalchatchawal, S. Samingprai, T. Shiono, P. Praserthdam, B. Jongsomjit, *Eur. Polym. J.* 48 (2012) 1304.
18. F. M. B. Coutinho, J. L. Xavier, *Eur. Polym. J*. 33 (1997) 897.
19. J. Wang, R. Cheng, X. He, Z. Liu, Z. Tian, B. Liu, *Macromol. Chem. Phys.* 216 (2015) 1472.
20. F. Huang, J. Wang, R. H. Cheng, X. L. He, Z. Liu, N. Zhao, B. P. Liu, *Macromol. React. Eng.*, 10 (2016) 10.
21. W. Zhu, Z. Tian, R.H. Cheng, X.H. He, Z. Liu, N. Zhao, B.-p. Liu, Chine. *J. Polym. Sci.* 35 (2017) 1474.
22. J. Wang, R. Cheng, X. He, Z. Liu, N. Zhao, B. Liu, *J. Organomet. Chem.* 798 (2015) 299.
23. J. Wang, R. Cheng, X. He, Z. Liu, N. Zhao, B. Liu, *Macromol. React. Eng.* 10 (2016) 246.
24. N. Kashiwa, *Journal of Polymer Science Part A: Polymer Chemistry* 42 (2004) 1.
25. L. C. D. Maria, *Polymer* 36 (1995) 2845.
26. Y. V. Kissin, *J. Catal.* 292 (2012) 188.
27. D. Fregonese, S. Bresadola, *J. Mol. Catal. A: Chem.* 145 (1999) 265.
28. K. A. K. L. C. F. Bell, ''Modern Approach to Inorganic Chemistry", 3rd edition, Tokyo KagaKu Dozin-Butterworth Co. Ltd., Tokyo 1976, p. 142, P. 153.
29. K. S. Y. Doi, M. Murata, E. Suzuki, Y. Ono, T. Keii, *Polym. Commun.* 24 (1983) 244.
30. Y. Zeng, A. Matta, S. Dwivedi, T. Taniike, M. Terano, *Macromol. Rea. Eng.* 7 (2013) 668.
31. X. Jiang, H. Wang, X. Tian, Y. Yang, Z. Fan, *Ind. & Eng. Chem. Res.* 50 (2011) 259.
32. R. Bazvand, N. Bahri-Laleh, M. Nekoomanesh, H. Abedini, *Des. Monomers Polym*. 18 (2015) 599.
33. T. Niyomthai, B. Jongsomjit, P. Praserthdam, *Polym. Bull.* (2017) 1.
34. H. Mori, K. Hasebe, M. Terano, *J. Mol. Catal. A: Chem.* 140 (1999) 165.
35. Y. Jin, R. Cheng, X. He, Z. Liu, N. Zhao, B. Liu, *Macromol. Chem. Phys.* 218 (2017) 1600443.

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