ESR studies indicate that in Mo–Ti oxide catalysts prepared via the addition of ammonium paramolybdate to pasted titanium hydroxide, Mo$^{5+}$ ions are observed in three states: in heteropoly blue, disperse MoO$_3$ and a solid substitutional solution in TiO$_2$.

It has been shown previously /1/ that upon supporting molybdenum by reacting Ti–Mo HPA with TiO$_2$, the thermal stability of HPA significantly increases, i.e. HPA bound to the TiO$_2$ surface is retained after calcination at 723 K. It has also been revealed that the peculiarities in the ESR spectra of Mo$^{5+}$ ions are good evidence for the existence of HPB on the TiO$_2$ surface. In the present study we have investigated the ESR spectra of Mo–Ti oxide catalysts prepared via the addition of ammonium paramolybdate (APM) to pasted titanium hydroxide and the supporting of APM on TiO$_2$ (anatase).

**EXPERIMENTAL**

To prepare Mo–Ti catalysts (series A), the pasted titanium hydroxide prepared via the precipitation of TiCl$_4$ from aqueous hydrochloric acid with ammonium at pH = 7, was washed from Cl$^-$ ions and mixed with an APM solution. It was then evaporated in a water bath under stirring, dried at 373 K and heated in air for 4 h at 723 K. A sample containing 2 wt.% Mo, was recalcined at 117 K for 6 h. APM was supported via impregnation according to the water capacity of TiO$_2$.
calcined at 723 K in air (series C). Samples were reduced by hydrogen at a pressure of 40 Torr and temperatures of 523 and 723 K for 30 min. ESR spectra were recorded on a JES-3BX spectrometer at 77 K; the parameters were compared with DPPH.

RESULTS AND DISCUSSION

Typical ESR spectra of reduced samples illustrated in Fig. 1 are the superpositions of several ESR signals due to Mo$^{5+}$ ions. Variations in the ESR spectra depending on the Mo content and the treatment conditions permitted to distinguish three types of axial signals for Mo$^{5+}$ ions, whose parameters are listed in Table 1. Because of overlapping of the spectra, it was not possible to resolve the h. f. s. due to Mo ions.

ESR spectra of the samples containing 10 wt. % and less Mo, before treatment by hydrogen, exhibit traces of type I and II ions, whereas signal III is significantly more intense. With increasing the Mo content, the intensity of signals I and II increases and at a Mo content of 15 wt. %, their intensity is similar to that of the signals of type III ions (Fig. 1b).

Reduction of the samples with H$_2$ at 373 K increases the intensity of all signals. With further increase in the reduction temperature the intensity of all signals increases, the maximum increase being observed for signal I (Fig. 1d). After reduction at 723 K, the spectrum exhibits only a broadened signal of type I ions; signals II and III cannot be distinguished against the background (Fig. 1e).

For samples with Mo contents of more than 10 wt. %, signal I is nonuniform.

In supporting APM on TiO$_2$, ESR spectra exhibit signal I (Fig. 1c).

Nature of type I ions. If the catalyst whose ESR spectrum is the superposition of three signals, is treated by water or hydrogen, the spectrum exhibits only signals II and III and signal I vanishes. ESR spectra of alcohol solutions exhibit an absorption in the region of 32 000 cm$^{-1}$, typical for HPA /2/. The absorption of H$_2$O and NH$_3$ on the samples prepared via supporting APM on TiO$_2$, leads to insignificant coordination, manifesting itself in a small increase of $g_\parallel$ and a decrease in $g_1$ of type I ions. This change in the ESR parameters indicates a symmetry increase in the Mo$^{5+}$ environment and the respective decrease of the “yl” bond. Prolonged treatment with water (for 24 h) leads to the disappearance of signal I on both samples prepared from the pasted titanium hydroxide and those prepared via supporting APM on TiO$_2$, which is typical for Mo$^{5+}$ ions in hydrogenated HPB /1/.