Polymer Bulletin 43, 231–238 (1999)

Polymer Bulletin

Study of the $MgCl_2$ recrystallization conditions on Ziegler-Natta catalyst properties

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Received: 14 December 1998/Revised version: 17 August 1999/Accepted: 17 August 1999

Summary

Magnesium dichloride supported titanium catalysts were prepared by dissolving anhydrous $MgCl_2$ in 1-hexanol/isooctane. Then recrystallization took place through different techniques such as evaporation of the solvent, quick cooling, precipitation with silicon tetrachloride and precipitation with titanium tetrachloride. The FT-IR analysis showed that several degrees of dealcoholation took place as a result of the adducts of $MgCl_2 \bullet XROH$. Moreover, it was found that the most active catalysts in the polymerization of ethylene were those obtained recrystallizing $MgCl_2$ by precipitation with $SiCl_4$. On the other hand, those directly recrystallized with $TiCl_4$ were the least reactive and the ones that produced polyethylenes with the highest molecular weights and the lowest degrees of crystallinity.

Introduction

Since the excellent properties of $MgCl_2$ supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of $MgCl_2$ have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between $MgCl_2$ and $TiCl_4$. These treatments have been the ball-milling (1-5), the chemical conversion (6) and the recrystallization methods (7-15). The ball-milling method allows to reduce the size of $MgCl_2$ crystallites increasing, as a consequence, the surface area of the catalyst and its activity. Nevertheless, its major disadvantage is a prevalent difficulty in controlling the polymer morphology (9-14).

On the other hand, the recrystallization method, starting from $MgCl_2$ solutions, is the most recent and offers the possibility of controlling the polymer morphology through that of the catalyst (12-14). Frequently, alcohols which react with $MgCl_2$ to give adducts of different stoichiometry, depending on the lenght of alkyl group of alcohol, are used to dissolve the $MgCl_2$ (16). In the case of the adducts of $MgCl_2 \bullet XROH$, it is convenient to remove the alcohol since, during the impregnation phase, this reacts with $TiCl_4$ and produces titanium chloride alcoxides that are inactive to polymerization. Therefore, the removal of the alcohol is very important to achieve high activities. In previously published works, the recrystallization of the support has been made by the evaporation of the solvent (11, 12, 14,15) or by cooling (7-10, 13), followed by the washing of the substratum before the impregnation phase; however, only a partial removal of the alcohol occurs through these techniques.

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In this work, catalysts starting from solutions of $MgCl_2$ in 1-hexanol/isooctane were prepared. $MgCl_2$ support was recrystallized by evaporation of the solvents, by cooling, by precipitation with $SiCl_4$ and by precipitation with $TiCl_4$. The catalysts, in turn, were tested in the polymerization of ethylene. The effects of the recrystallization technique on the catalyst performances were therefore investigated.

Experimental Part

Triethylaluminium (Schering) and titanium tetrachloride (Aldrich) were used as received. The $MgCl_2$ (Aldrich) was dried by heating at 150°C under vacuum during 48 h. The n-hexane and isooctane were dried and distilled on sodium. The 1-hexanol was used after distillation and dried on molecular sieve. The ethylene (Matheson 99.7%) was used after passing through columns of molecular sieve. Standard Schlenk techniques and high-purity nitrogen were used for the handling all the compounds.

Four different types of catalysts, consisting of $TiCl_4$ supported on $MgCl_2$, were prepared for this study. The four catalysts differ in the technique used to prepare the support. In the first step, common for all catalysts, the $MgCl_2$ was dissolved in a mixture of 1-hexanol/isooctane, with or without ethylbenzoate (EB), used as internal donor, at 100°C for 2 h, to obtain solution A:

$$\mathrm{MgCl_2+C_6H_{12}OH+C_8H_{18}} \xrightarrow{\mathrm{2h/100°C}} \mathrm{A}$$

Then, in order to prepare the different catalysts, solution A was treated in different ways:

For the first one, the $MgCl_2$ was recrystallized from solution A by cooling at -5°C until a white precipitate was formed; the resulting catalyst was designated as RT. For the second one, the $MgCl_2$ was recrystallized from solution A by evaporation of solvents under vacuum; the resulting catalyst was designated as RE. For the third type, the $MgCl_2$ was slowly precipitated from solution A with a mixture of $SiCl_4$/n-hexane until a gelatinous precipitate was formed; the resulting catalyst was designated as RSi. Then, the recrystallized supports were four times washed with n-hexane to remove the remaining alcohol. Next, they were refluxed with $TiCl_4$, in a molar relation Ti/Mg=1, for 2 h at 90°C and with constant stirring. The resulting suspensions were left to cool to room temperature and the precipitates were washed several times with n-hexane in order to remove not bonded $TiCl_4$. The washing process was repeated until no traces of titanium were detected in the washing liquid. Finally, the catalyst samples were suspended in heptane to be used in the polymerization of ethylene.

For the fourth type, the $MgCl_2$ was precipitated directly, without alcohol removal from solution A, by dropwise addition of pure $TiCl_4$ and then by 2 h heating and stirring at 90°C. The suspension was left at rest until a gelatinous precipitate was formed; then, it was four times washed with n-hexane. The washed catalyst was suspended in heptane and designated as RTi. These catalysts are listed in Table 1.

Afterwards, in order to measure the catalyst activity, polymerizations of ethylene were carried out in a 100 mL glass reactor with magnetic agitation, in 50 ml of n-hexane at a Al/Ti = 100 relation and 10 µmol Ti. Ethylene was continuously supplied at a pressure of 1 atm at 25°C for 1 h.

The content of Ti in the catalysts was determined using the colorimetric method. A Perkin Elmer 1725 spectrophotometer was used to measure the IR spectra under nitrogen atmosphere. For samples containing $MgCl_2$, Nujol mulls were prepared and held between NaCl plates. Intrinsic viscosity, $[\eta]$, of polyethylene in decaline at 135°C was measured with a PVS1 Lauda automatic viscosimeter. DSC measurements were made using a Rheometric Scientific DSC at a heating rate of 10°C/min.

Results and Discussion

As it is widely known, anhydrous $MgCl_2$ reacts with aliphatic alcohols to form adducts of different stoichiometry, depending on the type of alcohol. For example, methanol and ethanol give the hexakis adduct (9, 16); hexanol, in turn, gives bis adduct (16). Traditionally, the extraction of the alcohols such as methanol (9,12) and ethanol (11,13,14) has been performed by heating under vacuum. Nevertheless, in spite that the removal of the alcohol has not been complete through this method, the results have shown that a progressive removal of Lewis bases from the adduct by heating produces structural randomization in the magnesium dichloride chains and this, in turn, originates a highly disordered structure. Such supports have been used for the incorporation of $TiCl_4$ in order to produce catalysts for the polymerization of olefins with a high yield (12-15).

In this work, physical and chemical methods have been used in order to extract alcohol from the adduct of 1-hexanol-magnesium dichloride. The physical ones were performed through evaporation with heating under vacuum and through precipitation both followed by repeated washing. On the other hand, the chemical one was performed through the use of silicon tetrachloride as reactant. The selection of silicon tetrachloride was based on the fact that it reacts with alcohol to produce alkoxysilanes which can act as internal Lewis bases (16). In this case, the catalyst is produced through the following equations:

$$MgCl_2 + ROH \xrightarrow{2\ h/100°C} MgCl_2 \bullet ROH \xrightarrow{+\ ROH} MgCl_2 \bullet 2ROH \qquad (a)$$

$$MgCl_2 \bullet 2ROH + SiCl_4 \xrightarrow[-\ HCl]{12h/20°C} MgCl_2 \bullet Si(OR)_nCl_{4-n} \qquad (b)$$

$$MgCl_2 \bullet Si(OR)_nCl_{4-n} + TiCl_4 \xrightarrow{2h/90°C} MgTi\text{-}cat \qquad (c)$$

Studies of FT-IR

The analysis of the IR spectrum of the initial $MgCl_2$ revealed that this is not completely dehydrated since water, probably ocluded within $MgCl_2$ structure, is responsible for the IR bands at 3200-3550 cm^{-1} (O-H ν_a and ν_s) and 1600 - 1630cm^{-1} (attributed to H-O-H deformation).

In Fig. 1, the IR spectra of 1) pure $TiCl_4$, 2) the product of reaction of $TiCl_4$ with 1-hexanol, 3) the product of reaction of $SiCl_4$ with 1-hexanol and 4) the $MgCl_2 \bullet$ (1-hexanol)$_2$ adduct are shown.

The IR spectrum of ROH/$TiCl_4$ system (2) presents a centered band at 3369 cm^{-1}, corresponding to the O-H vibrations, as well as a strong band at 1071 cm^{-1}, typical of a C-O single bond stretching mode of titanium alkoxide (17).

In the IR spectrum of ROH/$SiCl_4$ (3), the band corresponding to the hydroxyl group dissapears; this indicates that dealcoholation has been completed. It shows a strong band, slightly displaced at 1098 cm^{-1}, typical of C-O that must correspond to alkoxysilane.

The IR spectrum of $MgCl_2 \bullet$ (hexanol)$_2$ adduct (2) presents some small variation in relation to the starting compounds. It is observed that the band corresponding to O-H group was displaced at a lower frequency, showing a wide band, centered on 3306 cm^{-1} and a doublette at 1058 and 1018 cm^{-1}.

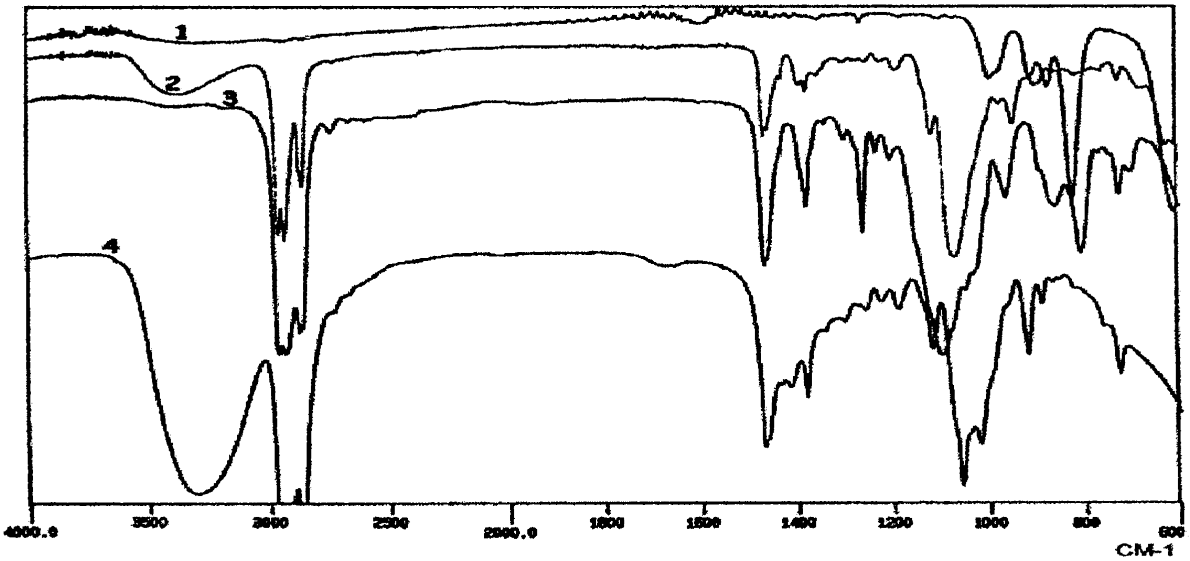

Fig. 1. FT-IR for 1)$TiCl_4$; 2)$TiCl_4$ + ROH; 3)$SiCl_4$ + ROH; 4)$MgCl_2$ + ROH.

In Fig. 2, the FT-IR spectra of catalysts 1) RSi, 2) RE and 3) RT are shown. The RE, RT and RTi (not shown) IR spectra were remarkably similar. They show bands around 3500 cm^{-1} corresponding to the hydroxyl group, a weak peak at 1620 cm^{-1} due to moisture traces, and a more strong peak at 1065 cm^{-1} corresponding to C-O of titanium chloride alkoxide. In the IR spectrum of RSi (1), the band of the OH group disappears and shows a band centered at 1590 cm^{-1} of the C-O, corresponding to the formation of alkoxysilanes.

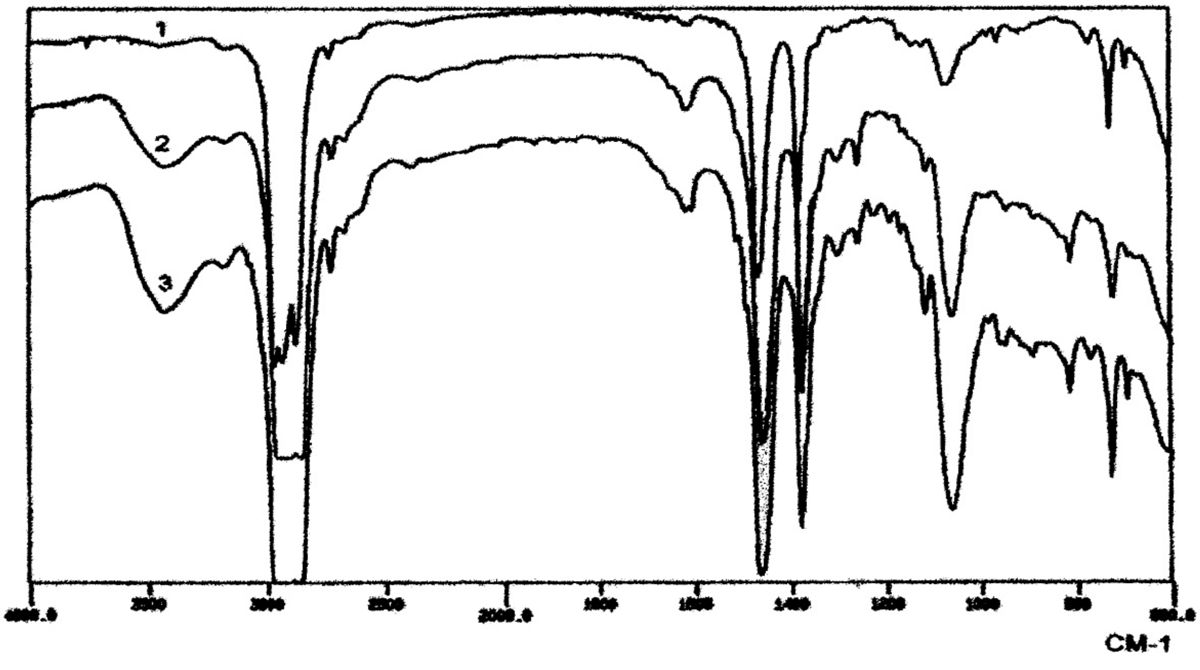

Fig. 2. FT-IR for Catalysts 1)RSi; 2)RE; 3)RT.

The FT-IR spectra in the region of 600-1800 cm^{-1} for 1) ethylbenzoate, 2) RE1 and 3) RSi1 catalysts, modified with the donor base, are shown in Fig. 3. EB presents a strong band at 1718 cm^{-1}, corresponding to the C=O vibration. On the other hand, RE1 catalyst shows a less intense peak at 1681 cm^{-1}, while RSi1 catalyst contains a strong band at 1698

cm^{-1}. These bands might correspond to the C=O vibrations of the respective $MgCl_2 \bullet EB$ complexes (1680-1695cm^{-1}) (18).

Other important bands are the ones at 1328 and 1306 cm^{-1} (in RE1) and at 1332 and 1309 cm^{-1} (in RSi1), which according to Ferreira et al (18) are interpreted as the shift on the bands at 1278 and 1108 cm^{-1}, corresponding to the vibrations of the C-O-C groups of the free EB. The RE1 catalyst shows a smaller peak centered at 1078 cm^{-1} corresponding to titanium chloride alkoxide. The FT-IR spectra of the catalysts of the RT and RTi with donors were quite similar to RE1 one. The RSi1 catalyst shows a broad band centered at 1094 cm^{-1} corresponding to the alkoxysilanes.

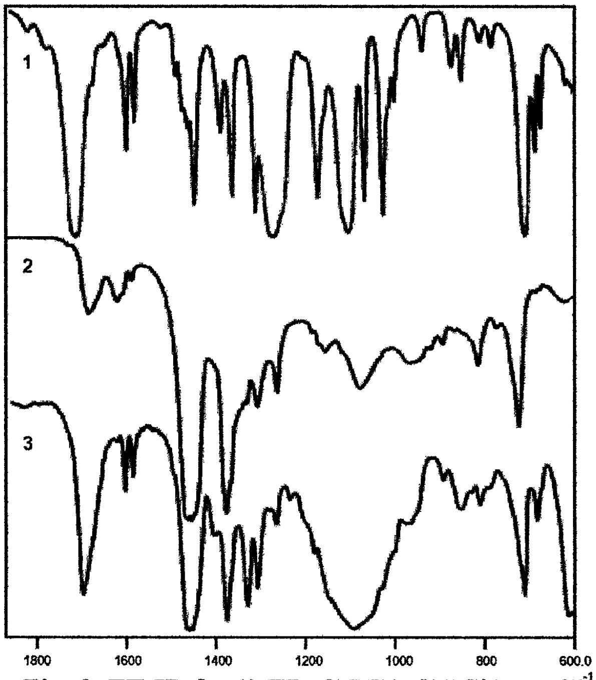

Fig. 3. FT-IR for 1) EB; 2)RE1; 3)RSi1

Titanium Content

In Table 1, the effect of recrystallization techniques of support upon the percentages of supported titanium, the activities of the catalysts, the thermal properties and the molecular weights of polymers are shown. The amount of supported titanium for the different catalysts depended on the particular preparation conditions. The catalysts obtained by the recrystallization of $MgCl_2$ through the precipitation with $TiCl_4$ (RTi) and by cooling (RT) presented the lowest values. Then the ones recrystallized by evaporation (RE) showed intermediate values. Finally, the ones recrystallized by precipitation with $SiCl_4$ (RSi) showed the highest contents.

This behavior can partially be related to both the disorder level of the crystalline structure and the size of $MgCl_2$ crystals. Besides, it can also be related to the degree of dealcoholation of the adducts during the impregnation process; this, dealcoholation, in fact, seems to be the determinant factor. According to the mentioned IR results, the dealcoholation for the catalyst RSi was complete due to the reaction between $SiCl_4$ and alcohol; while, for other catalysts, it was partial. In fact, dealcoholation affects the capacity of interaction of the $TiCl_4$ with the $MgCl_2$, which, probably occurs through a complexation on the faces (110) or (101) on the $MgCl_2$ (19).

On the other hand, the presence of the base reduced the content of titanium. As reported in literature, EB may block $TiCl_4$ fixation to certain parts of the $MgCl_2$ crystallite. The (100) and (110) faces have different Lewis acidities (the latter being more acid). Therefore, EB would be more easily removed from the (100) face and $TiCl_4$ should bind there more easily, though it might be inhibited somewhat from fixing to the (110) face (19). In the case of the catalyst RSi, the decrease of the content of titanium was higher; this may be due to the alkoxisilane formated that acts as internal Lewis base (16) reinforcing the effect of EB. In general terms, the percentages of supported titanium are relatively high and superior to those that have been reported in literature for catalysts obtained by support milling, whose values are not higher than 5% in weight (1-5), and by chemical conversion, that are around 2.4% in weight (6). The values obtained through this work are similar to those reported in literature for catalyst systems where support has been recrystallized by solvent evaporation or by cooling and where the titanium contents are in the 0.6 up to 12.5% range (7-15).

Table 1. Performances of different catalysts for ethylene polymerization

Cat	Mole ratio ED/Mg	wt % Ti(sup)[a]	Activity[b]	T_m °C	%Cr[c]	$\bar{M}$vx10^{-4}
RT	----	7.02	29.40	135.1	73.20	39.90
RT1[d]	0.16	7.01	20.47	135.0	69.20	35.10
RE	----	9.86	23.54	136.1	69.90	39.20
RE1[d]	0.16	8.01	16.25	136.0	77.30	39.30
RSi	----	11.30	49.41	135.5	67.50	40.30
RSi1[d]	0.16	7.86	26.38	136.0	70.30	38.20
RTi	----	6.94	4.96	143.1	55.80	131.00
RTi1[d]	0.16	6.26	1.74	143.4	51.10	187.90

Polymerization conditions: 25 °C for 1 h in 50 ml n-heptane, $P(C_2)$ = 1 atm, Al/Ti = 100.

a) The titanium content in support

b) In kgPE/gTi.atm.h

c) Crystallinity determined by DSC

d) EB Ethylbenzoate

Activity

The technique used in the recrystallization had a significant influence on the activities of catalysts. According to the results, it is possible to find the following order: RSi > RE > RT > RTi. The activity drops drastically from 50 Kg/gTi for the first one to about 5 kg/gTi for the last one. It is obvious that the amount of inactive titanium is increased in the same order as a consequence of the lower degrees of dealcoholation.

In the case of the catalyst RTi, the amount of alcohol present is greater than in the other samples due to the fact that the support was not washed before impregnation. For this reason, it is clear that the $TiCl_4$ tends to react considerably with alcohol, leaving very little for any other reaction. This explains its lower catalytic activity due to the formation of Cl_3Ti-O(1-hexyl), that is less active for polymerization, as well as for the lower presence of free $TiCl_4$. According to T. Garoff (20), the reaction product like Cl_3Ti-OR is inactive for polymerization. This product not only increases the weight of the catalyst but also blocks the active centers in the supported material.

The catalysts RSi type showed the higher activity due that $SiCl_4$ reacts with alcohol to form $SiCl_{4-n}$-(0-1-hexyl)$_n$ which blocks the reaction of $TiCl_4$ with alcohol during impregnation and therefore, $TiCl_4$ remains free for the polymerization.

This statement is corroborated through the result of the studies by FT-IR of the intermediary compounds and catalysts which have been discussed previously. Furthermore, it was found that the presence of the base reduced the activity of catalysts; a fact that, in turn, can be attributed to the poisoning of the nonstereospecific active centers.

Properties of Polyethylenes

The treatment afforded to the support affected the characteristics of the catalysts which, as a consequence, were reflected on the properties of polyethylenes. These can, in turn, be classified into two groups. The first one is formed by those polyethylenes obtained through RT, RE, RSi catalysts that showed fusion points, crystallinity degrees and molecular weights very similar; the second one is composed by those polyethylenes obtained through the RTi catalysts that presented the lowest values of crystallinity, near a 20% lower, and the highest molecular weights, in the order of 3 to 5 times when compared to the former group. The increase of molecular weights can be due to the formation of few active centers, in spite of high concentrations of Ti, since titanium is predominantly found forming titanium chloride alkoxide that is inactive, as it has been previously discussed. On the other hand, the high molecular weights may be responsible for the production of a great tangle of chains that tend to lower the degree of crystallinity.

Acknowledgements- The authors thank Consejo Nacional de Investigaciones Científicas (CONICIT) and Consejo de Desarrollo de La Universidad del Zulia (CONDES-LUZ) for financial support.

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