Investigation of paramagnetic centers in supported catalysts based on mixed heteropolycompounds with d-metals

1. Investigation of the SiO_2-supported Fe—Mo heteropolyacid catalyst

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The ESR method was used to study bulky samples of the Fe—Mo heteropolycomplex and the related supported catalyst. The supported catalyst manifests a considerably higher thermal stability than the bulky sample of the individual heteropolycompound. The high thermal stability of paramagnetic centers in the supported Fe—Mo catalyst under the high-temperature action (up to 823 K) of water vapor was discussed.

Key words: catalyst, heteropolycomplex, paramagnetic centers, structure, thermal stability.

Interest in heteropolycompounds (HPC) as catalysts of different processes has increased in recent years.[1–6] So-called mixed 12-heteropolyacids with ions of Ni, Co, Cr, and other d-metals in the inner coordination sphere of a heteropolycomplex were the subject of special attention. Syntheses of these metallocomplexes with different compositions make it possible to affect the character of Me—O and Me—O—Me bonds in MeO_6 octahedra in Me_3O_{10} triads. These octahedra are structural units of HPC (in a standard HPC of the 12th row, M is a metal of VB or VIB groups, Mo, W, or V).[4–6]

At elevated (500—700 °C) temperatures of the catalytic process, the reaction mixture can substantially affect the state of HPC and change the state of metal sites and catalyst activity. It can be suggested beforehand that the support would markedly affect the stability of HPC under catalytic conditions. In particular, according to the earlier data,[7,8] SiO_2-supported Si—Mo and P—Mo HPC decompose at considerably higher (by 100—300 °C) temperatures than bulky HPC.

In this work, we studied the change in the state of mixed HPC on heating. ESR was used as the main method of investigation.[9–11] Mixed iron-containing sodium molybdosilicate (1) and related supported catalysts are the objects of the study. Earlier high activity in the selective oxidation of methane was shown for $Na_4[PMo_{11}FeO_{39}]$.[6]

Experimental

HPC was synthesized according to the general scheme suggested by Tourne.[12] The iron-containing complex was obtained by adding $FeCl_3$ (in the form of a saturated solution or dry powder) to a 0.03 *M* solution of potassium 11-molybdosilicate in a ratio $Fe : SiMo_{11} = 1 : 1$. The reaction mixture was heated at 70—80 °C for 2 h with stirring. The pH value of the solution was maintained about 4.5 by the addition of HCl (1 : 5). Then the solution was concentrated to obtain yellow crystals of $Na_4[PMo_{11}FeO_{39}] \cdot 21H_2O$ (the content of admixtures determined in the synthesized samples of mixed HPC did not exceed 1%).

The supported catalyst was prepared by the impregnation method using aqueous solutions of the synthesized mixed HPC. Powdered SiO_2 (Merck, $S_{sp} = 300$ m^2 g^{-1}) was used as the support. The support powder was kept in a 5% solution of HPC at 80—100 °C for 2 h; then the catalyst was dried and subjected to further tests. The content of the active Fe metal in the samples prepared was 0.5 wt.%.

ESR spectra were recorded on a Jeol-JES-3BS-Q radiospectrometer in the X-band at 77 K. The Mn/MgO samples and DPPH were used as the internal standards. The relative integral intensity of ESR signals was determined with an accuracy of ±15% (taking into account that the shape of the signal observed remained unchanged during all treatments).

The spectra were obtained after evacuation of air-dried samples. The redox thermal treatment of samples was carried out in an adsorption unit under a vacuum of 10^{-3} Pa. The reduction by hydrogen was performed as follows: a sample was

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held at the desired temperature for 1 h in the vacuum system then it was contacted with hydrogen passed from a vessel (~2.7 kPa) supplied with a trap cooled with liquid nitrogen for absorption of water vapor. Then the sample was allowed to stay for 0.5 h in hydrogen. Hydrogen was again introduced, and the sample was evacuated. The procedure was repeated 3—4 times until no hydrogen was absorbed by the sample. Then the ampule with the catalyst was cooled at 77 K for 40 min, and ESR spectra were recorded.

The samples were oxidized. The first oxidation route (method 1) was similar to the reduction procedure. In the second procedure (method 2), flowing dry air was passed through an ampule with the catalyst at a given temperature for 2—3 h with a flow rate of 60 mL min^{-1} (procedure 2). Then the sample was evacuated at the same temperature for 1 h and cooled at 77 K for 40 min, and ESR spectra were recorded.

All adsorption measurements were also carried out under vacuum conditions.

Results and Discussion

Investigation of thermal stability of bulky and SiO_2-supported samples of the Fe—Mo-heteropolycomplex catalyst. After evacuation of the starting air-dried samples of bulky and supported Fe—Mo-HPC at 293 K for 1 min, we obtained a narrow asymmetrical signal with $g = 4.20$ and ΔH ~70 G characteristic of isolated Fe^{3+} ions in diamagnetic oxide matrices[13] (Fig. 1, spectrum *1*). A similar signal has been observed previously[9] for the $Na_5[SiW_{11}FeO_{39}] \cdot 16H_2O$ heteropolycomplex. Comparing the ESR data and structural parameters of the complex, the authors of Ref. 9 established that the signal observed is related to the isolated Fe^{3+} ions in the distorted octahedral coordination typical of the Keggin structure. The absence of ESR signals from Fe^{3+} ions in the low-frequency fields for the sample of the starting SiO_2 support allows us to assign the observed signal with $g = 4.20$ and ΔH ~70 G to the Fe^{3+} ions localized in the Keggin structure.

Evacuation for 1 h at higher temperatures to 823 K did not change the shape of the ESR spectrum. The thermal stability of HPC can be evaluated, in particular, by comparing absorption bands in the IR spectra of the starting HPC sample and samples calcined at 400, 500, 600, and 750 °C (Fig. 2). The analysis of the spectral data shows that all the absorption bands, which appear after thermal treatments at temperatures as high as 500 °C and reflect the character of Mo—O and Si—O bonds in the heteropolyanion,[4] retain the same positions of maxima as those found for for the starting tungstenosilicate. This implies that the matrix typical of the Keggin structure persists up to temperatures around 500 °C. The XRD patterns of the samples calcined at 250, 400, and 500 °C are identical, and these samples are entirely soluble in water and when crystallized retain all properties of the starting compound. Partial decomposition of the heteropolyanion occurs after the HPC samples were heated at higher temperatures (>500 °C). The endoeffects on the DTA curves at 580—600 °C, the shapes of the IR spectra (see Fig. 2), and the data of

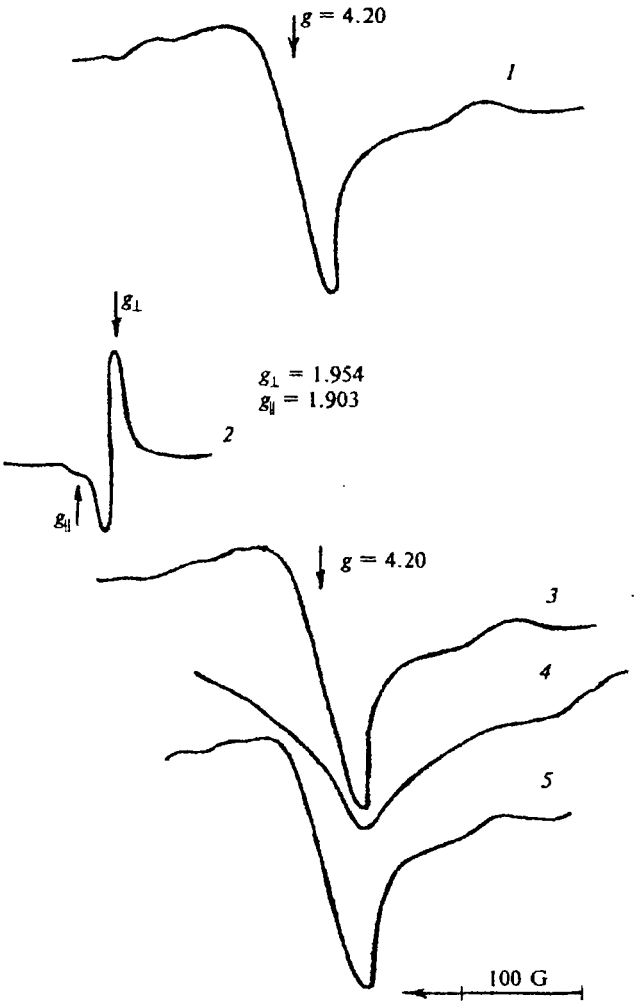

Fig. 1. ESR spectra of the supported Fe—Mo-HPC sample at 77 K: *1*, after oxidation by O_2 and evacuation at 550 °C; *2*, after reduction by H_2 and evacuation at 550 °C; *3*, reduced sample after oxidation by O_2 and evacuation at 550 °C; *4*, after admission of H_2O at 550 °C and evacuation at ~20 °C; and *5*, after admission of H_2O and evacuation at 550 °C.

X-ray phase analysis provide evidence for this decomposition.

The reduction of the bulky and supported Fe—Mo-HPC samples by hydrogen at 373—823 K results in the appearance of another narrow anisotropic signal with the parameters $g_\parallel = 1.903$ and $g_\perp = 1.954$ related to isolated ions with the d^1 configuration of the tetragonally distorted octahedron (or a square pyramid): Mo^{5+} ions (see Fig. 1, spectrum *2*).[9] A similar signal typical of ions with the d^1 configuration has been observed previously[10,11] for HPC $K_3[PMo_{12}O_{40}]$ and $H_{3+x}[PMo_{12-x}V_xO_{40}]$. This signal was correctly assigned to the Mo^{5+} ions formed during the partial reduction of the Keggin structure. It should be mentioned that the intactness of the Keggin structure in

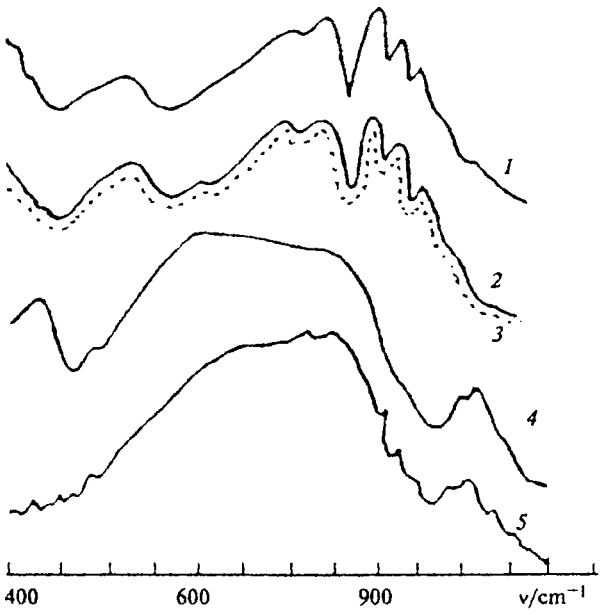

Fig. 2. IR spectra of the starting Fe-containing 12-HPC before (*1*) and after heating at T/°C = 400 (*2*), 500 (*3*), 600 (*4*), and 750 (*5*).

the bulky and supported samples of 12-HPC at relatively low reduction temperatures of 300—400 K was confirmed by IR spectroscopy and XRD phase analysis.[6,11] Thus, it can be assumed that the spectral data obtained under the reduction conditions outlined above also correspond directly to HPC with the Keggin structure.

The study of the influence of redox treatments on changes in the ESR spectra of the mixed HPC samples made it possible to reveal the following regularity (see Fig. 1). When the supported Fe—Mo-HPC/SiO_2 sample is reduced by hydrogen in the 373—823 K temperature range, the ESR spectrum exhibits a sharp decrease in the intensity of the signal with g = 4.20 from Fe^{3+} ions along with a narrow anisotropic signal with the parameters $g_{\parallel}$ = 1.903 and $g_{\perp}$ = 1.954 from Mo^{5+} ions. The subsequent oxidation of the catalyst by oxygen (method 1) at 473—823 K completely restored the initial pattern of the spectrum. Further multiple redox cycles in the 473—823 K temperature range (up to 8—10 treatment cycles) did not change the sample. During oxidation, the signal with g = 4.20 from Fe^{3+} ions was observed (with the unchanged intensity of $\sim 2 \cdot 10^{19}$ g^{-1}), whereas the signal from Mo^{5+} ions disappeared. After reduction, the signal from Mo^{5+} (with the intensity of $\sim 1 \cdot 10^{20}$ g^{-1}) appeared, and the signal from Fe^{3+} almost disappeared.

Reproducibility of the spectra following multiple redox treatments, reversibility of transformations of paramagnetic centers (PC), and the lack of changes in shapes and parameters of the signals imply retention of the HPC structure and high redox thermal stability of the supported complexes. Similar signals from the Mo^{5+} ions in the support matrix (SiO_2) are formed only at high temperatures ≥ 823 K. Assuming that the signal from Mo^{5+} can be assigned to centers localized in the support (SiO_2), we should mention the absence of the signal from the O_2^- radical ions, which is typical of the supported Mo/SiO_2, Mo,W/Al—Si, and Pd/Al—Si catalysts, after the adsorption of O_2 (293 K) on the reduced samples. The stabilization of these ions in the HPC complex confirms that the HPC structure is retained up to high temperatures.

If the decomposition of the Keggin structure of HPC is assumed,[4] the ESR spectrum would contain signals of iron oxide clusters instead of those of isolated iron ions,[9,13,14] or the signal from the Fe^{3+} ions would broaden due to the interaction with other magnetic species and hence, the intensity of the signal would decrease. We obtained these ferromagnetic signals for the bulky Fe—Mo-HPC sample after its calcination at 1073 K for 0.5 h in flowing dry air followed by evacuation. First, a distortion of the anisotropic signal from Mo^{5+} was observed, the intensity of the signal from Fe^{3+} decreased irreversibly, and a broad signal with $g \cong 2.02$ and ΔH = 1.5 kG from the ferromagnetic Fe_3O_4 clusters appeared.[14] Subsequent thermal treatment for 1 h resulted in the complete disappearance of the signals from Fe^{3+} and Mo^{5+} and the appearance of one broad ferromagnetic (FM) wave. According to the ESR data for the bulky Fe—Mo-HPC sample, the distortion of the Keggin structure of individual HPC starts even at 573 K. Thus, the difference between the distortion temperatures needed to distract the supported and bulky Fe—Mo-HPC samples is 250 °C.

According to the intensity of the signals observed, the content of PC is 30—40% of the total number of Fe^{3+} and Mo^{5+} ions in the prepared HPC samples, which is an order of magnitude higher than the amount of possible admixtures in the HPC samples used. Some difference is associated, on the one hand, with the previously established[9-11] effect of aggregation of HPC molecules and related broadening of the ESR signals. On the other hand, the results of this work and previously published data[9,13] indicate the effect of partial reduction of the Keggin structure for 12-HPC treated with hydrogen. It is shown[9,13] that the hydrogen treatment of the 12-HPC at 400—550 K results in a partial (3—4$\bar{e}$) reduction of the heteropolyanion with retention of the Keggin structure. An increase in the temperature of hydrogen treatment leads to the decomposition of the heteropolycomplex and to the appearance (in the XRD spectra) of many lines corresponding to the decomposition products, although lines typical of amorphous Keggin structure are also present in the XRD patterns. Retention of the Keggin structure for 12-HPC was experimentally confirmed[14] under conditions of partial reduction of the heteropolycomplex corresponding to ~30—40% of the total number of Mo (or W) atoms in the HPC

lattice. The heteropolyanion also decomposed when the regime of reductive thermal treatment became more rigid.[14]

Investigation of the influence of water vapor on the thermal stability of the Fe—Mo-heteropolycomplex catalyst. The hydrothermal stability of aluminosilicate catalysts with d-metals is low, as a rule, and after a short interaction with steam at 573—673 K, Fe atoms leave the aluminosilicate lattice to form ferromagnetic iron oxide clusters on the crystal surface.[14] The same FM signals are detected for iron-containing SiO_2, aluminosilicates, and zeolites after the reduction by hydrogen at 770 K and re-oxidation of the samples.

On the other hand, it is known that water molecules, which compose the hydrate shell of the heteropolycomplex, play an important role in the stabilization of the Keggin structure in 12-HPC.[4] The study of P—V—Mo-HPC by ESR also stressed the special role of water in the stabilization of the Keggin structure.[10]

Adsorption of water vapor on the supported Fe—Mo-catalyst sample was performed in a wide temperature range (293—823 K). The analysis of the ESR spectra (see Fig. 1) showed that in the given temperature region, adsorption of water has almost no effect on the character of PC (isolated Fe^{3+} ions); however, beginning from 573 K, the reduction of the Mo^{6+} ions to Mo^{5+} is observed. Subsequent evacuation at 823 K did not change the spectrum, which most likely indicates the chemical interaction of water molecules and Mo^{6+} ions, which prevents the desorption of water molecules from the catalyst surface under these conditions. As a whole, the data obtained indicate an increased stability of active sites of the d-metal (iron) in the supported HPC at temperatures as high as 823 K both to redox and hydrothermal treatments. The absence of FM signals in the case of the supported Fe-containing complexes suggests the double stabilization of ions of the d-metal by the complex and support.

Thus, the supported catalyst based on mixed Fe—Mo-HPC exhibits a higher thermal stability than the bulky sample of individual HPC. Redox cycles at 823 K do not decompose the Keggin structure of supported mixed HPC. The high stability of metal sites in the supported Fe—Mo-catalyst under the high-temperature action (up to 823 K) of water vapor was established.

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