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Interaction of α-$TiCl_3$ with organoaluminium compounds and its correlation with propylene polymerization

II. Characterization by IR

B.V. Kokta and R.G. Raj

Center for research in pulp and paper, University of Quebec at Three-Rivieres, C.P. 500,
Three-Rivieres, Quebec, Canada G9A 5H7

SUMMARY

The characterization of interaction between the catalytic components of a Ziegler-Natta sterospecific system formed by $TiCl_3$ and $AlEt_3$ in heptane was performed by IR spectroscopy. The extent of interaction was determined quantitativly by the analysis of chlorine exchange in liquid and solid phase.

INTRODUCTION

The reaction mechanism of α-$TiCl_3$ with $Al(C_2H_5)_3$ was described in our previous communication (1). The first step of reaction between α-$TiCl_3$ with $Al(C_2H_5)_3$ is an alkylation of the solid phase (exchange of Cl for ethyl) and formation of $Al(C_2H_5)_3$. This reaction was quantitatively treated in the work of Miotto (2), Simon et.al (3) and by Van Looy et.al (4). The conversion of exchange reaction was calculated indirectly from the amount of chlorine found in liquid phase by Mejzlik et.al (5). In this communication a direct measurment of the exchange reactions was perfomed by using IR spectroscopy.

EXPERIMENTAL

Chemicals and their purification

Titanium trichloride was prepared by the reduction of titanium teterachloride with hydrogen on tungsten sprial and ground under inert atmosphere in an Attritor-type ball mill (6). Triethylaluminium, diethylaluminium chloride and heptane were purified as described earlier (1).

Apparatus and Procedure

The apparatus and procedure of following the exchange reaction (alkylation) by conversion of chlorine in liquid phase has been described in the previous communication (1). In the present study, in addition to the liquid phase, the analysis of chlorine in solid phase after interaction was carried out. The solid phase was washed with the stripped heptane several times and the solid was dissolved in dilute sulphuric acid. Photometry and potentiometry were employed to determine aluminium, titanium and chlorine. IR studies were done on a two ray Spectrophtometer UR-10 (Zeiss). Sampling was done by means of hypodermic syringes, under throughly purified nitrogen, using special closed vessels under nitrogen blanket.

RESULTS AND DISCUSSION

The following are the reported (7) IR bands for Al_2Et_6 and $Al_2Et_4Cl_2$:

Al_2Et_6 : 662, 545 and 447 cm^{-1}

$Al_2Et_4Cl_2$: 673, 544 and 438 cm^{-1}

The differences between $AlEt_3$ and $AlEt_2Cl$ can be seen from the absorption region at 550-660cm^{-1} (Fig. 1). The absorption band at 675 cm^{-1} is assigned to $AlEt_2Cl$, which is in accordence with the reported value (7). The variation in $AlEt_2Cl$ concentration is shown in Fig. 1B. At lower concentrations of $AlEt_2Cl$, the absorption band at 675 cm^{-1} was not observed (curve 1). During interaction the concentration of $AlEt_3$ is constant (Figs. 1A and 1B, curves 1 and 2), so there is no change in the band at 580 cm^{-1}. For qualitative determination of $AlEt_2Cl$, the region characterized by bands at 800-825 cm^{-1} can be used.

For quantitative evaluation of chlorine in the liquid and solid phase, the band at 675 cm^{-1} was used. From the values of Fig. 1(B) a calibration curve has been constr ted (Fig. 2). The calibration curve is linear in the region considered.

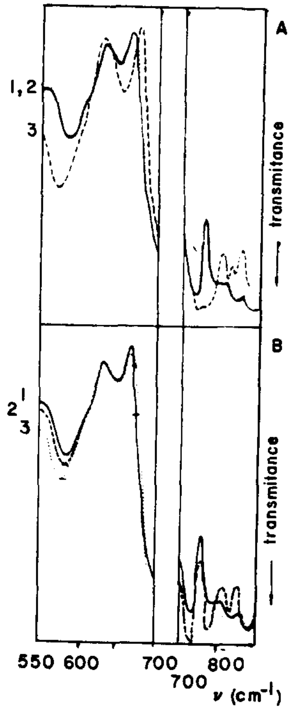

Fig. 1 IR spectra of AlEt$_3$ and AlEt$_2$ Cl

A

curves 1 and 2; AlEt$_3$ = 0.438 mole/l
curve 3; AlEt$_2$Cl = 0.482 mole/l

B

curve 1 ; AlEt$_3$ = 0.438 mole/l
AlEt$_2$Cl = 0
curve 2 ; AlEt$_3$ = 0.428 mole/l
AlEt$_2$Cl = 0.0117 mole/l
curve 3 ; AlEt$_3$ = 0.324 mole/l
AlEt$_2$Cl = 0.125 mole/l
d = 0.016
reference : heptane

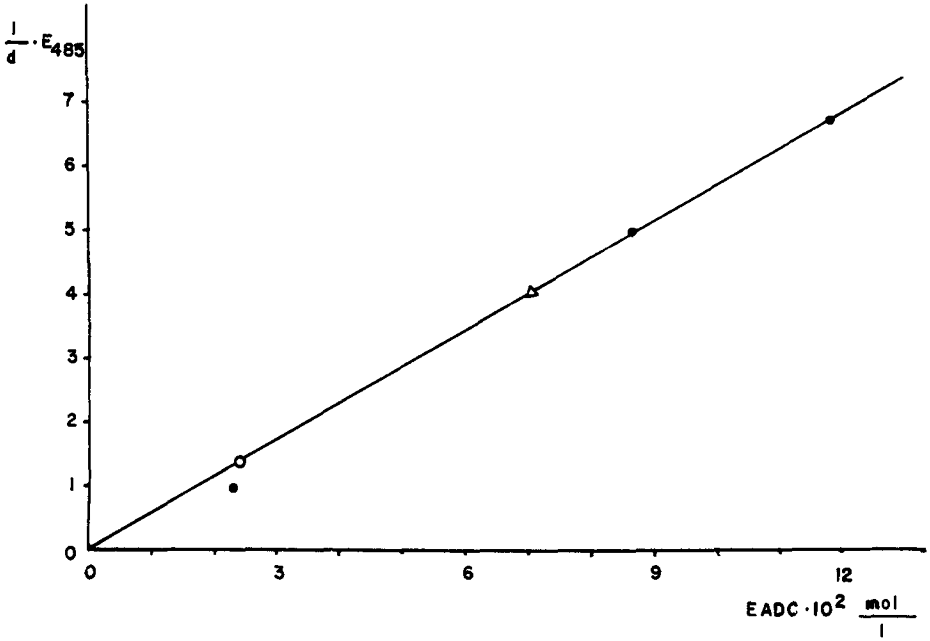

Fig. 2 The dependence of $\frac{1}{d} \ln \frac{I_0}{I}$ of $\mu = 675$ cm^{-1} on $AlEt_2Cl$ concentration

● - - - - calibration values from Fig. 1A

△ - - - - calibration value from Fig. 3, curve 2

o - - - - calibration value from Fig. 3, curve 3

The concentration of $AlEt_3$ during interaction is almost constant and therefore comparable to the calibration curve. The calibration curve also satisfies the value at 675 cm^{-1} for solution $AlEt_2Cl$ (0.482 mole/l).

The changes in IR bands after the interaction of α-$TiCl_3$ non-activated (s=5m²/g) and activated (s=80m²/g) with $AlEt_3$ in liquid phase is shown in Fig. 3.

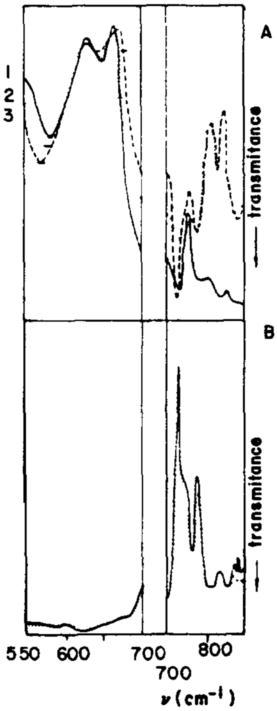

Fig. 3 IR spectra of interaction of $TiCl_3$ with $AlEt_3$

<u>A</u>

curve 1; $AlEt_3$ in heptane
$AlEt_3$ = 0.438 mole/l

curve 2; liquid phase after interaction of α-$TiCl_3$ (s= 5m²/g) with $AlEt_3$
$TiCl_3$ = 0.167 mole/l; $AlEt_3$ = 0.438 mole/l

curve 3; liquid phase after interaction of α-$TiCl_3$ (s= 80m²/g) with $AlEt_3$
$TiCl_3$ = 0.142 mole/l; $AlEt_3$ = 0.438 mole/l

<u>B</u>; heptane

The peak at 570 cm^{-1} (Fig. 3A) indicates that the amount of chlorine found in liquid phase after interaction is high in α-$TiCl_3$ activated with $AlEt_3$ (curve 3) compared to non-activated $TiCl_3$ (curve 2). The IR spectra of heptane is shown in Fig. 3B. No absorption peaks were observed in the case of pure heptane or the heptane from which the solid $TiCl_3$ was removed by centrifuging.

Table 1 Interaction of α-$TiCl_3$ with $AlEt_3$. Comparison of $AlEt_2Cl$ found by IR and by coulometric titration.

α-$TiCl_3$	$AlEt_2Cl$ after interaction (IR) mole/l	Quantity of Cl found in liquid phase (%) titration	IR
non-activated (s=5 m^2/g)	0.013	2.1	2.2
activated by milling (s=80 m^2/g)	0.138	32.6	32.3

Table 1 shows the comparison of the values of $AlEt_2Cl$ found by IR and the values calculated from the analysis of chlorine in hepatane phase. The results show a good agreement with the quantity of Cl found in the liquid phase by coulometric titration. The correlation between the chlorine lost from the solid phase and the chlorine found in liquid phase is shown in Table 2.

Table 2 Interaction of α-$TiCl_3$ with $AlEt_3$. Correlation of chlorine in solid phase and liquid phase

α-$TiCl_3$	% Cl lost from the solid phase	% Cl found in the liquid phase
non-activated (s=5 m^2/g)	2.7	2.5
activated by milling (s=80 m^2/g)	30.1	32.8

The results shown in Tables 1 and 2 confirm the validity of calculations of $AlEt_2Cl$ conversion using the % of chlorine found by coulometric titration in the liquid phase. Also, it was found that values obtained by coulometric titration, in solid and liquid phase, is more accurate than IR.

CONCLUSION

The IR spetroscopy can be used to follow $AlEt_2Cl$ formation during the interaction of catalytic components in Ziegler-Natta catalytic system. The % Cl found in liquid and solid phase after interaction by IR corresponds well with the values obtained by coulometric titrations.

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