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CATALYTIC ACTIVITY AND EPR SPECTRA OF MOLYBDENUM OXIDE CATALYSTS FOR ETHYLENE POLYMERIZATION

Previously we studied, by the EPR method, chromium oxide catalysts for ethylene polymerization ([1–4]). In these works, as well as in works by other authors ([5,6]), it was shown that in the process of catalyst preparation Cr^{5+} ions are formed, giving characteristic signals in the EPR spectrum. These ions apparently are active centers in the reaction of catalytic polymerization of ethylene ([4,7,8]) and centers for adsorption of the reacting substances ([9]). For the polymerization of olefins, in addition to chromium oxide catalysts, catalysts based on oxides of other metals of variable valence are also used ([10]). The present communication is devoted to studying the relationship between EPR spectra and the activity of molybdenum oxide catalysts with respect to the ethylene polymerization reaction.

As supports we used activated charcoal, magnesium oxide, zirconium dioxide, aluminum oxide, silica gel, and aluminosilica gels of various composition. Catalysts based on activated charcoal, aluminosilica gels, technical aluminum oxide, fluorinated aluminum oxide, and aluminum borate were prepared by impregnating the support with a solu-

Table 1

Dependence of the activity of molybdenum catalysts (8% MoO_3 by weight) on different supports on the degree of reduction of MoO_3 and on the signal in the EPR spectrum

Sample no.	Support	Intensity of the EPR line, unpaired electrons per 1 g of catalyst	Calculated from the EPR spectrum, amount of Mo^{5+}, % of total Mo content in the catalyst	Composition of oxides in the catalyst, after reduction with hydrogen according to chemical analysis	Calculated composition of Mo oxides	Polymer yield, g per 1 g catalyst per hour
1	Charcoal	No line		$MoO_{2.50}$		No polymer
2	SiO_2	No line		$MoO_{2.50}$		0.1
3	MgO	Very weak line		$MoO_{2.58}$		0.2
4	ZrO_2	Line of medium intensity		$MoO_{2.58}$		0.7
5	Al_2O_3 (precipitated catalyst)	10^{20}	30	$MoO_{2.61}$	$MoO_{2.15}$	3.0
6	Al_2O_3, technical	10^{20}	30			
7	Al_2O_3, fluorinated	$4.5 \cdot 10^{19}$	13.5	$MoO_{2.61}$	$MoO_{2.15}$	5.0
8	90% $Al_2O_3$10% BO_3	$4 \cdot 10^{19}$	13	$MoO_{2.35}$	$MoO_{2.06}$	4.1
9	13% $Al_2O_3$87% SiO_2	$4 \cdot 10^{19}$	13	$MoO_{2.15}$	$MoO_{2.06}$	4.1
10	30% $Al_2O_3$70% SiO_2	10^{19}	3	$MoO_{2.00}$	$MoO_{2.06}$	3.0

Sample no.	Support	Intensity of the EPR line, unpaired electrons per 1 g of catalyst	Calculated from the EPR spectrum, amount of Mo^{5+}, % of total Mo content in the catalyst	Composition of oxides in the catalyst, after reduction with hydrogen according to chemical analysis	Calculated composition of Mo oxides	Polymer yield, g per 1 g catalyst per hour
11	3% $Al_2O_3$97% SiO_2	$5 \cdot 10^{18}$	1.5	$MoO_{2.20}$	$MoO_{2.02}$	2.6
12	Without support	No line		$MoO_{2.00}$	$MoO_{2.01}$	No polymer

with an ammonium molybdate solution of the corresponding concentration. Samples in which MgO, SiO_2, and Al_2O_3 served as supports were prepared by coprecipitation from salt solutions at a constant pH equal to 9 for silica gel and alumina, and 11 for MgO.

To obtain alumomolybdenum catalysts containing more than 20% MoO_3, freshly precipitated aluminum hydroxide was mixed with a concentrated solution of ammonium molybdate. All catalysts were dried at 110°, calcined in air at 500°, and then reduced in a stream of hydrogen at 490° to constant composition. After reduction, the catalyst was transferred into glass ampoules, evacuated at 450° with a fore-vacuum pump, washed twice with hydrogen, and, after evacuation, sealed. Samples obtained by depositing MoO_3 on carbon were reduced at 300°. For each catalyst, several parallel samples were prepared. One of them was studied by the EPR method; for the others the catalytic activity in the ethylene polymerization reaction was determined. The procedure for measuring catalytic activity and for purifying the starting substances is described in ([11]). The catalytic activity was determined at: a) a temperature of 250° and a pressure of 50 atm; b) a temperature of 130° and a pressure of 35 atm. In the first case xylene was used as the solvent, and in the second, cyclohexane. The catalytic activity was characterized by the amount of polymer formed on 1 g of catalyst over 1 hour.

Fig. 1. EPR spectra of molybdenum catalysts for ethylene polymerization. *a* –spectrum of catalyst–8% MoO_3 on alumina; *b* –spectrum of catalyst–8%

Fig. 1. EPR spectra of molybdenum catalysts for ethylene polymerization. a –spectrum of catalyst –8% MoO_3 on alumina; b –spectrum of catalyst –8% MoO_3 on aluminosilicate (13% Al_2O_3 87% SiO_2)

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MoO_3 on aluminosilicate (13% Al_2O_3, 87% SiO_2)

To determine the content of molybdenum oxides, a weighed portion of catalyst was dissolved in dilute sulfuric acid (1 : 4), and then molybdenum was precipitated with α-benzoin oxime according to the method of ([13]). To determine the degree of reduction of MoO_3, after calcination in a stream of hydrogen, a weighed portion of catalyst was treated with a solution of $Fe_2(SO_4)_3$, the support was filtered off, and the ferrous iron was titrated with permanganate ([14]).

The degree of reduction of molybdenum in the catalysts was determined before the reaction. During polymerization, additional reduction of the molybdenum oxides is possible. However, as treatment of the catalysts with solvents at the temperature of the polymerization reaction showed, this additional reduction is small.

The EPR spectra were recorded on an EPR-2 radiospectrometer ([12]) at room temperature and at the temperature of liquid nitrogen.

As already noted above, the EPR spectra of active oxide-chromium olefin-polymerization catalysts contain narrow signals, the intensity of which correlates with activity. The present study showed that, in the case of active samples of oxide-molybdenum catalysts, characteristic signals are also observed in the EPR spectrum. The form of the spectrum depends on the nature of the support. Figure 1*a* presents the spectrum of an alumomolybdenum catalyst containing 8% MoO_3. As can be seen, the signal has a symmetrical form; the g-factor of the signal is 1.933, the width is 80 oersteds. The signal intensity is approximately 10^{20} spins/g.

of the catalyst, which corresponds to one unpaired electron for every 3 Mo atoms in the sample. In the case of the aluminosilicate support, the signal is asymmetric; its width is 60 oersteds (Fig. 1b), $g_{\parallel} = 1.879$, $g_{\perp} = 1.935$. Asymmetric signals are also observed in catalysts based on ZrO_2 and $ZrO_2 \cdot SiO_2$. The narrow line in the spectrum of the catalyst on magnesium oxide is very weak, and its shape is difficult to determine.

During the polymerization reaction the signals persist.

It is known that unreduced samples of molybdenum catalysts are inactive and that, in order to obtain active contacts, their preliminary reduction is necessary. However, as follows from the data in Table 1, no direct relationship is

Fig. 2. Comparison of the activity of alumomolybdenum catalysts with the intensity of the EPR signal (temperature 250°C, pressure 50 atm, solvent—xylene). *a*—polymer yield, g/g cat. per hour; *b*—signal intensity

Figure 2: Fig. 2. Comparison of the activity of alumomolybdenum catalysts with the intensity of the EPR signal (temperature 250°C, pressure 50 atm, solvent—xylene). *a*—polymer yield, g/g cat. per hour; *b*—signal intensity

Fig. 3. Comparison of the activity of the catalyst—molybdenum on aluminosilicate (30% Al2O3)—with the intensity of the EPR line (reaction temperature 130°C, pressure 35 atm, solvent—cyclohexane). Designations as in Fig. 2

Figure 3: Fig. 3. Comparison of the activity of the catalyst—molybdenum on aluminosilicate (30% Al2O3)—with the intensity of the EPR line (reaction temperature 130°C, pressure 35 atm, solvent—cyclohexane). Designations as in Fig. 2

observed between catalytic activity and the degree of reduction of molybdenum in partially reduced catalysts. Indeed, highly active sample 6 (support—technical alumina) has almost the same degree of oxidation of molybdenum as low-active sample 3 and completely inactive sample 1. Catalysts 5 and 9 have the same activity at different degrees of oxidation.

Fig. 2. Comparison of the activity of alumomolybdenum catalysts with the intensity of the EPR signal (temperature 250°C, pressure 50 atm, solvent—xylene).
a—polymer yield, g/g cat. per hour; *b*—signal intensity.

Qualitative comparison of the line intensity in EPR spectra with catalytic activity shows that there is a similarity between these quantities. Catalysts that do not give a signal have no catalytic activity, for example: silica gel, activated carbon. With an increase in signal intensity the polymer yield increases. It is difficult to establish a quantitative relationship between catalytic activity and EPR signals from the data in Table 1 because of the superposition of the influence of the nature of the supports—their porous structure and the different chemical properties of the surface. Therefore, a quantitative comparison with the intensity was carried out by us for catalyst samples on one and the same support.

Figure 2 shows the dependence of catalyst activity and EPR signal intensity on the content of molybdenum oxide in the sample. It is seen from the figure that the activity of alumomolybdenum catalysts reaches a maximum at 20% MoO_3. The EPR signal intensity changes in the same way. A similar correspondence of changes in catalytic activity and EPR signal intensity is also observed for MoO_3 on aluminosilicate supports with 30% Al_2O_3 (Fig. 3) and with 13% Al_2O_3 (Table 2).

Fig. 3. Comparison of the activity of the catalyst—molybdenum on aluminosilicate (30% Al_2O_3)—with the intensity of the EPR line (reaction temperature 130°C, pressure 35 atm, solvent—cyclohexane). Designations as in Fig. 2.

These observations allow the conclusion that the catalytically active

component of the catalysts studied proves to be a molybdenum compound having a characteristic signal in the EPR spectrum.

The Mo^{6+} ion has no unpaired electrons and gives no EPR signal. The Mo^{4+} ion has two unpaired electrons and, according to Kramers' theorem, may either give no EPR signal or, in polycrystalline samples, give very broad lines with a g-factor differing greatly from 2. Indeed, EPR spectra of this ion have not been described in the literature up to the present.

Table 2

Comparison of the activity of a molybdenum catalyst (aluminosilicate support: 13% Al_2O_3, 87% SiO_2) with the intensity of EPR signals.
Solvent —cyclohexane, $t = 130°$,
$p = 35$ atm.

MoO_3 concentration, wt.%	Polymer yield, g/g cat. per hour	EPR line intensity, arbitrary units	Surface area, m^2/g
0	Traces	No line	400
3	1.2-1.3	1.6	297
8	2.6-3.0	4.3	219
15	3.5-6.0	10.3	146
20	1.0-1.5	0.5	149

The formation of Mo^{3+} appears unlikely, since oxides of trivalent molybdenum are not formed when MoO_3 is reduced with hydrogen ([15]). Therefore we believe that the active component of the catalyst is a Mo^{5+} compound. Thus, the nature of the active component of an oxomolybdenum catalyst is analogous to the nature of oxochromium catalysts, for which it was established earlier that catalytic activity and the EPR signal are due to the presence of Cr^{5+} compounds on the surface. Table 1 gives calculations of the composition of molybdenum oxide in the catalyst, based on the assumption that the signal in the EPR spectra is due to $MoO_{2.5}$ oxides, while the remaining molybdenum is present as MoO_2. Comparison of the oxide compositions calculated in this way with the results of chemical analysis shows that the assumption of the presence in the catalysts of oxides of Mo^{5+} ions does not conflict with the chemical-analysis data. Since oxides of pentavalent molybdenum are unknown, the formation of Mo^{5+} in oxomolybdenum catalysts should be explained by interaction of molybdenum oxides with the support, leading to stabilization of these ions. The change in the

shape of the EPR signal of molybdenum ions depending on the type of support also indicates a bond between the Mo^{5+} ions and the substrate.

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Note: Figure translations are in progress. See original paper for figures.