

Studies on the Formation of New, Highly Active Silica-Supported Ziegler–Natta Catalyst for Ethylene Polymerization

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Highly active ethylene polymerization catalysts based on a new four-component catalyst-system Ti/Mg/THF/improver ($\text{Cl}_3\text{CCH}_2\text{OH}$) and with SYLOPOL948 or SMR49-4049 silica as carrier were prepared and studied. Compared with the corresponding catalysts based on a three-component catalyst system (Ti/Mg/THF), these new catalysts were improved in catalytic performances such as catalytic activity and hydrogen response. In particular, the catalysts based on the four-component catalyst system and SMR49-4049 silica had very high catalytic activity. The effects of improver $\text{Cl}_3\text{CCH}_2\text{OH}$ were investigated. The investigations into the catalyst formation mechanism showed that after dehydrated silica was treated with AlEt_3 , the average pore diameter of silica was enlarged from 20.3 to 26.2 nm for SMR49-4049 silica and from 25.3 to 34.9 nm for SYLOPOL948 silica. This transformation favors the impregnation of catalyst components on silica. After the catalyst was prereduced with alkyl-aluminum, the pore diameter of the final catalyst was enlarged from 17.5 to 26.4 nm for the catalyst based on SMR49-4049 silica, and from 27.6 to 45.2 nm for the catalyst based on SYLOPOL948 silica. This transformation favors high catalytic activity. © 2002 Elsevier Science (USA)

Key Words: Ziegler–Natta; silica; catalyst; mechanism; ethylene; polymerization.

INTRODUCTION

A fluidized-bed gas-phase process for ethylene polymerization has been developed and has become an important new direction for ethylene polymerization technology because of its strong points, such as a relatively low investment requirement, simple technologic processes, and excellent suitability for production of LLDPE (linear low-density polyethylene), compared with other polyethylene processes, such as the slurry process and the solution process. For example, both the UCC Company and the BP Company have developed fluidized-bed gas-phase polymerization technology which has been applied and licensed widely in the world, and which has contributed significantly

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to worldwide total polyethylene productivity. It is reported that by the year 2000 the UCC Company licensed 82 sets of production line in the world, with distributions in P. R. China, USA, Saudi Arabia, Russia, Canada, Sweden, Japan, and so forth. When the condensation and supercondensation techniques of the fluidized bed were developed, productivity increased 60–200%, showing more excellent developing foreground. Therefore researching and developing new catalysts suitable for fluidized-bed processes became very important and aroused extensive research interests (1).

Both the UCC Company and the BP Company have researched and developed silica-supported catalysts for the fluidized-bed process. These two kinds of catalysts have different characteristics and both of them have been industrialized and commercialized. The catalyst of the UCC Company, based on a three-component-system Ti/Mg/THF, had moderate catalytic activity, good hydrogen response, and a comonomer incorporation property, and the productive cost is low (2–5). The catalyst of the BP Company was prepared by using alkyl magnesium as starting material, and therefore the cost was relatively high; the hydrogen response and comonomer incorporation property, however, were good (6, 7). The Shanghai Research Institute of the Chemical Industry (P. R. China) first prepared alkyl magnesium chloride by a reaction of magnesium powder with halocarbon. The catalyst was subsequently prepared through a magnesium-containing complex, and the catalyst had high activity (8). Zhongshan University, P. R. China, has also carried out much research work on silica-supported gas-phase polymerization catalysts, a new kind of mixed support based on $\text{MgCl}_2/\text{ZnCl}_2$, and the corresponding catalyst were developed. The catalyst had high activity, excellent hydrogen response, and a comonomer incorporation property; in particular, the regulation ability to MWD (molecular weight distribution) was enhanced significantly (9–12). In the catalyst preparation process, a $\text{ZnCl}_2\text{–AlEt}_3$ mixed and reacted solution was used to treat dehydrated silica, and then the catalyst was prepared by supporting MgCl_2 and TiCl_4 . The polyethylene produced with this catalyst had a bimodal peak in DSC spectroscopy, which may be due to the bimetal Mg/Zn in mixed support. This polyethylene

probably has an improved processing ability (13, 14). In conclusion, a silica-supported and titanium-based Ziegler-Natta catalyst plays a very important role in the fluidized-bed gas-phase polymerization of ethylene.

There is much research reported on silica-supported vanadium-based catalysts. For example, the UCC Company has developed a series of silica-supported vanadium-based catalysts for gas-phase polymerization of ethylene (15–18). The catalyst has a good comonomer incorporation property, and the produced polyethylene resins are surprisingly broad in MWD: Mw/Mn may range from 7 to 12. But certain halocarbons must be used as promoters to reach high activity. CHCl_3 , CFCl_3 (15, 16), CH_2Cl_2 and $\text{CF}_2\text{ClCFCl}_2$ (17), $\text{C}_3\text{H}_2\text{Cl}_6$, and C_3Cl_8 (18) are all very efficient promoters which have been reported. When they studied the effect of halocarbons on vanadium-based catalysts, Cann *et al.* found that only CH_2Cl_2 could boost the activity of a titanium-based catalyst by approximately 50%, but the other halocarbons, such as CFCl_3 and CCl_4 , significantly poisoned the titanium-based catalyst in the same amount to the same catalyst (19). By making use of this characteristic, that CFCl_3 and CHCl_3 promote vanadium-based catalysts and restrain titanium-based catalysts in the same amount, the UCC company developed a Ti/V bimetal catalyst for the production of polyethylene resins having bimodal MWD (20). Then Wu and Wu (21) found that CHCl_3 could also boost the activity of a titanium-based catalyst with a CHCl_3/Ti molar ratio of between 0.5 and 4. When the CHCl_3/Ti molar ratio is above 5, CHCl_3 poisoned the activity of titanium-based catalysts greatly. In our research work, we found that monochloroalkanes, such as chlorocyclohexane, chlorobenzene, and chlorobutane, have a weak influence on vanadium-based catalysts but a great promotion effect on the activity of titanium-based catalysts (22, 23), indicating clearly that halocarbons suitable for vanadium-based catalysts are very different from those suitable for titanium-based catalysts in molecular structure and the amount used.

An obvious characteristic of silica is that it has plentiful hydroxyl on the surface. Because a hydroxyl group is very chemically active, through chemical reactions a catalyst or catalyst component could be bonded to silica to produce a heterogeneous catalyst. For example, tetramethyl cyclopentadiene could be bonded to silica, with which silica-supported metallocene catalyst could be prepared (24). BF_3 could be bonded to silica through the reaction of BF_3 with silicon-hydroxyl; in this way, the amount of cocatalyst MAO could be decreased for the prepared metallocene catalyst (25, 26). $\text{Cl}_3\text{CCH}_2\text{OH}$ could be introduced to the silica surface to prepare a supported vanadium-based catalyst; this kind of catalyst has high catalytic activity without the addition of halocarbons (27). Therefore chemical modification to the surface of silica is a very efficient method to use to prepare supported catalyst or to introduce some catalyst component to a solid catalyst.

In order to research and develop silica-supported titanium-based Ziegler-Natta catalysts with increased catalytic activity, improved hydrogen response, a good comonomer incorporation property, and better granular morphology for producing high-quality polyethylene resins, we developed a new class of four-component catalyst-system Ti/Mg/THF/improvers ($\text{Cl}_3\text{CCH}_2\text{OH}$ or Cl_3CCOCl), and selected SYLOPOL948 silica or SMR49-4049 silica as carriers (28–30), which have improved granular morphology compared with SYLOPOL955 silica. Four kinds of new catalysts were prepared, including Ti/Mg/THF/improver/SYLOPOL948 catalyst, Ti/Mg/THF/improver/SMR49-4049 catalyst, Ti/Mg/THF/improver/SYLOPOL948 catalyst without AlCl_3 , and Ti/Mg/THF/improver/SMR49-4049 catalyst without AlCl_3 . Compared with a Ti/Mg/THF/SYLOPOL955 catalyst reported in the literature, these new catalysts have higher catalytic activity, improved hydrogen response, a good comonomer incorporation property, and better granular morphology. Here the studies on the formation of the above-described new catalysts are presented.

EXPERIMENTAL

General Considerations

All of the chemicals used were purchased from the market. Solid chemicals, such as MgCl_2 , TiCl_3 (AA grade), were used directly as commercial grade. Liquid chemicals, such as tetrahydrofuran (THF), iso-pentane, hexane, 1,1,1-trichloroethanol ($\text{Cl}_3\text{CCH}_2\text{OH}$), chlorocyclohexane, chlorobenzene, and chlorobutane, were dehydrated with a 4-Å molecular sieve before use. Silica was purchased from Grace Davison Company. AlEt_3 was diluted with hexane to 1 mmol/ml before use, $\text{Al}(n\text{-C}_6\text{H}_{13})_3$ was diluted with hexane to 1.5 mmol/ml before use, and AlEt_2Cl was diluted with hexane to 2.21 mmol/ml before use. MgBu_2 was purchased as a heptane solution of 1 mmol/ml to be used directly.

Catalyst Preparation

The catalyst was prepared via five steps (28, 29), including (i) heat activation of silica at 600°C, (ii) chemical treatment to silica with AlEt_3 , (iii) preparation of catalyst mother liquor, (iv) impregnation of catalyst components on silica, and (v) catalyst prereduction with alkyl-aluminum. These are described in more detail in the following.

(i) *Heat activation of silica.* First, 11 g silica was weighed and put in a quartz boat, which was then laid into a tube furnace. Under a N_2 flow the tube was heated to 200°C within 30 min and was maintained at this temperature for 2 h. Then the temperature was increased to 600°C within 30 min and was kept at this temperature for 4 h. Finally the tube was cooled to room temperature, and silica was removed and preserved under N_2 for further use.

(ii) *Chemical treatment of silica.* Under N₂ ambience, to a 300-ml flask equipped with a mechanical stirrer 10 g heat-activated silica was added, with 100 ml low alkane, such as hexane or iso-pentane, added as diluent. Under stirring the suspended solution was adjusted to 25°C and then the desired amount of AlEt₃ solution (1 mmol/ml) was added slowly. The mixture was reacted at 25°C for 30 min, followed by slow drop addition of the desired amount of improver (Cl₃CCH₂OH or Cl₃CCOCl). After completion of the addition, the mixture was reacted for 30 min and then was dried by sweeping with N₂, thereby obtaining flowable powders.

(iii) *Preparation of catalyst mother liquor.* To another flask equipped with a stirrer were added desired amounts of MgCl₂ and AA-grade TiCl₃ or TiCl₄ using tetrahydrofuran as solvent. The mixture was heated under stirring to reflux for 5 h, thereby obtaining a catalyst mother liquor with a deep purple–black color for AA-grade TiCl₃ or with a pale yellow color for TiCl₄. The Mg/Ti molar ratio was controlled at 3.14.

(iv) *Impregnation of catalyst component on silica.* The silica obtained in step (ii) was mixed with the catalyst mother liquor from step (iii). The mixture was stirred under refluxing for 1 h, followed by drying by sweeping with N₂, thereby obtaining flowable, pale yellow solid powders. Percentage of THF was controlled at the desired range.

(v) *Catalyst prereduction with alkyl-aluminum.* The product from step (iv) was prereduced by first adding in drops the desired amount of AlEt₂Cl (2.21 mmol/ml) with 100 ml low alkane, such as hexane or iso-pentane, as diluent. After the completion of addition at room temperature, the mixture was reacted for 30 min, followed by drop adding the desired amount of Al(*n*-C₆H₁₃)₃ (1.5 mmol/ml). After completion of the addition, the mixture was heated to the boiling point and reacted for 30 min, then dried by sweeping with N₂, thereby obtaining a flowable powder catalyst, which was the final catalyst product.

General Procedure for Slurry Polymerization of Ethylene

Slurry polymerization of ethylene was carried out in a 2-L stainless steel autoclave with a mechanical stirrer. The stirring rate was adjustable. The autoclave was heated by recycling hot water. First, the autoclave was purified with H₂ at least three times; then hexane, cocatalyst, and catalyst were introduced in turn. When the autoclave was heated to 70°C, H₂ was introduced to the desired pressure within 5 min, and then C₂H₄ was introduced to the desired pressure and the temperature was raised to 80°C. In the process of polymerization, the temperature and pressure were controlled automatically by a computer. After reaction for 1–3 h, the autoclave was cooled to below 35°C by cool water, the pressure was vented, the slurry was discharged, and the polymer was filtrated and dried in air. Finally the polymer was weighed and the reaction rate was calculated in grams of PE/(g Ti) or PE/gram of catalyst. Bulk density (BD) was measured as grams of PE/cubic centimeters. When necessary, the melt index (MI) and flow index (FI) were tested as grams of PE/10 min, and the MFR (FI/MI) was calculated.

Slurry polymerization conditions. Condition I was as follows: total pressure 0.73 MPa; pressures of H₂ and C₂H₄, 0.25 and 0.48 MPa, respectively; 1 ml AlEt₃ (1 mmol/ml) as cocatalyst; 1 L hexane as diluent; and polymerization carried out at 80°C for 2 h.

Condition II was as follows: total pressure, 1.03 MPa; pressures of H₂ and C₂H₄, 0.28 and 0.75 MPa, respectively; 1 ml AlEt₃ (1 mmol/ml) as cocatalyst; 1 L hexane used as diluent; and polymerization carried out at 85°C for 2 h.

RESULTS

Catalyst Preparation with SYLOPOL948 Silica as Carrier (28)

In order to improve catalyst performances, including increasing catalytic activity and enhancing hydrogen response

TABLE 1
Evaluation Results of Catalyst Based on SYLOPOL948

The amount of improver and the introduction method	Catalyst system	Activity (×10 ⁴ g PE/g Ti)	BD (g/cm ³)
Cl ₃ CCH ₂ OH/Ti = 2, used in chemical modification	Ti/Mg/THF/Cl ₃ CCH ₂ OH	13.8	0.32
Cl ₃ CCH ₂ OH/Ti = 2, used in catalyst pre-reduction	Ti/Mg/THF/Cl ₃ CCH ₂ OH	12.8	0.31
Cl ₃ CCOCl/Ti = 2, used in chemical modification	Ti/Mg/THF/Cl ₃ CCOCl	16.1	0.35
Cl ₃ CCOCl/Ti = 2, used in catalyst pre-reduction	Ti/Mg/THF/Cl ₃ CCOCl	14.0	0.31
No	Ti/Mg/THF	11.2	0.30

Note. Catalyst preparation: Silica was dehydrated at 200°C for 2 h and at 600°C for 4 h. The dehydrated silica was treated with 5 ml AlEt₃ solution in 100 ml hexane, and then the desired amount of improver was added. The catalyst mother liquor was prepared with 1.1 g MgCl₂ and 0.4 ml TiCl₄ dissolved in 100 ml tetrahydrofuran. Catalyst components were impregnated on silica and THF was evaporated until THF% was between 10 and 15%. The catalyst was prereduced with two kinds of alkyl aluminum in 100 ml hexane. The molar ratio of AlEt₂Cl/THF and Al(C₆H₁₃)₃/THF was controlled at 0.40. Catalyst evaluation: with slurry polymerization condition (I) described in experimental section.

TABLE 2

Studies on Different Amounts of Cl_3CCOCl
in Catalyst Preparation

$\text{Cl}_3\text{CCOCl}/\text{Ti}$ molar ratio	Activity		
	Ti (%)	($\times 10^4$ g PE/g Ti)	BD (g/cm^3)
0.5	0.99	9.7	0.34
1	0.93	10.6	0.31
2	0.96	16.1	0.35
4	0.94	14.9	0.31
8	0.81	12.9	0.30

Note. Catalyst preparation and evaluation conditions were the same as that in Table 1.

and comonomer incorporation property, a new component was introduced to the catalyst system as improver to form a new class of four-component-catalyst system: $\text{Ti}/\text{Mg}/\text{THF}/\text{Cl}_3\text{CCH}_2\text{OH}$ or Cl_3CCOCl . The experimental results were shown in Table 1. Table 1 shows that the new catalyst had higher catalytic activity; at the same time BD was also increased.

In Table 1, two different methods to introduce the improver were investigated. The results showed that the improver could be added in the silica chemical modification step or in the catalyst prereluction step. The catalytic activity and polyethylene BD were all improved. Obviously, it is better that improver be introduced in the silica chemical modification step.

The effect of different amounts of Cl_3CCOCl added to the catalyst were investigated; the results are listed in Table 2. Table 2 showed that when the $\text{Cl}_3\text{CCOCl}/\text{Ti}$ molar ratio was near 2, the corresponding catalyst had high catalytic activity and polyethylene powder had high BD; this result is pretty coincident with CHCl_3 added to the polymerization.

Catalyst Preparation with SMR49-4049 as Carrier (29)

SYLOPOL948 silica has definite and limited pore volume and surface area; therefore the amount of catalyst component impregnated on silica was restricted. Normally the content of the catalyst component was controlled to remain under 28%; a too-much-higher content would lead to bad flowing property. In order to increase the content of the catalyst component to improve the catalytic activity further, and to prepare a highly efficient catalyst to suit a fluidized bed operated under condensation state, we selected SMR49-4049 silica, which has bigger pore volume and surface area. With SMR49-4049 silica used as carrier, the content of the catalyst component could be increased from 28 to 38% and Ti% could be increased from 0.95 to above 1.10%; in addition, the catalyst had good flowing property and the catalytic activity was improved greatly, with the catalyst containing the improver also having a good hydrogen response and comonomer incorporation property.

Based on SMR49-4049 silica as carrier, the evaluation results of catalyst prepared with TiCl_4 and AA-grade TiCl_3 are listed in Tables 3 and 4, respectively.

From the results in Tables 3 and 4, it can be concluded that when SMR49-4049 silica was used instead of SYLOPOL948 silica, but without an improver in the catalyst preparation, although the catalytic activity was increased greatly, from 1200 to 3946 g/g cat in Table 3 and from 1160 to 2402 g/g cat in Table 4, the MI of the polyethylene resin was decreased, evidently from 0.51 to 0.18 g/10 min in Table 3 and from 0.52 to 0.20 g/10 min in Table 4. Therefore this catalytic activity enhancement has no significance for production of polyethylene of certain grades with settled MI; probably this MI decrease is due to the smaller pore diameter of the catalyst prepared with SMR49-4049 compared with the catalyst prepared with SYLOPOL948 (31), and the activity enhancement is due to the increase of catalyst components

TABLE 3

Experimental Results of Catalysts Prepared with TiCl_4 using SMR49-4049 as Carrier

Improver	Ti (%)	Activity		BD	MI	FI	MFR	Remarks
		g/g cat	$\times 10^4$ g/g Ti					
$\text{Cl}_3\text{CCH}_2\text{OH}/\text{Ti} = 2$	1.26	6667	52.9	0.35	0.53	15.92	30.0	High activity
$\text{Cl}_3\text{CCOCl}/\text{Ti} = 2$	1.29	6160	47.8	0.34	0.53	16.44	31.0	High activity
No	1.36	3946	29.0	0.32	0.18	5.41	30.1	For comparison
No	0.90	1200	13.3	0.32	0.51	15.40	30.2	For comparison (SYLOPOL948)

Note. Catalyst preparation: Silica was dehydrated at 200°C for 2 h and at 600°C for 4 h. Dehydrated silica (10 g) was treated with 5.6 ml AlEt_3 solution in 100 ml iso-pentane, and then the desired amount of improver was added. The catalyst mother liquor was prepared with 1.74 g MgCl_2 and 0.64 ml TiCl_4 dissolved in 174 ml tetrahydrofuran. Catalyst components were impregnated on silica and THF was evaporated until THF% was between 15 and 20%. The catalyst was prerelucted with two kinds of alkyl aluminum in 100 ml iso-pentane and the $\text{AlEt}_2\text{Cl}/\text{THF}$ molar ratio was controlled at 0.45 and the $\text{Al}(\text{n-C}_6\text{H}_{13})_3/\text{THF}$ molar ratio was controlled at 0.20. Catalyst evaluation: with slurry polymerization condition (II) described in experimental section.

TABLE 4

Experimental Results of Catalysts Prepared with AA-Grade TiCl_3 using SMR49-4049 as Carrier

Improver	Ti (%)	Activity		BD	MI	FI	MFR	Remarks
		g/g cat	$\times 10^4$ g/g Ti					
$\text{Cl}_3\text{CCH}_2\text{OH}/\text{Ti} = 2$	1.14	4955	43.5	0.37	0.52	17.20	33.1	High activity
$\text{Cl}_3\text{CCOCl}/\text{Ti} = 2$	1.10	4649	43.4	0.38	0.52	15.30	29.4	High activity
No	1.26	2402	19.1	0.37	0.20	6.78	33.9	For comparison
No	0.95	1160	12.2	0.38	0.52	16.30	31.3	For comparison (SYLOPOL 948)

Note. Catalyst preparation and evaluation conditions were the same as that in Table 3, except that 1.16 g AA-grade TiCl_3 was used instead of 0.64 ml TiCl_4 to prepare catalyst mother liquor.

impregnated on silica from 28 to 38% and the increase of surface area. This will be probed further in the following.

In order to overcome the defect described above, here improver ($\text{Cl}_3\text{CCH}_2\text{OH}$ or Cl_3CCOCl) was introduced into the catalyst system to form a new class of catalyst-system $\text{Ti}/\text{Mg}/\text{THF}/\text{improver}$. It was surprising to find that the activity enhancement due to the use of improver and SMR49-4049 appeared in the same catalyst. Thus the catalytic activity was further greatly increased, which reached five times the catalytic activity of catalyst based on the $\text{Ti}/\text{Mg}/\text{THF}$ catalyst system and SYLOPOL948; at the same time the MI of the polyethylene resin was also increased evidently. For example, for the catalyst prepared with TiCl_4 in Table 3, when $\text{Cl}_3\text{CCH}_2\text{OH}$ or Cl_3CCOCl was incorporated, the catalytic activity was increased from 3946 to 6667 and 6160 g/g cat, respectively; simultaneously the MI of the polyethylene resin was increased from 0.18 to 0.53 g/10 min. For the catalyst prepared with AA-grade TiCl_3 in Table 4, when $\text{Cl}_3\text{CCH}_2\text{OH}$ or Cl_3CCOCl was incorporated, the catalytic activity was increased from 2402 to 4955 and 4649 g/g cat, respectively; simultaneously the MI of the polyethylene resins was increased from 0.20 to 0.52 g/10 min. These results clearly showed that $\text{Cl}_3\text{CCH}_2\text{OH}$ and Cl_3CCOCl favor the increase of both activity and MI. Therefore new catalysts based on the new catalyst system $\text{Ti}/\text{Mg}/\text{THF}/\text{improver}$ and SMR49-4049 silica have very high catalytic activity and good hydrogen response.

TABLE 5

Investigation of Content of Catalyst Components Impregnated on Silica

Content (%)	Ti (%)	Activity (g/g cat)	BD (g/cm^3)
28	0.96	2879	0.36
33	1.16	3118	0.39
38	1.20	3681	0.37
43	1.42	4503	0.38
45	1.87	5130	0.39

Note. Catalyst preparation and evaluation conditions were the same as that in Table 3, except that AA-grade TiCl_3 was used instead of TiCl_4 . $\text{Cl}_3\text{CCH}_2\text{OH}/\text{Ti} = 2$.

In order to optimize the catalyst preparation and to search for an efficient way to regulate the catalytic activity, the amount of catalyst components impregnated on silica was investigated when AA-grade TiCl_3 was used and $\text{Cl}_3\text{CCH}_2\text{OH}/\text{Ti}$ molar ratio was 2. The experimental results were shown in Table 5 and Fig. 1.

Table 5 shows that with the increase in the content of the catalyst component from 28 to 45% gradually, Ti% was increased from 0.96 to 1.87%, and catalytic activity was increased from 2879 to 5130 g/g cat, showing that to increase the content of catalyst components impregnated on silica was a very efficient method to use to increase the catalytic activity.

Studies on Catalytic Polymerization Behaviors

In order to understand the catalyst more deeply, the catalytic polymerization behaviors were investigated by using the catalyst prepared with AA-grade TiCl_3 and $\text{Cl}_3\text{CCH}_2\text{OH}$ ($\text{Cl}_3\text{CCH}_2\text{OH}/\text{Ti} = 2$). The hydrogen response, the effect of polymerization temperature, and polymerization time were investigated. The experimental results were listed in Tables 6–8 and Figs. 2–4.

Table 6 and Fig. 2 show that with the increase in hydrogen pressure from 0.28 to 0.58 MPa, catalytic activity was decreased from 4515 to 1418 g/g cat. BD was also decreased, from 0.38 to 0.33 g/cm^3 , but MI was increased significantly, from 0.35 to 3.13 g/10 min, showing clearly that the catalyst has good hydrogen response. Table 7 and Fig. 3

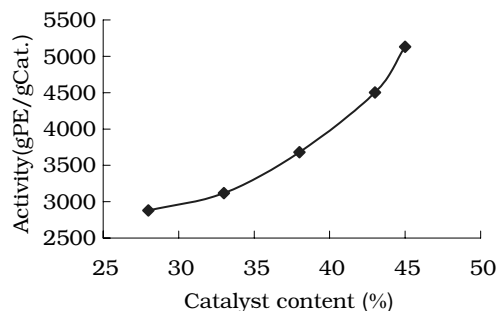


FIG. 1. The relationship between catalyst content and catalytic activity.

TABLE 6

Investigation of Hydrogen Response

P_{H_2} (MPa)	$P_{C_2H_4}$ (MPa)	Activity (g PE/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
0.28	0.75	4515	0.38	0.35	10.3	29.4
0.38	0.65	3211	0.35	1.00	27.5	27.5
0.48	0.55	2748	0.35	1.83	49.8	27.2
0.58	0.45	1418	0.33	3.13	78.5	25.3

Note. Slurry polymerization in 2-L autoclave; polymerization at 85°C for 2 h.

TABLE 7

Investigation of Polymerization Temperature

T (°C)	Activity (g PE/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
65	3702	0.34	0.05	2.15	43.0
75	3556	0.35	0.13	4.06	31.2
85	4515	0.38	0.35	10.3	29.4
95	2642	0.32	0.47	11.8	25.1

Note. Slurry polymerization in 2-L autoclave; polymerization for 2 h. Pressure of H₂ and C₂H₄ were 0.28 and 0.75 MPa, respectively.

TABLE 8

Investigation of Polymerization Time

Time (h)	Activity (g PE/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
1.0	2110	0.33	0.67	18.4	27.5
2.0	4515	0.38	0.35	10.3	29.4
2.5	5273	0.39	0.35	10.8	30.9

Note. Slurry polymerization in 2-L autoclave; polymerization at 85°C. Pressure of H₂ and C₂H₄ were 0.28 and 0.75 MPa, respectively.

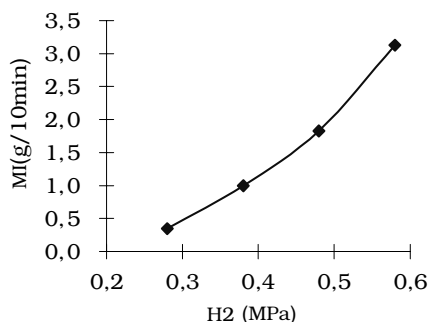


FIG. 2. The relationship between hydrogen pressure and MI.

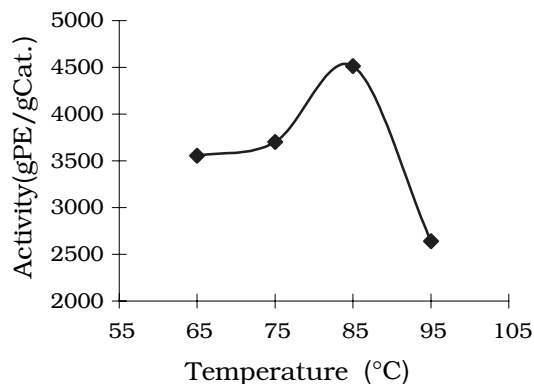


FIG. 3. The relationship between temperature and catalytic activity.

show that the catalytic activity and BD had a peak value at 85°C. High temperatures favor chain transformation, and therefore with the increase of temperature from 65 to 95°C, Mn was decreased and MI was increased from 0.05 to 0.47. Table 8 and Fig. 4 show that within 2.5 h, the reaction time and the catalytic activity almost had a linear relationship, indicating the catalytic activity is very uniform.

Catalyst Preparation by Reducing Titanium Tetrachloride with MgBu₂ In Situ to TiCl₃ (30)

Although the catalyst prepared with AA-grade TiCl₃ has high catalytic activity, excellent hydrogen response, and a good comonomer incorporation property, when it was used to catalyze the copolymerization of ethylene with high α -olefins, such as hexene-1 and octene-1, it was found that AA-grade TiCl₃ promoted the production of undesirable high hexane extractable content which influenced the production stabilization of the fluidized bed greatly (32, 33). This is believed to be caused by mixed crystal of TiCl₃ with AlCl₃, because AA-grade TiCl₃ contains 1/3 molar ratio AlCl₃. In order to overcome this defect, Jorgensen (32, 33)

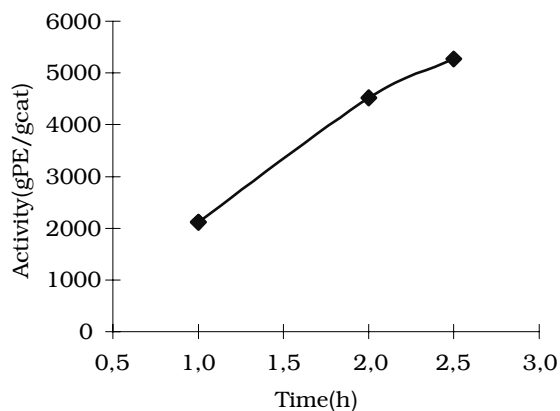


FIG. 4. The relationship between polymerization time and catalytic activity.

TABLE 9
Catalyst Preparation by Reducing TiCl₄ to TiCl₃ In Situ with MgBu₂^a

Run	Silica	Silica chemical treatment	Preparation of mother liquor	Ti (%)	Activity (g/g cat)	BD (g/cm ³)	Remarks
1	SMR49-4049	10 g dehydrated SiO ₂ , 6.1 ml AlEt ₃	1.42 g MgCl ₂ , 0.64 ml TiCl ₄ , 2.8 mmol MgBu ₂ , 142 ml THF	1.28	5770	0.36	High activity
2 ^b	SMR49-4049	10 g dehydrated SiO ₂ , 6.1 mmol AlEt ₃	1.42 g MgCl ₂ , 0.64 ml TiCl ₄ , 2.8 mmol MgBu ₂ , 142 ml THF	1.37	5349	0.34	High activity
3	SMR49-4049	10 g dehydrated SiO ₂ , 6.1 ml MgBu ₂	1.42 g MgCl ₂ , 0.64 ml TiCl ₄ , 2.8 mmol MgBu ₂ , 142 ml THF	1.40	4609	0.34	High activity
4	SMR49-4049	10 g dehydrated SiO ₂ , 6.1 ml AlEt ₃	1.74 g MgCl ₂ , 1.16 g AA-grade TiCl ₃ , 174 ml THF	1.14	4955	0.37	For comparison
5	SYLOPOL948	10 g dehydrated SiO ₂ , 6.1 mmol AlEt ₃	0.93 g MgCl ₂ , 0.4 ml TiCl ₄ , 1.8 mmol MgBu ₂ , 100 ml THF	1.22	3049	0.34	High activity
6	SYLOPOL948	10 g dehydrated SiO ₂ , 6.1 mmol AlEt ₃	1.1 g MgCl ₂ , 0.73 g AA-grade TiCl ₃ , 110 ml THF	0.90	1800	0.36	For comparison

^a In silica chemical treatment step: Cl₃CCH₂OH/Ti = 2. In catalyst prereduction step: AlEt₂Cl/THF = 0.45, Al(*n*-C₆H₁₃)₃/THF = 0.20. Catalyst evaluation: with slurry polymerization condition(II) described in experimental section.

^b In catalyst prereduction step: Cl₃CCH₂OH/Ti = 2.

prepared catalyst by reducing TiCl₄ with Mg powder *in situ* to TiCl₃; therefore AlCl₃ was not introduced to the final catalyst. When this catalyst was used to produce the copolymer of ethylene with hexene-1, the hexane extractable content was reduced significantly. This is very important for enhancing the production stabilization and the productivity of the fluidized bed. Therefore research for a highly active catalyst without AlCl₃ has great industrial significance.

In the literature (32, 33), it is pointed out that when dialkylmagnesium was used to reduce TiCl₄ to TiCl₃, undesirable chlorinated alkane was produced and it had to be separated out from the desired TiCl₃ product before it could be used. But in our research works, we found that monochloroalkane not only had no negative influence, but also it could promote catalytic activity; therefore to reduce TiCl₄ *in situ* to TiCl₃ with MgBu₂ is a good method to use to prepare catalyst without AlCl₃. The advantages are that by-products MgCl₂ and chlorobutane can be used *in situ*, and the residue of chlorobutane favors the increase of activity (30). The experimental results are listed in Table 9.

Table 9 shows that compared with the catalyst based on AA-grade TiCl₃, for the catalyst prepared by reducing TiCl₄ to TiCl₃ *in situ* by MgBu₂, both the catalytic activity and the percentage Ti were increased again. For the SYLOPOL948-supported catalyst, the catalytic activity was increased from 1800 to 3049 g/g cat. Percentage Ti was increased from 0.90 to 1.22%. For the SMR49-4049-supported catalyst, the catalytic activity was increased from 4955 to 5770 g/g cat. Percentage Ti was increased from 1.14 to 1.28%. Cl₃CCH₂OH can be incorporated into the silica chemical treatment step (run 1), or into the catalyst prereduction step (run 2), and in the silica chemical treatment step, AlEt₃ can be replaced by MgBu₂ (run 3). The final catalysts are all highly active. Therefore catalysts having highly catalytic activity and without AlCl₃ were prepared.

In order to investigate the effect of chloroalkane on catalytic polymerization, we selected the catalyst in Table 9, run 2, which has contained Cl₃CCH₂O⁻ of two molar ratio times of titanium and a small amount of chlorobutane. Slurry ethylene polymerization was performed with

TABLE 10
Investigation on the Effect of Added Chlorobutane on Catalytic Polymerization

No.	Chlorobutane/Ti molar ratio	Catalyst (mg)	Activity (g/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
1	0	37.8	5349	0.34	0.39	11.3	29.1
2	10	30.2	5979	0.35	0.50	14.1	28.3
3	50	24.9	5563	0.34	0.31	9.53	30.7
4	100	33.2	4988	0.32	0.30	8.27	27.6
5	200	23.8	5253	0.36	0.36	10.4	29.0

Note. Total pressure was 1.03 MPa. Polymerization was performed at 85°C for 2 h with 1 L hexane as diluent; 1 ml AlEt₃ solution (1 mmol/ml) was used as cocatalyst. Chlorobutane was made up to hexane solution (1 mmol/ml) before being used.

TABLE 11

Investigation of the Effect of Added Chlorocyclohexane on Catalytic Polymerization

No.	Chlorocyclohexane/Ti molar ratio	Catalyst (mg)	Activity (g/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
1	0	37.8	5349	0.34	0.39	11.3	29.1
2	5	29.8	5968	0.36	0.30	9.46	31.5
3	10	51.0	6907	0.36	0.83	23.4	28.2
4	20	19.5	7664	0.35	0.57	17.1	30.0
5	30	28.8	822	0.22	0.15	4.01	26.7

Note. Total pressure was 1.03 MPa. Polymerization was performed at 85°C for 2 h with 1 L hexane as diluent; 1 ml AlEt₃ solution (1 mmol/ml) was used as cocatalyst. Chlorocyclohexane was made up to hexane solution (1 mmol/ml) before being used.

added different amounts of different chloroalkanes, such as chlorobutane, chlorocyclohexane, or chlorobenzene, to investigate the influence of chloroalkane on catalytic polymerization. The experimental results are listed in Tables 10–12. Tables 10–12 show that under the condition that the catalyst has already contained Cl₃CCH₂O⁻ of two molar times of titanium and a small amount of chlorobutane, the addition of a small amount of chloroalkane increased the catalytic activity slightly. But monochloroalkane promotes the catalytic activity greatly for the catalyst without Cl₃CCH₂O⁻ or chloroalkane (22, 23). Table 11 also shows that too much chlorocyclohexane will decrease the catalytic activity and MI evidently. But even when a large amount of chlorobutane or chlorobenzene was added, there were no evident changes in activity and MI. The above description shows that the small amount of the by-product chloroalkane that formed in the reduction of TiCl₄ to TiCl₃ with dialkylmagnesium not only had no negative effect, but also it could promote catalytic activity.

For catalyst preparation by reducing TiCl₄ to TiCl₃ *in situ* with MgBu₂, in which Cl₃CCH₂OH was incorporated in the catalyst prereluction step, the amount of Cl₃CCH₂OH incorporated was investigated with SMR49-4049 and SYLOPOL948 as support. The experimental results are listed in Tables 13 and 14, respectively. In Table 13, for the SMR49-4049-supported catalyst, with the increase

in Cl₃CCH₂OH/Ti molar ratio from 0.5 to 4, first the activity was increased from 3057 to 5349 g/g cat. (Cl₃CCH₂OH/Ti = 2), and then the activity was decreased to 2396 g/g cat. In Table 14, for the SYLOPOL948-supported catalyst, with the increase in Cl₃CCH₂OH/Ti molar ratio from 1 to 4, first the activity was increased from 2540 to 3049 g/g cat. (Cl₃CCH₂OH = 2), and then the activity was decreased to 1949 g/g cat. This is coincident with the rule of the effect of Cl₃CCOCl shown in Table 2 and the rule of the effect of CHCl₃ added to titanium-based Ziegler–Natta catalyst (20). The above experimental results show clearly that suitable amounts of Cl₃CCH₂OH had a significant effect on catalytic activity, but too much Cl₃CCH₂OH restricted the catalytic activity, evidently. The optimized Cl₃CCH₂OH/Ti molar ratio was 2.

DISCUSSION

Heat Activation of Silica

As carrier, the granule performances and the flowing ability of silica decide the granule performances and the flowing ability of the prepared catalyst, and because the granule size and morphology of polyethylene powder is an enlarged replica of the corresponding catalyst, selection for suitable silica is very important for preparation of catalyst

TABLE 12

Investigation of the Effect of Added Chlorobenzene on Catalytic Polymerization

No.	Chlorobenzene/Ti molar ratio	Catalyst (mg)	Activity (g/g cat)	BD (g/cm ³)	MI (g/10 min)	FI (g/10 min)	MFR
1	0	37.8	5349	0.34	0.39	11.3	29.1
2	10	16.6	5885	0.34	0.36	12.1	33.5
3	30	13.3	5506	0.33	0.55	17.2	31.3
4	100	31.1	4190	0.32	0.33	9.21	27.9
5	300	27.2	4588	0.33	0.32	9.21	28.8

Note. Total pressure was 1.03 MPa. Polymerization was performed at 85°C for 2 h with 1 L hexane as diluent; 1 ml AlEt₃ solution (1 mmol/ml) was used as cocatalyst. Chlorobenzene was made up to hexane solution (1 mmol/ml) before being used.

TABLE 13
Investigation of the Effect of Cl₃CCH₂OH
for SMR49-4049-Supported Catalyst

Cl ₃ CCH ₂ OH ^a /Ti	Ti (%)	THF ^b (%)	Activity (g/g cat)	BD (g/cm ³)
0.5	1.33	17.5	3057	0.35
1	1.26	16.8	4408	0.36
2	1.37	17.4	5349	0.36
3	1.43	16.8	4350	0.31
4	1.35	16.4	2396	0.30

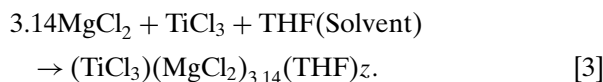
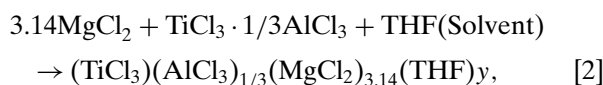
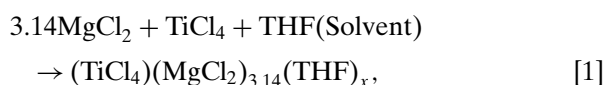
^a Added in catalyst prereduction step.

^b Product of step (iv).

having excellent granular performances. Both SMR49-4049 and SYLOPOL948 are spherical and have excellent flowing ability, providing a good basis for catalyst preparation. Silica has a plentiful hydroxyl group on the surface. Before silica can be used, most of the hydroxyl group must be gotten rid of, usually by dehydration at 200°C for 2 h and subsequently at 600°C for 4 h. The residual hydroxyl group is about 0.6 mmol/g SiO₂ (25, 26, 34). This dehydration process is called "silica heat activation." The residual hydroxyl group can be reacted with excess AlEt₃; this process is called chemical treatment to silica. The experimental results show that this favors high BD of polyethylene powder.

Preparation of the Catalyst Mother Liquor

By dissolving MgCl₂ and TiCl₃ together in THF, a complexation system was formed *in situ*:



In solution or solid state, the complexes in Eqs. [1]–[3] may be different. This difference will affect the catalyst

TABLE 14

Investigation of the Effect of Cl₃CCH₂OH for SYLOPOL948
Supported Catalyst

Cl ₃ CCH ₂ OH ^a /Ti	Ti (%)	THF ^b (%)	Activity (g/g cat)	BD (g/cm ³)
1	1.20	11.7	2540	0.37
2	1.22	13.3	3049	0.34
3	1.24	12.1	2969	0.35
4	1.10	11.8	1949	0.37

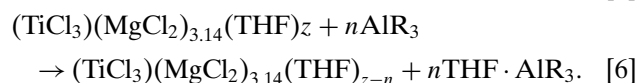
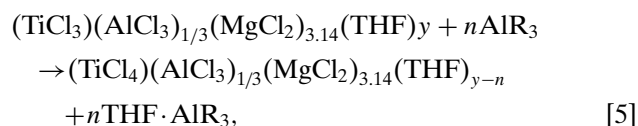
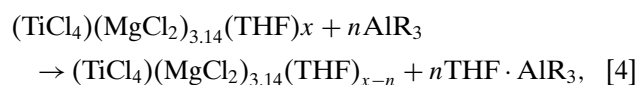
^a Added in catalyst prereduction step.

^b Product of step (iv).

properties directly. In solution, *x*, *y*, and *z* are all relatively big. This is because THF will occupy all the coordination sites of Ti, Mg, and Al together with Cl. In solid state, the percentage of THF is closely related to *x*, *y*, and *z*; therefore to control the percentage of THF in a suitable range is very important for catalyst preparation.

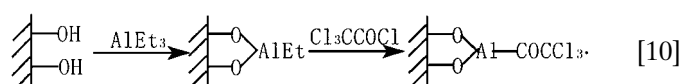
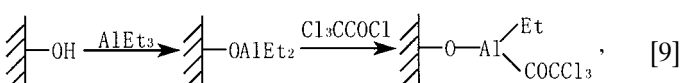
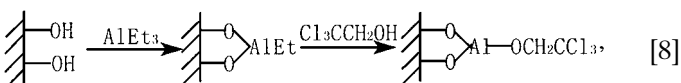
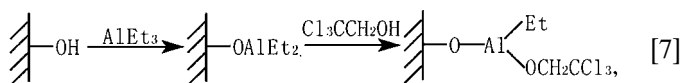
Prereduction of Catalyst

Prereduction of the catalyst with alkyl aluminum has at least two effects. First, it reduces Ti(IV) to Ti(III) so that the catalyst has very uniform activity to suit the fluidized bed to enhance production stabilization and favor the granule morphology of the produced polyethylene powder. Second, THF occupies the coordination sites of Ti to make Ti a center with no activity; alkyl aluminum can also coordinate with THF, and probably there exists a dynamic equilibrium in which Al and Ti compete for coordination of THF. Therefore some THF would be moved from the Ti center by alkyl aluminum, and the Ti center will exhibit high catalytic activity:



The Incorporation Method of Improver

The improver can be incorporated into the silica chemical treatment step after AlEt₃ is added and reacted for a period of time. Under this condition, the improver probably reacts with the residual AlEt group and thus bonds to silica (Eqs. [7]–[10] show the possible reactions):



The improver can also be incorporated into the catalyst prereduction step after Al(*n*-C₆H₁₃)₃ is added and reacted

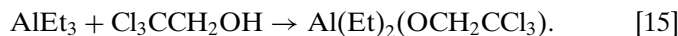
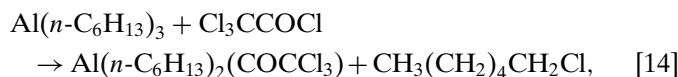
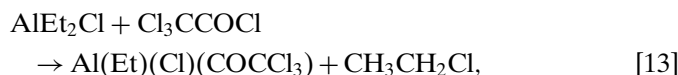
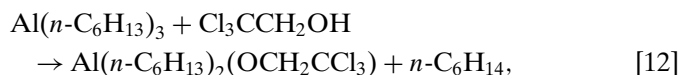
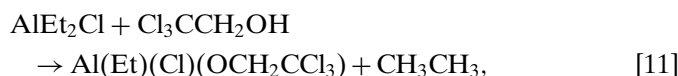
TABLE 15

Ethylene Polymerization Results of Three Different Catalysts with Modified Cocatalysts

Catalyst	Cocatalyst	Activity ($\times 10^4$ g/g Ti)	BD (g/cm ³)
TiCl ₄ /MgCl ₂ /THF/ SYLOPOL948 (2-5)	AlEt ₃	12.0	0.32
	Modified AlEt ₃	15.3	0.32
Ti/SiO ₂ (6, 7)	AlEt ₃	14.2	0.35
	Modified AlEt ₃	20.1	0.35
TiCl _n (OCH ₂ CH ₃) _{4-n} /MgCl ₂ , n = 1, 2	AlEt ₃	80	0.28
	Modified AlEt ₃	85	0.29

Note. With slurry polymerization conditions I.

for a period of time. The possible reactions are



The improver can also be added into the cocatalyst AlEt₃ to form a modified cocatalyst. For example, a desired amount of Cl₃CCH₂OH was added slowly to an AlEt₃ solution (1 mmol/ml) under stirring, and a quick exquisite heat-generation reaction occurred (see Eq. [15]). By controlling the amount of added Cl₃CCH₂OH, exactly 5% of AlEt₃ could be reacted and transferred to AlEt₂(OCH₂CCl₃). The polymerization results of three different titanium-based catalysts with the modified cocatalyst are listed in Table 15.

The Contributions of Improver to Catalyst Improvement

Tables 3 and 4 show clearly that the incorporation of improver increased the catalytic activity greatly and improved the hydrogen response evidently. The copolymerization of ethylene with butene-1 in a fluidized bed showed that the catalyst also had a good comonomer incorporation property. Therefore the synthetical property of the new catalyst is excellent.

Actually, the incorporation of the improver formed a new catalyst system, Ti/Mg/THF/Cl₃CCH₂OH or Ti/Mg/THF/Cl₃CCOCl. Impregnation of this new catalyst system in silica with excellent granule morphology formed a new kind of catalyst having high catalytic activity, excellent hydrogen response, and a comonomer incorporation property; therefore it has great significance in industrial application.

Investigation of Catalyst Formation Process

In fact, ethylene polymerization performed on the surface and in the pore of silica; therefore the surface area and the pore of the catalyst will affect catalyst performances directly. In particular the diameter of the pore could affect the catalytic activity and MI of polyethylene by affecting the diffusion of ethylene. Therefore the solid products of the four steps in catalyst preparation were followed, and the surface area, pore volume, and pore diameter were characterized. The results are listed in Table 16.

Table 16 shows that after chemical treatment of silica with AlEt₃, the pore diameter of both SMR49-4049 and SYLOPOL948 were enlarged evidently (for SMR49-4049, from 20.3 to 26.2 nm; for SYLOPOL948, from 25.3 to 34.9 nm). Probably this change was caused by the reaction of AlEt₃ with a silicon-hydroxyl group. After the catalyst was prereduced, the pore diameters of the catalysts based on both SMR49-4049 and SYLOPOL948 were also enlarged significantly (for the catalyst based on SMR49-4049, from 17.5 to 26.4 nm; for the catalyst based on SYLOPOL948, from 27.6 to 45.2 nm). Probably this change was caused by the coordination of the alkyl-aluminum with THF. These

TABLE 16

The Changes of Solid Properties in Catalyst Preparation Process

Items	Silica grade	Dehydrated SiO ₂	Chemically treated SiO ₂	Impregnated catalyst	Prereduced catalyst
Total intrusion volume (ml/g)	SMR49-4049	3.34	4.18	3.02	2.41
	SYLOPOL948	3.73	4.07	2.45	1.72
Total pore area (m ² /g)	SMR49-4049	658	639	690	364
	SYLOPOL948	590	466	356	153
Median pore diameter (volume) (nm)	SMR49-4049	838.2	2929.0	617.8	761.2
	SYLOPOL948	416.7	10616.5	9022.5	11802.1
Median pore diameter (area) (nm)	SMR49-4049	4.9	5.3	5.1	5.9
	SYLOPOL948	9.1	9.0	9.3	11.4
Average pore diameter (4 V/A) (nm)	SMR49-4049	20.3	26.2	17.5	26.4
	SYLOPOL948	25.3	34.9	27.6	45.2

results probably showed that alkyl-aluminum has a pore-enlargement function for silica and for the catalyst. The pore enlargement of silica favors the impregnation of a catalyst component on silica. The pore enlargement of catalyst favors the activity improvement.

Table 16 also shows that the pore volume and surface area of the catalyst based on SMR49-4049 are bigger than that of the catalyst based on SYLOPOL948 ($2.41 > 1.72$ ml/g, $364 > 153$ m²/g). Probably this is one reason why the catalyst based on SMR49-4049 has much higher activity than the catalyst based on SYLOPOL948. The pore diameter of the catalyst base on SMR49-4049 is smaller than that of the catalyst based on SYLOPOL948 ($26.4 < 45.2$ nm); therefore the catalyst Ti/Mg/THF/SMR49-4049 has a lower hydrogen response than catalyst Ti/Mg/THF/SYLOPOL948 (30). Therefore Cl₃CCH₂OH must be incorporated; then the catalyst Ti/Mg/THF/Cl₃CCH₂OH/SMR49-4049 has not only high catalytic activity but also a good hydrogen response; thus it has significant value in industrial application.

CONCLUSIONS

1. Highly active silica-supported titanium-based Ziegler-Natta catalysts based on a new catalyst system, Ti/Mg/THF/improver with SMR49-4049 and SYLOPOL948 as carriers, were prepared and studied. These new catalysts include the following:

Ti/Mg/THF/improver/SYLOPOL948 catalyst.

Ti/Mg/THF/improver/SMR49-4049 catalyst.

Ti/Mg/THF/improver/SYLOPOL948 catalyst without AlCl₃.

Ti/Mg/THF/improver/SMR49-4049 catalyst without AlCl₃.

Compared with the reported corresponding catalyst based on the three-component-catalyst-system Ti/Mg/THF, new catalysts incorporated with improver had increased catalytic activity, improved hydrogen response, and a good comonomer incorporation property. The synthetical performance was excellent. In particular the catalyst based on the new catalyst system and SMR49-4049 silica had very high catalytic activity; at the same time the catalyst had also an excellent hydrogen response and comonomer incorporation property.

2. Improver Cl₃CCH₂OH at least had two effects. First, it increased the catalytic activity and, second, it improved the hydrogen response.

3. The optimized improver/Ti molar ratio was 2, including Cl₃CCH₂OH and Cl₃CCOCl. At this point the improver had the best activity promotion effect. When improver/Ti molar ratio was under 2, the catalytic activity was increased with an increase in improver/Ti molar ratio; when improver/Ti molar ratio was above 2, the catalytic activity decreased with an increase in improver/Ti molar ratio. This

rule is coincident with that of CHCl₃ added to polymerization.

4. It is proved that a highly efficient catalyst without AlCl₃ can be prepared by reducing TiCl₄ to TiCl₃ *in situ* with MgBu₂; the catalytic activity and Ti content were increased further compared with the catalyst prepared with AA-grade TiCl₃.

5. Improver Cl₃CCH₂OH can also be used to modify the cocatalyst AlEt₃. With the modified cocatalyst, the catalytic activity of the titanium-based Ziegler-Natta catalyst was increased evidently.

6. In the silica chemical treatment step, AlEt₃ had a pore-enlargement function. For SMR49-4049 silica, the average pore diameter was enlarged from 20.3 to 26.2 nm, while the pore volume was also increased, from 3.34 to 4.18 ml/g. For SYLOPOL948 silica, the average pore diameter was enlarged from 25.3 to 34.9 nm, while the pore volume was also increased, from 3.73 to 4.07 ml/g. These results favor the impregnation of the catalyst component on silica.

7. In the catalyst prerduction step, AlEt₂Cl and Al(*n*-C₆H₁₃)₃ also had a pore-enlargement function. For the catalyst based on SMR49-4049 silica, the average pore diameter was enlarged from 17.5 to 26.4 nm; for the catalyst based on SYLOPOL948 silica, the average pore diameter was enlarged from 27.6 to 45.2 nm. These results favor high activity and a hydrogen response.

8. Compared with the Ti/Mg/THF/SYLOPOL948 catalyst, the catalyst Ti/Mg/THF/improver/SMR49-4049 had much higher catalytic activity. This was probably caused by three main factors: first, the increase in catalyst component content from ~28 to ~38%; second, the promotion of improver; third, the increase in pore volume and surface area from 1.72 and 153 m²/g (catalyst based on SYLOPOL948) to 2.41 and 364 m²/g (catalyst based on SMR49-4049). In conclusion, the high activity of the catalyst Ti/Mg/THF/improver/SMR49-4049 was the synergism of the above described three factors.

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