INTERACTION OF ETHYLENE WITH Ti(III) IONS IN SUPPORTED ORGANOTITANIUM CATALYSTS

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The interaction of ethylene with Ti(III) ions in ethylene polymerization catalysts prepared by the interaction of Ti(CH₂C₆H₅)₄ with silica has been studied by the ESR method. It has been found that at low temperatures (120 K) ethylene is reversibly adsorbed on titanium ions with further ethylene insertion into the Ti-C bond upon increasing temperatures.

Методом ЭПР исследовано взаимодействие этилена с ионами Ti(III) и катализаторах полимеризации этилена, полученных при взаимодействии Ti(CH₂C₆H₅)₄ с силикателем. Установлено, что при низких (120°K) температурах этилен обратимо адсорбируется на ионах титана с последующим внедрением этилена при повышении температуры по связи Ti–C.

INTRODUCTION

The interaction of organometallic compounds of transition metals with oxide carriers is known to give highly active ethylene polymerization catalysts /1, 2/. It has been found /1, 3/ that during the interaction of organotitanium compounds with the carrier hydroxyl groups, surface Ti(IV) compounds \( \{O_x\}_{TiR_{4-x}} [x = 1-3]\) are formed, which include the carrier oxygen and the organic ligand \( %\). As noted in Refs. /1, 3/ the propagation centers in supported organometallic catalysts may be formed due to the elimination of organic ligands during the decomposition of initial surface organometallic compounds. In the case of organotitanium catalysts Ti(III) compounds are formed /3/. In the present work the state of Ti(III) ions in the catalysts prepared by supporting tetrabenzyltitanium on silica, and their interaction with ethylene has been studied by the ESR method.
MAKIMOV et al.: ETHYLENE WITH Ti(III)

EXPERIMENTAL

Ti(CH₂C₆H₅)₄ was synthesized by the procedure of Ref. /4/. The catalyst was prepared by treating SiO₂ (S = 250 m²/g), predehydrated in vacuum at 250 °C, with tetrabenzyltitanium in pentane solution. The excess complex was washed from the catalyst with pentane and then the catalyst was dried in vacuum. Titanium content of the catalyst was 1.5 wt.%. ESR spectra were recorded on a JES-3BX spectrometer at 77 K. Ethylene adsorption was carried out directly in the tube used for recording ESR spectra.

RESULTS AND DISCUSSION

1. The state of Ti(III) ions in the catalyst

The ESR spectra of the catalyst samples show a Ti(III) signal of axial symmetry (Fig. 1a) with the following parameters \(g_x, y = 1.986-1.995; g_z = 1.923-1.935\). The concentration of Ti(III) ions accounts for about 2% of the total titanium in the catalyst.

In accordance with known results /5, 6/, the \(g_{av}\) values for the complexes of d¹ ions increase with increasing number of metal-carbon bonds. For Ti(III) complexes with two organic ligands \(g_{av} > 1.98\). The value \(g_{av} = 1.972\) for Ti(III) ions in the initial catalyst suggests that these ions have one Ti-R bond.

Ti(III) compounds may be formed due to the elimination of benzyl ligands from part of the Ti(III) surface compounds according to reaction (1):

\[
\begin{align*}
4^+ \quad R \\
\text{Ti} \\
\text{R} \quad \rightarrow \\
4O₂^+ \quad \text{Ti}^{3+} \cdot \text{R} + \text{R*}
\end{align*}
\]

where \(R = (-\text{CH}_2\text{C}_6\text{H}_5)\)

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