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CATALYSIS IN CHEMICAL  
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## Effect of Titanium–Magnesium Catalyst Morphology on the Properties of Polypropylene upon Propylene Polymerization in a Liquid Monomer

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**Abstract**—The effect of the particle size of an IK-8-21 domestic titanium-magnesium catalyst on the properties of polypropylene (PP) produced during the polymerization of propylene in a liquid monomer is studied. Catalysts with particle sizes of 20 to 64 μm are shown to have high activity and identical sensitivity to hydrogen and allow PP to be obtained with a narrow distribution of particles over size, high isotacticity, and close values of crystallinity, melting temperature, and physicomechanical properties. A slight decrease in the activity and bulk density of PP powder is observed when the average size of catalyst particles is increased from 20 to 43 μm. A more notable reduction in the activity and bulk density of PP powder is observed for catalyst with particle sizes of 62 to 64 μm. IK-8-21 catalyst is not inferior to its foreign analogues with respect to the properties of the resulting PP.

**Keywords:** Ziegler–Natta catalyst, titanium-magnesium catalyst, polymerization, propylene, polypropylene properties

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### INTRODUCTION

The production of polypropylene (PP) requires high-activity catalysts that ensure PP with high stereoregularity and improved powder morphology (low content of a small fraction less than 200 μm in the polymer) and have a high sensitivity to molecular weight regulators, particularly hydrogen. Stable production requires powder with high yield strength and bulk density (i.e., particles close to spherical in shape) with no dust fraction and a narrow particle size distribution.

It is known that the morphology of PP particles is determined by that of catalyst particles [1, 2], due to replication. The size of the catalyst particles used in the production of PP depends on the PP production technology and product requirements. A catalyst larger than those employed in obtaining a homopolymer is thus used at PAO Nizhnekamskneftekhim to obtain shockproof propylene/ethylene block copolymers. Russian companies currently use imported cat-

alysts to produce PP. The aim of using domestic catalysts for olefin polymerization is part of an import substitution program. IK-8-21 magnesium–titanium catalyst (MTC) was developed at the Boreskov Institute of Catalysis for the PP polymerization process [4, 5]. A number of tests were performed with catalysts for the polymerization process in a liquid monomer and they showed that IK-8-21 catalyst is not inferior to its foreign analogues in terms of activity and the quality of the resulting PP [6].

The aim of this work was to determine how the properties of IK-8-21 catalyst can change during polymerization in a liquid monomer, and how some characteristics of the obtained PP depend on the size of catalyst particles in the range of 20 to 64 μm.

### EXPERIMENTAL

IK-8-21 MTC samples with the composition TiCl<sub>4</sub>/D<sub>1</sub>/MgCl<sub>2</sub> (D<sub>1</sub> is an internal donor, dibutyl

**Table 1.** Properties of our IK-8-21 MTC samples

| Property  | Catalyst sample |       |       |       |       |
|---|-----------------|-------|-------|-------|-------|
|   | MTC-1           | MTC-2 | MTC-3 | MTC-4 | MTC-5 |
| Average size of catalyst particles, $\mu\text{m}$ | 20              | 34    | 47    | 62    | 64    |
| Amount of (in wt %):                              |                 |       |       |       |       |
| titanium  | 2.5             | 2.2   | 2.5   | 2.4   | 2.5   |
| magnesium   | 19.2            | 18.3  | 17.7  | 18.5  | 18.0  |
| internal donor, DBP                               | 11.8            | 9.7   | 10.2  | 9.2   | 10.5  |
| SPAN = $(d_{90} - d_{10})/d_{50}$                 | 0.5             | 0.3   | 0.5   | 0.4   | 0.4   |

**Table 2.** Properties of PP powders obtained using MTC with different particle sizes

| Property  | Catalyst sample |       |       |       |       |
|---|-----------------|-------|-------|-------|-------|
|   | MTC-1           | MTC-2 | MTC-3 | MTC-4 | MTC-5 |
| Average size of MTC particles, $\mu\text{m}$                | 20              | 34    | 47    | 62    | 64    |
| Catalyst activity, kg of PP per 1 g of catalyst             | 63              | 60    | 57    | 52    | 48    |
| Bulk density of PP powder, $\text{g}/\text{cm}^3$           | 0.470           | 0.460 | 0.450 | 0.440 | 0.430 |
| Average PP particle size, $\mu\text{m}$                     | 800             | 1270  | 1720  | 2100  | 2280  |
| SPAN = $(d_{90} - d_{10})/d_{50}$                           | 0.4             | 0.3   | 0.4   | 0.4   | 0.4   |
| Content of small fraction (less than 200 $\mu\text{m}$ ), % | 0.1             |       |       | No    |       |
| Isotacticity (XI), wt %                                     | 98.2            | 98.3  | 98.0  | 97.9  | 98.1  |
| Melting temperature, $^{\circ}\text{C}$                     | 166             | 164   | 165   | 166   | 165   |
| Crystallinity, %  | 32              | 30    | 29    | 31    | 30    |

phthalate) were prepared following the procedure described in [7]. Five samples with average particle sizes of 20 to 64  $\mu\text{m}$  were synthesized.

The distribution of the catalyst's particle size was determined by means of laser diffraction on a Mastersizer 2000 unit. The contents of titanium and magnesium in the samples was determined via atomic emission spectrometry with inductively coupled plasma on an Optima 4300 DV spectrometer, while the mass fraction of dibutyl phthalate was measured through liquid chromatography on a LC-20 Prominence chromatograph.

The propylene was polymerized in a steel autoclave with a capacity of 5  $\text{dm}^3$  using a liquid monomer at 70 $^{\circ}\text{C}$  and a pressure of 30  $\text{kgf}/\text{cm}^2$  for 2 h. Propylene of polymerization purity (PAO Nizhnekamskneftekhim) with a 99.8% volume fraction of the main substance was used for polymerization. The standard conditions were propylene weight (1300 g); the weight of the catalyst sample  $m_{\text{cat}}$  (0.015 g); the Al/Ti mole ratio (1500); and the Al/D<sub>2</sub> mole ratio (2), where D<sub>2</sub> was cyclohexylmethyldimethoxysilane as the external donor. To control the molecular weight of the synthe-

sized polymer, equal amounts of hydrogen (3.5 L) were introduced into the reactor in all our experiments. A catalytic complex was prepared in a glass flask by mixing a calculated amount of triethylaluminum (TEA), cyclohexylmethyldimethoxysilane, and MTC in *n*-hexane. After the reactants were introduced into the flask and stirred for 5 min, the catalyst complex was loaded into the reactor. To preserve the catalyst's morphology, a preliminary polymerization step was conducted at 20 $^{\circ}\text{C}$  for 5 min, and the temperature was then raised to 70 $^{\circ}\text{C}$ .

The isotacticity of PP (XI) was determined by dissolving a PP sample in *o*-xylene, with subsequent slow cooling of the solution down to 25 $^{\circ}\text{C}$ , separation of the solid phase via filtration, evaporating *o*-xylene from the solution, and determining the content of the atactic PP fraction to be soluble in xylene (XS, wt %). The isotacticity of PP was calculated as  $\text{XI} = 100 - \text{XS}$  (wt %).

The particle size of the PP powder was determined from the particle size distribution using an Octagon Digital sieve machine according to ASTM D 1921, while the bulk density of the PP powder was measured according to GOST (State Standard) 11035.1-93. The melting temperature and crystallinity were measured

**Table 3.** Physicomechanical properties of the PP samples obtained using MTCs with different particle sizes

| Property                                  | Catalyst sample |       |       |       |       |
|---|-----------------|-------|-------|-------|-------|
|   | MTC-1           | MTC-2 | MTC-3 | MTC-4 | MTC-5 |
| MFI, g/10 min                             | 3.8             | 4.1   | 3.9   | 4.2   | 4.0   |
| Bending elasticity modulus, MPa           | 1145            | 1140  | 1145  | 1120  | 1160  |
| Notched Izod impact strength at 23°C, J/m | 66              | 68    | 69    | 66    | 67    |
| Ultimate tensile yield strength, MPa      | 33.3            | 33.6  | 33.8  | 33.6  | 33.5  |

by means of differential scanning calorimetry (DSC) on a DSC 204F1 Phoenix unit (Netzsch), in accordance with ASTM E 794–85.

The melt flow index (MFI) of the polymer was measured on a Ray-Ran extrusion rheometer according to ASTM 1238 at 230°C and a constant load of 2.16 kg. The Izod impact strength test was performed according to ASTM D 256. The bending elasticity modulus was measured according to ASTM D 790 and yield strength under tension was determined according to ASTM D 638.

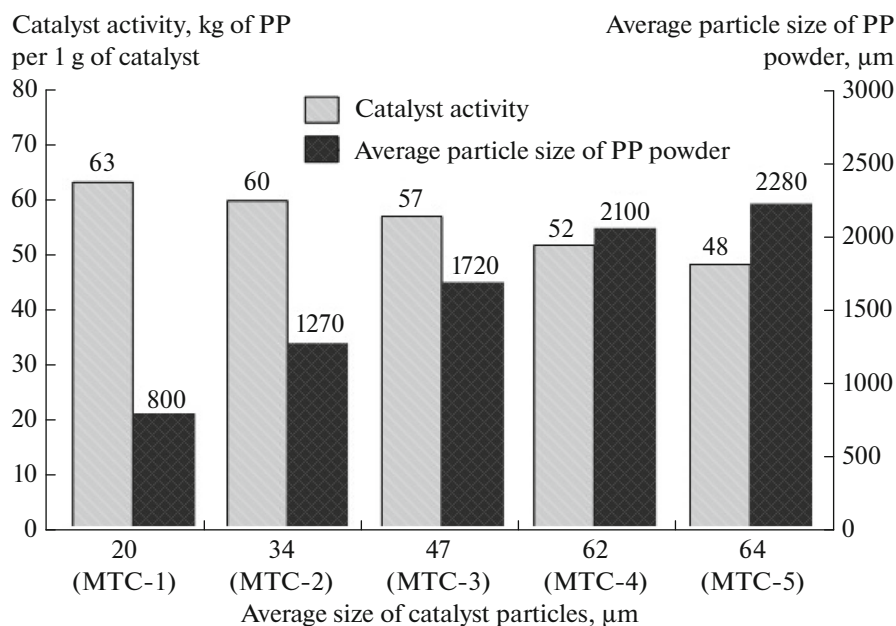
## RESULTS AND DISCUSSION

Table 1 contains data on the composition and particle sizes of IK-8-21 MTC samples studied during the polymerization of propylene in liquid monomer. The amounts of titanium, magnesium, and dibutyl

phthalate were 2.2–2.5, 17.7–19.2, and 9.2–11.8 wt %, respectively.

As was mentioned above, the polymerization process is stable in liquid monomer along with MTC samples having sizes of 20 to 64  $\mu\text{m}$ . The data on propylene polymerization on MTC samples are given in the figure and in Table 2. They indicate that all the samples would allow us to obtain high yields of PP—more than 45 kg per one gram of catalyst. In addition, the smaller the size of the catalyst's particles, the greater its activity in PP synthesis. The samples with, e.g., particle sizes of 20 and 34  $\mu\text{m}$  yielded 60 kg of PP per one gram of catalyst. The drop in activity when the particle size was 62–64  $\mu\text{m}$  was probably due to diffusion limitations.

The morphology of the obtained PP powder is of great significance, since it determines the operational stability of industrial machines. It is important that the



Activity of the IK-8-21 catalyst samples and average particle size of the PP powders obtained upon polymerization in liquid propylene on MTCs with different particle sizes.

catalyst has the optimum average size of PP particles and minimal amounts of the small polymer fraction. The granulometric composition of powders formed on the MTC samples showed that when the average size of the catalyst particles is raised, the average size of the PP particles grows as well (figure). The data from Table 2 indicate that there was no fraction of small particles (<200  $\mu\text{m}$ ) in our PP powders (0.1 wt % for MTC-1 with a particle size of 20  $\mu\text{m}$ ), while the distribution of PP particles over size was narrow (SPAN = 0.3–0.4). When the average size of catalyst particles was raised from 20 to 64  $\mu\text{m}$ , a slight reduction in the bulk density of our PP powder was observed: from 0.47 to 0.43  $\text{g}/\text{cm}^3$ .

Table 2 clearly shows that the content of the atactic fraction of our PP samples dissolved in *o*-xylene, obtained on IK-8-21 catalyst with different particle sizes, did not change significantly and was within 1.8–2.1 wt %, indicating that the catalyst's morphology did not influence the stereoregularity of the PP. Neither did the catalyst's morphology have any effect on the viscosity characteristics of the PP samples synthesized on MTC samples with particle sizes of 20 to 64  $\mu\text{m}$  under comparable propylene polymerization conditions; the MFI values are within 3.8–4.2 g per 10 min (Table 3). This indicates that the IK-8-21 catalyst samples with different particle sizes had a similar sensitivity to hydrogen. The PP samples obtained with our MTC samples had similar melting temperatures and crystallinities (see Table 2).

Our study of the physicomechanical properties of PP samples obtained on IK-8-21 catalyst samples with different particle sizes showed that when the MFIs are close, PP samples have similar bending elasticity moduli upon bending, Izod impact strength at 23°C, and ultimate tensile yield strengths under tension (see Table 3). Particle size thus had a weak impact on the physicomechanical properties of the obtained polymers.

## CONCLUSIONS

The effect of the particle size of IK-8-21 catalyst on its properties during propylene polymerization in a liquid monomer, and the characteristics of the obtained polypropylene, were studied. Catalyst samples with particle sizes of 2 to 64  $\mu\text{m}$  were shown to have high activity and similar sensitivity to hydrogen, and allow us to obtain polypropylene with high isotac-

ticity, bending elasticity moduli, and Izod impact strengths.

When the particle size of the catalyst was raised from 20 to 64  $\mu\text{m}$ , the size of the resulting polypropylene's particles was found to grow from 800 to 2280  $\mu\text{m}$ , and a powder with a narrow particle distribution over size and no pulverulent fraction (less than 200  $\mu\text{m}$ ) formed.

A slight drop in activity and bulk density were observed upon raising the average particle size of the catalyst from 20 to 43  $\mu\text{m}$ . A more notable drop in catalyst activity and the bulk density of our polypropylene powder was observed upon raising the average size of the catalyst particles from 62 to 64  $\mu\text{m}$ .

This way of synthesizing domestic IK-8-21 magnesium–titanium catalyst enables us to obtain highly active catalysts with particle sizes of 20 to 64  $\mu\text{m}$ , and to use them in the production of homo- and static polypropylene, and shockproof propylene/ethylene block copolymers. Our results from studying catalysts with different morphologies offer the possibility of choosing the optimum particle size of polypropylene powder to prevent the formation of agglomerates and deposits in reactors during propylene polymerization and the extraction of polypropylene powder.

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