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A study of the formation process of titanium–magnesium catalyst for propylene polymerization

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ABSTRACT

The catalyst formation by reacting magnesium diethoxide with titanium tetrachloride in the presence of stereoregulating electron donor – di-*n*-butylphthalate (DBP) – is studied by sampling the intermediate products during catalyst synthesis. Chemical and phase composition, porous structure, activity and stereospecificity of these products are investigated. It is show that before DBP adding the X-ray amorphous product consisting of $MgCl_2$ and $TiCl_3(OEt)$ is formed. This product has micro-mesoporous structure, very high surface area, but low activity and low stereospecificity. DBP has a significant effect on both the chemical composition of the catalyst due to removing inactive $TiCl_3(OEt)$, entering DBP and $TiCl_4$ in solid product and formation of $MgCl_2$ crystallites with mesoporous structure. At the same time the significant increase of the activity and stereospecificity is observed. Following $TiCl_4$/chlorobenzene treatment of solid product completes these processes, provides some increasing the surface area at similar mesoporous structure and additionally increases activity and stereospecificity.

1. Introduction

At present, polypropylene (PP) is produced using supported titanium-magnesium catalysts (TMCs) of $TiCl_4/D_1/MgCl_2$ composition, which comprise an $MgCl_2$ support with the adsorbed $TiCl_4$ (active component) and an electron donor compound (D_1 is a stereoregulating component) commonly represented by a phthalate. TMCs can be synthesized by various methods differing mainly in the composition of initial magnesium compound used to obtain $MgCl_2$ with the required structural characteristics. $Mg(OEt)_2$ is among the most efficient precursors for TMC synthesis. TMCs produced with $Mg(OEt)_2$ have been studied in a series of works [1–14].

In elucidating the catalyst formation mechanism and the role of individual compounds used for TMC synthesis, of great importance are data on intermediate products formed in the multistep synthesis of TMCs. In particular, the data on their chemical and phase compositions, porous structure and catalytic properties in propylene polymerization are needed.

TMCs synthesized with magnesium diethoxide as a precursor have been studied in many works; nevertheless, only scarce information on the composition and structure of intermediates produced during the TMC synthesis and on theirs catalytic properties is available in the literature. Data on the chemical composition are presented for the final catalyst synthesized either by a single step process [1,8] or in several steps [3–7,9,10]. Information on the products obtained after intermediate steps of the synthesis are restricted to the data presented in Refs. [2,4]. Therewith, results of the chemical analysis are not used to calculate the composition of titanium-containing compounds ($TiCl_{4-x}(OEt)_x$, $x = 0-2$) produced at different steps of the synthesis and to estimate their effect on the catalytic properties in propylene polymerization. Noteworthy is also the lack of data on the activity of intermediate solid products formed at individual steps of the synthesis and on their texture characteristics, except for the values of specific surface area reported in [2,4]. Texture characteristics (phase composition, porous structure, and morphology of catalyst particles) are important parameters affecting the catalyst activity and fragmentation in the course of polymerization. Data on the catalyst porous structure and, in particular, on the pore size distribution are of great importance taking into account work [15], which demonstrated that the kinetic features and morphology of polymer particles depend to a greater extent on the pore size distribution than on the absolute value of total pore volume.

In the present work, the chemical and phase composition, porous structure and catalytic properties in propylene polymerization were investigated for the solid products formed at different steps of the catalyst synthesis.

Objects of the study were represented by solid products sampled during the synthesis of catalyst obtained by the interaction of magnesium diethoxide with a $TiCl_4$ solution in chlorobenzene in the presence of DBP and the final catalyst.

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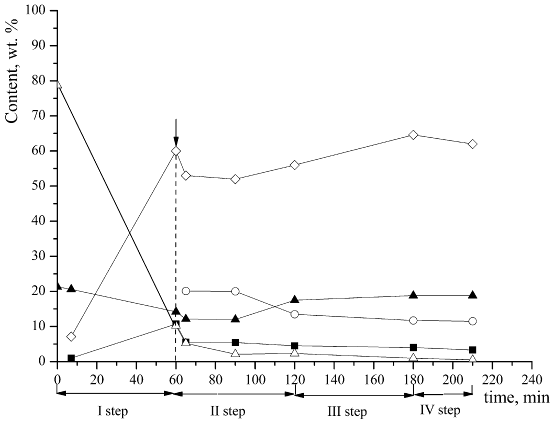

Fig. 1. Data on chemical composition of solid intermediate products formed during TMC synthesis: Ti (–■–), Mg (–▲–), DBP (–○–), Cl (–◇–), OEt (–△–). Arrow shows the moment of DBP addition at 110 °C.

2. Experimental

2.1. Materials

Isopentane (i-C_5), chlorobenzene (ChB), DBP and heptane reagents were preliminarily kept over molecular sieves and stored in an atmosphere of argon. Commercial titanium tetrachloride, propylene and $AlEt_3$ as well as $PrSi(OMe)_3$ (from Aldrich) and $Mg(OEt)_2$ (from Aldrich, particle size ~0.5 mm) were used without additional purification.

2.2. Catalyst synthesis

TMCs were prepared by reacting $Mg(OEt)_2$ with $TiCl_4$ in a ChB solution at a volume ratio $TiCl_4$:ChB = 1:1 and molar ratios $TiCl_4$/Mg = 13 and DBP/Mg = 0.15 for sequential four steps. At step I, at room temperature under argon, a $TiCl_4$/ChB solution and $Mg(OEt)_2$ were introduced into reactor equipped with mechanical and magnetic stirrers and placed in a thermostatic bath. After 7 min, a suspension was sampled from the reactor to a vessel with heptane. Then the reactor temperature was raised to 110 °C during 60 min. At attaining 110 °C, the second sample was taken from the reactor. At step II, DBP was added into reactor. Samples were taken from the reactor in 5, 30 and 60 min after the DBP introduction (scheme of catalyst synthesis – steps and solid sampling during synthesis time – can be seen in Fig. 1). Then it was followed by sedimentation of the solid product and decantation of the mother liquor. At step III, the new $TiCl_4$/ChB solution was added into reactor. The reaction mixture was stirred at 110 °C for 60 min and sampled. Then after sedimentation the mother liquor was decanted. At step IV, a $TiCl_4$/ChB solution was again added and carried out at 110 °C for 30 min. Finally, the solid product was washed with heptane 5 times at gradual lowering of the washing temperature from 70 °C to room temperature. Solid samples taken during the synthesis were washed in a similar way. For some analyses the solid products were additionally washed with *i*-C_5 and dried under a vacuum at room temperature for 60 min and at 50 °C for another 60 min.

2.3. Chemical analysis

The contents of Ti and Mg were measured by inductively coupled plasma atomic emission spectrometry (ICP AES) on an Optima 4300 DV (Perkin-Elmer) spectrometer, and the content of Cl—by potentiometric titration with an $AgNO_3$ solution after preliminary dissolution of the solid product in a 5% solution of sulfuric acid. The content of ethoxy groups was determined by gas chromatography (NetChrom v2.0 software) with respect to ethanol after preliminary dissolution of the sample in methyl cellosolve containing decyl alcohol as the internal standard. The contents of dialkyl phthalates (DBP, ethylbutyl phthalate (EBP), diethyl phthalate (DEP)) and phthaloyl dichloride (1,2-benzenedicarbonyl dichloride) were analyzed by liquid chromatography. The measurements were made on a LC-20 Prominence (Shimadzu) liquid chromatograph after extraction of dialkyl phthalates and phthaloyl dichloride from the solid product using acetonitrile.

2.4. X-ray diffraction analysis

The XRD study of the samples was performed on a HZG-4C diffractometer. Cu $K\alpha$-radiation ($\lambda = 1.54184$ Å) and graphite monochromator in the diffraction beam were used. The diffraction patterns were recorded with a 0.1° scanning step at an angle range of 2θ from 10 to 70° and accumulation period of 10 s in every point.

To prevent contacting with air, samples were transferred in an atmosphere of argon into sealed cuvettes with the teflon windows weakly adsorbing X-rays. The phase composition (the presence of $MgCl_2$) was determined by comparing the positions and intensities of diffraction peaks with the data of ICDD and ICSD databases. The sizes of coherent scattering range (c.s.r.) were calculated by the Selyakov–Scherrer formula with allowance for the instrumental half-width from the broadening of diffraction peak in the region of 50° (2θ).

2.5. Porous structure

Porous structure of the samples was analyzed by the low-temperature nitrogen adsorption using an ASAP 2400 Micromeritics instrument. The results of adsorption measurements were used to calculate the surface area (S_{BET}, m^2/g) and total pore volume (V_{Σ}, cm^3/g).

The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the isotherm. The cumulative pore volume was calculated as the sum of incremental pore volumes for the pore sizes from 2 to 100 nm.

The prevailing pore size was found as a pore diameter (*d*, nm) corresponding to the maximum value of $V_i/V_i^{\max}$ on the curve $V_i/V_i^{\max}$–d, where V_i is the incremental volume of pores corresponding to the *i*th range of pore sizes, and $V_i^{\max}$ is the maximum incremental pore volume.

2.6. Morphology

The average size of catalyst particles and the particle size distribution (SPAN) were measured by laser diffraction on a Malvern 2000SM instrument. The SPAN value was found as SPAN = $(d_{90} - d_{10})/d_{50}$, where d_{10}, d_{50} and d_{90} are the particle sizes corresponding to the catalyst volume fractions of 10%, 50% and 90%, respectively.

2.7. Polymerization of propylene

Polymerization of propylene was carried out in a 0.7 L autoclave in a heptane medium at 70 °C and total pressure 7 bar for 1 h; $[AlEt_3] = 4$ mmol/L; molar ratio Al/$PrSi(OMe)_3$ = 20; [catalyst] = 0.03–0.04 g/L; and hydrogen content in the gas phase 2.1 vol%. Stereospecificity of the catalyst was estimated from the content of atactic PP (APP), which was determined as a fraction of polymer dissolved in the heptane that was employed for polymerization.