The state of metals in the supported bimetallic $Pt-Pd/SO_4/ZrO_2$ system

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The behavior of the metals in the $Pt-Pd/ZrO_2$ and $Pt-Pd/SO_4/ZrO_2$ systems was studied by DRIFT spectroscopy. After reduction of $Pt-Pd/ZrO_2$ at 100 °C, the states of the metals are mainly Pt^0 and Pd^0 with a minor admixture of positively charged forms of Pt^+ or Pd^{2+}. An increase in the temperature of reduction leads to the formation of a bimetallic alloy. In the $Pt-Pd/SO_4/ZrO_2$ system, the effects of alloy formation and the interaction of the surface SO_4 groups superimpose. At low reduction temperatures, the surface SO_4 groups interact mainly with palladium. The influence of the surface sites on both supported metals increases with increasing reduction temperature.

Key words: platinum, palladium, bimetallic systems, superacids, SO_4/ZrO_2, metal—support interaction, alloy formation, diffuse-reflectance FTIR spectroscopy.

Bimetallic catalytic systems containing Pt and Pd are used in hydrogenation, dehydrogenation,[1,2] cyclization, dehydrocyclization,[3,4] oxidation,[5] and other catalytic processes. These systems are characterized by an enhanced resistance toward sulfur compounds as compared to that of monometallic catalysts.[6] Monometallic systems based on Pt supported on the superacidic carrier SO_4/ZrO_2 are promising catalysts for isomerization of lower alkanes.[7,8] Unfortunately, these systems are easily deactivated due, in particular, to covering of the platinum surface with sulfur compounds formed during reduction.[9]

The physicochemical properties of Pt—Pd bimetallic systems supported on oxides[10—12] and zeolites[6,13,14] have previously been studied. It has been shown that Pt—Pd alloy forms on the catalyst surface in a wide region of metal concentrations, and the surface of bimetallic particles is enriched with palladium atoms. It has been established by study[15—17] of the properties of monometallic SO_4/ZrO_2-supported systems that modification of the zirconium oxide surfaces by $SO_4{}^{2-}$ anions facilitates the interaction of metal with protons and SO_4 groups and stabilizes charged forms of the metal on the surface. Thus, it can be expected that in $Pt-Pd/SO_4/ZrO_2$ systems, the effects of alloy formation and interaction of the metals with active sites of the SO_4/ZrO_2 surface appear simultaneously.

In this work, we studied the state of Pt and Pd supported in combination on the superacidic SO_4/ZrO_2 carrier at different concentrations of the components of the systems and reduction conditions.

Experimental

$Pt-Pd/SO_4/ZrO_2$ catalysts were prepared on the basis of SO_4/ZrO_2 synthesized by the previously described[15—17] procedure. Platinum and palladium were supported from solutions of H_2PtCl_4 and $PdCl_2$ by combined incipient wetness impregnation. The total content of metals was 0.5 wt.%, and the Pt : Pd atomic ratio varied from 1.5 : 1.0 to 1 : 6. The catalyst was dried for 6 h at 120 °C and calcined in an air flow for 2 h at 400 °C.

During pre-treatment, samples were evacuated, oxidized, and then reduced in a hydrogen flow (the consumption of H_2 was 30 mL min^{-1}) at temperatures of 100—300 °C during 2 h.[15,17]

DRIFT spectra were recorded on a Nicolet Impact 410 spectrophotometer with a diffuse-reflectance attachment.[18] The spectra were quantitatively processed using the Kubelka—Munk equation by the OMNIC® program according to the known procedures.[19,20] Computer simulation also included smoothening of the spectra, subtraction of the background, and deconvolution of the spectra by their approximation with a combination of mixed Gauss—Lorentz functions.

Results and Discussion

When studying the behavior of metals supported in combination on SO_4/ZrO_2, one should evaluate the influence of surface sites formed by the SO_4 groups on the state of monometallic systems and elucidate the behavior of Pt and Pd in the system containing no SO_4 groups.

Monometallic catalysts Pt/ZrO_2, $Pt/SO_4/ZrO_2$ and Pd/ZrO_2, $Pd/SO_4/ZrO_2$

The IR spectra of CO adsorbed on monometallic Pt and Pd catalysts supported on ZrO_2 and SO_4/ZrO_2 and

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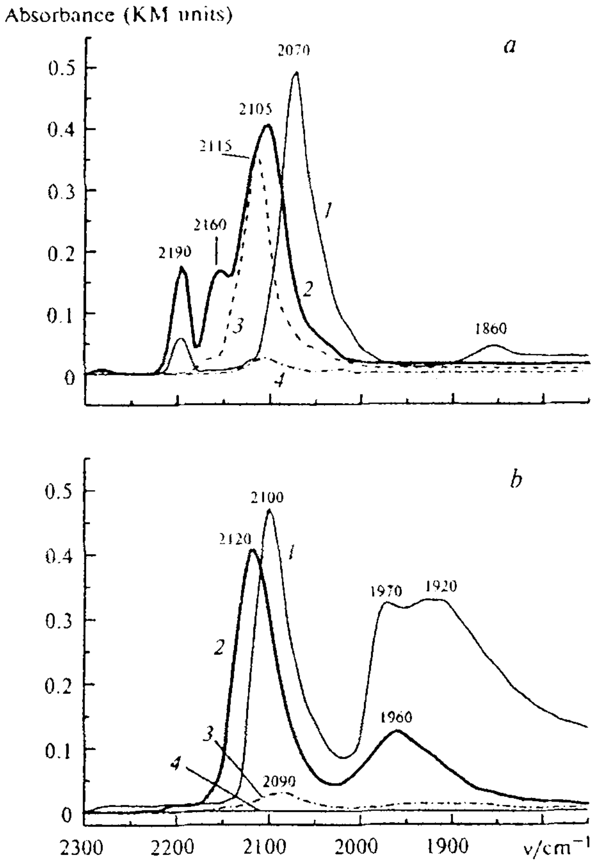

Fig. 1. IR spectra of CO adsorbed on samples: *a*, Pt/ZrO_2 (*1*) and $Pt/SO_4/ZrO_2$ (*2—4*); *b*, Pd/ZrO_2 (*1*) and $Pd/SO_4/ZrO_2$ (*2*, *3*) reduced at 200 °C before (*1*, *2*) and after evacuation at 20 (*3*) and 100 °C (*4*).

reduced at 200 °C are presented in Fig. 1. The spectrum of the Pt/ZrO_2 system (see Fig. 1, *a*) contains two characteristic absorption bands (AB) at 2070 and 1860 cm^{-1} corresponding to vibrations of CO adsorbed on Pt^0 in the linear and bridging forms, respectively.[21,22] The spectrum of Pd/ZrO_2 (see Fig. 1, *b*) exhibits AB at 2100 cm^{-1} corresponding to vibrations of CO adsorbed in the linear form on Pd^0, as well as AB at 1970 and 1920 cm^{-1} with a shoulder at ~1830 cm^{-1}, which are characteristic of polycarbonyl bridging, monocarbonyl bridging, and three-centered forms of CO adsorption on Pd^0.[16,21,22]

Modification of ZrO_2 by SO_4^{2-} anions results in the suppression of the bridging forms of adsorption and the shift of the AB corresponding to the linear forms of CO adsorption toward higher frequencies. For the Pt-containing systems, the introduction of SO_4^{2-} anions favors the electron deficiency of platinum species, which results in the high-frequency shift of maxima of AB of CO adsorbed in the linear form, suppression of the formation of bridged CO complexes with the metal, formation of positively charged $Pt^{\delta+}$ species, and stabilization of Pt^+ ions during reduction. The mechanism of formation of the positively charged forms of the metal can include the interaction of acidic protons with the metal particles.[15,16] For the palladium-containing systems, these processes are accompanied by the partial redox interaction of the metal with the SO_4 groups and blocking of the adsorption sites of the metal with reduced forms of sulfur.[17]

Bimetallic catalysts $Pt—Pd/ZrO_2$

The IR spectra of CO adsorbed on the $Pt—Pd/ZrO_2$ sample (atomic ratio Pt : Pd = 1 : 1) reduced at 100, 200, and 300 °C are presented in Fig. 2. The spectra of the sample reduced at 100 °C exhibit AB at 2155, 2095, 1970, 1930, and 1880 cm^{-1}. According to the published data,[21] AB at 2155 cm^{-1} can be attributed to vibrations of CO on unreduced Pt^+ or Pd^{2+} ions; the AB at 2095 cm^{-1} is also a superposition of the bands corresponding to vibrations of CO adsorbed on the metal species Pt^0 or Pd^0.[21,22] The intense AB at 1970 and 1880 cm^{-1} characterize the polycarbonyl and monocarbonyl bridging forms of CO adsorption, respectively.[21,22] The band at 1930 cm^{-1} corresponds, most likely, to the monocarbonyl bridging form of adsorption of CO on sites arranged near oxidized metal forms. Evacuation with a stepwise temperature increase results in a decrease in the intensity of AB, and bands at 2130, 2080, and 2060 cm^{-1} can be isolated in the region of vibrations of linear carbonyl groups in the spectrum. The two latter AB can indicate the presence of isolated platinum (2060 cm^{-1}) and palladium (2080 cm^{-1}) particles on the ZrO_2 surface. In the region of bridging vibrations, the high-frequency AB characteristic of polycarbonyl forms of adsorption on palladium atoms and the bands attributed to sites arranged near charged forms disappear first. The other AB, at 1900 and 1830 cm^{-1}, corresponding to the two-centered and three-centered forms of CO adsorption on Pd^0 indicate the presence of sufficiently large palladium species.

An increase in the reduction temperature to 200 °C results in some increase in the intensity of the AB at 2160 cm^{-1} attributed to charged forms of the metal and appearance of an AB at 2190 cm^{-1} characterizing CO complexes with the Lewis acidic sites (LAS) on the ZrO_2 surface.[23] Perhaps, at temperatures below 200 °C, the adsorption centers are neutralized by H_2O molecules that are formed during reduction of palladium. The further increase in the reduction temperature to 300 °C results in the disappearance of the first AB and further increase in the intensity of the second AB, which agrees with the assumption about a gradual removal of adsorbed water at temperatures >200 °C. No considerable changes are observed in the region of vibrations of the linear carbonyl groups (Pt^0, Pd^0). At the same time, the bridging CO groups are characterized by an increase in the intensity of AB at 1970 cm^{-1} relative to other bands. The spectra of the samples reduced at 200 and 300 °C

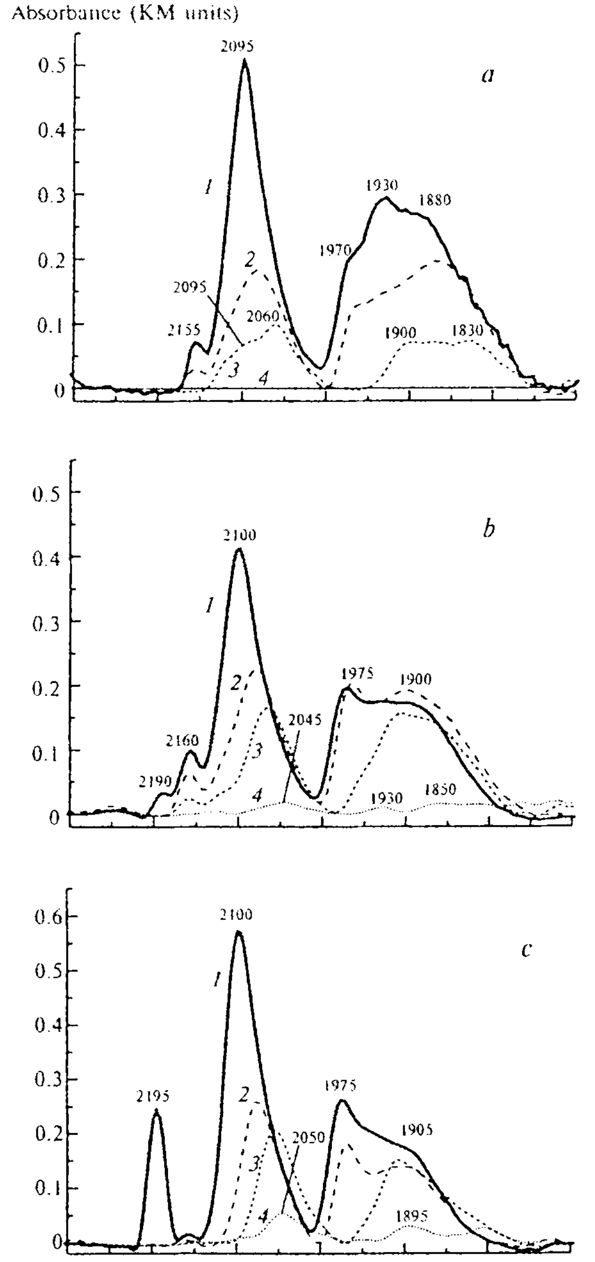

Fig. 2. IR spectra of CO adsorbed on a Pt—Pd/ZrO$_2$ sample reduced at 100 (*a*), 200 (*b*), and 300 °C (*c*) immediately after adsorption (*1*) and after evacuation at 20 (*2*), 100 (*3*), and 200 °C (*4*).

exhibit a decrease in the intensity of AB at 1830—1850 cm^{-1} that characterizes both the two- and three-centered forms of CO adsorption on Pt^0 and Pd^0, respectively.

Thus, after the reduction of the Pt—Pd/ZrO$_2$ system, Pt^0 and Pd^0 with a minor admixture of the charged forms Pt$^+$ or Pd^{2+} are the main states of the metals. The latter species are completely reduced only at 300 °C.

Analysis of the spectra of the sample reduced at 100 °C makes it possible to distinguish the regions of vibrations of bridging and linear carbonyl groups. In the first of them, the behavior of AB is typical of monometallic Pd/ZrO$_2$ systems.[17] In the second region, AB characterizing adsorption on the individual Pt^0 and Pd^0 sites can be distinguished. All these data can indicate the existence of separate Pt^0 and Pd^0 phases, *i.e.*, give no evidence for the formation of uniform Pt—Pd alloy.

An increase in the reduction temperature results in the shift of the maximum of adsorption of CO adsorbed in the linear form on Pt^0 and Pd^0 toward low frequencies relative to the position of a similar AB in the spectrum of the monometallic samples. This is accompanied by a decrease in the intensity of the bands characteristic of bridging forms of adsorption and, in particular, the disappearance of the three-centered forms (AB at 1830 cm^{-1}). This can indicate the partial formation of the alloy at high temperatures.

Bimetallic catalysts Pt—Pd/SO$_4$/ZrO$_2$

The IR spectra of CO adsorbed on Pt—Pd/SO$_4$/ZrO$_2$ samples (Pt : Pd = 1 : 1) reduced at 100, 200, and 300 °C are presented in Fig. 3. The complex AB at 2105 cm^{-1} contributes mainly to the spectra of the sample reduced at 100 °C (see Fig. 3, *a*). Deconvolution of the spectrum allows one to pick out two components (at 2115 and 2080 cm^{-1}), which can be assigned to Pd$^{\delta+}$ and Pt^0, respectively. Evacuation at 20 and 100 °C results in the redistribution of CO on the adsorption centers, which is evidenced by the disappearance of AB at 2115 cm^{-1} and an increase in the intensity of the AB at 2080 cm^{-1}.

After reduction at 100 °C, insignificant amounts of oxidized forms of Pt and Pd are present in the system, which is indicated by the AB at 2190 and 2160 cm^{-1}. The first of them characterizes vibrations of CO adsorbed on Pt^{2+} ions, whereas the second band is a superposition of vibrations of CO adsorbed on Pt$^+$ and Pd^{2+}. Evacuation at 20 °C results in the resolution of the band attributed to vibrations of CO adsorbed on Pd$^+$ in the form of a shoulder at 2135 cm^{-1}. It is noteworthy that after reduction at 100 °C, a higher concentration of positively charged forms of platinum and palladium than in the corresponding nonsulfated Pt—Pd/ZrO$_2$ systems is observed in the Pt—Pd/SO$_4$/ZrO$_2$ system (Pt : Pd = 1 : 1).

The spectrum of the Pt—Pd/SO$_4$/ZrO$_2$ system in the region of vibrations ν(CO) < 2000 cm^{-1} exhibits a considerable decrease in the intensity of AB of bridging vibrations as compared to the spectrum of Pt—Pd/ZrO$_2$. In addition, a complex band with a maximum at 1905 cm^{-1} appears, which is a superposition of AB at 1905 and 1860 cm^{-1} corresponding to the two-centered forms of CO adsorption on Pd and Pt, respectively.

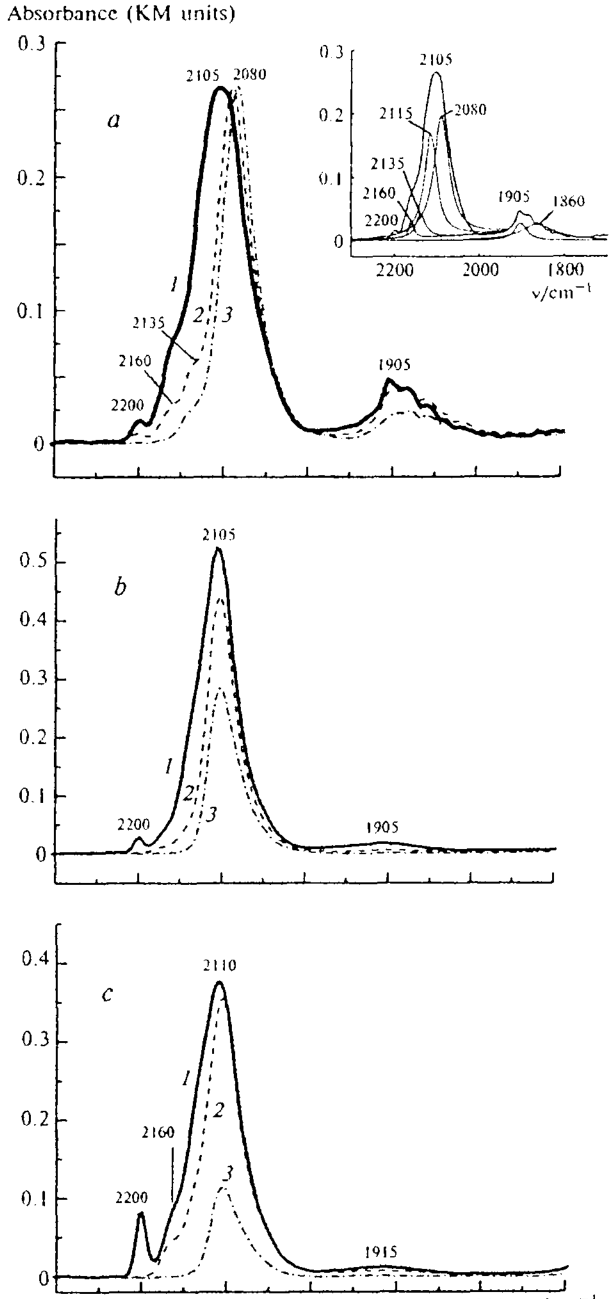

Fig. 3. IR spectra of CO adsorbed on a Pt—Pd/SO_4/ZrO_2 sample (Pt : Pd = 1 : 1) reduced at 100 (*a*), 200 (*b*), and 300 °C (*c*) immediately after adsorption (*1*) and after evacuation at 20 (*2*) and 100 °C (*3*). Deconvolution of spectrum 1, *a* is presented in the insert.

Thus, the Pt—Pd/SO_4/ZrO_2 system (Pt : Pd = 1 : 1) after reduction at 100 °C is characterized by two phases: the $Pd^{\delta+}$ phase, presumably formed due to the interaction of the metal species with superacidic protons of the surface active centers, and the Pt^0 phase, whose behavior is typical of systems containing no sulfur.

Reduction at 200 °C results in the suppression of bridging forms of CO adsorption on the metals (see Fig. 3, *b*) and complete reduction of charged forms of the metals. The spectrum of the sample contains an intense AB at 2105 cm^{-1} whose position remains almost unchanged during evacuation. Probably, with an increase in the reduction temperature, the adsorption sites become more uniform, although they differ from those formed under similar conditions in the Pt—Pd/ZrO_2 system. It can be assumed that processes of alloy formation begin to occur in the system; however, they are disguised by the action of the surface acidic sites, which is indicated by a decrease in the stability of the carbonyl complexes.

The increase in the reduction temperature to 300 °C (see Fig. 3, *c*) results in the further decrease in the stability of CO complexes with the metals. At the same time, the AB at 2160 cm^{-1}, which disappeared during reduction at 200 °C, appears again in the spectra. This indicates the formation of charged forms of the metals, presumably Pd^{2+}, at elevated temperatures. The effect observed can be explained by redox processes between the metal atoms and the surface SO_4 groups with the

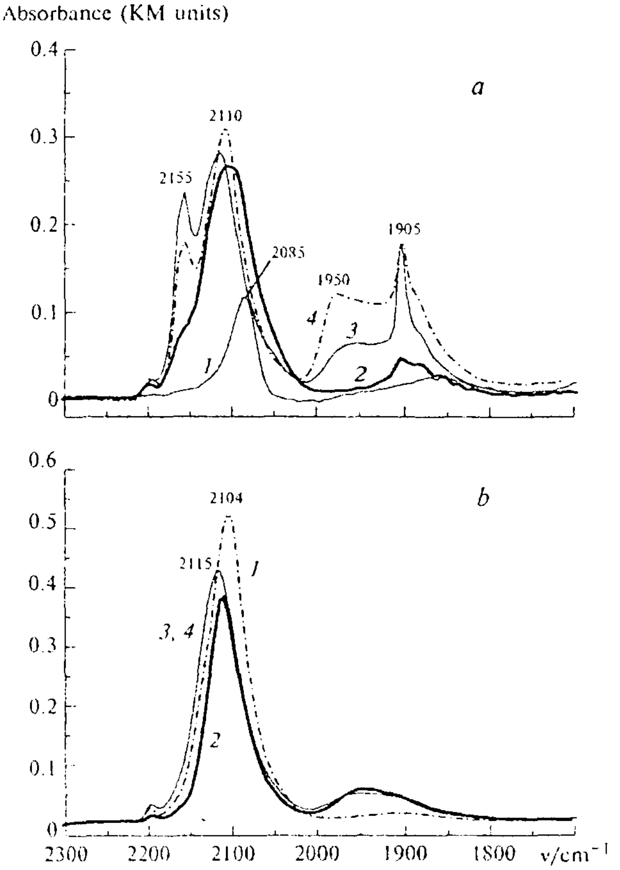

Fig. 4. IR spectra of CO adsorbed on Pt—Pd/SO_4/ZrO_2 samples at the atomic ratio Pt : Pd = 1.5 : 1.0 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), and 1 : 6 (*4*) reduced at 100 (*a*) and 200 °C (*b*).

formation of platinum and palladium compounds with the products of transformation of the SO_4 groups. These products can contain both sulfides and oxygen-containing compounds of sulfur with oxidation states from 6+ to 2−. In the monometallic systems containing SO_4^{2-} anions, the phenomenon of metal re-oxidation was not observed. This can indicate a change in the behavior of the metals upon combined support.

To evaluate the influence of the Pt/Pd ratio on the state of metals, we studied systems with the atomic ratio Pt : Pd from 1.5 to 0.15 (Fig. 4). An increase in the relative content of platinum in the Pt—Pd/SO_4/ZrO_2 sample (Pt : Pd = 1.5 : 1.0) results in the removal of aggregated palladium during reduction at 100 °C, which is indicated by the disappearance of AB that characterize bridging forms of CO adsorption on Pd^0. In this region, only the AB at 1860 cm^{-1} corresponding to the bridged CO complex with Pt^0 is observed. At the same time, the shoulder at 2120 cm^{-1} indicates the presence of palladium with an excessive positive charge $Pd^{\delta+}$. The behavior of platinum is typical of the systems containing no sulfur.

An increase in the relative content of palladium noticeably changes the spectral pattern. The spectra exhibit an increase in the intensity of AB at 2155—2160 cm^{-1}, which is typical of metal ions. At the same time, the intensity of the AB at 1950 cm^{-1} increases, which can be attributed to bridging forms of adsorption on palladium particles that are affected by the surface SO_4 groups. For the ratio Pt : Pd = 1 : 6, the AB at ~1975 cm^{-1} appears, which is characteristic of polycarbonyl bridging forms of CO adsorption on Pd^0.

An increase in the reduction temperature results in a decrease in the number of AB. The spectra contain AB at 2105—2115 and 1950 cm^{-1} whose behavior is similar to that of the corresponding bands for the Pt—Pd/SO_4/ZrO_2 system (Pt : Pd = 1 : 1).

The results obtained are summarized in Table 1. The behavior of metals in the Pt—Pd/SO_4/ZrO_2 system differs from those observed for the Pt—Pd/ZrO_2 and monometallic Pt(Pd)/SO_4/ZrO_2 systems. On the one hand, in the Pt—Pd/SO_4/ZrO_2 system, the three-centered forms of CO adsorption (characteristic of Pt—Pd/ZrO_2) are completely absent, and the formation of polycarbonyl bridged complexes begins only at a high content of palladium. On the other hand, the Pt—Pd/SO_4/ZrO_2 sample contains the Pt^0 phase, which is not characteristic of the SO_4/ZrO_2-supported system.

It can be assumed that two mechanisms of changing the state of metals are possible for the Pt—Pd/SO_4/ZrO_2 system. The first mechanism involves the alloy formation, and the second mechanism is related to the interaction of the metals with the surface SO_4 groups. It is difficult to separate the contributions of these effects, because the alloy formation and interaction of Pt and Pd with the surface SO_4 groups are superimposed.

Table 1. Frequencies of vibrations of linear and bridged CO complexes in IR spectra of mono- and bimetallic systems

System	T_{red}	ν/cm^{-1} (for different states of metal and adsorption forms)											
(Pt : Pd)	/°C	Pt^{2+}	Pd^{2+}	Pt^{+}	Pd^{+}	$Pt^{\delta+}$	$Pd^{\delta+}$	Pt^0	Pd^0	$M_2(CO)_n$	$M_2^{\delta+}(CO)$	$M_2(CO)$	$M_3(CO)$
Pt/ZrO_2 [a]	200	—	—	—	—	—	—	2070	—	—	—	1860	—
Pd/ZrO_2 [b]	200	—	—	—	—	—	—	—	2100	1970	—	1920	1830
Pt—Pd/ZrO_2	100	—	2155		2135	—	—	2060	2095	1970	1930	1880	1830
	200	—	2160		2135	—	—	2045	[c]	1975	—	1900	—
	300	—	—		—	—	—	2050	[c]	1975	—	1905	—
Pt/SO_4/ZrO_2 [a]	200	—	—	2160	—	2115	—	—	—	—	—	—	—
Pd/SO_4/ZrO_2 [b]	100	—	2150	—	2130	—	2120	—	[c]	—	1960	1900	—
	200	—	—	—	—	—	2120	—	—	—	1960	—	—
Pt—Pd/SO_4/ZrO_2	100	2200	2160	2160	2135	—	2115	2080	—	—	—	1905, 1860	—
(1 : 1)	200	—	—	—	—	2105	[c]	—	—	—	—	1905	—
	300	—	2160	—	—	2110	[c]	—	—	—	—	1915	—
Pt—Pd/SO_4/ZrO_2	100	—	—	—	—	—		2070	—	—	—	1860	—
(1.5 : 1.0)	200	—	—	—	—	—	[c]	2080	—	—	—	—	—
	300	—	2155	—	—	2100	[c]	—	—	—	—	—	—
Pt—Pd/SO_4/ZrO_2	100	2190	—	2160	—	—	2115	2080	[c]	—	1950	1905	—
(1 : 2)	200	—	—	—	—	2095	2115	2080	—	—	1950	—	—
	300	—	—		—	2105	2115	—	—	—	1950	—	—
Pt—Pd/SO_4/ZrO_2	100	—	2155	2155	2135	—	2115	2070	[c]	1975	1950	1905	—
(1 : 6)	200	—	—	—	—	—	2115	2085	—	—	1950	—	—
	300	—	2160	—	—	2100	2115	—	—	—	1950	—	—

[a] Ref. 15.

[b] Ref. 17.

[c] Individual bands in the region of vibrations of linear carbonyl groups are not observed; however, the metallic phase is present, which is indicated by bridging carbonyl groups.

In the Pt—Pd/SO_4/ZrO_2 system reduced at low temperatures, palladium is subjected to the same effect as in the Pd/SO_4/ZrO_2 system. At the same time, the behavior of Pt is characteristic of the metal supported on systems without a strong metal—support interaction. Pt^0 remains the main state of platinum in all samples. This specific feature is observed at different Pt/Pd ratios. In the systems with a low palladium content, it exists almost completely in the form of $Pd^{\delta+}$ and is prone to the effect of the surface SO_4 groups. An increase in the palladium content in the catalyst results in the appearance of a Pd^0 metallic phase; however, the behavior of platinum remains unchanged. It can be assumed that in the bimetallic systems the surface SO_4 groups interact predominantly with palladium species, and the effect of the SO_4 groups on platinum weakens. An increase in the reduction temperature results in the enhancement of the effect of surface acidic sites on both supported metals, which is indicated by the formation of the $Pt^{\delta+}$ form and a decrease in the stability of adsorption complexes.

At the same time, a decrease in the vibration frequencies of CO adsorbed on platinum in the bimetallic system can be explained by dilution of the platinum phase with palladium due to alloy formation. Analysis of the region of vibrations of the bridging carbonyl groups is less unambiguous, because a decrease in the intensity of AB characterizing multicentered forms of adsorption in the spectra of Pt—Pd/SO_4/ZrO_2 can be related to both alloy formation and blocking of adsorption centers by surface sulfur compounds.

Thus, the behavior of platinum and palladium supported in combination on SO_4/ZrO_2 was studied by diffuse-reflectance FTIR spectroscopy. It is established that after reduction of Pt—Pd/ZrO_2 at 100 °C Pt^0 and Pd^0 with a minor admixture of charged Pt^+ or Pd^{2+} forms are the main states of the metals. An increase in the reduction temperature results in dilution of the Pt^0 phase with a Pd^0 phase, which indicates alloy formation. An alloy can also form in the Pt—Pd/SO_4/ZrO_2 system; however, effects of alloy formation are screened by the influence of the surface SO_4 groups.

The surface SO_4 groups interact predominantly with palladium, and their effect on platinum weakens. An increase in the reduction temperature results in the enhancement of surface acidic sites on both supported metals.

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