Polymer Bulletin 30, 529–535 (1993)

Polymer Bulletin

Effects of external Lewis base on the performance of $MgCl_2$ supported catalysts in propylene polymerization

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SUMMARY

The effects of four different external Lewis bases on propylene polymerization using the $MgCl_2$-supported $TiCl_4$ catalyst were studied in the context of the variation of the chemical complexes formed between catalyst, catalyst support and internal Lewis base, and the interactions between complexes and external Lewis base. The internal Lewis base used in this study was dioctyl phthalate. With ethyl benzoate as the external donor no change in activity was observed, but the interaction between ethyl benzoate and $MgCl_2$·phthaloyl chloride complex resulted in a decrease of isotacticity. Increasing the bulkiness of the external Lewis base hindered the monomer coordination. It was found that the relative amount of the phthaloyl chloride complex to other complexes played an important role in the formation of active sites.

INTRODUCTION

The development of $MgCl_2$-supported catalysts has been a major breakthrough in the production of polyolefins. By choosing a proper combination of Lewis bases as internal and external electron donors, high isotacticity as well as high activity can be achieved. An excellent review was published recently by Barbé et al. (1)

Continuing research into improving catalyst performance has led to the uncovering of a new family of catalysts in which an aromatic diester and an alkoxy silane are used as an internal and an external donor, respectively (2,3,4). Compared with a typical monoester-containing catalyst, the new catalysts are more stable and of higher activity and stereoregularity, but the complexation of an internal base with both support and catalyst makes analysis much more involved (5,6). The catalyst performance is believed to be greatly influenced by the relative amounts of various Lewis-base complexes formed on the catalyst surface. The proportion of different complexes varies depending on the conditions under which the catalyst is prepared (5,6).

This communication presents our recent results in propylene polymerization with $MgCl_2$-supported catalyst using dioctyl

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regularity. Four different types of Lewis bases were studied in the context of the variation of complex distribution in the catalsyt and the interactions between the complex and the external Lewis base.

EXPERIMENTAL

Analytical grade n-heptane from BDH, propylene from Union Carbide, 2,2,6,6-tetramethylpiperidine from Aldrich and t-butylmethyl ether also from Aldrich were dried before use. Dioctyl phthalate, $MgCl_2$, triethylaluminum (TEA) and $TiCl_4$ all from Aldrich, and phthaloyl chloride and dimethoxydiphenyl silane from Tokyo Kasei were used as received.

In catalyst preparation, 15 g of $MgCl_2$ was mixed with dioctyl phthalate (DOP) to give a 0.075 molar ratio of DOP/$MgCl_2$. The mixture was ground for 120 h at room temperature in a 1.1 L porcelain jar, 1/4 to 1/3 filled with burundum grinding cylinders. Four grams of the ground solids were refluxed with $TiCl_4$ (about 8 mL) for 2 h at a prescribed temperature, a temperature that will be referred to later as the activation temperature. The solids were filtered hot and washed with 50 mL heptane five times at 80-95°C. After washing, the catalyst was dried in a stream of dry nitrogen for 2 h and then under vacuum for another 30 min at room temperature. The content of Ti in catalyst was determined using the colorimetric method (7).

Polymerization of propylene was carried out in a 250 mL stainless steel autoclave at 50°C. The reactor system was assembled while still hot and was thoroughly purged with dry nitrogen. Dry n-heptane was then drawn into the reactor. The temperature control was set in and monomer was introduced. Once the temperature was stablized and the solvent was saturated with propylene, a known volume of TEA together, when an external donor was employed, with a Lewis base were added. Finally the catalyst was introduced to initiate polymerization. During the run propylene was fed continuously to maintain a constant pressure (118 kPa) in the reactor. The monomer flow rate was monitored by an electronic mass flowmeter and recorded as the rates of polymerization as a function of time. The isotactic index (I.I.) of propylene products was measured as the percent of polymer insoluble in boiling heptane after 12 h in a soxhlet extractor.

The relative amounts of the Lewis base complexes in catalysts prepared at different activation temperatures were determined from IR spectra of the catalysts. The catalyst samples were prepared as nujol mull.

RESULTS AND DISCUSSION

In a separate study of the IR spectroscopy of the catalysts

(6) we identified three Lewis base complexes formed during the catalyst impregnation process, namely $MgCl_2 \cdot POC$ (phthaloyl chloride), $MgCl_2 \cdot DOP$ and $TiCl_4 \cdot DOP$ and their corresponding $\nu(C{=}O)$ absorptions were assigned at 1755, 1682 and 1648 cm^{-1}, respectively. In this study, three IR spectra of the catalysts prepared at activation temperatures of 80, 95 and 105°C were obtained and are presented in Figure 1. The origin of the POC complex is believed to be formed from the reaction of DOP and $TiCl_4$ (5,6).

It can be seen from the figure that the 1755 cm^{-1} peak increases as the activation temperature increases, accompanied by a proportional decrease of the $MgCl_2 \cdot DOP$ peak. No apparent

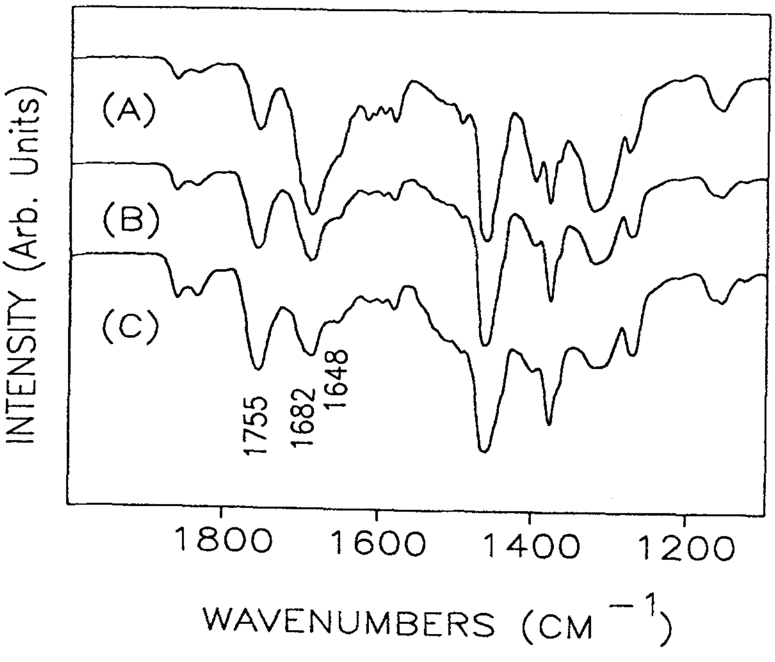

Figure 1. IR spectra of catalysts in nujol mull. Catalysts were prepared at the activation temperatures of: (A) 80°C, (B) 95°C, and (C) 105°C. The absorptions at 1755, 1682 and 1648 cm^{-1} are assigned to complexes $MgCl_2 \cdot$phthaloyl chloride (POC), $MgCl_2 \cdot$dioctyl phthalate (DOP) and $TiCl_4 \cdot$dioctyl phthalate, respectively.

change of $TiCl_4$·DOP absorption was detected. The relative variation of $MgCl_2$ complexes with DOP and POC is reported in Table 1 in terms of the absorpton ratio of ν(C=O) of $MgCl_2$·POC to ν(C=O) of $MgCl_2$·DOP. The polymerization results using different external donors are given in Table 2.

Table 1. Titanium contents in three catalysts synthesized at different activation temperatures and the relative amounts of $MgCl_2$·POC/$MgCl_2$·DOP complexes as measured by the ν(C=O) absorptions in IR spectra (Figure 1).

	Activation Temperature (°C)		
	80	95	105
Ti content, %	1.92	1.94	2.33
$MgCl_2$·POC/$MgCl_2$·DOP	0.34	0.45	0.65

Table 2. Results of propylene polymerization carried out at 50°C in heptane. Other conditions are: Monomer partial pressure = 118 kPa; [Ti] = 0.6 mmol /L; TEA/Ti = 50 in mole; external donor/TEA = 0.05.

	Activation Temperature, °C		
	80	95	105
	Activity, kg PP/g Ti·h		
Without external donor	9.6	11.0	7.6
With external donor*			
EB	8.4	8.6	7.1
DMDPS	8.4	7.4	6.8
TMPIP	9.2	10.3	6.9
TBME	9.8	9.4	10.1
	I.I., % insoluble in boiling heptane		
Without external donor	91.7	91.2	89.9
With external donor			
EB	93.1	92.4	84.1
DMDPS	96.4	95.6	95.5
TMPIP	96.0	95.7	93.7
TBME	90.0	89.8	88.7

*EB=ethyl benzoate; DMDPS=dimethoxydiphenyl silane; TMPIP=2,2,6,6-tetramethylpiperidine; TBME=t-butylmethyl ether.

From Tables 1 and 2, it is apparent that the complexes together with an external donor play a rather complicated role in polymerization. Without an external donor the catalyst activated at 95°C shows the highest activity. High relative concentration of the POC complex seems to have an adverse effect on catalyst activity. To isolate the effect of POC complex on catalyst performance a catalyst containing only POC was prepared by ball-milling $MgCl_2$ with POC alone. The same POC/$MgCl_2$ molar ratio of 0.075 was used. Polymerizations were conducted under exactly the same conditions given in Table 2. This catalyst gave an activity of 1.1 kg/g Ti·h and 93% isotactic index; the yield is much lower than any others reported in Table 2. Clearly, POC complex in excess is harmful to catalyst performance.

In an attempt to understand the interactions between those complexes with an external donor and their role in polymerization, four external donors of different types were investigated, namely ethyl benzoate (EB), dimethoxydiphenyl silane (DMDPS), 2,2,6,6-tetramethylpiperidine (TMPIP) and t-butylmethyl ether (TBME). Interestingly, the results shown in Table 2 clearly indicate that each type of external donors affects the polymerization differently. With EB, activity decreases slightly for the first two catalysts with corresponding increases in isotacticity. For the catalyst with a high ratio of POC/DOP complexes (0.65) no appreciable decrease in activity was observed, but the isotacticity drops from 89.9% in the absence of an external base to 84.1% when EB is present. This is contrary to the general belief that EB poisons atactic sites, resulting in a decrease in activity but an increase in isotacticity. At high concentrations of POC complex as in this case, EB in the presence of TEA may interact with POC without poisoning atactic sites, but converting some isotactic sites into atactic ones. No specific reason for this observation can be offered at this time.

The addition of DMDPS improves significantly the stereoregularity, but the activity suffers in all three cases. Likely DMDPS blocks the atactic sites from monomer insertion more effectively than it does the isotactic sites. On the other hand, the addition of TMPIP, as shown by Langer et al. (8), effectively transforms atactic sites to isotactic ones, resulting in an increase in isotacticity without affecting activity much.

The results with TBME as an external donor are interesting. Table 2 shows that both activity and isotacticity remain virtually unchanged with the exception of the catalyst activated at 105°C, where a significant increase in activity from 7.6 to 10.1 kg PP/g Ti·h was recorded. This is in agreement with the results of Ohnish et al. (9).

Further polymerization experiments were conducted by varying TBME concentration, and the results are shown in Figure 2. All three catalysts exhibit an optimum activity with respect to TBME concentration, whereas isotacticity remains constant.

The maximum activity, however, is shifted to higher TBME concentration, as the ratio of ν(C=O) of $MgCl_2 \cdot POC$ to ν(C=O) of $MgCl_2 \cdot DOP$ increases. A close examination of the activity plots in Figure 2 reveals that the relative proportion of the maximum yields in the three cases with or without an external donor is well preserved. This may suggest the possible replacement of POC in the complex by TBME which results in increasing the number of active sites.

The quantitative effects of POC complex on polymerization kinetics is under investigation and the result will be reported later.

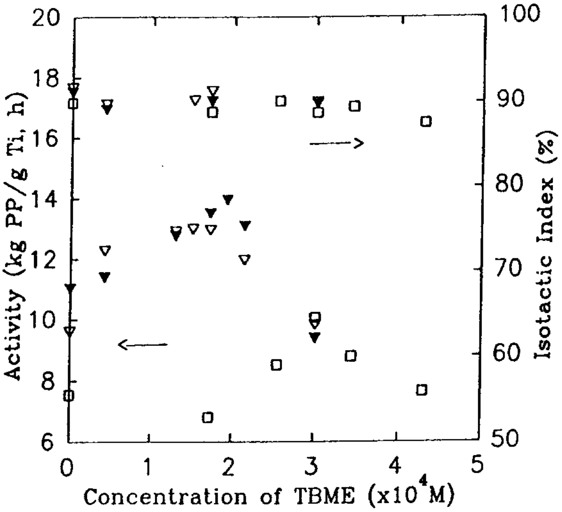

Figure 2. Effect of the external Lewis base, t-butylmethyl ether (TBME), on the catalyst activity and the polymer isotactic index, I.I., determined as the percent insoluble in boiling heptane. The catalysts were activated at 80°C (▽), 95°C (▼) and 105°C (□).

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Accepted March 10, 1993 K