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The state of metals in the Pt/Al_2O_3 and $(Pt—Cu)/Al_2O_3$ catalysts as indicated by IR spectroscopy with isotope dilution of $^{12}C^{16}O$ with $^{13}C^{18}O$ molecules

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Adsorption of $^{13}C^{18}O+^{12}C^{16}O$ mixtures on the Pt(2.9%)/γ-Al_2O_3, (Pt(2.6%)+Cu(2.7%))/γ-Al_2O_3, and (Pt(2.6%)+Cu(5.1%))/γ-Al_2O_3 catalysts was studied by FTIR spectroscopy. On the metallic Pt surface at coverages close to saturation, CO is adsorbed both strongly and weakly to form linear species for which the vibrational frequencies of the isolated $^{13}C^{18}O$ molecules adsorbed on Pt are ~1940 and ~1970 cm^{-1}, respectively. The redistribution of intensities of the high- and low-frequency absorption bands in the spectra of adsorbed $^{13}C^{18}O$ indicates that these linear forms are present on the adjacent metal sites. The weak adsorption is responsible for the fast isotope exchange between the gaseous CO and CO molecules adsorbed on metal. The Pt—Cu alloys, in which the electronic state of the surface Pt atoms characteristic of monometallic Pt remains unchanged, are formed on the surface of the reduced Pt—Cu bimetallic catalysts. The decrease in the vibrational frequencies of the isolated C=O bonds in the isolated Pt—CO complexes suggests that the CO molecules adsorbed on the Cu atoms affect the electronic properties of Pt.

Key words: adsorption, IR spectroscopy, catalysts.

The monometallic platinum catalysts exhibit high activity in various hydrocarbon conversions.[1] The addition of the second metal component to the catalyst can result in the formation of alloys and intermetallic compounds that strongly change the activity and selectivity of the bimetallic systems.[2] Similar changes were observed when studying the behavior of the Pt—Cu bimetallic catalysts in the reactions of hydrocarbon reforming,[3—5] paraffin dehydrogenation,[6—8] CO oxidation,[9,10] and hydrodechlorination of vicinal chlorohydrocarbons.[11—14] The bimetallic catalysts often served as model systems to obtain information on the electronic states and interactions between Pt and Cu.[11,12,15—18]

An analysis of the IR spectra of CO adsorbed on metals is widely used for investigation of the electronic and structural characteristics of the surface of bulky and supported metals. Information on the state of metals is obtained by examining vibrational frequencies of non-interacting (isolated) molecules of CO linearly adsorbed on the metals (singleton frequencies) and shifts of the frequencies of absorption band (AB) maxima, which appear due to the dipole-dipole interaction between the neighboring CO molecules adsorbed on metals.[19—21] Under the conditions when the dipole-dipole interaction between the adsorbed molecules is absent, the frequency of the AB maximum defined as the singleton frequency depends on the electron density on the metal atom that forms an adsorption complex with a CO molecule. Thus, the singleton frequency characterizes the electronic donor-acceptor properties of the adsorption sites on metals.[22] When the metal surface is covered with the adsorbed CO molecules, a dipole-dipole shift is observed, the magnitude of which is determined by the number of interacting adjacent vibrating dipoles,[4] and for adsorption close to saturation it characterizes the size of ensembles of atoms of the same nature.

At this saturation of the metal surface, the singleton frequencies and dipole-dipole shifts for CO adsorbed on the bulk[15,22,23] and supported metals[12,16,24—26] can be measured according to the method of isotope dilution usually using $^{13}C^{16}O+^{12}C^{16}O$ mixtures of different composition. Since the vibrational frequencies of the C≡O bonds in the $^{13}C^{16}O$ and $^{12}C^{16}O$ molecules differ by ~50 cm^{-1}, there is no dipole-dipole interaction between the adjacent $^{13}C^{16}O$ and $^{12}C^{16}O$ molecules. Therefore, the vibrational frequency of the adsorbed $^{12}C^{16}O$ molecules at low concentrations, when each $^{12}C^{16}O$ molecule is surrounded by the $^{13}C^{16}O$ molecules only, corresponds

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to the singleton frequency. The difference between the vibrational frequencies of $^{12}C^{16}O$ at coverages of the metal surface close to saturation and the singleton frequency corresponds to the dipole-dipole shift caused by the dipole-dipole interaction of the adsorbed $^{12}C^{16}O$ molecules. A similar approach can be used for the determination of the singleton frequencies and dipole-dipole shifts for the $^{13}C^{16}O$ molecules.

However, it is known[16,18,20,22] that for $^{13}C^{16}O$ and $^{12}C^{16}O$ adsorbed on VIII Group metals the AB intensity redistribution is observed. This redistribution and the overlapping of the AB of $^{13}C^{16}O$ and $^{12}C^{16}O$ adsorbed on metals in the linear form do not allow one to determine (with a sufficient accuracy) the position of the AB maximum of $^{13}C^{16}O$ at low concentrations of adsorbed $^{13}C^{16}O$.

For the Pt/SiO_2 catalyst we have shown[27] that difficulties in measuring the singleton frequencies and dipole-dipole shifts using the isotope dilution method can be avoided if the $^{13}C^{18}O+^{12}C^{16}O$ mixtures of different composition are used instead of the $^{13}C^{16}O+^{12}C^{16}O$ mixtures. It is found that the spectra of $^{13}C^{18}O$ adsorbed in the linear form on platinum can distinctly be observed at the $^{13}C^{18}O$ concentration in the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixture as low as a few per cent. At this concentrations, the dipole-dipole interaction of the $^{13}C^{18}O$ molecules is absent, which allows one to determine the singleton frequencies of $^{13}C^{18}O$ and dipole-dipole shifts of $^{12}C^{16}O$, using one measurement of the spectrum of the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixture with a low content of $^{13}C^{18}O$.

In the present work, we describe the spectral study of the state of metals in the monometallic Pt and bimetallic Pt—Cu catalysts supported on alumina using the isotope dilution method with the $^{13}C^{18}O+^{12}C^{16}O$ mixtures of different composition.

Experimental

The catalyst support was γ-Al_2O_3 (Vista-B, specific surface 300 $m^2 g^{-1}$, average pore size 55 Å). The monometallic Pt catalyst was prepared by the impregnation of the support with aqueous solutions of H_2PtCl_6. The Pt content in the catalyst was 2.9 wt.%. The bimetallic Pt—Cu catalysts, namely, (Pt—Cu(1 : 3))/Al_2O_3 and (Pt—Cu(1 : 6))/Al_2O_3 containing Pt(2.6%)+Cu(2.7%) (Cu/Pt = 3) and Pt(2.6%)+Cu(5.1%) (Cu/Pt = 6), respectively, were prepared by the impregnation of the support with a mixture of aqueous solutions of H_2PtCl_6 and $CuCl_2$. Before spectral measurements, the catalysts were calcined in air at 500 °C, cooled to ~20 °C, and compacted into pellets with a "thickness" of ~20 mg cm^{-2} under a pressure of 830 atm. The pellets were placed in an IR cell, whose design has been described earlier,[28] reduced for 1 h in a hydrogen flow (60 mL min^{-1}) at 350 °C, and then evacuated for 1 h at this temperature.

The IR spectra of the adsorbed $^{13}C^{18}O$ (^{13}C, 99%; ^{18}O 95%+) and $^{12}C^{16}O$ (99.99+%) mixtures were measured at ~20 °C and an equilibrium pressure of the mixture of $1.6 \cdot 10^3$ Pa on a Research Series II FTIR spectrophotometer. The spectra were recorded with a resolution of 4 cm^{-1}, and the number of scans was 400. First, the $^{13}C^{18}O+^{12}C^{16}O$ mixture was introduced to the reduced sample. After the catalysts were stored in the mixture for 20 min, the IR spectrum was measured in the presence of the gas phase. Then the gaseous mixture was evacuated at ~20 °C for 20 min and the IR spectrum of chemisorbed CO was recorded in the absence of the gas phase. Systematically repeating these experiments and changing the composition of the isotope mixture, the effect of the composition of the $^{13}C^{18}O+^{12}C^{16}O$ mixture on the spectra of adsorbed CO was investigated.

The singleton frequencies $\nu_{Pt}(^{13}C^{18}O)$ of the Pt—$^{13}C^{18}O$ linear complexes were determined directly from the spectra of the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixtures containing $^{13}C^{18}O$ in very low concentrations. The singleton frequencies $\nu_{Pt}(^{12}C^{16}O)$ for the Pt—$^{12}C^{16}O$ complexes were calculated by the formula $\nu_{Pt}(^{13}C^{18}O)$ + 100 cm^{-1}, where 100 cm^{-1} is the difference between the vibrational frequencies of the C=O bonds in the $^{12}C^{16}O$ and $^{13}C^{18}O$ molecules. The dipole-dipole shifts $\Delta\nu_{Pt}(^{12}C^{16}O)$ were determined as the difference between the frequencies of the AB maxima of $^{12}C^{16}O$ at near saturation coverages of the Pt surface with the mixtures with the low content of $^{13}C^{18}O$ and the calculated singleton frequency of $^{12}C^{16}O$.

Results and Discussion

The IR spectra of the $^{13}C^{18}O+^{12}C^{16}O$ mixtures of different composition adsorbed on the Pt(2.9%)/Al_2O_3 catalyst measured in the presence of the gas phase under an equilibrium pressure of $1.6 \cdot 10^3$ Pa are shown in Fig. 1. The spectrum of adsorbed $^{12}C^{16}O$ contains AB at 2085 and 1845 cm^{-1} assigned to the linear and bridged $^{12}C^{16}O$ complexes with metallic Pt.[29] The spectra of the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixture with a low $^{12}C^{16}O$ content exhibit AB at 1985 and 1760 cm^{-1}. Since the vibrational frequency of the C≡O bond in the $^{13}C^{18}O$ molecule is by 100 cm^{-1} lower than that in the $^{12}C^{16}O$ molecule, the indicated AB should be ascribed to the linear and bridged

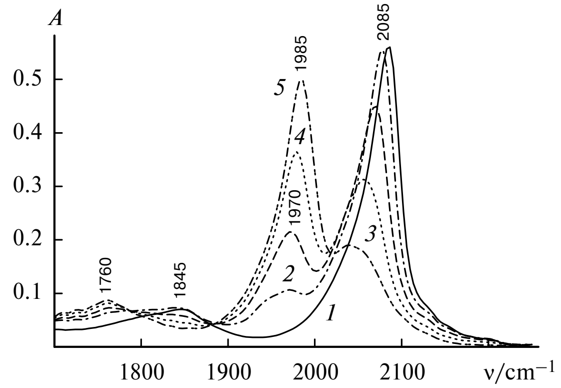

Fig. 1. FTIR spectra of $^{13}C^{18}O+^{12}C^{16}O$ mixtures with the $^{13}C^{18}O$ content 0 (*1*), 24 (*2*), 37 (*3*), 76 (*4*), and ~100% (*5*) adsorbed on the Pt(2.9%)/γ-Al_2O_3 catalyst in the presence of the gas phase. Hereinafter the spectra are measured at ~20 °C and the equilibrium pressure of the mixtures $1.6 \cdot 10^3$ Pa.

$^{13}C^{18}O$ complexes with metallic Pt, respectively. The spectrum of the $^{13}C^{18}O+^{12}C^{16}O$ mixture at a low $^{12}C^{16}O$ concentration also contains the AB at 2040 cm^{-1} characteristic[29] of the singleton of the Pt—$^{12}C^{16}O$ linear complexes.

The IR spectra of the linear Pt—$^{13}C^{18}O$ complexes appeared upon the adsorption of the $^{13}C^{18}O+^{12}C^{16}O$ mixtures with a low $^{13}C^{18}O$ concentration on the Pt/Al_2O_3 catalyst are shown in Fig. 2. The spectra were measured in the presence of the gas phase under an equilibrium pressure of the mixtures of $1.6 \cdot 10^3$ Pa. These spectra were obtained by the subtraction of the spectrum of adsorbed $^{12}C^{16}O$ from the spectra of the adsorbed mixtures. Since the monometallic Pt catalyst contains two types of sites of $^{13}C^{18}O$ adsorption in the linear form to which the AB at 1940 and 1970 cm^{-1} correspond, it can be assumed that the sites on the Pt surface are nonuniform. The frequencies of the AB maxima at the minimum $^{13}C^{18}O$ concentration in the mixture can be considered as singleton frequencies. After the gas phase was evacuated at room temperature for 20 min, the AB at 1970 cm^{-1} disappears from the spectra. Therefore, this band is attributed to the Pt—$^{13}C^{18}O$ linear complexes unstable at room temperature.

The intensities of the both AB increase with an increase in the $^{13}C^{18}O$ concentration in the mixture. In this case, the intensity of the high-frequency AB increases more strongly than the intensity of the AB at 1940 cm^{-1} (see Fig. 2). At the $^{13}C^{18}O$ concentrations in the mixture higher than 37%, the spectrum of the linear Pt—$^{13}C^{18}O$ complexes contains the single AB with a maximum at 1970—1985 cm^{-1} (see Fig. 1). These changes in the spectra indicate the redistribution of intensities of the low- and high-frequency absorption bands.

The intensity redistribution of the low- and high-frequency AB occurs if the difference in the frequencies of CO adsorbed on the closely spaced sites of two types is relatively low. This effect can distinctly be traced for the AB of the linear Pt—$^{13}C^{16}O$ and Pt—$^{12}C^{16}O$ complexes formed when the $^{13}C^{16}O+^{12}C^{16}O$ mixtures are adsorbed on the surface of Pt single crystals (see Ref. 30) and on Pt supported on alumina.[16] The intensity redistribution is also observed for the AB of the Pt—$^{13}C^{18}O$ and Pt—$^{12}C^{16}O$ complexes generated by the adsorption of the $^{13}C^{18}+^{12}C^{16}O$ mixtures on Pt supported on silica gel but it is much weaker than that for the Pt—$^{13}C^{18}$ and Pt—$^{12}C^{16}O$ complexes.[13] This difference in the effect of redistribution of the AB intensities is related to the fact that the difference in the vibrational frequencies of the C≡O bonds in the $^{13}C^{16}O$ and $^{12}C^{16}O$ molecules (50 cm^{-1}) is by two times lower than that for the $^{13}C^{18}O$ and $^{12}C^{16}O$ molecules (100 cm^{-1}). The effect of the AB intensity redistribution for the strong and weak Pt—$^{13}C^{16}O$ linear complexes should be more pronounced than that for the Pt—$^{13}C^{16}O$ and Pt—$^{12}C^{16}O$ complexes, because the difference in the vibrational frequencies of the $^{13}C{\equiv}^{18}O$ bonds for the $^{13}C^{18}O$ molecules adsorbed on the catalyst in the strong and weak forms is only ~30 cm^{-1}, *i.e.*, much lower than that for the complexes involving $^{13}C^{16}O$ and $^{12}C^{16}O$ (50 cm^{-1}).

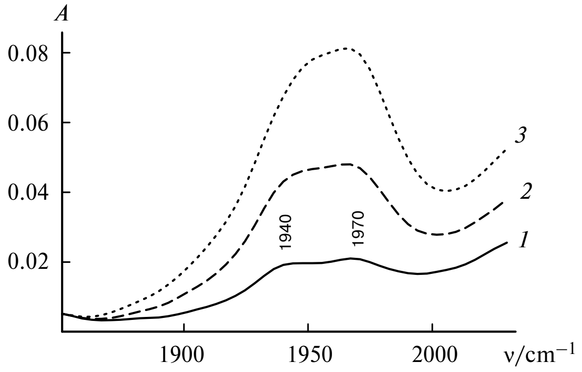

Fig. 2. FTIR spectra of the Pt—$^{13}C^{18}O$ complexes formed during adsorption on the Pt(2.9%)/γ-Al_2O_3 catalyst of $^{13}C^{18}O+^{12}C^{16}O$ mixtures with the $^{13}C^{18}O$ content 7 (*1*), 15 (*2*), and 25% (*3*) in the presence of the gas phase.

The phenomenon of the AB intensity redistribution impedes and often makes it impossible to determine the dipole-dipole shifts for different linear Pt—$C^{13}O^{18}$ complexes localized on the adjacent metal sites. In fact, at high $^{13}C^{18}O$ concentrations in the mixtures in the presence of the gas phase, the AB at 1940 cm^{-1} is transformed into the AB corresponding to $^{13}C^{18}O$ weakly adsorbed in the linear form on Pt (see Fig. 2). Thus, the examination of the IR spectra of the $^{13}C^{18}+^{12}C^{16}O$ mixtures of different composition adsorbed on Pt/Al_2O_3 in the presence of the gas phase makes it possible to determine the singleton frequencies for both the strong (1940 cm^{-1}) and weak (1970 cm^{-1}) Pt—$^{13}C^{18}O$ linear complexes (at low concentrations of $^{13}C^{18}O$ in the mixtures) but the dipole-dipole shift of 15 cm^{-1} (see Figs 1 and 2) can be detected only for weak complexes. At the same time, the measurement of the spectra of the adsorbed mixtures in the absence of the gas phase (Fig. 3), when the weak form of adsorbed CO is absent, makes it possible to determine both the singleton frequency (1943 cm^{-1}) and dipole-dipole shift (37 cm^{-1}, Table 1) for the strong Pt—$^{13}C^{18}O$ complexes.

The effect of the intensity redistribution of the low- and high-frequency AB of adsorbed CO have theoretically been interpreted earlier.[20,31,32] This effect is caused by the fact that the CO molecules adsorbed on the metal with a high vibrational frequency of the C≡O bond screen the external oscillating electrical field on the site of occurrence of a molecule with a low vibrational frequency of the C≡O bond.[23] This decreases the absorption of the electromagnetic radiation by the molecules with low vibrational frequencies of the C≡O bond. At the same time, the molecules with low vibrational frequencies of C≡O enhance the external electrical field at the position of the

Table 1. Spectral characteristics (ν/cm^{-1}) of the CO complexes with Pt and Cu in the presence (I) and absence (II) of the gas phase

Catalyst	$\nu_{Pt}(^{13}C^{18}O)$		$\nu_{Pt}(^{12}C^{16}O)$		$\Delta\nu_{Pt}(^{13}C^{18}O)$		$\Delta\nu_{Pt}(^{12}C^{16}O)$		$\nu_{Cu}(^{13}C^{18}O)$		$\nu_{Cu}(^{12}C^{16}O)$	
	I	II	I	II	I	II	I	II	I	II	I	II
Pt/Al_2O_3	1940, 1970	1942	2040	2042	15	37	15	37	—	—	—	—
$(Pt—Cu(1:3))/Al_2O_3$	1935, 1967	1942	2035, 2017	2042	20	15	20	15	2035	2037	2135	2135
$(Pt—Cu(1:6))/Al_2O_3$	1925	1940	2025	2040	15	14	15	14	2035	2035	2135	2136

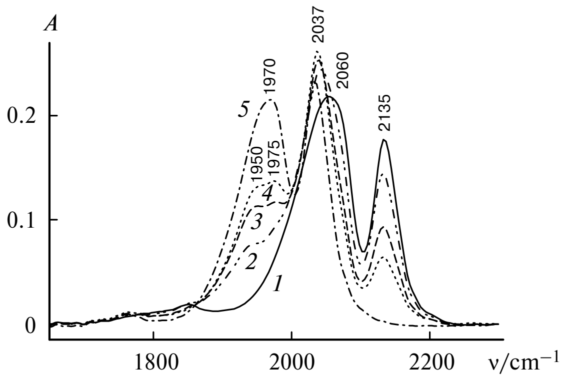

Fig. 3. FTIR spectra of $^{13}C^{18}O+^{12}C^{16}O$ mixtures with the $^{13}C^{18}O$ content 0 (*1*), 25 (*2*), 50 (*3*), 65 (*4*), and ~100% (*5*) adsorbed on the (Pt—Cu(1 : 3))/γ-Al_2O_3 catalyst in the presence of the gas phase.

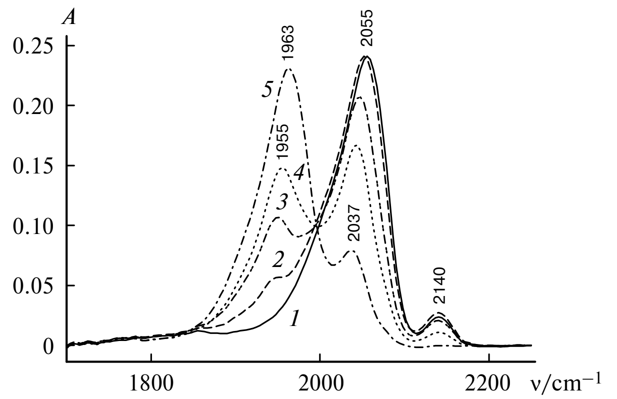

Fig. 4. FTIR spectra of $^{13}C^{18}O+^{12}C^{16}O$ mixtures with the $^{13}C^{18}O$ content 0 (*1*), 15 (*2*), 38 (*3*), 65 (*4*), and ~100% (*5*) adsorbed on the (Pt—Cu(1 : 3))/γ-Al_2O_3 catalyst in the absence of the gas phase.

molecules adsorbed on the sites with high vibrational frequencies of the C≡O bonds,[33] increasing their absorption of the electromagnetic radiation. Therefore, in the case of adsorption of the $^{13}C^{16}+^{12}C^{16}O$ mixtures on platinum, the integral intensity of the high-frequency AB of the Pt—$^{12}C^{16}O$ complexes increases due to a decrease in the AB intensity of the Pt—$^{13}C^{16}O$ complexes.

The weakly bound forms of CO adsorption on metallic platinum supported on silica gel and alumina are described.[34—36] The calorimetric studies of the heats of CO adsorption on Pt/SiO_2 at 673 K showed[37] that, when the surface coverage is close to saturation (0.7 of the monolayer), the heat decreases from 180—190 to 75 kJ mol^{-1} with an increase in the coverage of the metal surface. The same decrease in the heats is observed for CO adsorption on the single-crystal Pt(111) surface.[38] As shown by the calculations,[37] for the molecules adsorbed with a heat of 75 kJ mol^{-1} the desorption rate constant at room temperature should be ~1 s^{-1}. Therefore, for the coverages of the Pt surface close to saturation (0.6—0.7 of the monolayer), the gaseous and adsorbed CO molecules are rapidly equilibrated even at room temperature. This is indicated, in particular, by the strong dependence of the frequencies of the maxima and intensities of the AB of the Pt—$^{13}C^{18}O$ complexes on the $^{13}C^{18}O$ concentration in the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixtures (Figs 1, 3, and 4). Evidently, these effects are caused by the fast isotope exchange between the gaseous phase and molecules adsorbed on Pt and, most likely, this exchange involves weakly adsorbed CO species.

The presence of weakly bound CO on the Pt surface can be explained as follows. It was found[39—43] that at high coverages of the Pt surface the layer of adsorbed CO is compressed. In the compacted layer, the CO molecules are closely packed and their orbitals begin to overlap. This results in the intermolecular repulsion due to which the electron density on the 2π*-orbitals of CO decreases. As a result, the C=O bond becomes stronger (the vibrational frequency of the C=O bonds increases) and the Pt—C bond becomes less stable (the heat of CO adsorption decreases). Thus, the CO molecules weakly bound to Pt corresponding to a singleton frequency of 1970 cm^{-1} should be localized on terraces deeply inside the CO adsorption layer. The strongly bound CO molecules with the singleton frequency 1940 cm^{-1} are arranged, most likely, at the periphery of the compressed islands of CO.

The IR spectra of the mixtures of different composition adsorbed on the (Pt—Cu(1 : 3))/Al_2O_3 catalysts measured in the presence and absence of the gas phase are shown in Figs 3 and 4. The spectrum of adsorbed $^{12}C^{16}O$ recorded in the presence of the gas phase exhibits the intense AB at 2060 and 2135 cm^{-1} assigned to the Pt—$^{12}C^{16}O$ [15] and Cu—$^{12}C^{16}O$ [16] linear complexes (see Fig. 3). The bridged forms of CO adsorbed on platinum are virtually absent. When the $^{13}C^{18}O$ concentration in the mixture increases, the intensity of the AB at 2135 cm^{-1} decreases monotonically. Then this AB transforms into the AB at 2037 cm^{-1} assigned to the $^{13}C^{18}O$ complexes with copper. At the $^{13}C^{18}O$ concentrations in the adsorbed mixtures higher than 40%, in addition to the AB at 1950 cm^{-1}, the AB at 1975 cm^{-1} appears distinctly (see Fig. 3), which is removed from the spectra by evacuation of the sample at room temperature (see Fig. 4). Therefore, this band corresponds to unstable linear Pt—$^{13}C^{18}O$ complexes. For a mixture with the $^{12}C^{16}O$ concentration close to zero, one AB at 1970 cm^{-1} is detected in the spectrum of the Pt—$^{12}C^{16}O$ linear complexes, indicating the intensity redistribution of the AB of the strong and weak Pt—$^{13}C^{18}O$ linear complexes. Therefore, these complexes are arranged in the immediate vicinity to each other.

At low $^{13}C^{18}O$ concentrations in the mixtures, the spectra obtained by the subtraction of the spectrum of adsorbed $^{12}C^{16}O$ from the spectra of the adsorbed mixtures contain the AB at 1935 cm^{-1} and a less intense AB at 1967 cm^{-1}, which is removed from the spectrum by the evacuation of the sample at room temperature for 20 min (the spectra are not presented). The maxima of these AB correspond to the singleton frequencies of the stable and unstable at room temperature $Pt^{13}C^{18}O$ linear complexes, respectively.

For the (Pt—Cu(1 : 6))/Al_2O_3 catalyst, no weak forms of the linear Pt—CO complexes and no bridged forms of adsorbed CO on Pt are observed. Therefore, at any $^{13}C^{18}O$ concentrations in the adsorbed mixtures in the presence and absence of the gas phase, the spectra of $^{13}C^{18}O$ and $^{12}C^{16}O$ adsorbed on platinum consist of single lines. In the presence of the gas phase with a high content of $^{12}C^{16}O$, the spectra contain the AB at 2136 cm^{-1}, which, as in the case of the (Pt—Cu(1 : 3))/Al_2O_3 catalyst, corresponds to the $^{12}C^{16}O$ complexes with copper.

The plots of the vibrational frequency of $^{13}C^{18}O$ adsorbed on Pt for the (Pt—Cu(1 : 6))/Al_2O_3 catalyst *vs.* $^{13}C^{18}O$ concentration in the $^{13}C^{18}O+^{12}C^{16}O$ adsorbed mixture recorded in the presence and absence of the gas phase are shown in Fig. 5. In the presence of the gas phase, the singleton frequency and dipole-dipole shift are 1925 and 15 cm^{-1}, respectively. When the gas phase is removed, the singleton frequency increases by 15 cm^{-1} and becomes equal to 1940 cm^{-1}. In this case, the dipole-dipole shift remains unchanged within the measurement error (±2 cm^{-1}).

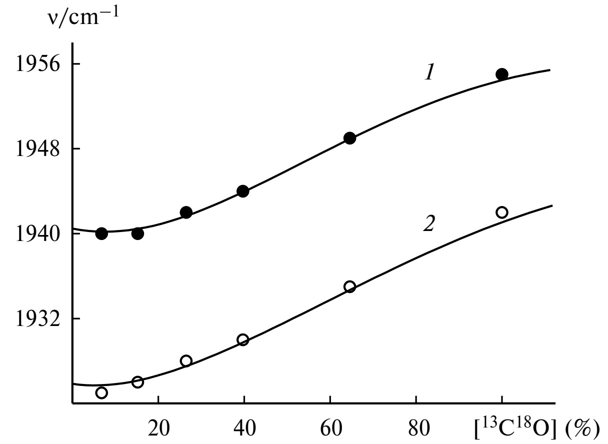

Fig. 5. Dependences of the frequencies of absorption band maxima of the stable Pt—$^{13}C^{18}O$ complexes on the $^{13}C^{18}O$ concentration in $^{13}C^{18}O+^{12}C^{16}O$ mixtures adsorbed on the (Pt—Cu(1 : 6))/γ-Al_2O_3 catalyst. The spectra were measured at ~20 °C in the absence (*1*) and presence (*2*) of the gas phase.

As shown by the data presented in Figs 1—5, during adsorption of the $^{13}C^{18}O+^{12}C^{16}O$ mixtures one can distinctly detect the spectra of metal-adsorbed $^{13}C^{18}O$ at its low concentrations in the mixtures. This is related to the fact that at low concentrations the adsorbed $^{13}C^{18}O$ molecules are far apart and there is no dipole-dipole interaction between the $^{13}C^{18}O$ molecules. Due to the high difference in the vibrational frequencies of the C≡O bonds in the $^{12}C^{16}O$ and $^{13}C^{18}O$ molecules (100 cm^{-1}), the intensity redistribution of the AB of the adsorbed $^{13}C^{18}O$ and $^{12}C^{16}O$ molecules is low. Thus, the spectra of the adsorbed mixtures with a low content of $^{13}C^{18}O$ allow one to determine the singleton frequencies of $^{13}C^{18}O$ adsorbed on the metal in the linear form, which are by 100 cm^{-1} lower than the singleton frequencies of $^{12}C^{16}O$. This differences between the frequencies of the maxima of $^{12}C^{16}O$ adsorbed at the coverages of the metal surface close to saturation and the singleton frequency of $^{12}C^{16}O$ correspond to the dipole-dipole shift of the $^{12}C^{16}O$ molecules.

When CO is adsorbed on copper, *i.e.*, in the presence of the $^{13}C^{18}O+^{12}C^{16}O$ gaseous mixture, the singleton frequency for the strong CO complexes with platinum of the Pt—Cu bimetallic catalysts decreases (see Table 1) for (Pt—Cu(1 : 3))/Al_2O_3 and (Pt—Cu(1 : 6))/Al_2O_3 by 7 and 15 cm^{-1}, respectively. A similar phenomenon has been observed previously[16,31—33] and explained by the increase in the reverse donation of the electron density from Pt to the 2π*-antibonding orbital of CO in the Pt—CO complexes during CO adsorption on the adjacent Cu atoms.[8] This effect should be observed for the formation of Pt—Cu alloys.

Carbon monoxide is weakly adsorbed on Cu and its most part can be removed by evacuation at room temperature (*cf.* curves in Figs 3 and 4). As a result, the singleton frequencies of the Pt—CO complexes increase. In the absence of the gas phase, the singleton frequencies of the Pt—CO complexes virtually coincide for all the catalysts (see Table 1).

It can be concluded from these data that copper does not modify the electronic properties of Pt. The decrease in the dipole shifts for CO adsorbed on Pt in the bimetallic catalysts is caused by the dilution of surface platinum with copper, *i.e.*, formation of a platinum alloy with copper. In the surface of the alloy particles the electronic properties of the Cu atoms are strongly modified by platinum. This appears as an increase in the vibrational frequency of the C≡O bonds in the Cu—CO complexes by 30—40 cm^{-1} compared to that for non-modified copper.[29,44]

Thus, an increase in the singleton frequency of the Pt—CO complexes upon CO removal from the copper atoms and a decrease in the dipole-dipole shift due to the dilution of Pt with copper from 37 cm^{-1} (for Pt/Al_2O_3) to 15 cm^{-1} (for the Pt—Cu bimetallic catalysts) indicate the formation of platinum—copper alloys rather than individual Pt and Cu crystallites upon the reduction of the bimetallic catalysts.

* * *

The low dipole-dipole interaction between the $^{13}C^{18}O$ and $^{12}C^{16}O$ molecules adsorbed on Pt makes it possible to detect the Pt—$^{13}C^{18}O$ complexes formed due to the adsorption of the $^{13}C^{18}O+^{12}C^{16}O$ mixtures with a low content of $^{13}C^{18}O$ on the catalysts. This allows one to determine the singleton frequencies of the Pt—$^{13}C^{18}O$ complexes and dipole-dipole shifts from the single spectrum of this adsorbed mixture.

On the surface of metallic Pt at coverages close to saturation, both strongly and weakly adsorbed linear species of CO are observed for which the singleton frequencies of Pt—$^{13}C^{18}O$ are 1940 and 1970 cm^{-1}, respectively. These both forms can exist on the adjacent Pt atoms, due to which the intensities are redistributed between the high- and low-frequency AB in the spectra of adsorbed $^{13}C^{18}O$. The weak adsorption form is responsible, most likely, for the fast isotope exchange between the gaseous and metal-adsorbed CO molecules at room temperature.

When the Pt—Cu bimetallic catalysts are reduced, platinum—copper alloys are formed on their surface. In this case, no direct electron modification of the surface Pt atoms occurs but platinum is diluted with copper. The CO molecules adsorbed on the Cu atoms decrease the singleton frequency of the Pt—CO complexes, *i.e.*, modify the electronic properties of platinum.

The electronic properties of the Cu atoms on the alloy surface are strongly modified by platinum. This appears as the increase by 30—40 cm^{-1} in the vibrational frequency of the C≡O bonds in the Cu—CO complexes compared to similar CO complexes with non-modified copper.[29,44]

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