# Catalysis of Ethylene to Linear Low-Density Polyethylene with Iron-Based Diimine Complex Immobilized on Calcosilicate and Silica-Supported *rac*-Et(Ind)₂ZrCl₂

**Feng-Wen Yan,**[1] **Hao Xu,**[1] **Cun-Yue Guo,**[1] **Ming-Ge Zhang,**[1]* **Xiao-Hui Zhang,**[1] **Hai-Jian Yang,**[2] **Guo-Qing Yuan**[1]

[1]*Beijing National Laboratory for Molecular Sciences, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[2]*Key Laboratory of Catalysis and Materials Sciences of Hubei Province, College of Chemistry and Materials Sciences, South-Central University for Nationalities, Wuhan 430074, People's Republic of China*

**ABSTRACT:** Iron-based diimine complex was immobilized on calcosilicate (CAS-1) to form heterogeneous precatalyst, which oligomerized ethylene to α-olefins even without the use of aluminum alkyl compounds as activators. The α-olefins, upon the catalysis of another catalyst, i.e., silica-supported *rac*-Et(Ind)₂ZrCl₂, copolymerized with ethylene to produce linear low-density polyethylene (LLDPE). The copolymerization reactions could be performed with the addition of triethylaluminum alone because of the introduction of methylaluminoxane to CAS-1 and silica during the supporting process. In addition to the formation of more α-olefins with lower molar mass, the layered structure of CAS-1 acted well in the controlled release of α-olefins in the copolymerization process. The simultaneous employment of the aforementioned two catalysts hence resulted in high catalytic activities, smooth kinetic process, well-regulated branching degree, higher molecular weights ($M_n$), improved thermal stability, and better morphology of the LLDPE obtained. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2298–2304, 2009

**Key words:** catalysis; ethylene; LLDPE; calcosilicate; silica

## INTRODUCTION

Formation of linear low-density polyethylene (LLDPE) from ethylene monomer alone is of great significance for both academic research and industrial applications. *In situ* copolymerization of ethylene to LLDPE, since its first appearance as "tandem reaction" in 1984,[1] has been developing into an ever updating methodology in the field of LLDPE production. Advantage of this methodology lies in the fact that the comonomers, i.e., α-olefins, which are needed to incorporate into the backbone and form branches of polyethylene, are formed directly from ethylene itself under the catalysis of one complex that is capable of performing ethylene oligomerization with the cocatalyst methylaluminoxane (MAO). The as-formed α-olefins can be simultaneously copolymerized with ethylene *in situ* to produce LLDPE catalyzed by another organometallic compound, which is activated with the cocatalyst.[1,2] Benefits from this method are obvious due to the employment of a single feedstock—ethylene and two catalysts in one reactor. Following the aforementioned original work, several attempts adopting different combinations of ethylene oligomerization and copolymerization catalysts had been performed.[3–9] However, such catalytic systems had problems like interferences between the oligomerization catalyst and copolymerization catalyst, the catalysts and activators, and moreover, inferior control over the distribution of α-olefins and branching degree of the LLDPE obtained.

The emergence of late-transition metal (LTM) complexes brought about opportunities of producing α-olefins with high catalytic activities and selectivities toward ethylene oligomerization with the cocatalyst MAO. Employment of iron-based diimine complex and zirconocene compound produced structure-

adjustable LLDPE.[10–12] Other catalytic systems were also successfully attempted to form LLDPE taking similar routes.[13–16]

The difficulties like reactor fouling and implosion standing in the breach, which frequently accompany the utilization of homogeneous dual-functional catalyst systems, have to be tackled with great efforts to make the present LLDPE production process accessible to industry. Heterogenization of homogeneous catalysts by immobilizing on supports such as silica, $MgCl_2$, and montmorillonite (MMT)[16–19] has proved to be examples in coping with the aforementioned disadvantages to some extent.

As found in previous research, the employment of MMT as the support of $(acac)_2ZrCl_2$ tripled the catalytic selectivity for 1-hexene when compared with the homogeneous analog mainly due to the confinement effect of the layered structures of MMT.[17] It is known to many researchers that the facile adjustment of the selectivity to *in situ*-formed α-olefins is significant in forming well-defined chain structures of LLDPE. To further investigate the effects of supports with layered structures, CAS-1, a calcosilicate synthesized and structurally confirmed recently,[18,19] has been effectively used to support ethylene polymerization catalysts[20,21] and is introduced herein to immobilize iron-based diimine complex to form supported ethylene oligomerization catalyst. Taking advantage of this strategy and silica-supported zirconocene complex, both improved control over the selectivity for α-olefins from ethylene oligomerization and better morphology of the resulting LLDPE from the *in situ* copolymerization, in addition to a smooth kinetic process, are expected for sure.

## EXPERIMENTAL

### Materials

All manipulations of air- and/or moisture-sensitive compounds were carried out using dry-box procedures or standard Schlenk techniques. 2,6-Diacetylpyridine (97 wt %), 4-oxymethyl-2-methylaniline, and *rac*-Et(Ind)$_2$ZrCl$_2$ were procured from J&K Chemical Ltd. (Beijing, China). Ethylene of polymerization grade was generously provided by Yanshan Petro-Chemical (Beijing, China) and was used without further purification. MAO solution in toluene (1.4 mol L$^{-1}$, MAO = 10 wt %, TMA = 10–20 wt %) was purchased from Albemarle Corp. (Baton Rouge, LA). Toluene, hexane, and tetrahydrofuran (THF) were refluxed with sodium/benzophenone and freshly distilled before use. Grace 955 silica was purchased from the Aldrich Chemical (Milwaukee, WI). All other chemicals were obtained commercially and used without further treatment unless indicated otherwise.

### Synthesis of CAS-1

CAS-1 was synthesized as follows: 2 g of Ca(N-O$_3$)$_2$·4H$_2$O (≥96 wt %; Beijing Hongxin Chemical Factory, Beijing, China) was dissolved in 25 mL of distilled water. Then, 10.43 mL of colloidal silica (6.05 mol L$^{-1}$ aqueous solution; Qingdao Chemical Factory, Qingdao, China) was added to the solution. Finally, 2.41 g of KOH (≥82 wt %; Beijing Chemical Factory, Beijing, China) was added at room temperature and the mixture was stirred for 30 min. The gel composition was 0.28 K$_2$O : 0.13 CaO : 1 SiO$_2$ : 22 H$_2$O. This gel was transferred to a teflon-lined stainless steel autoclave, and the crystallization was carried out at 220°C under autogenetic pressure without stirring for 6 days. The autoclave was then removed from the oven and cooled, and the product was separated by centrifuge, washed with distilled water six times and dried at 110°C subsequently in air. The structure of CAS-1 had been reported in the literature.[19]

### Synthesis of {[(2-ArN═C(Me))$_2$C$_5$H$_3$N]FeCl$_2$} (Ar = 2─CH$_3$─4─OCH$_3$(C$_6$H$_3$))

2,6-Diacetylpyridine (0.5 g, 3.06 mmol) and 4-oxymethyl-2-methylaniline (1.7 mL, 12.24 mmol) were added to a round-bottom flask with 30 mL of 1,2-dichloroethane. A stirring bar and five drops of 97% formic acid were added, and the solution was stirred for 48 h at 50°C. After removing the solvent in vacuum, the resulting viscous oil was washed with cold methanol prior to the formation of a yellow solid, which was confirmed to be the desired ligand after filtration isolation and identification by $^1$H-NMR.

Ligand (C$_{25}$H$_{27}$N$_3$O$_2$) $^1$H-NMR (CDCl$_3$): δ = 8.26 (d, Py-*m*-H), 8.02 (t, Py-*p*-H), 6.99 (d, Aryl), 6.72 (m, Aryl), 3.79 (s, Aryl─OCH$_3$), 2.83 (s, N═C─CH$_3$), 2.34 (s, Aryl─CH$_3$). Elemental Analysis: Calc. (%): C = 74.8, H = 6.73, N = 10.47, O = 7.98; Found (%): C = 74.25, H = 6.72, N = 10.20, O = 7.69.

The precatalyst complex was formed by the addition of the ligand to FeCl$_2$·4H$_2$O in THF. Details about the ligand synthesis and complex formation could be found in the literature.[22]

### Preparation of CAS-1-immobilized ethylene oligomerization catalyst

CAS-1 was dried in vacuum at 120°C to constant weight and reacted with MAO at 60°C overnight prior to being washed with large amount of toluene. Then, desired amount of oligomerization catalyst dissolved in toluene was added and reacted at 50°C for 8 h. The supported catalyst was washed several times with toluene until the upper layer turned colorless, and then dried in vacuum at 50°C to give azury powder. Loading of aluminum in the MAO-

treated CAS-1 was 13.6 wt %. Loading of iron in the resultant supported catalyst was 185 $\mu$mol g$^{-1}$.

## Supporting of *rac*-Et(Ind)$_2$ZrCl$_2$ on silica

Silica was dried at 400°C under nitrogen atmosphere overnight and then at 150°C in vacuum for 6 h. The product was suspended in a solution of MAO in toluene and reacted at 60°C for 8 h. The suspension was filtered in a Schlenk apparatus and washed several times with toluene until no more Al was detected in the washing. This MAO/SiO$_2$ was added to certain amount of *rac*-Et(Ind)$_2$ZrCl$_2$ dissolved in toluene, stirred overnight, washed with toluene and filtered until no more Zr was found in the washing prior to drying in vacuum. Loading of aluminum in the MAO-treated silica was 18.9 wt %. Loading of zirconium in the resultant SC was 67 $\mu$mol g$^{-1}$.

## Ethylene oligomerization

To an ethylene-purged 250 mL three-necked flask, equipped with a magnetic stirrer and thermostated in a silicone bath, 100 mL of toluene and predetermined amount of triethylaluminum (TEA) were added. The mixture was stirred until the solution was saturated with ethylene of constant pressure controlled by an electromagnetic valve. Desired amount of supported iron-based complex was then transferred to initiate ethylene oligomerization at an ethylene pressure of 0.1 MPa. The reaction was quenched after certain period of time by stopping the supply of ethylene. The catalytic activity for ethylene oligomerization was calculated on the pressure drop of the ethylene buffer tank. For the lower $\alpha$-olefins like 1-butylene and 1-hexene not to escape the resultant oligomers along with the sealed flask were placed in a cooling bath for more than 2 h before GC-MS measurement.

## Ethylene catalysis to LLDPE

To an ethylene-purged 250 mL three-necked flask, equipped with a magnetic stirrer and thermostated in a silicone bath, 100 mL of toluene and desired amount of TEA were added. The mixture was stirred until the solution was saturated with ethylene of constant pressure controlled by an electromagnetic valve. Then desired amounts of CAS-1-supported oligomerization catalyst and silica-supported copolymerization catalyst were introduced to start *in situ* copolymerization of ethylene under atmospheric pressure. The reaction was quenched with 10 wt % acidified ethanol after certain period of time (0.5 h in general). The polymer was kept in an excess of acidified ethanol overnight, filtered and washed with ethanol and water, separated and dried

at 70°C in vacuum to constant weight before characterization.

## Characterization

$^1$H-NMR (300 MHz) spectra and $^{13}$C-NMR (300 MHz) were detected on a Bruker DMX-300 spectrometer. Mass spectra were carried out with an electron impact (EI) instrument (Kratos AEI MS-50). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. GC-MS analyses were performed on an HP-5890/HP-5971 apparatus with an HP-1 capillary column (30 m × 0.25 mm). The column temperature was started with 35°C (10 min), heated at 10°C min$^{-1}$ to 280°C and kept for 10 min. Molecular weights ($M_w$ and $M_n$) and molecular weight distribution ($M_w/M_n$) were determined on high-temperature gel permeation chromatography (GPC) with a PL-GPC220 instrument at 140°C in trichlorobenzene, and the data were analyzed relative to polystyrene standards. The melting temperatures ($T_m$) of polyethylene were determined by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 operating under nitrogen at a heating rate of 10°C min$^{-1}$ from 50 to 160°C, and $T_m$ was recorded for the second scan. The onset decomposition temperatures ($T_{onset}$) were performed on a Perkin-Elmer 7 series system at a heating rate of 10°C min$^{-1}$ from 50 to 800°C in air. Loadings of aluminum in the MAO-treated supports and loading of iron and zirconium in the supported catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES POEMS TJA). SEM images of LLDPE morphology were recorded on a JEOL JSM-6700F field-emission scanning electron microscope.

## RESULTS AND DISCUSSION

### Ethylene oligomerization with CAS-1-supported catalyst

To investigate the effects of the layered structure of CAS-1 on the catalytic performance of {[(2-ArN=C(-Me))$_2$C$_5$H$_3$N]FeCl$_2$}(Ar = 2—CH$_3$—4—OCH$_3$(C$_6$H$_3$)) ethylene oligomerization was carried out with only TEA. As reflected in Table I, the immobilization of oligomerization catalyst on MAO-modified CAS-1 bettered the oligomerization performance at elevated temperatures even without the addition of MAO as in the case of adopting homogeneous oligomerization catalyst. Moreover, high selectivity for $\alpha$-olefins from ethylene oligomerization with the oligomerization catalyst was still maintained. The results indicated that layers of CAS-1 effectively prevented the active sites of oligomerization catalyst from being deactivated due to bimolecular interaction as in the case of homogeneous catalysts.[23–26] Different from

**TABLE I**
**Data of Ethylene Oligomerization with CAS-1-Supported Catalyst[a]**

| Entry[b] | Activator | Al/Fe[c] (mol/mol) | Temp. (°C) | Yield (g) | Activity $\times 10^{-7}$ [g (mol Fe)$^{-1}$ h$^{-1}$] | $\alpha$-olefins (wt %) | $C^=_4 - C^=_{10}$ (wt %) |
|---|---|---|---|---|---|---|---|
| 1 | – | 0 | 35 | 0 | – | – | |
| 2 | MAO | 1000 | 35 | 6.38 | 0.85 | 96.2 | 85.3 |
| 3 | TEA | 100 | 35 | 5.18 | 0.69 | 98.5 | 89.2 |
| 4 | TEA | 1000 | 35 | 8.40 | 1.12 | 98.1 | 90.3 |
| 5 | MAO | 1000 | 35 | 10.20 | 1.36 | 97.3 | 89.5 |
| 6 | TEA | 1000 | 75 | 7.13 | 0.95 | 98.2 | 91.2 |
| 7 | MAO | 1000 | 75 | 9.45 | 1.26 | 98.7 | 90.8 |
| 8 | TEA | 2000 | 35 | 17.93 | 2.39 | 98.2 | 90.1 |
| 9 | MAO | 2000 | 35 | 20.10 | 2.68 | 98.3 | 89.7 |
| 10 | TEA | 2000 | 75 | 13.88 | 1.85 | 98.6 | 91.3 |
| 11 | MAO | 2000 | 75 | 16.95 | 2.26 | 98.5 | 90.8 |

[a] Reaction conditions: Fe = 1.5 μmol (8.1 mg of CAS-1 supported catalyst); solvent = 100 mL toluene; ethylene pressure = 0.1 MPa; polymerization time = 30 min.
[b] Homogeneous oligomerization catalyst is used for entries 1 and 2.
[c] Al herein only refers to that from MAO or TEA added during the oligomerization process excluding that already present in CAS-1.
= represent double bond in defines.

homogeneous iron-based diimine complexes, there is no need for external addition of MAO to initiate the oligomerization of ethylene under such circumstances. The reason for this is that the MAO chemically bound with the silanol groups on layers of CAS-1 during the immobilization process has already been capable of activating the catalytic precursors, and TEA employed here is mainly to scavenge polar impurities in the reaction system.

The selectivity for low molar-mass $\alpha$-olefins increased to some extent (Fig. 1). Reason for this might be that the protection from CAS-1 layers improved the stability of oligomerization catalyst, and MAO-activated LTM complexes-catalyzed ethylene oligomerization tended to experience more β-H elimination than chain propagation when performed at higher temperatures.[27,28] Additional possible explanation for the reduced formation of higher $\alpha$-olefins might be the confinement effect of layered structures of CAS-1 with the essence further probed.[17]

## Catalysis of ethylene to LLDPE

As mentioned in ethylene oligomerization catalyzed by CAS-1-supported iron-based catalyst upon activation by TEA, oligomers with the selectivity above 99 wt % for linear $\alpha$-olefins could be formed in between layers of CAS-1. Herein we took advantage of the improved selectivity for lower molar-mass linear $\alpha$-olefins formed with supported oligomerization catalyst/TEA in the formation of LLDPE by the combination of supported oligomerization catalyst and silica-supported zirconocene catalyzed *in situ* copolymerization also with TEA. Table II shows that the copolymerization activities increased with rising reaction temperature for whichever molar ratios of

Fe/Zr. Figure 2 shows the formation of LLDPE in this case.

Because the immobilization of oligomerization catalyst in between layers of CAS-1 bettered the thermal stability of supported oligomerization catalyst and $\alpha$-olefins of lower molar mass, they were advantageously formed at elevated temperatures, the $\alpha$-olefins together with the high catalytic activities of silica-supported zirconocene complex in a relatively broad temperature range were much prone to copolymerize *in situ* with ethylene.[17] The branches along the main chains included mainly ethyl (ca. 28%), butyl (ca. 40%), hexyl (ca. 19%), and minor amount
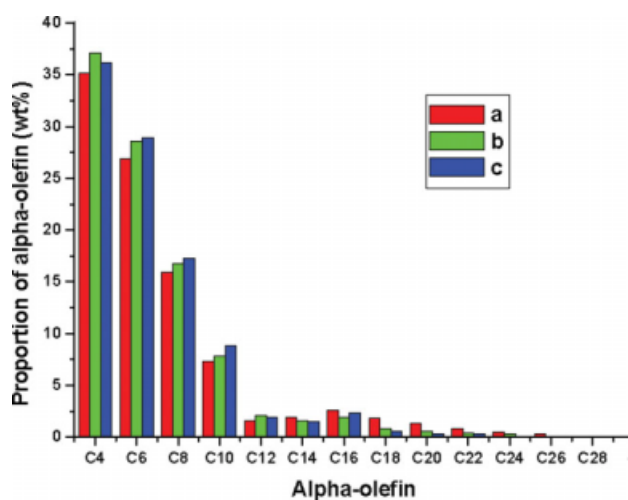


**Figure 1** Distribution of $\alpha$-olefins produced from homogeneous oligomerization catalyst/MAO at 35°C, entry 2 in Table I (a); CAS-1 supported oligomerization catalyst/TEA at 35°C, entry 4 in Table I (b); CAS-1 supported oligomerization catalyst/TEA at 75°C, entry 6 in Table I (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE II**
**Results of Ethylene Copolymerization to LLDPE with Supported Catalysts[a]**

| Entry[b] | Activator | Fe/Zr (mol/mol) | Al/(Zr + Fe)[c] (mol/mol) | Temp. (°C) | Activity[d] | $T_m$(°C) | $T_{onset}$ (°C) | $M_n \times 10^{-4}$ (g mol$^{-1}$) | $M_w/M_n$ | Branching degree CH$_3$/1000C |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MAO | 1/9 | 1500 | 50 | 1.36 | 109.3 | 418.3 | – | – | 32 |
| 2 | MAO | 1/9 | 1500 | 80 | 1.38 | 118.2 | 420.5 | 3.9 | 2.1 | – |
| 3 | TEA | 1/9 | 1500 | 50 | 3.19 | 103.1 | 448.1 | 3.6 | 2.3 | 39 |
| 4 | MAO | 1/9 | 1500 | 80 | 4.16 | 115.2 | 452.6 | 3.5 | 3.4 | 46 |
| 5 | MAO | 1/3 | 1500 | 80 | 4.52 | 102.3 | 455.3 | 3.1 | 3.1 | 59 |
| 6 | TEA | 1/9 | 1500 | 80 | 3.56 | 113.6 | 452.9 | 6.9 | 3.2 | 40 |
| 7 | TEA | 1/9 | 1000 | 50 | 2.98 | 112.8 | 451.3 | – | – | – |
| 8 | TEA | 1/3 | 1500 | 80 | 4.36 | 116.5 | 453.1 | 5.1 | 2.6 | 63 |

[a] Reaction conditions: Zr = 2.0 μmol (29.9 mg of silica-supported zirconocene); solvent = 100 mL toluene; ethylene pressure = 0.1 MPa; polymerization time = 30 min.

[b] Homogeneous oligomorization catalyst and copolymerization catalyst were used for entries 1 and 2; CAS-1-supported oligomerization catalyst/silica-supported copolymerization catalyst was used for entries 3–8.

[c] Al herein only refers to that from MAO or TEA added during the copolymerization process excluding that already bound to CAS-1 or silica.

[d] $10^6$ [g (mol(Zr + Fe))$^{-1}$ h$^{-1}$].

of even longer side chains (ca. 13%). Also observed from the experiments is the much smoother kinetic behavior of ethylene copolymerization process, which was catalyzed by the supported two-catalyst system (Fig. 3). Herein, the relatively high reaction rates still remained for the whole copolymerization process, which was somewhat different from the kinetic behavior as in the case of adopting homogeneous catalytic system.

Because ethylene molecules have to diffuse around layers of CAS-1 to perform the oligomerization and copolymerization, as a result, the polymerization reaction proceeded in a moderate way. There was no abrupt exothermic phenomenon accordingly because the reaction heat had to transfer to the outside through tortuous CAS-1 layers. As to high Fe/Zr molar ratios (1/3) (Table II, Fig. 3), higher polymerization activities were obtained when compared with the case of employing low Fe/Zr molar ratios. Reason for this was that there were abundant α-olefins from higher amount of active sites of iron due to high Fe/Zr molar ratios. In comparison with homogeneous catalysts/MAO system, which exhibited low activity in ethylene copolymerization at higher temperatures, the supported catalysts/TEA avoided the deactivation of oligomerization catalyst under such conditions and resulted in good catalytic activities even without extra addition of MAO. In all cases, the copolymerization proceeded at decreasing rate of ethylene absorption due to the difficulty of monomer diffusion in large quantity of the already formed LLDPE.

Being a lasting and effective catalyst, the supported ones did not decay over the time frame of the experiments. The homogeneous catalyst showed very high initial activity, but it sharply fell down in the course of copolymerization. However, the catalytic activities of the supported two-catalyst system decreased slowly after the peak value and maintained steady yet high values when compared with their homogeneous analogs. This phenomenon could be attributed to the steric hindrance of CAS-1's layers around the active sites that effectively
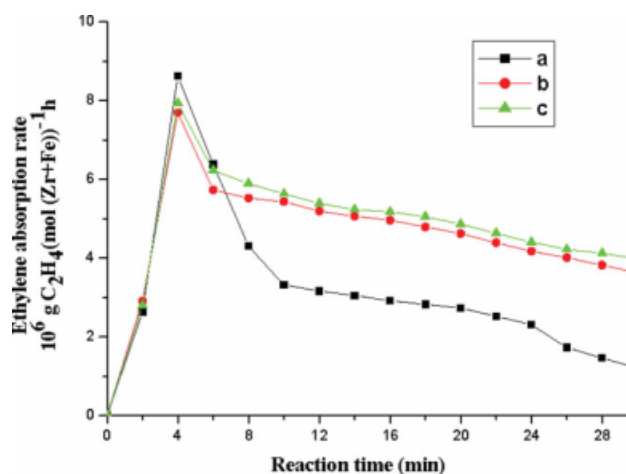


**Figure 3** Relationship between ethylene absorption rate and reaction time: homogeneous oligomerization catalyst/homogeneous copolymerization catalyst/MAO, entry 2 in Table II (a); CAS-1 supported oligomerization catalyst/silica-supported copolymerization catalyst/TEA, entry 3 in Table II (b); CAS-1 supported oligomerization catalyst/silica-supported copolymerization catalyst/TEA, entry 6 in Table II (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
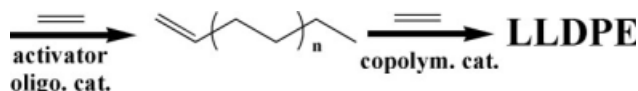


**Figure 2** Ethylene catalysis to the formation of LLDPE by two catalysts.
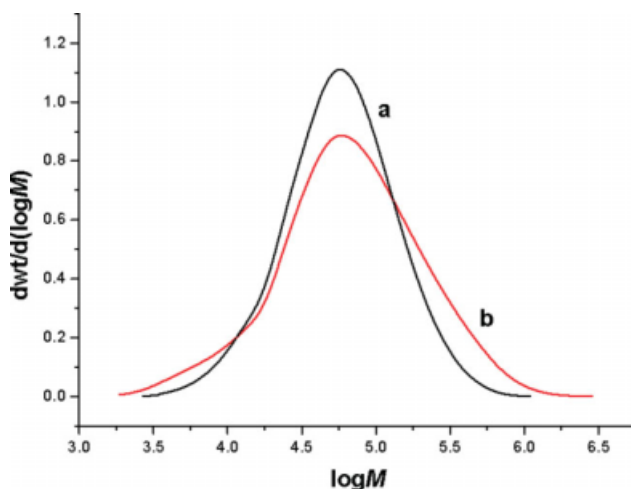
**Figure 4** GPC curves of LLDPE prepared from homogeneous oligomerization catalyst/homogeneous copolymerization catalyst/MAO, entry 2 in Table II (a); CAS-1-supported oligomerization catalyst/silica-supported copolymerization catalyst/MAO, entry 4 in Table II (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

prevented the aggregation of active species of the system, a situation that might lead to sudden release of great quantity of heat during the copolymerization process. The steric effect of the layered structure might also hinder the activation process of supported catalysts/TEA, thus prolonged the induction period of the supported catalysts.

Compared with homogeneous catalysts, the supported catalytic system produced LLDPE with high molecular weights ($M_n$ and $M_w$) (Fig. 4), which might be attributed to the suppression of β-H transfer because the interaction between the support and TMA contained in the MAO solution impeded TMA to act as a transfer agent.[29–31] Moreover, the molecular weights depended significantly on the concentration of TEA and decreased with increasing Al/(Fe+Zr) molar ratio. The results can be attributed to

the frequently occurred chain-transfer reaction to Al especially at high concentrations.[32]

The molecular weight distribution ($M_w/M_n$) slightly increased in the case of employing supported catalytic systems. One reason for this might be the dissociation of some active metal sites from the supports and became homogeneous again, hence leading to the formation of LLDPE from different active centers. Generally, the higher molecular weights and broader molecular weight distribution were originated mainly from the low rates of chain termination and transfer reactions when supported catalyst system was used.[33]

As to polymeric materials, another benefit of broad molecular weight distribution plus high molecular weight is the improvement of mechanical properties and processability.

Structure analyses reveal that the resultant LLDPE possessed considerable branching degrees (Table II) because the lower molar-mass α-olefins, such as 1-butene, 1-hexene, and 1-octene, etc., were more prone to form branches when compared with higher molar-mass α-olefins, which contain more than 10 carbon atoms. More obvious is the case at elevated reaction temperatures as indicated by the DSC data (Table II). Moreover, the introduction of CAS-1 into LLDPE matrix played similar roles as MMT in the improvement of the onset decomposition temperatures ($T_{onset}$) of the polymers because the layers of CAS-1 formed tortuous pathway for small molecules like oxygen and other volatile degradation products to get across.[34,35]

SEM images in Figure 5 reflects that the regulated stacking of layers of CAS-1 [Fig. 5(a)] became dispersed and completely invisible [Fig. 5(c)] after the formation of LLDPE. Moreover, the resultant LLDPE exhibited morphologies of compact particles because the adoption of silica as the support for *rac*-Et(Ind)$_2$ZrCl$_2$ and the "support duplicating effect." In contrast, LLDPE from homogeneous oligomerization
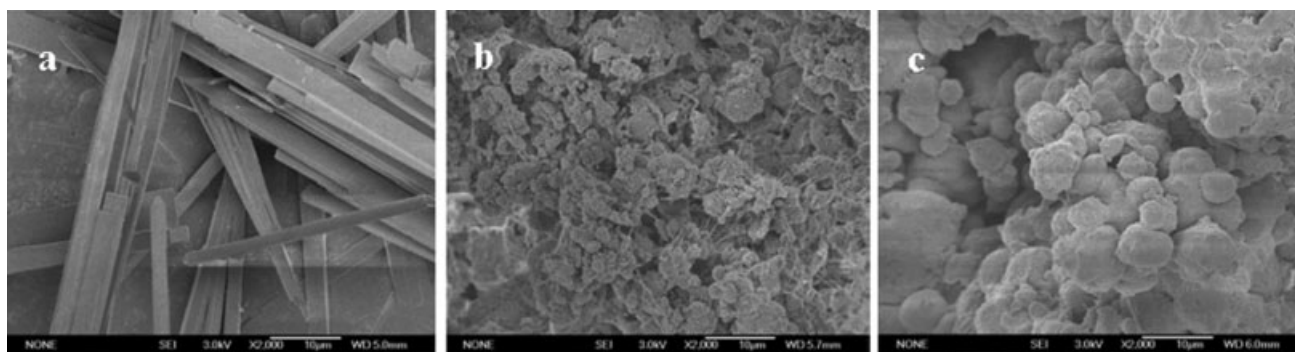


**Figure 5** SEM images of CAS-1 (a), LLDPE prepared from homogeneous oligomerization catalyst/homogeneous copolymerization catalyst/MAO, entry 2 in Table II (b); LLDPE prepared from CAS-1-supported oligomerization catalyst/silica-supported copolymerization catalyst/TEA, entry 4 in Table II (c).

catalyst/copolymerization catalyst/MAO catalyst was still a loosely stacking appearance [Fig. 5(b)].

## CONCLUSION

CAS-1 was successfully employed to support {[(2-ArN=C(Me))$_2$C$_5$H$_3$N]FeCl$_2$}(Ar = 2—CH$_3$—4—OCH$_3$ (C$_6$H$_3$)) and exhibited high catalytic activities in ethylene oligomerization in addition to improved selectivity for lower α-olefins at elevated reaction temperatures with only TEA. Silica-immobilized *rac*-Et(Ind)$_2$ZrCl$_2$ in combination with CSA-1-supported oligomerization catalyst performed well in ethylene catalysis to LLDPE with TEA. The combined catalytic system resulted in smoother kinetic process and formed LLDPE of particle morphology. What is more remarkable is that the as-prepared LLDPE possessed high yet adjustable molecular weights and branching degree in addition to improved thermal stability because of the uniform dispersion of CAS-1 layers in the LLDPE matrix.

## References

1. Beach, D. L.; Kissin, Y. V. J Polym Sci Polym Chem Ed 1984, 22, 3027.
2. Kissin, Y. V.; Beach, D. L. J Polym Sci Polym Chem Ed 1986, 24, 1069.
3. Liu, Z. Y.; Jia, M.; Guo, C. Y.; He, D. W.; Hu, Y. L. Acta Polym Sinica 2001, 751.
4. Liu, Z. Y.; Xu, D. M.; Guo, C. Y.; Wang, J.; He, D. W.; Hu, Y. L. Chin Sci Bull 2001, 46, 2051.
5. Liu, Z. Y.; Wang, J.; Li, X. H.; He, D. W.; Hu, Y. L.; Yan, W. D. Chem J Chin Univ 2001, 22, 1271.
6. Liu, Z. Y.; Yang, L.; Tan, Z. J.; He, D. W.; Hu, Y. L. Acta Polym Sinica 2001, 471.
7. Liu, Z. Y.; Wang, J.; Xu, D. M.; He, D. W.; Hu, Y. L. Acta Polym Sinica 2001, 509.
8. Barnhart, R. W.; Bazan, G. C. J Am Chem Soc 1998, 120, 1082.
9. Junges, F.; de Souza, R. F.; Zimnoch dos Santos, J. H.; Casagrande, O. L., Jr. Macromol Mater Eng 2005, 290, 72.
10. Quijada, R.; Rojas, R.; Bazan, G. C.; Komon, Z. J. A.; Mauler, R. S.; Galland, G. B. Macromolecules 2001, 34, 2411.
11. Komon, Z. J. A.; Fiamond, G. M.; Leclerc, M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. J Am Chem Soc 2002, 124, 15280.
12. Komon, Z. J. A.; Bu, X. H.; Bazan, G. C. J Am Chem Soc 2002, 122, 1830.
13. Liu, Z. Y.; Guo, C. Y.; Ma, Z.; Wang, J.; Xu, D. M.; He, D. W.; Hu, Y. L. Chin Sci Bull 2001, 46, 2054.
14. Wan, H.; Ma, Z.; Ke, Y. C.; Hu, Y. L. Polym Int 2003, 5, 2.
15. Zhu, B. C.; Guo, C. Y.; Liu, Z. Y.; Yin, Y. Q. J Appl Polym Sci 2004, 94, 2451.
16. Zhang, Z. C.; Guo, C. Y.; Cui, N. N.; Ke, Y. C.; Hu, Y. L. J Appl Polym Sci 2004, 94, 1690.
17. Wang, J.; Liu, Z. Y.; Guo, C. Y.; Chen, Y. J.; Wang, D. Macromol Rapid Commun 2001, 22, 1422.
18. Xue, C. F.; Liu, G. H.; Li, J. P.; Dong, J. X. Front Solid State Chem 2002, 233.
19. Jordá, J. L.; Prokic, S.; McCusker, L. B.; Baerlocher, C.; Xue, C. F.; Dong, J. X. C R Chim 2005, 8, 331.
20. Xu, H.; Guo, C.-Y.; Zhang, M.; Yang, H.-J.; Dong, J.; Yuan, G. Catal Commun 2007, 8, 2143.
21. Xu, H.; Guo, C. Y.; Xue, C.; Ma, Z.; Zhang, M.; Dong, J.; Wang, J.; Hu, Y. Eur Polym J 2006, 42, 203.
22. Wang, H.; Yan, W. D.; Jiang, T.; Liu, B. B.; Xu, W. Q.; Ma, J. J.; Hu, Y. L. Chin Sci Bull 2002, 47, 1616.
23. Ko, Y. S.; Han, T. K.; Park, J. W.; Woo, S. I. Macromol Rapid Commun 1996, 17, 749.
24. Looveren, L. K.; Geysen, D. F.; Vercruysse, K. A.; Wouters, B. H.; Grobet, P. J.; Jacobs, P. A. Angew Chem Int Ed 1998, 37, 517.
25. Kaminsky, W.; Strübel, C. J Mol Catal A Chem 1998, 128, 191.
26. Chu, K. J.; Soares, J. B. P.; Penlidis, A. J Polym Sci Part A: Polym Chem 2000, 38, 462.
27. Small, B. L.; Brookhart, M.; Bennett, A. M. A. J Am Chem Soc 1998, 120, 4049.
28. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. Chem Commun 1998, 849.
29. Bouilhac, C.; Cramail, H.; Cloutet, E.; Deffieux, A.; Taton, D. J Polym Sci Part A: Polym Chem 2006, 44, 6997.
30. Bouilhac, C.; Cloutet, E.; Deffieux, A.; Taton, D.; Cramail, H. Macromol Chem Phys 2007, 208, 1349.
31. Bouilhac, C.; Cloutet, E.; Cramail, H.; Deffieux, A.; Taton, D. Macromol Rapid Commun 2005, 26, 1619.
32. Kaminsky, W.; Renner, F. Makromol Chem Rapid Commun 1993, 14, 239.
33. Woo, S. I.; Ko, Y. S.; Han, T. K. Macromol Rapid Commun 1995, 16, 489.
34. Tidjani, A.; Wilkie, C. A. Polym Degrad Stab 2001, 74, 33.
35. Fischer, H. R.; Gielgens, L. H.; Koster, T. P. M. Acta Polym 1999, 50, 122.