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## Silica powder obtained by sol-gel method as a support of organometallic vanadium catalyst for ethylene polymerization

### RAPID COMMUNICATION

**Summary** — Sol-gel technique was employed to obtain the silica-type powder, which after modification procedure was applied as a support of organometallic catalytic system for ethylene polymerization. The powder product was synthesized using hydrolysis and condensation of TEOS, catalyzed by ammonia. Obtained material and a reference support (commercial silica Davisil) were characterized to determine their particle size distributions, BET surface area, pore volume and diameter. Gas-phase adsorption of vanadium catalyst on analyzed support materials as well as adsorption from the solution in hexane were carried out. Both carrier materials were thermally pretreated prior catalytic systems syntheses and the influence of modification method applied on resulting organometallic catalyst character was estimated in low-pressure slurry polymerization of ethylene. Obtained results prove that sol-gel material, due to its advantageous morphology with wide and shallow pores, allows to obtain catalytic systems of higher activity in low-pressure ethylene polymerization, in comparison with commercial silica Davisil.

**Key words:** silica support, sol-gel technique, ethylene polymerization, supported vanadium catalyst, support porous structure.

Organometallic catalytic systems for ethylene polymerization and copolymerization require being heterogeneous for application in modern gas-phase industrial plants. Furthermore heterogenization gives the possibility to regulate polymer product morphology as a result of "replication" phenomena, which occur during polymer particle growth [1]. As support materials magnesium dichloride [2–5] and oxide-type compounds (silica or alumina) are widely used, however recent reports concern mainly SiO<sub>2</sub> [6, 7].

Behavior of supported catalytic system depends on carrier physical and chemical properties as well. For example oxide-type material needs to be modified to achieve desired concentration and arrangement of superficial hydroxyl groups, what in addition should affect the activity of supported catalytic system and properties of polymer obtained.

Looking for new, chloride free carriers we have applied a product of a common sol-gel technique. This sim-

ply procedure, depending on synthesis conditions, allows to obtain the products that can significantly vary in form [8]. Starting with orthosilicate precursor *i.e.* tetraethyl orthosilicate (TEOS), the fibers, glasses, thin layers and bulk powders can be produced, where the powder seems to be most useful form for organometallic catalyst heterogenization.

We have applied mentioned sol-gel technique to produce successfully silica-type powder. Received material and commercial silica (for comparison) were used in supported vanadium catalyst preparation by VOCl<sub>3</sub> precursor deposition performed in gas-phase adsorption and slurry impregnation. Supported vanadium catalysts after activation with diethylaluminum chloride were used in low-pressure polymerization of ethylene.

### EXPERIMENTAL

#### Materials

Ethylene for polymerization was of polymerization grade, delivered by PKN Orlen.

Support and catalytic system has been prepared from the following components:

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- tetraethylorthosilicate (TEOS,  $\geq 98\%$ , Fluka),
- ammonia (aqueous 25 %, POCh Gliwice),
- vanadium oxytrichloride ( $\text{VOCl}_3$ , 99 %, Aldrich),
- diethylaluminum chloride ( $\text{AlEt}_2\text{Cl}$ , solution in hexane, Aldrich).

As a reference material commercial silica Davisil (Grade 645, Aldrich) was used.

### Preparation and characterization of catalysts

All operations, except for sol-gel material synthesis, were performed under dry and oxygen free, argon atmosphere. The procedure of sol-gel powder synthesis was taken from the literature, where colloidal silica-gel suspension was obtained as a first step in high transparency glass production [9]. Water, TEOS, ethanol (solvent) and ammonia (catalyst) were mixed together in molar ratios 4.5:1:6:0.07 and stirred for 24 hours. Final powder product was obtained by solvent evaporation from received suspension.

Applied carrier materials were modified by annealing them at temperature 200 or 800 °C for 3 hours in air atmosphere and then for 1 hour in argon.

Particle size distribution was determined using laser diffraction technique.

The surface area and pore size distributions of support materials were determined using nitrogen adsorption by Micromeritics ASAP 2000 instrument at 77 K.

Thermal analysis of support samples was performed using TA 2050 TGA instrument at the heating rate 10 deg/min.

Chemisorption of  $\text{VOCl}_3$  on support surface was realized by successive introduction of catalyst components ( $\text{VOCl}_3$  and then  $\text{AlEt}_2\text{Cl}$ ) from gas-phase and control of the amounts of chemically adsorbed compounds using gravimetric technique [10].

Supported catalysts for slurry polymerization were prepared by reaction of thermally pretreated support with  $\text{VOCl}_3$  in hexane at room temperature. Received supported precatalyst was washed with hexane ( $5 \times 20$  mL), dried and dispersed in solvent again. Amount of adsorbed  $\text{VOCl}_3$  was determined by atomic absorption spectroscopy (AAS) using Solaar AAS spectrometer.

### Polymer synthesis and testing

Polymerization process was carried out in Büchi glass reactor, in hexane slurry, at 45 °C and under constant ethylene pressure (0.5 MPa). The precatalyst slurry was activated by addition of organoaluminum co-catalyst ( $\text{AlEt}_2\text{Cl}$ ). Reaction was initiated by introducing ethylene and quenched after 30 min by addition of methanol containing 5 wt. % of HCl.

Molecular weight and molecular weight distribution of investigated samples were determined by gel permeation chromatography (PL GPC220) at 150 °C in trichlorobenzene as a solvent.

Melting points and the degrees of crystallinity of polymers were measured by differential scanning calorimetry using TA Instruments 2010 DSC calorimeter at the heating rate 10 deg/min. Polymer particle size distribution was determined using Fritsch vibratory sieves shaker with set comprising 11 sieves varying from 0.063 to 1.6 mm.

## RESULTS AND DISCUSSION

### Catalytic system

Silica powder obtained by sol-gel synthesis shows particle size distribution with dominant particle dimension about 5–20  $\mu\text{m}$  (Fig. 1). Taken as reference sample commercial Davisil silica exhibits "bulky" distribution with the highest contribution of particles ranging 100–200  $\mu\text{m}$ . Thus grinding of Davisil in ball-mill was applied to approach desired powder size composition (granulation). Hence two powder materials of grain diameter around 10  $\mu\text{m}$  were obtained, however Davisil was slightly shifted to larger diameter (Fig. 1).

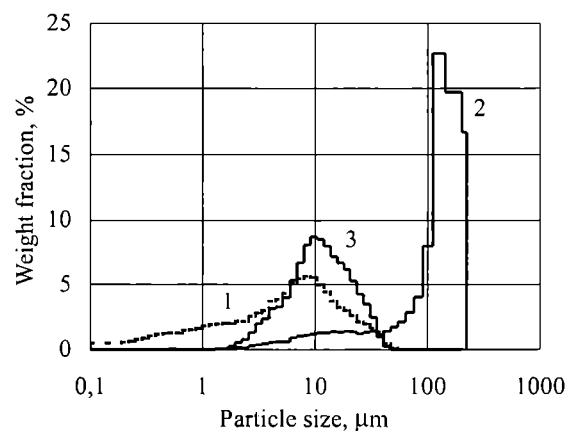


Fig. 1. Particle size distribution of silica powders: 1 — prepared in this work, 2 — raw Davisil, 3 — milled Davisil

Both obtained powder materials were characterized using low-temperature nitrogen adsorption. Results of surface investigations show that raw powder synthesized by sol-gel technique shows similar surface area and smaller pore volume and diameter in comparison with commercial Davisil (Table 1). Grinding operation applied for Davisil and following calcination in 200 °C keeps these properties almost unchanged, contrary to sol-gel powder, which demonstrates almost double BET surface area drop and contemporary increase in pore's volume and diameter in case of calcinations at the same temperature (200 °C). However it should be stressed that further increase in annealing temperature up to 800 °C does not cause important changes in sol-gel material morphology.

**Table 1.** Morphological properties of applied support materials<sup>\*)</sup> and results of catalyst syntheses and slurry polymerization of ethylene; polymerization conditions:  $[AlEt_2Cl] = 20 \text{ mmol/dm}^3$ , temp.  $45 \text{ }^\circ\text{C}$ , time 30 min

Support	Calcination temp., $^\circ\text{C}$	$S_{BET}$ $\text{m}^2/\text{g}$	$d_p$ nm	$V_p$ $\text{cm}^3/\text{g}$	$d_p/V_p$	$\text{VOCl}_3$ [mmol/g]		$\text{VOCl}_3$ [ $\mu\text{mol}/\text{m}^2$ ]		Yield g PE/g <sub>cat</sub>	Activity kg PE/molv
						gas-phase	AAS	gas-phase	AAS		
Sol-gel silica	—	266	8.4	0.26	32.3	—	—	—	—	—	—
	200	143	21.4	0.61	33.4	0.30	0.31	2.10	2.17	141	455
	800	116	21.4	0.63	34.0	0.10	0.19	0.86	1.64	110	579
Davisil silica	—	280	12.9	1.18	10.9	—	—	—	—	—	—
	200	262	13.3	1.12	11.9	1.03	1.29	3.93	4.92	425	329
	800	—	—	—	—	0.37	0.55	—	—	246	447

<sup>\*)</sup>  $S_{BET}$  – surface area,  $d_p$  – pore diameter,  $V_p$  – pore volume.

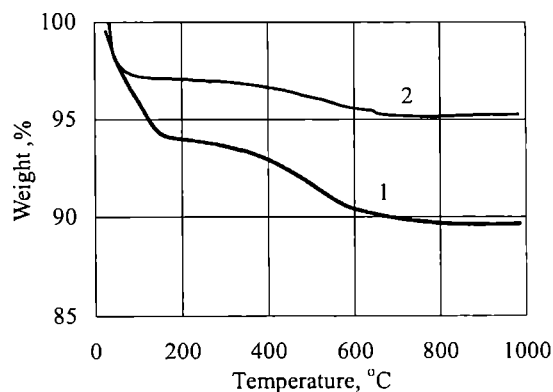
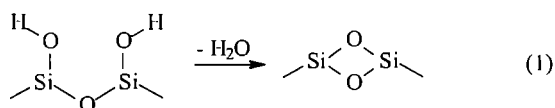


Fig. 2. TG curves of materials applied as supports, heating rate  $10 \text{ deg/min}$ ; 1 — sol-gel silica, 2 — Davisil silica

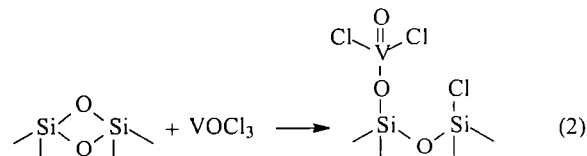
Observed surface physical property variation is probably caused by changes in gel structure. To trace the changes that occur during heating, the thermogravimetric analysis was performed (Fig. 2). A stronger decrease in initial weight in case of sol-gel silica, in comparison with Davisil silica, during the heating at the temperature up to  $100 \text{ }^\circ\text{C}$ , indicates higher water (and probably ethanol) content in sol-gel material, as a synthesis residue. Removal of water molecules is very important in case of organometallic catalysts, which require special handling in dry, oxygen free atmosphere. Thus material annealing at temperature up to  $200 \text{ }^\circ\text{C}$  should eliminate majority of water molecules, leaving certain concentration of superficial hydroxyls, which are postulated to be vicinal, geminal or isolated [8, 11]. At temperature above  $200 \text{ }^\circ\text{C}$  a progressive removal of hydroxyls takes place, what results in partially dehydroxylated silica as a result of removing vicinal OH groups in condensation reaction.



Finally, at higher temperature, due to migration of individual hydroxyl groups, further dehydration is possible what results in almost fully dehydroxylated surface with remaining siloxane groups and not numer-

ous geminal and isolated OH groups. Thus annealing at specific temperature allows to obtain the desired concentration of superficial hydroxyls, what is important in case of oxide-type materials.

Prepared support materials were used in chemisorption of transition metal component —  $\text{VOCl}_3$ . Results of gas-phase precursor adsorption on the carrier surface, according to calcination temperature, are presented in Table 1 and compared with corresponding vanadium content in catalysts obtained by impregnation. Received results demonstrate that different techniques used for catalyst preparation give similar results: sol-gel silica calcined at  $200 \text{ }^\circ\text{C}$  shows  $0.3 \text{ mmol}_V/\text{g}_{\text{cat}}$  (determined by gravimetric technique) and  $0.31 \text{ mmol}_V/\text{g}_{\text{cat}}$  (determined by AAS), respectively. Davisil silica treated in the same conditions exhibits triple higher vanadium content, what may be caused by its higher surface area. Both support materials annealed at  $800 \text{ }^\circ\text{C}$  show almost triple concentration of precursor fall in comparison with these that were calcined at  $200 \text{ }^\circ\text{C}$ . Observed decrease is obviously caused by reduction of superficial hydroxyl groups concentration. However it should be stressed that even the support calcined at  $800 \text{ }^\circ\text{C}$ , which seems to be strongly dehydroxylated, is still efficient to bind a lot of vanadium precursor. This situation may be explained by participation of siloxane bridges in reaction with  $\text{VOCl}_3$ , but it should be noticed that one bridge, which is formed from two hydroxyl groups, is able to react with one  $\text{VOCl}_3$  molecule only.



## Polymerization

Investigated catalytic systems were applied in low-pressure ethylene polymerization process. Catalyst supported on carrier (Davisil or sol-gel silica) calcined at  $200 \text{ }^\circ\text{C}$  shows significantly higher productivity (expressed in  $\text{g PE}/\text{g}_{\text{cat}}$ ) in comparison with counterparts

where support was annealed at 800 °C. It seems to be clear when we realize that quantity of vanadium active species that are potentially formed depends directly on the quantity of transition metal compound, which is present in catalytic system. Differences in polymer yield obtained with use of catalysts supported on different materials but annealed in the same conditions may be explained the same way. Higher productivity of catalyst supported on Davisil silica is caused evidently by nearly triple higher vanadium loading on supports surface, in comparison with sol-gel material.

However comparison of activities of investigated systems (expressed in kg PE/mol<sub>V</sub>, Table 1) prove that catalytic systems obtained with sol-gel silica are more efficient. Differences in activities between Davisil and sol-gel supported catalysts, annealed at the same temperature, may be explained by differences in vanadium loading on support surface. Taking into consideration the amount of vanadium compound fixed and supports surface area as well we can see that Davisil supported catalysts exhibits clearly more dense distribution of precursor (μmol<sub>V</sub>/m<sup>2</sup>). As a result, active species that are formed on Davisil support surface may be less accessible for co-catalyst and monomer molecules, in comparison with sol-gel systems.

Additionally Davisil demonstrates the surface with narrow and deep pores — expressed by low value of the diameter-to-volume ratio ( $d_p/V_p$ ) — while for sol-gel silica this parameter is triple higher; independently on applied calcination temperature (Table 1). As a result the major part of Davisil surface area may be located inside the pores. Vanadium active sites that are formed in the "internal" part of the support surface may still be accessible for co-catalyst and monomer molecules, but the growth of macromolecule chain inside deep pores may be strongly restricted [12].

Obtained results prove that sol-gel material, due to its advantageous morphology with wide and shallow pores, allows to obtain the catalytic systems with higher activity in low-pressure ethylene polymerization in comparison with commercial Davisil silica.

Molecular weight of polyethylene obtained with use of sol-gel (calcinated at 200 °C) supported catalysts is relatively high ( $\overline{M}_w > 2 \cdot 10^6$ ). It is not surprising, because vanadium catalysts are known to produce the polymers of extremely high molecular weights and broad molecular weight distributions [13]. However analyzed sample shows quite narrow molecular weight distribution ( $MWD < 4$ ) what points to low heterogeneity of surface vanadium species. Discussed conclusions are confirmed by polymer properties listed in Table 2. Melting point (139–140 °C) and crystallinity (39–40 %) values seem to be independent on carrier type used and way of its modification. It may be caused by the affinity of active sites, which are always created in reaction of VOCl<sub>3</sub> with hydroxyl groups or siloxanes — in any case vanadium atom is fixed *via* oxygen [eq. (2)].

Table 2. Selected properties of polymer products<sup>1)</sup>

Support	Calcination temp., °C	$T_m$ , °C	$C_{DSC}$ , %	Bulk density g/dm <sup>3</sup>
Sol-gel silica	200	139.8	40	181
	800	139.5	39	138
Davisil silica	200	138.9	39	180
	800	—	—	120

<sup>1)</sup>  $T_m$  — melting temperature,  $C_{DSC}$  — crystallinity determined by DSC.

If we look at polymer morphology it shows relatively high bulk density (almost 200 g/dm<sup>3</sup> for 30 min polymerization time) what is beneficial for industrial polymerization processes. Additionally it is known that polymer particles should exhibit controlled spherical morphology with desired size and uniformity. Heterogeneous (especially supported) catalysts give the opportunity of polymer particle control known as "catalyst particle replication" phenomenon.

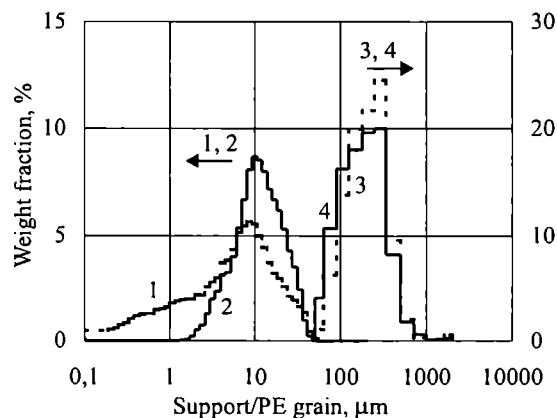


Fig. 3. Particle size distribution of catalysts carriers and resulting polyethylene: 1, 3 — sol-gel silica and PE obtained with its use, respectively; 2, 4 — Davisil and PE obtained with its use, respectively

Results of carrier particle distribution and related polymers granule distribution (obtained with corresponding catalytic systems) are presented on Fig. 3. It can be noticed, that both supported systems produce the polymer of fine particles and uniform distributions. Comparison of support material granulation with adequate polyethylene granules distribution shows that these values match in ratio 1:10.

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