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NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPIC STUDIES OF THE STRUCTURE OF UNSUPPORTED TITANIUM-MAGNESIUM CATALYST FOR OLEFIN POLYMERIZATION

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The reaction of magnesium dichloride and titanium trichloride in the composition of an unsupported titanium-magnesium catalyst for olefin polymerization has been studied by nuclear quadrupole resonance spectroscopy.

Методом спектроскопии ядерного квадрупольного резонанса исследовано взаимодействие дихлорида магния с трихлоридом титана в составе массивного титан-магниевого катализатора полимеризации олефинов.

As is known /1/, the reduction of titanium tatrachloride by organomagnesium compounds (OMC) provides titanium – magnesium catalysts (TMC), which, in combination with organoaluminium compounds (OAC) as cocatalysts, are highly effective for ethylene polymerization. By its chemical composition, TMC is mainly a combination of $TiCl_3$ and $MgCl_2$ and characterized by a disordered (X-ray amorphous) structure /1/.

This study is our first attempt to examine the TMC structure by nuclear quadrupole resonance spectroscopy (NQR) by using Violet modifications of the unsupported TMC prepared via the reduction of $TiCl_4$ by ethylmagnesium bromide with the subsequent prolonged heating of the product in excess $TiCl_4$ (the approximate chemical composition of this catalyst is $TiCl_3 \times 1.1\ MgX_2$, where X=Cl, Br /2/). For comparison, a titanium-aluminium catalyst (TAC) ($TiCl_3 \times 0.3\ AlCl_3$) was prepared, which is used for the commercial production of polypropylene. ^{35}Cl-NQR spectra of catalyst samples sealed in glass cells filled with argon, were recorded on a regenerative spectrometer in the range of 1–12 MHz at 77 K. For both catalysts the ^{35}Cl signal belonged to titanium trichloride. Blank experiments with different

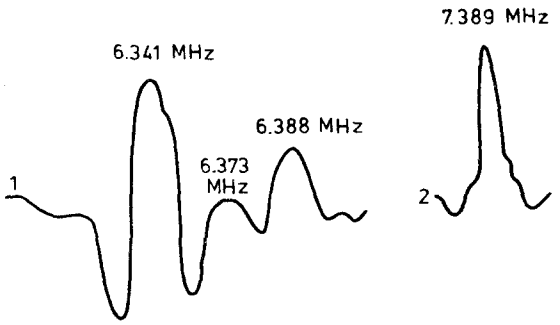

Fig. 1. Second derivative of the ^{35}Cl-NQR signal for the catalysts: 1 – TMC; 2 – TAC

samples of anhydrous $MgCl_2$, including those prepared by organomagnesium synthesis, did not show any magnesium dichloride in the frequency range (ν) for the ^{35}Cl signal /3/.

^{35}Cl-NQR spectra of TAC and TMC samples are illustrated in Fig. 1. As is seen, the TAC spectrum consists of one line at ν = 7.389 MHz, which is in good agreement with literature data for "pure" $TiCl_3$, (ν = 7.39 MHz) /4/. Unlike TAC, the similar spectrum of TMC exhibits three lines of different intensity with the average frequency of 6.367 MHz.

A sharp decrease (> 1 MHz) in the frequency of ^{35}Cl-titanium trichloride in TMC compared with the TAC and "pure" $TiCl_3$ indicates the reaction of $TiCl_3$ with $MgCl_2$ in TMC formation leading to significant rearrangement in the $TiCl_3$ structure. To our mind, this reaction can be the coordination of titanium and chlorine ions of $MgCl_2$ and, apparently, Br, whose presence is possible taking into account the nature of the applied OMC. It should be mentioned that due to this reaction, a common X-ray amorphous phase is formed /2/, whereas the diffractograms of TAC and naturally of "pure" $TiCl_3$ indicate the presence of a separate phase of $TiCl_3$. This reaction of $TiCl_3$ with $MgCl_2$ in the TMC composition is likely to influence the geometric features of the polymerization active centers (AC) and the electronic state of their titanium-carbon bond. This can be supported by the increase not only of the number of AC in TMC compared with TAY in ethylene polymerization /5/, but also by the increase of AC reactivity in elementary steps of polyethylene macrochain propagation and of the chain transfer selectivity in the copolymerization of ethylene and propylene /2/.

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