Influence of support acidity on electronic state of platinum in oxide systems promoted by SO_4^{2-} anions

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The electronic state of platinum supported on SO_4/ZrO_2, SO_4/TiO_2, SO_4/Al_2O_3, and SO_4/SiO_2 systems and on systems unpromoted by sulfur was investigated by diffuse-reflectance IR spectroscopy using CO as the probe molecule. The introduction of SO_4^{2-} anions increases the electron deficit on platinum particles. This suppresses the formation of bridging CO complexes with the metal, leads to the high-frequency shift of absorption maxima of CO adsorbed in the linear form, and stabilizes positively charged metal species ($Pt^{\delta+}$ and Pt^+) during the reduction process. The formation of the positively charged species includes the interaction between the acidic protons and the metal particles yielding $[Pt—H]^{\delta+}$ adducts. The extent of the influence of the support on the electronic state of the metal increases in the series $SO_4/SiO_2 < SO_4/Al_2O_3 < SO_4/TiO_2 < SO_4/ZrO_2$ in parallel with an increase in the strength of the acid sites in the system.

Key words: platinum; superacids, SO_4/ZrO_2, SO_4/TiO_2, SO_4/SiO_2, SO_4/Al_2O_3, metal—support interaction; diffuse-reflectance IR spectroscopy.

The studies related to the activation of C—H and C—C bonds in hydrocarbon molecules have shown that new systems, including SO_4^{2-}-promoted metal oxides with strong acidic or superacidic properties, can be considered as promising catalysts. The Pt-promoted superacidic systems are of the greatest interest, but despite this, the state of the metal and oxide surface and the role of the metal in promotion of catalytic reactions have not yet been elucidated.[1]

It is established that the state of platinum on the $Pt/SO_4/ZrO_2$ system and that of platinum supported on the traditional oxide supports are different. X-ray photoelectron spectroscopic (XPS) data suggest that platinum is mainly present as the metal with the surface covered by sulfur.[2] It is shown that the initial formation of the metal follows calcination of the $Pt/SO_4/ZrO_2$ sample in air at 600 °C. EXAFS data also indicate that the metal phase of platinum is present after the activation of the catalyst in air at 725 °C. The size of platinum particles is not less than 100 Å, and the coordination number of platinum (N_{Pt} = 10—13) coincides with that of Pt in foil.[3]

The existence of the metal state described as a state with "strong metal—support interaction" is also assumed.[4] It is shown that after the reduction with hydrogen at 400 °C, the concentration of the metal phase is low, and platinum is mainly present in the form of cations (a mixture of PtO and $PtSO_4$), *i.e.*, additives of SO_4^{2-} anions suppress strongly the processes governing reduction to the metal.[5] The stability of platinum on SO_4/ZrO_2 toward reduction can be probably explained by the redox metal—support interaction caused by the acidic properties of the support.

The systems studied[2—5] were characterized by a high metal concentration (> 2 wt.%), while the $Pt/SO_4/ZrO_2$-based catalysts usually contain ~0.5 wt.% Pt. IR spectroscopy is very efficient for studying the state of metals supported on oxide and zeolite systems at the metal concentration <0.5 wt.%.[6] The previous transmission IR spectroscopic study[5,7] of CO adsorption on the metal surface has established that the presence of sulfur almost completely suppresses the CO adsorption. However, this was not confirmed in our works,[8,9] where the state of the surface of SO_4/ZrO_2-supported metals was studied by diffuse-reflectance IR spectroscopy using CO as the probe molecule. Sulfate additives were established to change the electronic state of ZrO_2-supported platinum and facilitate the formation of $Pt^{\delta+}$ species. An increase in the surface metal concentration results in the weakening of the proton action due to which two forms of platinum can co-exist: $Pt^{\delta+}$ and Pt^0.

It was of interest to study and compare Pt-containing systems based on different metal oxides promoted by SO_4^{2-} anions in order to determine the influence of acidity and surface sulfur compounds on the state of platinum. In this work, we studied the metal state in the $Pt/SO_4/ZrO_2$, $Pt/SO_4/TiO_2$, $Pt/SO_4/Al_2O_3$, and $Pt/SO_4/SiO_2$ systems and compared them with similar nonsulfated systems (Pt/ZrO_2, Pt/TiO_2, Pt/Al_2O_3, and Pt/SiO_2).

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Experimental

The following starting supports were used: (1) $Zr(OH)_4$ (S_{sp} = 150 $m^2\ g^{-1}$, Magnesium Electron Co., grade XZ0706/03); (2) $Ti(OH)_4$ synthesized from an aqueous solution of $TiCl_4$ by precipitation with an aqueous solution of ammonium hydroxide; the precipitate formed was washed with distilled water until a negative reaction to Cl^- ions (the reaction with $AgNO_3$) was observed and dried at 120 °C for 6 h; (3) Al_2O_3 (γ-Al_2O_3, A-64K trade mark, S_{sp} = 180 $m^2\ g^{-1}$, Ryazan' refinery); and (4) SiO_2 (KSK-2-5 trade mark, S_{sp} = 300 $m^2\ g^{-1}$).

To prepare 5% SO_4/M_xO_y systems (SO_4/ZrO_2, SO_4/TiO_2, SO_4/Al_2O_3, and SO_4/SiO_2), dried (2 h at 120 °C) samples of $Zr(OH)_4$, $Ti(OH)_4$, Al_2O_3, and SiO_2 were treated with a 1 *N* aqueous solution of H_2SO_4 until a 5 wt.% concentration of SO_4^{2-} was achieved. The samples were dried at 120 °C for 6 h and calcined in a dry air flow at 550—650 °C for 2 h.

Platinum-promoted (0.5 wt.%) samples were prepared by the impregnation of SO_4/M_xO_y with an aqueous solution of H_2PtCl_6. The catalyst was dried at 120 °C for 6 h and heated in an air flow at 450 °C for 2 h.

Pt/M_xO_y (0.5 wt.%) systems without superacidic properties were prepared by the impregnation of the starting hydroxides and oxides with an aqueous solution of H_2PtCl_6. The catalysts were dried at 120 °C for 6 h and heated in a dry air flow at 500 °C for 2 h.

Activation and reduction. Prior to measurements, samples 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 400 °C *in vacuo*. After a residual pressure of 10^{-4} Torr was achieved, the samples were treated with O_2 (30 Torr) at 400 °C to prevent the reduction of the metal and SO_4^{2-} ions. Then the system was evacuated again and cooled to ~20 °C.

To obtain the reduced form of platinum, the catalysts were treated in a hydrogen flow (the flow rate of H_2 was 30 mL min^{-1}) at 200—300 °C for 2 h. Then the samples were evacuated at the reduction temperature to a pressure of 10^{-4} Torr and cooled to ~20 °C.

Measurements of IR spectra. Carbon monoxide (30 Torr) was adsorbed on pre-activated and evacuated samples. IR spectra were recorded on a Nicolet Impact 410 spectrophotometer equipped with a diffuse-reflectance attachment.[10] After the spectrum was recorded, the sample was evacuated with a stepwise temperature increase (50 °C-increment), and the spectra were recorded at each temperature of evacuation.

The spectra were quantitatively processed by the Kubelka—Munk equation using the OMNIC® program (see Refs. 11 and 12). The computer simulation also included smoothening of the spectra, subtraction of the background, and deconvolution of the spectra by approximation by doublets, which are a combination of the mixed Hauss—Lorentz functions.

Results and Discussion

Pt/ZrO_2 and $Pt/SO_4/ZrO_2$ systems. The IR spectra of CO adsorbed on the Pt/ZrO_2 and $Pt/SO_4/ZrO_2$ samples are presented in Fig. 1. After CO was adsorbed on the Pt/ZrO_2 sample, three absorption bands (AB) were observed in the spectrum: at νCO 2190, 2070, and 1855 cm^{-1}. The first AB is characteristic of CO complexes with Lewis acid sites (LAS) on the ZrO_2 surface.[13] The remaining AB correspond to vibrations of

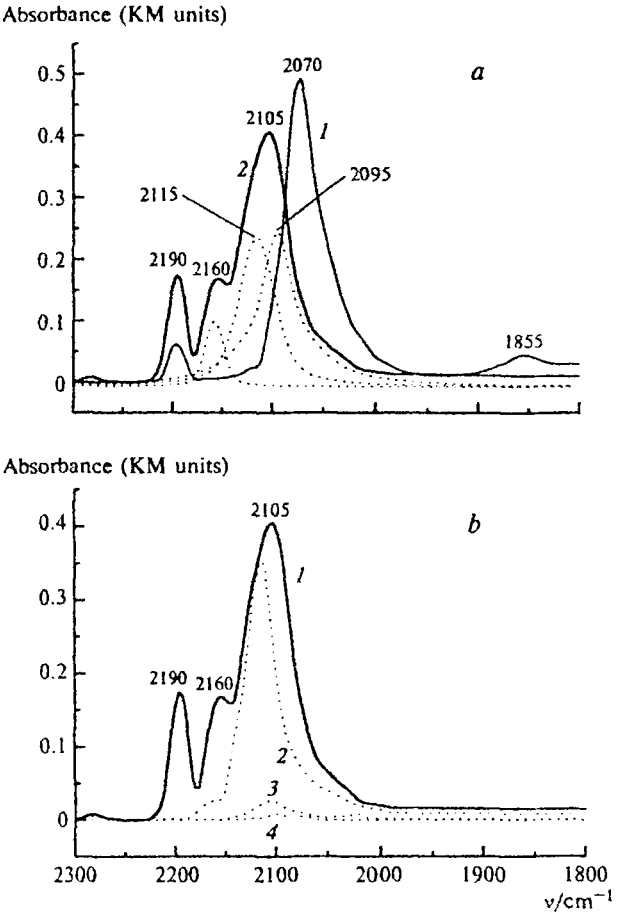


Fig. 1. *a*. IR spectrum of CO (20 Torr) after adsorption on Pt/ZrO_2 (*1*) and $Pt/SO_4/ZrO_2$ (*2*) samples and deconvolution of spectrum *2* into components. *b*. IR spectrum of CO adsorbed on $Pt/SO_4/ZrO_2$ samples before (*1*) and after evacuation at 20 °C (*2*), 100 °C (*3*), and 200 °C (*4*).

CO adsorbed in the linear and bridging forms on platinum particles.[14] A decrease in the coverage of the platinum surface by CO molecules caused by a stepwise increase in the evacuation temperature results in a shift of the AB maximum at 2070 cm^{-1} to the frequency of a singleton (2040 cm^{-1}). Under these conditions, dipole-dipole interactions of adsorbed molecules are absent due to the low coverage of the surface.[15]

After CO was adsorbed on the $Pt/SO_4/ZrO_2$ sample (Fig. 1, *a*, spectrum *2*), three AB with maxima at 2190, 2160, and 2105 cm^{-1} were observed in the spectra. The first of them is characteristic of CO complexes with LAS on the SO_4/ZrO_2 surface[16] and CO complexes with Pt^{2+} ions.[14] The band at 2160 cm^{-1} can be assigned to linear complexes of CO with Pt^+ ions, which can be incorporated in the near-surface (O—Pt)—CO complexes. In this case, however, the maximum of this band is localized at higher frequencies than those in the spectra of the zeolite systems.[17,18] The absorption band at 2105 cm^{-1} is a superposition of several bands. Deconvolution of the spectrum makes it possible to distinguish two components

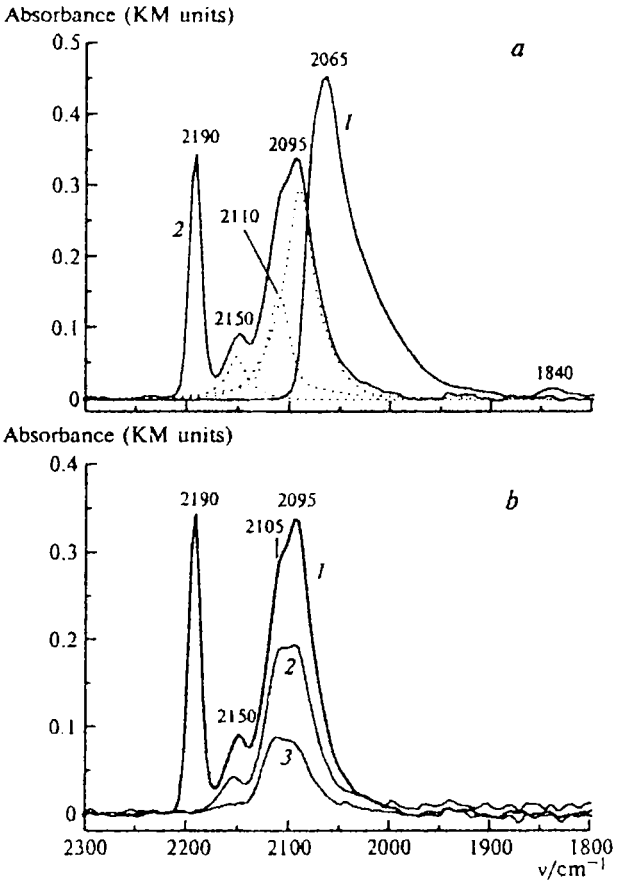


Fig. 2. *a*. IR spectrum of CO (20 Torr) after adsorption on Pt/TiO_2 (*1*) and $Pt/SO_4/TiO_2$ (*2*) samples and deconvolution of the low-frequency region of spectrum *2* into components. *b*. IR spectrum of CO adsorbed on $Pt/SO_4/TiO_2$ samples before (*1*) and after evacuation at 20 °C (*2*) and 100 °C (*3*).

at 2115 and 2095 cm^{-1}, which can be assigned, according to the data obtained previously,[9] to the frequencies of CO adsorbed in the linear form on the $Pt^{\delta+}$ and Pt^0 species, respectively. The assignment of these AB to vibrations of CO in the Pt_9—Pt_{15} clusters is less probable, because other AB of these clusters in the 1700—1900 cm^{-1} region are not observed in the spectra.[19]

Evacuation during the stepwise temperature increase (Fig. 1, *b*) results in a decrease in the intensity of all AB; however, no shifts of the maxima to lower frequencies are observed, which indicates an insignificant dipole-dipole interaction of the CO molecules adsorbed on platinum. This can probably be accounted for by the small size of the metal particles. The AB intensity decreases to zero after evacuation at temperatures >100 °C. This provides evidence for the lower stability of the surface CO complexes with the metal particles as compared to the systems containing no sulfur.

Pt/TiO_2 and $Pt/SO_4/TiO_2$ systems. As in the case of Zr-containing systems, the spectra of CO adsorbed on Pt/TiO_2 (Fig. 2, *a*, spectrum *1*) exhibited two AB at 2065 and 1840 cm^{-1} corresponding to vibrations of CO

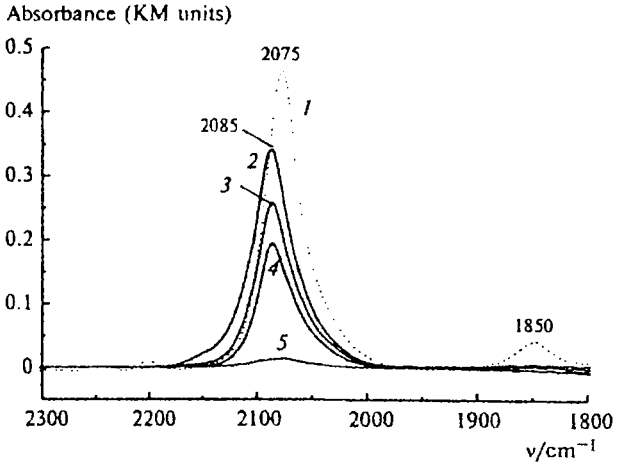


Fig. 3. IR spectrum of CO (20 Torr) adsorbed on Pt/Al_2O_3 (*1*) and $Pt/SO_4/Al_2O_3$ samples before (*2*) and after evacuation at 20 °C (*3*), 100 °C (*4*), and 200 °C (*5*).

adsorbed in the linear and bridging forms on the metal particles. Evacuation during the stepwise temperature increase results in the shift to frequencies as low as 2060 cm^{-1} for the AB maximum corresponding to vibrations of CO adsorbed in the linear form.

After CO was adsorbed on the $Pt/SO_4/TiO_2$ sample (see Fig. 2, *a*, spectrum *2*), three main AB at 2190, 2150, and 2095 cm^{-1} were observed in the spectra. The high-frequency AB can be assigned to vibrations of CO in surface complexes with LAS.[20,21] The band at 2150 cm^{-1} can be ascribed to surface complexes of CO with Pt^+ ions. The high-frequency shoulder of the AB at 2095 cm^{-1} indicates the complicated character of this band. Deconvolution of the spectrum makes it possible to isolate two components with maxima at 2110 and 2095 cm^{-1}. The assignment of these bands is similar to that presented above for the $Pt/SO_4/ZrO_2$ system and corresponds to vibrations of CO in complexes with $Pt^{\delta+}$ and Pt^0.

Evacuation of $Pt/SO_4/TiO_2$ with adsorbed CO during the stepwise temperature increase (see Fig. 2, *b*) results in a decrease in the intensity of all AB. The bands at 2105 and 2095 cm^{-1} disappear at temperatures >100 °C; and as the intensity of the band decreased, no shifts of their maxima to low-frequencies were observed.

Pt/Al_2O_3 and $Pt/SO_4/Al_2O_3$ systems. The spectrum of CO adsorbed on the Pt/Al_2O_3 sample exhibited two intense AB at 2075 and 1850 cm^{-1}, which characterize complexes of CO with Pt metal (Fig. 3, spectrum *1*). Evacuation of the sample during the stepwise temperature increase leads to the shift of the band maximum to the singleton frequency at 2040 cm^{-1}.

When CO was adsorbed on the $Pt/SO_4/Al_2O_3$ sample (Fig. 3, spectra *2*—*5*), the IR spectra exhibited only one intense AB at 2085 cm^{-1}, indicating the presence of Pt^0 as the only state of platinum. The stability of the complexes of CO adsorbed in the linear form is also higher than that of the complexes after adsorption on the $Pt/SO_4/ZrO_2$ and $Pt/SO_4/TiO_2$ samples. The traces of the AB are

observed even after evacuation at 200 °C with the maximum shifted to low frequencies (to 2080 cm^{-1}).

Pt/SiO_2 and $Pt/SO_4/SiO_2$ systems. Adsorption of CO on the Pt/SiO_2 systems unpromoted by SO_4^{2-} anions was well studied and, hence, we used for comparison the results in Ref. 22, the authors of which established that the AB at 2070 cm^{-1} corresponded to the vibration of CO adsorbed in the linear form on platinum particles.

The IR spectra of CO adsorbed on the $Pt/SO_4/SiO_2$ sample are presented in Fig. 4. The spectra exhibit only one AB at 2075 cm^{-1} ascribed to vibrations of CO adsorbed in the linear form on platinum particles. After evacuation of the sample during the stepwise temperature increase, the AB decreases sharply and disappears completely at 100 °C. This indicates the low stability of the surface complexes of CO with the metal. However, no changes in the position of the AB maximum were observed.

The experimental results related to the electronic state of platinum on the surface of the systems containing SO_4^{2-} anions and based on the data obtained by diffuse-reflectance IR spectroscopy with CO as a probe molecule are summarized in Table 1.

The analysis of the data on the electronic state of platinum supported on metal oxides unpromoted by sulfate anions shows that platinum ions are completely reduced in a hydrogen atmosphere at 200 °C. The positions of maxima of AB corresponding to vibrations of adsorbed CO indicate that the metal state is characteristic of systems with a weak metal—support interaction.

The addition of the SO_4^{2-} anions suppresses the formation of the bridging CO complexes with the metal, it induces the shift of the maxima of AB corresponding to CO adsorbed in the linear form on the Pt^0 particles to high frequencies and stabilizes positively charged platinum ions ($Pt^{\delta+}$ and Pt^+) during the reduction. All systems are characterized by a decrease in the stability of the surface CO complexes with the metal particles as compared to the systems containing no sulfur.

When the SO_4^{2-} anions were added, the behavior of platinum changes, which is manifested in the spectra of

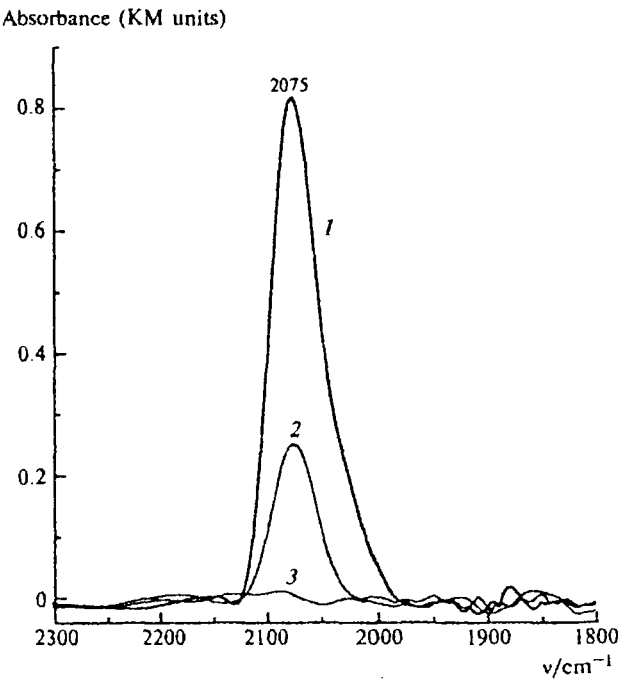


Fig. 4. IR spectrum of CO (20 Torr) adsorbed on $Pt/SO_4/SiO_2$ samples before (*1*) and after evacuation at 20 °C (*2*) and 100 °C (*3*).

adsorbed CO. The absorption bands in the region of 2075—2115 cm^{-1} indicate unambiguously the presence of reduced platinum, the state of which, however, is affected strongly by acid sites. The effect of the SO_4 groups on the electronic state of the metal depends on the oxide nature. For example, the results obtained for the adsorption of CO on the $Pt/SO_4/SiO_2$ sample almost coincide with the published data[22] on the adsorption of CO on the Pt/SiO_2 samples. This indicates that the addition of the SO_4^{2-} anions affects the stability of the CO complexes rather than the electronic state of platinum. The difference between the frequency of the vibration of CO adsorbed in the linear form on

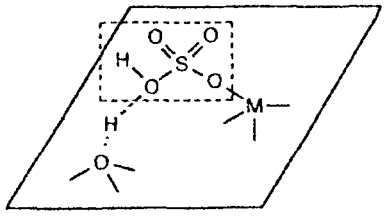
Table 1. Vibration frequencies of CO adsorbed on Pt supported on M_xO_y and SO_4/M_xO_y (M = Zr, Ti, Al, Si)

Catalyst	νCO/cm^{-1}			ΔνCO/cm^{-1}	
	Pt^+	$Pt^{\delta+}$	Pt^0 (Pt^0_{sing})	$Pt^{\delta+} - Pt^0_{sing}$	$Pt^0 - Pt^0_{sing}$
Pt/ZrO_2	—	—	2070 (2040)	—	—
$Pt/SO_4/ZrO_2$	2160	2115	2095 (2095)	75	55
Pt/TiO_2	—	—	2065 (2060)	—	—
$Pt/SO_4/TiO_2$	2150	2110	2095 (2095)	50	35
Pt/Al_2O_3	—	—	2075 (2040)	—	—
$Pt/SO_4/Al_2O_3$	—	—	2085 (2080)	—	40
Pt/SiO_2	—	—	2070*	—	—
$Pt/SO_4/SiO_2$	—	—	2075 (2075)	—	5

* Published data.[22]

$Pt/SO_4/ZrO_2$ and $Pt/SO_4/TiO_2$ and that observed in the IR spectrum of the $CO—Pt/SO_4/Al_2O_3$ system exceeds 10 cm^{-1}. At the same time, the stabilization of positively charged forms of platinum was also observed for the $Pt/SO_4/ZrO_2$ and $Pt/SO_4/TiO_2$ systems. Therefore, the interaction of sulfur with metal particles and formation of surface sulfides affect only the electronic state of the metal and its adsorption properties. The nature and properties of active sites, in particular, those gaining superacidic properties under certain treatment regimes, exert probably the maximum effect on the metal state.[1,23]

The structure of the active sites should be taken into account for a deeper understanding of the mechanism of the modifying action of the surface on the platinum state. Based on the spectral results, we have previously suggested[16,24] two alternative structures of the active sites (**1** and **2**) responsible for the superacidic properties of the SO_4/M_xO_y systems.



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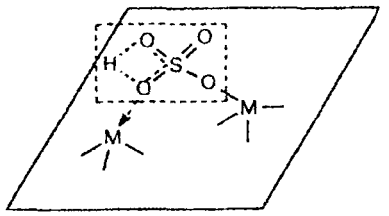

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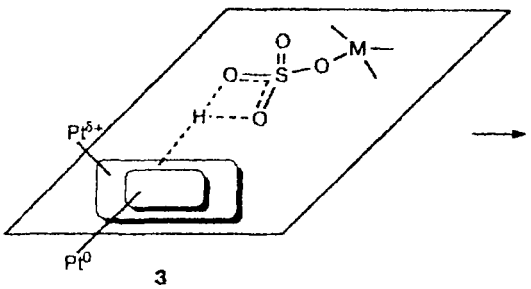
The strength of the acid centers formed depends on the nature of oxides and crystal lattice parameters. It was established that the addition of the SO_4^{2-} anions led to the enhancement of the Brönsted acid sites (BAS) in the ZrO_2- and TiO_2-based systems and LAS in the Al_2O_3-based systems, and the strength of BAS decreased in the series $SO_4/ZrO_2 > SO_4/TiO_2 > SO_4/Al_2O_3$.[24] No enhancement of the acid centers was observed for the SO_4/SiO_2 system.[23]

Comparison of these results with the data in Table 1 shows that the value of the shift of the AB maximum of CO adsorbed in the linear form on the platinum particles in the sulfated systems decreases in the same sequence. It can be assumed that BAS have the most significant effect on the electronic state of the metal. The interaction of the metal particles with the acid centers can be accompanied by the formation of surface sulfides due to side reactions of the metal with H_2S, which is formed during the reduction of the surface SO_4 groups. This could be the reason for the decrease in the stability of the surface CO complexes and shifts of the frequencies of vibrations of CO adsorbed in the linear form as compared to the samples containing no sulfur. However, as has been established previously,[9] the effect of these processes at reduction temperatures below 200 °C can be considered negligible: it becomes noticeable only after the reduction at 300 °C.

Taking into account the content and distribution of platinum in different electronic states on the surface of the SO_4/ZrO_2, SO_4/TiO_2, and SO_4/Al_2O_3 samples and the published data on the mechanism of interaction of platinum-promoted systems with hydrogen, we can suggest the following mechanism of formation of the charged forms of the metal in the $Pt/SO_4/M_xO_y$ systems.

When the metal is supported on the SO_4/M_xO_y surface, centers of two types are formed. The centers of the first type are the SO_4 groups separated from the metal particles. The centers of the second type are BAS localized in the vicinity of the metal particles and capable of interacting directly with them to change their electronic states. Depending on the strength of the acid centers, the interaction can proceed in two steps.



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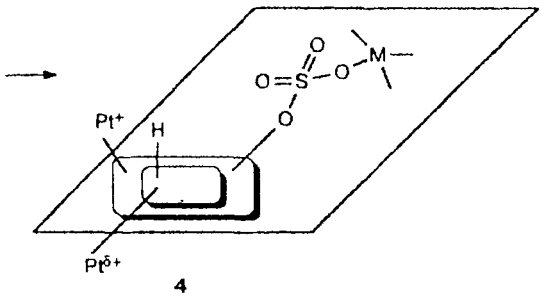

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At the first step (structure **3**), BAS interact with the metal particle to form the $[Pt—H]^{\delta+}$ adduct. The frequencies of the vibration of CO adsorbed in the linear form increase by 35—75 cm^{-1} compared to the systems containing no SO_4 groups. Other Pt-containing systems, in particular, zeolites,[26,27] are also characterized by a change in the frequency of CO vibrations induced by the difference in the acidities of the system. Thus, the value of the shift of the AB maximum of CO adsorbed in the linear form depends on the polarization extent of the $Pt...H...OSO_3$ bond and can serve as a measure for the strength of the acid centers of the system.

Stronger protonic sites can be released from the acid center to migrate over the metal surface (structure **4**). The OSO_3^- group reacts with the platinum particles to

form compounds of the $[Pt^+—OSO_3]$ type in which the platinum atom is positively charged. This agrees with the EXAFS data, which confirm the presence of compounds with Pt—O bond lengths that are different from those in conventional platinum oxides Pt—O—Pt.[28] It can be assumed that the Pt atoms with the charge 1+ remain to be bound to the particle of the reduced Pt^0 to form a sequence of charged states $Pt^+ \rightarrow Pt^{\delta+} \rightarrow Pt^0$. These compounds form complexes with CO giving AB in the 2150—2160 cm^{-1} region, which are observed upon CO adsorption on the $Pt/SO_4/ZrO_2$ and $Pt/SO_4/TiO_2$ samples. At the same time, weaker acid sites, like those in SO_4/Al_2O_3, cannot participate in proton transfer and, accordingly, no formation of positively charged forms of the metal ions is observed.

The proton transfer from the acid center to the metal is the reverse stage of the formation of the acid centers on the surface of the $Pt/SO_4/ZrO_2$ system in a hydrogen atmosphere described previously.[1,29] Hydrogen can generate new acid centers, while an inert environment favors a decrease in acidity of the surface centers due to the interaction with metal particles. This phenomenon is clearly seen in the catalytic processes of isomerization of *n*-butane on $Pt/SO_4/ZrO_2$ when hydrogen used as the carrier gas is replaced by helium or nitrogen.[24,30]

Thus, the electronic states of platinum supported on the SO_4/ZrO_2, SO_4/TiO_2, SO_4/Al_2O_3, and SO_4/SiO_2 systems and the systems containing no SO_4 groups were studied by diffuse-reflectance IR spectroscopy using CO as the probe molecule. In the nonsulfated systems, platinum is completely reduced in a hydrogen atmosphere at 200 °C, and the state of Pt is similar to that in the systems with a weak metal—support interaction.

The addition of the SO_4^{2-} anions suppresses the formation of bridging CO complexes with the metal and results in the stabilization of positively charged metal ions ($Pt^{\delta+}$ and Pt^+) during the reduction. Maxima of AB in the IR spectra of CO adsorbed in the linear form are shifted to the high-frequency region. All these effects are explained by the action of acidic protons at the surface, and the influence of the support on the electronic state of the metal increases in the following series: $SO_4/SiO_2 < SO_4/Al_2O_3 < SO_4/TiO_2 < SO_4/ZrO_2$, *i.e.*, it increases as the acidity of the system increases.

The mechanism of formation of positively charged forms of the metal most likely includes the interaction of the acidic protons with the metal particles to form the $[Pt—H]^{\delta+}$ adduct followed by the detachment of the most strong acidic protons and their migration over the metal surface.

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