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Effect of carrier nature and monomer pressure on polymerization of ethylene with high activity catalyst system

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Summary

The effects of monomer pressure, texture of amorphous SiO_2 carrier used and stoichiometry of surface titanium complexes on the profile of the kinetic curves obtained by polymerization of ethylene with high activity catalyst system $TiCl_4/SiO_2$-$(C_2H_5)_2AlCl$-$(C_4H_9)_{1.5}(C_8H_{17})_{0.5}Mg$ were studied. It was found that constant polymerization rate was reached for different times but their values did not depend on pressure and carrier used. The results obtained suggest that surface complexes with mole ratio $Cl^-/Ti^{4+}=2$ generate higher number of active centers and higher polymerization rate. A relationship between kinetic studies and productivity, microstructure of polymers synthesized and their physico-mechanical properties is shown.

Introduction

With Ziegler-Natta supported catalysts, polymerization rate depends on carrier texture and its preliminary thermal treatment. The carrier of the active component must have well developed surface, large volume and radius of pores and should be easily disintegrated by the growing polymer to the initial particles forming its porous structure (1-3). Amorphous SiO_2 obeys all these requirements (4). Furthermore, the reactivity of its surface hydroxyl groups, connected with its thermal prehistory, is well studied on the way to develop the molecular deposition method (5,6).

The papers published recently on polymerization of ethylene show that the introduction of an organomagnesium component in the composition of Ziegler-Natta titanium catalyst systems provides a possibility to increase their catalytic activity. However, the good results announced by the authors refer mainly to non-supported catalysts (7-9). With titanium catalysts deposited on amorphous SiO_2, this approach is still less studied (4,10). Besides, there are no papers so far on the use of titanium catalysts in combination with two co-catalysts (organoaluminium and organomagnesium compounds) and the factors affecting the profile of the kinetic curves during polymerization and the properties of the polyethylene synthesized.

The kinetics of polymerization of ethylene with high activity catalyst systems is characterized by high initiation rate and clearly demonstrated non-stationarity (11-13). Hence, it is important to find ways to maintain high polymerization rate during polymerization time by retarding the irreversible deactivation of active centers. With supported catalyst systems, possibilities can be sought by selecting a suitable texture of the carrier and regulating monomer pressure.

The aim of the present work is to study the suspension polymerization of ethylene with the catalyst system $TiCl_4/SiO_2-(C_2H_5)_2AlCl-(C_4H_9)_{1.5}(C_8H_{17})_{0.5}Mg$ and reveal the dependence between the nature of the carrier, polymerization conditions, process kinetics and polymer properties.

Experimental

Two commercial products of amorphous SiO_2 were used as carriers of the active component: silica gel (KSK, Russia) - S=230 m^2/g; V_{pore}=0.90 cm^3/g and vulcasil (Bayer, Germany) - S=158 m^2/g; V_{pore}=0.40 cm^3/g. The carriers were dehydroxylated at 600°C for 8 h. The preparation of deposited catalysts and their characterization was reported earlier (6).

The polymerizations were carried out with first co-catalyst $(C_2H_5)_2AlCl$ (Ethyl Co., USA) - 0.5M solution in petrol and second co-catalyst $(C_4H_9)_{1.5}(C_8H_{17})_{0.5}Mg$ (Shering, Germany) - 0.14M solution in hexane. Ethylene (Neftochim Ltd., Bulgaria) was with 99.9% purity. The catalytic activity of the samples synthesized was studied by suspension polymerization in petrol medium in 1 l reactor. The polymerizations were carried out with 0.05 g catalyst at 60°C and ethylene pressure 0.25 and 0.8 MPa for 60 min.

The structure characteristics of the polymers synthesized were studied by mercury porometer Model 1500 (Carlo Erba, Italy). Molecular weight of polyethylene was determined viscosimetrically (3) and its degree of crystallinity - by differential scanning calorimeter (Setaram, France) (14).

The physico-mechanical characteristics of the samples synthesized were studied on dynamometer (Instron, UK) using 1 mm thick samples of standard form obtained by pressing polymer powder at 180°C and 18 MPa for 10 min.

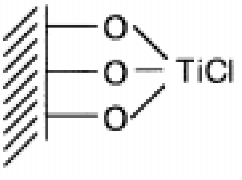
Results and discussion

The structure characteristics and chemical composition of the supported catalysts synthesized can be assesed from the data presented in Table 1. It can be seen that the catalyst with silica gel carrier had higher specific area and almost twice larger volume and average radius of pores compared to the catalyst deposited on vulcasil. As it has been discussed by other authors (3,4) it should affect the accessibility of the active centers located within the catalyst to the monomer.

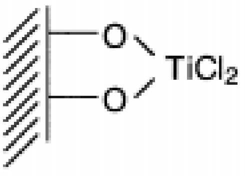
Table 1. Structure characteristics and chemical composition of catalysts synthesized

Carrier	Spesific area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (Å)	Ti^{4+} (mmol/g)	Cl^- (mmol/g)	Cl^-/Ti^{4+}
Vulcasil	148	0.30	40	0.42	0.59	1.40
Silica gel	217	0.70	70	0.58	1.25	2.16

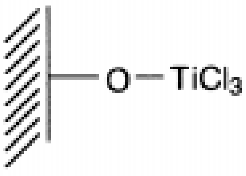
The different values of the mole ratio of Cl^-/Ti^{4+} found indicated a different mechanism of interaction between $TiCl_4$ and surface hydroxyl groups of vulcasil and silica gel. The results obtained show that the first two types of the following possible surface complexes were formed on the amorphous SiO_2:



type A



type B



type C

The presence of type C complexes in catalysts can be ignored, since they are formed mainly at temperature of preliminary thermal treatment above 600°C (4,6). The ratio Cl^-/Ti^{4+}=1.40 obtained for vulcasil shows that complexes types A and B are formed on its surface. In contrast, complexes type B are mainly formed on the surface of silica gel (Cl^-/Ti^{4+}=2.16). The possibility for formation of type A complexes on vulcasil was proved by the twice higher content of hydroxyl groups on this carrier at 600°C (4.03 OH-gr/nm^2) compared to silica gel (1.95 OH-gr/nm^2) (6).

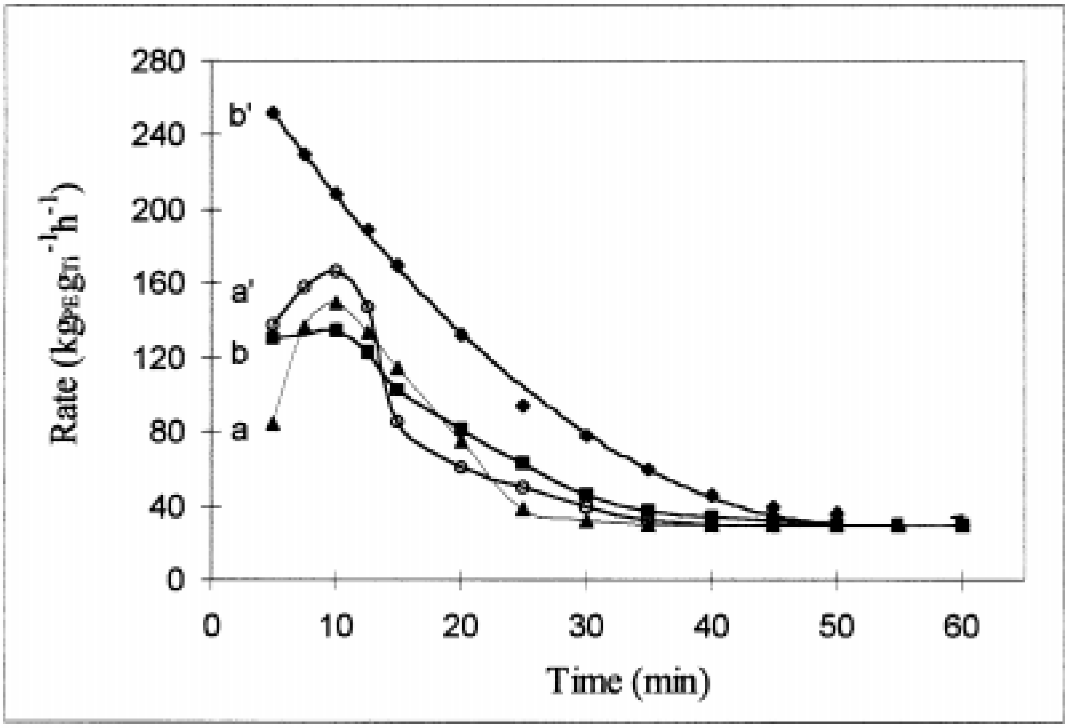


Fig. 1. Kinetic curves for polymerization of ethylene with different carriers:
vulcasil ($C_{Ti^{4+}}$=0.021 mmol/l), P=0.25 MPa (a) and P=0.8MPa (a′);
silica gel ($C_{Ti^{4+}}$=0.029 mmol/l), P=0.25 MPa (b) and P=0.8MPa (b′)

The titanium complexes on the surface of amorphous SiO_2 are potential sites for the formation of active centers after the introduction of the co-catalysts. It should be expected that their different stoichiometry would affect polymerization rate and catalyst system productivity to certain extent. Therefor, preliminary experiments were carried out and it was found that maximum catalytic activities can be reached at mole ratio of catalyst components Ti:Al:Mg=1:50:30 when deposited on vulcasil and Ti:Al:Mg=1:40:35 when deposited on silica gel. Polymerization kinetics with both supported catalysts was studied at these mole ratios and at ethylene pressure 0.25 and 0.8 MPa (Fig.1).

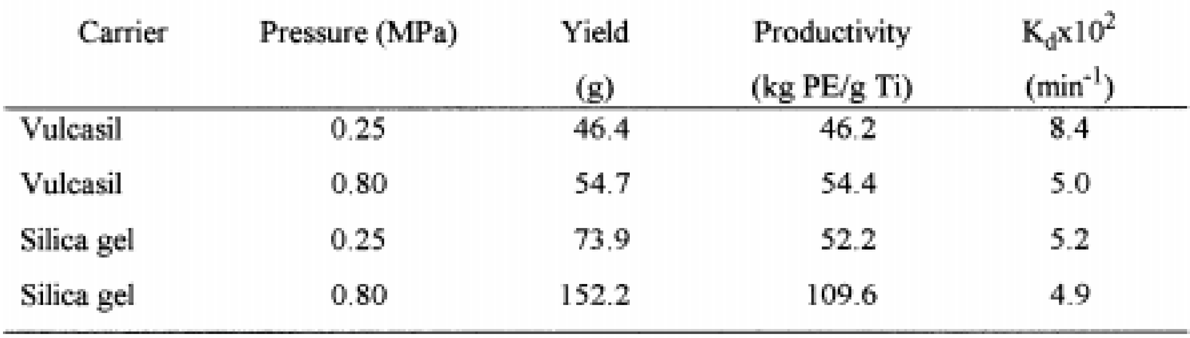
Fig 1 (a and a') shows that for catalysts deposited on vulcasil, the kinetic curves are similar, despite ethylene pressure. They have an induction period until time τ=10 min and a period of decrease of polymerization rate to reach stationary polymerization at τ=35 min for both samples. The induction period can be explained with slow disintegration of the catalyst and initiation of polymerization on newly uncovered areas (4). The non-stationary region (after reaching the maximum rate) in the case of vulcasil carrier can be attributed manly to the smaller volume and radius of pores which are blocked by the growing polymer chains. As a result, the mass transfer of monomer to the active centers on the inner surface of the growing polymer particles becomes harder. Besides, there is also a chemical reason for this effect - a deep reduction of Ti^{4+} ions to a low valency inactive state (12). The consideration of the kinetic curves (Fig.1-a,a') shows also that after 35 min stable active centers only take part in the process. These are the centers which are not chemically deactivated or capsuled within polyethylene chains.

The high specific area and larger volume and radius of pores of the catalyst deposited on silica gel affects process kinetics, as illustrated in Fig.1-b,b'). At a pressure of 0.25 MPa (curve b) the induction period is very short and at 0.8 MPa and τ=5 min it is absent (curve b'). Therefore, the texture of the catalyst deposited on silica gel (Table 1) combined with the increased pressure, intensifies the synthesis of polyethylene in the initial stage of the polymerization. At 0.8 MPa, the polymerization rate decreases up to τ=50 min but remains higher compared to the rate with catalyst deposited on vulcasil.

It should be noted also that, for all the four kinetic curves, the constant polymerization rate was reached for different periods of time but its value is almost the same (30 $kg_{PE}g_{Ti}^{-1}h^{-1}$) and it was not affected by carrier nature and pressure. It means that the working stable active centers are of the same type. Most probably they are centers formed on surface complexes type B. This assumption is based on the fact that with silica gel carrier the polymerization rate (despite pressure) after τ=20 min remains high and constant rate was reached later (Fig.1-b,b'). As it has been already discussed, complexes type B are mainly formed on silica gel. These conclusions are asserted also by the discussion in (15) where the structure of type B complexes was supposed to ease the formation of bimetallic complex (which is more stable) after the introduction of the co-catalyst.

The regions of the kinetic curves in Fig.1, representing the decrease of polymerization rate, give linear dependence when drawn in (lnR)/τ co-ordinates and conform to the kinetic equation of first order. This made possible to determine the deactivation constant (K_d) of the active centers before constant rate of the polymerization process was reached (Table 2). It can be seen that the highest value of K_d shows vulcasil carrier at 0.25 MPa, which determined the lower productivity of this catalyst system. At 0.8 MPa for the same carrier, K_d decreases and is close to the value for silica gel.

Table 2. Dependence of productivity and deactivation constant on carrier nature and pressure

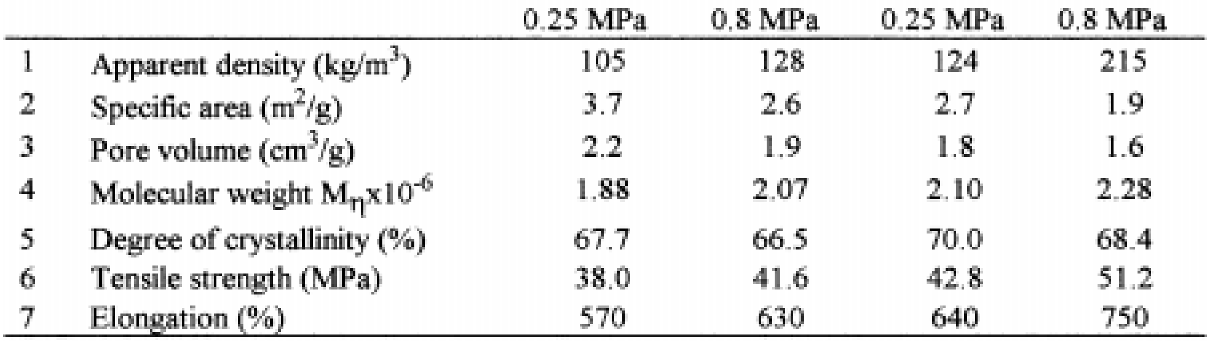


Carrier	Pressure (MPa)	Yield (g)	Productivity (kg PE/g Ti)	$K_d x10^2$ (min^{-1})
Vulcasil	0.25	46.4	46.2	8.4
Vulcasil	0.80	54.7	54.4	5.0
Silica gel	0.25	73.9	52.2	5.2
Silica gel	0.80	152.2	109.6	4.9

The question here is why for similar values of K_d (~5x10^{-2} min^{-1}) the highest productivity observed was with silica gel at 0.8 MPa. It can be explained with the formation of very high number of active centers in the initial period of the polymerization. Despite the equal deactivation rate, their concentration on catalyst surface remains comparatively high for longer time (Fig.1-b').

The results from the study of the apparent density and microstructure of the polymers synthesized showed increased density of the polymer particles with the increase of pressure for both carriers. This is illustrated by the increase of apparent density and decrease of specific area and volume of pores (Table 3). With silica gel carrier (for both ethylene pressures studied), apparent density is higher as a result of the polymer chains growing over accessible active centers placed in the pores of the growing polymer particles. This is directly connected with the larger volume and bigger radius of pores of the catalyst deposited on silica gel. The results obtained for the molecular weight of the polymers synthesized show that high molecular weight polyethylene was obtained with all the four polymerizations. The increase of pressure gave very high productivity with silica gel carrier and the polyethylene obtained was relatively with the highest molecular weight.

Table 3. Dependence of synthesized polymer characteristics on carrier nature and ethylene pressure



No	Feature	Carrier vulcasil		Carrier silica gel	
		0.25 MPa	0.8 MPa	0.25 MPa	0.8 MPa
1	Apparent density (kg/m^3)	105	128	124	215
2	Specific area (m^2/g)	3.7	2.6	2.7	1.9
3	Pore volume (cm^3/g)	2.2	1.9	1.8	1.6
4	Molecular weight $M_\eta x10^{-6}$	1.88	2.07	2.10	2.28
5	Degree of crystallinity (%)	67.7	66.5	70.0	68.4
6	Tensile strength (MPa)	38.0	41.6	42.8	51.2
7	Elongation (%)	570	630	640	750

It can be seen from Table 3 that a slight decrease of the degree of crystallinity of the polymers with increase of pressure for both carriers was registered. It can be explained with the difficult orientation and folding into crystallites of the longer macrochains due to the increase of the molecular weight. The results obtained for the physico-mechanical properties of the samples showed that the best characteristics had the polymer synthesized with silica gel supported catalyst at ethylene pressure 0.8 MPa.

Conclusions

As a result from the study carried out it may be concluded that the introduction of butyloctylmagnesium as second co-catalyst in the supported Ti/SiO_2 catalysts leads to the formation of highly active catalyst systems for syntesis of polyethylene. It is shown that the different texture of the amorphous SiO_2 carriers (vulcasil and silica gel) exerts significant effect on the stoichiometry of the surface titanium complexes and the profile of the kinetic curves of polymerization. For the vulcasil carrier, the latter involve an induction period, irrespective of ethylene pressure, while for the catalysts deposited on silica gel no induction period was registered. The highest polymerization rate was observed with the higher monomer pressure used and silica gel carrier. It is connected with the higher stability of the active centers forming on the surface complexes in mole ratio $Cl^-/Ti^{4+}=2$.

The results obtained clearly show that the titanium catalyst deposited on silica gel can succesfully be used in the industry. In this case, at a monomer pressure of 0.8 MPa, the catalyst system $TiCl_4/SiO_2-(C_2H_5)_2AlCl-(C_4H_9)_{1.5}(C_8H_{17})_{0.5}Mg$ would give high polymerization rate and productivity above 100 kg PE/g Ti. The polyethylene synthesized would have comparatively the highest apparent density and molecular weight, as well as very good physico-mechanical properties.

References

1. Weist EL, Ali AH, Naik BG, Conner WC (1989) Macromolecules 22: 3244
2. Kim I, Kim J, Woo S (1990) J Appl Polym Sci 39: 837
3. Munoz-Escalona A, Hernandez JG, Gallardo JA (1984) J Appl Polym Sci 29: 1187
4. Ermakov UI, Zaharov VA, Kuznetsov BN (1980) Zakreplennye kompleksy na okisnyh nositelyah v katalize, Nauka, Novosibirsk (Russ)
5. Aleskovski VB (1976) Stehiometriya i sintez tverdyh soedinenii, Nauka, Moscow (Russ)
6. Damyanov D, Velikova K, Ivanov I, Vlaev L (1988) J Non-Cryst Solids 105: 107
7. Petkov L, Kyrtcheva R, Radenkov Ph, Dobreva D (1978) Polymer 19: 567
8. Choi KY, Ray WH (1985) J Macromol Sci C25: 1
9. Krenzel BA, Nehaeva LA (1990) Uspehi chimii 59: 2034
10. Brant P, Speca A (1987) Macromolecules 20: 2740
11. Munoz-Escalona A, Villalba J (1977) Polymer 18: 179
12. Valendo AY, Kostyan LP, Utrobina OA (1986) Docl AN BSSR 30: 527
13. Badley RD, Johnson MM (1993) J Catal 141: 524
14. Minkova L, Velikova M, Damyanov D (1990) Eur Polym J 26: 1161
15. Arhipova ZV,Grigoriev VA, Veselovskaya EV, Andreeva IN, Semenova AS, Severova NN, Shagilova AV (1980) Polietilen nizkogo davleniya, Khimiya, Leningrad (Russ)