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INFLUENCE OF THE PREPARATION TECHNIQUE OF $MgCl_2/TiCl_4$ ZIEGLER-NATTA CATALYST ON THE PERFORMANCE IN ETHYLENE AND PROPYLENE POLYMERIZATION

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Abstract. Different methods to remove the alcohol of adduct $MgCl_2 \cdot nEtOH$ were studied to obtain Ziegler-Natta catalysts for evaluation in ethylene and propylene polymerization. Thus, the adduct $MgCl_2 \cdot nEtOH$ was submitted to thermal dealcoholation, as well as chemical dealcoholation with different substances: titanium tetrachloride, triethylaluminum, and dichlorodimethylsilane. Thermogravimetric analyses (TGA) were performed to obtain information on the thermal characteristics of adducts and prepared supported catalysts. Ethylene and propylene homopolymerization were carried out with the prepared catalysts and the polymers were characterized.

Keywords: polyethylene, polypropylene, dealcoholation, fourth-generation Ziegler-Natta catalyst.

1. Introduction

Polyolefin represents approximately 60 % of all thermoplastic market. There are hundreds of commercially available grades with an incredible variety of properties, and the amount of them is still steadily growing. With a proper choice of catalyst system and reaction conditions it is possible to produce materials with several applications. Polyethylene and polypropylene are typical semicrystalline plastics mainly manufactured using fourth-generation Ziegler-Natta type catalysts. The process for preparing Ziegler-Natta catalysts based on titanium compound supported on magnesium chloride is of great commercial interest because it may influence the catalytic activity, kinetics of olefin polymerization, and polymer properties. Generally, the industrial productivity of polyolefins strongly depends on the morphology of the polymer particles, which reflects the shapes of support particles in many cases. Therefore support, type of treatment, and preparation process of these catalysts are important parameters. Although massive research effort resulted in

major improvements of catalyst performance, it has to be admitted that the approach was purely empirical.

A typical Ziegler-Natta catalyst system, particularly that for propylene polymerization, consists of $MgCl_2$ -supported $TiCl_4$ with an internal donor (ID) such as phthalate, a cocatalyst such as triethylaluminum (TEA) and an external donor (ED) like alkoxysilane [1]. The use of electron donors is mainly to improve the catalyst stereospecificity. The most recently developed method for the activation of support is through chemical activation, which allows particle morphology control, and includes: (i) low temperature recrystallization of $MgCl_2$ from an emulsion with a fixed amount of ethanol, using methylsiloxane oil and paraffin oil; (ii) precipitation of the $MgCl_2$ complexes in alcoholic solutions or other polar solvent, followed by thermal or chemical decomposition of the complexes with the formation of microcrystalline $MgCl_2$; (iii) chemical synthesis of $MgCl_2$ from dialkylmagnesium compounds or Grignard reagents [2, 3].

Because of the importance of $MgCl_2 \cdot nEtOH$ adduct in the field of Ziegler-Natta catalyst, great effort has been devoted to the studies on its composition and structure [4-6]. Moreover, researches on the preparation of active support using this adduct as precursor is still being conducted. For example, in the treatment of adduct $MgCl_2 \cdot nEtOH$ with a solution of alkylaluminum reaction between ethanol and alkylaluminum molecules occurs, forming alkoxy aluminum free or fixed on the support surface, releasing ethane [7].

Currently, the use of $SiCl_4$ for the dealcoholation of adduct has been reported in the literature. The silicon tetrachloride reacts with $MgCl_2 \cdot nROH$ to form $MgCl_2 \cdot SiCl_{4-n}(OR)_n$. Then, $TiCl_4$ is supported on the alcohol-free recrystallized $MgCl_2 \cdot SiCl_{4-n}(OR)_n$. Thus, after a complete dealcoholation, the alkoxysilanes formed remain grafted in the solid catalysts and act as electron donor in the catalytic polymerization [8].

Other reports describe the preparation of $MgCl_2 \cdot nEtOH$ liquid adducts, followed by a controlled

regeneration of the active support through recrystallization by quick cooling [1, 9-11] or by solvent evaporation [11-14], with subsequent substratum washing. However, alcohol elimination is not complete through these techniques and their presence in the support is undesirable as they react with TiCl_4 during impregnation producing titanium alkoxides that are inactive for polymerization [15].

In the study reported in the present paper, we have prepared Ziegler-Natta catalysts differing in the dealcoholation method of the MgCl_2 -adduct and examined the adduct composition and their thermal stability by thermogravimetric analysis (TGA) with the aim to understand the relations between the structure of the support precursor and properties of the catalysts. These catalysts were employed in ethylene and propylene homopolymerization in slurry phase under mild reaction conditions and the catalyst activity and polymers properties were compared.

2. Experimental

2.1. Materials

All the reagents were manipulated under inert atmosphere of nitrogen using the Schlenk technique. Ethylene, propylene, and nitrogen were purified by sequential passage through columns containing 4A molecular sieves and copper catalyst to remove oxygen, carbon dioxide, and moisture. Toluene was refluxed over metallic sodium/benzophenone and was distilled under a nitrogen atmosphere prior to use. *n*-Hexane was obtained from Petroflex S.A., Brazil, anionic polymerization-grade; ethanol (Vetec Quimica Fina Ltda, Brazil) was dried with 4A molecular sieves. Triethylaluminum (TEA) (10 wt % solution in hexane, obtained from Akzo Nobel, USA) was used as received; *n*-butyl phthalate was treated in column containing silica for chromatography and anhydrous MgSO_4 . Diphenyl-dimethoxysilane from Tokyo Kasei Kogyo Co., LTD, Japan, was used as received. Dichloro-dimethylsilane obtained from Aldrich, Brazil, has undergone treatment in molecular sieve. TiCl_4 was distilled under a nitrogen atmosphere prior to use. Isoparaffin (provided by Unipar Commercial, Brazil) was treated in molecular sieve.

2.2. Preparation of MgCl_2 Support

A volume of 140 ml of anhydrous ethanol (treated in the molecular sieve and bubbled with nitrogen for 10 min) was introduced in a Schlenk and then 5 g of anhydrous magnesium chloride were added. The system was kept under stirring at 500 rpm and a flow of nitrogen, until complete dissolution of magnesium chloride in anhydrous ethanol. Then, the solution was transferred under inert atmosphere to an addition funnel, and it was added dropwise

under nitrogen flow into a flask containing 250 ml of dry isoparaffin at 233 K and stirred at 60 rpm. For a complete precipitation of the solution in isoparaffin, the system was maintained at 233 K for 1 h. Afterwards, the supernatant was removed and the adduct $\text{MgCl}_2 \cdot n\text{EtOH}$ was washed with dry hexane and transferred to a Schlenk.

2.3. Dealcoholation of Adduct

Different types of thermal and chemical dealcoholation were performed in the adduct $\text{MgCl}_2 \cdot n\text{EtOH}$.

Thermal dealcoholation. 80 ml of dry toluene were added on the catalytic precursor ($\text{MgCl}_2 \cdot n\text{EtOH}$) and this system was kept under reflux for 4 h.

Chemical dealcoholation with TiCl_4 . 30 ml of isoparaffin and then 30 ml of TiCl_4 were added, maintaining the temperature of 283 K for 10 min.

Chemical dealcoholation with TEA. 30 ml of dry hexane were added and then 150 ml of solution of TEA (10 wt % in hexane) were added on the precursor. The system was kept under stirring of 300 rpm at room temperature for 4 h.

Chemical dealcoholation with dichloro-dimethylsilane. To remove the alcohol in the support precursor, 30 ml of dry hexane and then 8.22 ml of dichloro-dimethylsilane were added, which corresponds to the same number of most used in chemical dealcoholation with TEA. The system was kept under 300 rpm at room temperature for 4 h.

After the end of each dealcoholation, the support was washed with toluene at 363 K and then dried under nitrogen flow.

2.4. Preparation of Ziegler-Natta Catalyst

1750 μl of *n*-butyl phthalate (internal donor) were added on the dealcoholated support at 363 K and then the temperature was raised to 373 K with stirring speed of 300 rpm, and the system was kept under these conditions for 2 h. Then, 30 ml of isoparaffin and 30 ml of TiCl_4 were added on the support at 383 K for 2 h, under nitrogen atmosphere. After the time of impregnation, the supernatant was removed and the catalytic solid was washed with dry toluene at 363 K until no residue of HCl was observed. The catalyst obtained was dried until constant weight under nitrogen flow.

2.5. Polymerization

Ethylene and propylene homopolymerization were carried out in a 1000 ml glass reactor. The reagents were added into the reactor in the following order: hexane, TEA solution as cocatalyst, diphenyl-dimethoxysilane as external donor; the suspension of the supported catalyst was injected into the reactor and the pressure of ethylene or propylene was increased to 200 kPa, ethylene or propylene polymerization was conducted under 600 rpm and 343 K.

The reaction was interrupted after one hour and polymer was transferred to a solution of HCl/ethanol. After 24 h under magnetic stirring, the polymer was filtrated, washed with $NaHCO_3$ solution and ethanol, and dried at 333 K to constant weight.

2.6. Adduct, Support and Catalyst Characterization

The chemical characteristics of the adduct, supports and catalysts were evaluated through thermogravimetric analysis (TGA) in a TA Instruments – model Q500. The samples were heated from room temperature to 973 K with heating rate of 10 K/min under nitrogen atmosphere. The determination of the titanium content in the catalyst was carried out by the colorimetric method. The absorbance reading was performed in a Turner SP 870 UV-Vis spectrophotometer using a wavelength between 370–410 nm. The specific area (S_g), average pore volume (V_p) and average pore diameter (D_p) of the adduct, supports and catalysts were determined by N_2 physisorption at 77 K. The S_g was calculated by the BÉT method (Brunauer, Emmett and Teller), and the V_p and D_p (in the range of 2 to 100 nm) were calculated by the BJH method (Barrett, Joyner and Halenda) in the adsorption branch.

2.7. Polymer Characterization

2.7.1. Thermal analysis (DSC)

The polymers thermal characteristics such as melting temperature (T_m) and crystallinity degree (X_c) were obtained by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 at a heating rate of 10 K/min. Approximately 3.0 mg of polymer sample was sealed in aluminum pan. The temperature was raised from 313 K to 423 K at a rate of 10 K/min under nitrogen atmosphere. The sample was kept for 10 min at this temperature to eliminate the heat history before cooling at a rate of 10 K/min.

2.7.2. Infrared spectroscopy (FTIR)

This technique was used for determination of the isotactic index using accessory ATR (Attenuated Total Reflectance). 100 scans were performed with a resolution of 4 cm^{-1} . According to Burfield and Loi [14] this technique can replace ^{13}C -NMR to obtain the isotactic index of polypropylene. The authors constructed a calibration curve relating the ratio of the absorbance at 998 cm^{-1} (associated to alpha-helix conformation of the isotactic chains) and 973 cm^{-1} (internal standard), according to Eq. (1). In this technique the stereoregularity of the polymer is defined by dyads (mm).

$$\frac{A_{998}}{A_{973}} = 1.08(I.I.) - 0.15 \quad (1)$$

where A_{998} and A_{973} are absorbance obtained in FTIR spectrum; $I.I.$ is isotactic index, %.

3. Results and Discussion

3.1. Thermogravimetric Analysis

By thermogravimetric analysis, information about structure and mechanism of thermal decomposition can be obtained. Fig. 1a presents the thermogram of the sample of the adduct ($MgCl_2 \cdot nEtOH$), which shows the lost 67.3 % of the initial mass when the temperature was raised from room temperature to the first plateau at 573 K. According to [16], in this range of temperature molecules of HCl may have been released in addition to ethanol, during the adduct decomposition.

The peak temperatures of the derivative of TGA (DTG) were about 323, 365, 405, 436 and 495 K until the plateau at 573 K, and lastly, a broad peak at 724 K. There is no decomposition till 558 K, indicating the absence of the species $MgCl_2 \cdot nH_2O$.

The peak at 724 K is probably caused by decomposition of $Mg(OH)Cl$. When the temperature was increased to 973 K, only 16.4 % of mass of the sample was left. Possibly this is the mass of magnesium oxide (MgO).

Whereas the decomposition of the adduct to 573 K leads to the formation of $Mg(OH)Cl$ and that at 723 K results in MgO , we can calculate the ethanol content of the adduct (n), according to Eq. (2) presented below. The value of n was calculated and resulted 3.0, then the adduct obtained in this work has the composition $MgCl_2 \cdot 3EtOH$.

$$n = \frac{100MW_{Mg(OH)Cl} - MW_{MgCl_2}}{MW_{EtOH}} \quad (2)$$

where $MW_{Mg(OH)Cl} = 76.8\text{ g/mol}$; $MW_{MgCl_2} = 95.3\text{ g/mol}$; $MW_{EtOH} = 46.0\text{ g/mol}$; $\%Mg(OH)Cl = 100 - \%$ volatile to 573 K.

Moreover, we can confirm the amount of MgO residue after the loss at 723 K according to Eq. (3). The content of MgO was calculated to be 17.1 %, which is very close to the value obtained at the end of heating (973 K), which was 16.4 %.

$$\%MgO = \frac{100MW_{MgO}}{MW_{MgCl_2 \cdot nEtOH}} \quad (3)$$

where $MW_{MgO} = 40.3\text{ g/mol}$; $MW_{MgCl_2 \cdot nEtOH} = 233.3\text{ g/mol}$.

After thermal dealcoholation of the adduct, the support I was also analyzed by TGA (Fig. 1b), and a lack of the peak at 323 K was observed, although a peak at 335 K and the appearance of a fine peak of 389 K in this

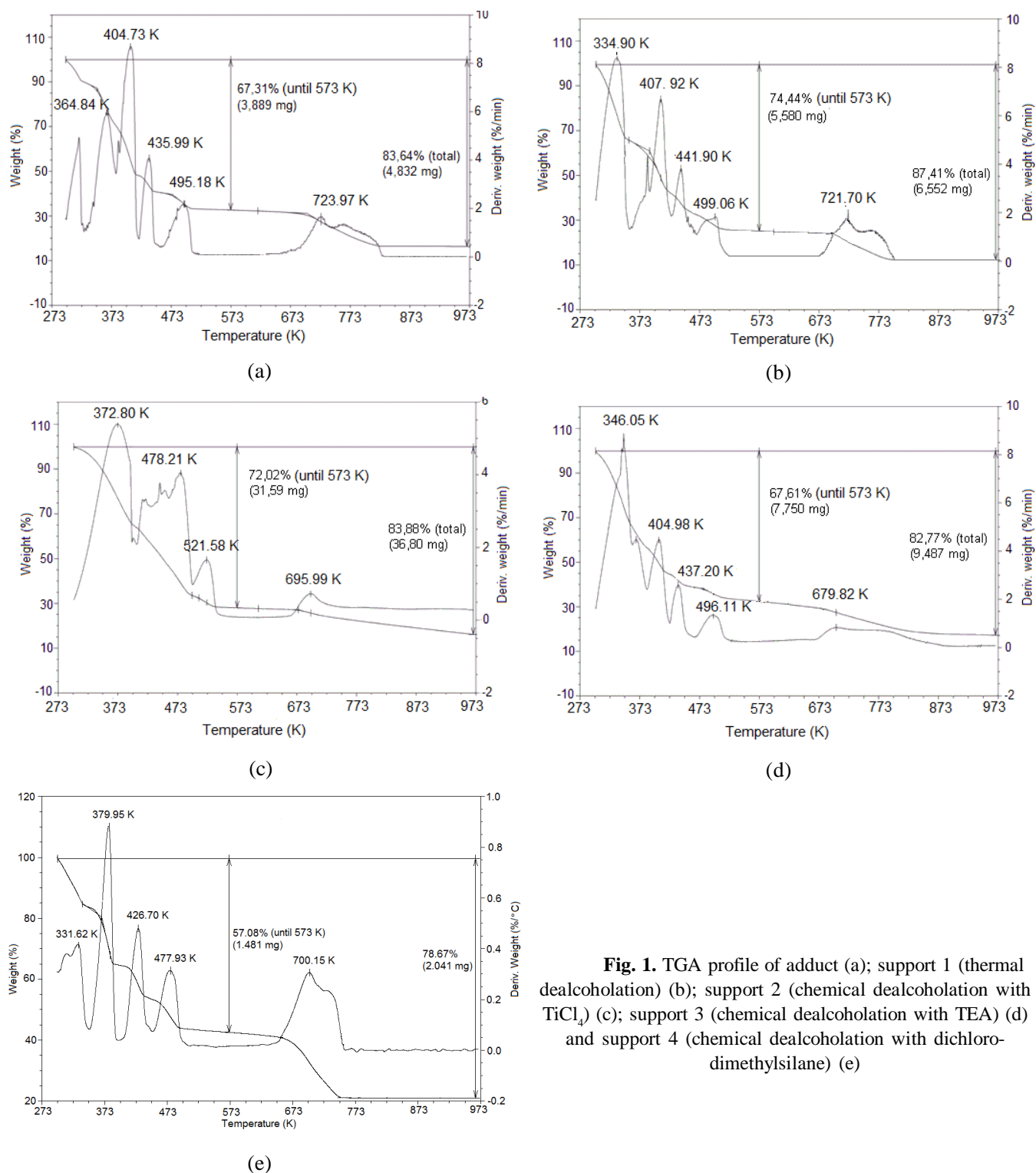


Fig. 1. TGA profile of adduct (a); support 1 (thermal dealcoholation) (b); support 2 (chemical dealcoholation with TiCl_4) (c); support 3 (chemical dealcoholation with TEA) (d) and support 4 (chemical dealcoholation with dichlorodimethylsilane) (e)

support is noticed. The other peaks (408, 442 and 499 K) appear at temperatures slightly higher than those of the adduct. The peak at 722 K is very similar to that of the precursor. Moreover, it can be seen that the volatile content of the support 1 was higher than in the analysis of the

adduct. This may be due to the presence of residual toluene in the treated adduct.

In the case of support 2 (Fig. 1c), the peaks found in the DTG were around 373 K, a very broad peak with maximum at 478 K, a peak at 522 K, and finally a narrow

peak at 696 K. The volatile content from 398 to 478 K may be due to the evolution of HCl arising from treatment with $TiCl_4$.

Support 3 (Fig. 1d) showed peaks at 346, 367, 405, 437, 496, and 702 K, which are very similar to the profile of the adduct, probably due to the formation of aluminum alkoxides fixed in the support surface. Finally, support 4 (Fig. 1e) showed a different profile of degradation, with peaks at 332, 380, 427, 478, and 700 K. This support seems to be less thermally stable than the others.

3.2. Textural Characterization of Supports and Performance of Catalysts

Although the physisorption technique is not highly sensitive to low specific area values, according to the results presented in Table 1, support 1 presented the highest specific area, pore volume and size values. Therefore, its catalyst presented a high titanium content and high catalytic activity for both ethylene and propylene polymerizations (Fig. 2).

The heat treatment of the adduct (support 1) caused the pore size to increase, with a consequent decrease in the specific area. Treatment with $TiCl_4$ (support 2) before impregnation led to a marked reduction of the texture properties of the material, showing that apparently the titanium chloride alkoxide was not effectively washed from the support surface, occupying sites where the potentially active titanium could be fixed after impregnation. So, the final Ti content was lower (cat 2) than in cat 1 and its activity was relatively low in both ethylene and propylene polymerizations. On the other hand, dealcoholation with TEA (support 3) slightly decreased the texture properties and the Ti content fixed on this support was the lowest among the catalysts obtained. Nonetheless, cat 3 was very active.

The treatment with dichloro-dimethylsilane in support 4 led to formation of catalyst with low polymerization activity. It is possible that due to the presence of two chlorine atoms in the structure of dichloro-dimethylsilane this compound was fixed on the surface defects of $MgCl_2$ in the form of diethoxysilane, filling positions where potentially active titanium would be fixed, which explains the decreased activity of catalysts 4.

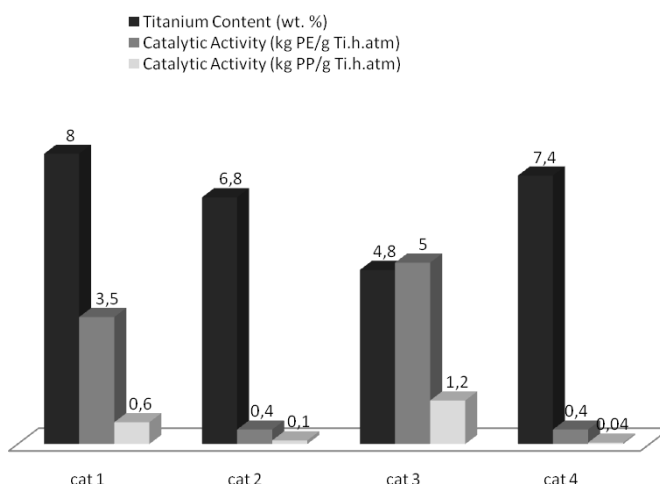


Fig. 2. Titanium content and catalytic activity in ethylene and propylene polymerization. Polymerization conditions: TEA/ED = 50; $m_{cat} = 0.05$ g; $n_{TEA} = 7.5$ mmol; hexane (100 ml); $T_{polym} = 343$ K; $t = 1$ h; $p = 200$ kPa).

3.3. Polymer Characterization

3.3.1. Thermal analysis and isotactic index

Fig. 3 shows the result of the DSC of the polyethylenes synthesized with the obtained catalysts. Polymers PE 1 and PE 2 showed higher values of T_m and X_c . On the other hand, the results of the DSC and isotactic index (I.I.) of the polypropylenes obtained with different catalysts synthesized are presented in Fig. 4. Polymers PP 1 and PP 2 showed higher values of I.I., T_m , and X_c . This means that catalysts 1 and 2 were the most stereospecific ones. These results may be related to the fact that both catalysts are very alike, since their preparation procedure employed reaction only with $TiCl_4$, not involving reaction with other compound. The performance of catalyst 3 was also remarkable, especially regarding the catalyst activity.

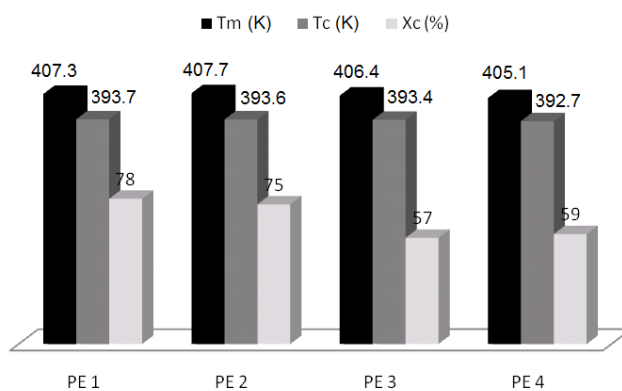


Fig. 3. Results of thermal analysis of polyethylenes obtained with synthesized catalysts

Table 1

Values of specific area, volume and pore size of the supports

Adduct and supports	Type of dealcoholation of the adduct	S_g , m^2/g	V_p , cm^3/g	D_p , \AA
1	Thermal	17.6	0.1	209.8
2	$TiCl_4$	7.0	0.005	53.6
3	TEA	18.4	0.05	147.5
4	$Cl_2(CH_3)_2Si$	7.2	0.04	208.4

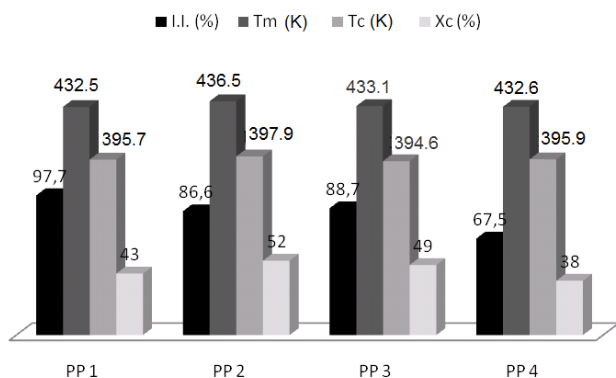


Fig. 4. Results of thermal analysis and isotactic index of polypropylenes

4. Conclusions

The prepared catalysts employing supports with thermal activation (catalyst 1) of the adduct $MgCl_2 \cdot nOEt_2$, as well as chemical activation with $TiCl_4$ (catalyst 2), showed high Ti content. However, the catalyst obtained with the adduct treated with $AlEt_3$ (catalyst 3) presented the highest activity for both ethylene and propylene polymerizations, although this catalyst showed relatively low Ti amount fixed on the support surface.

Regarding the characteristics of the synthesized polymers, polyethylene prepared with the first two mentioned catalysts presented improved thermal characteristics. On the other hand, polypropylene obtained with catalysts 1, 2 and 2 showed the highest values of melting temperatures, isotacticity, and crystallinity degree.

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ВПЛИВ ТЕХНОЛОГІЇ ПРИГОТУВАННЯ $MgCl_2/TiCl_4$ КАТАЛІЗАТОРА ЦИГЛЕРА-НАТТА НА ПЕРЕБІГ РЕАКЦІЇ ПОЛІМЕРИЗАЦІЇ ЕТИЛЕНУ І ПРОПІЛЕНУ

Анотація. Вивчено різні методи вилучення спирту з адукту $MgCl_2 \cdot nEtOH$ для одержання каталізаторів Циглера-Натта, які використовуються при полімеризації етилену і пропілену. Адукт $MgCl_2 \cdot nEtOH$ піддавали термічній та хімічній dealкоголізації з різними речовинами: тетрахлоридом титану, триетилалюмінієм та дихлоро-диметилсиланом. З використанням термогравіметричного аналізу одержано термічні характеристики адуктів та каталізаторів на їх основі. Проведена гомополімеризація етилену, а також пропілену в присутності приготованих каталізаторів та охарактеризовано отримані полімери.

Ключові слова: поліетилен, поліпропілен, dealкоголізація, каталізатор Циглера-Натта четвертого покоління.