

NdCl₃/MgCl₂ BISUPPORTED CATALYST FOR OLEFIN POLYMERIZATION

WANG Hai (王海), XIAO Shijing (肖士镜) and CAI Shimian (蔡世绵)

(Institute of Chemistry, Academia Sinica, Beijing, 100080)

ABSTRACT

The NdCl₃/MgCl₂ bisupported catalyst was prepared by using NdCl₃, MgCl₂, (CH₃)₂CH(CH₂)₂OH and TiCl₄. It is shown that the structure of bisupported catalyst was different from those of either NdCl₃ or MgCl₂ single supported catalyst. A peculiar type of kinetic curve for ethylene polymerization was found.

INTRODUCTION

It is well known that high active catalysts for olefin polymerization can be prepared by MgCl₂-supported titanium catalysts. In the previous paper¹¹, we have reported the structural feature of NdCl₃ supported catalyst prepared from anhydrous NdCl₃, C₂H₅OH and TiCl₄ and the results for ethylene and propene polymerization in the presence of such catalysts together with MgCl₂ supported catalyst prepared by the same procedure for comparison. It was found that the NdCl₃/MgCl₂/TiCl₄-AlEt₃ catalyst system exhibits high activity for ethylene polymerization.

In this work we report the preliminary investigation on the NdCl₃/MgCl₂ bisupported catalyst prepared by using NdCl₃, MgCl₂, (CH₃)₂CHCH₂CH₂OH and TiCl₄.

EXPERIMENTAL

Catalysts preparation

NdCl₃/MgCl₂ bisupported catalysts (NMSC): Anhydrous NdCl₃ and MgCl₂ ([Nd]/[Mg]=1) was suspended in isoamyl alcohol at the molar ratio [ROH]/[Nd+Mg]=4. The mixture was stirred at 80 °C for 2hr. The alcoholate was formed and dissolved in heptane. The solution was added dropwise with stirring into excess TiCl₄ at -20 °C. At the end of addition, the temperature was raised to 80 °C, the liquid mixture was allowed to react for 2hr. After removal of all supernatant, the solid was treated again in excess amount of TiCl₄ at 100 °C for 2hr. The solid catalyst was separated by filtration, washed five times with heptane and dried in vacuum. For preparing NdCl₃ supported catalyst (NSC) or MgCl₂ supported catalyst (MSC), the above procedure was repeated by using NdCl₃ or MgCl₂ and isoamyl alcohol.

The Ti content of catalysts was determined calorimetrically. The IR spectra were recorded as plaster which was made by mixing solid with paraffin oil between two pieces of CsI crystalline flat on PE 983 spectrophotometers.

The polymerization of olefin was carried out in a 500 ml glass flask equipped with a stirrer, using 100 ml heptane as solvent, with AlEt_3 as cocatalyst. During the polymerization at 60°C , the pressure was maintained at 1 Bar by continuous feeding of olefin.

The isotactic index of the polymer is expressed as percent of polymer insoluble in boiling n-heptane and the isotactic polymer content of the polymer fraction soluble is determined from the triad peaks of the methyl carbon in the expanded ^{13}C NMR spectra using the polymer fraction soluble in boiling heptane. ^{13}C NMR spectra of the polymer were recorded at 140°C in o-dichlorobenzene- d^4 solution with a JEOL JNMFX-100 spectrometer operating in the Fourier transform mode at 25MHz.

X-ray powder diffraction patterns were recorded on a Rigaku 3010 X-ray diffractometer using $\text{CuK}\alpha$ radiation. The samples were sealed on a sample frame by Scotch tape under inert atmosphere.

RESULTS AND DISCUSSION

Table 1 Titanium content in catalyst and their behavior for olefin polymerization^{a)}

Catalysts	Ti content in wt.	Ethylene polymerization in Kg PE/g.Ti.h	Propylene polymerization		
			Activity in Kg.PP/g.Ti.h	Isotacticity in%	
$\text{NdCl}_3/\text{C}_5\text{H}_{11}\text{OH}/\text{TiCl}_4$	3.0	2.24	0.05	88	75 ^{b)}
$(\text{NdCl}_3 + \text{MgCl}_2)/\text{C}_5\text{H}_{11}\text{OH}/\text{TiCl}_4$	4.7	5.06	10.58	80	46
$\text{MgCl}_2/\text{C}_5\text{H}_{11}\text{OH}/\text{TiCl}_4$	9.0	21.0	1.15	83	29

a) Polymerization condition: mole ratio $\text{Al}/\text{Ti}=40$, temp. = 60°C , time = 2hr

b) Determined from ^{13}C NMR spectra of the methyl carbon of the polymer fraction soluble in boiling heptane

The Ti content of $\text{NdCl}_3/\text{MgCl}_2$ bisupported titanium catalyst and the results of olefin (ethylene and propene) polymerization with NMSC- AlEt_3 catalyst system are given in Table 1 together with those obtained using NSC/ AlEt_3 and MSC/ AlEt_3 system for comparison. It is seen that the Ti content of NMSC is higher than that of NSC but lower than MSC, viz. the order $\text{MSC} > \text{NMSC} > \text{NSC}$. The catalytic activity of catalyst for olefin polymerization have the same order and the isotacticity of polypropene should be $\text{MSC} \approx \text{NMSC} < \text{NSC}$.

Fig.1 shows the $1400 - 200\text{ cm}^{-1}$ IR spectra of NSC, NMSC and MSC. They have different band patterns. In the far infrared zone, the NSC and MSC give band at 196 cm^{-1} and 279 cm^{-1} respectively. The strong band at 196 cm^{-1} for NSC and strong broad band at 279 cm^{-1} for MSC could be assigned to $\text{Nd}-\text{Cl}$ stretching^[2] and $\text{Mg}-\text{Cl}$ stretching^[3] respectively. The band patterns for NMSC are different from those of NSC and MSC. The NMSC give band at 197, 210 and 240 cm^{-1} , whereas the 279 cm^{-1} band is not observed.

To check the differences in structure among the NSC, MSC and NMSC the anhydrous NdCl_3 was cogrounded with MgCl_2 at various molar ratio in a ball-milled vibrator for 36h. The IR data in the far IR region for comilled products are given in Table 2.

The bands at $214 - 219\text{ cm}^{-1}$ and 240 cm^{-1} occurred in comilled products at all molar ratio. These are different from the diffraction patterns of NdCl_3 and

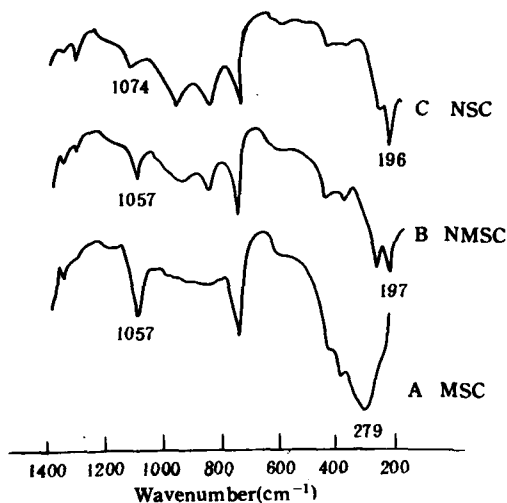


Fig.1 The IR spectra of (A) MSC
(B) NMSC (C) NSC

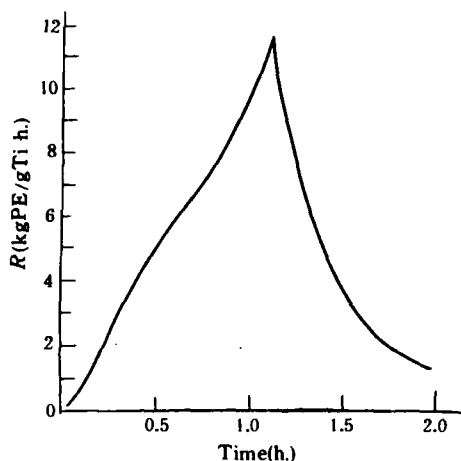


Fig.2 Kinetic curve of ethylene polymerization
with NMSC-AlEt₃ system

Table 2 The IR spectra of comilled products of NdCl₃ and MgCl₂

NdCl ₃ /MgCl ₂ molar ratio	1.8/1	1/1	1/1.8	NdCl ₃	MgCl ₂
IR in cm ⁻¹	240/219	214(wide)	275, 240, 218	206	279

Table 3 Data of X-ray analysis of NdCl₃, MgCl₂ and its comilled product

NdCl ₃		MgCl ₂		NdCl ₃ /MgCl ₂ (molar ratio=1)	
in 2θ	in I°	in 2θ	in I°	in 2θ	in I°
9.06	(80)			9.58	(98)
		13.66	(9)		
13.84	(100)			13.98	(100)
		15.12	(100)	24.18	(75)
24.20	(72)				
25.30	(83)			25.32	(79)
28.00	(46)	30.42	(71)	32.18	(49)
32.22	(41)	32.54	(3)		
		35.04	(10)	35.16	(74)
35.26	(96)				
37.24	(34)			43.04	(58)
42.46	(50)				
43.14	(77)			45.16	(27)
45.16	(24)	46.10	(3)		
49.58	(24)			49.44	(26)
		50.54	(9)		
51.56	(22)				
56.22	(23)				
57.86	(20)				

I°: line intensity in relative units

a new material may be formed. It is found that the 279 cm⁻¹ band is not observed at [Nd]/[Mg] = 1.0 and 1.8, indicating that all the MgCl₂ has been destroyed. The X-ray data (in Table 3) demonstrates also that comilling of MgCl₂ with NdCl₃ results in a complete destruction of the crystal structure of MgCl₂.

The kinetic curve of ethylene polymerization with NMSC-AlEt₃ system shows a rather peculiar type curve (Fig. 2). The rate of polymerization rises rather moderately to a maximum value and then decreases rapidly with time after about 65min. it is different from the decay-type for NSC-AlEt₃ system and the acceleration-type for MSC-AlEt₃. The difference in the behavior of ethylene polymerization rate also suggests that the bisupported catalyst NMSC has the different structure.

Keywords:

NdCl₃; MgCl₂; Bisupported catalyst; Olefin polymerization

REFERENCES

- [1] Xiao, S.J.; Wang, H. and Cai, S. M., *Makromol. Chem.*, **1991**, 192, 1059.
- [2] Taylor, M.D., Cheung, T.T. and Hussein, M. A., *J. Inorg. Nucl. Chem.*, **1972**, 34, 3073.
- [3] Xiao, S.J.; Cai, S. M.; Chen, Z. and Liu, H. L., "Catalytic Polymerization of Olefin", T. Keii, K. Soga eds., Elsevier, Tokyo, **1986**, 413.