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INTERACTION OF HYDROGEN SULFIDE WITH MOLYBDOPHOSPHORIC HETEROPOLYACID

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The effect of hydrogen sulfide on P-12Mo heteropolyacid has been studied using ESR, IR spectroscopic and thermal analysis methods. It has been established that hydrogen sulfide can be chemisorbed like water and no entering of sulfur into the anion structure takes place.

С помощью методов ЭПР, ИКС и ТА исследовано воздействие сероводорода на P-12Mo гетерополикислоту. Показано, что сероводород может хемосорбироваться аналогично воде. Вхождение серы в структуру аниона не происходит.

Heteropolyacids (HPA) find an ever increasing application as catalysts for various homogeneous and heterogeneous processes, e.g. hydrogenation of propylene, methanol conversion to hydrocarbons, hydration of olefins, etc. [1, 2]. Our studies [3] showed that HPA supported on TiO_2 are active catalysts for hydrodesulfurization. Under hydrodesulfurization conditions two types of the effect of reaction medium on HPA are realized: HPA

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reduction and its partial sulfurization. It was also shown [4] that interaction of the hydrogen sulfide produced by hydrogenolysis thiophene with the HPA anion provides the quasi-steady activity of samples.

The aim of the present study was to investigate the effect of hydrogen and hydrogen sulfide on molybdophosphoric acid to establish the nature of this effect.

EXPERIMENTAL

We have studied chemical grade bulk molybdophosphoric heteropolyacid $H_3PMo_{12}O_{40}nH_2O$ (PMA).

Treatment with hydrogen sulfide was carried out for 0.5 h in a flow of 20 vol.% H_2S in helium at various temperatures. Physically adsorbed hydrogen sulfide was blown off by helium at room temperature. Reduction by hydrogen was carried out at 100-300°C with a space velocity of 300 h^{-1}. Reoxidation of samples was performed in flowing oxygen at 100-240°C for 1 hour.

IR spectra of catalysts were recorded on UR-20 and SPECORD IR-75 spectrometers. Samples for recording were pressed with KBr (1 mg sample per 200 mg KBr).

ESR spectra were recorded on JES-3BX radiospectrometer at 77 and 300 K. Parameters were determined from comparison with DPPH.

Thermal analysis was performed on a MOM (Hungary) system with a heating rate of 5K/min in air over platinum plates.

X-ray phase analysis was carried out on a DRON-15 diffractometer with CuK_α radiation monochromatized by graphite.

RESULTS AND DISCUSSION

X-ray phase analysis. PMA anion in the solid state is characterized by the Keggin (primary) structure and a secondary structure which is due to the three-dimensional arrangement of anions, water molecules and cations. It is known that the secondary structure of PMA is to a great extent determined by the degree of its dehydration [5]. XPA performed in the region of Keggin anion existence, shows the occurrence of two types of crystal lattice: type A corresponds to the larger content of water (at temperatures T < 300°C) and type B corresponds to the more dehydrated state of PMA and is present at 300°C together with phase A. Remnants of phase B are observed after PMA sulfurization at 400°C. Also appeared a phase of molybdenum sulfide and non-stoichiometric molybdenum oxide.

IR spectra. HPA of the 12th series having the Keggin structure (including PMA) have several typical bands at 600-1100 cm^{-1}: bands at 960 cm^{-1} are vibrations of 12 terminal Mo=O bonds and those at 860 and 780 cm^{-1} are asymmetric stretching vibrations of 12 almost linear Mo-O -Mo bonds between triplets and 12 corner bridges between MoO_6 octahedra in the triplets, respectively. Asymmetric stretching vibrations of the PO_4 tetrahedron are observed at 1060 cm^{-1} and deformational vibrations appear at 590 cm^{-1} [6].

IR spectra of the initial, sulfurized and reoxidized HPA are illustrated in Fig. 1. Typical spectrum of the Keggin structure was also preserved after heating up to 300°C. PMA reduction by hydrogen at T < 300°C does not affect the appearance of typical bands of the Keggin structure either. Only after prolonged 4 h reduction by hydrogen at 300°C does the IR spectrum of the sample broaden. Sample treatment by hydrogen sulfide at the same temperatures causes no principal changes in the spectrum: it broadens. Heating of PMA at 300°C and further sulfurization at the same temperature for 0.5 h broadens the band at 960 cm^{-1} and leads to disappearance of the bands at 860 and 1060 cm^{-1}. Further reoxidation of this sample partly restores its initial structure. Heating of PMA at 400°C and further treatment by hydrogen sulfide at the same temperature leads to destruction of the anion structure. The IR spectrum exhibits only a weak band at 960 cm^{-1}.

ESR spectra. After heating a sample of the initial PMA in flowing hydrogen at 100 and 200°C, there appears an anisotropic ESR

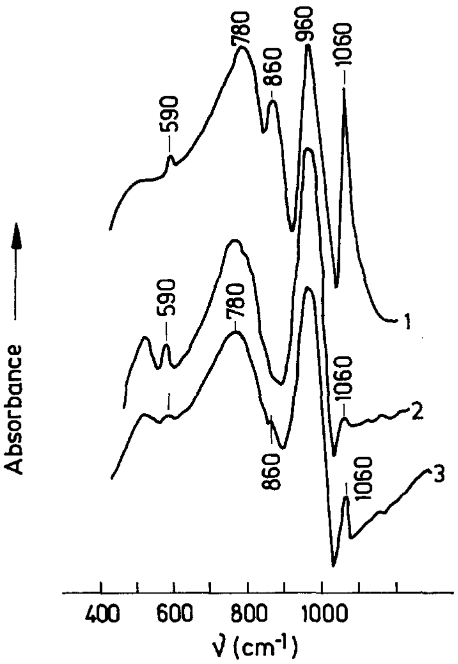

Fig. 1. IR spectra of PMA: 1) initial sample (100°C, air); 2) sample treated by H_2S at 300°C; 3) sample 2 reoxidized by air at 50°C for 4 h

signal of Mo^{5+} ions with $g_{\perp}=1.96$ and $g_{\parallel}=1.94$ (Fig. 2). Parameters of this signal show that it belongs to Mo^{5+} ions in weakly dehydrated HPA: Heating of the initial samples of PMA in flowing hydrogen at higher temperatures is accompanied by observation of a spectrum with $g_{\perp}=1.95$-1.96 and $g_{\parallel}=1.86$ with traces of the spectrum of weakly dehydrated HPA.

Treatment of PMA in air at 200°C leads to the appearance of an anisotropic ESR spectrum with $g_{\perp}=1.94$ and $g_{\parallel}=1.87$ (Fig. 2) Further treatment of this sample in flowing hydrogen sulfide at 150°C considerably increases the intensity of its ESR spectrum (approximately by an order of magnitude) due to the appearance of a new isotopic spectrum with $g=1.93$. Its intensity rises with temperature and time of treatment. Heating of the sample

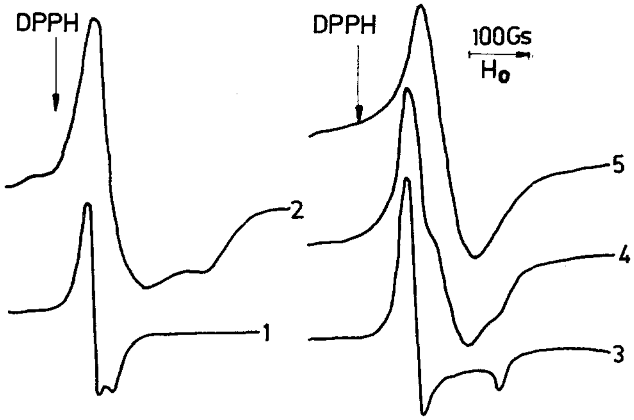

Fig. 2. ESR spectra of PMA: 1) sample heated in hydrogen at 200°C for 0.5 h; 2) sample heated in hydrogen at 300°C for 0.5 h; 3) sample heated in air at 200°C for 2 h; 4) sample treated by H_2S at 200°C; 5) sample 4 reoxidized at 200°C by air

in air at 200°C is accompanied by a decrease of the ESR spectrum intensity due to almost complete disappearance of the isotopic signal with g=1.93. During the second step of treatments (hydrogen sulfide, air) the intensity of the axial signal changes only slightly.

As to the singlet signal of Mo^{5+} ions with g=1.93, the absence of anisotropy makes its interpretation difficult. It can, however, be stated that its appearance indicates the disordering of its structure and the formation of regions with the increased local concentration of Mo^{5+} ions of dehydrated PMA.

Thermal analysis. Thermal analysis data for the initial PMA and those sulfurized at various temperatures are represented in Fig. 3. Data for the initial acid agree well with the results obtained in Ref. [7]. At 100-200°C one can observe endothermic effects due to dehydration. Exothermic peak at 410°C is attributed to the loss of the last molecules of water entering into the PMA structure and its transition into the polyoxide state with further

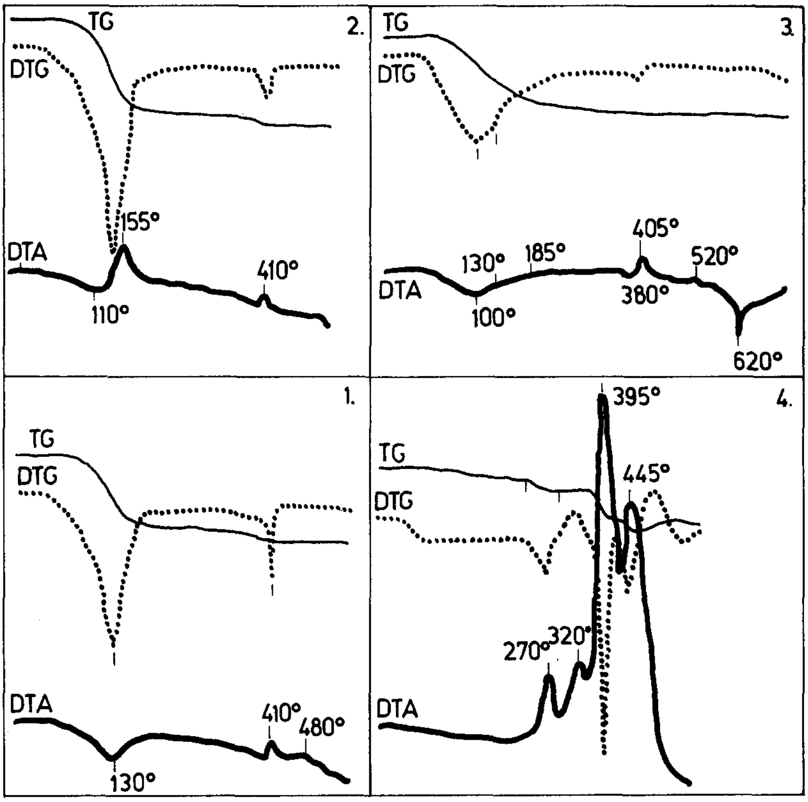

Fig. 3. Thermograms of PMA: 1) initial sample (100°C, air); 2) sample treated by H_2S at 100°C; 3) sample treated by H_2S at 200°C; 4) sample treated by H_2S at 400°C

conversion to molybdenum trioxide at 480°C. Beside the above effects, the thermogram of the sample sulfurized at 100°C demonstrates an exothermic effect at 155°C accompanied by weight losses. It is most likely to be due to the evolution of weakly bound hydrogen sulfide. The effect at 155°C is not observed for the samples sulfurized at higher temperatures. The DTA curves of the sample heated at 400°C and sulfurized at 300°C, demonstrates weak exothermic peaks at 280, 320 and 400°C accompanied by weight losses. These effects considerably are strengthened when the sulfurization temperature is elevated to 400°C. They are most probably due to the decomposition of partly sulfurized products of PMA destruction.

The analysis of the data obtained shows considerable stability of the Keggin structure in the PMA studied to the effect of hydrogen and hydrogen sulfide. The effect of crystallization water on the structure of a crystallographic cell is well known. Our data show that the same effect can be produced by hydrogen sulfide. Calculation of thermograms for PMA heated at 100°C and sulfurized at the same temperature, shows that on the average 8 moles of adsorbed water and 5 moles of hydrogen sulfide are liberated corresponding to the exothermic effect at 155°C.

It is known that HPA reduction by hydrogen is a two-step process and it depends on the reduction conditions [8]. At low temperatures Mo^{6+} reduces to Mo^{5+} due to electron transfer from hydrogen to Mo^{6+} and the proton thus formed is bound with the PMA anion. The second step is associated with the detachment of oxygen from the anion to produce an anion vacancy and to liberate water. We think, preservation of the intensity of the IR spectrum for PMA reduced by hydrogen at $T < 300°C$, indicates the unaltered Keggin structure and the absence of oxygen vacancies in the anion structural in this temperature range. Symmetry distortion in the nearer coordination environment of molybdenum observed in the ESR spectra of the samples treated at these temperatures, can be ascribed to sample dehydration like in Ref.[9]. Broadening of the IR spectrum for the sample reduced for a long time at 300°C is apparently due to an increase in sample inhomogeneity resulting from the formation of oxygen vacancies in the anion structure. In this case the decrease of $g_{\parallel}$ can be ascribed to the decreased covalency of equatorial Mo-O bonds.

The effect of hydrogen sulfide on the catalyst is stronger compared to hydrogen. Short-term reduction of the anion by hydrogen sulfide at 300°C takes place with the formation of oxygen vacancies. The observed restoration of the IR spectrum after reoxidation of the sample treated by hydrogen sulfide indicates that under reduction the main Keggin structure of the anion is preserved. Absence of the ESR signals associated with the substitution of oxygen ligands by sulfur, indicates that the coordination sphere of Mo^{5+} contains no sulfur. But broadening of the ESR spectrum can indicate the increase of inhomogeneity of crystal fields near Mo^{5+} ions with the adsorption of hydrogen sulfide, i.e. adsorbed hydrogen sulfide leads to stronger distortion of the anion structure. This is also confirmed by the considerably higher value of Δg between $g_{\perp}$ and $g_{\parallel}$ for the sample treated with hydrogen sulfide ($\Delta g=0.071$) compared to Δg for the sample reduced by hydrogen ($\Delta g=0.038$).

Elevation of the temperature for preliminary treatment of the sample up to 400°C decreases the structure stability to the effect of hydrogen sulfide. In this case besides reduction one can observe the partial destruction of the HPA anion with further sulfurization of destruction products.

CONCLUSION

Analysis of the results suggest that in the region of thermal stability of PMA, treatment by hydrogen sulfide does not lead to sulfur insertion into the HPA structure. Like water, at low temperatures hydrogen sulfide can only be chemisorbed and partly substitute water. Besides chemisorption, PMA reduction also takes place. At low temperatures of reduction the structure does not alter. At temperatures above 300°C reduction takes place with the removal of oxygen ions from the HPA anion. Sulfur-containing phases are formed only when HPA is destroyed due to sulfurization of destruction products of the HPA anion.

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