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Highly active and stereospecific catalyst based on β-$TiCl_3$ for propylene polymerization

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A method was developed to prepare a crystalline structure of β-$TiCl_3$ (brown) using an electron-donor compound as an internal Lewis base, namely, diisoamyl ether (DIAE). β-$TiCl_3$ combined with triethylaluminium (TEA) resulted in highly active and stereospecific catalyst systems close to those based on violet $TiCl_3$ (α-, γ- or δ-$TiCl_3$) for propylene polymerization. The influence of solvent and amount of Lewis base employed in the catalyst synthesis on the catalyst properties and structure was investigated. The catalyst structure was examined by X-ray diffraction.

Introduction

There are four known polymorphic structures of $TiCl_3$, namely, α-, γ- and δ-$TiCl_3$, which are similar layered structures, all being violet, and β-$TiCl_3$ (brown) with a non-layered structure[1]. The crystal of β-$TiCl_3$ consists of infinite parallel chains packed in a hexagonal symmetry[2]. The formation of highly isospecific active centres on the surface of the heterogeneous Ziegler–Natta catalyst based on $TiCl_3$ for 1-alkene polymerization is mostly attributed to the layered structure similar to those exhibited by the violet forms (α-, γ- and δ-$TiCl_3$)[3,4]. In fact, most catalysts, even the $MgCl_2$-supported catalysts which are highly active, satisfy this description. On the other hand, the β-$TiCl_3$ form is rather atypical. Despite the fact that more than three decades have passed since discovery of the coordination catalyst for olefin polymerization, the β-$TiCl_3$ form is ill-defined. Its structural description has not been fully refined. However, recently Corradini and co-workers have re-examined the catalytic behaviour and structure of β-$TiCl_3$[3,5] and clarified some obscure features about it.

Over the last four years, we have also been interested in $TiCl_3$ catalyst systems modified with electron-donor compounds. We have already developed a highly active and stereospecific catalyst for propylene polymerization[6-8]. It is now our aim to show that a highly active and stereospecific catalyst based on β-$TiCl_3$ can be produced.

More recently, data on the effect of these electron-donating compounds, usually ethers, on the process of $TiCl_3$ catalyst synthesis have been reported in the literature[9,10]. Bukharkina *et al.*[9] related that the use of ether in different synthetic routes contributed to elucidation of the influence of these types of Lewis bases in the formation of various $TiCl_3$ modifications, in the catalyst surface area, in the number of defects on the catalyst surface, etc. That study showed the connection between catalyst properties and composition. Hence, the judicious choice of Lewis bases allows control of the catalyst properties for both supported and non-supported catalysts.

In this article, some routes for catalyst synthesis have been described, differing in the type of solvent and in the concentration of Lewis base. The investigation of $TiCl_3$ catalyst formation in presence of ether (DIAE) led to elucidation of the role of this base in the production of various $TiCl_3$ modifications, and enabled us to determine the relationship between the catalyst properties and its structure. In order to understand the behaviour of $TiCl_3$ polymorphism, in the polymerization process, a thorough investigation of some specific features of the catalyst was considered worthwhile. Thus, one of the objectives of this work was to try to elucidate the function and influence of some synthesis parameters on the catalyst structure, chemical composition and properties.

The main purpose of the present work was to investigate the effect of some reagents (solvent and electron-donor) on β-$TiCl_3$ catalyst properties and structure, as well as to describe the catalytic behaviour of propylene polymerization.

Experimental

Materials. All operations were conducted under dried nitrogen atmosphere using Schlenk techniques.

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Anhydrous solvents and ether (DIAE) were freshly refluxed for several hours over sodium and distilled before use in the catalyst synthesis. Commercial $TiCl_4$ was previously distilled. $Al(C_2H_5)_2Cl$ (DEAC) and $Al(C_2H_5)_3$ (TEA) were donated by Polibrasil S.A. and used as received. Propylene and nitrogen (from White Martis S.A.) were used after passing through 3 Å molecular sieve columns.

Preparation of β-$TiCl_3$. DEAC complexed with DIAE in toluene solution (System A) or in isooctane (C_8) solution (System B) was added dropwise (until the chosen DIAE/$TiCl_4$ mole ratio was attained) to a toluene/$TiCl_4$ solution (System A) or to an isooctane/$TiCl_4$ solution (System B) cooled at −10°C. After 1.5 h addition, the temperature of the solution was raised to 0°C (1°C min^{-1}) and then kept at this temperature for 1 h. After thermal treatment at 60°C for 1.5 h, the catalyst was thoroughly washed with isooctane. The aluminium content of the catalyst was determined by atomic absorption spectroscopy (AAS) and the titanium content by calorimetry. The X-ray diffraction patterns of the catalysts were obtained using HZG-UEB Freiberger Präzisionsmechamk equipment under the following conditions: Ni filter, 40 kV, 20 mA, step angle 0.4°, Cu-radiation and camera provided with nitrogen flux[11]. Moreover, characterization of this catalyst system was conducted very carefully as the $TiCl_3$ itself is only stable in an inert atmosphere or in vacuum.

Propylene polymerization. Propylene polymerization was performed at 50°C in a 1 dm^3 glass reactor equipped with a mechanical stirrer. Determined amounts of TEA and catalyst were added to the reactor containing 0.5 dm^3 of C_8. Propylene was then continuously fed in order to maintain a positive pressure of 100 mmHg for 1 h. The reaction mixture was cooled and the polypropylene filtered off, washed with hexane and dried. For each polymer sample, the isotacticity index (I.I., weight % of polymer insoluble in boiling C_8) was determined by Soxhlet extraction with C_8 for 6 h. The soluble polymer content in the reaction medium (isooctane) was determined by evaporation of 10 ml isooctane (polymerization dilutent) solution and the results were expressed as a percentage of total polymer.

Results and discussion

The problem of establishing the relationship of the chemical composition, the crystalline forms of catalysts based on $TiCl_3$ and their properties, in spite of many investigations in this field, has received injudicious analysis. Several differences among the crystalline modifications of $TiCl_3$ are observed the β-modification is brown with a fibre-shaped structure; the α-, γ- and δ-modifications are violet with lamellar-shaped structures. Although numerous investigations on non-supported Ziegler–Natta catalysts have been carried out with the objective of obtaining high stereospecificity and activity, they are mostly in the patent literature[12–14]: fundamental knowledge of the influence of the chemical composition on the nature of the catalyst sites, catalyst crystalline structures and the role of the ubiquitous Lewis bases almost always employed in this system is still insufficient.

In former papers[15–17], we concluded that the use of Lewis bases is useful for solubilizing the system during catalyst synthesis and therefore, when $TiCl_3$ crystallizes in presence of these bases, it is reasonable to expect a disordered structure. Furthermore, catalysts prepared in presence of Lewis bases have low aluminium contents, while catalysts prepared by ether treatment of pre-formed β-$TiCl_3$[14] showed higher aluminium contents, although they have been washed and have become less ordered and more porous as a result of ether treatment. Thus, it is preferable to add the ether before forming the catalyst structure (still in solution during the synthesis) because once it has been formed, it requires additional treatments to drive the structure change, i.e. ordered β-$TiCl_3$ to disordered crystalline structures.

$TiCl_3$ can be produced by the reduction of $TiCl_4$ with aluminium-alkyls in a hydrocarbon solvent. Ideally, one mole of $TiCl_4$ is able to react with 1/3 mole of AlR_3. Products of this reaction depend strongly on the $TiCl_4$/AlR_3 mole ratio and on the reduction temperature. In fact, the $TiCl_4$/AlR_3 mole ratio plays a major role in the preparation of β-$TiCl_3$, in particular. It is obtained only when equimolar amounts of $TiCl_4$ and AlR_3 are employed; lower Al/Ti mole ratios yield amorphous products containing a high content of aluminium, and at higher ratios, over-reduction of $TiCl_3$ is observed.

Table 1 shows the corresponding data for catalyst synthesis parameters and catalyst characterization (chemical composition). The aluminium content diminished when the amount of DIAE employed in the catalyst synthesis increased. This decrease in aluminium content confirms the base ability of extracting the aluminium compounds from the catalyst structure. This can be ascribed to the preferential solubility of the aluminium compounds in relation to titanium compounds, the former being stronger Lewis acids than the latter.

It should be noted that the amount of DIAE employed in the catalyst synthesis played a marked role in the catalytic activity (*Table 1*). The productivity was enhanced with an increase in the amount of DIAE for both catalysts synthesized in isooctane and in toluene. It can also be observed that the maximum values of catalyst activity were obtained at DIAE/$TiCl_4$ = 0.5 for the catalyst synthesized in osooctane and 0.35 for the catalyst synthesized in toluene. It is well known that ether with short chains, such as di-n-butyl ether and diisoamyl ether, are more soluble in aromatic solvents than in aliphatic solvents. Thus, inasmuch as toluene was employed as the solvent in the synthesis of these catalysts (Cat. 05, Cat. 06, Cat. 07 and Cat. 08), it resulted in a more homogeneous system during the catalyst preparation. This homogeneity has probably caused exposure of a higher number of active sites, giving increased catalytic activity.

Comparing the values of isotacticity index of the polymers obtained with the catalysts synthesized in both solvents (*Table 1*), one observes the opposite tendencies on the catalyst stereospecificty when the DIAE/$TiCl_4$ mole ratio varied. While the stereospecificity of the catalyst synthesized in isooctane tended to diminish, the stereoregularity of the polymer obtained with the catalyst prepared in toluene tended to increase. The values of isotacticity index report the percentage of insoluble polymer after isooctane extraction over 6 h. In this method, a polymer chain with higher molecular weight even with low stereoregularity is considered to be

Table 1 Catalyst synthesis conditions, characterization and evaluation in propylene polymerization

Catalyst synthesis conditions			Characterization		Evaluation in propylene polymerization		
Catalyst #	DIAE/TiCl$_4$ mole ratio	Solvent	Ti content[a] (mmol Ti/g cat.)	Al content[b] (weight %)	Catalyst activity (gPP/gTi.h)	Isotactic index[c] (weight %)	Soluble polymer[d] (weight %)
Cat. 01	0.25	isooctane	n.d.	n.d	17	n.d.	n.d
Cat. 02	0.35	isooctane	5.7	0.4	62	92	38
Cat. 03	0.40	isooctane	5.7	0.3	96	90	39
Cat. 04	0.50	isooctane	5.2	0.1	199	90	28
Cat. 05	0.25	toluene	4.9	0.9	18	96	29
Cat. 06	0.35	toluene	6.1	0.3	247	90	n.d.
Cat. 07	0.40	toluene	5.9	0.4	234	92	n.d.
Cat. 08	0.50	toluene	5.9	0.2	208	94	26

Polymerization conditions: temperature = 50°C; propylene pressure = 100 mmHg; TEA/Ti = 1; polymerization time = 1 h; polymerization dilutent = isooctane

n.d. = Not determined

[a] Determined by colorimetry

[b] Determined by atomic absorption spectroscopy (AAS)

[c] Determined by Soxhlet extraction with isooctane for 6 h

[d] Soluble polymer content in the polymerization dilutent

Table 2 Polymer properties

Catalyst #	Apparent density (g cm^{-3})	T_m[a] (°C)	ΔH_m[b] (cal g^{-1})	CI[c] (weight %)
Cat. 01	n.d.	n.d.	n.d.	n.d.
Cat. 02	0.32	156	13.6	27
Cat. 03	0.26	159	14.7	29
Cat. 04	0.23	155	14.5	29
Cat. 05	0.21	158	5.10	10
Cat. 06	0.21	158	13.8	28
Cat. 07	0.21	158	13.6	27
Cat. 08	0.20	156	12.1	24

n.d. = Not determined

[a] Melting temperature by d.s.c.

[b] Melting heat determined by d.s.c.

[c] Crystallinity index determined by d.s.c.

isotactic due to its insolubility. That could be the reason for the high value of isotacticity index (96%) found for the polymer obtained by the catalyst prepared with DIAE/TiCl$_4$ mole ratio of 0.25 (in toluene). This polymer sample obtained from Cat. 05 showed a low crystallinity index compared to the other polymers (see *Table 2*). The literature states that there is a close correlation between the polymer stereoregularity and its crystallinity index[18].

Table 2 shows that the apparent density of polymer obtained with the catalysts synthesized in isooctane decreased with an increase of the DIAE/TiCl$_4$ mole ratio. It seems that the use of DIAE at higher concentrations led to catalysts which are more porous and consequently more breakable. This increase in the porosity of catalyst particles was provoked as a consequence of the decrease of apparent density of polymers obtained with the catalysts prepared at higher DIAE/TiCl$_4$ mole ratios. On the other hand, the apparent density of polymers obtained with the catalyst synthesized in toluene did not change so much, keeping almost constant with an increase in the DIAE/TiCl$_4$ mole ratio.

Figures 1 and *2* show the X-ray diffraction patterns of some catalysts (Cat. 02, Cat. 03, Cat. 04, Cat. 05, Cat. 06

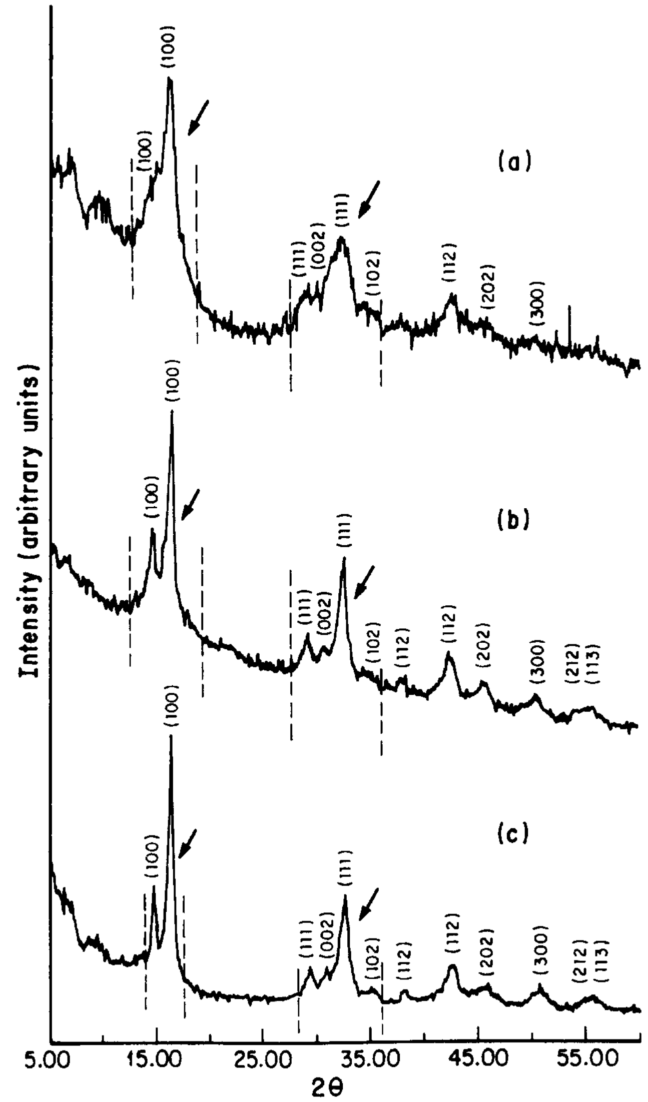

Figure 1 X-ray diffraction patterns of the catalysts prepared in isooctane: (a) Cat. 04, mole ratio DIAE/TiCl$_4$ = 0.50; (b) Cat. 03, mole ratio DIAE/TiCl$_4$ = 0.40; (c) cat. 02, mole ratio DIAE/TiCl$_4$ = 0.35

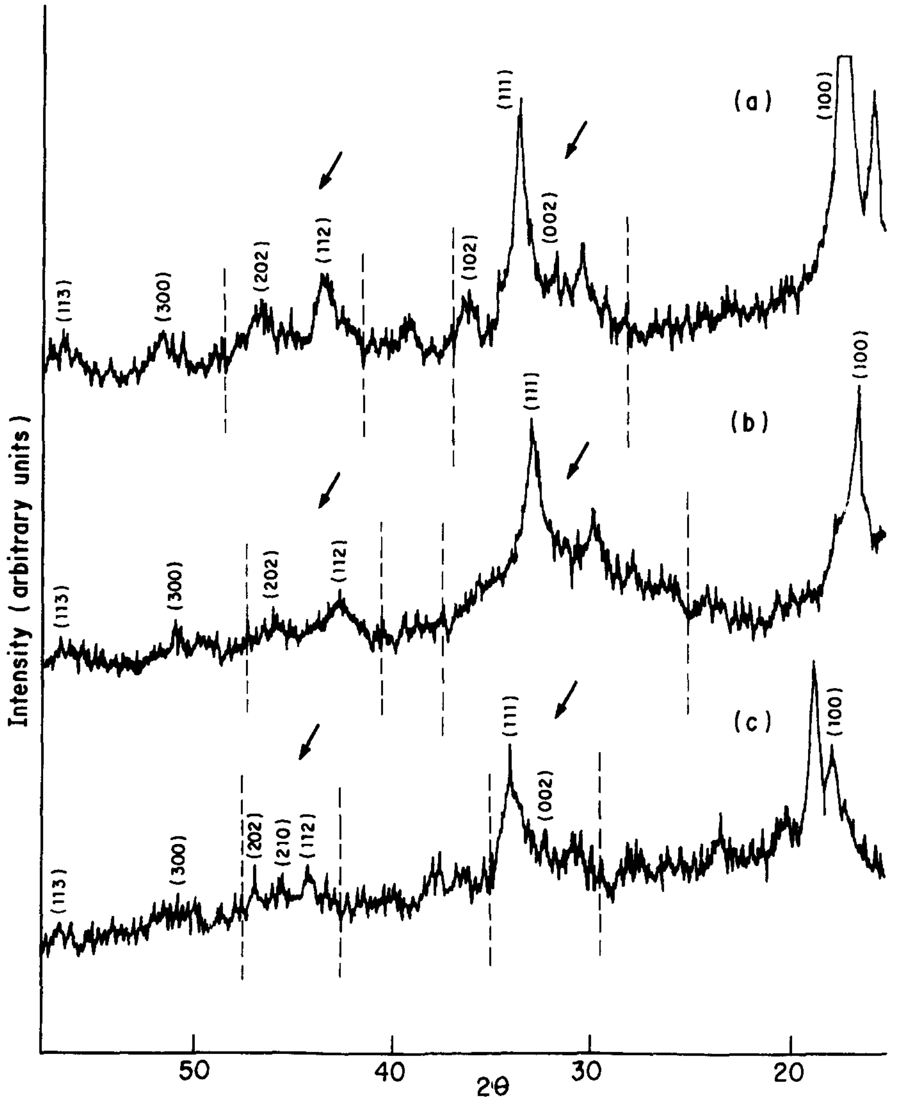

Figure 2 X-ray diffraction patterns of the catalysts prepared in toluene: (a) Cat. 07, mole ratio DIAE/TiCl$_4$ = 0.40; (b) Cat. 06, mole ratio DIAE/TiCl$_4$ = 0.35; (c) Cat. 05, mole ratio DIAE/TiCl$_4$ = 0.25

and Cat. 07). All these catalysts had the β-TiCl$_3$ crystalline structure as it can be confirmed by the main reflection planes (*h k l*) of this crystalline structure (100; 112; 300; 102 and 202). It can also be observed that the X-ray spectra present broad peaks, indicating that the crystalline structures are disordered. Moreover, at higher DIAE/TiCl$_4$ mole ratios, the peaks of the X-ray diffraction patterns became more broad, showing that the DIAE amount used in the catalyst synthesis produces more disordered structures. It can be concluded that these structures have a behaviour similar to that of δ-TiCl$_3$ which present the highest stereospecificity and productivity. These data are confirmed by the high catalytic stereospecificity and activity close to that attained with δ-TiCl$_3$ which is considered to be the best form for propylene polymerization. Thus, one of the main factors which seems to control the catalyst properties is that number of defects in the crystalline structure.

In conclusion, it was found that the catalysts based on β-TiCl$_3$ studied in this work are able to polymerize propylene with a performance comparable to the TiCl$_3$ modifications with layered structures. This similarity might be due to the presence of similar isospecific active sites among TiCl$_3$ modifications. Analysis of the catalyst structure by X-ray diffraction revealed highly disordered β-TiCl$_3$.

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