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Investigation of the state of palladium in the potassium palladium-11-tungstosilicate/alumina system by diffuse-reflectance IR spectroscopy

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The influence of redox treatments on the state of palladium in the $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O/\gamma\text{-}Al_2O_3$ system was investigated by diffuse-reflectance IR (DRIFT) spectroscopy using CO as a probe molecule. The $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$ heteropolycompound (HPC) and starting $\gamma\text{-}Al_2O_3$ support were studied for comparison. It was shown that palladium is present in HPC mainly in the form of Pd^{2+} ions. Treatment of HPC in an H_2 flow results in complete reduction of palladium to Pd^0. The HPC is unstable in redox cycles at temperatures above 373 K. When the HPC was supported on alumina, the Keggin units were stabilized on the support surface and Pd^+ formed in the oxidized sample. The supported $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O/\gamma\text{-}Al_2O_3$ catalyst displays higher thermal stability and does not decompose during redox treatments at temperatures up to 723 K.

Key words: heteropolycompound, heteropolyanion, Keggin unit, palladium, heteroatom, redox cycle, thermal stability, diffuse-reflectance FTIR spectroscopy, carbon monoxide, probe molecules.

Heteropolycompounds (HPC) are promising catalysts for various industrial processes and fine organic synthesis.[1–5] In particular, 12th row heteropolyacids (HPAc) with the Keggin unit and their salts with metal cations such as Ni, Cs, Fe, Pd, and Pt are used in hydroisomerization of alkanes.[2,3] However, metal sites of HPC are deactivated under catalytic conditions because the secondary structure of HPAc salts possesses a comparatively low thermal stability in redox media.

Mixed 12th row HPC containing ions of d-metals are of interest for the development of stable highly active catalysts with a specified position of the d-metal atom in the Keggin heteropolyanion (HPA). In this work, palladium was used as the heteroatom. In HPC of the $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$ type,[6,7] palladium occupies the position of the tungsten atom in one of the W_3O_{13} fragments.[4,5]

The purpose of this work is to study the influence of conditions of redox treatments on the state of palladium in the supported $HPC/\gamma\text{-}Al_2O_3$ system ($HPC = K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$). The state of palladium was studied by DRIFT spectroscopy using CO as a probe molecule. The bulky $K_6[SiW_{11}PdO_{39}] \cdot 11H_2O$ and starting support $\gamma\text{-}Al_2O_3$ were studied for comparison.

Experimental

Preparation of HPC. Catalyst samples were prepared according to the general scheme.[8] A saturated solution or solid $PdCl_2$ was added to a 0.03 *M* solution of potassium 11-tungstosilicate in a Pd : SiW_{11} ratio of 1 : 1. The reaction mixture was stirred for 2 h at 355—365 K, adjusting the pH to 4.5 by the addition of HCl. Then the solution was concentrated to obtain golden-brown crystals of potassium palladium-11-tungstosilicate,[7] which were dried for 4 h at 373 K. The content of palladium in the bulky HPC sample was 3 wt.%.

Preparation of $HPC/\gamma\text{-}Al_2O_3$. $\gamma\text{-}Al_2O_3$ (S_{sp} = 240—250 $m^2\ g^{-1}$) was used as the starting support. To prepare the $HPC/\gamma\text{-}Al_2O_3$ system, the mixed HPC (potassium palladium-11-tungstosilicate) was used. Granules of Al_2O_3 (0.2—0.5 mm fraction) were impregnated with a saturated solution of HPC and stored in the solution for 2 h at 365 K. Then the mixture was concentrated, 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 synthesized system was 30 wt.%, which is sufficient for the formation of the crystalline phase of HPC on the support surface.[4]

Samples of bulky and supported catalysts with a particle size of 0.2—0.5 mm were loaded in a quartz reactor with a CaF_2 window for measuring IR spectra and activated at 473—673 K in a vacuum for 1 h. Then the samples were exposed to

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O_2 (30 Torr) at the activation temperatures to prevent the reduction of palladium. Then the catalysts were evacuated for 1 h at the same temperatures to a residual pressure of 10^{-4} Torr and cooled to room temperature. To obtain the reduced form of palladium, activated samples (0.5 g) were treated for 2 h in a hydrogen flow (H_2 consumption was 30 mL min^{-1}) at 373—723 K, then evacuated at the corresponding temperatures of reduction to a residual pressure of 10^{-4} Torr, and cooled to room temperature.

Measurement of IR spectra. DRIFT spectra were recorded on a Nicolet Impact-410 spectrophotometer with a diffuse-reflectance attachment[9] at a resolution of 8 cm^{-1}. Oxidized or reduced samples were evacuated, and CO was adsorbed on them at a pressure of 25 Torr. After recording the spectrum, the sample was evacuated with a stepwise increase in temperature with an increment of 50 K, recording spectra for each temperature of evacuation.

Spectra were quantitatively processed using the Kubelka—Munk equation by the OMNIC® program according to the previously proposed procedure.[10] Computer simulation also included smoothening of spectra and subtraction of the background.

Results and Discussion

To reveal the state of palladium, the bulky HPC sample was studied during redox treatment under comparatively mild conditions. The oxidative treatment was carried out at 473, 523, and 573 K. CO is not sorbed on the sample pre-oxidized at 473 K, which can most likely be explained by the incomplete removal of coordination water that shields palladium ions in the Keggin unit from attack by CO. At higher temperatures, absorption bands (AB) with νCO 2155 and 2100 cm^{-1} appear in the IR spectrum of CO. When the temperature of treatment further increases, the intensity of the first AB increases, and that of the second band remains unchanged (Fig. 1, *a*, spectra *1* and *2*). According to the published data,[11,12] these bands can be assigned to linear complexes Pd^{2+}—CO and Pd^0—CO, respectively. The bands corresponding to bridged CO complexes with Pd^0 were not found because of a strong background in the lower-frequency region in the IR spectrum. The appearance of AB at νCO 2100 cm^{-1} indicates the reduction (in the CO medium) of Pd^{2+} ions in the Keggin unit to form palladium metal.

A stepwise increase in the temperature of evacuation of oxidized samples after CO adsorption results in the complete disappearance of AB at νCO 2155 and 2100 cm^{-1} at $T > 373$ K.

After reductive treatment of HPC in a hydrogen flow at 373 K, the IR spectrum of CO changes (see Fig. 1, *b*, spectrum *1*). AB at νCO 2070 cm^{-1} and the group of high-intensity bands appear in the frequency region from 1750 to 2000 cm^{-1} with maxima at 1825, 1910, and 1985 cm^{-1}. The IR spectrum of the reduced sample contains AB at 2155 cm^{-1}, which indicates the resistance of Pd^{2+} ions toward reductive treatment. The position of AB at 2070 cm^{-1} in the region characteristic of Pd^0 carbonyls indicates that this AB is attributable, as the AB at 2100 cm^{-1}, to linear CO complexes with Pd^0. It is known from the published data[13,14] that for the neutral environment of Pd^0 particles, vibrations of Pd^0—CO appear as a band in the 2095—2100 cm^{-1} region. In the presence of acid sites in the nearest environment of metallic particles, this band is shifted toward higher frequencies.[13] By contrast, the shift of AB from 2100 to 2070 cm^{-1} indicates that basic sites are present in the nearest environment of palladium. This can be related to the presence of potassium ions in the outer sphere of HPC. The group of high-intensity bands with maxima at 1825, 1908, and 1985 cm^{-1} characterizes bridged CO complexes with particles of palladium metal.[13—16]

An increase in the reduction temperature to 473 K results in an increase in the intensity of AB at νCO 2070 cm^{-1} and a change in the spectral pattern in the region that characterizes the bridged CO complexes with Pd^0. The intensity of AB at νCO 1825 cm^{-1} increases simultaneously with the appearance of new bands at

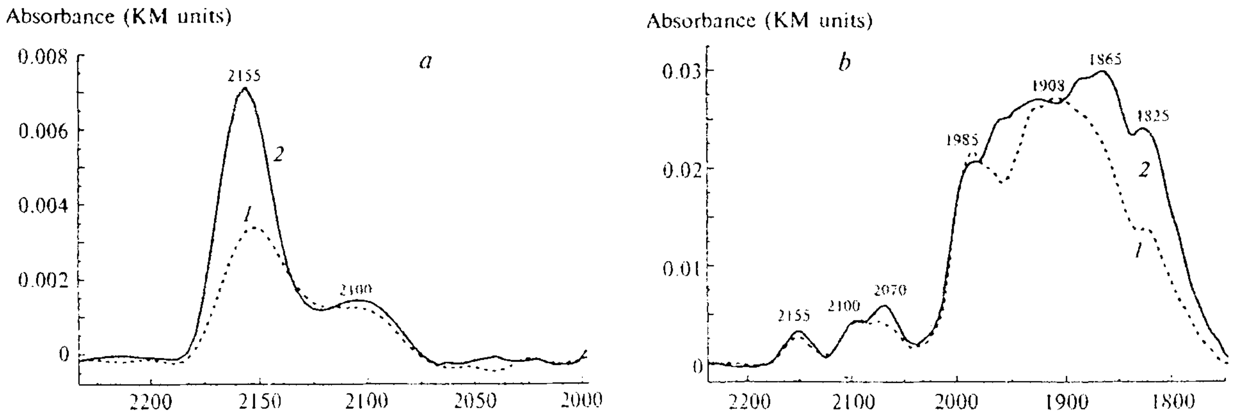

Fig. 1. IR spectra of CO (25 Torr) adsorbed on HPC samples (*a*) oxidized at 523 (*1*) and 573 K (*2*) and (*b*) reduced at 373 (*1*) and 473 K (*2*).

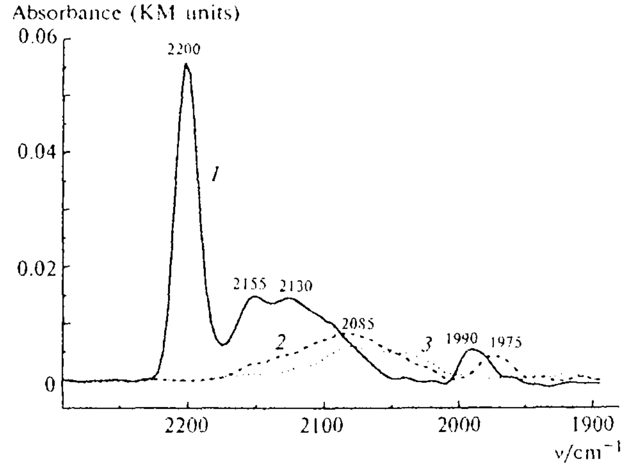

Fig. 2. IR spectra of CO (25 Torr) adsorbed on an $HPC/\gamma\text{-}Al_2O_3$ sample oxidized at 673 K (*1*) followed by evacuation at 293 (*2*) and 373 K (*3*).

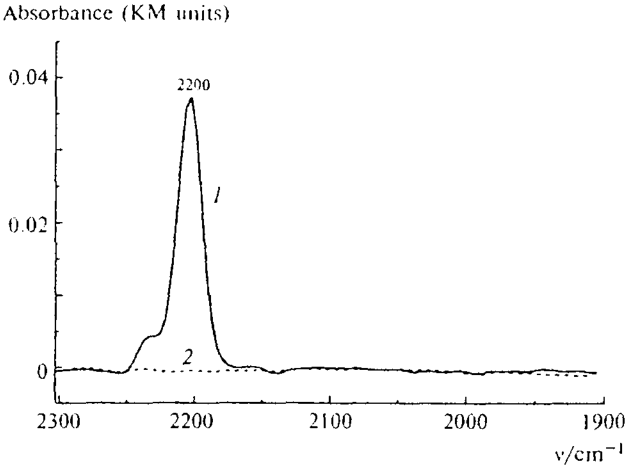

Fig. 3. IR spectra of CO (25 Torr) adsorbed on a $\gamma\text{-}Al_2O_3$ sample activated at 723 K (*1*) followed by evacuation at 293 K (*2*).

1930 and 1865 cm^{-1}, and the AB at 1908 cm^{-1} disappears. High intensity of the bands of this group indicates that the system contains palladium clusters, whose formation is due, most likely, to the compactness of Keggin heteropolyanions associated with the decomposition of the secondary structure of HPC under conditions of thermal reduction of the sample. The bridged CO complexes with palladium metal are unstable and disappear at evacuation already at 373 K.

Re-oxidation of the bulky HPC sample at 573 K followed by CO adsorption (25 Torr) does not result in the appearance of any bands in the IR spectral region characteristic of complexes with charged palladium particles. This can be related to sintering of the bulky sample and a sharp decrease in the number of surface palladium atoms accessible for CO adsorption. It is known that the structure of HPC of the 12th row is stable during not very deep redox transformations.[4] Our studies showed that the Keggin unit of bulky HPC begins to decompose when the redox treatments are carried out at temperatures higher than 373 K. Support of HPC on an inert carrier increases the thermal stability of the system and its resistance in redox cycles.[4–6]

The IR spectra of CO adsorbed on an $HPC/\gamma\text{-}Al_2O_3$ sample which was oxidized at 673 K (spectrum *1*) and evacuated at 293 and 373 K (spectra *2* and *3*, respectively) are presented in Fig. 2. Adsorption of CO (25 Torr) on the oxidized sample leads to the appearance of AB at 1990, 2130 (with a shoulder at 2095 cm^{-1}), 2155, and 2200 cm^{-1}. The position of the bands at νCO 2130 and 2155 cm^{-1} and their behavior during thermal vacuum treatment make it possible to assign them, according to the published data,[11–16] to linear CO complexes with Pd^+ and Pd^{2+} ions, respectively. The presence of the AB at νCO < 2000 cm^{-1} indicates the formation of complexes of the bridged type between metal particles and CO molecules.[13] The very intense AB at νCO 2200 cm^{-1} can be assigned to CO complexes with Lewis acidic sites (LAS) on the support surface.[11,12] This assignment is favored by the absence of this band in the IR spectra of the bulky sample and the presence of a similar AB in the spectrum of CO adsorbed on a clean support (Fig. 3).

The stepwise increase in the temperature of evacuation of the oxidized sample with pre-adsorbed CO results in the disappearance of AB at 2200 cm^{-1} already at 293 K and a decrease in the intensities of AB at 2155 and 2130 cm^{-1}, which almost completely disappear at 373 K. At 293 K, a new broad band appears at 2085 cm^{-1} in the IR spectrum. This band characterizes vibrations of CO adsorbed on Pd^0 particles, which may indicate reduction processes in a CO atmosphere and, correspondingly, an increase in the fraction of the reduced metal. The intensity of this band decreases at 373 K and vanishes with further temperature increase to 473 K. The band at νCO 1990 cm^{-1} is shifted during evacuation at 293 K by $\Delta\nu$ = 15 cm^{-1} toward low frequencies and disappears at 373 K. Analysis of the spectral pattern suggests that palladium in the $HPC/\gamma\text{-}Al_2O_3$ system is mainly present as Pd^+ and Pd^{2+} ions.

The band at νCO 2155 cm^{-1} in the IR spectra of bulky HPC and $HPC/\gamma\text{-}Al_2O_3$ subjected to oxidative treatment can be attributed to linear Pd^{2+}—CO complexes. Since adsorption of CO on the oxidized Pd/SiO_2 system, in which palladium exists as an oxide phase, does not result in the appearance of AB in this region,[16] the presence of the band at νCO 2155 cm^{-1} indicates, most likely, that the Pd^{2+} ions belong to the Keggin unit. An approximately twofold increase in the intensity of the band at νCO 2155 cm^{-1} in the spectrum of $HPC/\gamma\text{-}Al_2O_3$ is related to an increase in the total HPC surface upon support and, as a consequence, to an increase in the number of palladium atoms accessible for CO adsorption. The presence of the AB at νCO 2130 cm^{-1} characteristic of Pd^+—CO complexes can be explained by a partial

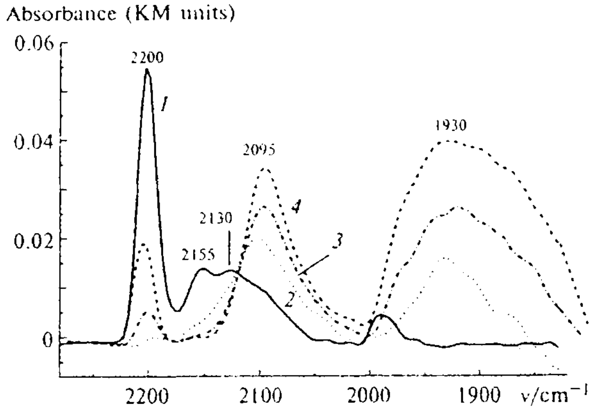

Fig. 4. IR spectra of CO (25 Torr) adsorbed on an HPC/γ-Al_2O_3 sample oxidized at 673 K (*1*) and reduced at 423 (*2*), 523 (*3*), and 623 K (*4*).

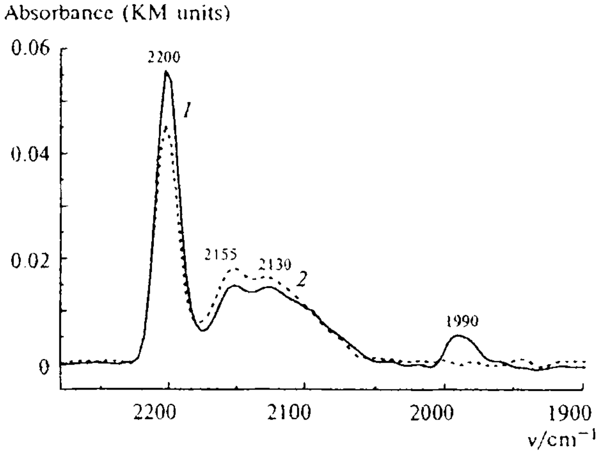

Fig. 5. IR spectra of CO (25 Torr) adsorbed on oxidized (*1*) and re-oxidized (*2*) HPC/γ-Al_2O_3 samples; the last reductive treatment was carried out at 723 K.

reduction of palladium during direct contact with the support surface.[11] This favors an easier reduction of palladium, which begins already during treatment with hydrogen at room temperature.

The treatment of HPC/γ-Al_2O_3 at 423 K in an H_2 flow results in complete reduction of palladium. This is indicated by the absence of AB typical of charged forms of palladium (Pd^+, Pd^{2+}) and the appearance of a new AB at νCO 2095 cm^{-1} attributed to linear Pd^0—CO complexes[11—16] (Fig. 4). The position of this band indicates a neutral environment of palladium particles. The spectrum also contains a broad band with a maximum at 1930 cm^{-1} corresponding to the two-centered bridging form of CO adsorption on particles of metallic palladium.[13] Under these conditions, palladium atoms in adjacent HPA aggregate, most likely, followed by the formation of polynuclear complexes. When the temperature of reduction of the sample is increased from 423 to 623 K followed by evacuation, AB at νCO 2200 cm^{-1} appears in the spectrum (Fig. 5, spectra *2*—*4*). The AB appears in this region due to the interaction of CO with LAS on the support surface. The absence of this AB at reduction temperatures below 423 K can be associated with blocking of LAS by water molecules, which are formed when Pd is reduced in an H_2 flow.

Examination of the spectrum of the reduced HPC/γ-Al_2O_3 system shows that an increase in the temperature of reduction results in an increase in the intensity of AB attributed to both the linear and bridged CO complexes with Pd^0. This can be explained by a more complete removal of coordination water from the catalyst surface. The increase in the intensity of AB with a maximum at 1930 cm^{-1} characteristic of the two-centered form of adsorption of CO molecules on palladium particles can also be related to an increase in the fraction of polynuclear palladium clusters. Some of them are formed due to the compactness of HPA, and others are formed because of the decomposition of HPA. However, these destructions are most likely insignificant, which is confirmed by the reproducibility of the spectra of CO adsorbed on the re-oxidized HPC/γ-Al_2O_3 sample after its numerous redox treatments (see Fig. 5).

The results of studying unsupported HPC and supported HPC/γ-Al_2O_3 samples by diffuse-reflectance FTIR allow us to draw the following conclusions.

(a) In oxidized bulky HPC, palladium exists in the form of Pd^{2+}. Treatment in an H_2 flow results in its complete reduction to Pd^0 clusters.

(b) No bands appear in the IR spectrum of CO in the 1750—2200 cm^{-1} region after the re-oxidative treatment of the bulky sample, which indicates sintering and characterizes instability of the HPC system in the redox cycles at reduction temperatures >373 K.

(c) Support of HPC on γ-Al_2O_3 results in a strong interaction of the Keggin HPA with the support surface.

(d) The main state of palladium in the oxidized HPC/γ-Al_2O_3 system corresponds to its charged forms Pd^+ and Pd^{2+}.

(e) The main form of palladium in the reduced HPC/γ-Al_2O_3 system is Pd^0 in the atomic state and in the form of clusters.

(f) The HPC/γ-Al_2O_3 system exhibits a higher thermal stability as compared to that of the bulky HPC sample and does not decompose during redox treatments at temperatures not lower than 723 K.

Synthesis of mixed HPC with different structures and, in particular, Keggin units produces inorganic complexes with platinoid ions stabilized by the oxygen environment. An enhanced stability of supported HPC at different temperatures of redox treatments makes it possible to achieve a high dispersity of platinum group metals (up to the dispersed-atomic state). This allows supported catalysts based on mixed HPC containing d-metal atoms in the inner coordination sphere to be used in acidic catalysis.

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