

Ethylene Oligomerization by 8-Aminoquinoline Nickel Dichloride Complex Supported on β -Cyclodextrin[#]

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β -Cyclodextrin was pretreated by methylaluminumoxane (MAO) and subsequently reacted with 8-aminoquinoline nickel dichloride complex to yield the supported catalyst, which was characterized by ICP, IR and XPS methods. Using MAO as cocatalyst, the catalytic activity of this supported catalyst was investigated at various reaction temperature and Al/Ni molar ratio. The results showed that, despite possessing a number of polar groups, the supported catalyst displayed relatively high activity over 1×10^5 g ethylene/(mol Ni·h) under mild conditions.

Keywords ethylene oligomerization, supported catalyst, β -cyclodextrin

Introduction

Since the excellent capability of late transition metal complexes for olefin polymerization, was discovered by Brookhart¹ and Gibson², the interest in these catalysts has greatly increased in both academic and industrial researches.³ Unfortunately, in the olefin polymerization process initiated by late transition metal complexes, the polyolefins produced often deposit at the reactor walls and stirring device, which will be disadvantageous to the further application of these catalysts. In order to overcome these problems, the heterogenization of the homogeneous compounds, such as immobilizing the active catalyst on the supports, has been widely employed. However, most of the supports are inorganic materials, and the organic supports are less involved. Recently, a few organic materials, such as polyolefin,^{4,6} starch^{4,7} and α -cyclodextrin,^{8,9} were reported as supports for olefin polymerization catalysts. More recently, the preparation of Cp₂ZrCl₂ catalyst supported on 4-vinylpyridine grafted polyethylene has been reported.¹⁰ Herein, we wish to report the versatile heterogenization technique to immobilize 8-aminoquinoline nickel dichloride complex on β -cyclodextrin, and this technique can be conveniently applied in other case of late transition metal complexes. We chose cyclodextrin as support materials for the simple reason that both ethylene¹¹ and olefins¹² can form in-

clusion complexes with cyclodextrin, which will enable us to adjust the activity of catalyst and the property of polymerization products to some extent. The catalytic activities of β -cyclodextrin-supported catalyst for ethylene oligomerization were examined at various temperature and Al/Ni molar ratio.

Experimental

Materials and apparatus

β -Cyclodextrin (Beijing Reagent Co.) was recrystallized twice from water and dried *in vacuo* for 24 h at 100 °C. Methylaluminumoxane (MAO, 10 wt% in toluene) was purchased from the Aybemarle Co. 8-Aminoquinoline nickel dichloride complex was prepared according to the reported method.¹³ Toluene was dried over 0.4 nm molecular sieves, and then refluxed with benzophenone over Na/K alloy for 24 h. Polymerization grade ethylene monomer, produced by Beijing Yanshan Petrochemical Co. was used without further purification. X-Ray photoelectron spectra (XPS) were recorded on an ESCA Lab220i-XL spectrometer using a monochromatic Al K α X-ray radiation (1486.6 eV). IR spectra were recorded on a Perkin-Elmer 2000 spectrometer. The chemical composition of supported catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Plasma-Spec (I) of the American Leeman Lab. The oligomers obtained were analyzed on a BF3400 GC instrument.

Preparation of β -cyclodextrin supported catalyst

All manipulations were carried out under an atmosphere of nitrogen. β -Cyclodextrin (3.0 g) was dispersed in toluene (100 mL), then MAO (15 mL) was added. The reaction mixture was stirred at 60 °C for 24 h. The solvent was filtered off and the residue was washed with toluene (50 mL \times 2). A solution of 8-aminoquinoline nickel dichloride complex (0.1

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g) in toluene (100 mL) was subsequently added to the reaction flask, and the mixture was stirred at 60 °C for 24 h. The solvent was filtered off, and the residue was washed with toluene (50 mL \times 2). Then the crude product was dried *in vacuo* to give the β -cyclodextrin-supported 8-aminoquinoline nickel dichloride complex (3.0 g) as white powder. The nickel content determined by ICP-AES was 0.224 wt% though 0.665% nickel complex was added for the supporting, which means that only 34% of nickel complex was supported on the MAO-treated β -CD.

Ethylene oligomerization

Ethylene oligomerization was carried out in a 200 mL Schlenk-type glass reactor equipped with a magnetic stirrer. Supported catalyst (0.15 g) and the appropriate amount of MAO were added to the reactor, and the system was exposed to 1×10^5 Pa of ethylene. The oligomerization started when 50 mL of toluene was added and allowed to proceed for 1–1.5 h at various temperatures as defined in Table 1. Then the acidic ethanol was added to stop the reaction, and the oligomers were determined by gas chromatograph.

Results and discussion

The supported catalyst can be conveniently obtained by coupling 8-aminoquinoline nickel dichloride complex with MAO-modified β -cyclodextrin (β -CD/MAO). Since the hydroxyl groups at the 6-position of β -cyclodextrin are known far active than other ones, the 6-OH groups of β -cyclodextrin are firstly modified by MAO to give the intermediate β -CD/MAO. Secondly, β -CD/MAO can react with 8-aminoquinoline nickel dichloride complex to yield the supported catalyst. As presented in Table 1, compared with the original C_{1s} binding energy of parent β -cyclodextrin, there appears a new peak at *ca.* 292 eV in the C_{1s} binding energy of β -CD/MAO and supported catalyst. Additionally, the O_{1s} binding energy of β -CD/MAO displays 0.15 eV lower than that of β -CD. These phenomena and the appearance of Al_{2p} binding energy in the case of β -CD/MAO and supported catalyst jointly indicate the introduction of MAO moieties. Additionally, after being treated with 8-aminoquinoline nickel dichloride complex, the sup-

ported catalyst displays relevant Ni_{2p} , Cl_{2p} and N_{1s} binding energies. Moreover, the O_{1s} and Al_{2p} binding energies of supported catalyst decrease 0.45 and 0.1 eV respectively as compared with β -CD/MAO. On the other hand, the Ni_{2p} binding energy of supported catalyst decreases 0.3 eV, while the Cl_{2p} and N_{1s} binding energy increase 0.25 and 1.0 eV, respectively, as compared with the 8-aminoquinoline nickel dichloride complex. These also confirm that 8-aminoquinoline nickel dichloride complex is supported through chemical bonding on the β -CD/MAO.

For traditional polyolefin catalysts such as metallocene, the presence of polar groups in the reaction system is known dramatically unfavorable to the catalytic activity. However, in the present case, β -cyclodextrin supported 8-aminoquinoline nickel dichloride complex can initiate the ethylene oligomerization with relatively high activity, despite there seems still a number of hydroxyl groups in the supported catalyst as exemplified in the IR spectra (Fig. 1). This may be attributed to the low oxophilicity of late transition metal complexes, which makes the catalyst tolerant to so many polar groups. Table 2 presents the ethylene oligomerization results of supported catalyst using MAO as cocatalyst, which shows a Schulz-Flory distribution of linear α -olefins. In the control experiment, β -CD/MAO exhibits less oligomerization activity under comparable conditions. As shown in Table 2 and Fig. 2, when Al/Ni molar ratio is defined, the supported catalyst displays

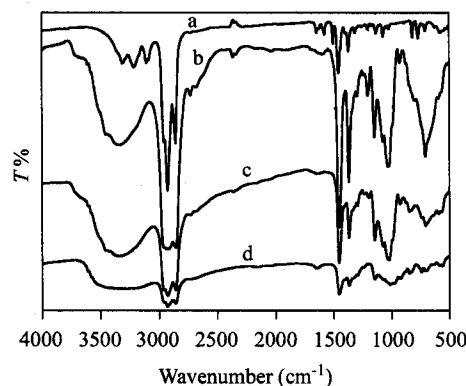


Fig. 1 IR spectra (from top to bottom) of (a) 8-aminoquinoline nickel dichloride complex, (b) supported catalyst, (c) β -CD/MAO and (d) β -CD.

Table 1 XPS results of β -cyclodextrin, β -CD/MAO and supported catalyst

	Binding energy (eV)					
	C_{1s}	O_{1s}	Al_{2p}	Ni_{2p}	Cl_{2p}	N_{1s}
β -CD	287.63, 286.13, 284.40	532.45				
8-Aminoquinoline $NiCl_2$ complex	285.49, 284.57	531.75		855.60	197.45	399.30
β -CD/MAO	291.98, 287.76, 286.15, 284.45	532.30	74.05			
Supported catalyst	291.85, 288.11, 286.03, 284.53	531.85	73.95	855.30	197.70	400.30

Table 2 Ethylene oligomerization by β -cyclodextrin supported catalyst

Catalyst	t ($^{\circ}\text{C}$)	Al/Ni ratio	Activity ^a	Oligomer distribution (wt%)										Schulz-Flory α
				C_4	$\alpha\text{-C}_4$ (%)	C_6	$\alpha\text{-C}_6$ (%)	C_8	$\alpha\text{-C}_8$ (%)	C_{10}	$\alpha\text{-C}_{10}$ (%)	C_{12}	$\alpha\text{-C}_{12}$ (%)	
β -CD/MAO	25	1500	trace ^b											
Supported catalyst	50	1500	1.23	53	100	17	75	17	50	9	40	4	20	0.21
	25	1500	1.81	51	100	16	78	18	47	10	30	5	16	0.21
	0	1500	1.69	47	100	18	80	18	50	12	30	5	20	0.24
	-10	1500	1.54	37	100	26	80	18	45	12	35	7	18	0.36
	0	2000	2.04	46	100	19	80	18	50	10	30	7	20	0.25
	0	1000	1.39	57	100	18	80	14	50	8	30	5	20	0.19
	0	750	0.38	73	100	16	80	11	50					0.13
	8-Aminoquinoline nickel dichloride complex	25	1000	6.1 ^c										

^a In unit of 10^5 g ethylene/(mol Ni \cdot h). ^b Trace means that the yield of oligomers is too small to evaluate activity. ^c Ref. 14, highest activity observed at 1×10^5 Pa.

the highest catalytic activity at 25 $^{\circ}\text{C}$. A lower or higher temperature will be unfavorable to the activity for ethylene oligomerization. However, the content of high-molecular-weight oligomers ($\text{C}_8\text{--C}_{12}$) shows certain temperature dependence in the range of -10 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$. Moreover, seen from Table 2 and Fig. 3, the activity of the supported catalyst enhances 3.7 times when increasing Al/Ni ratio from 750 to 1000. With further increasing the Al/Ni ratio to 2000, the

activity of the supported catalyst exhibits a relatively smooth enhancement from 1.39×10^5 to 2.04×10^5 g ethylene/(mol Ni \cdot h). In addition, the content of high molecular weight fraction ($\text{C}_8\text{--C}_{12}$) gradually enhances with the increase of Al/Ni ratio, which means, in a certain range, high Al/Ni ratio will favor the ethylene oligomerization initiated by β -cyclodextrin-supported catalyst.

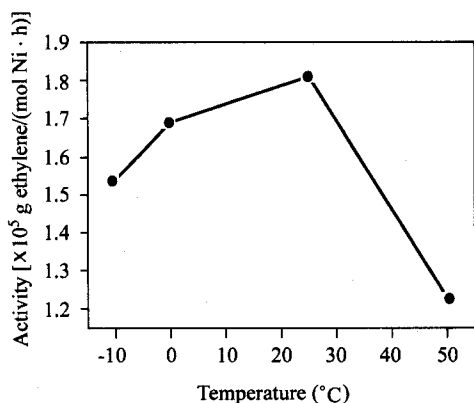


Fig. 2 Ethylene oligomerization activity of supported catalyst at various temperature (Al/Ni ratio 1500).

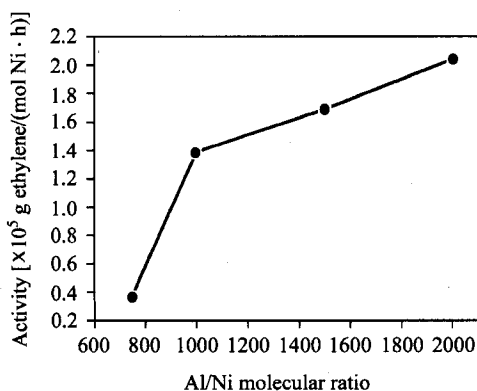


Fig. 3 Ethylene oligomerization activity of supported catalyst at various Al/Ni ratio ($t = 0$ $^{\circ}\text{C}$).

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