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IR spectroscopic investigation of structural hydroxyl groups in W—Si heteropolycompound supported on Al_2O_3

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Structural hydroxyl and deuteroxyl groups within the $K_4[SiW_{12}O_{40}]/Al_2O_3$ and $K_6[SiW_{11}PdO_{39}]/Al_2O_3$ systems were studied by diffuse-reflectance FTIR spectroscopy in a spectral range of fundamental stretching vibrations, first overtones, and combination bands of stretching and bending vibrations. For hydroxyl groups, the region of combination vibrations is the most informative. The calculated frequencies of bending vibrations of hydroxyl groups (865 and 730 cm^{-1}) are characteristic of acidic OH groups.

Key words: diffuse-reflectance FTIR spectroscopy, hydroxyl groups, W—Si heteropolycompound, combination vibrations, bending vibrations of OH groups.

Heteropolycompounds (HPC) are widely used as catalysts.[1,2] Activity of these systems is usually explained by the presence of Brönsted acid sites, OH groups associated with oxide polyhedra that form Keggin structure.[3]

IR spectroscopy remains the most informative method for studying structural OH groups in heterogeneous catalysts. In studies of the acidic properties of oxide systems, IR spectra are usually recorded in the region of fundamental stretching vibrations of the O—H bond. IR spectra of supported HPC and other catalysts with strong acid properties[4] are, as a rule, a superposition of broad lines, and the problem of differentiation of sites of different nature and strength is often difficult. Measurements of IR spectra in the region of combination bands of stretching and bending vibrations of structural OH groups (4000—5000 cm^{-1}) or overtones of stretching vibrations of the O—H bond (6500—7500 cm^{-1}) were found to be more efficient.[5] This approach is especially applicable for heterogeneous catalysts that are characterized by broad unresolved IR spectra in the region of fundamental stretching vibrations of OH groups.

This method has previously been successfully used for studying structural OH groups of laminated clays pillared by Al_2O_3 and SiO_2 columns[6] and some unstable forms of zeolites.[7] In this work, a similar approach was extended to tungsten-silicon HPC: $K_4[SiW_{12}O_{40}]$ and $K_6[SiW_{11}PdO_{39}]$ supported on aluminum oxide.

Experimental

Tungsten-silicon HPC were used for the preparation of samples: $K_4[SiW_{12}O_{40}]$ (reagent grade, Krasnyi Khimik Co., St. Petersburg) and $K_6[SiW_{11}PdO_{39}]$ synthesized by the known procedure.[8] Chemical analysis of potassium palladium-11-tungstosilicate was performed by atomic-absorption spectrophotometry. Found (%): WO_3, 78.95; SiO_2, 1.74; PdO, 3.7; K_2O, 8.61; H_2O, 7.0. Calculated (%): WO_3, 79.36; SiO_2, 1.87;

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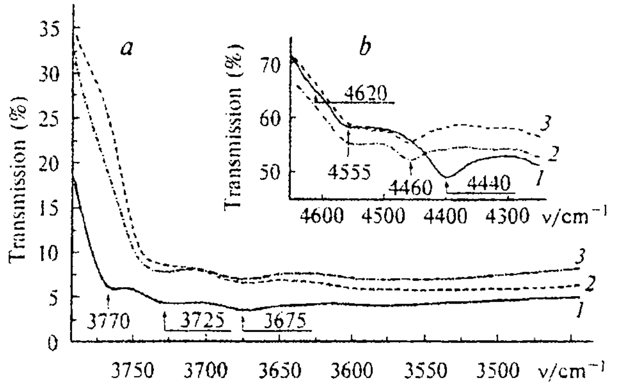

Fig. 1. IR spectra of hydroxyl groups of Al_2O_3 (*1*), $K_6[SiW_{11}PdO_{39}]/Al_2O_3$ (*2*), and $K_4[SiW_{12}O_{40}]/Al_2O_3$ (*3*) in the region of stretching (*a*) and combination bands of stretching and in plane bending vibrations (*b*).

PdO, 3.81; K_2O, 8.8; H_2O, 6.16. Spectral analysis of $K_6[SiW_{11}PdO_{39}]$ in the region of vibrations of Me—O bonds revealed the following bands characteristic of Si—W—HPC of the 12th row[1] (v/cm^{-1}): 990 (W=O); 938 (Si=O); 896 (W—O—W); 784 (W—O—W). γ-Al_2O_3 (S_{sp} = 240—250 m^2 g^{-1}) was chosen as a support. Pellets of Al_2O_3 (0.2—0.5 mm) were dried in air for 2 h at 393 K and impregnated with aqueous solutions of HPC, exposing them to the solution for 2 h at 365 K. Then the solution was concentrated, and the pellets were dried for 4 h at 373 K and calcined for 2 h in an air flow at 673 K. The content of HPC in the supported systems was 30 wt.%.

Before spectral studies, HPC samples were evacuated at 673 K, and the Al_2O_3 was evacuated at 723 K for 2—5 h directly in a quartz IR cell with a CaF_2 window. For preparation of deuterated samples, the supported systems were treated with C_6D_6 or D_2O vapor at 373—473 K followed by evacuation at 673 K to a residual pressure of 10^{-4} Torr.

IR spectra were recorded in the diffuse-reflectance mode with a Nicolet Impact 410 FTIR spectrometer according to known procedure.[9] Diffuse-reflectance FTIR spectra were processed using the OMNIC® program.

Results and Discussion

The IR spectra of the initial Al_2O_3 carrier and samples containing supported $K_4[SiW_{12}O_{40}]$ and $K_6[SiW_{11}PdO_{39}]$ are presented in Fig. 1. The spectra in the fundamental region are a superposition of poorly resolved absorption bands, and their maxima can hardly be determined. By contrast, resolved lines are observed in the region of combination bands, which evidently correspond to specific types of isolated structural OH groups.

The spectrum of the initial γ-Al_2O_3 sample in this region is presented by three bands with maxima at 4400, 4555, and 4620 cm^{-1}. The low-frequency band with a frequency of 4400 cm^{-1} is attributed to the terminal OH groups associated with the octahedrally coordinated aluminum ions.[10,11] The frequency of the in plane bending vibration for this type of OH groups calculated as a difference of frequencies of the combination (4400 cm^{-1}) and fundamental stretching (3770 cm^{-1}) vibrations[5,12] is equal to 630 cm^{-1}. The band of the fundamental stretching vibration with a maximum at 3725 cm^{-1} attributed to terminal OH groups related to tetrahedrally coordinated aluminum atoms corresponds, most likely, to the band of the combination vibration at 4555 cm^{-1}.[10,11] The frequency of bending vibrations δ for this type of OH groups is equal to 830 cm^{-1}. A low-intensity band at 4620 cm^{-1} can be attributed to bridging hydroxyl groups with a frequency of the fundamental stretching vibration of 3675 cm^{-1}.[11] In this case, the estimate of the frequency of the bending vibration gives 945 cm^{-1}.

According to previous data,[5—7,12] the frequency of bending vibrations of the isolated structural OH groups is a reliable characteristic of the acid properties of Brönsted acid sites. For OH groups of similar type with identical coordination of the metal ion to oxygen, an increase in the frequency of the bending vibration is directly related to an enhancement of the acid properties of the OH groups. Correspondingly, the acid properties of bridging OH groups are more pronounced than those of terminal OH groups, and the proton-donating ability of the OH groups associated with the tetrahedral Al atoms is higher than that of the terminal hydroxyl groups localized at the octahedrally coordinated Al atoms.

The weakest acid OH groups disappeared after tungsten-silicon HPC were supported on Al_2O_3. Among them are OH groups of the terminal type that are bound to octahedrally coordinated Al atoms, *i.e.*, the strongest basic OH groups. Probably, reactions, due to which the heteropolycompound is grafted on the support surface, occur on the Al_2O_3 surface between the OH groups of Al_2O_3 and the supported heteropolycompound. In the region of combination bands, an additional, sufficiently intense narrow band with a maximum at 4460 cm^{-1}

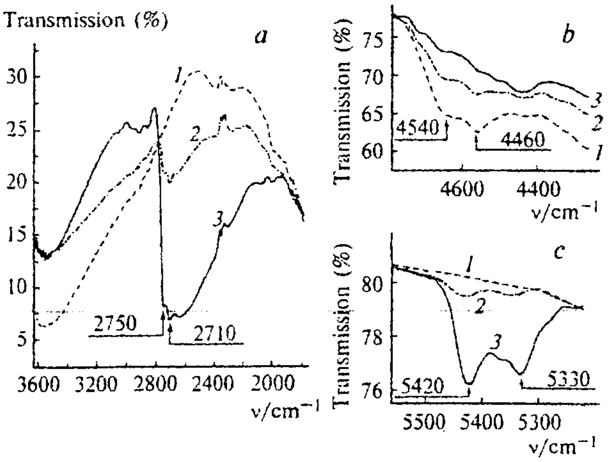

Fig. 2. IR spectra of hydroxyl (*1*) and deuteroxyl groups of $K_6[SiW_{11}PdO_{39}]/Al_2O_3$ after treatment with D_2O (*2*) and C_6D_6 (*3*) vapor. *a*, Region of fundamental stretching vibrations; *b*, region of combination bands of stretching and bending vibrations; and *c*, region of the first overtone of stretching vibrations.

appears simultaneously and can be assigned to isolated OH groups associated with the supported heteropolycompound. These are most likely OH groups of the terminal type localized at tungsten ions, which are in the Keggin structure. In addition, the spectra of the modified systems contain a band with a frequency of 4550 cm^{-1}. The intensity of this band increases as compared to that of the band at 4555 cm^{-1} in the spectrum of the starting support. This band can be attributed either to terminal Al—OH groups or OH groups bound to HPC.

Unfortunately, the spectra in the region of stretching vibrations of OH groups for supported HPC represent unresolved superposition of bands, and it is impossible to distinguish isolated narrow lines from this superposition. Therefore, the frequency of bending vibrations of OH groups can not be calculated, because the frequencies of the fundamental stretching vibrations, which could unambiguously be assigned to the corresponding bands in the region of combination frequencies, are unknown. To find these frequencies, the catalyst surfaces were deuterated using C_6D_6 and D_2O as deuterating agents. To avoid deep degrees of exchange, deuteration was carried out under sufficiently mild conditions. The spectra obtained in the region of fundamental stretching vibrations of OD groups and the first overtone of stretching vibrations of OD groups are presented in Fig. 2. Analysis of the spectra makes it possible to unambiguously attribute the absorption bands in the region of combination vibrations at 4550 and 4460 cm^{-1} to bands in the regions of fundamental stretching vibrations of OD groups with maxima at 2710 and 2750 cm^{-1} and first overtones of deuteroxyl groups at 5330 and 5420 cm^{-1}, respectively. Using the isotopic coefficient (1.357), one can find the frequencies of the fundamental stretching vibrations of the O—H bond. The frequency ν(OH) 3675 cm^{-1} corresponds to ν(OD) 2710 cm^{-1}, and ν(OH) 3730 cm^{-1} corresponds to the frequency ν(OD) 2750 cm^{-1}. In this case, the frequencies of bending vibrations of these two types of hydroxyl groups are equal to 875 cm^{-1} (4550—3675) and 730 cm^{-1} (4460—3730). These frequency values indicate that OH groups of the first type exhibit sufficiently strong acidic properties, whereas hydroxyl groups of the second type are moderate acidic sites.

Thus, hydroxyl groups in heteropolycompounds supported on Al_2O_3 and other supports can be characterized by the spectra in the near-IR region including combination frequencies of stretching and bending vibrations.

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