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Ethylene Polymerization with a Silica-Supported Iron-Based Diimine Catalyst

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ABSTRACT: A supported iron-based diimine catalyst (**SC**) was prepared by immobilization of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron chloride (**I**) on silica and employed in ethylene polymerization. The kinetic behavior of ethylene polymerization with **SC** was studied. The effects of the Al/Fe molar ratio, reaction temperature, and cocatalyst on the catalytic activity as well as the melting temperature, molecular weight, and morphology of the polymers obtained were also investigated. The results showed that good catalytic activities can be obtained even with a small amount of the cocatalyst methylaluminoxane (MAO) or triethylaluminum (AlEt$_3$). The polyethylenes obtained with a supported catalyst had higher molecular weight, higher melting temperature, and better morphology than those obtained with a homogeneous catalyst. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 466–469, 2003

Key words: catalysts; supports; polyethylene (PE); morphology

INTRODUCTION

In recent years, more attention has been paid to late transition-metal (LTM) catalysts for olefin polymerization.[1–7] One virtue of LTM catalysts is their less oxyphilic characteristic which may open up the possibility for preparing functionalized polyolefin materials via inserting polar comonomers.[8–11] This new generation of single-site catalysts can really impact the polyolefin industry if they can be used as a dropped addition at plants with a large capacity and the produced resins can be processed in the existing equipment without major modification. An efficient method is the supporting of new catalysts on suitable inorganic or organic carriers[12] such as SiO$_2$, MgCl$_2$, Al$_2$O$_3$, and polymers for dropping into a slurry and gas-phase process and producing polyolefin materials with better properties and good processability. However, there has been little research on supported LTM complex catalysts.[13] Herein, a silica-supported iron-based diimine catalyst (**SC**) was prepared and its behavior in ethylene polymerization combined with methylaluminoxane (MAO) or triethylaluminum (AlEt$_3$) as a cocatalyst was investigated.

EXPERIMENTAL

Materials

The catalyst of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron chloride (**I**) was synthesized following the method described in the literature.[5] Grace 955 silica was obtained from the Aldrich Chemical Co. (Milwaukee, WI). Ethylene for polymerization was obtained from the Yanshan Petro-Chemical Ltd. (Beijing, China) and used without further purification. A methyl aluminoxane (MAO) solution in toluene (1.4 mol/L) and AlEt$_3$ were purchased from the Albemarle Corp. (Pasadena, TX). Toluene and THF were distilled from sodium/benzophenone and degassed before use. All other chemicals were obtained commercially and used as received.

Preparation of silica-supported LTM catalysts

Grace 955 silica was calcinated at 400°C for 6 h and dried at 200°C for 2 h *in vacuo*; thereafter, it was cooled to room temperature. Under an argon atmosphere, 1.5 g of the silica treated above, 10 mL MAO, and 10 mL toluene were added to a two-neck flask and stirred at 50°C for 6 h. The mixture was washed several times

with toluene and then dried *in vacuo*. To the flask, 0.05 g of catalyst **I** in 20 mL toluene was added and stirred at 50°C for 12 h. The final supported catalyst was washed with toluene until the liquid layer above became colorless and then dried *in vacuo*. The resultant **SC** presented was 0.43 wt % Fe/SiO_2.

Characterization

The iron content of the supported catalyst was measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES POEMS TJA Co.) The changes of the binding energy (BE) in elements during the support process were traced by XPS (ESCALab220i-XL, VG Co. AlKα, 15 kV × 20 mA). The melting temperatures (T_m) of polyethylene were determined by differential scanning calorimetry (DSC) with a DSC-7 (Perkin–Elmer Co.) operating under nitrogen at a heating rate of 10°C min^{-1} from 20 to 150°C, and T_m was determined in the second scan. The molecular weight of polyethylene was measured by an AVS-300 viscometer (Shott Co.) in decahydronaphthalene (the residue SiO_2 was isolated by filtration) at 135 ±0.1°C and calculated from [η] according to eq. (1):

$$[\eta] = 2.3 \times 10^{-4} M_\eta^{0.82} \tag{1}$$

An SEM (HITACHI-530, Japan) was utilized to observe the appearance of polyethylenes obtained with supported and homogeneous catalysts.

Ethylene polymerization

A dried three-necked flask with a stirbar was purged with N_2 three times and ethylene once, then charged with 50 mL of toluene. The flask was heated in a bath up to the given reaction temperature and a prescribed amount of MAO or AlEt$_3$ was added via a syringe. After stirring for 5 min, the supported catalyst was added. The polymerization was quenched with 10% (wt %) acidified ethanol after 30 min. The purified polymer was dried at 60°C in a vacuum oven for characterizations.

RESULTS AND DISCUSSION

The XPS results in our other work[13b] showed the changes of the BEs in elements during the support process. After treated with MAO, the BEs of O_{1s} on silica increased from 532.9 to 533.9 eV, while a small change (0.1 eV) in the BEs of Si_{2p} was observed. The BEs of Si_{2p} and O_{1s} varied little after supporting catalyst **I** on the silica/MAO. **SC** had lower BEs of Fe_{2p} (710.4 eV) and Cl_{2p}(198.9 eV) than those of **I** (710.8 and 198.3 eV, respectively). In comparison with the BE of
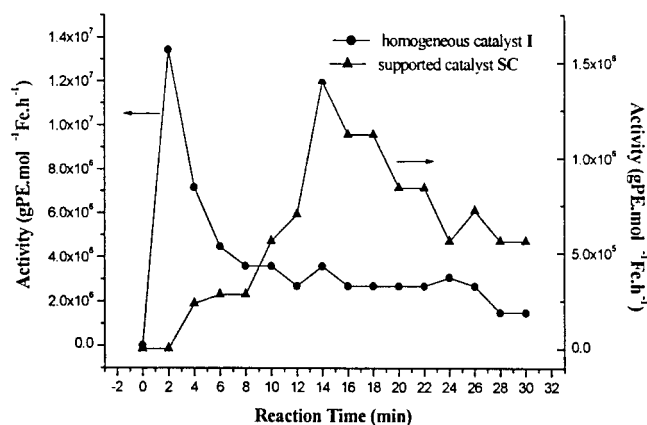

Figure 1 Relationship of catalytic activity to reaction time: amount of catalyst, 2 μmol; Al/Fe molar ratio, 1500 (MAO as cocatalyst); polymerization temperature, 40°C; polymerization time, 30 min.

74.8 eV in SiO_2/MAO, the BE of Al_{2p} in **I**/SiO_2/MAO was reduced to 74.2 eV. All these results confirmed that catalyst **I** was actually supported on silica through the "bridge" of MAO. The ionic species formed after the support were trapped and stabilized by multicoordinate "crown" aluminoxane against dissociation and formed a stable active site.

Ethylene polymerizations with **SC** and the homogeneous catalyst **I** were carried out under the same reaction conditions. Figure 1 shows an activity reduction due to catalyst immobilization.

It can be seen that there are two different polymerization kinetic curves for **SC** and **I** in Figure 1. For the homogeneous catalyst **I**, the catalytic activity increases rapidly to the maximum value with a very short induction period, followed by a sharp decay. However, a longer induction period of 14 min is shown in the kinetic curve for **SC** and the catalytic activity decreases gradually after the peak. Similar to the supported metallocene, this result can be attributed to the steric hindrance of a carrier's surface around the active site and the existence of inactive surface species or an inefficient number of active sites during the supporting process.[14] The steric effect on the surface of silica may also cause the hindered activation reaction of the catalyst **SC**, which, in turn, prolongs the induction period of the catalyst. In addition, both the α-hydrogen transfer and the bimolecular interaction, which result in the deactivation of the catalyst were suppressed by immobilizing **I** on silica,[15,16] so the **SC** lost relatively little activity over prolonged periods.

The data of ethylene polymerization catalyzed by **SC** combined with the MAO or AlEt$_3$ as cocatalysts are summarized in Table I. Although the activity of **SC** is lower than that of **I**, a good catalytic activity of **SC** with a smaller amount of MAO or AlEt$_3$ was obtained (entry 3 versus entry 4, entry 9 versus entry 10 in Table

TABLE I
Data of Ethylene Polymerization with SC and I

Entry	Catalyst/cocatalyst	Al/Fe (mol/mol)	T_p (°C)	Activity[a]	M_η (10^4 g/mol)	T_m (°C)
1	**SC**/MAO	500	40	9.14	24.26	135.5
2	**SC**/MAO	1000	40	9.91	24.64	135.1
3	**SC**/MAO	1500	40	9.60	23.74	134.8
4	**I**/MAO	1500	40	45.6	6.41	131.5
5	**SC**/MAO	1000	20	8.92	25.18	135.3
6	**SC**/MAO	1000	60	5.64	16.30	133.7
7	**SC**/AlEt$_3$	100	40	11.5	21.61	135.0
8	**SC**/AlEt$_3$	500	40	12.8	16.10	135.6
9	**SC**/AlEt$_3$	1500	40	8.34	8.47	134.3
10	**I**/AlEt$_3$	1500	40	58.5	4.85	131.2
11	**SC**/AlEt$_3$	500	20	11.2	18.30	135.2
12	**SC**/AlEt$_3$	500	60	2.78	9.50	133.9

Polymerization condition: amount of catalyst, 2 μmol (corresponding to Fe content); ethylene pressure, 1.013×10^5 Pa; polymerization time, 30 min.

[a] Activity, 10^5 g PE mol^{-1} Fe h^{-1}.

I). Some deactivation reactions[15] in the homogeneous catalyst system can be inhibited by a supporting catalyst on silica.[17,18] Therefore, more cocatalysts are unnecessary for protecting or reviving the active sites.

From the data in Table I, in general, with both MAO and AlEt$_3$ as cocatalysts, the molecular weight of the obtained polyethylene is much higher for the supported catalyst **SC** than for the homogeneous catalyst **I** because the β-hydrogen transfer was suppressed.[19] The polymers obtained by **SC** also have higher melting temperatures (T_m) than those by **I**.

Entries 1, 2, 7, and 8 in Table I indicate that the choice of a cocatalyst has an important effect on the catalytic activity. In the lower range of the Al/Fe molar ratio, **SC** activated with AlEt$_3$ has a higher activity than that activated with MAO. The possible explanation is that the less bulky AlEt$_3$ can easily enter into the multicoordinate "crown" aluminoxane complexes[20] and play a role of activating the supported catalyst. However, excess AlEt$_3$ may lead to large steric formation around the active site which inhibits the insertion of ethylene,[21] resulting a decrease in activity.

With either MAO or AlEt$_3$ as the cocatalyst, there was a maximum catalytic activity in the concentration range selected in the experiment, respectively,. In the case of using MAO, the molecular weight of the polymers has less dependence on the Al/Fe molar ratio (entry 1 versus entry 3 in Table I). However, polymers with a lower molecular weight are produced using AlEt$_3$ as the cocatalyst. Moreover, molecular weights are significantly dependent on the AlEt$_3$ concentration and decrease in an excess Al/Fe molar ratio. The results can be attributed to the frequently occurring chain-transfer reaction to AlEt$_3$, especially in high concentration.[21,22]

The reaction temperature (T_p) also has a significant influence on the catalytic activity and polymer characteristics. As shown in entries 2, 5, 6, 8, 11, and 12 (Table I), both of the two supported catalyst systems reached their maximum activity at 40°C and the highest molecular weight at 20°C. Generally, elevated temperatures will result in a higher chain-propagation rate which would be expected to increase the catalytic activity and the molecular weight, while the higher chain-transfer rate results in a decrease of the molecular weight. In addition, the reduction of ethylene solubility in toluene[23] and the accelerated deactivation rate of the catalyst at higher temperature might decrease the catalytic activity. The combination of these effects is likely to account for the different dependence of the catalytic activity and molecular weight on the temperature. From the SEM photographs in Figure 2, whether MAO or AlEt$_3$ acts as the cocatalyst, the polyethylenes obtained with the supported catalyst had a more compact morphology than those obtained with the homogeneous catalyst.

CONCLUSIONS

A smoother kinetic curve appears in ethylene polymerization with the silica-supported catalyst **SC** than with the homogeneous catalyst. Good catalytic activities can be obtained even with little MAO or AlEt$_3$. The polyethylenes obtained with the supported catalyst have a higher molecular weight, higher melting temperature, and better morphology than those obtained with the homogeneous catalyst.
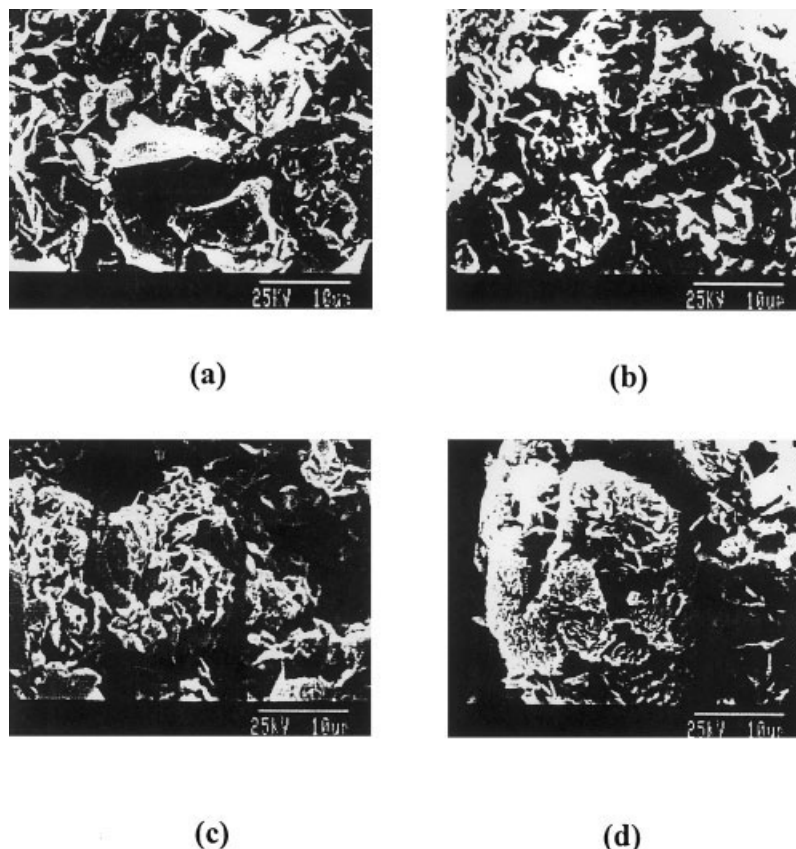
Figure 2 SEM photographs of polyethylenes obtained with (a) **I**/MAO, (b) **I**/AlEt$_3$, (c) **SC**/MAO, and (d) **SC**/AlEt$_3$.

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