Polymer Bulletin 38, 419–426 (1997)

Polymer Bulletin

Influence of the catalyst matrix structure of the supported Ziegler-Natta catalysts on the homo- and copolymerization of olefins

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Received: 2 October 1996/Revised version: 17 January1997/Accepted: 23 January 1997

SUMMARY

The vanadium catalytic complexes immobilized on the same support (aluminium hydroxide, AH) and distinguished by structure and composition have been compared for ethylene and propylene homo- and copolymerization to find relationship between the polymerization activity, copolymerization relative reactivity of comonomers and the supported catalyst structure. The catalytic complexes of vanadium with supported aluminoxanes (II) and catalysts with dispersed solid phase of vanadium compounds on the support surface (III) are more active than catalyst (I) in which vanadium has the covalent bond with surface of support. The relative reactivity of comonomers in copolymerization also depends on type of supported catalyst. The catalysts III unlike I and II can produce the ethylene and propylene copolymers with high content of propylene. The promoting effect of propylene on ethylene polymerization rate takes place only in the presence of catalysts III.

INTRODUCTION

The supported Ziegler-Natta type catalysts are used for synthesis of polyolefins [1] and composite materials on their base [2]. The catalysts of various structure, composition and with different properties are obtained depending on the nature of support, methods and conditions of immobilization of catalytic complexes on the support surface. The titanium catalysts representing isolated transition metal complexes on the support surface display lower activity in ethylene polymerization than supported catalysts involving n.$TiCl_3$ associates [3]. The catalytic properties of vanadium supported catalysts, $VOCl_3/SiO_2$ (Al_2O_3) - AlR_3, depend on the structure of surface compounds formed in reaction of $VOCl_3$ with the support OH'-groups [4]. For catalysts based on VCl_3 the dependence of specific activity in olefin polymerization on the surface concentration of the transition metal is extreme in nature [2].

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The difference in properties of supported catalysts is especially essential for α-olefin polymerization because it involves both activity and stereospecifity of catalyst. So, the content of atactic fraction in polypropylene obtained with the isolated titanium complexes amounts to 50 wt.% whereas in the case of catalyst with $TiCl_3$ associates it decreases to 10-15 wt.% [3]. The highly isotactic polypropylene is produced with titanium catalysts supported on materials with layered structure, graphite [5] and boron nitride [6] (unlike catalysts on alumina or SiO_2) without electron - donor modifiers.

The purpose of this work is to prepare the different types of supported vanadium catalysts using the same support AH and to compare their behaviour in the ethylene and propylene copolymerization and also in two-stage process of ethylene polymerization after preliminary ethylene - propylene copolymerization.

EXPERIMENTAL

The vanadium compounds were distilled under vacuum: $VOCl_3$ - at 18,5 °C (0,5mm Hg), VCl_4 - at 40 °C (15mm Hg). $Al(i\text{-}Bu)_3$ had the composition: Al -12,5 wt. %, (i-Bu) - 83,4 wt.%.

Aluminium hydroxide, AH, from Research Institute of Iodine-Bromine Industry, Saky TC 6-22-11-76-83 was used as support. The content of water on the surface of AH was determined by the method of Thermal Desorption Mass-Spectrometry (TDMS) [7]. The structure and composition of catalysts were investigated by elementary analysis , ESR [8] and ^{51}V NMR [9] spectroscopy.

Ethylene and propylene were of polymerization-grade. The polymerization and copolymerization were carried out in dried n-heptane of spectral purity grade. The methods of kinetics study were described in [10,11].

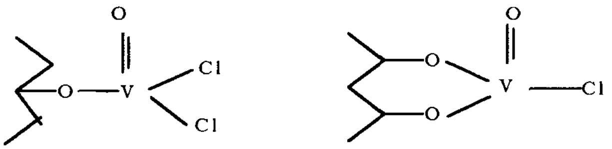
The ethylene was polymerized at 70°C and pressure of 0,19 and 4 atm. The ethylene and propylene copolymerization was carried out at 70°C, comonomer pressure of 0,19 and 2,8 atm and the feed mixture composition C_3H_6 / C_2H_4 (M) in the range 0,3-1,9. The composition of ethylene-propylene copolymers was established by the kinetic method [10] and IR-method [12]. IR-spectra were registered with Beckman IR 4260. The content of amorphous phase in copolymers was determined by X-ray method.

RESULTS AND DISCUSSION.

The known methods of immobilization of Ziegler-Natta catalysts were used for preparation of different types of vanadium catalysts supported on AH [2] .

The $VOCl_3$/AH-$Al(i\text{-}Bu)_3$ catalyst (catalyst I) was obtained in following way. The support (5 g) was heated for 4 h at 160°C in vacuum. The reaction of $VOCl_3$ vapour with OH-groups of support was carried out at 22°C. Then the product was blown with argon and evacuated for 1h at 100°C for removing the excess of $VOCl_3$. According to ^{51}V NMR spectra physically adsorbed $VOCl_3$ was absent in the samples of $VOCl_3$/AH. It was established by EPR method that interaction of $VOCl_3$ with OH-groups of AH occurs without side reaction of V^{+5} reduction. $VOCl_3$/AH contained 0,013 wt.% of V, the molar ratio Cl:V was equal 1,3:1. The assumed structures of the fixed vanadium compounds are in scheme I.

Scheme I.

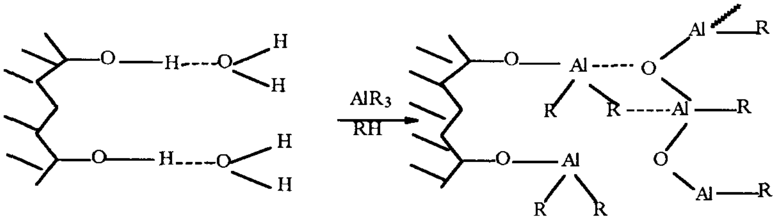


Appropriate amounts of $VOCl_3$/AH and Al(i-Bu)$_3$ were added into reactor, molar ratio Al:V was equal 10:1. It was shown previously that the covalent bond between V and support is kept when species $VOCl_3$/support react with aluminiumorganic compound (AOC) [2,4].

Unheated AH containing 0,3wt.% of physically absorbed water was used to prepare Al(i-Bu)$_3$/AH-$VOCl_3$ catalyst (catalyst II). AH (2 g) was suspended in 50 ml of n-heptane. Solution of Al(i-Bu)$_3$ (O,066 g in 20 ml of n-heptane) was added portionwise. Al(i-Bu)$_3$ reacted with the surface water of AH (molar ratio AOC:H_2O was 1:1). The gaseous products RH were evolved and alkylaluminoxanes were obtained on the surface. The formation of alkylaluminoxanes in this reaction was proved by us earlier [13,4]. We showed by elementary analysis that heptane solution after filtration of suspension of Al(i-Bu)$_3$/AH and washing of residue contained Al in amount of 4-8 wt. % of introduced amount. By this is meant that alkylaluminoxanes are bonded to support surface (scheme II). Immobilized alkylaluminoxanes contained reactive alkyl groups and, similarly to other AOC, entered into reactions of alkylation with transition metal compounds [13].

The supported on the surface of AH aluminoxanes [Al(i-Bu)$_3$/AH] were used as aluminiumorganic component of catalyst II. Appropriate amount of $VOCl_3$ was added into suspension of Al(i-Bu)$_3$/AH. Catalyst II contained 0.15 wt.% of V, molar ratio AL:V was equal 10:1. Vanadium had no covalent bond with support, it entered into composition of donor-acceptor complexes with fixed aluminoxanes.

Scheme II:



where R is i-Bu.

Aluminiumorganic component of catalyst IIIa, in contrast to catalyst II, was prepared with AH which had been treated with an excess of AOC in respect to amount of surface water (molar ratio AOC : H_2O was 2:1). It contained both fixed aluminoxanes and free AOC [Al(i-Bu)$_3$/AH+ Al(i-Bu)$_3$]. The dispersed solid phase of V^{+3} compounds was formed and deposited on support surface when unfixed Al(i-Bu)$_3$ reacted with $VOCl_3$. Catalyst IIIa contained 0.15 wt.% of V, molar ratio Al:V was equal 20:1.

For obtaining of the vanadium component (VCl_3/AH) of catalyst IIIb VCl_4 was decomposed to VCl_3 on the surface of support according to procedure given in [14]. AH was heated for 4 h at 160 °C in vacuum previously. Appropriate amounts of VCl_3/AH and Al(i-Bu)$_3$ reacted at 70 °C to form catalyst IIIb . It contained 0,3 wt.% of V, molar ratio AL:V was equal 10:1. Catalyst IIIb as well as IIIa contained the dispersed solid phase of V^{+3} compounds on the surface of support.

The variations of the rate of ethylene polymerization and of ethylene-propylene copolymerization (W) with time for different type catalysts are presented in Fig. 1a and Fig. 1b respectively. It is seen that vanadium catalysts exhibited different polymerization behaviour. The catalysts II, IIIa and IIIb are much more active than catalyst I. Evidently, the catalytic species of catalyst I, in which V has the covalent bond Al- O-V with support, are the least active in polymerization. One of the probable causes for low activity of these species may be the decreased reactivity of metal-carbon bond as a result of the chemical bonding of transition metal to the surface of support.

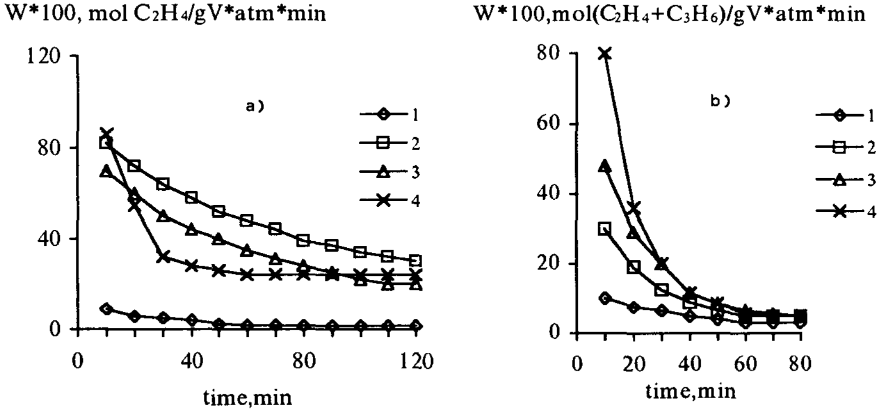


Fig 1. Kinetic curves of ethylene polymerization (a) and ethylene-propylene copolymerization (b).
70 ° C. Catalysts: 1 - I, 2 - II, 3 - IIIb, 4 - IIIa. Molar ratio C_3H_6 / C_2H_4 in feed mixture (M) 0,3.

Relative reactivity of comonomers in copolymerization also depends on the type of immobilized catalytic complexes. The compositions of copolymers obtained in the presence of vanadium catalysts at different compositions of feed mixture are presented in Table 1. As is seen, in the case of catalyst I the increase in M from 0,3 to 1,7 implies the increase in concentration of propylene in reaction zone (F is changed from o,8 to 20) and slightly affects the copolymer composition (f). The content of propylene in the copolymers was 3 and 6 mol. % respectively. Catalyst II behaved about in the same manner as I. At the same time the catalyst IIIb which contained the dispersed solid phase of vanadium compounds produced copolymers with high content of propylene when the feed mixtures enriched with propylene were used. The amount of propylene in copolymers was 18 mol.% at M=1,6 and 28 mol.% at M=1,9.

We compared all types of supported vanadium catalysts in the two-stage process where ethylene-propylene copolymerization was the first stage and ethylene homopolymerization was the second stage.

The copolymerization stage was carried out at M=0,3 for 40 min. The copolymers of approximate composition were obtained with each catalyst. The content of propylene was egual to 3 - 8 mol.% (Tab.1), the content of amorphous phase in all products was practically the same and egual to 59 ± 3 %. After copolymerization the mixture of comonomers was removed from reaction zone and ethylene was injected into reactor. The kinetic curves of ethylene polymerization (curves 1) and ethylene polymerization after ethylene-propylene copolymerization (curves 2) are presented in Fig. 2.

Table 1. The composition of ethylene-propylene copolymers obtained with supported vanadium catalysts

Catalyst	Molar ratio of comonomers in feed mixture, C_3H_6/C_2H_4 M	Molar ratio of comonomers in reaction zone, C_3H_6/C_2H_4 F	The content of C_3H_6 in copolymer, mol. % f
I	0,3	0,8	3
	1,7	20,0	6
II	0,3	0,7	8
	1,9	12,0	9
IIIb	0,3	0,8	5
	1,6	12,0	18
	1,9	16,0	28

As is seen the preliminary ethylene-propylene copolymerization has no effect on activity of catalysts I and II in the following ethylene polymerization (Fig. 2a and 2b, curves 2). While the rate of ethylene polymerization with catalysts IIIa and IIIb is increased after the stage of ethylene-propylene copolymerization (Fig. 2c and 2d, curves 2).

The promoting effect of propylene on ethylene polymerization in two-stage processe of sequential homopolymerization of propylene and ethylene with titanium-magnesium catalyst (TMC) was reported previously in [11,15,16]. It was shown that enhancement of TMC activity was due to increase in the number of active centres (AC) [15]. It may be attributed to increased (in respect to polyethylene) content of amorphous phase in polypropylene obtained on the catalyst surface in the first stage of process. That is why the greater number of AC was accessible for ethylene.

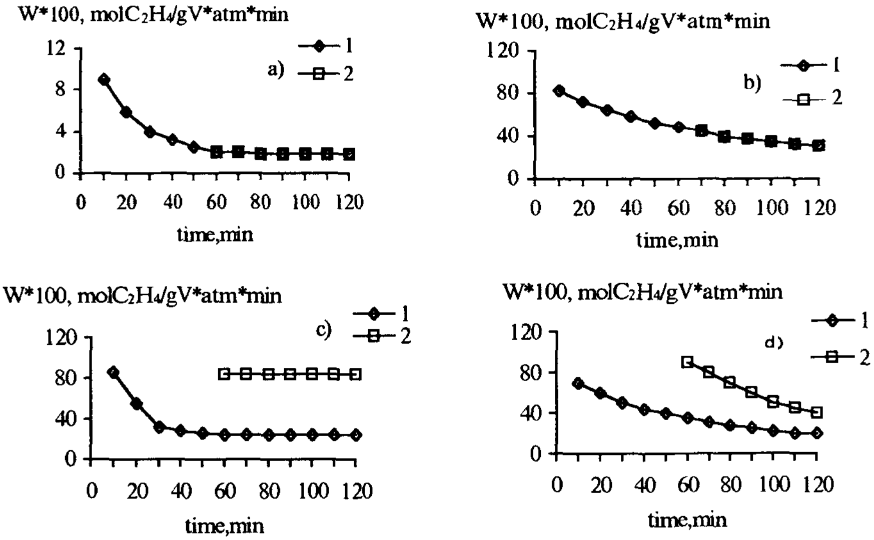


Fig 2. Kinetic curves of ethylene polymerization (1) and ethylene polymerization after the stage of ethylene - propylene copolymerization (2).

70°C. Catalyst: a - I; b - II; c - IIIa; d - IIIb.

In the case being considered the copolymers with the same content of amorphous phase were obtained on the surface of supported catalysts in the stage of copolymerization. However, the promoting effect of propylene on ethylene polymerization rate was observed in the presence of catalysts contained the dispersed solid phase of vanadium compounds only.

For explanation of these results the concept of fragmentation of catalyst matrix by nascent polymer product was used [17]. The scheme of fragmentation of supported vanadium catalysts is presented in Fig.3.

For catalysts I and II where vanadium is covalent bonded with support or constituents of fixed vanadium-aluminoxane complex the distribution of transition metal compound on the surface is determined by the distribution of OH-groups of support. The fragmentation of these catalysts is concerned mainly with the breakdown of support (Fig.3a) and depends on its nature (pore size and structure). It can not lead to increase in active centres number. So promoting effect of propylene on ethylene polymerization with catalysts I and II doesn't take place.

The active components of catalysts IIIa and IIIb are distributed as dispersed solid phase on the support surface. For IIIa and IIIb types of catalysts the process of catalyst matrix fragmentation by copolymer is concerned with crushing of this dispersed solid phase and results in the increase of the active surface of catalyst (Fig.3b) that is in the increase of number of active centers in ethylene polymerization after preliminary ethylene-propylene copolymerization.

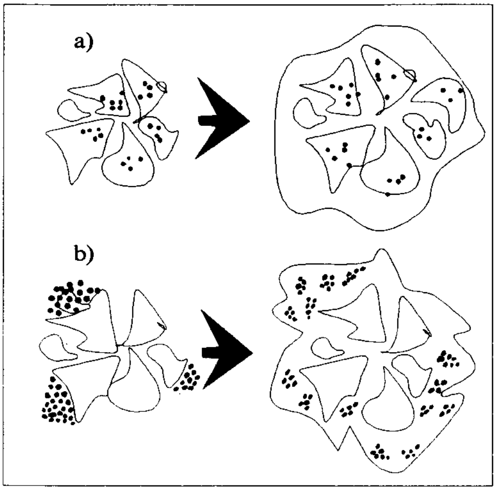


Fig 3. Scheme of catalyst matrix fragmentation for different types of supported vanadium catalysts.

Catalysts: a - type I and II; b - type IIIa and IIIb.

CONCLUSION

The features of supported vanadium catalysts behaviour in the ethylene homopolymerization, ethylene-propylene copolymerization and sequential ethylene and propylene co- and homopolymerization are determined by the structure of catalyst matrix. The activity of catalysts and the rate of comonomer inlet into polymer chain depend on the character of bond between transition metal in catalytic centres and support.

In the case of supported catalysts the promoting effect of propylene on ethylene polymerization concerns to the increase of the active centres number. It is determined by capacity of catalyst matrix for fragmentation by nascent polymer product.

ACKNOWLEDGEMENT

This work was supported by International Science Foundation (ISF) with Grants NEI000 and NEI300. The authors thank Dr. O.B.Lapina, Boreskov Institute of Catalysis, Novosibirsk, Russia, for investigation of catalysts by ^{51}V NMR method.

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