Cryosynthesis of catalysts for propylene oligomerization based on titanium tetrachloride and magnesium

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A highly dispersed catalyst for oligo- and polymerization of propylene was synthesized by the interaction of $TiCl_4$ with magnesium in the cocondensates of their vapor with benzene and pentane. The catalyst contains $MgCl_2$ and organotitanium and organomagnesium cluster derivatives. The transformations of propylene and hex-1-ene over the catalysts were studied. The direction of catalytic reactions and activity of the catalyst depend on the $TiCl_4$: Mg molar ratio and the hydrocarbon used. Systems with an equimolar ratio of the reactants obtained in a benzene matrix exhibit the highest activity. Propylene oligomers containing a considerable fraction of unsaturated bonds are formed in the presence of the catalysts at room temperature and a pressure of 300 Torr.

Key words: propylene, oligomerization, catalysts, titanium tetrachloride, magnesium, cryosynthesis, IR spectra.

Low-temperature condensation of metals with various reactants makes it possible to obtain a variety of organometallic compounds including those inaccessible by other methods.[1] This method seems to be promising for the synthesis of organometallic catalysts.[2] In this work, the method is used for the first time for the synthesis of the cryochemical analog of titanium—magnesium catalysts (TMC) for olefin polymerization. Titanium—magnesium catalysts are used on a large scale in the industrial production of polymeric plastics, isotactic polypropylene, and low-molecular wax-like products based on polypropylene.

The preparation procedure of TMC markedly affects their activity, stereospecificity, and stability.[3,4] The search for new ways to synthesize these catalysts is still of strong interest.[5] TMC are usually prepared by grinding magnesium chloride with $TiCl_4$ or by precipitating the components from nonaqueous solutions. By using the cryochemical interaction between $TiCl_4$ and atomic magnesium in organic matrices, it is possible to synthesize a highly dispersed catalyst containing $MgCl_2$, as well as cluster-like organometallic derivatives of magnesium that play the role of cocatalysts. The high activity and unusual chemical properties of the cluster derivatives offer new possibilities for organic synthesis and catalysis.[1]

Experimental

All reactants except for magnesium were purified according to standard procedures. Propylene of "polymerization" purity was used. The cryochemical synthesis was carried out in an ~1 L volume reactor of the immersion type[6] equipped with an resistive evaporator of magnesium and connected with a vacuum line. Magnesium was evaporated at 700—725 K. The reagents, 10^{-4}—10^{-5} mole of Mg, 10^{-4}—10^{-3} mole of $TiCl_4$, and $5 \cdot 10^{-4}$—10^{-2} mole of pentane or benzene, were condensed for 1—3 h onto the surface of a glass reactor that was evacuated and cooled with liquid nitrogen. Condensation of reactants at 80 K occurred in a regime of molecular beams with a rate of ~10^{16} molec. cm^{-2} s^{-1} to ensure the absence of reactions in the gaseous phase. The Mg : $TiCl_4$ ratio was varied from 10 : 1 to 1 : 10. *n*-Pentane or benzene was used as an organic matrix in a 10—50-fold excess with respect to magnesium. When cocondensation was finished, the reactor was heated to room temperature and the product obtained was used as the catalyst for propylene conversion. The catalytic experiments were performed directly in the same vacuum reactor at ~300 K in the gas phase. The olefin was fed into the reactor until an overall pressure of 200—300 Torr was reached.

IR spectroscopic study of the catalytic systems was carried out in a specially designed vacuum reactor.[7] $TiCl_4$, Mg, benzene, and propylene were condensed onto the surface of a copper parallelepiped cooled with liquid nitrogen in the glass vacuum reactor joined with a vacuum line. After cocondensing the reactants, the reactor was disconnected from the vacuum line and the spectra were recorded in the double refraction mode in the range of 4000—400 cm^{-1} at 80—293 K.

The catalytic activity of the systems was studied at ~300 K by admitting propylene or hex-1-ene vapor until an overall pressure of 200—300 Torr was reached. The rates of olefin consumption were determined from the drop in the pressure of the system. A gas-liquid chromatograph Chrom-5 with a flame-ionization detector was used for the analysis of light-weight products. After the catalytic run, the reactor was exposed to air and the polymeric fraction was separated from other reaction products and the catalyst. Oligomers were studied by

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IR spectroscopy. The molecular-weight distribution (MWD) and melting point were also determined. The extent of unsaturation was estimated by the bromine numbers method.[8]

For studies by ESR and scanning electron microscopy techniques, the catalyst was prepared in the same vacuum reactor additionally equipped with a glass or quartz ampule. After the synthesis, the catalyst was loaded into the ampules joined to the bottom of the reactor and then the ampules were sealed off. The ESR spectra were acquired on a Bruker-220D spectrometer. Micrographs were obtained with a Jeol-840 electron microscope. The samples for this investigation were prepared in a dry box filled with dried argon.

Results and Discussion

The catalyst is a dark fine powder extremely sensitive to oxygen and water. The dispersion and pore size depend on the conditions of its preparation, particularly on the nature of the hydrocarbon matrix. Figure 1 presents photomicrographs of the $TiCl_4$—Mg cocondensates prepared in benzene and *n*-pentane. As can be seen in Fig. 1, the cocondensate prepared in *n*-pentane contains spherical particles of 300—500 nm size with a rather smooth surface. The cocondensate prepared in benzene consists of porous associates of a columnar structure; their average size is ~300 nm.

On cocondensing the components of the catalytic system, $TiCl_4$ is reduced by magnesium at 80 K even in the absence of a matrix that prevents aggregation of the metal. In the IR spectrum, an absorption band at 420 cm^{-1} appeared at 80 K. The band is caused by the stretching vibrations of the Ti^{III}—Cl bond[9] and indicative of the titanium reduction. The depth of the titanium reduction depends on the $TiCl_4$: Mg ratio. At Ti : Mg < 1 the reaction occurs directly at the moment of cocondensation, and further annealing at 80 K and heating to room temperature do not increase the yield of Ti^{III}. On heating the sample prepared in an excess of $TiCl_4$ or in the presence of an organic matrix, an increase in the size of the band at 420 cm^{-1} is observed. Thus, when magnesium is diluted with other components of the cocondensate, *i.e.*, when the extent of its aggregation decreases, the depth of the titanium reduction significantly increases. A signal with parameters typical of isolated Ti^{III} ions, $g_\perp = 1.94$, $g_\parallel = 1.8$, appears in the ESR spectra of the $TiCl_4$—Mg system at 80 K. In the $TiCl_4$—Mg—*n*-pentane system, this signal disappears upon heating to room temperature. The cocondensates synthesized in benzene and heated to room temperature exhibit an ESR spectrum with the same parameters and an additional line with $g = 1.99$. Similar spectra have been observed during the study of TMC[10,11] prepared by the reduction of $TiCl_4$ with aluminum derivatives as well as with titanium—arene complexes.[12] A suggestion was made that this spectrum is due to the formation of the Ti^{III}—C bond.[10] We were able to confirm the formation of an organometallic derivative with data on the hydrolysis of the cocondensates prepared with benzene. Phenol was found in the reaction products by chromatographic and spectral analyses. However, on hydrolizing the cocondensate with *n*-pentane under similar conditions, *n*-pentanol was not detected.

Thus, $TiCl_4$ is reduced by magnesium during synthesis of the catalytic system in the organic matrix, and the reduction in the benzene matrix is accompanied by incorporation of hydrocarbon to form Ti^{III} organometallics.

The direction of catalytic reactions occurring in the presence of the catalysts is determined by the conditions of their synthesis. Typically, poly- and oligomerization of propylene and benzene alkylation occur. The most active catalyst for olefin oligomerization and benzene alkylation with propylene was prepared by cocondensation of $TiCl_4$ with magnesium in benzene. At 293 K and 200—300 Torr, this system readily consumes propylene forming the wax-like oligomerization product and the products of benzene alkylation, mainly cumene. The composition of the propylene oligomer prepared in the

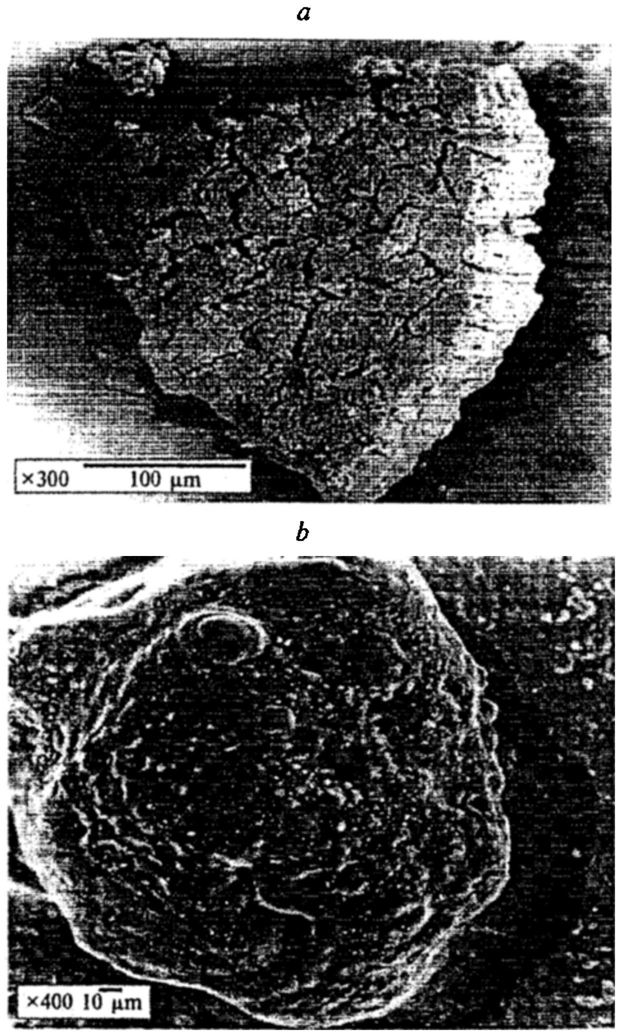

Fig. 1. Photomicrographs of the $TiCl_4$—Mg cocondensates prepared in benzene (*a*) and *n*-pentane (*b*).

presence of the $TiCl_4$—Mg (1 : 1) catalyst synthesized in the benzene matrix is presented below.

M	$> 2 \cdot 10^3$	$2 \cdot 10^3$—10^3	10^3—400	250
Content (%)	14	10	11	65

As can be seen, the main product of oligomerization is the propylene hexamer; however, the fraction of high-molecular products ($M > 10^3$) is sufficiently high (~25%).

The maximum rates of propylene consumption (20 mol (mol $TiCl_4$ min)$^{-1}$) are reached at an equimolar $TiCl_4$: Mg ratio in the cocondensate with benzene. They exceed the rates of the gas-phase polymerization of propylene over industrial TMC.[13]

Dependence of the selectivity of the process on the magnesium content at the step of cryochemical synthesis is given in Fig. 2. The highest selectivity is observed for the system with an equimolar ratio between magnesium and titanium. In the presence of the cocondensate of $TiCl_4$ with benzene without magnesium, the main direction of the propylene conversion is benzene alkylation, and the oligomer formed contains aromatic fragments in the chain. An intense IR band typical of benzene derivatives[14] arises near 820 cm^{-1}, confirming this conclusion. The content of magnesium in the catalyst affects also the physicochemical properties of the oligomer formed. In the absence of magnesium, an oligomer with a melting point of 116 °C is formed in the cocondensate of $TiCl_4$ with benzene. The introduction of an equimolar amount of magnesium with respect to titanium results in the formation of an unsaturated oligomer with a melting point of 104 °C. Fig. 3 shows the dependence of the number of double bonds in the oligomer on the magnesium content in the cocondensate. According to the IR data, the following types of double bonds are present in the oligomers studied: internal (*trans*-) (the band at 960 cm^{-1}), vinyl (905 cm^{-1}), and vinylidene (885 cm^{-1}). These bands are not observed in the spectra of the propylene oligomers prepared in the presence of the $TiCl_4$—Mg—*n*-pentane catalyst.

The results of the IR study of the propylene oligomers synthesized in the presence of the two types of catalysts mentioned are presented below:

Catalyst	IR spectrum, ν/cm^{-1}
$TiCl_4$—Mg—benzene (1)	1640, 1450, 1370, 1140, 960, 905, 885, 820
$TiCl_4$—Mg—*n*-pentane (2)	1450, 1370, 1140

It follows from the comparison of these data with those obtained previously[15] that the spectral characteristics of the oligomer formed in the presence of catalyst 1 are typical of products of anionic-coordination polymerization. An oligomer characterized by a similar spectrum has been obtained over the Ziegler catalyst $TiCl_4$—$AlBu^i_2Cl$.[15] The spectrum of the oligomer formed in the presence of catalyst 2 is typical of the products of a cationic process.[16] The bands at 1370 and 1140 cm^{-1} related to bending vibrations of the Me groups and skeletal vibrations in branched chains are observed in the spectra of this polymer.

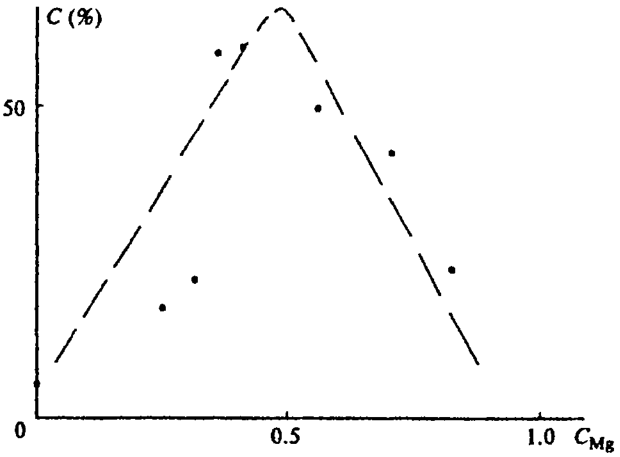

Fig. 2. Dependence of the selectivity of propylene oligomerization on the magnesium content in cocondensates with $TiCl_4$ in benzene (C is the weight fraction of oligomer in the products of propylene conversion, C_{Mg} is the molar fraction of magnesium).

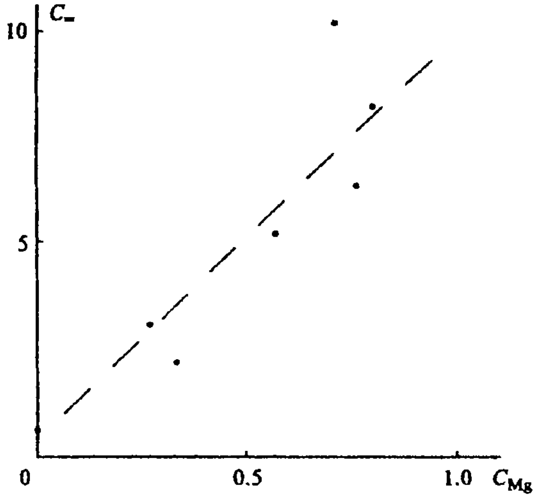

Fig. 3. Dependence of the content of double bonds ($C_=$) in the propylene oligomer per 100 C atoms on the molar fraction of magnesium (C_{Mg}) in cocondensates with $TiCl_4$.

The difference in the mechanisms of propylene conversion in the presence of catalysts 1 and 2 is also confirmed by a change in the molecular-weight distribution of the oligomers. A wax-like oligomer containing ~25% of heavy products is formed in the presence of catalyst 1 ($M > 10^3$), whereas only low-molecular oils are formed in the presence of catalyst 2 regardless of the $TiCl_4$: Mg ratio.

The difference in the mechanism of action of catalysts 1 and 2 is especially pronounced when hex-1-ene is used as the substrate. Thus, the catalyst synthesized in benzene converts hex-1-ene to an oily polymer.

The isomerization of hex-1-ene to hex-2-ene and hex-3-ene as well as the autohydrogenation to *n*-hexane become the main directions of the process in the presence of catalyst 2. However, these reactions are observed only during cocondensation, and after heating the sample, additional fractions of olefin are not involved in the reaction. This indicates that the process, in the strict sense, is not catalytic. Previously, we have observed similar conversions of olefin in magnesium—hexene cocondensates.[17] In this case, the interaction between active magnesium and olefin rather than the presence of titanium affects the pattern of the process.

Hence, magnesium can play a dual role in the systems outlined above. On the one hand, the interaction between Mg and $TiCl_4$ leads to the formation of $TiCl_3$ and highly dispersed $MgCl_2$, *i.e.*, a system similar to TMC. On the other hand, during the interaction between magnesium and organic molecules under the conditions of cryosynthesis, active magnesium derivatives are formed that can participate in olefin conversions, as well as in other reactions involving hydride transfer.[17] In the polymerization process under study, a significant yield of oligomers containing internal double bonds can be related to the participation of hydride derivatives at the step of chain termination.

Thus, depending on the nature of the hydrocarbon matrix and the fraction of magnesium in the catalyst, both cationic and anionic-coordination catalysts can be prepared by low-temperature cocondensation of $TiCl_4$ with Mg in an organic matrix. At an Mg : Ti ratio close to an equimolar ratio, benzene matrix produces an active catalyst that converts propylene to oligomers with a significant extent of unsaturation.

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