Ziegler–Natta MgCl$_2$-supported catalysts: relationship between titanium oxidation states distribution and activity in olefin polymerization

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Abstract

The chemical interaction between the procatalyst MgCl$_2$/TiCl$_4$/EB (EB = ethylbenzoate) and the cocatalyst triethylaluminium was investigated with the purpose to find a relationship between the degree of titanium reduction and the catalytic activity in ethene and propene polymerizations. This interaction was studied in dependence on Al/Ti molar ratio, activation temperature and aging time by measuring the changes of titanium oxidation states during either aging time and polymerization course. Ti(III) and Ti(II) were determined by two redox titrations, while Ti(IV) was calculated by difference, the total titanium amount being known. It was found that Ti(IV) undergoes reduction to lower oxidation states owing to treatment with AlEt$_3$ and this process is dependent on activation temperature, aging time and Al/Ti molar ratio. However, in contrast to literature reports, the Ti(IV) reduction appears to be incomplete also by using an excess of cocatalyst AlEt$_3$ or long aging times. Thus, a catalyst activated for 2 h at 70°C with a molar ratio Al/Ti = 200, showed the following distribution: Ti(IV):Ti(III):Ti(II) = 9:31:60. The activated catalysts were tested in the ethene and propene polymerizations carried out under the same conditions and the obtained activities were compared with the variation of the titanium oxidation state distribution. Whereas both Ti(III) and Ti(II) species appear to be active in the ethene polymerization, in the case of propene only the species in the higher oxidation states, such as Ti(III) and possibly Ti(IV), are catalitycally active. In particular, the variation of the catalyst activity in the propene polymerization is consistently parallel with the variation of the Ti(III) species.

Finally, in order to verify the possible influence of free monomer on the titanium reduction process, the changes in titanium oxidation states during the course of 1-hexene polymerization in heptane solution were measured. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ziegler–Natta catalysis; Supported catalysts; Titanium oxidation states; Olefin polymerization

1. Introduction

More than 40 years are passed since the Ziegler–Natta catalysts were discovered. A great deal of efforts has been made on the improvement of the catalyst performance, such as activity and stereospecifity [1]. In particular, a great effect in improving the efficiency of the olefin polymerization was reached by industrial applications of the MgCl$_2$-supported Ziegler–Natta catalytic systems, thus leading to an enormous economic outcome. In fact, the discovery that the active MgCl$_2$ (δ-form) behaves as an ideal support for the

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fixation of $TiCl_4$ allowed to prepare catalysts for the polyethene and polypropene production which brought about revolutionary industrial developments. The rapid set-up of the production plants was accompanied by a great deal of scientific publications and patents. However, many concepts, such as the structure of the active centers and the relationship between activity and oxidation states of titanium, are still under discussion. These catalytic systems are characterized by high activity and stereospecificity and are generally obtained by comilling active $MgCl_2$, $TiCl_4$ and an internal donor, followed by treatment with an Al-trialkyl as cocatalyst [2]. Although only few experimental data were so far reported, there is no doubt that Ti(IV) undergoes an extensive reduction whenever the procatalyst $TiCl_4/MgCl_2$ is treated with the cocatalyst. Thus, quantitative determination of the Ti^{n+} species carried out on the $TiCl_4/MgCl_2$ systems after contact with trietylaluminium by using potentiometric [3], polarographic [4] or EPR [5,6] methods or by redox titration [7] showed that approximately 90% of the initial Ti(IV) is rapidly reduced to Ti(III) and Ti(II). On the basis of these results it is reasonable to expect that also under polymerization conditions the reduction of Ti(IV) to Ti(III) and even to Ti(II) species may occur.

It is known that the performance of the $MgCl_2$-supported titanium catalysts in the ethene and propene polymerizations depends on both nature and oxidation states of titanium [4,8,9], but no any quantitative correlation between the degree of titanium reduction and catalytic activity was found [2]. Furthermore, no general consensus exists on the really active titanium species [8]. In particular, on the basis of EXAFS experiments [10] and of indication from industry [11], Ti(IV) was identified as the dominant catalytic species in the propene polymerization.

In this paper, we report the results of a study performed with the object to find a quantitative relationship between polymerization activity and the titanium oxidation state distribution in the catalysts, working under different polymerization conditions (activation temperature, aging time and Al/Ti molar ratio). The measurement of titanium oxidation state distribution was performed by using a modified version of the redox technique suggested by Chien et al. [7], that appeared the most suitable to carry out these measurements under polymerization conditions.

The EPR method was rejected, as it allows to determine only 20–25% of the Ti(III) species present, the remaining being EPR silent [1].

2. Experimental part

2.1. Reagents and instruments

1-Hexene, heptane, $NH_4Fe(SO_4)_2$, H_3PO_4, H_2SO_4, $Na_2Cr_2O_7$, H_2SO_4, N,N'-diphenylbenzidine, sodium diphenylamine sulfunate, 2-propanol, titanium trichloride were Aldrich Reagents Grade.

Propene and ethene (polymerization grade), the procatalyst $TiCl_4/EB/MgCl_2$ (EB = ethylbenzoate; Ti = 2.45%) and the cocatalyst triethylaluminium (TEA) were supplied by BASELL-Italia S.p.a. The solvents were purified by standard methods and refluxed over Na/K alloy for 8 h. Propene and ethene were treated with molecular sieves 4A and BASF catalyst R 3-11 in order to remove oxygen and water. TEA was used without further purification. The reagents used in the titration were only bubbled with dried nitrogen before use.

All the reagents were handled in a Braun dry-box MB 150-B-4-II under nitrogen atmosphere ($H_2O <$ 0.5 ppm and $O_2 < 2$ ppm). The ethene and propene polymerizations were carried out in a 2 l Büchi stainless steel reactor equipped with a thermostatic system and a turbine-stirrer.

Titanium was determined by ICP-AES Spectro Analytical USN-100 Instrument.

2.2. Determination of titanium oxidation states

In order to determine the titanium reduction grade in the activated catalysts, the procatalysts were treated with the cocatalyst TEA under rigorously inert atmosphere. A hexane solution of TEA (10 wt.%) was added under inert atmosphere to 0.5–0.6 g of procatalyst (0.2–0.4 mmol of Ti) suspended in 15–20 ml of hexane in a glass flask equipped with a magnetic stirrer and a graduate funnel. With the object to evaluate the effects of Al/Ti molar ratio, activation temperature and aging time on the titanium oxidation states distribution (OSD) and on the catalytic activity, the measurements were performed as follows: (i) the procatalyst was activated at 70°C by using different Al/Ti

molar ratios (15, 50, 100 and 200); (ii) operating with a constant molar ratio Al/Ti = 50 the activation was carried out at 20°, 40°, 55° and 70°C for 2 h; (iii) aging times of 10, 20, 30, 60 and 120 min were experienced at 70°C with a molar ratio Al/Ti = 50.

The activated catalysts were analyzed in order to determine the Ti(IV), Ti(III) and Ti(II) amounts following an improved titration method formerly suggested by Chien et al. [7]. This method implies a double redox titration (A and B) of the solution containing the activated catalyst. In such a way the Ti(III) and Ti(II) quantities were measured, whereas the remaining Ti(IV) could be calculated by difference, being known the initial Ti(IV) amount.

In particular, once the prearranged aging time was reached, the reaction mixture was quenched at 25°C and an overstoichiometric amount of isopropyl alcohol and 10 ml of deionized water were added. The titration procedures were as follows.

2.2.1. Titration A

0.1 N $NH_4Fe(SO_4)_2$ solution was added to the catalyst mixture until a 3 Fe/Ti molar ratio was reached. In such a way all the reduced titanium species were oxidized to Ti(IV) by Fe(III), which in turn was reduced to Fe(II). The solution was then treated with 55 ml of H_3PO_4 85% and heated at 70°C. Two milliliter of N,N'-diphenylbenzidine as indicator were added and Fe(II) formed was titrated with 0.3 N $K_2Cr_2O_7$ solution. Within ±0.03 ml of dichromate, a sharp color change from colorless to dark violet occurred at the end point. The dichromate equivalents $[n_{equiv}(K_2Cr_2O_7) = A]$ used corresponds at the end of the titration to $n_{equiv}Ti(III) + 2n_{equiv}Ti(II)$.

2.2.2. Titration B

After quenching, ca. 30 ml of a 10% H_2SO_4 solution were added to the mixture containing a precise amount of the activated catalyst. The Ti(II) species were oxidized by the protons:

$$Ti(II) + H^+ \rightarrow Ti(III) + \tfrac{1}{2}H_2$$
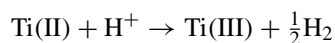
The solution was vigorously stirred for 30 min and then few drops of a solution of the indicator sodium diphenylamine sulfunate were added. The formed Ti(III) species are in turn titrated with the dichromate solution and the end point was shown by a sharp color change from purple to green occurring within ±0.02 ml. The dichromate equivalents $[n'_{equiv}(K_2Cr_2O_7) = B]$ used correspond to $n_{equiv}Ti(III) + n_{equiv}Ti(II)$.

The amounts of the three titanium species present in the activated catalyst can be calculated as follow: $n_{equiv}Ti(II) = A - B$; $n_{equiv}Ti(III) = 2B - A$; $n_{equiv}Ti(IV) = [n_{equiv}Ti(IV)]_0 - [n_{equiv}Ti(III) + n_{equiv}Ti(II)]$.

Since the titration method requires the addition of water we devised to verify the stability of Ti(II) during the time needed for its determination. Thus, we have prepared a sample of $TiCl_2$ by heating $TiCl_3$ at 475°C under vacuum [12]. This sample was dissolved in water and the solution obtained was analyzed at increasing times. Within the experimental errors, the analysis showed that the Ti(II) species is not oxidized in the course of the first 30 min, in spite of the literature indications [13]. Therefore, in the time required for the analysis (10–15 min) Ti(II) does not undergo oxidation and can be quantitatively determined.

2.2.3. Total titanium

The total titanium content was evaluated by ICP analysis and the standard deviation was ±0.3%.

2.2.4. Titration accuracy

The titrations were carried out in triplicate with an accuracy of 0.9% for Ti(II) and 1.2% for Ti(III). These results are very satisfactory on considering the complexity of the system and the difficulty to handle the samples.

2.3. Polymerization

The tests of propene and ethene polymerizations were carried out under slurry conditions at constant pressure and temperature in a 2 l Büchi stainless steel reactor equipped with a thermostatic system and a turbine stirrer. Heptane was used as reaction medium. The reactor was cleaned by heating at 105°C for 12 h under nitrogen and then filled with nitrogen and evacuated several times. The reactor was charged with 1.2 l of heptane. A weighed amount of procatalyst (0.05–0.1 g) suspended in mineral oil was injected into the reactor ($P_{olefin} = 1.2$ atm). Afterwards, pressure and temperature were raised up to the selected reaction value and the polymerization started when the required

amount of TEA (cocatalyst) was added. The reactor temperature and pressure were maintained constant within $\pm 0.5°C$ and ± 0.02 atm, respectively. The stirring speed was 1200 rpm in order to avoid effects due to monomer diffusion through the gas–liquid interface. The polymerization rate was determined by measuring the monomer consumption rate using a mass-flow meter. This procedure allowed to monitor the entire polymerization reaction course.

The 1-hexene polymerization tests were carried out in a glass flask using heptane as reaction medium under vigorous stirring at 60°C and inert atmosphere.

3. Results and discussion

The evolution of the titanium reduction in the MgCl$_2$-supported procatalyst, TiCl$_4$/MgCl$_2$/EB (EB = ethylbenzoate), caused by treatment with the cocatalyst triethylaluminium (TEA) was investigated in dependence on Al/Ti molar ratio, activation temperature and aging time.

Each of the catalytic systems so obtained was tested in the propene and ethene polymerizations with the purpose to find a correlation between the titanium oxidation state distribution (ODS) and the catalytic activity.

Table 1 reports the titanium oxidation states distribution and the activities found in the ethene and propene polymerization as function of the activation temperature.

The dependence on the Al/Ti molar ratio at 70°C of both titanium oxidation states distribution and activity in the polymerization of both ethene and propene is exhibited in Table 2.

These results appear to be in agreement with the idea that Ti(IV) fixed on the MgCl$_2$ support of the procatalyst undergoes extensive reduction, even to Ti(II), when the procatalyst is activated with a large excess of cocatalyst or by increasing the activation temperature. Moreover, the activities found in the propene polymerization carried out at 70°C with increasing Al/Ti molar ratio agree with the suggestion [5,8–10] that the active sites are formed by the titanium species in the oxidation states higher than Ti(II).

We studied also the influence of the aging time on the titanium OSD in the catalysts activated at constant temperature (70°C) and Al/Ti molar ratio (Al/Ti = 50). The obtained results are listed in Table 3. Unlike the literature reports [14,15] in which it is claimed that the equilibrium between the titanium oxidation states is reached in few minutes, we found that the reduction is remarkably time dependent and goes on especially at Ti(IV) expense, yielding increasing amounts of Ti(II).

Table 3 exhibits also the activities found at 70°C in the ethene and propene polymerizations in dependence on the aging time. It is to be observed that the activity in the propene polymerization decreases with

Table 1
Activation temperature effect on both OSD and activity in the propene and ethene polymerization[a]

T (°C)	Ti(IV)%	Ti(III)%	Ti(II)%	Activity (kg PP/g Ti h)	Activity (kg PE/g Ti h)
20	60	13	27	6.0	29.0
40	36	32	32	9.6	n.d.
55	18	44	38	10.7	n.d.
70	10	34	56	7.1	34.0

[a] Polymerization conditions: Al/Ti = 50; $P = 2$ atm; aging time: 2 h.

Table 2
Al/Ti molar ratio effect at 70°C on both titanium OSD and activity in the propene and ethene polymerization[a]

Al/Ti	Ti(IV)%	Ti(III)%	Ti(II)%	Activity (kg PP/g Ti h)	Activity (kg PE/g Ti h)
15	36	36	28	8.5	28.0
50	10	34	56	7.1	34.0
100	12	33	55	7.0	31.8
200	9	31	60	7.1	31.4

[a] Polymerization conditions: $P = 2$ atm; aging time = 2 h.

Table 3
Aging time effect at 70°C on both titanium OSD and activity in the propene and ethene polymerizations[a]

Aging time (min)	Ti(IV)%	Ti(III)%	Ti(II)%	Activity (kg PP/g Ti h)	Activity (kg PE/g Ti h)
10	30	56	14	14.3	25.0
20	19	59	22	13.7	31.4
30	15	40	45	12.7	32.0
60	12	30	58	10.2	33.2
120	10	34	56	7.1	34.0

[a] Polymerization conditions: Al/Ti = 50, $P = 2$ atm.

increasing the aging times to coincide with an increase of Ti(II) at expense of the higher titanium oxidation states. On the contrary, these catalysts exhibit a practically steady activity in the ethene polymerization with increasing aging times in the range 20–120 min. By operating in this range of activation times, a slow decrease of Ti(IV) amount, accompanied by a large decrease of Ti(III) and a more large increase of Ti(II), is observed. However, the total amount of the Ti(III) and Ti(II) species appear to be substantially constant on increasing the aging times.

This behavior is in agreement with the suggestion that the polymerization of ethene is catalyzed by both Ti(III) and Ti(II) species, while in the propene polymerization only titanium(III) and/or Ti(IV) species appear to be active. In order to confirm this deduction, in the course of polymerizations of ethene and propene we added to the polymerization bulk precise amounts of triethylaluminium at well defined times thus increasing the Al/Ti molar ratio. The rate of monomers consumption was recorded by a mass-flow meter. The obtained kinetic curves of ethene (Fig. 1) and propene (Fig. 2) polymerizations appear to be in agreement with the conclusions drawn by the analytical and polymerization data above reported.

In fact, with high Al/Ti molar ratios (≥ 850) the propene polymerization is stopped, while the ethene polymerization is only slowed down, so indicating that Ti(II) is inactive in the propene polymerization, but active, even though less, in the ethene polymerization. Furthermore, it is to be underlined that the data of Tables 1–3 are in agreement with this suggestion. In particular, the variation of Ti(III) and that one of the catalyst activity in the propene polymerization show a consistently parallel behavior.
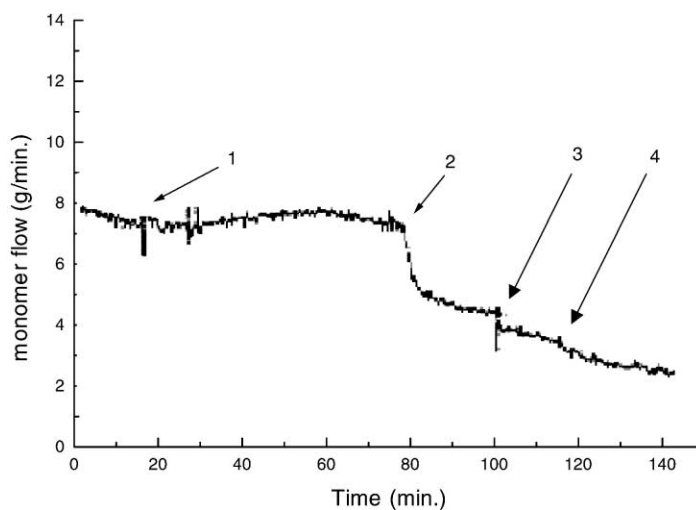

Fig. 1. Effect of the cocatalyst addition on the kinetics at 70°C of ethene polymerization catalyzed by MgCl$_2$/TiCl$_4$/EB-TEA ($P = 2$ atm; Al/Ti molar ratios: 50 (initial), 100 (1), 350 (2), 550 (3) and 850 (4)).
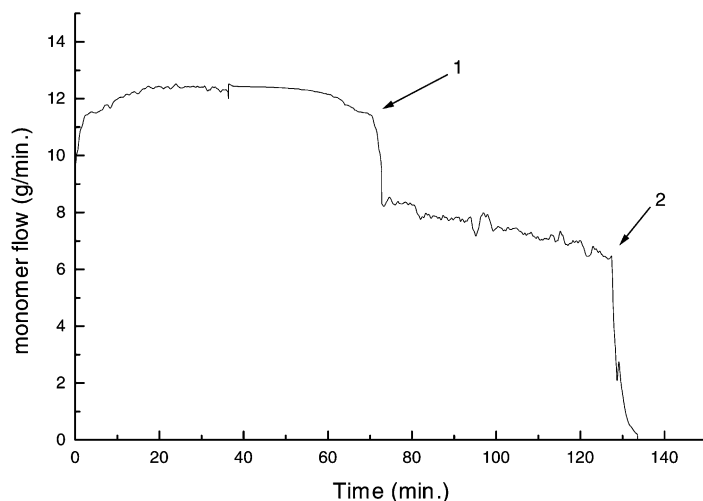
Fig. 2. Effect of the cocatalyst addition on the kinetics at 70°C of propene polymerization catalyzed by $MgCl_2/TiCl_4$/EB-TEA ($P = 2$ atm; Al/Ti molar ratios: 50 (initial), 450 (1), 850 (2)).

With the aim to determine the effect of the free monomer on the titanium OSD, we have also carried out the polymerization of 1-hexene at 60°C and measured the Ti^{n+} quantities at increasing times between 30 and 120 min. The results obtained show that the most important changes take place in the first 30 min. The small increase of Ti(IV)%, accompanied by a corresponding decrease of Ti(III)%, observed after 100 min (1.2% after 90 min versus 7.3% after 120 min), can be explained by assuming
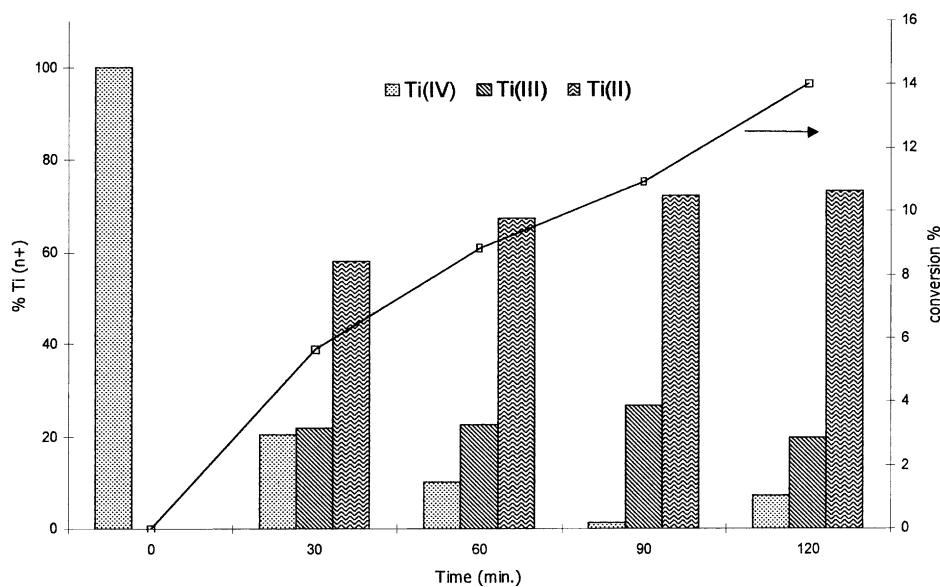

Fig. 3. Titanium oxidation state variation at 60°C during the course of 1-hexene polymerization (polymerization conditions: Al/Ti = 36; 10% hexene in heptane).

disproportionation of the Ti(III) species. Fig. 3 shows the changes of Ti^{n+} species versus time together with the conversion of monomer to polymer.

By comparing these results with those summarized in Table 3, one can observe that the reduction process of the supported titanium is very little affected by the presence of free monomer.

On the other hand, on the basis of these results it is not possible to exclude a certain participation of the monomer during the activation process. In fact, it is to be underlined that the percentage of titanium active as polymerization catalyst is very small respect to the total amount of titanium fixed on the $MgCl_2$ support. Of course, the knowledge of the mechanism controlling the formation of the catalytically active sites as well as of their nature and chemical structure is not yet exhaustive and more accurate researches are indeed required. In order to achieve such information, studies on these $MgCl_2$-supported catalytic systems are now in progress by employing XPS and EXAFS techniques.

Acknowledgements

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