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# Ethylene polymerization with heterogeneous Ziegler-Natta catalysts

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## Summary

**$TiCl_4/SiO_2$, $Ti(OC_4H_9)_4/SiO_2$, $MgCl_2/TiCl_4/SiO_2$ and $MgCl_2/Ti(OC_4H_9)_4/SiO_2$ catalysts were prepared by treating silica gel with $TiCl_4$, $Ti(OC_4H_9)_4$, $MgCl_2/TiCl_4$ or $MgCl_2/Ti(OC_4H_9)_4$ in tetrahydrofuran (THF) solution. Ethylene polymerization was performed with these catalysts activated by common alkylaluminum compounds. The influence of magnesium dichloride on catalyst performance was investigated. $MgCl_2$ has enhanced the catalyst activity for both titanium compounds. In addition, all catalyst systems were only active when they were washed with $AlCl(C_2H_5)_2$ (DEAC).**

## Introduction

The activity of Ziegler-Natta catalyst for α-olefins polymerization was substancially enhanced by supporting the titanium compounds on a solid carrier (1-6). A variety of metal halides was reported as carriers or modifier agents, and the most common and effective being magnesium dichloride treated with Lewis bases like ethyl benzoate.

In a previous paper (7), it was reported the preliminary results on the polymerization of ethylene and/or propene using the catalyst $TiCl_4/SiO_2$ activated by $Al(i\text{-}C_4H_9)_3$ which showed an increase of catalyst activity for ethylene and/or propene polymerizations when $MgCl_2$ was employed as catalyst modifier.

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This paper deals with the results of ethylene polymerization using catalysts based on $TiCl_4$ or $Ti(OC_4H_9)_4$ complexed with THF and supported on $SiO_2$. In addition, it was investigated the influence of magnesium dichloride used as catalyst modifier on the catalyst behavior. It is also described the method of the catalyst preparation.

## Experimental

**Materials** - Ethylene (genteelly donated by Research Center of Petrobras - CENPES), toluene and THF were purified according to the usual procedures. Nitrogen (White Martins S.A.) was used after passage through 3 Å molecular sieve columns. Silica gel (genteelly donated by Fuji Division Co.) was calcined at 400 °C for 8 h under argon flux. The other chemicals (research grade) were commercially purchased and used without further purification.

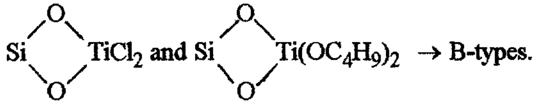
**Preparation of $SiO_2$-supported catalysts** - To a 200 mL glass reactor equipped with a magnetic stirrer and cooled at 0 °C were added 2 g of silica gel, 25 mL of fresh THF (recently distilled), 12 mmol of $MgCl_2$ and dropwise 6 mmol of $TiCl_4$ or $Ti(OC_4H_9)_4$ under nitrogen. The mixture was kept standing with vigorous stirring for 24 h at room temperature (r.t.). To the reactor were added 20 mL of THF and the mixture was again kept standing with vigorous stirring at r.t. overnight to remove the unreacted $TiCl_4$ or $Ti(OC_4H_9)_4$. Then, the precipitates were separated by decantation, adequately washed with fresh toluene (recently distilled). Then, the catalyst was washed with DEAC at mole ratio Al/THF = 2 for 1 h at r.t. The catalyst was washed several times with fresh toluene and dried. The catalyst was kept in toluene suspension with known concentration.

**Polymerization procedure** - The ethylene polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer. To the reactor were added 20 mL of fresh toluene, a prescribed amount of cocatalyst (Al/Ti = 5) and 0.1 mmol of Ti under nitrogen. Ethylene was then continuously fed to maintain a positive pressure of 100 mmHg for 15 min at 70 °C. The polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitate polymer was washed with iso-octane and dried at 80 °C for 3 h.

## Results and discussion

The reactions of $SiO_2$ with titanium compounds were already reported in the literature (8-10). When $TiCl_4$ or $Ti(OC_4H_9)_4$, for exemple, interact with a silica gel surface containing OH-groups, surface compounds of tetravalent titanium may be formed with the following compositions:

$Si\text{-}O\text{-}TiCl_3$ and $Si\text{-}O\text{-}Ti(OC_4H_9)_3$ → A-types
or



$Si\overset{O}{\underset{O}{\diamond}}TiCl_2$ and $Si\overset{O}{\underset{O}{\diamond}}Ti(OC_4H_9)_2 \rightarrow$ B-types.

In these compounds, the titanium ions are anchored by a covalent bond through oxygen to the silica gel skeleton (8). Depending on calcination temperature, the silica gel surface presents basically two types of OH-groups: single and/or neighboring ones. The silica gel calcined at 800 °C has only single hydroxyls and hence forms A-type surface compounds. When silica gel calcined at lower temperatures is used in the catalyst preparation, either A-type or B-type compounds may be formed. In the present work, the silica gel was calcined at 400 °C and treated with $TiCl_4$ or $Ti(OC_4H_9)_4$ in THF solution at r.t. where the deposition of titanium compounds proceeds mainly via compounds A- and B-types formation.

The maximum reached loading was 1.8 mmol-Ti/g-$SiO_2$, indicating that the majority of the OH-goups has reacted with titanium compounds (see Table 1). The use of $MgCl_2$ as catalyst modifier decreased the loading of titanium on silica gel, maybe due to the bimetallic complex formation between magnesium dichloride and titanium compounds anchored to silica structure.

**Table 1 - Catalyst characterization**

| Catalyst # | Catalyst type | Mg/Ti mole ratio | Ti content (mmol/g of catalyst)[a] |
|---|---|---|---|
| Cat.01 | $TiCl_4/SiO_2$ | 0 | 1.8 |
| Cat.02 | $Ti(OC_4H_9)_4/SiO_2$ | 0 | 1.6 |
| Cat.03 | $MgCl_2/TiCl_4/SiO_2$ | 2 | 1.5 |
| Cat.04 | $MgCl_2/Ti(OC_4H_9)_4/SiO_2$ | 2 | 1.3 |

**[a] Ti content was determined by colorimetric method**

The results of ethylene polymerization are summarized in Table 2. Indeed, the catalyst systems were only active when DEAC was employed as Lewis acid to form a soluble complex with THF and hence removing it from the titanium compounds. Probable, the ether had complex the titanium species preventing the polymerization process. As it can be seen the catalyst activity was markedly enhanced for both catalysts when magnesium dichloride was used as catalyst modifier.

**Table 2 - Results of ethylene polymerization[a)]**

| Catalyst # | DEAC/THF mole ratio | Cocatalyst type | Polymer yield (g) |
|---|---|---|---|
| Cat.01 | 0 | TIBA | - |
| Cat.02 | 0 | TIBA | - |
| Cat.01 | 2 | TIBA | 0.30 |
| Cat.02 | 2 | TIBA | 0.24 |
| Cat.03 | 2 | TIBA | 1.68 |
| Cat.03 | 2 | MAO | 1.07 |
| Cat.03 | 2 | TEA | 1.84 |
| Cat.03 | 2 | DEAC | 1.49 |
| Cat.04 | 2 | TIBA | 0.98 |
| Cat.04 | 2 | MAO | 1.54 |
| Cat.04 | 2 | TEA | 1.14 |
| Cat.04 | 2 | DEAC | 1.08 |

**[a)] Polymerization conditions: 70 °C, Al/Ti = 5, [Ti] = 0.1 mmol, 15 min and 100 mmHg of ethylene**
**TIBA - triisobutylaluminum, DEAC - diethylaluminum chloride, MAO - methylaluminoxane, TEA - triethylaluminum and THF - tetrahydrofuran**

This behavior has been attributed to the influence of metal chloride on the bimetallic complex formation between titanium site and other metal. The capability of electron-withdrawing of metal chloride is likely to modify the coordination of a monomer molecule with $Ti^{+3}$, depending on their electronegativities compared to Ti trivalent. As in the case of magnesium dichloride, the metal chloride should cause a favourable effect on the subsequent insertion of the coordinated monomer into the active Ti-polymer chain bond, considering that the back-donation of electron $Ti^{+3}$ to monomer is the main factor in the insertion of the Ti-monomer complex.

Table 3 shows that the catalyst activity decreased slightly when the Al/Ti mole ratio enhanced.

**Table 3 - Influence of Al/Ti mole ratio on catalyst activity for ethylene polymerization[a)]**

| Catalyst # | TEA/Ti mole ratio | Polymer yield (g) |
|---|---|---|
| Cat.04 | 1 | 1.22 |
| Cat.04 | 5 | 1.14 |
| Cat.04 | 10 | 0.81 |

**[a)]Polymerization conditions: 70 °C, [Ti] = 0.1 mmol, 15 min and 100 mmHg of ethylene, TEA - triethylaluminum**

The results described above have led to conclude that the $TiCl_4/SiO_2$ and $Ti(OC_4H_9)_4/SiO_2$ catalysts combined with common alkylaluminums used as cocatalysts can be markedly activated when they are modified with $MgCl_2$ in suitable conditions.

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