The state of platinum in the potassium platinum-11-tungstosilicate system on alumina studied by diffuse-reflectance IR spectroscopy

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The electronic state of platinum in the $K_4[SiW_{11}PtO_{39}]/Al_2O_3$ supported system and its thermal stability in redox cycles were investigated by diffuse-reflectance IR spectroscopy using CO as a probe molecule. The bulk sample of the $K_4[SiW_{11}PtO_{39}] \cdot 13H_2O$ heteropolycompound (HPC) was studied for comparison. It was shown that platinum is present in the oxidized HPC mainly as the Pt^{1+} and Pt^0 species. In the supported system, the ratio of these species strongly depends on the temperature of oxidative pretreatment. The reduced HPC contains mainly metallic platinum in the form of Pt^0 complexes with the bridged CO ligands. Supporting of the bulk sample HPC increases the thermal stability of its structure in an oxidative medium from ~600 to ≥820 K. The supported $K_4[SiW_{11}PtO_{39}]/Al_2O_3$ system exhibits a higher stability in the redox cycles compared to that of the bulk sample of individual HPC and preserves the Keggin structure and highly dispersed state of platinum up to $T \geq 670$ K.

Key words: heteropolycompound, Keggin structure, platinum, heteroatom, redox cycle, thermal stability, diffuse-reflectance IR spectroscopy, carbon monoxide, probe molecule.

Heteropolycompounds (HPC) are inorganic polyacids possessing some valuable properties,[1—3] due to which they are attractive for use in acid-type catalytic reactions.[3—5] The nature, strength, and number of acidic sites can be controlled by the selection of the outer-sphere cation, the replacement of the central atom and metal ion in the heteropolyanion (HPA) structure, the choice of supports with different structures, the change in the HPC concentration on the support, and by varying the conditions of catalyst pretreatment and the degree of dehydration of the compound.[3] HPCs containing both outer-sphere protons and transition metal cations can act as bifunctional catalysts, for example, in the skeletal hydroisomerization of alkanes on $(Pd,Pt)/H_3PW_{12}O_{40}$ [4] and $(Pd,Pt)/H_{0.5}Cs_{2.5}PW_{12}O_{40}$.[5] The partial replacement of protons by the Cs^+ or K^+ cations enhances[6,7] the HPC thermal stability. The introduction of transition metal atoms into the HPC structure (similarly to the systems $Na_4[PMo_{11}FeO_{39}]$ [8—10] or $H_4[SiW_{11}CrO_{40}]$[10,11] and others) enhances the thermal stability of highly dispersed metallic species.

Earlier[12] we studied the $K_6[SiW_{11}PdO_{39}]/Al_2O_3$ system and its bulk analog by diffuse-reflectance IR spectroscopy using CO as a probe molecule. The main states of palladium in the oxidized system were shown to be Pd^+ and Pd^{2+}, and the reduced system was shown to contain the Pd^{2+} ion along with metallic palladium. The bulk sample is thermally stable under oxidative conditions below 550—600 K but begins to decompose in the redox cycles already at ~400 K. Supporting of HPC on Al_2O_3 enhances the thermal stability up to ~700 K, and the system is reversible at 670 K in the redox cycles. Therefore, it seemed of interest to study analogous systems with other transition metals introduced into the Keggin structure.

The purpose of this work is to investigate the state of platinum in the $K_4[SiW_{11}PtO_{39}]/Al_2O_3$ system (hereinafter $Pt-HPC/Al_2O_3$) and its thermal stability in the redox cycles. The bulk analog $K_4[SiW_{11}PtO_{39}] \cdot 13H_2O$ (hereinafter $K_4[SiW_{11}PtO_{39}]$ or Pt-HPC) was studied under the same conditions for comparison. Diffuse-reflectance IR spectroscopy (CO as a probe molecule), being one of the most widely used and highly efficient methods for studying the surface of heterogeneous catalysts,[13] was applied as the main method of investigation.

Experimental

Samples of bulk HPC $K_4[SiW_{11}PtO_{39}] \cdot 13H_2O$ were prepared by complexation in solution using a standard procedure.[14]

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We have previously described the synthesis of $K_4[SiW_{11}PtO_{39}] \cdot 13H_2O$ in detail.[15,16] The platinum content in the prepared HPC was 6 wt.%. Supported samples were prepared by impregnation from an aqueous solution of HPC.[12] Granules of γ-Al_2O_3 (S_{sp} = 240—250 $m^2 g^{-1}$) with the particle size 0.2—0.5 mm were used as support. The HPC content in the synthesized $K_4[SiW_{11}PtO_{39}]/Al_2O_3$ system was 16.7 wt.%, which corresponds to ~1 wt.% Pt in the supported sample.

Samples of the bulk and supported catalysts with the particle size 0.2—0.5 mm were loaded in a quartz reactor with the CaF_2 window for recording IR spectra and activated at 470—920 K *in vacuo* for 1 h. Then the samples were exposed to O_2 (30 Torr) at the activation temperatures to prevent platinum reduction. The catalysts were evacuated at the same temperatures additionally for 1 h to a residual pressure of 10^{-4} Torr and cooled to ~20 °C. In order to obtain reduced platinum, the activated samples (0.5 g) were treated in an H_2 flow (30 mL min^{-1}) at 370—670 K for 2 h, and then the samples were evacuated at the corresponding reduction temperatures to a residual pressure of 10^{-4} Torr and cooled to ~20 °C.

IR spectra were recorded using a Nicolet Protégé-460 spectrophotometer equipped with the diffuse-reflectance attachment[17] at a resolution of 8 cm^{-1}. Carbon monoxide was adsorbed on the pre-evacuated oxidized or reduced samples at a pressure of 30 Torr. After the spectrum was recorded, the sample was evacuated with a stepwise temperature increase with an increment of 50 K, while recording the spectra for each temperature of evacuation.

The spectra were quantitatively processed using the Kubelka—Munk equation and the OMNIC® program acoording to a previously proposed procedure.[18] The computer processing of spectra also included smoothening of the spectra and subtraction of the background.

Results and Discussion

We studied the bulk $K_4[SiW_{11}PtO_{39}]$ compound to elucidate the electronic structure of the interstitial platinum. Oxidative treatment was carried out at 470 K. The IR spectrum of the adsorbed CO contains a broad absorption band (AB), which is a superposition of two unresolved bands with maxima at 2115 and 2085 cm^{-1} (Fig. 1, *a*). These bands can be assigned to the Pt^+—CO and Pt^0—CO linear complexes, respectively.[19—21] However, the frequencies of vibrations of the adsorbed CO are somewhat lower than those for the Pt/H-zeolite systems.[20,21] The stepwise temperature increase during vacuum treatment of the samples results in the disappearance of the band at 2085 cm^{-1} already at 370 K, whereas the band at 2115 cm^{-1} is observed up to 470 K. (Earlier,[19] a much higher stability of the Me^+—CO complexes compared to that of Me^0—CO was observed). The AB at 2115 cm^{-1} does not shift during evacuation, and the AB maximum at 2085 cm^{-1} shifts toward lower frequencies by $\Delta\nu$ = 20 cm^{-1}. This shift is related to the weakening of the dipole-dipole interaction between the CO molecules with a decrease in the coverage of the platinum surface with the adsorbate. The absence of the band shift in the case of the Pt^+—CO complexes evidences an insignificant dipole-dipole interaction of the CO molecules, indicating a high dispersity of the adsorption sites.

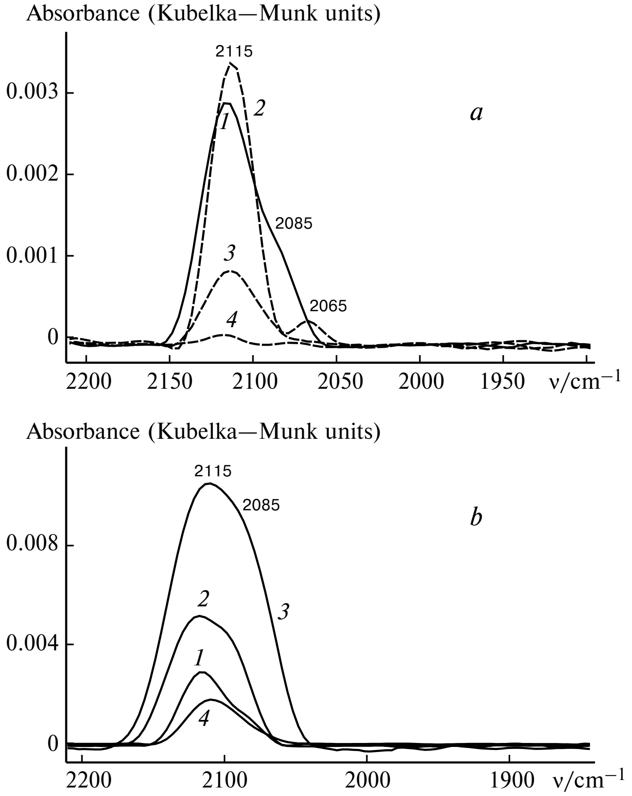

Fig. 1. IR spectrum of CO (30 Torr) adsorbed on the bulk Pt-HPC; *a*, Pt-HPC sample was oxidized at 470 K: before evacuation (*1*), after evacuation at 290 (*2*), 370 (*3*), and 470 K (*4*); *b*, oxidized at 470 (*1*), 520 (*2*), 570 (*3*), and 670 K (*4*).

To study the thermal stability of the bulk HPC, the temperature of oxidative treatment was successively increased from 470 to 520 and 570 K. As a result, the intensities of ABs at 2115 and 2085 cm^{-1} increased (Fig. 1, *b*). This effect is due to the complete removal of the structurally bound water with an increase in the treatment temperature from 470 to 570 K and the corresponding increase in the number of platinum cations accessible for CO adsorption. The further temperature increase to 670 K sharply decreases the intensity of the CO bands, which is likely related to the beginning of the thermal destruction of the HPC structure. In this case, the neighboring platinum atoms are aggregated to form polynuclear complexes, due to which the dispersity of the sites of CO adsorption decreases.

After the reductive treatment of the sample in an H_2 flow at 420 K, two broad bands with a complicated shape appear in the spectrum of the adsorbed CO (Fig. 2, *a*). One band with maxima at 2075, 2045, 2010, 1980, and 1920 cm^{-1} appears in the region characterizing the linear Pt^0—CO complexes (2090—1900 cm^{-1}).[19] The second

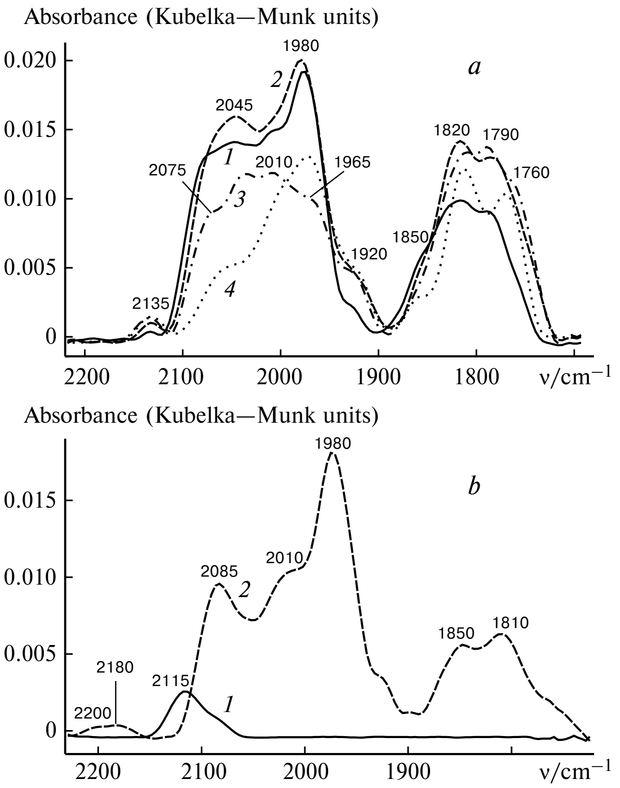

Fig. 2. IR spectrum of CO (30 Torr) adsorbed on the bulk Pt-HPC; *a*, Pt-HPC sample was reduced at 420 K (*1*) and then evacuated at 290 (*2*), 370 (*3*), and 420 K (*4*); *b*, oxidized (*1*) and reoxidized (*2*) at 470 K.

band is attributed to the bridged CO complexes (~1800 cm^{-1})[19] with maxima at 1850, 1820, 1790, and 1760 cm^{-1} corresponding to both two- and three-coordinated CO complexes with Pt^0. Commonly, platinum, unlike palladium, is not apt to form bridged CO complexes, and the ratio of the intensities for the linear and bridged forms substantially exceeds 2—3. However, in the case of the bulk platinum-containing HPC, this ratio is ~1.5. The unchanged positions of the bands upon thermal vacuum treatment at different temperatures (see Fig. 2, *a*, curves *2—4*) indicate that platinum retains its highly dispersed state under these conditions. The variety of peaks characterizing the linear forms of CO adsorption is related, first, to the nature of HPC and can be explained by the influence of the entire HPA framework and outer-sphere K$^+$ cations on Pt. The formation of the polycarbonyl Pt$_n$(CO)$_m$ complexes similar to the anionic Chini complexes previously found in zeolites cannot be excluded either.[22] The ABs at 2010 and 1980 cm^{-1} correspond to the most stable linear Pt^0—CO complexes, and the bands at 1820 and 1760 cm^{-1} correspond to the most stable bridged complexes. It is important that the reductive treatment of the sample does not result in the complete transition of platinum from the ionic to metallic form, which is indicated by the presence of the AB at 2135 cm^{-1} in the spectrum. This band can unambiguously be ascribed to the Pt$^+$—CO complexes.[19—21] Its shift by 20 cm^{-1} toward higher frequencies relatively to the analogous AB in the spectrum of the starting oxidized sample can indicate some changes in the nearest environment of platinum resulting in the stabilization of its charged form under the reductive conditions.

The oxidative treatment of the reduced sample at 470 K results in the appearance of the following bands in the IR spectrum of adsorbed CO (Fig. 2, *b*): the AB at 2200 cm^{-1} attributed to the linear CO complexes with Lewis acidic sites of the support,[12] the AB at 2180 cm^{-1} corresponding to the Pt^{2+}—CO complexes,[19] the AB at 2085 cm^{-1} characterizing the Pt^0—CO complexes, and the AB at 2010, 1980, and 1850, 1810 cm^{-1}, which can be ascribed to the linear and bridging CO species adsorbed on Pt^0. Thus, as follows from Fig. 2, *b*, platinum cannot completely be transformed into the initial ionic state by the reoxidation of the bulk system, and a new form of charged platinum species, *viz.*, Pt^{2+}, is formed instead of Pt$^+$. These data indicate the beginning of irreversible changes in the Pt-HPC structure during redox treatments already at ~470 K.

As follows from the detailed analysis of the spectra of the oxidized and reduced samples, the bands of CO adsorbed in both the linear and bridged forms are substantially shifted toward the low-frequency region compared to similar bands in the spectra of the Pt/Al$_2$O$_3$ and Pt/H-zeolite systems.[19,20] We have previously[12] observed a similar effect for potassium palladium-11-tungstosilicate, which is explained by the basic environment (formed by the K$^+$ ions and structural OH groups) of the platinum species resulting in the electron density redistribution in the nearest environment of Pt. A similar effect was also described[23] for CO adsorption on Pt zeolites modified by alkali metals. The position of the maximum of the CO band was concluded to correlate with the basic properties of the zeolite: the frequency of CO adsorbed in the linear form decreases in the series Pt/HY > Pt/HNaY > Pt/NaY > > Pt/NaX (Δν(CO) = 20 cm^{-1}) simultaneously with strengthening of the basicity of these systems. It has been found[24] that for Pt/H-mordenite calcined at 770 K and reduced at 370 K, CO adsorption in the presence of NH$_3$ results in the shifts of the AB at 2123 and 2092 to 2112 and 2080 cm^{-1}, which also confirms the influence of the basic properties of the catalyst on the position of the CO bands in the IR spectrum. Thus, the decrease in the CO vibration frequency with an increase in the charge on the O atom and, hence, in the basicity of the system for alkali metal salts of HPC can be explained by an increase in the inverse donating of electrons from Pt to CO due to the interaction of Pt with electron donors, being the negatively charged O atoms interacting with the alkali metal cations in the Keggin unit.

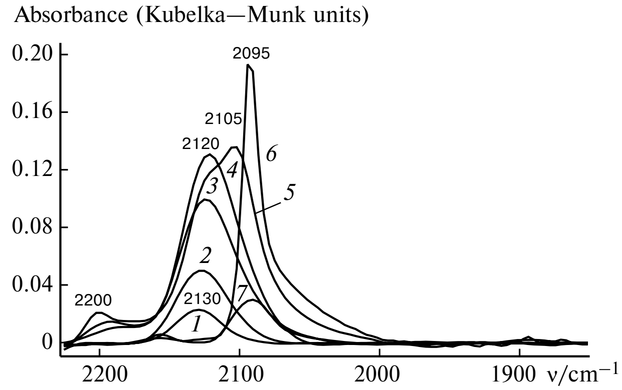

Fig. 3. IR spectrum of CO (30 Torr) adsorbed on the Pt-HPC/Al_2O_3 sample oxidized at 470 (*1*), 520 (*2*), 570 (*3*), 620 (*4*), 670 (*5*), 820 (*6*), and 920 K (*7*).

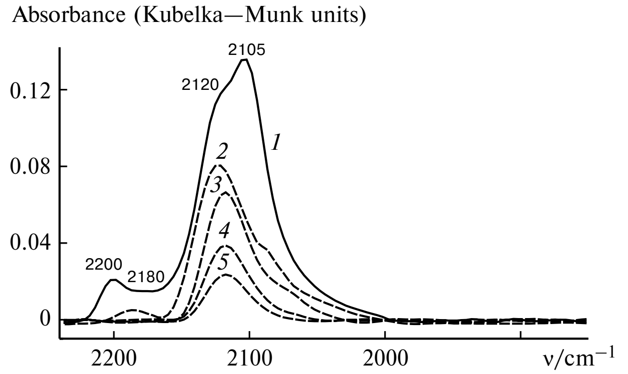

Fig. 4. IR spectrum of CO (30 Torr) adsorbed on the Pt-HPC/Al_2O_3 sample oxidized at 670 K: before evacuation (*1*) and after evacuation at 370 (*2*), 470 (*3*), 520 (*4*), and 570 K (*5*).

Supporting of the Pt-HPC on Al_2O_3 results in the appearance of the single AB at 2130 cm^{-1} in the spectrum of the sample oxidized at 570 K (Fig. 3, curve *1*). The behavior of this AB during the thermal vacuum treatment allows its unambiguous assignment to the Pt^+—CO complexes.[20,21] It is noteworthy that in the supported system the influence of the alkali K^+ cations on the electronic state of platinum is much weaker than that in the bulk HPC. This is manifested by the absence of the low-frequency shift of the band of adsorbed CO, unlike that of the bulk sample. Most likely, for monolayer HPC supporting, the outer-sphere K^+ cations form stronger bonds with the Al_2O_3 oxide surface than with the O atoms of the HPA lattice. Such an interaction favors the partial decrease in the basicity of the HPC and prevents the destruction of the HPC structure upon supporting. The increase in the oxidative treatment temperature from 470 to 620 K provides almost complete removal of the coordinatively bound water and, as a consequence, results in an increase in the intensity of the AB at 2130 cm^{-1}. The maximum of this band simultaneously shifts from 2130 to 2120 cm^{-1} (see Fig. 3, curves *2*—*4*).

The sample was subjected to the oxidative treatment at 670, 820, and 920 K to reveal the temperature limits of stability of the HPC structure in the $K_6[SiW_{11}PtO_{39}]/Al_2O_3$ system. In addition to the AB at 2120 cm^{-1} in the IR spectrum, a new AB (ν(CO) = 2105 cm^{-1}) with the same intensity and a low-intensity AB (ν(CO) = 2200 cm^{-1}) appear at 670 K (Fig. 3, curve *5*). The first of these bands is attributed to the Pt^0—CO complexes,[20,21] and the second band characterizes CO adsorption on the Lewis acid sites of the support.[12,19] Both types of the complexes are less stable than the Pt^+—CO complexes. The band at 2200 cm^{-1} disappears after thermal evacuation at 470 K, and the AB at 2105 cm^{-1} disappears at 520 K along with the appearance of the low-intensity AB at ~2075 cm^{-1} (Fig. 4). The Pt^+—CO complex manifests the highest thermal stability during the thermal vacuum treatment and is completely decomposed only at temperatures above 570 K. The position of the AB with ν(CO) = 2120 cm^{-1} remains unchanged (see Fig. 4). The oxidative treatment of the sample at 820 K qualitatively changes the spectral pattern (see Fig. 3, curve *6*): the spectrum is represented by a narrow intense band at 2095 cm^{-1}. This is caused by a change in the HPC structure, during which the system is transformed into the so-called "anhydride" state[25,26] caused by almost complete removal of the structurally bound water molecules. This state precedes the decomposition of the Keggin structure at higher pretreatment temperatures.[2] In this case, the high intensity of the band is explained by the liberation of an as large as possible number of the Pt sites, which are still in the highly dispersed state due to the fixed position in the HPC framework.

However, the subsequent temperature increase to 920 K more than fivefold decreases the intensity of the AB at 2095 cm^{-1} (see Fig. 3, curve *7*). The character of the spectral changes observed at 920 K indicates irreversible changes in the HPC structure accompanied by the formation of the PtO_2 phase, which is transformed into the PtO particles. The intense aggregation of metallic particles sharply decreases the number of platinum sites accessible for CO adsorption.

In order to study the possibility of regeneration of the supported $K_4[SiW_{11}PtO_{39}]/Al_2O_3$ system after its operation in a reductive medium, we carried out three redox cycles at different temperatures. The temperature of 570 K was chosen for the first cycle. We found that the HPC structure is stable at this temperature under the oxidative conditions. The reductive treatment of the oxidized sample favors the appearance of ABs at 2090 and 1850 cm^{-1} attributed to the linear and bridged CO complexes with metallic platinum,[19—21] respectively (Fig. 5). The subsequent reoxidation treatment at 570 K results in an approximately twofold decrease in the intensities of the ABs at 2090 and 1850 cm^{-1} and appearance of the AB at 2125 cm^{-1} characteristic of the spectrum of the oxidized

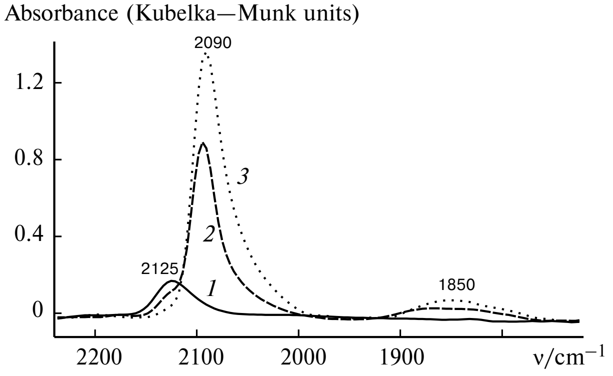

Fig. 5. IR spectrum of CO (30 Torr) adsorbed on the Pt-HPC/Al_2O_3 sample oxidized (*1*), reduced (*2*), and reoxidized (*3*) at 570 K.

sample. We failed to completely oxidize the reduced sample by increasing the time of the reoxidative treatment to 5 h, which indicates that platinum is transformed into a new state likely due to changes in the HPC structure in a reductive medium. However, the observed tendency of decreasing the amount of reduced platinum suggests the possibility of complete reversibility of the properties of the system upon reoxidation in a longer time scale or under more severe conditions (for example, in the presence of water vapor).

The next redox cycle was carried out at 670 K. The reduction of the preoxidized sample in an H_2 flow results in the disappearance of the spectral bands characterizing CO adsorption on charged platinum. Simultaneously the ABs with frequencies of 2075 and 2025 cm^{-1}, as well as 1850 and 1800 cm^{-1}, appear in the spectrum (Fig. 6, *a*). Two first AB are attributed to linear CO adsorption on Pt^0. However, the position of the AB at 2025 cm^{-1} indicates that the nearest environment of some platinum species contains K^+ cations enhancing the basicity of the system. Two other bands characterize the two- and three-coordinated bridged adsorption of CO on metallic platinum. The intense bands at 2125 and 2105 cm^{-1} appear in the spectrum (Fig. 6, *b*) due to the reoxidative treatment. A comparison of the data obtained with the spectrum of the primarily oxidized sample suggests the following. First, the AB at 2125 cm^{-1} corresponding to the Pt^+—CO complexes is almost completely reproduced upon reoxidation. Second, the spectrum of the reoxidized sample contains a very intense (compared to that of the oxidized sample) AB at 2105 cm^{-1} assigned to the linear Pt^0—CO complexes. This suggests that the metallic platinum sites in the supported HPC are retained upon the redox cycles at temperatures below 670 K.

The third redox cycle was carried out at the temperature corresponding to the beginning of destruction of the supported HPC to give the spectral pattern substantially different from those described previously. The spectrum of the sample oxidized at 920 K contains the highly intense AB at 2095 cm^{-1} (linear Pt^0—CO complexes) corresponding to the main state of the metal in the sample and the AB at 2155 cm^{-1} indicating the presence of the ionic form of platinum, possibly, Pt^{2+} (Fig. 7). The reductive treatment at 670 K induces a band at 2145 cm^{-1} (Pt^+—CO complexes), an AB at 2080 cm^{-1} with a shoulder at 2045 cm^{-1}, and an AB at 1990 cm^{-1} (all these AB characterize the linear Pt^0—CO complexes). As a result of

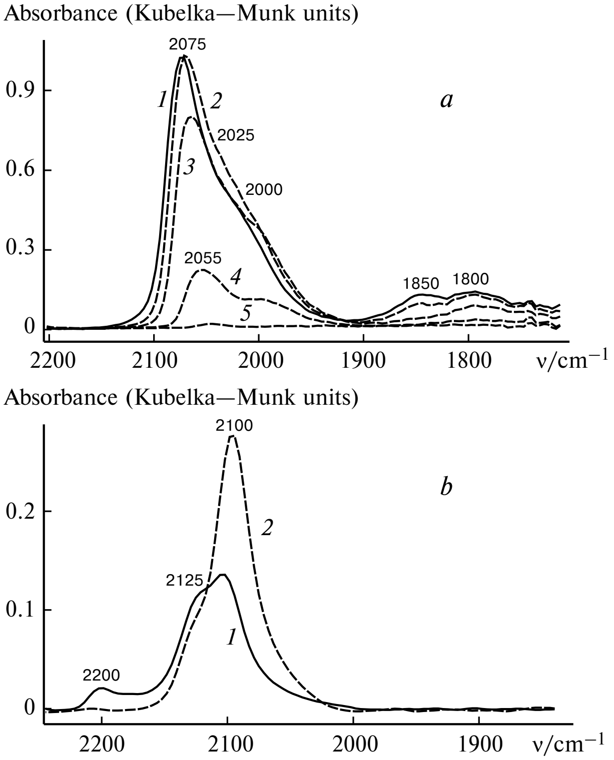

Fig. 6. IR spectrum of CO (30 Torr) adsorbed on the Pt-HPC/Al_2O_3 sample; *a*, Pt-HPC/Al_2O_3 sample was reduced at 670 K: before evacuation (*1*), after evacuation at 290 (*2*), 370 (*3*), 470 (*4*), and 570 K (*5*); *b*, oxidized (*1*) and reoxidized (*2*) at 670 K.

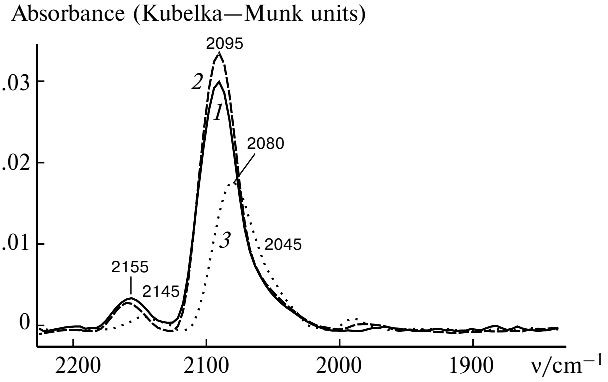

Fig. 7. IR spectrum of CO (30 Torr) adsorbed on the Pt-HPC/Al_2O_3 sample oxidized at 920 K (*1*), reduced at 670 K (*2*), and reoxidized at 920 K (*3*).

reoxidation at 970 K, the AB at 2155 and 2095 cm^{-1} are reproduced simultaneously with the appearance of a low-intensity AB at 1970 cm^{-1} resulted from the adsorption of CO on Pt^0 in the linear form). The findings in the third redox cycle (*viz*., a change in frequencies for adsorbed CO, an approximately twofold decrease in the intensity of the AB corresponding to reduced platinum compared to the AB of oxidized platinum, and the presence of the bridged CO complexes with Pt^0 in the reoxidized sample) indicate unambiguously the irreversible decomposition of the HPC structure and transition of platinum to a different state with a decrease in dispersion.

Thus, the study of the bulk $K_4[SiW_{11}PtO_{39}]$ system and similar HPC supported on γ-Al_2O_3 led us to conclude the following.

— Electronic state of platinum in the oxidized bulk sample corresponds to Pt^+ and Pt^0, and that in the reduced sample is Pt^0. The bulk HPC exhibits a low thermal stability at temperatures above 470 K.

— Supporting of the HPC on γ-Al_2O_3 results, most likely, in a strong interaction of the active phase with the support, weakening the influence of the outer-sphere K^+ cations on the electronic state of platinum. Under the oxidative conditions, the supported system is much more thermally stable than the bulk analog.

— Electronic state of platinum in the supported system depends, to a great extent, on the treatment temperature. For example, the main state is Pt^+ in the system oxidized in the 470 to 620 K temperature interval, oxidation at $T > 620—670$ K produces Pt^0 and Pt^+, whereas an increase in the treatment temperature to 820 K and above results in the stabilization of platinum in the single Pt^0 form.

The data obtained confirm the previous conclusion[12] that the synthesis of mixed HPC with the Keggin structure allows one to prepare inorganic complexes with platinoid ions stabilized by the oxygen environment. The enhanced stability of the supported HPC in the redox cycles at high temperatures opens new avenues for acid-type catalytic reactions mediated by the HPC-based highly dispersed platinoids.

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