

Polymerization of ethylene by oxide-supported titanium halide catalyst: kinetic model with a deactivation of active species

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Abstract

The effect of the calcination temperature of alumina, which was then used as a support for a titanium halide catalyst [TiCl₄/Et₂AlCl], on the catalyst activity in ethylene polymerization was investigated. α-Al₂O₃ was found to make a more advantageous catalyst support as compared to γ-Al₂O₃ despite the fact that the former offered a clearly lower specific surface area and its content of surface OH groups was inferior. The ethylene polymerization in the presence of the catalytic system on different alumina supports was investigated on the basis of a proposed kinetic model, taking into consideration the deactivation of active sites in the process. The improved activity was found to result from the better utilisation of adsorbed titanium chloride in the formation of active sites (increase of [C₀^{*}]) and from the higher stability of said sites (lower k_t), while their chemical nature underwent no significant change (k_p and k_{tr} remain unchanged). © 2000 Elsevier Science Ltd. All rights reserved.

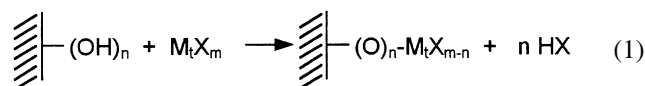
Keywords: Titanium Ziegler–Natta type catalyst; Oxide-type support; Polymerization of ethylene

1. Introduction

The supported organo-metallic catalysts are much more active in olefin polymerization than their non-supported counterparts. This could be expected to be from the superior dispersion of a transition metal compound employed over a developed surface of a support. The improved activity of a titanium–aluminium catalyst supported on silica has been explained in this way [1]. On the other hand, however, some studies find no correlation between the catalyst activity and the surface area of the support used for that catalyst production [2–5]. The structural requirements for the supports and their effects on the yields and properties of the polymer have not been clearly defined till date.

The investigation of various supported catalysts reveals that the support material frequently takes part in the formation of superficial metal complexes [6–9]. Thus, in the case of most inorganic supports, predominantly oxides, the hydroxyl groups remain on the surface after the adsorbed water has been removed therefrom. When a supported catalyst is synthesised, these groups are involved in the formation of surface-bounded chemical compounds where the metal atom is fixed to the support surface through the

oxygen atom, according to the following equation:



Further, the obtained superficial compound of, for example, titanium in the reaction with an organo-aluminium co-catalyst, yields the surface complexes, which are active in the polymerization reaction.

In the case of oxide-type supporting materials, the type, concentration and arrangement of ion sites over the surface, inclusive of OH groups, can be changed by the chemical modification of the support, and predominantly by changing the conditions of its calcination.

Alumina in the γ-form is generally employed as a catalyst support for various chemical processes, inclusive of olefin polymerization. This material is obtained by annealing at a temperature of up to 500°C. It offers a relatively high specific surface area (>200 m²/g) [10] and a relatively high number of OH groups (5.7 μmol/m²) [1]. Our investigations have revealed, however, that employing a higher temperature for alumina dehydration, above 500°C, improves the activity of the supported titanium catalyst in the ethylene polymerization process [11–13]. This effect is pretty surprising since any increase in the alumina annealing temperature is expected to reduce the specific surface area

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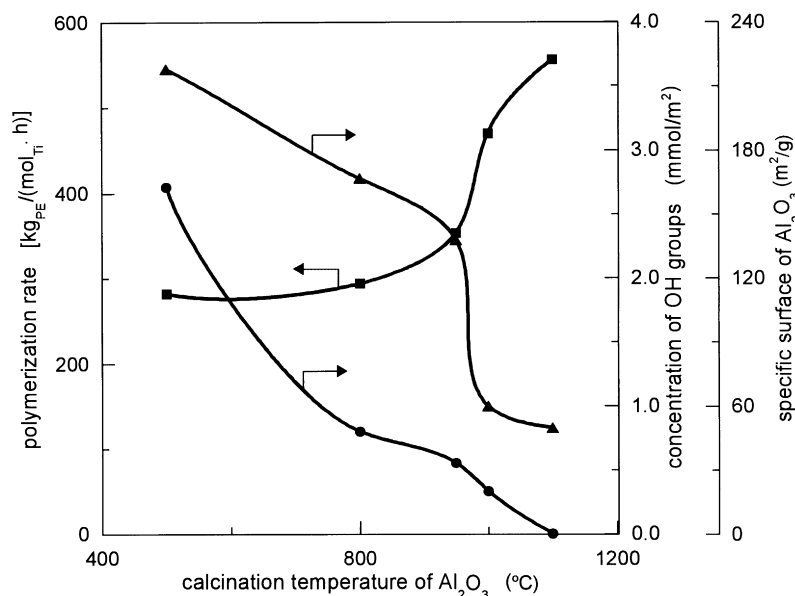


Fig. 1. Ethylene slurry polymerization rate (■). Concentration of surface OH groups (●) and specific surface of Al₂O₃ (▲) vs. calcination temperature of alumina support.

of the support material and the density of its coverage with hydroxyl groups. In order to explain that effect, this paper presents a more comprehensive investigation of the influence from the alumina calcination temperature on the preparation process of the supported titanium–aluminium catalyst and its catalytic properties in the slurry polymerization of ethylene.

2. Experimental

All the operations connected with the synthesis and investigations of the catalysts as well as the polymerization processes were carried out in dry and oxygen-free argon.

2.1. Materials

Polymerization grade ethylene (from Chemical Works “Blachownia” S.A., Kedzierzyn-Kozle, Poland) and pure argon (from “Liquid Carbonic”, Kedzierzyn-Kozle, Poland) were additionally purified by passing them through the beds of 4 Å molecular sieves. Pure hexane (from “Petrochemia” S.A. Plock, Poland) was refined with sulphuric acid, dried by refluxing in argon over the sodium metal and stored over 4 Å molecular sieves. TiCl₄ (from “Merck”) and Et₂AlCl (from “Fluka”) were used without further purification. Alumina (“Rhone-Poulenc” milled to reach the grain diameter below 2 mm) was modified, or not, by hydrochloric acid (25% (w/w) water solution) and calcined at high temperature, within the range of 500 to 1, 100°C (3 h in air and then 1 h in argon).

2.2. Catalyst preparation

The titanium pre-catalyst used in the slurry polymerization was prepared by ball-milling of Al₂O₃ with TiCl₄ in hexane at room temperature for 24 h. The pre-catalyst was activated by Et₂AlCl before use in the ethylene polymerization process. The adsorption studies for TiCl₄ on the Al₂O₃ surface were performed as described elsewhere [13].

2.3. Polymerization

The slurry polymerization reaction was carried out in a 1 dm³ reactor equipped with a stirrer, in hexane, at 50°C and under constant pressure of ethylene (0.5 MPa). Hexane (0.75 dm³) together with the required amounts of the titanium pre-catalyst and Et₂AlCl (mole ratio Al/Ti = 200) were charged into the reactor. After 15 min of ageing, the polymerization was initiated by introducing ethylene. The reaction was then quenched with methanol containing 5 wt% HCl, the polymer was filtered off, washed with methanol and dried.

2.4. Measurements

The concentration of hydroxyl groups on the surface of aluminium oxide was determined by titration of the oxide suspension in dry tetrahydrofuran with sodium naphthenide solution, as described elsewhere [14]. The molecular weights of the polymers produced were determined by the viscosity-measuring method [15], with the use of decalin at 135°C. The sample concentrations were kept very low, at 0.025% (w/v). Such a low concentration was necessary because of very high molecular weight and viscosity specifications for some samples.

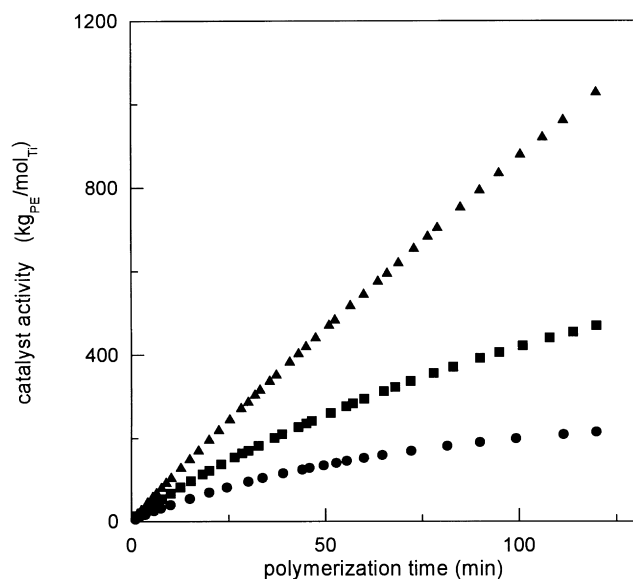


Fig. 2. Catalyst activity vs. polymerization time. Support of catalytic system; Al_2O_3 -500 (●), Al_2O_3 -1100 (■) and Al_2O_3 -Cl-1100 (▲).

3. Results and discussion

The results presented in Fig. 1 reveal that when the calcination temperature for alumina is increased above 500°C , the activity of the titanium–aluminium catalyst deposited on this support also increases in the ethylene polymerization process. At the same time the specific surface area of alumina is reduced which is especially the case above the temperature of 800°C . This is known to result from the phase transition of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$. The findings seem to negate the role of a support as an inert supporting material for the titanium active sites which is responsible for the improved dispersion of these sites only, which is suggested for a similar silica-supported catalytic system [1]. From Fig. 1, it is also seen that with increasing alumina calcination temperature over the range studied, the concentration of the surface OH groups decreases and at about 1100°C they completely disappear. And this, in turn, results in the reduced potential for the creation of superficial

titanium complexes according to Eq. (1). Hence, the catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ —as compared to its equivalent supported on $\alpha\text{-Al}_2\text{O}_3$ —should offer a different catalytic performance in the polymerization process as well.

3.1. Polymerization kinetic studies

The kinetic studies on ethylene polymerization were performed for the titanium catalyst supported on alumina which had been calcined either at 500°C (Al_2O_3 -500) or at 1100°C (Al_2O_3 -1100), and also alumina chlorinated and then calcined at 1100°C (Al_2O_3 -Cl-1100), (Fig. 2). The results presented indicate that the systems studied offer considerable stability in the course of the process and the kinetic stability of the active sites is dependent on the nature of the Al_2O_3 support. Our earlier studies [13] on the effect from the alumina type on the deactivation process of the supported titanium catalyst in the course of polymerization indicated that the active site deactivation rate was dependent on the catalyst concentration only, which can be expressed by a known equation:

$$d[C^*]/dt = k_t[C^*] \quad (2)$$

where, $[C^*]$ is the concentration of active sites, t is the time of polymerization and k_t is the termination reaction rate constant.

After separation of variables and integration of (2) within the time limits of 0 to t we obtain the equation which describes the changes of the concentration of active sites over the time of polymerization:

$$[C_t^*] = [C_0^*]\exp(-k_t \times t) \quad (3)$$

The experimental results for the yields (W_t) (Fig. 2) and polyethylene average molecular weight (\bar{M}_t) (Table 1) allow us to calculate the concentration of macromolecules after the time t , ($[N_t]$), from the relationship:

$$[N_t] = W_t/\bar{M}_{n,t} \quad (4)$$

It should be stressed here that the present work employed the viscosity-average \bar{M}_v instead of the number-average \bar{M}_n because of the very high molecular weight of polyethylene

Table 1
Influence of the alumina type support on ethylene polymerization results

Polymerization time, min	Type of alumina support					
	Al_2O_3 -500		Al_2O_3 -1100		Al_2O_3 -Cl-1100	
	$\bar{M}_{v,t}$ (10^{-6})	N_t (10^2 mol/mol Ti)	$\bar{M}_{v,t}$ (10^{-6})	N_t (10^2 mol/mol Ti)	$\bar{M}_{v,t}$ (10^{-6})	N_t (10^2 mol/mol Ti)
10	1.02	3.82	1.05	6.36	1.06	9.71
20	1.70	4.03	1.84	6.61	1.96	9.94
30	2.31	4.10	2.55	6.64	2.84	10.07
45	3.00	4.25	3.20	7.36	3.87	10.82
60	3.30	4.60	3.87	7.60	4.53	11.99
90	3.80	4.99	4.56	8.57	5.67	13.96
120	3.82	5.61	4.83	9.70	6.24	16.42

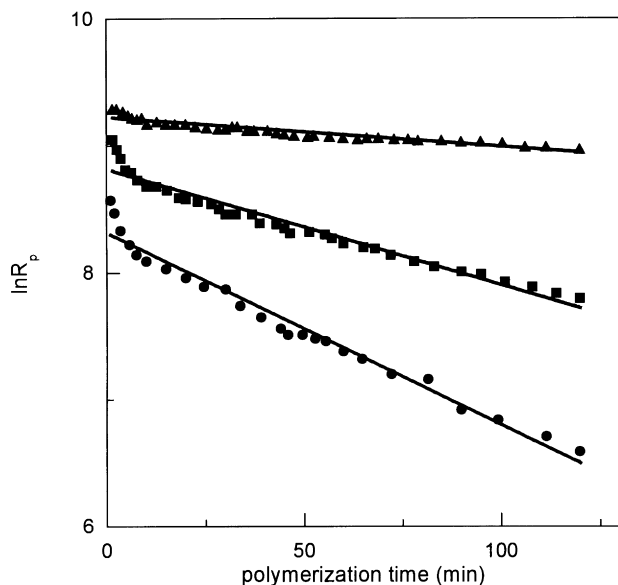


Fig. 3. Slurry polymerization rate (ln scale) $\ln R_p$ as a function of polymerization time. Designation of the curves as in Fig. 2.

obtained. In such a case only the viscosity method can be used for the determination of the molecular weight of polyethylene.

The results presented in Table 1 show that the number of macromolecules increases with the polymerization time. This suggests that the chain transfer reaction takes place in the system studied. This reaction terminates the macromolecule growth and restores the active site available for the initiation of a new polymer chain.

The macromolecule creation rate ($d[N]/dt$) is equal to the transfer reaction rate (R_{tr}), which can be expressed by the equation [16]:

$$dN_t/dt = R_{tr} = k_{tr} \times [C^*] \times [M] \quad (5)$$

where, k_{tr} is transfer reaction rate constant and $[M]$ is monomer concentration.

When Eq. (3), which describes the changes of concentration of active sites over the polymerization time, is introduced to Eq. (5), the following is obtained:

$$dN_t/dt = k_{tr} \times [C_0^*] \times \exp(-k_t \times t) \quad (6)$$

Then, after separation of variables, one obtains

$$\int_{N_0}^{N_t} d[N] = k_{tr} \times [C_0^*] \times [M] \times \int_0^t \exp(-k_t \times t) dt \quad (7)$$

and the subsequent integration gives:

$$[N_t] - [N_0] = \frac{k_{tr}}{k_t} \times [C_0^*] \times [M] \times \{1 - \exp(-k_t \times t)\} \quad (8)$$

As results from Fig. 2 indicate the initiation reaction is very fast and it is not limiting to the polymer chain growth. Hence, it can be assumed that

$$[N_0] = [C_0^*] \quad (9)$$

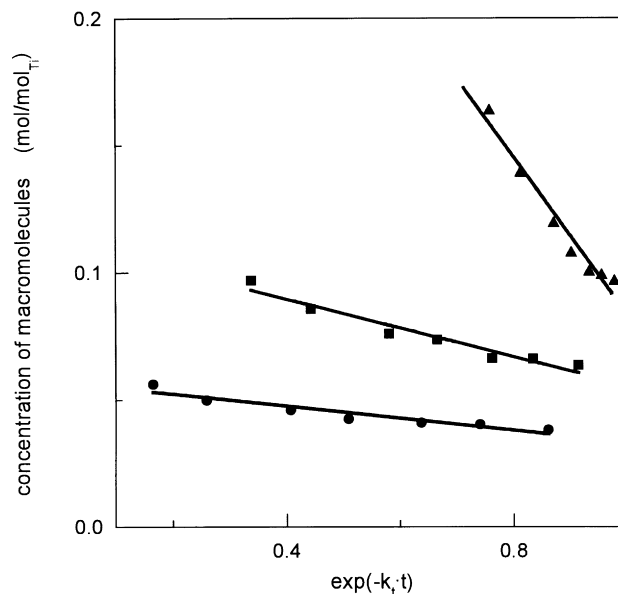


Fig. 4. Concentration of macromolecules formed (N_t) vs. $\exp(-k_t \times t)$ calculated according to Eq. (11). Designation of the curves as in Fig. 2.

So,

$$[N_t] = [C_0^*] + \frac{k_{tr}}{k_t} \times [C_0^*] \times [M] - \frac{k_{tr}}{k_t} \times [C_0^*] \times [M] \times \exp(-k_t \times t) \quad (10)$$

and finally

$$[N_t] = W_t/\bar{M}_t = A - B \times \exp(-k_t \times t) \quad (11)$$

where $A = [C_0^*] + B$, and $B = (k_{tr}/k_t) \times [C_0^*] \times [M]$.

Starting from the change of the number of macromolecules over the polymerization time (Eq. (4)) and making use of the non-linear regression method, it is possible to calculate from Eq. (11) the coefficients for this equation; then the values $[C_0^*]$, k_{tr} and k_t are sought. On the contrary, the known value of k_t can be used in Eq. (11) which can be found at higher accuracy (no error in finding the polyethylene average molecular weight (\bar{M}_t)) from the change of the polymerization rate versus time (Fig. 3), according to Eq. (12) [13]:

$$\ln R_p = \ln R_{p,0} - k_t \times t \quad (12)$$

where $R_{p,t}$ and $R_{p,0}$ are the polymerization rate after time t and its initial value, respectively.

Eq. (11) is then simplified to a linear dependence of the number of macromolecules $[N_t]$ on $\exp(-k_t \times t)$. The experimental findings presented in Fig. 4 make linear functions with high correlation coefficients ($R > 0.96$). This confirms applicability of the kinetic model suggested for the polymerization process and makes it possible to calculate the coefficients A and B for Eq. (11). On the basis of these, the values of $[C_0^*]$ and k_{tr} can be found. Then the propagation rate constant k_p can be calculated from the

Table 2
Kinetic parameters of ethylene polymerization depending on the type of alumina used as catalyst support

Type of alumina support	$[C_0^*]$ (10^2 mol/mol _{Ti})	k_p dm ³ /(mol × s)	k_{tr} (10^4 dm ³ /(mol × s))	k_t (10^4 /s)
Al ₂ O ₃ -500	3.37	155.50	3.43	2.12
Al ₂ O ₃ -1100	5.55	152.30	3.33	1.51
Al ₂ O ₃ -Cl-1100	8.24	154.0	3.24	0.47

known equation which describes the polymerization rate:

$$R_{p,t} = k_p \times [M] \times [C_t^*] \quad (13)$$

The computed values have been presented in Table 2. They prove that the catalyst activity changes with the form of the support employed which results from the change in the concentration of active sites $[C_0^*]$. However, it should be noticed that neither the propagation rate constant (k_p) nor the chain transfer constant (k_{tr}) are dependent in practice on the type of the Al₂O₃ support employed. Moreover, in both these cases the values of rate constants of the chain termination reactions, i.e. k_{tr} and k_t were by a few orders lower than the propagation rate constant k_p , which would give a polymer with a very high molecular weight—of the order of a few million.

These findings reveal that the superficial titanium complexes offer similar catalytic performance in the polymerization process irrespective of the structure of the surface of the Al₂O₃ support (whether the OH groups are present on the surface or they have been removed by calcination). This suggests that the bonds between the complexes and the support surface might be similar.

3.2. Studies on the synthesis of the Al₂O₃-supported titanium catalyst

It was observed that hydrogen chloride is evolved from the reaction between TiCl₄ and γ -Al₂O₃ hydroxyls. Additionally, the investigation of the adsorption process of a titanium compound on the surface of this support revealed that the amount of the metal bounded to said surface (Table 3) was comparable to the concentration of the superficial OH groups found earlier (2.71 μ mol/m²). Both these observations confirm that in this case titanium forms a superficial complex according to Eq. (1). However, the reaction between TiCl₄ and the support with no OH groups on its

surface (α -Al₂O₃) yields no by-product. This may suggest that only the physical adsorption of the titanium compound on the supporting surface takes place. And yet, the study on the adsorption process proved that, despite the lack of OH groups, the superficial concentration of the titanium compound permanently fixed to such a support is even higher (Table 3). (The physically adsorbed titanium compound was then removed from the surface by long-time evacuation.) However, attention should be paid to the fact that the higher calcination temperature of alumina considerably changes the specific surface of this material since γ -Al₂O₃ is converted into α -Al₂O₃. Thus, the amount of the titanium compound adsorbed on the surface of Al₂O₃-1100 is clearly lower than for the oxide calcined at 500°C (Table 3).

The alumina surface dehydration process, when the temperature exceeds 600°C, is known to break the bonds between the support and individual OH groups [17]; the groups then migrate which allows for further dehydration. The crystal lattice of alumina undergoes rearrangement in the process and the superficial layer of oxygen ions (Lewis base sites) and the layer with the exposed aluminium ions (Lewis acid sites) [18,19] are formed. Both the surface Lewis acid and base sites can form the co-ordinate bonds with a metal or with its substituent(s) [20,21]. However, these bonds should be remarkably weaker than the metal–oxygen σ -bonds formed in the reaction (1). Yet it was found that heating up the obtained superficial titanium compounds at 200°C, with subsequent long-time evacuation of the products with weaker fixation, led in both cases to only partial desorption of the titanium compound. The quantitative findings presented in Table 3 indicate that both the supports under comparison give similar relatively strong bonds with the titanium compound.

When the alumina surface is heated up, it undergoes dehydration wherein the neighbouring hydroxyl groups

Table 3
Effect of Al₂O₃ calcination temperature on the quantity of adsorbed Ti

Type of alumina	Specific surface area, m ² /g	[OH]		[Ti]			
				at 20°C		at 200°C	
		μ mol/m ²	mmol/g	μ mol/m ²	mmol/g	μ mol/m ²	mmol/g
Al ₂ O ₃ -500	218	2.71	0.59	2.50	0.55	1.68	0.37
Al ₂ O ₃ -1100	50	0	0	4.85	0.24	3.44	0.17
Al ₂ O ₃ -Cl-1100	35	–	–	5.44	0.19	4.13	0.15

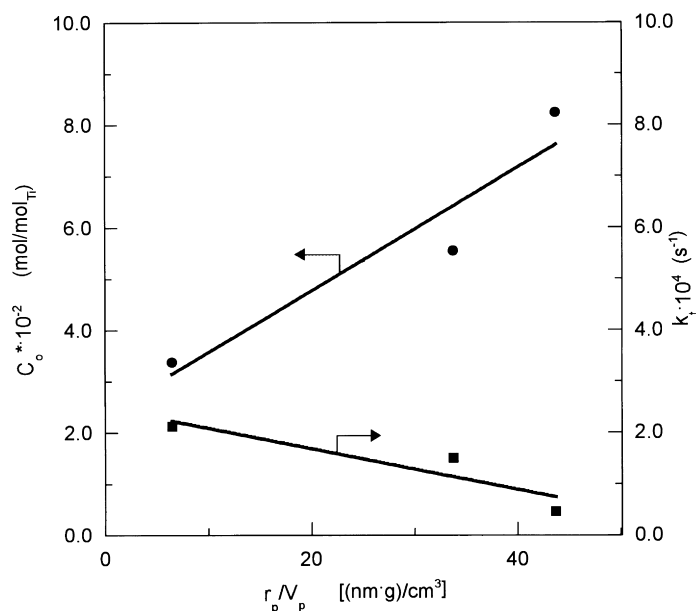
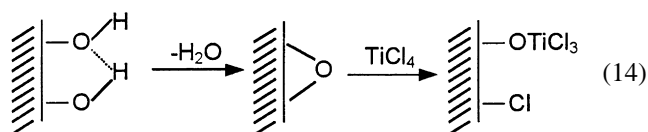


Fig. 5. Concentration of active species ($[C_0^*]$) (●) and termination reaction rate expressed by constant k_t (■) vs. ratio of pore radius to pore volume of the support r_p/V_p .

take part and condense to form oxide sites that can react with $TiCl_4$ according to:



Thus, no matter which type of the Al_2O_3 support is employed, whether it contains the hydroxyl groups or not, its reaction with $TiCl_4$ yields similar superficial titanium oxychlorides wherein the titanium atom is fixed to the support through the oxygen atom. The hypothesis presented seems to be confirmed by the determined quantity of adsorbed Ti (Table 3) which, for Al_2O_3 -1100, is less than one half of what is adsorbed on γ - Al_2O_3 (two hydroxyls condense to one oxide species). Moreover, the similar catalytic performance as found (k_p and k_{tr}) for the titanium sites supported on both the alumina forms, γ - Al_2O_3 and α - Al_2O_3 , also confirm this hypothesis. This proves that the closest chemical environment of the metallic active site is, in practice, independent from the type of alumina support. The different activities found for these systems result from different utilization of the titanium oxychlorides obtained (Eq. (1) or (14)) in the formation of catalytic active sites (increase of $[C_0^*]$). Additionally, this can result from the clearly slower decay of the sites in the polymerization process (reduction of k_t), as was found earlier [13].

The presented results are contrary to the expected trend, if the specific area was the dominant factor of the catalyst activity. The increase in the catalyst activity with decreasing specific area of a support may be evidence that not only the specific surface of the support but also its suitable porous

structure determine the catalyst activity. The internal surface of the support with narrow and deep channels may be inaccessible for catalyst components. The study on the support morphology seems to suggest that the active sites are favourably formed (increase of $[C_0^*]$) and they become more stable (reduction of k_t) in the presence of wide and shallow pores on the supporting surface (higher value of the radius-to-volume ratio, r_p/V_p) (Fig. 5). So, the active sites should be located close to the support external surface. Our results agree with those reported by other authors [22,23] and indicate that the porous structure of the support is also an important factor, since the access of the catalyst to the micropores seems to be limited.

4. Conclusions

The effect of calcination temperature of alumina, to be employed as a supporting material for the titanium–aluminium catalyst, on its activity in ethylene polymerization was studied. The results obtained reveal that when this temperature is increased above $500^\circ C$, the specific surface of the support and the concentration of the superficial OH groups are reduced, but the activity of the catalyst in the ethylene polymerization process is improved. The kinetic study of the ethylene polymerization for the catalysts on different support was based on the suggested kinetic model that considered the deactivation of active sites in the process. The results showed similar catalytic performance of the titanium species supported on various types of alumina (with or without OH groups). Improved activity was found to result from the better utilization of the titanium compound introduced in the formation of active sites as

well as from the better stability of these sites. Our results indicate that not only the specific area of the support but also its porous structure determine the catalyst activity, since the access of the catalyst to the micropores seems to be limited.

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