Influence of the support on the state of nickel in the Ni/SiO_2, Ni/ZrO_2, and $Ni/SO_4/ZrO_2$ oxide systems studied by diffuse-reflectance IR spectroscopy

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The Ni/SiO_2, Ni/ZrO_2, and $Ni/SO_4/ZrO_2$ systems were studied by diffuse-reflectance IR spectroscopy using CO as a probe molecule. The Ni/SiO_2 and Ni/ZrO_2 systems are similar in properties, and the state of nickel in the Ni/ZrO_2 system is determined by the specific surface area. In the $Ni/SO_4/ZrO_2$ system, the surface sulfur compounds affect substantially the state of nickel: $Ni^{\delta+}$ species with a partial positive charge are formed due to the strong electron-acceptor properties of the sulfur compounds.

Key words: nickel, silicon oxide, zirconium oxide, sulfate-promoted zirconium oxide, metal—support interaction; diffuse-reflectance IR spectroscopy.

The study of several catalysts based on SO_4/ZrO_2 promoted by transition metals[1–3] ($Pt/SO_4/ZrO_2$, $Pd/SO_4/ZrO_2$, and $Rh/SO_4/ZrO_2$) made it possible to establish that the physicochemical properties of the surface have a strong effect on the metal state *via* the stabilization of partially positive charged forms. The addition of a metal can result in a change in the acidic properties of the system at the stage of the metal reduction due to a decrease in the oxidation state of sulfur in the SO_4 group.

Ni-containing systems exhibit catalytic activity in hydrogenolysis of the C—C bonds.[4,5] Nickel-containing superacids based on SO_4/ZrO_2 were studied as catalysts for the isomerization of *n*-butane[4] and hydrocracking of polyolefins.[5] Although nickel in hydrogenation reactions is substantially less active than the platinum systems, an increase in the activity of the Ni-containing catalysts can make them promising from the viewpoint of replacement of platinum, for example, in hydroisomerization and hydrocracking of paraffins.

The study of the $Ni/SO_4/ZrO_2$ system by diffuse-reflectance IR spectroscopy, in particular, in the region of vibrations of adsorbed carbon monoxide, gives valuable information on the metal state under different conditions of treatment. At the same time, it is difficult to study reduced Ni-containing systems by the spectra of adsorbed CO, because nickel, unlike platinum and other noble metals, is prone to the formation of volatile carbonyl compounds $Ni(CO)_4$ upon CO adsorption. In addition, metallic nickel species formed by the reduction tend to coalescence and sinter to form large agglomerates for which the effect of properties of the support surface can be insufficient. Nevertheless, it is known that the SO_4/ZrO_2-supported metals are stabilized in the highly dispersed state[3] due to the interaction of the metal microparticles with the active centers of the SO_4/ZrO_2 surface.

In this work, we studied the $Ni/SO_4/ZrO_2$ and Ni/ZrO_2 systems by IR spectroscopy. For comparison, we also studied the Ni/SiO_2 system prepared and treated similarly to the ZrO_2-based systems. It is known that SiO_2 exhibits neutral properties, and the interaction of nickel with the silica surface resulting in the formation of silicates begins only after the treatment of the samples at $T > 700$ K. Therefore, the interaction of Ni with SiO_2 can be considered insignificant under the conditions chosen in this work.

Experimental

Preparation of Ni/ZrO_2. Samples of Ni/ZrO_2 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 $Ni(NO_3)_2$ to a concentration of Ni of 0.5 wt.%. The catalyst was dried at 390 K for 6 h and calcined at 790 K for 2 h in a flow of anhydrous air.

Preparation of $Ni/SO_4/ZrO_2$. Samples of $Ni/SO_4/ZrO_2$ were prepared by impregnation of the $Zr(OH)_4$ with a 1 *N* aqueous solution of H_2SO_4 to a concentration of SO_4^{2-} of 5 wt.%. The samples were dried at 390 K for 2 h, and Ni (0.5 wt.%) from an aqueous solution of $Ni(NO_3)_2$ was deposited. The catalyst was dried at 390 K for 6 h and calcined at 870 K for 3 h in an air flow.

Preparation of Ni/SiO_2. Samples of Ni/SiO_2 were prepared by impregnation of the starting SiO_2 ($S_{sp} = 400$ m^2 g^{-1}) with an aqueous solution of $Ni(NO_3)_2$ to a concentration of Ni of 0.5 wt.%. The catalyst was dried at 390 K for 6 h and calcined at 790 K for 2 h in a flow of anhydrous air.

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Reduced samples of Ni-catalysts ($Ni/SO_4/ZrO_2$, Ni/ZrO_2, and Ni/SiO_2). Prior to the measurements, samples (0.5 g) with particle size of 0.2—0.5 mm were placed in a quartz reactor with a CaF_2 window for recording IR spectra and then activated at 670 K *in vacuo* for 1 h. To obtain the reduced form of nickel, the starting catalysts were treated at 470, 570, or 620 K for 2 h in a hydrogen flow (the consumption of H_2 was 30 mL min^{-1}), evacuated at 620 K to the residual pressure of 10^{-4} Torr, and cooled to room temperature.

Measurements of IR spectra. Carbon monoxide (20 Torr) was admitted on the pre-activated and evacuated samples. IR spectra were recorded on Perkin—Elmer 580B and Nicolet Impact 410 spectrophotometers with diffuse-reflectance attachments.[6] After recording the spectrum, the samples were evacuated with a stepped temperature increase at increments of 50 K, and the spectra were recorded for each *T* value. The spectra were quantitatively processed by the Kubelka—Munk equation according to the previously described procedures.[7,8]

Results and Discussion

The treatment of all systems by hydrogen at 470—570 K does not result in a noticeable reduction of nickel, which is indicated by the IR spectra of the adsorbed CO. An increase in the treatment temperature to 620 K changes the shape of the spectra.

Ni/SiO_2 system. The IR spectrum of the CO adsorbed on the Ni/SiO_2 sample reduced at 620 K (Fig. 1, *a*) exhibits two main absorption bands (AB) of ν(CO) at 2060 and 2010 cm^{-1} and less intense AB at 2175, 2125, 1960, and 1850 cm^{-1}. The presence of weak high-frequency AB at 2175 and 2125 cm^{-1} attests to positively charged forms of nickel,[9,10] which can be due to the incomplete reduction of the sample. The other bands are assigned to the CO molecules adsorbed on the metallic nickel particles.[10,11] The absorption bands at 2060 and 2010 cm^{-1} correspond to the CO adsorbed in a linear form on the metal atoms on the surface of the metallic particles, while AB at 1960 and 1850 cm^{-1} can be attributed to the surface CO complexes corresponding to two-centered and three-centered forms of adsorption.[12] As known from the published data,[10,11,13] the adsorption of CO molecules on metallic nickel at room temperature can lead to the formation of carbonyl compounds $Ni(CO)_4$. The vibrations of $Ni(CO)_4$ are characterized by the ν(CO) frequency of 2057 cm^{-1}, which remains almost unchanged during the interaction with the surfaces of oxide and zeolite systems.[14] However, the high intensity of the AB at 2060 cm^{-1} and the reproducibility of the spectral pattern after the complete removal and repeated admission of CO do not allow one to assign the band at 2060 cm^{-1} to the volatile compound $Ni(CO)_4$. The assignment of this band to vibrations of the CO molecules adsorbed on the metallic nickel particles in the linear (Ni—CO) form seems more probable.[12] In this case, the AB at 2010 cm^{-1} can correspond to the vibrations of the CO adsorbed on the corners and edges of the metal particles.

Ni/ZrO_2 system. Three main AB of ν(CO) at 2185, 2060, and 1960 cm^{-1} and a less intense AB at 2135 and 1860 cm^{-1} are observed in the IR spectra of the CO adsorbed on the Ni/ZrO_2 sample reduced at 620 K (Fig. 1, *b*). The band at 2185 cm^{-1} is most likely related to the CO molecules adsorbed on the Lewis acidic sites (LAS) ZrO_2. The insignificant shift of its maximum from the frequency of 2190 cm^{-1}, which is characteristic of the oxidized ZrO_2-based samples (see also Ref. 15), to 2185 cm^{-1} can be explained by either superposition of

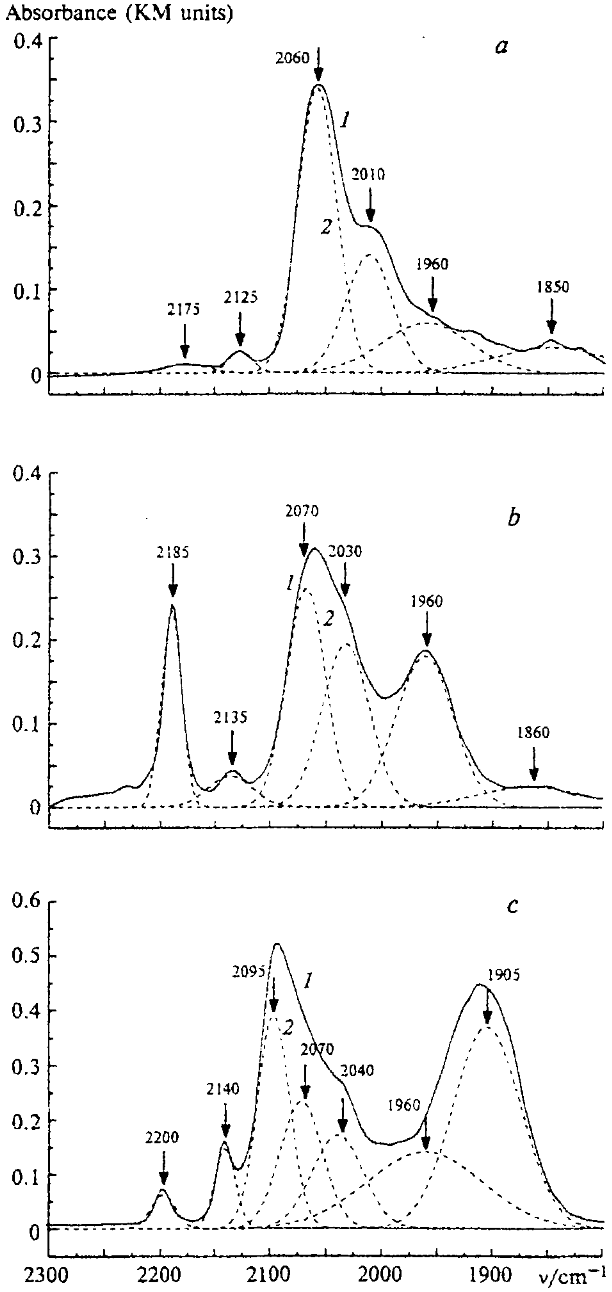


Fig. 1. IR spectra of CO (20 Torr) adsorbed at 300 K on the Ni/SiO_2 (*a*), Ni/ZrO_2 (*b*), and $Ni/SO_4/ZrO_2$ (*c*) samples reduced at 620 K (*1*) and decomposition of the spectra into components (*2*).

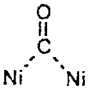
AB of the Ni^{2+}—CO complex (~2195 cm^{-1}) or partial reduction of Zr^{4+} to Zr^{3+} after treatment with hydrogen. The other bands can be assigned to vibrations of the CO adsorbed in the linear form on Ni^{+} (2135 cm^{-1}) and Ni^{0} (2060 cm^{-1}) and to surface complexes formed for the two-centered (1960 cm^{-1}) and three-centered (1860 cm^{-1}) forms of the CO adsorption on the metallic nickel particles. The analysis of the nonsymmetrical AB at 2060 cm^{-1} makes it possible to decompose it into two components: 2070 and 2030 cm^{-1}. The first band is similar to the AB at 2060 cm^{-1} in the spectrum of the Ni/SiO_2 sample; however, its maximum is shifted by 10 cm^{-1} toward high frequencies. The second band corresponds to the AB at 2010 cm^{-1} for the Ni/SiO_2 system, and its maximum is shifted by 20 cm^{-1} to the high-frequency region.

The analysis of the results obtained for the adsorption of CO on Ni/SiO_2 and Ni/ZrO_2 shows that the spectral parameters of these systems are close; however, differences related to the intensity and positions of the bands are observed. The IR spectrum of CO adsorbed on Ni/SiO_2 (see Fig. 1, *a*) indicates that small metallic nickel particles are formed on the SiO_2 surface. This is evidenced by the low intensity of the AB corresponding to multicentered forms of adsorption of the CO molecules (ν(CO) 1960 and 1850 cm^{-1}) and the position of the AB of the Ni^{0}—CO complex (ν(CO) 2010 cm^{-1}).

The following changes in the spectrum of the Ni/ZrO_2 system compared to that of Ni/SiO_2 can be mentioned: the shift of the AB corresponding to vibrations of the CO adsorbed on the metal particles in the linear form from 2010 and 2060 cm^{-1} (for Ni/SiO_2) and to 2030 and 2070 cm^{-1} (for Ni/ZrO_2), respectively, and an increase in the intensity of the AB at 1960 cm^{-1}, which characterizes bridged forms of adsorption. It is known that an increase in the intensity of the bands characteristic of bridged forms of adsorption relative to the intensity of the vibrations of the CO adsorbed in the linear form is possible in two cases: first, for an increase in the particle size[11] and, second, due to an increase in the electron density on the Ni atoms upon interaction with the surface.[16] The second reason should also result in the shift of the position of the maximum corresponding to vibrations of the linear form of the adsorbed CO to low frequencies (as in the case of the other metal-promoted systems[17,18]); however, the spectra exhibit shifts in the opposite direction. Thus, the differences between the spectra of the CO adsorbed on Ni/SiO_2 and Ni/ZrO_2 can be considered to be mainly due to geometrical factors and a change in the size of the metal particles. Different values of the specific surfaces of SiO_2 and ZrO_2 (S_{sp} = 400 and ~50 m^2 g^{-1}, respectively), which results in different surface concentrations of the metal, can be one of the reasons for this.

$Ni/SO_4/ZrO_2$ system. The IR spectrum of the CO adsorbed on the $Ni/SO_4/ZrO_2$ sample reduced at 620 K (Fig. 1, *c*) contains AB of ν(CO) at 2200, 2140, and 2090 cm^{-1} with a shoulder at 2050 cm^{-1} and broad AB at 1910 cm^{-1}. The band at 2200 cm^{-1} can be attributed to complexes of CO with LAS SO_4/ZrO_2, whose strength somewhat decreases due to the reduction of the surface SO_4 groups as compared to that of LAS of the oxidized sample (ν(CO) 2205 cm^{-1}).[19] The band at 2140 cm^{-1}, as in the case of the Ni/SiO_2 and Ni/ZrO_2 systems, can be assigned to complexes of CO with the Ni^{+} ions. The decomposition of the remaining part of the spectrum, taking into account the results obtained for the adsorption of CO on Ni/ZrO_2, allows one to distinguish components at 2095, 2070, and 2040 cm^{-1} in the regions of vibrations of the CO adsorbed in the linear form on metallic nickel and AB at 1960 and 1905 cm^{-1} in the region of vibrations of the bridged forms. The bands at 2040 and 2070 cm^{-1} are similar to the AB at 2010—2060 cm^{-1} for the Ni/ZrO_2 and Ni/SiO_2 systems; however, the spectra of $Ni/SO_4/ZrO_2$ exhibit a further shift of the positions of the maxima to the high-frequency region. The absorption band at 1960 cm^{-1} was also observed for the ZrO_2- and SiO_2-supported systems, which is typical of the bridged forms of the CO adsorption.

Two new AB of ν(CO) at 1905 and 2095 cm^{-1} appear in the spectrum of $Ni/SO_4/ZrO_2$. The band at 1905 cm^{-1} observed previously for crystalline nickel can correspond to the two-centered form of the CO adsorption (complex **1**). In this case, the AB at 1960 cm^{-1} in the spectra of the Ni/SiO_2 and Ni/ZrO_2 systems is referred to vibrations of the bridging CO in complex **2**.[11,13] Linear carbonyl fragments of complex **2** can contribute to the formation of AB in the region of 2060—2070 cm^{-1}.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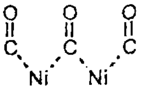
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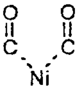
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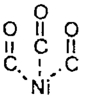
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The band at 2080—2090 cm^{-1} observed previously for the Ni/SiO_2 system treated with different sulfidizing agents[13] and nonsulfidized systems was assigned[10,13,20] to polycarbonyl forms of the adsorption of CO on Ni^{0} (complexes **3** and **4**).

However, as established in this work, $Ni(CO)_4$ is not formed in noticeable amounts. In addition, this AB in the spectra of the $Ni/SO_4/ZrO_2$ system is shifted to high frequencies up to 2095—2100 cm^{-1}, which is 5—10 cm^{-1} higher than the frequencies presented[10,13,20] for the Ni/SiO_2 system treated with hydrogen sulfide. Differences in the behavior of the sulfidized systems and samples containing the SO_4^{2-} anions were also observed[1-3] for other metals, such as Pt, Rh, and Pd. Thus, it can be assumed that AB of ν(CO) at ~2100 cm^{-1} is due to the interaction of the metal microparticles with the surface active centers SO_4/ZrO_2, resulting in the formation of the surface $Ni^{\delta+}$—CO complexes with an elevated frequency of the vibration of the C—O bond.

Changes in the properties of the support should be evaluated to better understand the reason for the change in the state of nickel in systems containing the SO_4^{2-} anions compared to samples containing no sulfur. The promotion of ZrO_2 by the SO_4^{2-} anions results in the appearance of the active centers, whose structure has been described previously,[19,21] on the surface. The superacidic properties of the active centers are described by protons bound by multicentered bonds to the oxygen atoms of the SO_4^{2-} anions and oxide lattice. Along with acidic properties, the active centers possess oxidation properties because of sulfur in the maximum oxidation state S^{6+}.

The SO_4 groups can affect the metal particles by two methods, first of which is the interaction of the metal with acidic protons of the surface HSO_4^- groups similar to that observed previously for the zeolite systems.[22] The study of the $Pt/SO_4/ZrO_2$ system has established that this interaction is also possible in the superacidic systems.[1] The strength of the acidic centers and, hence, the extent of their effect on the metal depend on the oxidation state of sulfur. The promotion of the Ni/ZrO_2 system by the SO_4^{2-} anions was shown[4] to result in an increase in the temperature of the beginning of the reduction of Ni to 670 K. However, our data (see Fig. 1, *c*) indicate that the reduction begins already at 620 K. The surface SO_4 groups are also reduced at this temperature, which can be seen in the IR spectra: the AB at 2760 cm^{-1} of the first overtone of vibrations of the sulfate anions[1] disappears. When the oxidation state of sulfur decreases due to the reduction, weakening of the strength of the acidic centers can be expected.

The second method seems to be more probable: the interaction of the metal atoms with the adjacent sulfur-containing groups with electron-acceptor properties. The surface sulfur-containing compounds, which contain both the starting active $HSO_{4(surf)}$ centers and the products of their reduction, which are localized in the immediate vicinity of the Ni atoms, block some adsorption centers on the metal surface. This effect is especially pronounced in the region of vibrations of the bridging CO and serves as a reason for the appearance of AB at 1905 cm^{-1} instead of the band at 1960 cm^{-1}. The high intensity of AB at 1905 cm^{-1} suggests that sulfur does not migrate to the metal particles, and the steric effect of the closely arranged surface sulfur compounds plays the main role and prevents the formation of complexes **2**. In the opposite case, a total decrease in the intensity of the AB of bridging carbonyls should be expected.

A decrease in the electron density on the nickel atoms due to the electron-acceptor effect of surface sulfur compounds results in the formation of positively charged metal particles $Ni^{\delta+}$ (ν(CO) 2100 cm^{-1}) on the $Ni/SO_4/ZrO_2$ surface.

Thus, the present study shows that the metal state in the Ni/ZrO_2 system is typical of the systems deposited on neutral supports, such as SiO_2. The differences in the behavior of Ni upon the CO adsorption are mainly determined by the specific surface of the support. In the $Ni/SO_4/ZrO_2$ system, by contrast, the state of nickel is mostly affected by the active centers, surface sulfur compounds favoring the formation of the $Ni^{\delta+}$ species. The sulfur compounds block the metal surface and result in the two-centered bridged form of the CO adsorption instead of the formation of the polycarbonyl bridged complexes observed in the systems that were not promoted by the SO_4^{2-} anions.

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