STUDY OF THE CHEMISORPTION OF MIXTURES OF ACETONE
WITH OXYGEN ON NICKEL MONOXIDE BY THE METHOD
OF INFRARED SPECTROSCOPY

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In our previously published works [1, 2], devoted to a study of the chemisorption of mixtures of acetone with CO according to the IR spectra, it was shown that a number of chemical transformations take place on the surface of NiO during the adsorption of these mixtures. In this work we present the results of a further investigation of the adsorption of mixtures on NiO, in particular, of a mixture of acetone and oxygen, using isotopic analogs of acetone — hexadeuteroacetone, hexafluoroacetone, and D_2O and H_2O. This permitted a more detailed interpretation of the spectra obtained after the adsorption of the investigated mixtures. A brief communication on these results has already been published [3].

EXPERIMENTAL

The method of preparation and conditioning of the nickel monoxide samples before conducting the adsorption was analogous to that of [3]; the specific surface of the samples was 90 m^2/g. The adsorption of the mixtures and individual components was conducted at room temperatures and initial acetone and oxygen pressures of ~15 mm Hg; the adsorption of the mixture was conducted at the same partial pressures. It was established experimentally that the formation of surface compounds after the adsorption of the individual components and a mixture of them on NiO ends in approximately 10 min. After conducting the adsorption, the samples were evacuated to a residual pressure of $\leq 10^{-4}$ mm Hg for an hour to remove adsorbed forms weakly bound to the surface.

The spectra were taken on the UR-10W two-beam spectrophotometer. The spectral slit width in the range 1200-1800 cm^{-1} (NaCl prism) varied from 5 to 6 cm^{-1}, in the range 2400-2800 cm^{-1} from 2 to 3 cm^{-1}. The spectra obtained were recalculated relative to the spectrum of the initial NiO and given in a percent transmission scale.

Adsorption of Oxygen on NiO. The spectrum, taken after the adsorption of oxygen on NiO in the ranges 1200-1800 and 2400-2800 cm^{-1}, does not differ from the spectrum of the initial nickel monoxide.

Adsorption of Acetone on NiO. In the spectrum of adsorbed acetone (a preliminary interpretation of this spectrum was given in [1, 2]), there are the following adsorption bands (Fig. 1): a) a band at ~1640 cm^{-1}, lying in the region of adsorption of the C=O bond, characteristic of the molecular complexes with acetone with BF_3 [4], $AlCl_3$, and $TiCl_2$, for the double bond C=C in olefins, and for the deformational vibration of coordination-bonded water [5]; b) absorption bands at 1570 and 1515 cm^{-1}, lying in the region characteristic of the valence vibrations of the C=O bond in the spectra of internal complex compounds of β-diketones with metals [5].

To establish what happens to acetone when it is adsorbed on nickel monoxide, we took the spectra of adsorbed hexadeuteroacetone, hexafluoroacetone, light and heavy water.

In the spectrum taken after the adsorption of hexadeuteroacetone on NiO (Fig. 2), absorption bands remained at ~1640 and 1515 cm^{-1}; moreover, the intensity of the band at ~1640 cm^{-1} was substantially reduced in comparison with the intensity of the band at 1515 cm^{-1}. The absorption bands at 1570, 1390, and 1360 cm^{-1}, consequently belonging to the vibrations in which hydrogen atoms participate, disappeared from the spectrum (see Fig. 1). The decrease in the intensity of the absorption band at 1640 cm^{-1} (Fig. 2) also indicates that this band in the spectrum of adsorbed "light" acetone consists of at least two absorption bands, one of which belongs to the vibrations with participation of the hydrogen atom. In the case of "light" acetone,
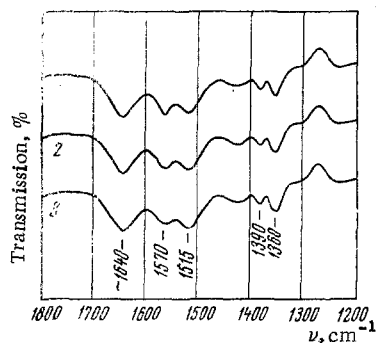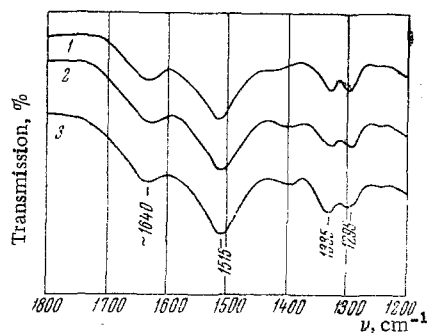
Fig. 1   Fig. 2

Fig. 1. IR spectra taken after the adsorption of acetone on NiO,
after: 1) 1 h; 2) 24 h; 3) 48 h.

Fig. 2. IR spectra taken after adsorption of hexadeuteroacetone on
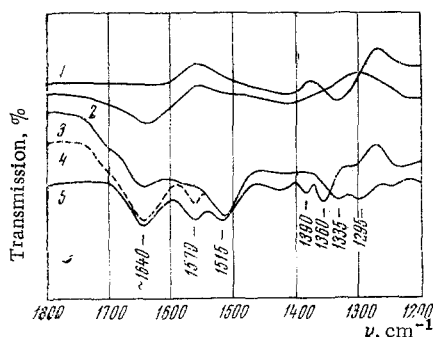NiO, after: 1) 1 h; 2) 24 h; 3) 48 h.

Fig. 3. IR spectra taken after adsorp-
tion on NiO of: 1) D_2O; 2) H_2O; 3) hexa-
deuteroacetone; 4) H_2O after prelimi-
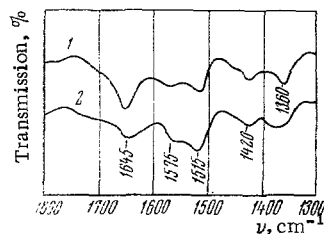narily adsorbed hexadeuteroacetone;
5) acetone.

Fig. 4. IR spectra taken
after adsorption of acetone
on NiO with preliminarily
adsorbed oxygen, after: 1)
1 h; 2) 24 h.

one of the components of the band at 1640 and the band at 1570
cm^{-1} can be assigned to the deformational vibrations of co-
ordination-bonded water. The absorption bands at 1335 and
1295 cm^{-1} belong to the analogs of these absorption bands in
the spectrum of adsorbed hexadeuteroacetone.

Figure 3 presents the spectra of adsorbed D_2O and H_2O. The absorption band at 1335 cm^{-1} belongs
to the deformational vibrations of D_2O (curve 1), while the absorption band at 1640 cm^{-1} belongs to the de-
formational vibrations of H_2O (curve 2). Consequently, one of the components of the band at 1640 cm^{-1} in
the case of acetone (absorption band at 1335 cm^{-1} in the case of hexadeuteroacetone) belongs to the deforma-
tional vibrations of coordination-bonded water. The absorption at 1570 cm^{-1} (see Fig. 1) (the band at 1295
cm^{-1} in the case of hexadeuteroacetone) also can be assigned to the deformational vibrations of coordination-
bonded water. The presence of this band is specific for the spectrum of adsorbed acetone, since there is no
such band in the spectrum of adsorbed H_2O.

Figure 3 (curve 4) presents a spectrum taken in the case of successive adsorption of hexadeuteroace-
tone (curve 3) and 8 mm Hg of H_2O on NiO. From the spectrum it is evident that the supplementary adsorp-
tion of water leads to a restoration of the absorption bands at ~1640 and 1570 cm^{-1}, characteristic of the
spectrum of adsorbed acetone (curve 5). The restoration of the absorption bands at ~1640 and ~1570 cm^{-1}
becomes appreciable only at an initial H_2O pressure of ~2 mm Hg. The appearance of the absorption bands
of water in the spectrum of adsorbed acetone may be explained by oxidation of the enol form of acetone by
the labile oxygen of NiO, forming the enolate complex and water, bound to the NiO surface. The absorption
band at 1515 cm^{-1} can be tentatively assigned to the valence vibration either of the C ═ O- or of the C ═ C-
bonds of the enolate complex of acetone. The second component of the absorption band at 1640 cm^{-1} can be
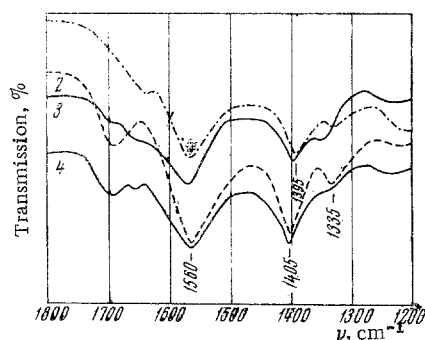
Fig. 5. IR spectra taken after adsorption on NiO of: 1) oxygen after preliminarily adsorbed hexadeutero-acetone; 2) oxygen after preliminarily adsorbed acetone; 3) a mixture of O_2 — $(CD_3)_2CO$; 4) a mixture of O_2 — $(CH_3)_2CO$.

assigned to the valence vibrations of $C=O$ in the molecular complex of acetone with the surface of NiO. To confirm the existence of enolate and molecular complexes of acetone on the surface of NiO, we took the spectrum of hexafluoroacetone, adsorbed on NiO. In contrast to the usual acetone, hexafluoro-acetone cannot exist in the enol form; therefore, in the "carbonyl" region we might have expected the appearance of only one absorption band characteristic of the valence vibration of $C=O$ in the molecular complex of hexafluoroacetone with the NiO surface. Actually, in this region only one absorption band is observed at 1660 cm^{-1}. The experiment with hexafluoro-acetone cannot serve as strict evidence of the formation of a molecular complex in the case of adsorption of acetone on NiO, since the introduction of fluorine atoms in place of hydrogen atoms into the acetone molecular sharply changes its adsorption and other characteristics. However, taking into consideration the literature data of [4] on the existence in the "carbonyl" region of the absorption of $C=O$, characteristic of molecular complexes of acetone and the spectra of adsorbed hexafluoroacetone and hexadeuteroacetone, we may assume that a molecular complex is formed on the surface of NiO when acetone is adsorbed.

Exposure of the sample to a vacuum of $\leq 10^{-4}$ mm Hg for 48 h leads to a decrease in the intensity of the band at 1570 cm^{-1} relative to the band at ~1640 cm^{-1} (see Fig. 1); exactly the same picture is also observed in the case of hexadeuteroacetone (see Fig. 2) for the absorption bands at 1335 and 1295 cm^{-1}. The decrease in the relative intensity of the absorption bands of water is probably due to its partial desorption from the surface of NiO, or to the transition of one adsorbed form of water on the surface of NiO to another.

Adsorption of Acetone on NiO with Preliminarily Adsorbed Oxygen. Figure 4 (curve 1) presents the spectrum taken after the adsorption of acetone on NiO with preliminarily adsorbed oxygen. As can be seen, in this case there was only a general increase in the adsorption in the region of the bands characteristic of coordination-bonded water and the enolate complex. The spectrum taken after exposure of the sample to a vacuum of $\leq 10^{-4}$ mm Hg for 24 h is represented by curve 2.

Adsorption of Oxygen on Nickel Monoxide with Preliminarily Adsorbed Acetone. Figure 5 (curve 3) presents the question taken after the adsorption of oxygen on NiO with preliminarily adsorbed acetone. Strong absorption bands at ~1570 and 1395 cm^{-1}, corresponding to the antisymmetrical and symmetrical valence vibrations of the carboxyl ion [5], appear in the spectrum. The absorption band at ~1640 cm^{-1} is masked by the strong band at 1570 cm^{-1}, but in the spectrum taken after the adsorption of oxygen on NiO with preliminarily adsorbed hexadeuteroacetone (curve 1), the weak band of the molecular complex at ~1640 cm^{-1} remains, and an absorption band appears at 1335 cm^{-1}, corresponding to the deformational vibrations of D_2O. The absorption bands at 1570 and 1395 cm^{-1}, assigned to the vibrations of the carboxyl ion, do not change their positions in the spectrum (curve 1). As was shown by spectral measurements, there are no appreciable changes with time in the adsorbed layer.

Simultaneous Adsorption of a Mixture of Acetone with Oxygen on NiO. The nature of the spectrum remains the same in the case of simultaneous adsorption of acetone and oxygen as in the case of the adsorption of oxygen after acetone, but the intensities of the absorption bands of the carboxyl ion (~1560 and 1405 cm^{-1}) increases (see Fig. 5, curve 4). In the spectrum taken after the adsorption of a mixture of oxygen and hexadeuteroacetone (curve 2), the absorption bands of the carboxyl ion remain, and an absorption band appears at ~1335 cm^{-1}, corresponding to the deformational vibrations of D_2O.

DISCUSSION OF RESULTS

A peculiarity of the acetone — oxygen system from the standpoint of the electronic theory of chemisorption is the different nature of the components, in the sense of charging of the surface. Although in the acetone — carbon monoxide system studied earlier [1, 2], both components are donors; in the acetone — oxygen system the latter behaves as an acceptor. Therefore, in the adsorption of acetone — oxygen mixtures, the "hyperadditivity" might be tentatively explained by the influence of macroscopic charging. However, the nature of the IR spectra obtained and their comparison with the IR spectra of the acetone — carbon monoxide
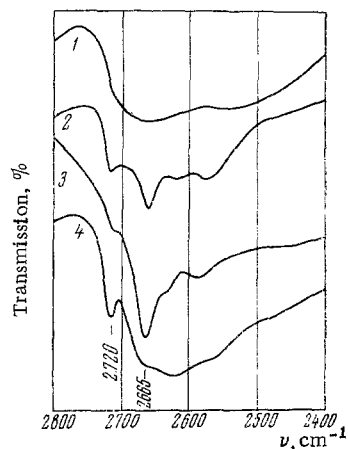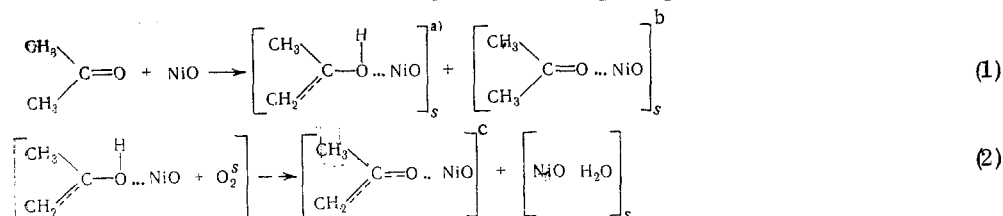
Fig. 6. Spectra taken after adsorption on NiO of: 1) hexa-deuteroacetone; 2) oxygen after preliminarily adsorbed hexa-deuteroacetone; 3) a mixture of $O_2 - (CD_3)_2CO$; 4) D_2O.

system shows that the adsorption of acetone and its mixtures with oxygen involves the occurrence of a number of chemical processes on the surface of NiO. In all cases except for the individual adsorption of oxygen, coordination-bonded water is formed. Figure 6 presents the spectra in the region of the valence vibrations of the O—D bonds for the case of individual adsorption of hexadeuteroacetone (curve 1), successive adsorption of oxygen and hexadeuteroacetone (curve 2), and simultaneous adsorption of oxygen and hexadeuteroacetone (curve 3). For comparison, the spectrum taken after the adsorption of D_2O on NiO at $p = 8$ mm Hg is cited (Fig. 4). In the spectrum of the initial NiO in the region of 3500–3800 cm^{-1} there are three absorption bands: ~3570, 3625, and 3685 cm^{-1}, corresponding to the valence vibrations of O—H of the undecomposed hydroxide. The ratio of the intensities of these bands depends upon the temperature of decomposition of nickel hydroxide under vacuum. The greatest intensity among these bands is possessed by the absorption band at 3685 cm^{-1}. The OH groups, the valence vibrations of which correspond to the absorption band 3685 cm^{-1}, most readily undergo exchange in the adsorption of D_2O on NiO. In the spectrum (curve 4), an absorption band at 2720 cm^{-1} corresponds to the vibration of O—D.

The coordination-bonded water formed as a result of the adsorption of hexadeuteroacetone and its mixtures with oxygen, appears in the spectra in the form of a broad absorption band in the region of the O—D valence vibrations (curves 1-3). The total absorption of OD groups increases as we pass from curve 1 to curve 3; moreover, beginning with curve 2, a narrow absorption band at 2665 cm^{-1} appears in the spectra. A broad absorption band of heavy water (4), adsorbed on NiO, has a close value of the integral absorption in this region.

The adsorption of acetone on NiO may be represented by the following simplified scheme:

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
C=O \\
\diagup \\
CH_3
\end{array}
+ NiO \longrightarrow
\left[
\begin{array}{c}
CH_3 \\
\diagdown \\
C-O\ldots NiO \\
\diagup \quad | \\
CH_2 \quad H
\end{array}
\right]_s^{a)}
+
\left[
\begin{array}{c}
CH_3 \\
\diagdown \\
C=O\ldots NiO \\
\diagup \\
CH_3
\end{array}
\right]_s^{b}
\tag{1}
$$

$$
\left[
\begin{array}{c}
CH_3 \quad H \\
\diagdown \quad | \\
C-O\ldots NiO \\
\diagup \\
CH_2
\end{array}
+ O_2^s
\right]
\longrightarrow
\left[
\begin{array}{c}
CH_3 \\
\diagdown \\
C=O\ldots NiO \\
\diagup \\
CH_2
\end{array}
\right]^c
+
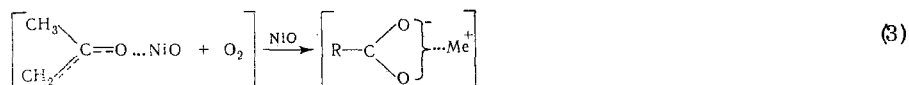\left[NiO \quad H_2O \right]_s
\tag{2}
$$

where S is the surface; a is the enol form; b is the molecular complex; c is the enolate complex.

Step 1 is accompanied by the formation of the enol form (a) and the molecular complex (b) of acetone (component of the absorption band at ~1640 cm^{-1}). The formation of the enolate complex (c) with the surface of NiO (absorption band 1515 cm^{-1}) and coordination-bonded water evidently proceeds through oxidation of the enol form of oxygen, the spectrum of which we did not observe, by the excess oxygen of the surface (step 2) From this it follows that an increase in the concentration of excess oxygen on the surface before the adsorption of acetone should lead to an increase in the amount of water and enolate complex formed. Actually, such a picture is observed in the spectrum (see Fig. 4, curves 1 and 2). The surface reaction of acetone (steps 1 and 2) can proceed along a different pathway. In the adsorption of acetone on NiO, one of the hydrogen atoms can be directly split out from the methyl group and can combine with the excess oxygen of the surface. The remainder of the acetone molecule can be adsorbed on the surface of NiO in the form of a π-complex

$$
\begin{array}{c}
CH_3 \\
| \\
CH_2=C=O \\
\downarrow \\
NiO
\end{array}
$$
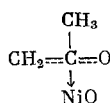
In the case of the adsorption of oxygen after acetone, evidently there is an oxidation of the enolate complex of oxygen from the gas phase, which leads to the appearance of the absorption bands of the carboxyl ion in the spectra (step 3)

$$
\left[
\begin{array}{c}
CH_3 \\
\diagdown \\
C=O\ldots NiO \\
\diagup \\
CH_2
\end{array}
+ O_2
\right]
\xrightarrow{NiO}
\left[
R-C\diagup\diagdown^{O^-}_{O}
\right]\ldots Me^+
\tag{3}
$$

In the case of simultaneous admission of acetone and oxygen, the enolate complex formed on the surface (steps 1 and 2) is immediately oxidized by the oxygen from the gas phase, forming the carboxyl ion (step 3).

A comparison of the results obtained with measurements of the contact potential difference shows that the adsorption of acetone on NiO leads to a decrease in the work function by approximately 100 mV, while in the presence of preliminarily adsorbed oxygen, the decrease is 300 mV. The decrease in the work function upon the adsorption of acetone on NiO may occur either on account of the dipole moment of acetone or on account of transfer of an electron to the lattice of NiO. The decrease in φ may also occur as a result of the formation of water (step 2), since evidently there is always some amount of excess oxygen on the surface of NiO. In addition, the change in the work function also continues after the complete adsorption of acetone, which is probably an indication of a change in the nature of the bond of the molecules to the surface or of their conversion. The adsorption of oxygen after acetone leads to a substantially larger increase in the work function than in the case of the adsorption of O_2 on the initial NiO. This may be explained by the formation of a negatively charged carboxyl ion as a result of oxidation of the surface enolate complex by oxygen from the gas phase.

The desorption of successively adsorbed acetone and O_2 on NiO at 250° under vacuum gives a larger amount of frozen out products than the amount of adsorbed acetone. From the rate of thawing, we can assume the presence of CO_2 in the condensate. An investigation of the interaction of acetone with O_2 on NiO by a pulsed chromatographic method at 220° indicated that the reaction products are CO_2, CH_4, and an unsaturated aliphatic hydrocarbon.

CONCLUSIONS

1. It may be concluded on the basis of the IR spectra obtained that the adsorption of mixtures of acetone with oxygen is accompanied by a number of chemical conversions on the surface of NiO, which leads to "hyperadditivity" in the case of adsorption.

2. The nature of the surface compounds formed during adsorption depends upon the order of admission of the components of the mixture.

3. The adsorption of a mixture of acetone and oxygen is characterized by the formation of enolate and molecular complexes of acetone, coordination-bonded water, and a surface carboxyl ion.

4. The process of formation of surface complexes at room temperature is of a "dead end" nature.

5. The greatest intensity of chemical conversions on the surface of NiO in the case of simultaneous adsorption of acetone and oxygen may be explained by the "presorption effect."

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