JOURNAL OF CATALYSIS 147, 367–369 (1994)

NOTE

Improvement of Stereospecificity of an $MgCl_2$-Supported Titanium Catalyst upon Treatment with $Al(C_2H_5)_3$

$MgCl_2$-supported titanium catalyst consisting of $MgCl_2$, $TiCl_4$, and an internal donor compound, when used with an $Al(C_2H_5)_3$/external donor combination, exhibits very high activity and stereospecificity in propylene polymerization (1, 2). In general, $MgCl_2 \cdot TiCl_4 \cdot$ diester/$Al(C_2H_5)_3$/alkoxysilane catalyst systems have superior catalyst activity in comparison with $MgCl_2 \cdot TiCl_4 \cdot$ monoester/$Al(C_2H_5)_3$/monoester systems, mainly due to a relatively low polymerization rate decrease with time (3). The interaction of $Al(C_2H_5)_3$ with alkoxysilane which is assumed to affect the propylene polymerization rate decrease was investigated by the ^{1}H-NMR method, and was compared with that of $Al(C_2H_5)_3$/monoester. In this study diphenyldimethoxysilane(DPMS) and ethylbenzoate (EB) were selected as the representative alkoxysilane and monoester, respectively.

The ^{1}H-NMR spectra of $Al(C_2H_5)_3$ and the mixtures of $Al(C_2H_5)_3$ with EB and with DPMS were measured under a constant concentration of $Al(C_2H_5)_3$ (50 mmol/liter) using cyclohexane or cyclopentane as solvents. The spectra were recorded with a JEOL FX-100 and a GX-270 spectrometer operating at 100 MHz and 270 MHz, respectively. Instrument conditions were as follows: pulse angle = 45°; pulse repetition time 5 = s; spectral width = 2 kHz for FX-100; 4 kHz for GX-270; the number of scans = 100, internal reference and lock solvent benzene, d_6(7.26 ppm downfield from tetramethylsilane, regardless of measurement temperatures).

The ^{1}H-NMR spectrum of the EB/$Al(C_2H_5)_3$ mixture (1 : 3 molar ratio) (Fig. 1b) is more complex than that of $Al(C_2H_5)_3$ (Fig. 1a). Broad peaks at −0.08 and 0.18 ppm due to the methylene groups of $Al(C_2H_5)_3$ appear in the mixture of EB and $Al(C_2H_5)_3$ instead of the sharp quartet peaks at 0.32 ppm for $Al(C_2H_5)_3$, indicating the formation of $Al(C_2H_5)_3$ derivatives (4) in the reaction of $Al(C_2H_5)_3$ with EB.

On the other hand, only small changes in the shape of the methylene peaks were observed in the spectra of the mixture of DPMS/$Al(C_2H_5)_3$ (1 : 3 molar ratio) (Fig. 1c) compared to that of $Al(C_2H_5)_3$. The quartet peaks of the methylene group of $Al(C_2H_5)_3$ for the mixture were shifted upfield with respect to $Al(C_2H_5)_3$. This upfield shift can be attributed to electron donation from DPMS to $Al(C_2H_5)_3$, suggesting the formation of a complex of $Al(C_2H_5)_3$ with DPMS.

In order to confirm the formation of the complex, ^{1}H-NMR spectra of the DPMS/$Al(C_2H_5)_3$ mixture with 1 : 1 and 1 : 5 molar ratios were measured at −76°C and at room temperature. For the 1 : 1 mixture of DPMS and $Al(C_2H_5)_3$, the shapes and the chemical shifts of the methylene peaks of $Al(C_2H_5)_3$ remained unchanged between room temperature and −76°C (Fig. 2). On the other hand, for the mixture of DPMS/$Al(C_2H_5)_3$ with a 1 : 5 molar ratio, quartet peaks observed at room temperature were split into seven peaks in −76°C (Fig. 3). These results imply that only one type of $Al(C_2H_5)_3$ exists in the 1 : 1 mixture, while at least two types of $Al(C_2H_5)_3$ coexist in the 1 : 5 mixture. In comparison to the chemical shifts of the methylene peak of $Al(C_2H_5)_3$ and DPMS/$Al(C_2H_5)_3$ mixtures (1 : 5, 1 : 1) measured at −76°C (Figs. 4a, 4b, 4c, respectively), the position of the upfield side quartet peaks of Fig. 4b is almost same as that of the DPMS/$Al(C_2H_5)_3$ 1 : 1 mixture, and that of the downfield peaks is almost same as that of the $Al(C_2H_5)_3$. Therefore, the spectrum of the DPMS/$Al(C_2H_5)_3$ 1 : 5 mixture apparently is the overlap of two spectra, those of $Al(C_2H_5)_3$ and the DPMS/$Al(C_2H_5)_3$ 1 : 1 complex. The peak area ratio of $Al(C_2H_5)_3$ and the DPMS/$Al(C_2H_5)_3$ 1 : 1 complex of Fig. 4b was estimated to be about 2.5. It has been reported (5) that $Al(C_2H_5)_3$ was a dimeric structure, and its methylene peaks are split into two quartet peaks assigned to the bridge methylene groups (1.08 ppm(p)) and the terminal methylene groups (0.08 ppm(p)) in the low-temperature ^{1}H-NMR spectrum. Therefore, two quartets of methylene peaks observed at −76°C in Fig. 4b are assigned to the terminal methylene groups of the $Al(C_2H_5)_3$ dimer and those of the $Al(C_2H_5)_3$ complex.

Assuming that DPMS and $Al(C_2H_5)_3$ form a complex with the 1 : 1 molar ratio, the chemical composition of the sample DPMS/$Al(C_2H_5)_3$ 1 : 5 complex is described

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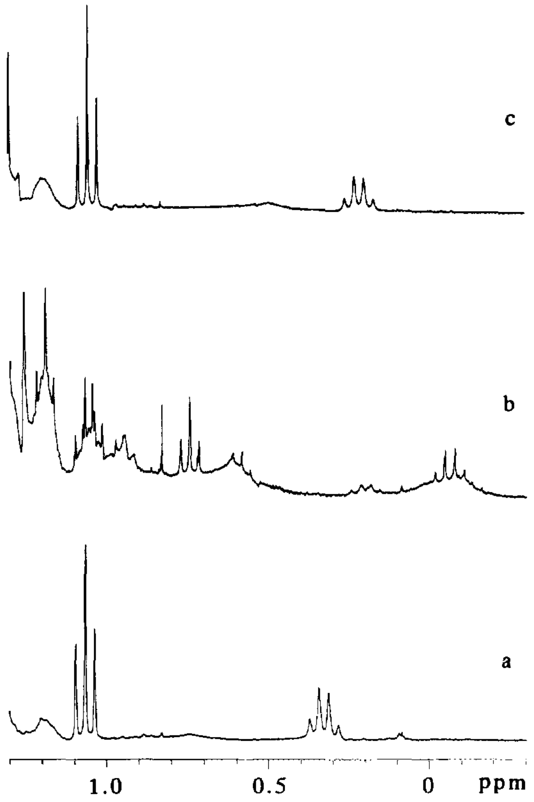


FIG. 1. ¹H-NMR spectra of $Al(C_2H_5)_3$ (a), EB/$Al(C_2H_5)_3$ = 1 : 3 (b), and DPMS/$Al(C_2H_5)_3$ = 1 : 3 (c) at room temperature.

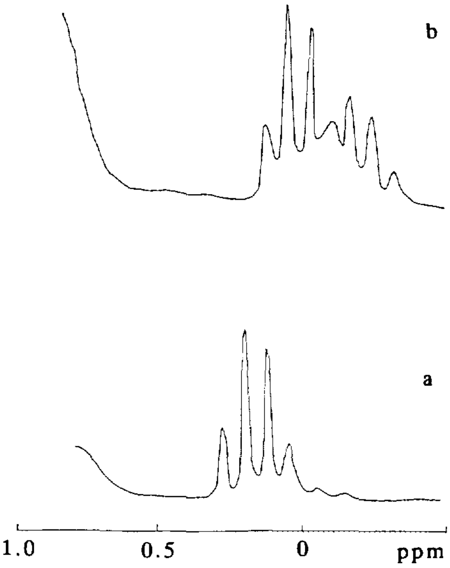


FIG. 3. ¹H-NMR spectra of the 1 : 5 mixture of DPMS/$Al(C_2H_5)_3$ at room temperature (a) and −76°C (b).

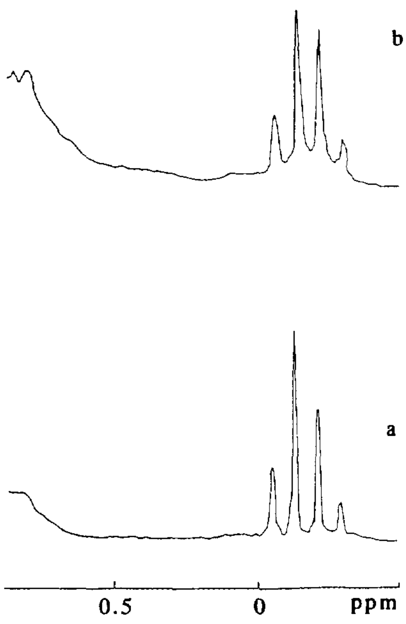


FIG. 2. ¹H-NMR spectra of the 1 : 1 mixture of DPMS/$Al(C_2H_5)_3$ at room temperature (a) and −76°C (b).

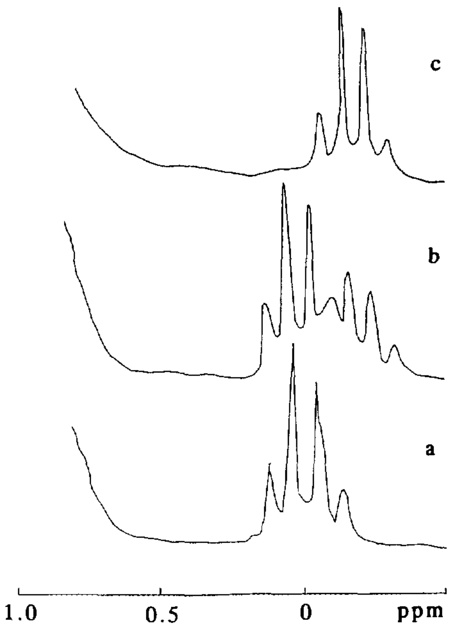
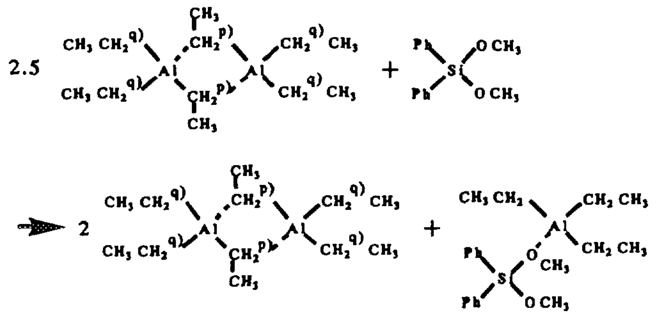


FIG. 4. ¹H-NMR spectra measured at −76°C. (a) $Al(C_2H_5)_3$; (b) DPMS/$Al(C_2H_5)_3$ = 1 : 5; (c) DPMS/$Al(C_2H_5)_3$ = 1 : 1.

as follows:



The exchange rate between dimeric $Al(C_2H_5)_3$ and the complex is slow enough at −76 °C to observe the terminal methylene peaks separately. The ratio of the terminal methylene groups in the $Al(C_2H_5)_3$ dimer and the $Al(C_2H_5)_3 \cdot$ DPMS complex in the 1 : 5 mixture is calculated to be 2.66, which roughly corresponds to the 2.5 value in Fig. 4b.

The chemical shifts of the terminal methylene peaks in DPMS/$Al(C_2H_5)_3$ mixtures (1 : 20, 1 : 5, 1 : 1), in the spectra measured at room temperature calculated on the basis of the assumption that DPMS and $Al(C_2H_5)_3$ form a complex with a 1 : 1 molar ratio, are consistent with the observed peak positions shown in Table 1.

Based on these results, we conclude that $Al(C_2H_5)_3$ reacts with DPMS and forms a stable 1 : 1 complex, the rest of $Al(C_2H_5)_3$ existing in the dimeric form.

Stability of the DPMS/$Al(C_2H_5)_3$ complex may be one of the reasons for a low rate decrease in propylene polymerization with DPMS-containing catalyst systems.

TABLE 1

Chemical Shifts of Methylene Groups in $Al(C_2H_5)_3$

$Al(C_2H_5)_3$/DPMS	$\delta(CH_2)$ obsv. (ppm)	$\delta(CH_2)$ calc. (ppm)
1	−0.08	—
5	0.32	0.34
20	0.41	0.42
$Al(C_2H_5)_3$	0.45	—

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Received September 20, 1993; revised November 22, 1993