

SILICA-SUPPORTED NICKEL AND ZIRCONIUM CATALYSTS FOR BRANCHED POLYETHYLENE*

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Abstract 8-Aminoquinoline nickel dichloride and bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) were supported simultaneously on silica to produce branched polyethylene successfully by combined polymerization. The supported polymerization results showed that the molecular weight of polyethylene increased while the molecular weight distribution became wider and the molecular chains of oligomers remaining in the final solution became shorter as compared to the oligomers obtained in polymerization processes with pure 8-aminoquinoline nickel dichloride catalysis, as well as the Cp_2ZrCl_2 and nickel combination system. With decreasing amount of Ni catalyst in the supported catalyst, the molecular chains of oligomers in the resulting solution became shorter, while α -olefin selectivity increased.

Keywords 8-Aminoquinoline nickel dichloride, Cp_2ZrCl_2 , Silica supported catalysts, Branched polyethylene

INTRODUCTION

Generally, there are three procedures for making branched polyethylene by coordination polymerization. The first method is the commercialized copolymerization of ethylene and α -olefins using Ziegler-Natta catalysts or metallocene catalysts^[1–3]. The second method is to use one designed catalyst to polymerize ethylene monomer under special polymerization conditions^[4, 5, 6], in which the structure of the catalyst affects the branches of the resulting polyethylene. The third method is to use a combined catalytic system, in which there are two active sites, one for ethylene oligomerization and the other for copolymerization. Compared to copolymerization of ethylene with α -olefins using the classic Ziegler-Natta catalysts, the combining catalytic system produces a blend of homopolyethylene and/or ethylene/ α -olefins copolymer^[7]. The third procedure is a research field of growing interest^[8–12]. In this combination of catalyst systems, the two kinds of catalysts should be compatible with each other under the same reaction conditions of temperature, monomer pressure and solvent.

It is very important to support the homogeneous catalysts of polyolefins when considering their industrial application. We studied the preparation of branched polyethylene with combined catalysts of 8-aminoquinoline nickel dichloride and Cp_2ZrCl_2 in homogeneous system. In this work, we attempted to support the catalysts on silica. The ethylene polymerization behavior of supported catalyst and the structure and properties of the obtained branched polyethylene were investigated.

EXPERIMENTAL

Materials

Methylaluminoxane (MAO) in toluene (10 wt%) was purchased from Aybemarle Co. (USA). The ethylene

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monomer, polymerization grade, was available from Beijing Yanshan Petrochemical Co. (China) without further purification. Toluene was dried with 4 Å molecular sieves and then refluxed over Na/K alloy in the presence of benzophenone. Cp_2ZrCl_2 was bought from Aldrich Co. 8-Aminoquinoline nickel dichloride was prepared according to the method in the literature^[13]. Grace 955 silica was obtained from Daqing Petro-Chemical Co. (China).

Characterization

The elemental analysis of supported catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (POEMS TJA Co.). Differential scanning calorimetric (DSC) results were obtained in the second scan on a Perkin-Elmer 7 Series Thermal Analysis System at a heating rate of 10 K/min. Gel permeation chromatography (GPC) of the polyethylene was performed on a Waters Alliance GPCV 2000 system (USA) at 135°C in 1,2,4-trichlorobenzene as solvent. Scanning electron microscopy (SEM) was conducted with a JEOL JAX-840 instrument (Japan). ^{13}C -NMR spectra of polymers were measured on a Bruker MSL-300 spectrometer (Switzerland) in 1,2-dichlorobenzene- d_4 at 135°C.

Preparation of Supported Catalysts

15 mL MAO as the scavenger and 60 mL toluene were placed in a reactor to treat the silica. The MAO-SiO₂ support was collected by filtration and washed several times with toluene. Then 60 mL toluene and the appropriate amount of Cp_2ZrCl_2 and 8-aminoquinoline nickel dichloride catalyst were introduced into the reactor. After reacting for about 12 h with stirring at 60°C, the final catalyst was collected by filtration and washed with toluene several times, dried under vacuum, then the light gray supported catalyst was obtained. All operations mentioned above were carried out under a dry nitrogen atmosphere.

Polymerization of Ethylene

Ethylene polymerization was carried out in a 200 mL Schlenck-type glass reactor equipped with a stirring bar. After carefully heating and evacuating air and moisture from the reactor for about 30 min, ethylene, 50 mL toluene and MAO were led into the reactor sequentially. Polymerization of ethylene was started when the appropriate amount of the suspended silica-supported catalyst was introduced. After the polymerization was terminated by adding acidified ethanol (5 wt%), part of the transparent solution was measured by gas chromatography-mass spectroscopy GC-MS, while the precipitated polymer was filtered and washed with ethanol several times and dried under vacuum at 50°C for 24 h.

RESULTS AND DISCUSSION

Effect of Ni/Zr in the Silica-Supported Catalysts

With the increase of the Ni/Zr ratio in the supported catalyst (from Cat 340 to Cat 440), the polyethylene obtained had lower melting point (T_m), crystallinity and more branches because the lower melting point of polyethylene indicates higher branching value^[1, 4, 5, 8, 9], and the amount of oligomers produced increased. The distribution of the oligomers catalyzed by the supported catalysts is different from that produced by pure Ni catalyst. With the decrease of Ni/Zr ratio in the supported catalyst, the carbon chain of oligomers became shorter, only C4 oligomers were determined when Ni/Zr < 2.5 (Cat 340 and Cat 440). The molecular chains of oligomers produced by silica-supported Ni catalyst (Cat 441) became shorter; interestingly, the α -olefins selectivity increased. This polymerization behavior is similar to that of the homogeneous combined catalytic system of 8-aminoquinoline nickel dichloride and Cp_2ZrCl_2 ^[9].

Effect of Al/(Ni + Zr) on Ethylene Polymerization

With increasing Al/(Ni + Zr) ratio, the molecular weight increased from 2.60×10^5 to 10.7×10^5 g/mol, while the molecular weight distribution became wider. At lower Al/(Ni + Zr) ratio, the polyethylene had more chains.

Table 1. Properties of the silica supported early/late transition metal catalyst

Samples	Al/(Zr+Ni) Molar ratio	Ni/Zr Molar ratio	A ^a	Oligom (g)	T _m (°C)	M _w (× 10 ⁻⁵)	M _w /M _n B ^b	Distribution of oligomers								
								C ₄	α-C ₄	C ₆	α-C ₆	C ₈	α-C ₈	C ₁₀	α-C ₁₀	C ₁₂
Cat340 ^c	1000	1.44	4.10	0.01	127.8	12.22	3.65	2.1	100	100						
Cat460 ^c	1000	3.76	2.56	0.03	126.3	18.50	3.19	3.4	100	100						
Cat440 ^c	1000	6.87	0.55	0.21	125.5	31.31	6.75	7.2	62.5	33.4	37.5	20				
Cat441 ^c	1000	–	–	0.66	–	–	–	–	35.5	33.4	39.5	7	25.0	0		
Cat441 ^d	1000			0.23					100	92.3						
Ni Cat ^e	1000			1.22		–			0	0	0	0	72.7	15.0	27.1	7.6
Cp ₂ ZrCl ₂	1000		12.46	0	133.8	2.65	2.33	0								0.2
Ni+Zr ^f	1000	1.50	1.14	0	128.6	0.26	2.62	–								
Cat340	300	1.44	1.13	0.53	122.9	2.60	2.98	9.8	100	100						
Cat340	500	1.44	2.72	0.14	125.5	6.74	3.09	6.2	100	100						
Cat340	1500	1.44	11.78	0.25	127.7	3.52	3.81	1.6	100	100						
Cat340	2000	1.44	3.60	0.62	126.1	10.73	3.47	1.9	100	100						

Polymerization conditions: 25 °C, 30 min, 50 mL toluene

^a Activity: × 10⁻⁵ gPE/molZr • h;^b Branches: CH₃/1000CH₂;^c Determined by ICP-AES, Cat 340, Ni: 4.37, Zr: 4.73 mg/g; Cat 460, Ni: 4.60, Zr: 1.90 mg/g; Cat 440, Ni: 8.40, Zr: 1.90 mg/g; Cat 441, Ni: 4.37, Zr: 4.73 mg/g;^d 80 °C;^e 3 μmol Ni catalyst;^f 3 μmol Ni cat and 2 μmol Cp₂ZrCl₂ added at the same time;

— Not determined

With increasing of Al/(Ni + Zr) ratio, the supported catalyst showed the polymerization behavior of the pure Cp_2ZrCl_2 . In addition, the more MAO could impart higher activity to Cp_2ZrCl_2 than the Ni catalyst. These phenomena were apparent from the branches of resulting polyethylene^[14]. The ^{13}C -NMR spectra of polyethylene produced by using Cat 340 with Al/(Ni + Zr) ratio of 300 and 2000 are shown in Fig. 1. The molecular weight of polyethylene produced by supported catalyst was greatly increased compared to that obtained from a homogeneous catalytic system, although the Ni catalyst and Cp_2ZrCl_2 were added to the reactor at the same time for supporting on silica (Table 1).

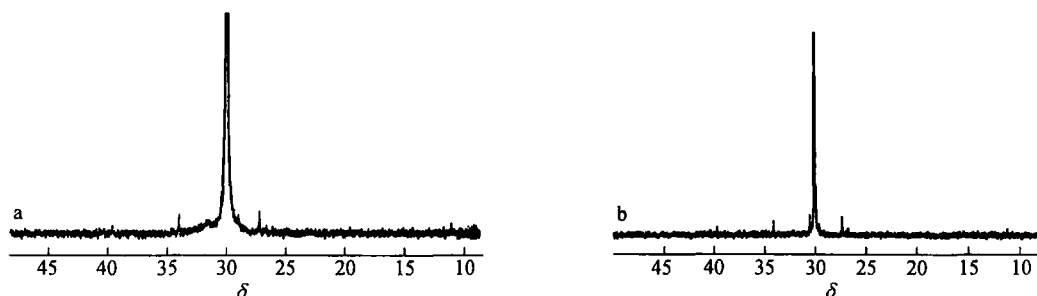


Fig. 1 ^{13}C -NMR spectra of PE by Cat340 with Al/(Ni+Zr) ratio of 300 (a) and 2000 (b)

It was also found that the branched chains of the polyethylene obtained with supported catalysts were fewer than were obtained by homogeneous catalyst, and the branches belonged to the most frequent short branched alkyl groups, and same trend occurred on the silica supported Brookhart's Ni catalyst^[15].

The morphology of polyethylene produced with supported catalyst had a granular form and compact arrangement, showing replicability of the shape of supported catalyst (Fig. 2b); however, the polyethylene produced with homogeneous catalyst had worse morphology (Fig. 2c). When Ni catalyst and Cp_2ZrCl_2 were used simultaneously (Fig. 2d), the resulting polyethylene showed a loose surface.

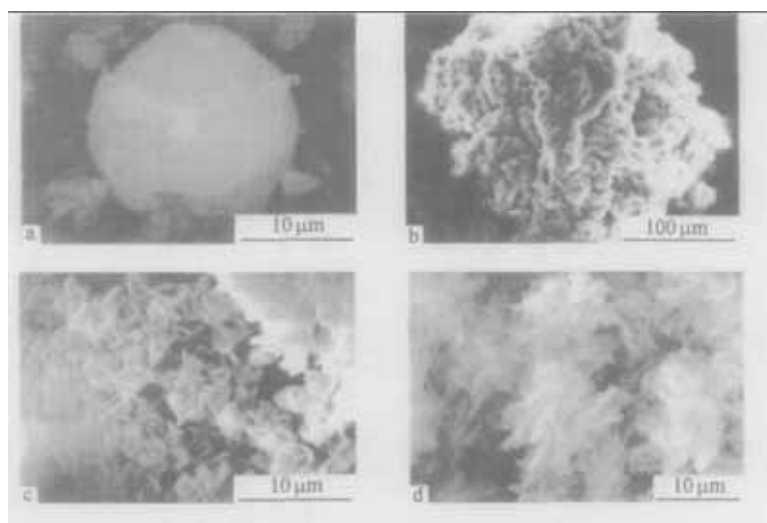


Fig. 2 SEM microphotography of Cat340 catalyst (a), PE by supported Ni/Zr catalyst, Cat340 (b), PE by homogeneous Ni/Zr catalyst (c), PE by Cp_2ZrCl_2 (d)
Polymerization condition: Al/M = 1000, 25°C, 50 mL toluene

In the case of the homogeneous system, no activity was found above the temperature 80°C^[13], probably due to the catalyst decomposition or dissociation. However, the supported catalysts are more stable, and activities were found though much decreased at temperatures higher than 80°C (Table 1).

CONCLUSIONS

8-Aminoquinoline nickel dichloride and Cp_2ZrCl_2 were simultaneously supported on silica to form a combined supported catalyst for the preparation of branched polyethylene. The corresponding polyethylene had higher molecular weight with wider molecular weight distribution comparing to their homogeneous catalytic system. In addition, the oligomers produced by supported catalysts had shorter chains with better selectivity of α -olefins than the homogeneous results. Moreover, the supported catalysts were more stable even up to 80°C.

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