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The nature of the promoting effect of propylene on ethylene polymerization over supported Ziegler—Natta catalysts^{*)}

Summary — The promoting effect of α -olefin (propylene) on polymerization of ethylene over Ziegler—Natta catalysts was investigated in a two-stage homo- and co-polymerization of ethylene and propylene, ethylene and 3-methyl-1-butene over titanium—magnesium catalysts and aluminum hydroxide-supported vanadium catalysts differing in structure and composition. With the catalysts, the enhancement effect is related to the increase in the number of ethylene active centers. This increase is related to the catalyst matrix structure and morphology of the nascent polymer and is determined by the liability of the catalyst matrix to become fragmented by the nascent polymer.

Key words: enhancement effect, Ziegler—Natta catalysts, ethylene—propylene copolymerization, titanium—magnesium catalysts, aluminum hydroxide-supported vanadium.

The promoting effect of α -olefin on ethylene polymerization is one of the many interesting phenomena of the Ziegler—Natta catalysis. Copolymerization of ethylene with an α -olefin over heterogeneous [1], supported [1—4] and homogeneous [5] catalysts is known to be enhanced in terms of the ethylene polymerization rate by small amounts of comonomers like propylene, 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene.

This "enhancement effect" (ethylene rate increase) has been observed in slurry [1—5], gas-phase [4], and solution-phase [6] copolymerizations. The magnitude of the effect depends on the nature of the catalytic system and on the length of the carbon chain of the α -olefin comonomer (Table 1). The effect has been attributed to various chemical and physical factors:

(i) modification of the propagation rate constant (formation of new active centers by reaction involving α -olefin molecules);

(ii) an increase in the amount of active sites (activation of dormant or potential centers by an α -olefin comonomer; physical disintegration of catalyst matrix particles);

(iii) diffusion phenomena (change in monomer concentration near the active site).

The major objective of the present study is the kinetic study of the "enhancement effect" due to propylene and ethylene polymerization over various supported Ziegler—Natta catalysts. Ethylene—propylene copolymeri-

Table 1. The enhancement effect with different catalysts

Catalyst	Comonomer	Rate Increase	Reference
δ -TiCl ₃ 0.33 AlCl ₃ + Al(<i>i</i> -Bu) ₃	1-octene	3.5 (max)	[1]
CrO ₃ /SiO ₂ Al ₂ O ₃	1-hexene	2.5—3.0	[2]
TiCl ₄ /MgCl ₃ /TGF/SiO ₂ + AlEt ₃	1-hexene	1.9	[3]
VCl ₃ (TGF) ₃ /SiO ₂ + AlEt ₃	1-hexene	2	[3]
	1-butene	3.4	
	propylene	5.8	
TiCl ₄ /MgCl ₂ + AlEt ₃ TiCl ₄ /MgCl ₂ /EB + Al(<i>i</i> -Bu) ₃	1-hexene	2.5—3.0	[2]
	1-octene	6.5 (init)	[2]
	4-methyl-1-pentene	4.5 (init)	[1]
TiCl ₄ /MgCl ₂ /DIBP—AlEt ₃	propylene	2.0	[4]
Cp ₂ ZrCl ₂ /MAO	1-hexene	2.0	[5]
	propylene	1.5	

zation and two-stage sequential homo- and copolymerization of ethylene and propylene, ethylene and 3-methyl-1-butene (3M1B) were studied in the presence of a titanium—magnesium catalyst and supported vanadium catalysts differing in structure and composition.

To determine the number of active sites, the polymerization of ethylene was preceded by a preliminary "CO-inhibited polymerization" of propylene.

The effect was tentatively explained by the data on the specific rate of polymerization (R_p), the specific rate of comonomer incorporating into copolymer chain (R_{cop}), the reactivity ratios of comonomer for ethylene

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(r_1) and for propylene (r_2) and the number of active centers.

To estimate the specific rate of polymerization and of incorporation of monomer into the copolymer chain in the copolymerization process, it was necessary to determine the monomer concentration in the vicinity to the centers of polymer chain propagation.

In our opinion the monomer can penetrate toward active centers through a polymer film covering the catalyst particles, and the concentration of the monomer near the active sites depends on the monomer solubility in the nascent polymer product. The solubility of ethylene and propylene in isotactic polypropylene and in UHMWPE has been reported elsewhere [7].

EXPERIMENTAL

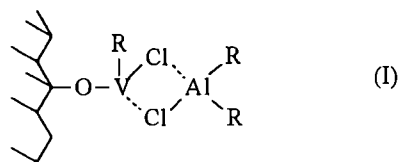
Supported catalysts

$\text{MgCl}_2/\text{DIBP}/\text{TiCl}_4$ (TMC) (Institute of Catalysis, Siberian Branch of RAS, Novosibirsk) contained 2.3 wt % titanium. AlEt_3 and phenyltriethoxysilane (PTES) were used as a cocatalyst and a stereoregulating agent, respectively. The AlEt_3/Ti and $\text{AlEt}_3/\text{PTES}$ mole ratios were 320 and 20, respectively.

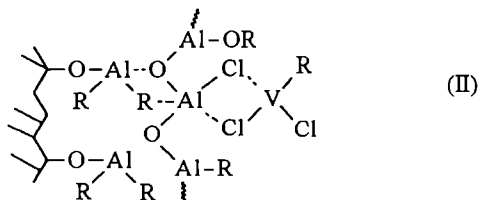
Vanadium supported catalysts were obtained on aluminum hydroxide (AH) (Research Institute of the Iodine—Bromine Industry, Saky TC 6-22-11-76-83) used as support.

The components of vanadium catalysts were: VOCl_3 (b.p., $18.5^\circ\text{C}/0.5$ mm), VCl_4 (b.p., 148.5°C), AlEt_3 ($[\text{Al}] = 23$ wt %, $[\text{R}] = 76.2$ wt %) and $\text{Al}(i\text{-Bu})_3$ ($[\text{Al}] = 12.5$ wt %, $[\text{R}] = 83.4$ wt %).

The vanadium supported catalysts were prepared in three types: (1) $\text{VOCl}_3/\text{Al}(\text{OH})_3\text{—Al}(i\text{-Bu})_3$ (I), with va-



anium covalently bonded to the support [8–10]; (2) $\text{Al}(i\text{-Bu})_3/\text{Al}(\text{OH})_3\text{—VOCl}_3$ (II), with vanadium incorporated into the donor—acceptor complex formed with supported aluminoxane (product of partial hydrolysis of alkylaluminum by support's surface water) [8, 9]; and



(3) Catalysts containing the dispersed phase of V^{+3} compounds on the support surface, $\text{VCl}_3/\text{Al}(\text{OH})_3\text{—Al}(i\text{-Bu})_3$ (IIIa) [11] and $[\text{Al}(i\text{-Bu})_3/\text{Al}(\text{OH})_3\text{Al}(i\text{-Bu})_3]\text{—VOCl}_3$ (IIIb).

The structure and composition of the catalysts were investigated by elementary analysis, IR, ESR and ^{51}V -NMR spectroscopy and by thermodesorption and mass-spectrometry methods (for results see [8–11]).

Homo- and copolymerization of ethylene and propylene

Ethylene, propylene and 3-methyl-1-butene were of polymerization-grade purity. Slurry polymerization and copolymerization were carried out in dried n-heptane of spectral purity grade. The homo- and copolymerization conditions were as follows: 70°C ; the $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4$ mole ratios in the feed mixture, 0.18–5.5; monomer pressure in the reaction zone of copolymerization, 0.19–3 atm. The experimental procedure of polymerization has been described elsewhere [12].

The kinetic method [13] was used to study copolymerization. In the multistage sequential polymerization and copolymerization the first stage of polymerization was performed in n-heptane (or liquid propylene); subsequent stages were carried out in the gas phase. In addition to the kinetic method [13], ^{13}C -NMR spectra were used as described elsewhere [14] to establish the composition of ethylene—propylene copolymers. The degree of crystallization of polymer products was determined by the X-ray method.

RESULTS AND DISCUSSION

Our kinetic investigation of the "enhancement effect" with titanium—magnesium catalysts gave the following results:

(i) Ethylene polymerization is activated by a propylene comonomer as well as after a preliminary polymerization of propylene followed by removal of the residual propylene from the reaction zone and introduction of ethylene (Fig. 1);

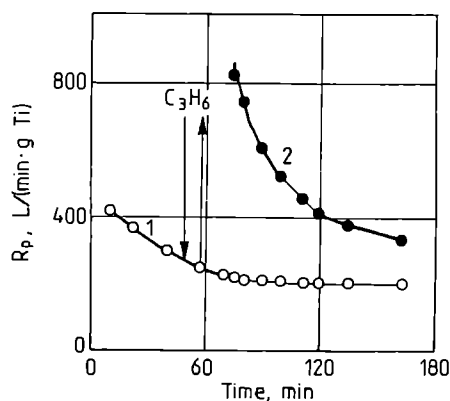


Fig. 1. Kinetic plots of ethylene polymerization (1) and of ethylene polymerization after propylene polymerization (2) by TMC

(ii) The ethylene specific rate increases irrespectively of the length of time of propylene polymerization and of the quantity of polypropylene coating catalytic particles;

(iii) The preliminary homopolymerization of propylene has no influence on the specific rate of ethylene introduction into the polymer chain in the course of copolymerization (Fig.2);

(iv) Ethylene polymerization fails to occur after 3-methyl-1-butene polymerization (Table 2).

Copolymers with identical compositions are obtained in one-stage copolymerization of ethylene and propylene and in two-stage copolymerization preceded by a preliminary polymerization of propylene. The copolymerization constants r_1 and r_2 for those processes are close in value, as confirmed by the variation of copolymer composition with the mole ratio of comonomers concentrations in the reaction zone plotted in the Fineman—Ross coordinates [4].

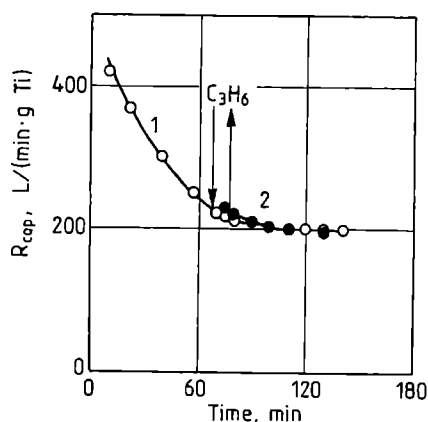


Fig. 2. Specific rates of ethylene incorporation into the copolymer chain in copolymerization of C_2H_4 with C_3H_6 (1) and of C_2H_4 with C_3H_6 after propylene polymerization (2) by TMC

Table 2. The influence of previous 3M1B polymerization stage on ethylene polymerization rate

[TMC + $AlEt_3$]-PTES; mole ratios: $AlEt_3:Ti = 320$; $AlEt_3:PTES = 20$; $50^\circ C$]

Run	Polymerization	$P_{C_2H_4}$, atm	$Rp^{C_2H_4}$, L/min / gTi**)
1	Ethylene polymerization	1.8	40
2	Ethylene polymerization after 3M1B polymerization ^{*)}	9.0	0.8

^{*)} Poly-3M1B coating on TMC particles, 8 g/g TMC.

^{**) R_p^{C₂H₄} were compared in 150 min, when 3M1B was replaced by ethylene in Run 2.}

From this data the nature of ethylene active center has been inferred to remain unaffected by the action of propylene. Thus, the "enhancement effect" could not be related to modification of active centers. Most probably, it results from a change in the number of active sites. There is an interrelation between the morphology of the nascent polymer product on the catalyst surface and the

activity of catalyst in ethylene polymerization. On passing from high-crystalline poly-3-methyl-1-butene to semicrystalline UHMWPE and polypropylene and to practically amorphous ethylene—propylene copolymers, the content of the amorphous phase rises in the nascent polymer product. As a result, the catalytic surface accessible to monomers increases and accordingly, the number of centers active in ethylene polymerization can increase, too.

The method of CO-inhibited polymerization allowed to demonstrate that, after the preliminary propylene polymerization, the number of active centers, was actually greater than that in ethylene homopolymerization [7].

To study the activation of ethylene polymerization by α -olefin, we investigated sequential homo- and copolymerization over types I, II and IIIa,b of supported vanadium catalysts.

The copolymerization stage was carried out when the mole ratio of propylene to ethylene in the feed mixture was equal to 0.3. With each catalyst the resulting copolymers were approximately equal in composition. The contents of propylene and of the amorphous phase in the product were 3—8 mol % and about 60%, respectively.

The kinetic curves of ethylene polymerization (1) and ethylene polymerization preceded by the stage of ethylene—propylene copolymerization (2) are presented in Fig.3.

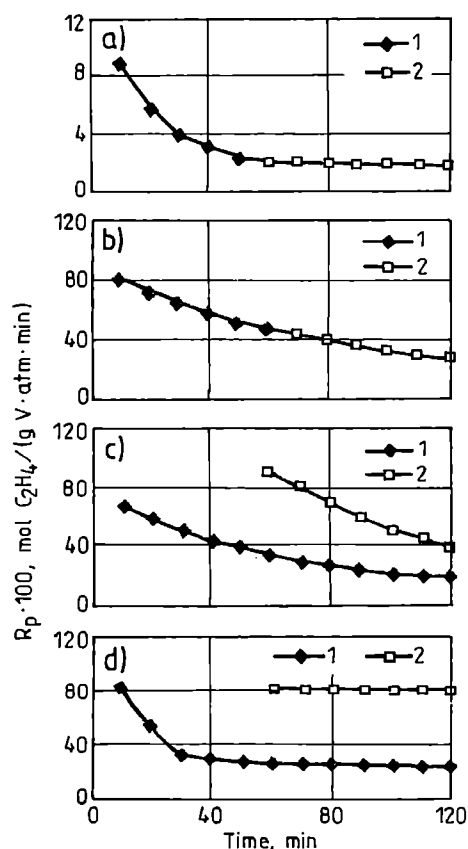


Fig. 3. Kinetic curves of ethylene polymerization (1) and ethylene polymerization after copolymerization of C_2H_4 with C_3H_6 ; catalyst: a — I; b — II; c — IIIa; d — IIIb

The preliminary ethylene—propylene copolymerization is seen to have no effect on the activity of catalysts I and II (Figs. 3a and 3b, curves 2) and to result in increased rate of ethylene polymerization over catalysts IIIa and IIIb (Figs. 3c and 3d, curves 2).

To explain these results resort is taken in the concept of catalyst matrix fragmentation by the resulting polymer [15]. The possible fragmentation scheme of different types supported vanadium catalysts is shown in Fig. 4.

For catalysts I and II, where vanadium is covalent-bonded with the support or with the constituents of the supported vanadium—aluminoxane complex, the distribution of the transition metal compound on the surface is determined by the distribution of the support's OH-groups.

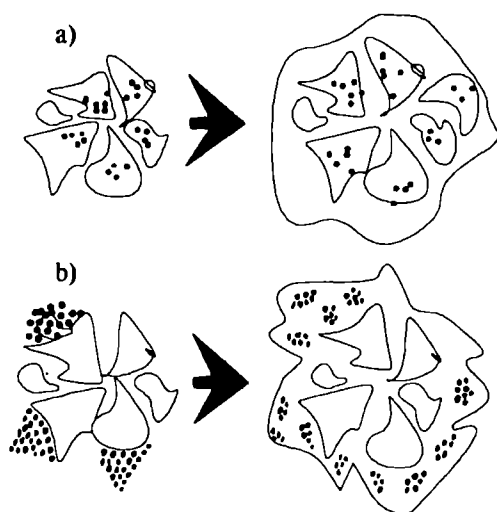


Fig. 4. Fragmentation scheme of different types of supported vanadium catalysts and TMC; catalyst: a — type I and II; b — type IIIa, IIIb and TMC

Fragmentation of these catalysts (Fig. 4a) is related primarily to the breakdown of the support and depends on its nature (pore size and structure). Therefore, it can not give rise to an increase in the number of active centers and to catalyst activation.

The catalytic species in the IIIa and IIIb systems are solid phase species dispersed on the support surface. For these type of catalysts, the process of catalyst matrix fragmentation by the copolymer consists in crushing the dispersed phase and thus in increasing the catalyst active surface (Fig. 4b), i.e., increasing the number of active centers.

The present kinetic results obtained for the two-stages process of ethylene and propylene co- and homo-polymerization on supported vanadium catalysts permit to conclude that fragmentation of the catalyst matrix is the major cause of increase in the number of active centers.

CONCLUSIONS

We compared the results of our investigation with the data of other authors, who studied ethylene and

α -olefin copolymerization over homogeneous and heterogeneous Z—N catalysts, and concluded that it is impossible to give a unified explanation of the "enhancement effect" valid for all types of Z—N catalysts. In contrast to homogeneous zirconocene system [5], in the heterogeneous [1] and the supported [4] catalysts, ethylene active centers fail to become modified by α -olefin. The main reason of enhancement of the ethylene polymerization rate is the increase in the number of active centers involved in polymer chain propagation [1, 7], associated with the catalyst matrix fragmentation caused by the nascent polymer.

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