

# Preparation of spherical $\text{MgCl}_2$ supported bis(imino)pyridyl iron(II) precatalyst for ethylene polymerization

Rubin Huang<sup>a, 1</sup>, Dongbing Liu<sup>a</sup>, Shibo Wang<sup>a, b</sup>, Bingquan Mao<sup>a, \*</sup>

<sup>a</sup> Polyolefin National Engineering and Research Center, Beijing Research Institute of Chemical Industry (BRICI),  
China Petroleum and Chemical Corporation, Beijing 100013, PR China

<sup>b</sup> Science College, Beijing University of Chemical Technology, Beijing 100029, PR China

Received 28 September 2004; received in revised form 26 January 2005; accepted 2 February 2005

## Abstract

The immobilization of the soluble precatalysts  $[(\text{ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ , where Ar = 2,4,6-trimethylphenyl (A) or 2,6-diisopropylphenyl (B), on supports derived from a spherical  $\text{MgCl}_2$ -alcohol adduct yields active supported systems for ethylene polymerization. The activity of the supported catalysts and the resultant polymer properties are strongly dependent on the method of preparation. The highest activities are obtained using supports obtained by pretreatment of the  $\text{MgCl}_2$ -alcohol adduct with triethylaluminium (TEA). In addition, it was found that precatalyst A, having less steric bulk at the *ortho*-aryl position of the ligand, gave higher activity than precatalyst B, in line with the different behaviours of these precatalysts in homogeneous polymerization, while precatalyst B gave polyethylene with lower polydispersity. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Precatalyst A; Precatalyst B; Ethylene polymerisation; TEA

## 1. Introduction

In 1998, Brookhart and co-workers [1] and Gibson and co-workers [2–5] independently described olefin polymerization and oligomerization catalyzed by the well-known class of compounds [6], diiminopyridine complexes of iron and cobalt, with an activator, such as methylaluminoxane (MAO) [7–10]. Common alkylaluminium compounds, such as triisobutylaluminium (TIBA) and triethylaluminium (TEA) have also been used as activators [11,12] for homogeneous catalysts in ethylene polymerization. However, the practical use of homogeneous catalyst systems in slurry or gas phase polymerization processes is generally limited by the lack of control over polymer morphology, reactor fouling and short catalyst lifetimes.

These shortcomings can be avoided by catalyst immobilization on a suitable support. Significant efforts have been made to support homogeneous metallocene catalysts on inorganic (most often silica) or polymeric materials [13–17]. Late transition metal catalysts have also been supported using silica [18] and silica–alumina derivatives [19]. Recently, however, several groups have investigated the use of magnesium chloride either as support or as activator for various single-site catalysts, including both early and late transition metal systems [20–22]. We have recently reported that supported iron catalysts, using TEA-treated spherical  $\text{MgCl}_2$  as support, had high activity in a slurry process for ethylene polymerization, while the morphologies of the resulting polyethylene particles strongly depended on the supported catalyst preparation procedure and the polymerization conditions [23].

The previous studies were carried out using  $[(\text{ArN}=\text{C}(\text{Me}))_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$  (Ar = 2,4,6-trimethylphenyl) as precatalyst component. In the present work, we have used both this component, denoted precatalyst A, and a more sterically hindered component, precatalyst B, in which Ar = 2,6-diisopropylphenyl. Different methods of supporting these

\* Corresponding author. Fax: +86 10 64228661.

E-mail address: [maobingquan@brici.ac.cn](mailto:maobingquan@brici.ac.cn) (B. Mao).

<sup>1</sup> Present address: Dutch Polymer Institute/Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

iron precatalysts on thermally pretreated and TEA-pretreated spherical  $\text{MgCl}_2$  supports have been investigated, along with the effects of different aluminium alkyls in ethylene polymerization with these systems. In addition, the supports used have been characterized by X-ray diffraction, both before and after immobilization of the precatalyst.

## 2. Experimental

### 2.1. Materials

Triethylaluminium (TEA) was purchased from Witco, and diluted to a 2.0 M solution in hexane before use. The spherical  $\text{MgCl}_2$ -alcohol adduct support precursor of composition  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  was prepared according to the literature [24]; the average particle diameter was 59.6  $\mu\text{m}$ . Precatalysts A and B (Scheme 1) were prepared according to literature procedures [5]. Ethylene (polymer grade) was obtained from the Yanshan Petrochemical Corporation, Beijing, China. Hexane and toluene were purified by refluxing over sodium and distilled under nitrogen prior to use.

### 2.2. Catalyst preparation

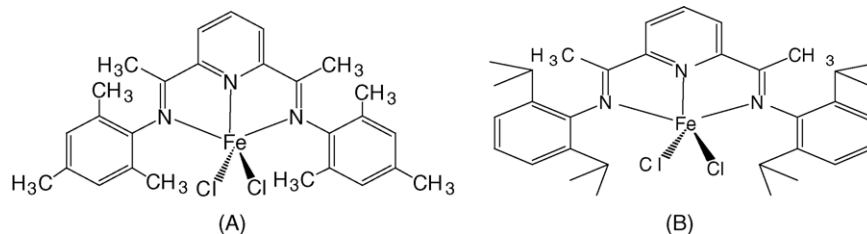
All manipulations involving air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques.

#### 2.2.1. Preparation of supported catalyst A-1 (SCA-1)

The spherical  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  adduct was first thermally pretreated at 100 °C under nitrogen for 4 h. An amount of 15 mL of a toluene solution of precatalyst A ( $[\text{A}] = 0.01 \text{ M}$ , corresponding to 0.2 wt.% Fe/support) was added over 30 min to a slurry of the thermally pretreated support (4 g) in 40 mL toluene at room temperature. After reaction for 4 h, the slurry was filtered through a fritted disk. The resultant solids were washed several times with toluene until the liquid phase was colourless. The solid catalyst was dried under  $\text{N}_2$  until free flowing conditions were reached.

#### 2.2.2. Preparation of supported catalyst B-1 (SCB-1)

SCB-1 was prepared similarly, according to the procedure for catalyst SCA-1, using a toluene solution of precatalyst B.



Scheme 1. Structures of bis(imino)pyridyl iron(II) catalysts.

#### 2.2.3. Preparation of supported catalyst A-2 (SCA-2)

SCA-2 was prepared using previously described methods [23]. Typically, 20 mL of a 2 M solution of  $\text{AlEt}_3$  in hexane was added over a period of 60 min to a slurry of 4.93 g spherical  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  adduct in 40 mL hexane at  $-60^\circ\text{C}$ . Reaction was continued at  $-60^\circ\text{C}$  for 4 h, after which the slurry was filtered under  $\text{N}_2$  and the solid was washed with  $2 \times 20 \text{ mL}$  *n*-hexane and dried under  $\text{N}_2$ . The resultant powder was slurried in 20 mL toluene at 20 °C and a solution of precatalyst A (97.4 mg) in toluene (18.5 mL) was added over a period of 30 min. After stirring for 4 h at 20 °C, the liquid phase was removed and the solid residue was washed with toluene until the liquid phase was colourless. The solid catalyst was dried under  $\text{N}_2$  until free flowing.

#### 2.2.4. Preparation of supported catalyst B-2 (SCB-2)

SCB-2 was prepared similarly according to the procedure of SCA-2, using precatalyst B.

#### 2.2.5. Preparation of supported catalyst A-3 (SCA-3)

SCA-3 was prepared using previously described methods [23]. The spherical  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  adduct was first thermally pretreated at 100 °C under  $\text{N}_2$  for 4 h. Subsequent reaction with  $\text{AlEt}_3$  at  $-60^\circ\text{C}$ , followed by the catalyst immobilization, was carried out as described for SCA-2.

#### 2.2.6. Preparation of supported catalyst A-4 (SCA-4)

SCA-4 was prepared using the same method as that described for SCA-3, but the thermal pretreatment of the  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  adduct was carried out at 130 °C.

### 2.3. Polymerization reactions

The polymerization of ethylene was performed in hexane slurry in a stainless steel autoclave (2 L capacity) equipped with gas ballast through a solenoid valve for continuous feeding of ethylene at constant pressure. Purified hexane (1 L) was transferred to the reactor under nitrogen atmosphere. The required amounts of cocatalyst ( $\text{AlR}_3$ ) and the suspension of supported catalysts were injected into the reactor using a syringe. After the set temperature was reached, the reactor was pressurized with ethylene to initiate the polymerization for a set reaction time. At the end of the reaction, ethylene pressure was released and the granular polyethylene was separated.

rated from the reaction mixture by filtration and dried in an oven under N<sub>2</sub>.

#### 2.4. Characterization of supported catalysts and polyethylene

The morphologies of the catalysts and PE particles were examined in a JSM-35C SEM and Cambridge S-250MK3 SEM. Elemental analysis was performed with an ICP–AES. Powder X-ray diffraction (XRD) patterns of the supports and supported catalysts were obtained with a Rigaku D/max 2500 VB2+/PC n instrument equipped with a source using a Cu anode, operating at 40 kV and 200 mA for Cu  $\kappa_1$  radiation. The dried sample was covered with a thin PE film to avoid contact with air and moisture. The diffraction pattern was recorded in the range,  $5^\circ < 2\theta < 60^\circ$ . Weight-average ( $\bar{M}_w$ ), number-average ( $\bar{M}_n$ ) molecular weights and molecular weight distributions ( $\bar{M}_w/\bar{M}_n$ , PDI) of the PE were measured by means of gel permeation chromatography on a PL-GPC 220 at 150 °C with 1,2,4-C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> as the eluant. Melting points of the polymers were obtained on a Perkin-Elmer DSC-7 in the standard DSC run mode. The instrument was initially calibrated for the melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample, about 5 mg, was firstly equilibrated at 0 °C, and then heated to 160 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled down to 0 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min.

### 3. Results and discussion

#### 3.1. Effect of the preparation route on the catalytic activity and polymer properties

It is well known that different preparation routes in supporting homogeneous catalysts have a great influence on catalytic activity and polymer properties. Table 1 presents the iron, aluminium and magnesium loadings on the different immobilized systems used in the present work. The results indicate that the preparation route has a remarkable effect on

Table 1  
Al, Mg and Fe loading on the supported catalyst

Catalyst	Al (wt.%)	Mg (wt.%)	Fe (wt.%)
SCA-1	–	32.30	0.27
SCB-1	–	47.03	0.16
SCA-2 <sup>a</sup>	4.76	15.30	0.30
SCB-2	4.40	16.80	0.29
SCA-3 <sup>a</sup>	0.92	16.04	0.23
SCA-4	0.51	18.30	0.15

<sup>a</sup> Reported previously [23].

the metal loadings. It is also apparent that a lower Al loading contributes to a lower Fe loading. The results of ethylene polymerization using the supported catalysts are summarized in Table 2, which reveals that the activities obtained with precatalyst A were higher than those obtained with precatalyst B. These differences are in line with the relative activities of these catalysts under homogeneous polymerization conditions after activation with MAO [5]. The data in Table 2 also indicate broader molecular weight distributions for the polymers prepared using precatalyst A. The highest activities were obtained with supports which had undergone both thermal pretreatment and a pretreatment with TEA prior to contact with the precatalyst, but reasonable activity was obtained with only a thermal pretreatment of the support. X-ray diffraction studies indicated (vide infra) the presence of some residual ethanol in the support after thermal pretreatment at 100 °C, but evidently this did not lead to excessive deactivation of the catalyst. This might be due to the relatively low oxophilicity of late-transition metals, such as iron, making such systems more robust than catalytic systems based on titanium, zirconium or other early-transition metal precatalysts. In any case, subsequent contact with TEA before polymerization will result in the conversion of residual ethanol to alkylaluminium ethoxide species. Supports prepared by in situ reaction of an aluminium alkyl with an adduct of MgCl<sub>2</sub> and 2-ethyl-1-hexanol have been shown to be effective for immobilization and activation of various single-site olefin polymerization precatalysts [20,25].

#### 3.2. Effect of cocatalyst

Table 3 presents the results of ethylene polymerizations with SCA-1 using different cocatalysts. The order of cata-

Table 2  
Ethylene polymerization using supported catalysts<sup>a</sup>

Entry	Catalyst	Charge (mg)	Activity (g(PE)/g(cat) h)	Activity (kg(PE)/g(Fe) h)	Bulk density (g/mL)	$\bar{M}_w (\times 10^{-4})$	PDI	$T_m$ (°C)
1	SCA-1	116	1877	695	0.29	47.0	15.0	136.2
2	SCB-1	149	431	270	0.31	73.9	8.5	136.0
3 <sup>b,c</sup>	SCA-2	38	2429	810	0.30	43.9	17.2	136.5
4 <sup>d</sup>	SCB-2	106	786	271	0.25	38.8	5.9	135.7
5 <sup>b,c</sup>	SCA-3	31	4895	2128	0.28	48.1	13.0	136.4
6 <sup>b</sup>	SCA-4	70	1156	770	0.34	58.3	14.5	136.4

<sup>a</sup> Polymerization conditions: ethylene pressure = 1.0 MPa, temperature = 70 °C, time = 1 h, Al/Fe (mol/mol) = 500, solvent = 1 L hexane, TEA as the scavenger and alkylating reagent.

<sup>b</sup> Polymerization time = 2 h, other conditions unchanged.

<sup>c</sup> Reported previously [23].

<sup>d</sup> Al/Fe (mol/mol) = 150, other conditions unchanged.

Table 3  
Ethylene polymerization using supported catalyst SCA-1<sup>a</sup>

Entry	Charge (mg)	Cocatalyst	Activity (g(PE)/g(cat) h)	Activity (kg(PE)/g(Fe) h)	Bulk density (g/mL)	$\bar{M}_w (\times 10^{-4})$	PDI	$T_m$ (°C)
1	116	AlEt <sub>3</sub>	1877	695	0.29	47.0	15.0	136.2
2	140	Al <sup>i</sup> Bu <sub>3</sub>	1365	506	0.28	40.1	17.4	135.9
3	128	AlEt <sub>3</sub>	980	363	0.25	45.5	19.1	135.9
4 <sup>b</sup>	124	AlEt <sub>3</sub>	2701	1000	0.28	40.4	18.6	135.5
5 <sup>c</sup>	123	AlEt <sub>3</sub>	2239	829	0.27	35.2	16.6	135.5

<sup>a</sup> Polymerization conditions: ethylene pressure = 1.0 MPa, temperature = 70 °C, time = 1 h, Al/Fe (mol/mol) = 500, solvent = 1 L hexane.

<sup>b</sup>  $P_{H_2}/P_{C_2H_4}$  (MPa/MPa) = 0.05/0.95, other conditions unchanged.

<sup>c</sup> 1-hexene = 5 mL, other conditions unchanged.

lyst activity with the different alkylaluminiums used is as follows: AlEt<sub>3</sub> > Al<sup>i</sup>Bu<sub>3</sub> > AlEt<sub>3</sub>. Broad polyethylene molecular weight distributions, illustrated in Fig. 1, are obtained in each case, but there is no evidence of the formation of the very low molecular weight fraction obtained in homogeneous polymerization [23]. Iron-catalyzed ethylene polymerization using homogeneous systems typically gives a bimodal polymer molecular weight distribution, the formation of the low molecular weight fraction being ascribed to chain transfer to aluminium [1,5], although it has been reported [26] that the use of TIBA can give polyethylene with relatively narrow molecular weight distribution.

Table 3 also contains the results of ethylene polymerizations carried out in the presence of either hydrogen or a small quantity of 1-hexene. It has been reported that the addition of hydrogen to the iron-catalyzed polymerization can lead to significant increases in catalyst activity but has relatively little effect on polymer molecular weight [27,28]. This is also apparent on comparing entries 1 and 4 in Table 3. A significant increase in activity is also observed when polymerization is carried out in the presence of a small quantity of 1-hexene. Entry 5 in Table 3 reveals that the increase in activity was not accompanied by any significant decrease in the  $T_m$  of the resulting polymer. This indicates a low copolymerization ability of this catalyst system, although comonomer incorporation in ethylene/1-hexene copolymerization using iron catalysts has been reported [29]. The origin of the comonomer

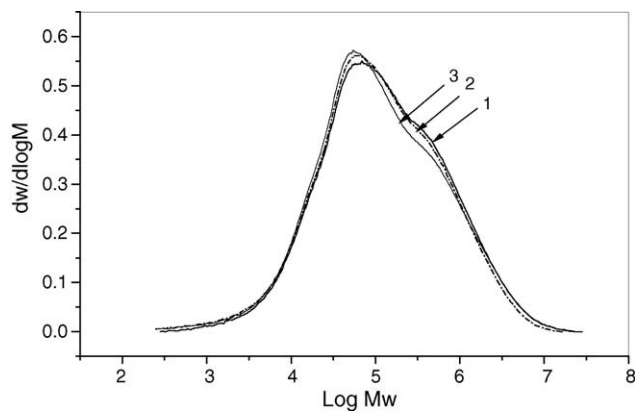


Fig. 1. GPC curves of PE prepared with SCA-1 with different cocatalysts. (1) cocatalyst = AlEt<sub>3</sub>; (2) cocatalyst = Al<sup>i</sup>Bu<sub>3</sub> and (3) cocatalyst = AlEt<sub>3</sub> (numbers of the curves correspond to entries in Table 3).

activation effect observed in the present work is as yet unclear; the high melting point of the polymer gives no indication that the increased activity arises from easier monomer diffusion through a less crystalline polymer.

In a previous study, we reported that the spherical morphology of the starting support material was retained after pretreatment with TEA, subsequent contact with the precatalyst leading to uniform distribution of Al and Fe throughout the particle [23]. Retention of morphology was also obtained in the thermally pretreated support used in the present work for the systems SCA-1 and SCB-1. The morphology of the support after thermal pretreatment at 100 °C is shown in Fig. 2a. A rough and porous surface of the pretreated support, beneficial for catalyst immobilization, is apparent at higher magnification (Fig. 2b). Similar spherical morphologies are apparent for the immobilized catalyst (Fig. 2c) and the resulting polyethylene (Fig. 2d), confirming that the morphology of the starting support has been replicated during the polymerization.

### 3.3. Effect of polymerization temperature

Previous results with the system SCA-2 showed that high catalyst activities could be obtained at a polymerization temperature of 50 or 70 °C, the activity decreasing when the temperature was raised to 85 °C [23]. The results in Table 4 indicate similar effects for the supported catalyst SCB-2, the main differences with the previously reported catalyst SCA-2 being the lower activities and the narrower polymer molecular weight distributions. It is also apparent, as shown in Fig. 3, that increasing polymerization temperature resulted in a lowering in molecular weight and a broadening in molecular weight distribution. The lower activities obtained with catalyst SCB-2, as opposed to SCA-2, reflect the effect of changes in the ligand environment around the metal centre in the precatalyst, an increase in steric bulk at the *ortho* positions of the aryl ring attached to the imino nitrogens generally resulting in decreased activity and increased polymer molecular weight [5].

### 3.4. Support characterization using X-ray diffraction

Anhydrous MgCl<sub>2</sub> has a cubic close packing structure which gives a strong X-ray diffraction pattern at  $2\theta = 15^\circ, 35^\circ$

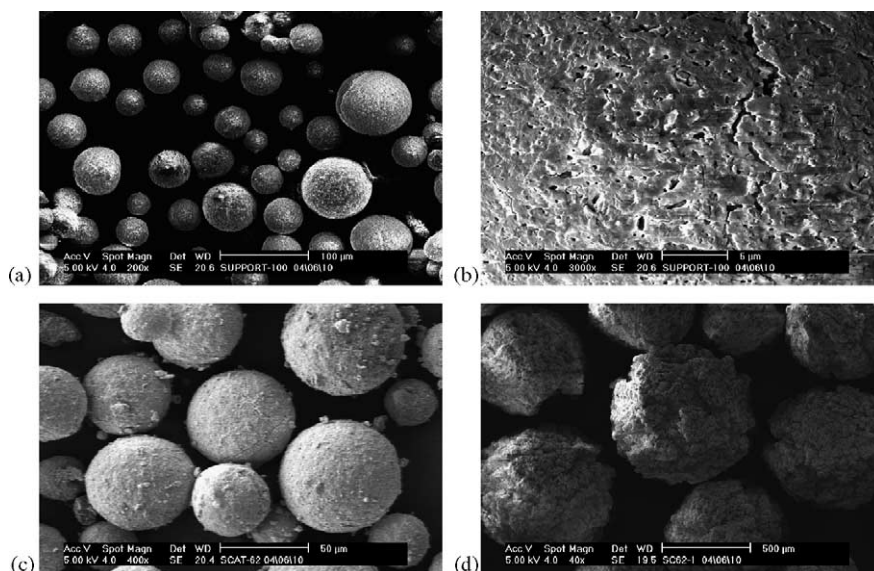


Fig. 2. SEM images of: (a) the support thermally pretreated at 100 °C, magnification 200×; (b) the same support, magnification 3000×; (c) supported catalyst SCA-1, magnification 400× and (d) the resulting polyethylene, entry 1 in Table 3, magnification 40×.

and 50°; the XRD patterns of magnesium chloride supports vary depending on their composition and method of preparation [30–32]. Characterization by X-ray powder diffraction of a number of adducts of magnesium chloride and ethanol has been described by Bart and Roovers [33], while Sozani et al. [34] have recently reported the use of advanced solid-state NMR techniques to determine the various components present in  $\text{MgCl}_2 \cdot n\text{EtOH}$  adducts. The XRD pattern of the starting  $\text{MgCl}_2 \cdot 2.56\text{C}_2\text{H}_5\text{OH}$  support used in the present work is shown in Fig. 4, along with the XRD patterns obtained after thermal and TEA pretreatments of the support. It is evident that the diffraction pattern of the starting support is more complicated than those of the thermally and TEA-treated supports and those of the supported catalysts. In the case of the support subjected to thermal pretreatment at 100 °C under a flow of nitrogen, the XRD pattern reflects substantial dealcoholation of the original support.  $\text{MgCl}_2 \cdot n\text{EtOH}$  adducts are known to undergo progressive loss of ethanol on heating [33]. Compared to the support pretreated at 100 °C, the diffraction pattern of the support pretreated with TEA at –60 °C, with broad peaks at  $2\theta = 9.47^\circ$ ,  $30.1^\circ$  and  $50.4^\circ$ , is more similar to that of activated magnesium chloride com-

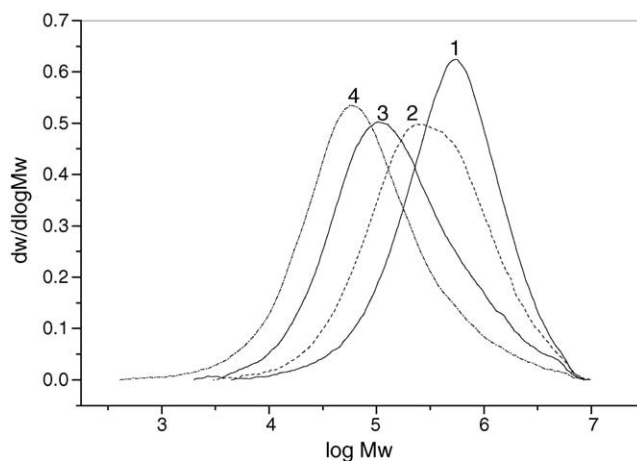


Fig. 3. GPC curves of PE prepared with SCB-2 at various temperatures ( $T$ ). (1) 30 °C; (2) 50 °C; (3) 70 °C and (4) 85 °C (numbers of the curves correspond to entries in Table 4).

monly used as a support material in Ziegler–Natta catalysts [35]. An irregular structure, high porosity and small primary crystallite size will be beneficial for effective catalyst immobilization. The similarity of the XRD patterns before

Table 4  
Ethylene polymerization using supported catalyst SCB-2<sup>a</sup>

Entry	Charge (mg)	Temperature (°C)	Activity (g(PE)/g(cat) h)	Activity (kg(PE)/g(Fe) h)	Bulk density (g/mL)	$\bar{M}_w$ ( $\times 10^{-4}$ )	PDI	$T_m$ (°C)
1	110	30	199	69	0.21	80.3	3.58	136.2
2	112	50	890	307	0.24	60.8	4.60	136.4
3	106	70	786	271	0.25	38.8	5.90	135.7
4	109	85	354	122	0.15	22.7	7.48	134.7
5 <sup>b</sup>	–	35	–	85	–	64.7	107	–

<sup>a</sup> Polymerization conditions: ethylene pressure = 1.0 MPa, time = 1 h, solvent = 1 L hexane, cocatalyst =  $\text{AlEt}_3$ ,  $\text{Al/Fe}$  (mol/mol) = 150.

<sup>b</sup>  $[\text{Fe}] = 1.07 \times 10^{-5}$  M,  $\text{Al/Fe}$  (mol/mol) = 200,  $P = 0.1$  MPa,  $t = 30$  min, using homogeneous catalyst.

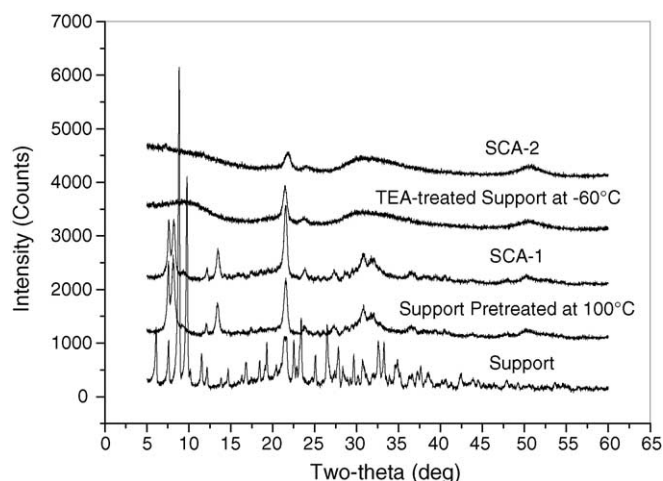


Fig. 4. XRD patterns of support, treated support and supported catalysts.

and after catalyst immobilization indicates that little change takes place during the process of supporting the iron complex.

#### 4. Conclusions

We have developed novel spherical  $\text{MgCl}_2$ -supported iron-based catalyst systems for ethylene polymerization, without the use of MAO or borate activators, starting from an adduct of magnesium chloride and ethanol. The particle morphology of the original support is retained and replicated throughout the supported catalyst preparation and ethylene polymerization, giving spherical polymers with high bulk density. The method of preparing the supported catalyst has a great influence on catalytic activity and polymer properties. An increase in steric bulk around the metal centre in the iron precatalyst leads to reduced polymerization activity, as is also observed in homogeneous polymerization, but the activities of the  $\text{MgCl}_2$ -immobilized systems are much higher than those of their homogeneous counterparts. The molecular weight distribution of PE produced with the immobilized systems was dependent on the catalyst and was narrowest when a sterically hindered precatalyst was used. The pronouncedly bimodal MWD obtained in homogeneous polymerization was not apparent after catalyst immobilization. Further studies, including elucidation of the supporting mechanism and an extension of the use of spherical  $\text{MgCl}_2$  as support for the immobilization of other single-site catalysts, are in progress.

#### Acknowledgements

Financial support from the State Key Fundamental Research Project of China (G1999064801) is appreciated. In

addition, the authors thank Dr. J.C. Chadwick of DPI for valuable suggestions and assistance with the manuscript.

#### References

- [1] B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* 120 (1998) 4049.
- [2] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, *Chem. Commun.* (1998) 849.
- [3] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem.* 111 (1999) 448.
- [4] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428.
- [5] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, *J. Am. Chem. Soc.* 121 (1999) 8728.
- [6] E.C. Alyea, P.H. Merrell, *Synth. React. Inorg. Chem.* 4 (1974) 535.
- [7] A. Koppl, H.G. Alt, S.J. Palackal, M.B. Welch, US patent 6,458,905 (2002), Phillips Petroleum Co.
- [8] A. Andresen, H.G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.J. Vollmer, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 630.
- [9] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* 18 (1980) 99.
- [10] H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, US patent 4,404,344 (1983), BASF AG.
- [11] L.C. Simon, R.S. Manler, R.F. Souza, *J. Polym. Sci., Part A: Polym. Chem.* 37 (1999) 4656.
- [12] Q. Wang, H.X. Yang, Z.Q. Fan, *Macromol. Rapid Commun.* 23 (2002) 639.
- [13] J.C.W. Chien, D.W. He, *J. Polym. Sci., Part A: Polym. Chem.* 29 (1991) 1603.
- [14] G.G. Hlatky, *Chem. Rev.* 100 (2000) 1347.
- [15] G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* 100 (2000) 1377.
- [16] F. Ciardelli, A. Altomare, M. Michelotti, *Catal. Today* 41 (1998) 149.
- [17] M. Kanminaka, K. Soga, *Polymer* 33 (1992) 1105.
- [18] Z. Ma, W.H. Sun, N. Zhu, Z.L. Li, C.X. Shao, Y.L. Hu, *Polym. Int.* 51 (2002) 349.
- [19] K.-Y. Shih, WO Patent 01/32723 (2001), W.R. Grace & Co.
- [20] Y. Nakayama, H. Bando, Y. Sonobe, T. Fujita, *J. Mol. Catal. A* 213 (2003) 141.
- [21] J.R. Severn, J.C. Chadwick, *Macromol. Rapid Commun.* 25 (2004) 1024.
- [22] J.R. Severn, J.C. Chadwick, V. Van Axel Castelli, *Macromolecules* 37 (2004) 6258.
- [23] R.B. Huang, D.B. Liu, S.B. Wang, B.Q. Mao, *Macromol. Chem. Phys.* 205 (2004) 966.
- [24] B.Q. Mao, J.X. Yang, Z.L. Li, A.C. Yang, Y. Zheng, X.Z. Xia, CN Patent 1,091,748 (1994) SINOPEC (BRICI).
- [25] Y. Nakayama, H. Bando, Y. Sonobe, T. Fujita, *Bull. Chem. Soc. Jpn.* 77 (2004) 617.
- [26] K. Radhakrishnan, H. Cramail, A. Deffieux, P. François, A. Momtaz, *Macromol. Rapid Commun.* 24 (2003) 251.
- [27] T.B. Mikenas, V.A. Zakharov, L.G. Echevskaya, M.A. Matsko, Proceedings of the International Olefin Polymerization Conference on MOSPOL 2004: Catalytic Olefin Polymerization, Poster No. 61, June 22–25, 2004.
- [28] R. Schmidt, M.B. Welch, S.J. Palackal, H.G. Alt, *J. Mol. Catal. A* 179 (2002) 155.
- [29] R. Souane, F. Isel, F. Peruch, P.J. Lutz, *CR Chim.* 5 (2002) 43.
- [30] B. Keszler, G. Bodor, A. Simon, *Polymer* 21 (1980) 1037.

- [31] D.N.T. Magalhães, O. Do Coutto Filho, F.M.B. Coutinho, Eur. Polym. J. 27 (1991) 827.
- [32] P. Galli, P. Barbè, G. Guidetti, R. Zannetti, A. Martorana, A. Marigo, M. Bergozza, A. Fichera, Eur. Polym. J. 19 (1983) 19.
- [33] J.C.J. Bart, W. Roovers, J. Mater. Sci. 30 (1995) 2809.
- [34] P. Sozzani, S. Bracco, A. Comotti, R. Simonutti, I. Camurati, J. Am. Chem. Soc. 125 (2003) 12881.
- [35] U. Giannini, Makromol. Chem. 5 (Suppl.) (1981) 216.