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The state of palladium in the system potassium palladium-11-tungstosilicate on aluminosilicate as studied by DRIFT spectroscopy

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The influence of redox treatments on the state of palladium in the heteropoly acid $K_6[SiW_{11}PdO_{39}]$ supported on amorphous aluminosilicate was studied by diffuse-reflectance IR spectroscopy using CO as a probe molecule. A bulk sample of the $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$ heteropoly compound (HPC) was studied for comparison. The deposition of the bulk sample on aluminosilicate leads to the partial decomposition of Keggin structure and to the removal of palladium cations from the HPC framework. The metal introduced into the $K_6[SiW_{11}PdO_{39}]/SiO_2$-$Al_2O_3$ system within HPC displays higher thermal stability in redox cycles compared to that of the bulk HPC. A highly dispersed state of palladium persists up to 573 K.

Key words: heteropoly compound, potassium palladium-11-tungstosilicate, Keggin structure, palladium, electronic state of metal, thermal stability, diffuse-reflectance FTIR spectroscopy.

The stability to redox treatments and stabilization of initial dispersion are the most important demands to efficient supported metal catalysts. Palladium systems are widely used in industry but palladium often undergoes sintering in the course of thermal treatments and its dispersion markedly decreases. It of interest to develop catalysts with a stable metal state. The stabilization of palladium in Keggin heteropoly anion (HPA) is one of the methods to fix palladium in the structure. Palladium can be introduced in the form of mixed heteropoly compounds (HPC) such as potassium palladium-11-tungstosilicate ($K_6[SiW_{11}PdO_{39}]$)[1] in which Pd replaces the W atom in one of the W_3O_{10} fragments.[2—4]

Dispersing HPC on a support enhances the catalytic activity but distorts the secondary and tertiary structures of HPC and sometimes decomposes Keggin structure.[5,6] These changes can make an impact on the properties of metallic sites introduced in the catalytic system within the mixed HPC.

The aim of this work is to study the role of a support and the effect of the conditions of redox treatments on the state of palladium in $K_6[SiW_{11}PdO_{39}]$ supported on SiO_2-Al_2O_3. The state of palladium was studied by diffuse-reflectance IR spectroscopy using CO as a probe molecule.

Experimental

Synthesis of $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$. The starting salt was prepared according to a common scheme.[7] Solid $PdCl_2$ or its saturated solution was added to a 0.03 *M* solution of potassium 11-tungstosilicate in the ratio Pd : SiW_{11} = 1 : 1. The reaction mixture was stirred for 2 h at 355—365 K at constant pH 4.5, which was maintained by adding HCl. The solution was evaporated and dried for 4 h at 373 K to yeild the golden-brown crystals of potassium 11-tungstosilicate. The palladium concentration in the bulk sample was 3 wt. %.

System $K_6[SiW_{11}PdO_{39}]/SiO_2$-$Al_2O_3$. A dedicated synthetic high-silica aluminosilicate (S_{sp} = 850 $m^2\ g^{-1}$, pore diameter 28—30 Å, Si : Al = 30) was used as the support. The aluminosilicate grains (fraction 0.2—0.5 mm) were impregnated with a saturated aqueous solution of $K_6[SiW_{11}PdO_{39}]$ for 2 h at 365 K. The mixture was evaporated, and the sample obtained was dried for 4 h at 373 K and heated in an air flow for 2 h at 673 K. The content of HPC in the system synthesized was 30 wt. %.

Oxidation and reduction of samples. To oxidize the bulk and supported samples, they were placed in a quartz reactor and heated in a vacuum up to 473—673 K for 1 h at a residual pressure of 10^{-3} Torr followed by treatment with O_2 (30 Torr) at activation temperatures. The catalysts were then evacuated for 1 h at the same temperatures and cooled to room temperature. To reduce palladium species, the activated samples were treated with hydrogen for 2 h in a hydrogen flow (H_2 consumption was

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30 mL min^{-1}) at 323—723 K, evacuated at the same temperatures down to a residual pressure of 10^{-4} Torr, and cooled to room temperature.

Recording IR spectra. The spectra were recorded at 20 °C on a Nicolet Protégé 460 IR Fourier-spectrometer with a diffuse reflectance attachment; resolution was 4 cm^{-1}.

The electronic state of palladium was determined from the analysis of vibration frequencies of the adsorbed CO. The adsorption of CO (20 Torr) was carried out at room temperature. After recording the initial spectrum, the sample was evacuated at a stepwise temperature rise with a step of 50 °C and the spectra were also recorded at each step.

The spectra were processed using the Kubelka—Munk equation according to the OMNIC® software. Computational treatment included smoothing the spectra, subtraction of the background, and deconvolution of the spectra by approximation with the combination of the Gauss—Lorentz functions.

Results and Discussion

The first task was to study the HPC state before and after deposition on SiO_2-Al_2O_3. IR spectra in the region of vibrations of Keggin structure (600—1100 cm^{-1}) in both bulk and supported samples of $K_6[SiW_{11}PdO_{39}]$ are presented in Fig. 1. The spectrum of the initial 12-tungstosilicic acid is shown for comparison. The absorption bands (AB) at 1018, 980, 925, 885, and 790 cm^{-1} were observed in the spectrum of the initial acid $H_4SiW_{12}O_{40}$. According to the reported data, they can be attributed to vibrations of the W=O (980 and 1018(?) cm^{-1}) and Si—O (925 cm^{-1}) bonds and fragments of the blocks $[W_2O_6]$ W—O—W with the shared O atoms (885 and 790 cm^{-1}).[8]

In the palladium-containing systems, the replacement of one WO_3 block by PdO_2 results in the distortion of the symmetry of Keggin structure. A narrow AB from the vibrations of the Si—O bonds in the SiO_4 fragment splits into two components with maxima at 892 and 915 cm^{-1}. The replacement of protons by K^+ ions shifts the absorption bands from the vibrations of the W=O bonds down to lower frequencies of 1010 and 960 cm^{-1}. These bonds participate in the formation of the secondary structure.

The deposition of the salt on aluminosilicate decreases the intensities of the bands from the W=O bonds and the band at 892 cm^{-1} from the vibrations of the SiO_4 tetrahedra. As a result, the absorption bands typical of the HPC structure become narrower and the total spectrum becomes similar to that of bulk $H_4SiW_{12}O_{40}$. The reconstruction of the structure results in a partial loss of crystallinity, as evidenced by the appearance of new bands at 1075 cm^{-1} and in the region of 700—750 cm^{-1}, which are typical of the vibrations of the Si—O and W=O bonds in amorphous oxide systems.

When CO is adsorbed on a dehydrated salt $K_6[SiW_{11}PdO_{39}]$ evacuated at 373 K, the AB at 2155 cm^{-1} typical[9] of the CO complexes with Pd^{2+} appears in the spectrum of the oxidized system (Fig. 2). Treatment with hydrogen at 333 K results in the complete reduction of palladium species. The elimination of the AB from the charged species (2155 cm^{-1}) and the appearance of the AB in the region of 1900—1980 cm^{-1} corresponding to the vibration of bridging CO complexes with Pd^0 (see Ref. 9) are indicative of this process. An increase in the reduction temperature to 373 K is accompanied by the growth of the metal particles as suggested by the broadening of the ABs which are due to the vibrations of the bridging carbonyl groups.

Since the formation of the bridging carbonyl groups involves several palladium atoms, it is obvious that during reduction, palladium leaves the HPC structure to form the metal particles. The absence of the ABs of the linear carbonyl groups (2000—2100 cm^{-1}) typical of CO adsorbed on Pd points to the strong interaction of the metal particles with the HPC fragments (K^+ ions), which enhances the electron density on the metal particles.

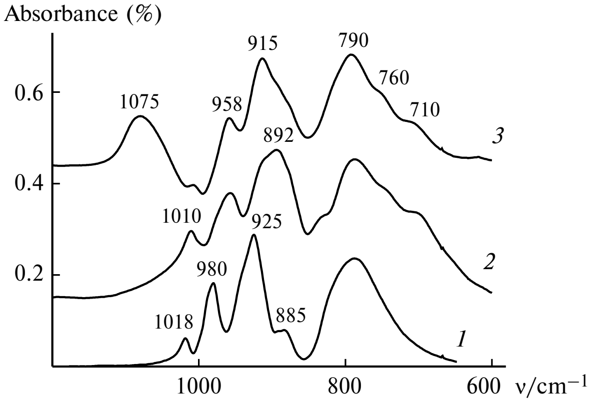

Fig. 1. IR spectra of $H_4SiW_{12}O_{40}$ (*1*), $K_6[SiW_{11}PdO_{39}]$ (*2*) and $K_6[SiW_{11}PdO_{39}]/SiO_2$-$Al_2O_3$ (*3*) after subtraction of background spectrum of SiO_2-Al_2O_3.

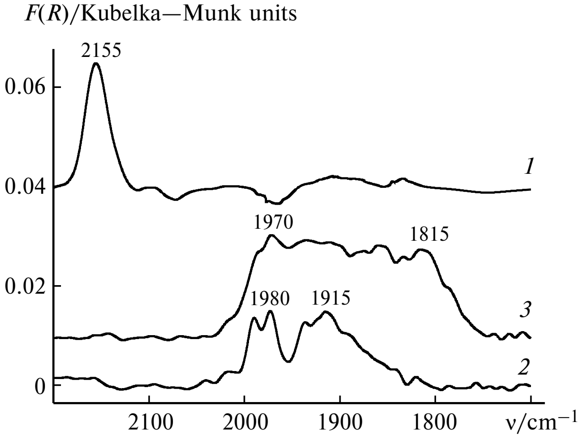

Fig. 2. IR spectra of CO adsorbed on the sample $K_6[SiW_{11}PdO_{39}]$ oxidized at 573 K (*1*) and reduced at 333 (*2*) and 373 K (*3*).

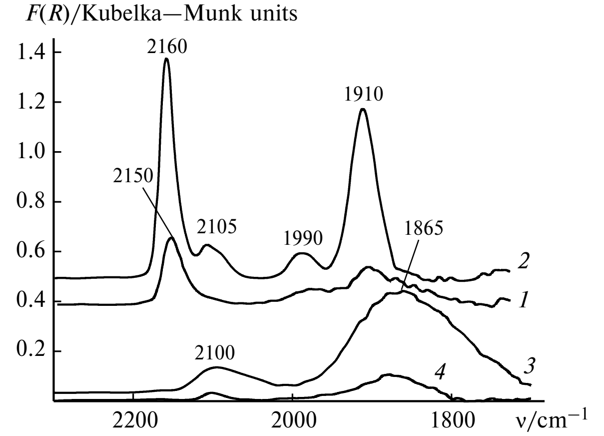

Fig. 3. IR spectra of CO adsorbed on the sample $K_6[SiW_{11}PdO_{39}]/SiO_2$-$Al_2O_3$ oxidized at 573 (*1*) and 773 K (*2*) and reduced at 473 (*3*) and 673 K (*4*).

In the spectra of CO adsorbed on the supported systems, ABs typical of CO complexes with palladium are only observed. This fact indicates a blockage of all adsorption sites of the support caused by the complete coverage of its surface with HPC. Figure 3 presents IR spectra of CO adsorbed on the Pd-HPC/SiO_2-Al_2O_3 sample oxidized at 573 (spectrum *1*) and 773 K (spectrum *2*). In the first case, the AB at 2150 cm^{-1} and weak ABs at 1990 and 1910 cm^{-1} were found. The presence of the low-frequency bands attributed to the carbonyl complexes gives evidence that in the case of the supported system, unlike the oxidized bulk HPC, the metal particles are formed as early as at the step of the evacuation of the sample preceded by oxidative treatments (ABs at 1990 and 1910 cm^{-1}). An increase in the temperature of oxidative treatment and evacuation up to 773 K increase intensities of these bands typical of complexes with the Pd^0 particles (see Fig. 3, spectrum *2*).

The above findings are in agreement with the data on the structural changes that occur during the HPC deposition. As follows from the IR spectra (see Fig. 1), a partial desintegration of the structure and the removal of palladium atoms from the lattice weaken the stabilizing effect of HPC on the metal atoms and facilitate their reduction in CO atmosphere and during evacuation.

Spectrum *3* in Fig. 3 indicates the complete reduction to the metal upon the reductive treatment of HPC with hydrogen at 473 K followed by the addition of CO. This is confirmed by the absence of the ABs typical of the charged palladium species (Pd^+ and Pd^{2+}) and the presence of the bands typical of the linear and bridging CO complexes with the Pd^0 particles (AB at 2100 cm^{-1} and broad AB in the 1750—2000 cm^{-1} region, respectively). The higher intensity of the ABs of the bridging carbonyl groups (1750—2000 cm^{-1}) compared to that of the linear complexes (2100 cm^{-1}) indicates the formation of particles with the enhanced electron density, which can be due to the presence of K^+ ions in the outer sphere of HPC.

An increase in the reduction temperature to 673 K (see Fig. 3, spectrum *4*) leads to the nearly complete disappearance of the ABs of the linear and bridging carbonyl groups. Two explanations for this phenomenon can be proposed: either palladium particles experience sintering or the metal surface decreases because of a blockage by the HPC fragments formed upon destruction during reductive treatments.

Destructions caused by redox treatments are not so dramatic when the samples are reduced at lower temperature, and the blockage of the metal particles does not occur in this case. Palladium is capable of restoring its properties upon reoxidation. The spectra of CO adsorbed on the reoxidized sample Pd-HPC/SiO_2-Al_2O_3 after numerous redox treatments at 573 K (Fig. 4) confirm this fact. In the spectrum of the reoxidized sample, the intense AB from the charged Pd^{2+} species (2150 cm^{-1}) appears again and its intensity and half-width coincide in fact with the corresponding parameters of the initial sample.

Thus, the deposition of the palladium-containing HPC on aluminosilicate stabilizes the metal particles compared to the bulk sample and enhances their resistance to sintering. This is achievable due to grafting the metal particles on the fragments of the partially distorted Keggin structure.

In general, the findings of the comparative study of the bulk and supported samples of $K_6[SiW_{11}PdO_{39}]$ by diffuse-reflectance IR spectroscopy lead us to the following conclusions:

1. In the oxidized bulk HPC, palladium occurs as Pd^{2+} and only a small fraction of the metal ions is present on the surface and accessible to the adsorptive molecules.

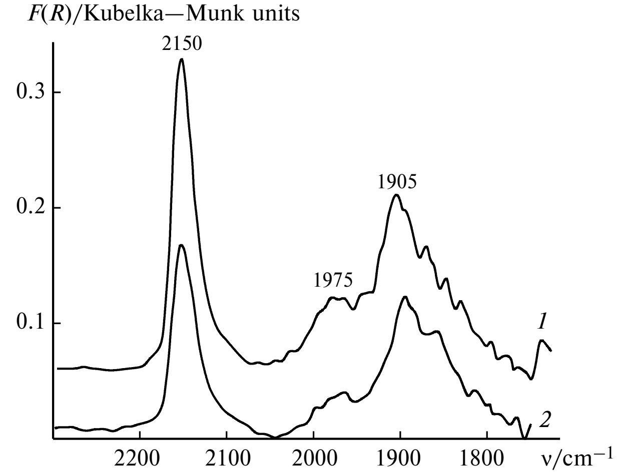

Fig. 4. IR spectra of CO adsorbed on the sample $K_6[SiW_{11}PdO_{39}]/SiO_2$-$Al_2O_3$ oxidized at 573 K (*1*) and reoxidized after reduction at 573 K (*2*).

The reductive treatment results in the complete reduction of accessible palladium to Pd^0 and the partial destruction of HPC at temperatures above 373 K.

2. The deposition of the bulk HPC on SiO_2-Al_2O_3 causes strong interaction of the Keggin HPA with the support surface accompanied by the release of palladium atoms from the HPC structure.

3. In the oxidized system HPC/SiO_2-Al_2O_3, palladium occurs predominantly as the charged species Pd^{2+}, whereas in the reduced system palladium is present as Pd^0.

4. The palladium particles in the HPC/SiO_2-Al_2O_3 system are more thermally stable than those in the bulk HPC sample and do not experience sintering upon redox treatments at the temperatures up to 573 K.

The synthesis of mixed HPC including those with Keggin structure allows the formation of inorganic complexes with the platinum metal ions stabilized by oxygen environment. The enhanced stability of the supported HPC to redox treatments provides a high metal dispersion. This creates fresh opportunities for using in catalysis the supported catalysts based on the mixed HPC containing the d-metal atoms in the inner coordination sphere.

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