Investigation of the state of palladium in the $Pd/SO_4/ZrO_2$ system by diffuse-reflectance IR spectroscopy

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The Pd/ZrO_2 and $Pd/SO_4/ZrO_2$ systems were investigated by diffuse-reflectance IR spectroscopy using CO as the probe molecule. For the Pd/ZrO_2 system, the behavior of the metal is characteristic of the weak metal—support interaction. Intense bands attributed to the bridging CO species indicate the formation of large metal particles in the reduced systems. Modification of the ZrO_2 support with SO_4^{2-} anions leads to an increase in the metal—support interaction and makes the metal more resistant to reduction. On the surface promoted by SO_4^{2-} anions, metal particles with a positive charge (Pd^+ and $Pd^{\delta+}$) were observed. The smaller the size of the metal clusters and the higher degree of oxidation of sulfur, the stronger the influence of acidic protons and surface sulfur compounds on the metal.

Key words: palladium, zirconia, superacids, metal—support interaction; diffuse reflectance IR spectroscopy.

The study of the nature of the metal—support interaction in the SO_4/ZrO_2 systems promoted by transition metals is of great importance for the explanation of catalytic properties of solid superacids. Data on physicochemical and catalytic properties of the systems based on VIII Group metals such as Pd, Rh, Os, Ir, and Ni supported on sulfated zirconia are almost nonexistent, although it has been established that they can be used in catalysis.[1–3]

In previous works,[4–6] we have studied the $Pt/SO_4/ZrO_2$ and $Rh/SO_4/ZrO_2$ systems by diffuse-reflectance IR spectroscopy and shown that the superacidic support stabilizes charged forms of the metal and makes the reduction of the metal ions difficult. In this work, we studied the metal—superacidic support interaction in the $Pd/SO_4/ZrO_2$ system at different metal concentrations and reduction temperatures by diffuse-reflectance IR spectroscopy using CO as the probe. The Pd/ZrO_2 system without superacidic properties was studied for comparison.

Experimental

Preparation of Pd/ZrO_2. The Pd/ZrO_2 samples were prepared by impregnation of the starting $Zr(OH)_4$ (Magnesium Electron Co., XZ0706/03, S_{sp} = 150 m^2 g^{-1}) with an aqueous solution of $PdCl_2$ to the Pd concentration of 0.5 wt.%. The catalyst was dried at 393 K for 6 h and calcined in a flow of dry air at 793 K for 2 h.

Preparation of $Pd/SO_4/ZrO_2$. Samples of the catalyst were prepared according to standard procedures[1–4,6] by impregnation of $Zr(OH)_4$ with a 1 *N* aqueous solution of H_2SO_4 to the concentration of SO_4^{2-} equal to 5 wt.%. The samples were dried at 393 K for 2 h and calcined at 873 K for 2 h. Palladium (0.1, 0.5, or 2.5 wt.%) from an aqueous solution of $PdCl_2$ was supported on the samples. The catalyst was dried at 393 K for 6 h and calcined in an air flow at 673 K for 2 h.

Samples with a grain size of 0.2—0.5 mm were placed in a quartz reactor with a CaF_2 window for recording IR spectra and activated at 673 K in a vacuum for 1 h. Then the samples were treated with O_2 (30 Torr) at 673 K to prevent the possible reduction of Pd and SO_4^{2-}. To obtain the reduced form of palladium, the activated samples (0.5 g) were treated in an H_2 flow (30 mL min^{-1}) for 373—573 K for 2 h, evacuated at 473 K to the residual pressure of 10^{-4} Torr, and cooled to room temperature.

Measurement of IR spectra. Pre-evacuated samples were treated with CO (20 Torr). IR spectra were recorded on a Perkin—Elmer 580B spectrophotometer with a diffuse-reflectance attachment.[7] After the measurement of the spectrum, the sample was evacuated with a stepped temperature increase with an increment of 50 K recording the spectra for each *T* value. The spectra were quantitatively processed using the Kubelka—Munk (KM) equation according to previously suggested procedures.[8,9]

Results and Discussion

The analysis of published data shows that the state of ZrO_2-supported palladium was insufficiently studied. Therefore, the study of the state of the metal in the Pd/ZrO_2 system containing no SO_4^{2-} anions was the first stage of our work.

The IR spectra of CO adsorbed on the Pd/ZrO_2 samples (oxidized and reduced at 470 K) are presented in Fig. 1. The adsorption of CO (20 Torr) on the oxidized sample results in the appearance of the ν(CO)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 57—61, January, 1998.

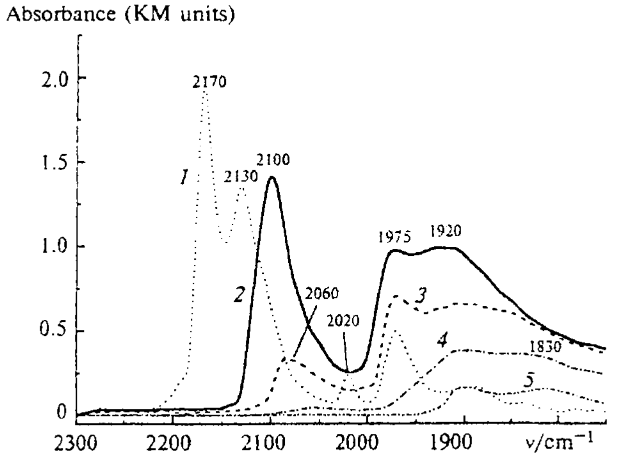


Fig. 1. IR spectra of CO (20 Torr) adsorbed on the Pd/ZrO_2 samples: oxidized (*1*) and reduced at 470 K before (*2*) and after evacuation at 300 (*3*), 370 (*4*), and 470 K (*5*).

absorption bands (AB) in the IR spectra at 2170, 2130, 2020, 1970, and 1890 cm^{-1} (see Fig. 1, spectrum *1*). The position of the bands at 2170 and 2130 cm^{-1} and their behavior during the thermal vacuum treatment allow one to assign them to linear CO complexes with the Pd^{2+} and Pd^{+} ions, respectively, which is in accord with the published data.[10—12] The band at 2020 cm^{-1} cannot be attributed to linear CO complexes with the Pd^0 particles, because the frequency of vibrations of the adsorbed CO is considerably lower than that observed for the adsorption on the Pd/Al_2O_3 systems (ν(CO) 2070—2100 cm^{-1}).[10] Therefore, this band can correspond to the antisymmetrical vibration of CO in the $Pd^{+}(CO)_2$ complex, and the AB of the symmetrical vibration is overlapped by the intense ν(CO) band at 2110—2130 cm^{-1}. The bands at 1970 and 1890 cm^{-1} likely correspond to the bridging CO species in the complexes with the Pd^0 metal particles (see Refs. 11 and 12).

When the temperature of evacuation increases during removal of CO, the intensity of AB characterizing the vibrations of CO adsorbed on the Pd^0 metal particles increases. This can indicate reductive processes facilitating an increase in the fraction of the reduced metal. The treatment of the samples in an H_2 flow at 370 K results in the complete reduction of the metal on the ZrO_2 surface. This is evidenced by the disappearance of the bands that characterize the charged forms of palladium from the spectra.

The spectral pattern remains unchanged after the reduction of the samples at 470 K (see Fig. 1, spectra *2*—*5*). The spectrum of CO adsorbed on reduced Pd/ZrO_2 contains three main ν(CO) AB at 2100, 1975, and 1920 cm^{-1}. The position of the high-frequency AB makes it possible to attribute it to CO adsorbed in a linear form on the Pd^0 metal particles.[13] During evacuation, when the temperature increases stepwise, the position of the maximum of this band is shifted to 2060 cm^{-1}, and the band disappears after evacuation at $T > 370$ K. The bands at 1975 and 1920 cm^{-1} are attributed to the bridging CO species in the complexes with the metal particles.[11,12] These bands are more stable and observed in the spectrum even after evacuation at 500 K. A new band at 1830 cm^{-1} appears during evacuation: first, as a shoulder and then as a resolved band. It can be assigned to the three-centered form of the CO adsorption, which is typical of Pd particles.[11,12]

Thus, the behavior of the metal in the Pd/ZrO_2 system is typical of weak metal—support interaction which is observed in the systems similar to Pd/SiO_2.[14—16] The presence of intense bands characterizing polydentate-coordinated CO molecules can indicate the formation of large metal particles in the reduced systems. These particles can appear in the oxidized samples.

The introduction of the SO_4^{2-} anions in the system results in significant changes in the spectrum and, hence, in the state of the metal on the surface. The IR spectra of CO adsorbed on the 0.5% $Pd/SO_4/ZrO_2$ samples (oxidized and reduced at 370, 470, and 570 K) are presented in Fig. 2. The spectrum of CO adsorbed on 0.5% $Pd/SO_4/ZrO_2$(ox) (see Fig. 2, spectrum *1*) contains the ν(CO) AB at 2170 cm^{-1} with shoulders at 2205 and 2140—2130 cm^{-1} and two bands with frequencies less than 2000 cm^{-1}: ν(CO) 1980 and 1910 cm^{-1}. According to the published data,[4,6,17] the shoulder at 2205 cm^{-1} can characterize the vibrations of CO adsorbed on the SO_4/ZrO_2 surface. The high intensity of the AB at 2170 cm^{-1} indicates that Pd^{2+} is the main state of the metal on the oxidized sample surface. At the same time, the presence of AB with frequencies less than 2000 cm^{-1} is evidence for particles of the metal characterized by the formation of CO-bridged complexes.

The treatment of the system with an H_2 flow at 370 K results in the partial reduction of Pd, which is accompanied by the corresponding changes in the spectrum (see Fig. 2, spectrum *2*). After the adsorption of CO, the ν(CO) AB at 2150 cm^{-1} with the shoulder at

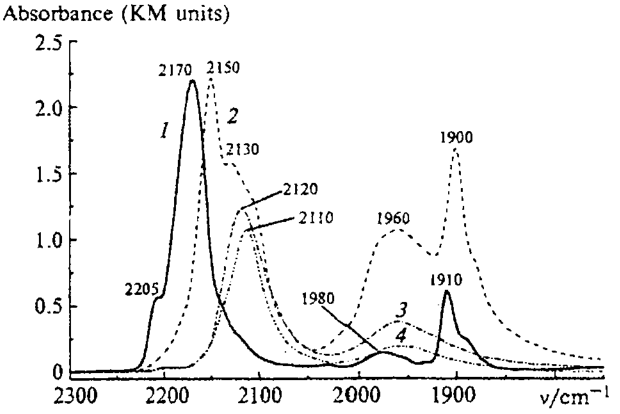


Fig. 2. IR spectra of CO (20 Torr) adsorbed on the 0.5% $Pd/SO_4/ZrO_2$ samples: oxidized (*1*) and reduced at 370 (*2*), 470 (*3*), and 570 K (*4*).

2130 cm^{-1} and two bands in the frequency region of vibrations of bridging carbonyls (broad at 1960 cm^{-1} and narrow at 1900 cm^{-1}) are observed. The analysis of the IR spectrum allows one to conclude that Pd^{2+} is absent; however, a considerable amount of Pd^+ is present in the system, that is evidenced by the high intensity of AB at 2150 cm^{-1}. At the same time, metal particles are formed, which is characterized by an increase in the intensity of AB of the bridging forms of CO adsorbed on the metal particles, (ν(CO) 1960 and 1900 cm^{-1}) and the appearance of a new AB at 2130 cm^{-1}.

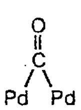
The increase in the reduction temperature to 470 K (see Fig. 2, spectrum *3*) results in the complete disappearance of the positively charged forms of the metal (Pd^{2+} and Pd^+). The band at 2120 cm^{-1} attributed to a linear complex of CO with the metal particles and the band at 1960 cm^{-1} corresponding to bridging carbonyls are observed in the IR spectrum. The further increase in the reduction temperature (see Fig. 2, spectrum *4*) does not change the whole spectral pattern, however, some decrease in the intensity of all AB is observed. All forms of the adsorbed CO are not stable, and they are removed after evacuation at 290 K.

Thus, the SO_4/ZrO_2-supported palladium particles possess high resistance to reduction as compared to the systems supported on the starting ZrO_2. Let us consider the differences in the spectral behavior of CO adsorbed on the Pd/ZrO_2 and Pd/SO_4/ZrO_2 systems to explain the reason for this phenomenon and determine the degree of the influence of the sulfated surface on the metal. In the region of vibrations of the bridging forms of CO adsorbed on the 0.5% Pd/ZrO_2(ox) system, the intensity of AB at 1970 cm^{-1} is higher than that of AB at 1920 cm^{-1}; the spectra of the sulfur-containing samples exhibit an increase in the intensity of AB at 1900 cm^{-1} as compared to the band at 1960 cm^{-1}, and the low-frequency AB does not appear at all.

After the reduction of the SO_4^{2-}-containing samples at 470 K, the band of CO adsorbed in the linear form on the metal particles is shifted by 15—20 cm^{-1} to high frequencies relative to the AB observed for the nonmodified sample. The position of the maximum of this band (ν(CO) 2120—2110 cm^{-1}) is higher than the frequencies characteristic of the surface Pd^0—CO complexes but lower than the frequencies of vibrations of CO in the Pd^+—CO complex. In the region of vibrations of the bridging forms of CO adsorbed on 0.5% Pd/SO_4/ZrO_2, the spectral pattern depends on the reduction temperature: two AB at 1960 and 1900 cm^{-1} for the systems reduced at 370 K and only one broad band at 1960 cm^{-1} for the samples treated in an H_2 flow at higher temperatures. The Pd/ZrO_2 system is characterized by three ν(CO) AB at 1975, 1920, and 1830 cm^{-1} at any reduction temperature.

First, let us consider the reasons for the change in the position of the maximum of the absorption band of CO adsorbed in the linear form. It is known that the shift of the frequencies of CO adsorbed on metals is due to electronic and geometrical factors.[18] The geometrical effect is related to an increase in the size of metal clusters, which results in the high-frequency shift of the band as the coverage of the surface with molecules increases. The electronic effect is caused by the chemical interaction of metal atoms with the active centers of the support surface. It is difficult to explain the shift of the frequencies for linear carbonyls by geometrical factors in the case of the SO_4^{2-}-promoted samples. For large particles, which are characterized by higher frequencies of the CO vibrations at a considerable coverage of the surface, the shift of the bands to low frequencies is observed as the coverage of the metal surface by adsorbed molecules increases due to weakening of the dipole-dipole interaction. This phenomenon is pronounced for the Pd/ZrO_2 sample (see Fig. 1), for which the bands of both the linear and bridging forms of the adsorbed CO are shifted to low frequencies by 15—25 cm^{-1} due to evacuation with a stepped temperature increase leading to a decrease in the coverage. The SO_4^{2-}-promoted samples are characterized by a sharp decrease in the intensity of the bands, while the shifts of the maxima corresponding to the linear form of adsorption are not substantial.

Thus, we can conclude that the electronic factor related to the interaction between the metal clusters and the support surface is mainly responsible for the shift of the positions of the absorption maxima of CO adsorbed on Pd/SO_4/ZrO_2 system relative to the position of the bands in the spectrum of Pd/ZrO_2. The direct contact of active centers of the SO_4/ZrO_2 surface with the metal particles should be expected during this interaction. This is confirmed by the IR spectra of the adsorbed CO. Let us consider the behavior of AB, which characterize the bridging forms of CO adsorbed on the metal particles. Three types of bridged complexes between CO and the palladium surface are known:[11—13]



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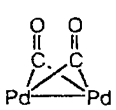

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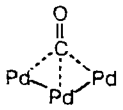

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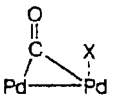
The ν(CO) AB at 1890—1920, 1975—1960, and 1830 cm^{-1} in the IR spectra correspond to complexes **1—3**, respectively. At low reduction temperatures, Pd/SO_4/ZrO_2 is characterized by the presence of complexes **1** and **2**, and only complex **2** is present at higher temperatures. This can be reasoned by the partial shielding of adsorption centers on the metal surface. In this case, the formation of the complex of type **3** is suppressed, and surface compound **4** is formed instead of complexes **1** and **2**, where a fragment of the active center of the SO_4/ZrO_2 surface can act as X. The frequency of the vibration of the C—O bond in complex **4** is higher than the ν(CO)



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values characteristic of normal bridging forms of type **1**, and approaches the frequencies of the CO vibrations in complex **2**.

The structure and properties of the active centers on the SO_4/ZrO_2 surface should be considered to elucidate the nature of shielding groups. Based on the IR spectral data, we have previously suggested two probable structures of the active centers, which can possess both strongly acidic and redox properties.[17,19] Therefore, two types of the interaction of metal particles with the surface centers of the support are possible. In the first case, metal microparticles can interact with strongly acidic protons of the surface to form adducts of the $[Pd-H]^{\delta+}$ type. In the second case, a chemical reaction with the surface SO_4 groups is possible. The previous studies showed that in the case of the $Pt/SO_4/ZrO_2$ system, the first type of the interaction takes place, while the effect of the second type is weaker and manifests itself at the reduction temperature >620 K.[4] For the $Rh/SO_4/ZrO_2$ system, the second type of the interaction is likely more preferable and appears at lower temperatures.[6]

It is noteworthy that the effect of protons occurs mainly at the metal—support interface and is maximum for metal microparticles, while the interaction with the surface SO_4 groups can also change the behavior of the larger particles. When the SO_4/ZrO_2 system is reduced by hydrogen, several parallel redox processes can occur at the surface. During one of these processes, the surface SO_4 groups are reduced by hydrogen to form several compounds containing sulfur in degrees of oxidation from 4+ to 2− (see Refs. 4, 20, and 21). The surface $S^0{}_{surf}$ species, which is mobile and can migrate to the metal particles, appears due to the deep reduction of the SO_4 groups. The product of the deeper reduction (H_2S) can also interact with the surface of the metal particle to form PdS.

Systems with different metal concentrations were studied to investigate the nature of the effect of the active centers of SO_4/ZrO_2 on the state of the metal.

The IR spectra of CO adsorbed on the $Pd/SO_4/ZrO_2$ samples containing 0.1, 0.5, and 2.5 wt.% Pd reduced at 470 K are presented in Fig. 3. The spectrum of CO adsorbed on Pd/ZrO_2 is presented for comparison.

The spectra of CO adsorbed on the 0.1% $Pd/SO_4/ZrO_2$ sample (see Fig. 3, spectrum *2*) contain the ν(CO) AB at 2200 and 2140 cm^{-1} and a broad low-intensity absorption in the regions of 1900—1980 cm^{-1}. The first AB is characteristic of the CO molecules interacting with the support surface, while the other bands are related to the surface CO complexes with the metal and can indicate strong metal—support interaction. This spectral pattern testifies that the metal is almost completely prone to the effect of the active centers on the SO_4/ZrO_2 surface.

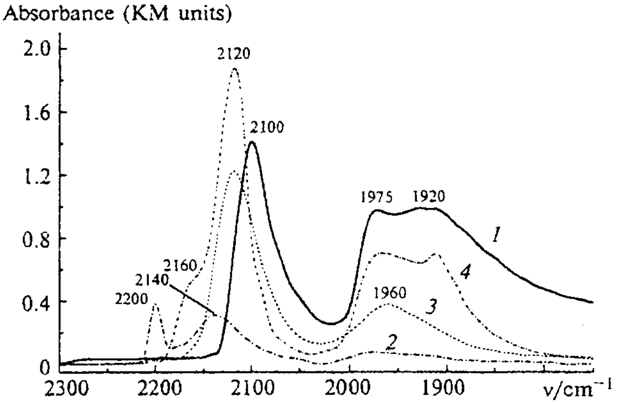

Fig. 3. IR spectra of CO (20 Torr) adsorbed on the 0.5% Pd/ZrO_2 (*1*), 0.1% $Pd/SO_4/ZrO_2$ (*2*), 0.5% $Pd/SO_4/ZrO_2$ (*3*), and 2.5% $Pd/SO_4/ZrO_2$ (*4*) samples reduced at 470 K.

The increase in the metal concentration to 0.5 wt.% (see Fig. 3, spectrum *3*) results in weakening of the effect of the support (expressed as the shift of the maximum of AB), which is characteristic of CO adsorbed in the linear form, to low frequencies (ν(CO) 2120 cm^{-1}) and an increase in the intensity of AB of the bridging forms of adsorbed CO.

The further increase in the metal concentration to 2.5 wt.% (see Fig. 3, spectrum *4*) results in the appearance of the metal phase, which is unaffected by the surface active centers. This is testified by the appearance of AB at 1910 cm^{-1} in the region of vibrations of the bridging forms of adsorbed CO. As a result, after the adsorption of CO on the 2.5% $Pd/SO_4/ZrO_2$ sample, the spectral pattern approaches the spectrum of CO adsorbed on Pd/ZrO_2 (see Fig. 3, spectrum *1*).

Thus, the interaction of the metal with the SO_4/ZrO_2 surface can be schematically presented as follows:

5 **6**

Here S_{surf} represents both the initial SO_4 groups of the active centers and the products of their reduction. Structure **5** is typical of the systems containing not more than 1 wt.% of the metal, while complex **6** is formed at higher concentrations.

Examination of the results allows one to conclude that no noticeable migration of sulfur to the surface of the metal particles occurs during the reduction process, and the effect of the support is performed at the metal—support interface. Therefore, acidic protons, the products of the proton substitution in the superacidic center, and the products of mild reduction of the SO_4 groups, which remain unattached to the support surface, affect mainly the state of the metal. An increase in the temperature of the hydrogen treatment leads to the more complete reduction of the surface SO_4 groups and, correspondingly, to weakening of the effect of the active centers. This is indicated by the shift of AB of CO adsorbed in the linear form on the metal in the $Pd/SO_4/ZrO_2$ system (see Fig. 2, spectra *2—4*). The increase in the reduction temperature from 370 to 570 K results in the shift of the ν(CO) maximum from 2120 to 2110 cm^{-1}.

Thus, the results of the comparative study of the Pd/ZrO_2 and $Pd/SO_4/ZrO_2$ systems by diffuse-reflectance IR spectroscopy makes it possible to draw the following conclusions.

1. The behavior of the metal in the Pd/ZrO_2 system is typical of the weak metal—support interaction, which is observed in the systems similar to Pd/SiO_2. Intense bands characterizing polydentate-coordinated CO molecules can indicate the formation of large metal particles in the reduced systems.

2. Modification of the ZrO_2 surface by the SO_4^{2-} anions results in an increase in the metal—support interaction, which is accompanied by an increase in the stability of the metal toward reduction. Metal particles with the charge of +1 (Pd^+) and partial positive charge ($Pd^{\delta+}$) are observed on the SO_4^{2-}-promoted surface of the system.

3. Protons and the surface compounds of sulfur in different oxidation states have the main effect on the state of the metal. The smaller the size of the metal cluster and the higher the degree of oxidation of sulfur, the stronger the effect on the metal.

In conclusion, it should be mentioned that we studied systems in which the metal was supported by the traditional impregnation method from the salt solution. In this case, the metal particles can be distributed by size over a wide range. Undoubtedly, the introduction of the metal in the form of a cluster with the structure formed beforehand can open up a new way of studying the metal—support interaction, because the metal particles formed possess a more narrow size distribution[22] and the behavior of adsorbed CO is caused only by the interaction between the metal and active surface centers.

A. V. Ivanov thanks the Haldor Topsoe A/S Company for the financial support (Haldor Topsoe Post Graduate Grant) of this study.

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Received June 30, 1997;
in revised form August 28, 1997