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Polymerization of ethylene over zeolite-supported catalysts[*)]

Summary — Zeolites including Na-form ZSM-5 (Si/Al = 42) and natural zeolite (Shivyrtuisk deposit: clinoptilolite 60 ± 6%, water 14.2%) were studied as supports for olefin polymerization organometallic catalysts. Zeolite-fixed aluminoxanes, *viz.*, anchored to the surface of the support, were prepared by partially hydrolyzing alkylaluminums ($AlMe_3$, $AlEt_2Cl$) with zeolite's internal water. Thus modified, the zeolites were made to react with transition metal compounds like Cp_2ZrCl_2 or $VOCl_3$. The product of the reaction of zeolites' internae water with $AlMe_3$ was made to react with Cp_2ZrCl_2, and the resulting product was found to be active in the polymerization of ethylene with no additional activation carried out with MAO. In this way, an active metallocene catalyst was prepared without the use of MAO. Yet, when added as cocatalyst, MAO still activated the system, unlike the other conventional organoaluminum cocatalysts. The PE produced over the ZSM-5 $(H_2O)/AlMe_3/Cp_2ZrCl_2$ system had a higher *M* and a higher melting point than PE prepared over a homogeneous Cp_2ZrCl_2 + MAO catalyst system.

Key words: polymerization of ethylene, zeolites, fixed alkylaluminoxanes, supported metallocene and vanadium catalysts, polyethylene.

Immobilization of organometallic catalysts for olefin polymerization arose as a problem immediately after they have been discovered and it continues to be of particular significance. Most relevant reports are concerned with the catalysts immobilized on inorganic carriers like silica and alumina. The first works involving zeolites as supports appeared as recently as the mid-1990s [1—4]. The unique properties of zeolites as supports for olefin polymerization catalysts comprise the possibility of varying the composition of a zeolite support (Si:Al ratio in zeolite framework structure) over a relatlvely wide range; the multitude of available structures ranging from very narrow to large pore systems; and the capability of absorbing metal ions, small metal clusters, or transition metal complexes.

This report sets out to describe the application of different types of zeolites as supports for metallocene and vanadium catalysts in the polymerization of ethylene. One important problem solved in this work is the preparation of the alkylaluminoxanes anchored to the support by partial hydrolysis of organoaluminum compounds (OAC) with the aid of zeolite's internal water and their use as cocatalysts. The study is concerned with partial hydrolysis of OAC ($AlMe_3$, $AlEt_2Cl$) with water contained in the inorganic supports; with formation of the heterogenized complexes based on Cp_2ZrCl_2 or $VOCl_3$ and of the aluminoxanes anchored to a zeolite (zeolite (H_2O)/OAC); and with polymerization of ethylene over ZSM-5$(H_2O)/AlMe_3/Cp_2ZrCl_2$ and NZ$(H_2O)/AlEt_2Cl/VOCl_3$ catalysts (NZ = natural zeolite).

EXPERIMENTAL

Zeolite-supported catalysts

Supports

The Na-form ZSM-5 had the ratio Si:Al = 42; the total volume of pores, 0.287 cm^3/g; the specific surface (on benzene), 40 m^2/g; and the internal water content, 8.9 wt %.

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The NZ from the Shivyrtuisk deposit (Russia) contained 60 ± 6 wt % of clinoptilolite and 14.2 wt % of zeolites' water. An NZ fraction 50—60 µm in particle size and a nonfractionated NZ with particles lower than 60 µm in size were used.

Kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, contained 13.8 wt % of structure water and 0.5 wt % of surface water; the specific surface of kaolin was 12.2 m^2/g.

Tuff contained 0.3 wt % of water and had a specific surface of 6.7 m^2/g.

The zeolites and other supports were examined by thermogravimetry (TGA) with the aid of a Q-1500 D derivatograph.

Components of catalysts

Aldrich's Cp_2ZrCl_2 was used as supplied.

$VOCl_3$ was prepared from V_2O_5 and $SOCl_2$ and was distilled in vacuum (0.5 mm Hg) at 18.5°C. Alkylaluminums $AlMe_3$, $AlEt_2Cl$ (from GNIIHTEOS, Moscow) and MAO (Aldrich's 10 wt % solution in toluene) were used without further purification; their composition was: $AlMe_3$ (Al, 37.2; Me, 60.6 wt %); $AlEt_2Cl$ (Al, 22.3; Et, 47.9; Cl, 29.2 wt %).

Aldrich's toluene and spectral-purity dried *n*-heptane were used as solvents.

Preparation of zeolite supported catalysts

This preparation involved two steps: the preparation of alkylaluminoxanes anchored to the support by partial hydrolysis of OAC with the zeolite's internal water and the formation the heterogenized complexes from zirconocene (or vanadium compound) and alkylaluminoxanes. Alkylaluminum was added dropwise to uncalcined zeolite suspended in toluene (or *n*-heptane) at room temperature. The end of the reaction of the alkylaluminum with the zeolite water was recognized by cessation of the evolution of gaseous products. The composition and quantity of the gaseous products were determined with a Chrom-5 gas chromatograph. After removal of the gaseous products from the reaction zone, the zirconocene or vanadium compound and then the monomer were added.

Polymerization of ethylene

Ethylene was of polymerization-grade purity. Slurry polymerization of ethylene was carried out in a 0.4 L glass reactor, the same in which the catalytic complex had been prepared. The reactor was equipped with a stirrer and a water jacket. The monomer concentration, temperature, and the rate of stirring were kept constant during a polymerization run. The molecular weight characteristics of PE samples were obtained by GPC in *o*-dichlorobenzene at 140°C (Waters, 150C). The melting point of PE was determined on a Dupont differential scanning calorimeter (DSC 910) used with a heating rate of 10 K min^{-1} from 20 to 150°C.

RESULTS AND DISCUSSION

The formation of catalytic complexes with aluminoxanes anchored to zeolite

Supported catalysts including the supported metallocene catalysts can be prepared by the following main methods: direct adsorption of transition metal compounds on inorganic support materials like SiO_2, Al_2O_3, zeolite, $MgCl_2$, *etc.*; adsorption of transition metal compounds on a support modified by AlR_3, MAO or other compounds; adsorption of the complexes of a metallocene and MAO on silica or other carriers. All these methods require a long-duration high-temperature treatment of carriers and, what is most important, introduction of additional amounts of the free organoaluminum component (MAO or AlR_3) to activate the supported catalyst. As a result, the alkylaluminum concentration in the system involving a supported catalyst is practically the same and sometimes greater than that in homogeneous catalytic systems.

Our method of preparing organometallic catalysts on the surface of hydrated supports has been reported elsewhere [5]. In this method, the fixed alkylaluminoxanes formed in the reaction of the surface or the support's internal water with OAC are used as cocatalysts in the system for ethylene polymerization. Extensive investigations on the reaction of alkylaluminums with water of various inorganic supports (kaolin, aluminum hydroxide, crystalline KBr, and zeolites) [6—8] have shown the organoaluminum compounds formed in the reaction of OAC with the support water to be predominantly bonded to the surface; according to the data of elemental analysis, the Al content in the solution was found not to exceed 4—5% of the total quantity of the Al introduced into the reaction zone; the fixed OAC failed to become completely released into the solution, even in the presence of strong electron donors (Et_3N). Partial hydrolysis of an alkylaluminum with the support water is accompanied by evolution of gaseous hydrocarbon products (RH). The yield of RH (CH_4 and C_2H_6 on hydrolysis of $AlMe_3$ and $AlEt_2Cl$, resp.) is related to support type (Fig. 1).

Reports [9, 10] and our investigations [11] have shown various organoaluminum products such as dialkylaluminum hydroxide, an aqua-complex of alkylaluminoxane, and alkylaluminoxane to form in the reaction of alkylaluminum with water. The formation of alkylalumoxane on the surface in the system support (H_2O)/OAC was evidenced by IR spectra. A strong band at 780—810 cm^{-1} due to asymmetric vibrations of Al-O bonds in the alumoxane molecule [10] was found to be assignable to the products of the reaction of $AlEt_2Cl$ with water adsorbed on KBr crystals. The absorption bands (680, 620, 1460 cm^{-1}) characteristic of alkylaluminum compounds were also observed. Thus, the alkylaluminoxanes formed on the support surface are

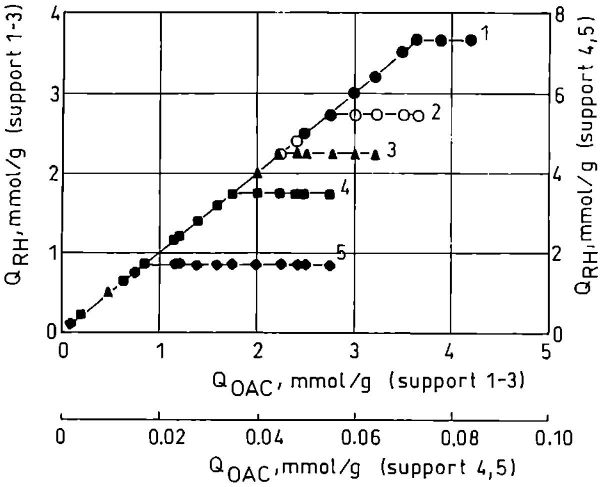

Fig. 1. The RH (C_2H_6) yield in the reaction of OAC with the support water; 22°C; n-heptane; uncalcined supports: (1) ZSM-5, (2) natural zeolite, (4) kaolin, (5) tuff, (3) natural zeolite calcined at 300°C; OAC: (1) $AlMe_3$, (2—5) $AlEt_2Cl$

believed to contain the reactive alkyl groups. Similarly as other organoaluminum compounds, they enter into the reactions of alkylation with transition metal compounds as shown by our IR study on the reaction of $VOCl_3$ with supported aluminoxanes [11].

Zeolites are peculiar in that their internal water is highly mobile. In contrast to the structure water of other high-hydrated supports (*e.g.*, kaolin), the zeolite water is completely removed on heating at 800—1000°C without any destruction of the zeolite structure and can be easily reabsorbed. The consumption of OAC in the dehydration of zeolites and gas evolution processes (Fig. 1, curves 1—3) is markedly higher than that in the dehydration of other inorganic supports (Fig. 1, curves 4, 5). Gas evolution data show the whole of zeolite water (from the external surface and from channels) to react with OAC. Actually, the amount of ZSM-5 water that reacted with $AlMe_3$ was equal to 9.1 wt %, *i.e.*, to the total amount of water (8.9 wt %) in the zeolite according to TGA analysis.

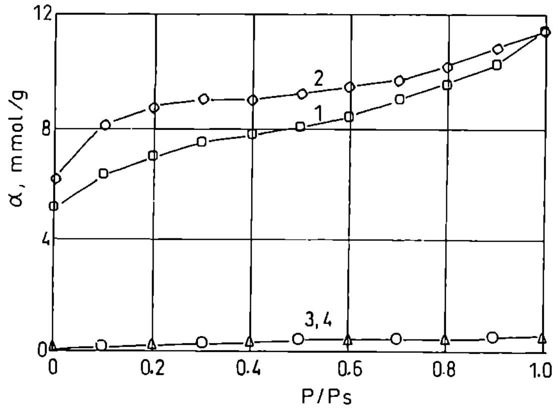

Fig. 2. Isotherms of (1) adsorption and (2) desorption of H_2O, (3) adsorption of $AlMe_3$ and (4) of $VOCl_3$ on natural zeolite heated in vacuo at 300°C

The sorption properties of the zeolite were studied with respect to the catalyst components $AlMe_3$ and $VOCl_3$. The adsorption isotherms are presented in Fig. 2. In contrast to water (Fig. 2, curve 1), gaseous $VOCl_3$ and $AlMe_3$ (Fig. 2, curves 3 and 4) are seen not to penetrate into the micropores of the zeolite; they are sorbed only by secondary pores and on the external surface of the zeolite. The fact that $AlMe_3$ does not penetrate into the micropores of the zeolite and the whole water of this support reacts with OAC allows to infer that, in the reaction with OAC, the zeolite's mobile water migrates from zeolite channels and the fixed aluminoxanes and then their complexes with transition metal compounds are formed at the external zeolite surface.

Polymerization of ethylene over zeolite supported catalysts

The high content of zeolite's internal water and its mobility allow aluminoxanes to be formed at the zeolite surface in amounts high enough to activate zirconocene and vanadium components of the catalyst. The $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ and $NZ(H_2O)/AlEt_2Cl/VOCl_3$ systems are active in the polymerization of ethylene with no addition of MAO nor any other organoaluminum component. The kinetic curves of ethylene polymerization run over these catalysts are presented in Figs. 3 and 4.

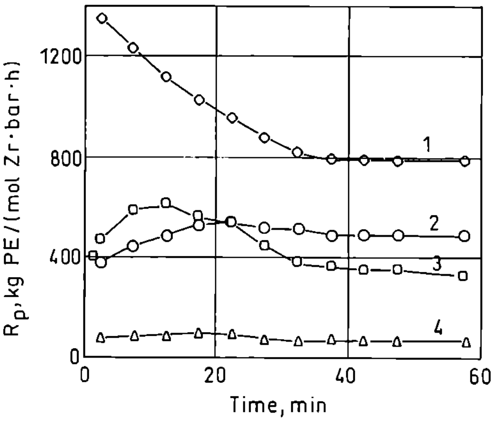

Fig. 3. Rate vs. time profiles for ethylene polymerization over homogeneous system (1) Cp_2ZrCl_2—MAO and (2—4) zeolite supported catalyst $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$; polymerization conditions: toluene; 0.46 bar; 34°C; 1 hour; [Zr] · 10^5, mol/L; (1) 14; [Zr], wt % = (2) 0.024; (3) 0.03; (4) 0.3; OAC: (1) MAO, (2—4) $AlMe_3$; mole ratio Al:Zr = (1) 470, (2) 1650, (3) 1090, (4) 140

The activity of the zeolite-supported zirconocene catalyst is lower than that of the homogeneous Cp_2ZrCl_2—MAO catalyst prepared under similar conditions (Fig. 3, curves 1, 2—4 and Table 1). The ethylene

Table 1. **Polymerization of ethylene over zeolite-supported and homogeneous catalysts based on Cp_2ZrCl_2*)**

Run	Catalyst	[Zr], wt %	Al/Zr, mole ratio	Activity, kg PE/(mol Zr · bar · h)	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Melting point °C
1	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$	0.007	4620	82	202750	22	133.5
2	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$	0.024	1650	475	273810	10	132.5
3	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$	0.028	1090	455	280620	4.8	135
4	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$	0.16	160	80	—	—	—
5	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$	0.03	3000	370	—	—	—
6	$ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ + MAO	0.16	320**)	500	52900	18	123.5
7	Cp_2ZrCl_2—MAO	0.14***)	470	1000	133750	4.8	127
8	Cp_2ZrCl_2—MAO	0.17***)	556	1500	57540	4.6	126.5

*) Polymerization conditions: 34°C (runs 1—4 and 6—8), 75°C (run 5); toluene; ethylene pressure, 0.46 bar (runs 1—7), 0.23 bar (run 8).
**) Al:Zr = $AlMe_3$:Zr + MAO:Zr = 160 + 160 = 320.
***) [Zr], mmol/L.

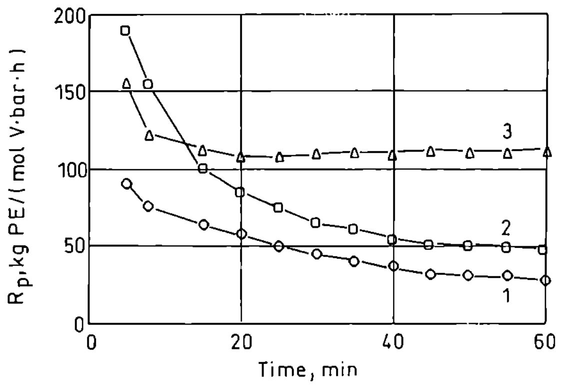

Fig. 4. Rate vs. time profiles for ethylene polymerization over zeolite-supported catalyst $NZ(H_2O)/AlEt_2Cl/VOCl_3$; polymerization conditions: n-heptane; 0.2 bar; 50°C, 1 hour; [V], wt % = (1) 1, (2) 0.08, (3) 0.16; mole ratio Al:V = (1) 43, (2) 35, (3) 70

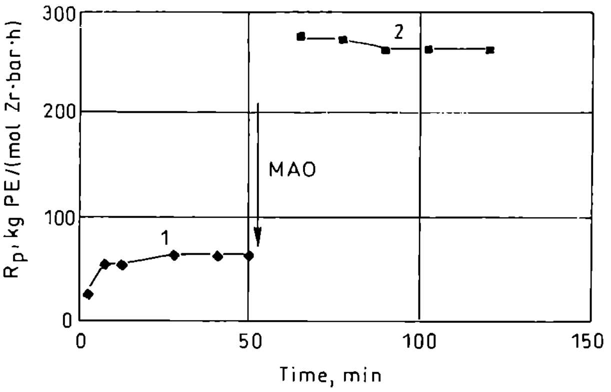

Fig. 5. Effect of MAO addition on ethylene polymerization over zeolite-supported catalyst $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$: polymerization conditions: toluene, 34°C; 0.46 bar; 3 hours; [Zr], wt % = 0.16; Al/Zr = (1) 160, (2) 320; catalysts: (1) $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$, (2) $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ + MAO

polymerization rate over $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ did not change after addition of $AlMe_3$ and increased after introduction of free MAO (Fig. 4).

The molecular weight and the melting point of PE formed over the $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ catalyst were higher than those of PE prepared over the homogeneous Cp_2ZrCl_2—MAO catalyst (Table 1). Addition of MAO to the $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ catalyst decreased the molecular weight and the melting point of PE formed (Table 1, run 6), and increased the rate of polymerization (Fig. 5).

For zeolite-supported catalysts, the MAO concentration in the reaction zone has been reported to exceed 100 mmols/L [1, 2, 4, 12]. Moreover, the consumption of MAO in the chemical treatment of zeolites ranges up to about 30 mmols/L. Contrary to these catalysts, the present $ZSM\text{-}5(H_2O)/AlMe_3/Cp_2ZrCl_2$ catalyst allows to replace MAO by $AlMe_3$ and to exclude addition of free MAO to the zeolite-supported zirconocene complex. Furthermore, we suppose that the synthesis of MAO directly on the zeolite support may be one of the ways to reduce leaching of the supported zirconocene catalyst. In this case, the homogeneous active centers are made less likely to appear in the reaction zone. The increase in the molecular weight and melting point of the polyethylene prepared over the novel zeolite-supported zirconocene catalyst, as compared with PE produced over the homogeneous zirconocene system, favors this view.

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KALENDARZ IMPREZ

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27—29 maja 2002 r. Lyon-Villeurbanne, Francja. Sympozjum europejskie **„7th European Symposium on Polymer Blends"**.

Organizator: Centre Nationale de la Recherche Scientifique, Laboratoire des Matériaux Macromoléculaires, Lyon.

Tematyka: termodynamika mieszania, zmiany morfologii podczas mieszania i przetwarzania, środki kompatybilizujące, mieszanie reaktywne, materiały, zależność struktura-właściwości, nowe kierunki rozwoju, strategie i zastosowania przemysłowe mieszanin.

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16—20 czerwca 2002 r. Guimarães, Portugalia. **„Eighteenth Annual Meeting — PPS-18 Polymer Processing Society"**.

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