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Mutual Displacement of NO, CO, and CO_2 Adsorbed on NiO, Shown by Infrared Spectra

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Adsorption of two gases in alternative sequence does, or does not eliminate the infrared bands of the preadsorbed species, which are replaced in the first case by those of the second one. Qualitative inference on the relative adsorption strength of NO, CO, and CO_2 molecules on NiO is made. A peculiar shift of the CO_2 bands upon NO co-adsorption has been noticed.

In the course of a study of gas adsorption on metal oxides with the infrared technique, carried out in this laboratory, it has been noticed that the bond strength of NO, CO, and CO_2 with the oxide surface is different for the separate bands produced by several possible adsorption types. Some of the bands are removed on evacuation at room temperature, the other ones require additional heating.

In the present study, being a continuation of the previous one (*1*), the behavior of adsorbed molecules has been investigated by means of adsorption on NiO of two of the above-mentioned gases in succession.

EXPERIMENTAL

Two kinds of NiO samples were used. They were obtained by decomposition of $NiCO_3$ and $Ni(NO_3)_2 \cdot 6H_2O$ ("pure for analysis" brand) in air at 400°C, 4 hr. In the first case the resulting powder was black (on account of an oxygen excess above the stoichiometric content), in the second one it was gray-green. The results obtained with both were similar; however, priority was given to NiO from the nitrate, since it was more transparent in the spectral range studied, and moreover, according to ref. (*2*), the adsorption rate and the total CO adsorbed amount is greater for it, than for the black NiO.

A weighed amount of freshly prepared powder was placed between CaF_2, or NaCl plates. The thickness of the layer (by weight) was 5–10 mg/cm^2 for NiO from the carbonate, and 10–40 mg/cm^2 for that from the nitrate. The transmittance of the samples of this thickness amounted to from 2 to 10% at 2000 cm^{-1}.

The subsequent thermal treatment of the samples was carried out in a cell, described in ref. (*3*), under continued pumping (*ca.* 10^{-5} mm Hg) at 400°C (3–4 hr). This procedure has been chosen in order to remove from NiO the oxygen excess. Some reduction of the oxide was, however, inevitable, the samples acquiring a lighter color. In previous research, done under milder preparation conditions (*6, 7*) definite divergences in the spectra of CO adsorbed on NiO have been found, depending on the calcination temperature, or on oxygen addition.

After this procedure the sample was allowed to cool down to room temperature, and the spectrum recorded; then gas was admitted to the sample and another spectrum recorded. The gas pressure mostly reached 20 mm Hg; in some experiments a pressure range from 5 to 60 mm Hg has been used. At such pressures, the dead space in the cell being 2–3 mm, the spectrum of the gas phase itself was not observed.

The spectral apparatus used was the single-beam spectrometer IKS-12 with a

NaCl prism (the container of the spectrometer was desiccated with P_2O_5). The lamp current in the amplifier was stabilized with the help of a device, described in ref. (*4*). The scale of the recorder (EPP-09) was 2 mV. The slit spectral width did not exceed 30 cm^{-1}. The spectral transmittance curves for the adsorbed gases reproduced below were calculated from the transmittance curves of the adsorbent before and after gas adsorption. The spectral range investigated was from 1500 to 2200 cm^{-1}.

The first adsorbed gas taken in excess was always pumped out of the cell during about 1 min, before the second gas was admitted. Thus on the adsorbent only relatively strongly adsorbed molecules remained. When the pumping lasted 20–30 min the bands of all adsorbed gases, except NO, disappeared. Thus the removal (desorption) of the preadsorbed gas (when observed) took place in an excess of the second gas during its adsorption.

RESULTS AND DISCUSSION

A. Adsorption of Separate Gases

CO gas has an absorption band at 2150 cm^{-1}. When adsorbed on NiO at room temperature, bands at 2050, 1985, and 1925 appear, together with a broad band at 1600–1700 cm^{-1} (curve 1 in Fig. 1 and curve 2 in Fig. 2). According to the results of Eischens and Pliskin (*5*) for CO adsorbed on metals, the 2050 band is to be assigned to chemisorbed CO molecule,

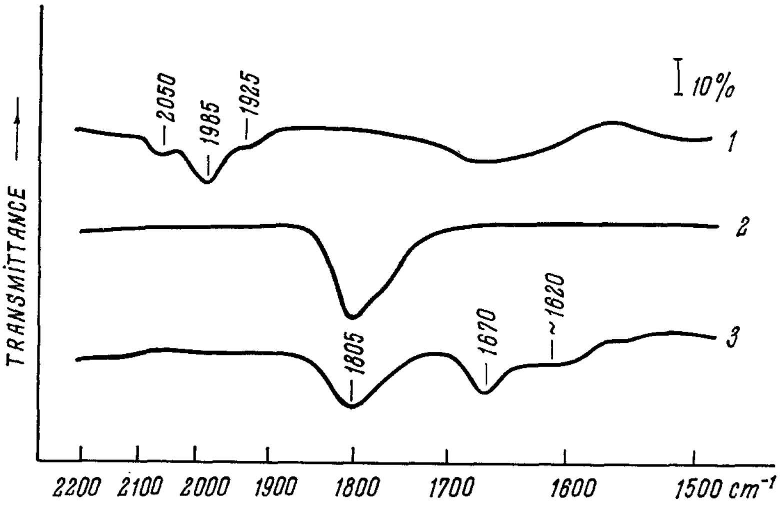


FIG. 1. Infrared spectra of CO (curve 1), NO (curve 2), and CO_2 (curve 3), adsorbed in succession on a NiO sample, with evacuation at 20°C between. Pressures of the admitted gases 20 mm Hg.

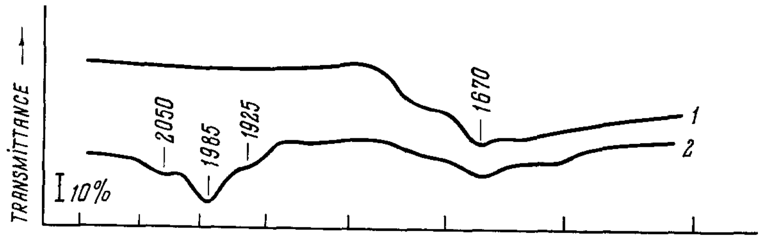


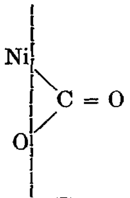
FIG. 2. Infrared spectra of CO (curve 2) and CO_2 (curve 1), adsorbed on NiO in succession. Pressure of the admitted gases 20 mm Hg. Spectral slitwidth 15 cm^{-1}. Sample thickness 30 mg/cm^2.

linearly bound to a surface Ni atom, whereas the 1985 band belongs to a bridged structure of CO bound to two Ni atoms. These authors did not observe on NiO any bands of adsorbed CO (*5*a). Courtois and Teichner (*6*), who have observed on NiO the same bands at 2060 and 1965, suppose that the adsorption sites are Ni^{2+} cations. O'Neill and Yates (*7*) suggest that these sites are Ni metal atoms, formed as the result of a partial reduction of the NiO surface. We are of the same opinion, taking into consideration the high-temperature post-treatment *in vacuo* used by us (cf. ref. *10*).

When the CO pressure is increased from 20 to 60 mm Hg the 1925 band is obliterated by the 1985 band.

Courtois and Teichner did not observe the 1925 band, which can be explained by the fact that they used a higher CO pressure of 40 mm Hg for the adsorption. O'Neill and Yates (*7*a) have mentioned a band at 1920, however the adsorbent used by them was NiO (cf. Fig. 6 in ref. *7*a), or Ni metal (cf. Fig. 5, ref. *7*b) supported on TiO_2 in both cases.

The additional 1925 band observed by us can be assigned to a bridged structure of another kind than that for the 1985 one, *viz.*



(1925 cm^{-1})

(I)

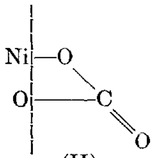
The assignment of the 1925 band to the bridged structure (I) is based on the consideration that its frequency must lie between that of a bridged structure with two surface Ni atoms (1985) and that of another bridged structure with two surface O atoms (III, cf. below). The frequencies of the latter are in the range 1700–1600 cm^{-1} and thus the frequency for structure (I) must be shifted towards lower frequencies, relative to that of a bridge with Ni atoms only.

It is, however, possible that the 1925 band, like the 1985 one is similarly formed by a bridged structure with two Ni atoms, but is shifted to lower frequencies, owing to the expected different nature of the Ni sites on NiO, as compared with Ni metal. It must be noted that the NiO samples used by us were different from those of the other authors mentioned. Courtois and Teichner (*6*) thermally decomposed pellets of Ni hydroxide pressed with finely ground SiO_2 as additive at 200°C *in vacuo*.

They noticed the substantial influence of the calcination temperature of $Ni(OH)_2$ on the infrared spectrum of adsorbed CO. O'Neill and Yates (*7*a) used NiO, obtained by oxidation at 300°C of the metal, dispersed on various carriers (SiO_2, Al_2O_3, TiO_2).

CO_2 adsorbed on NiO samples of our preparation exhibit two bands, at 1620 and 1670 (Fig. 3, curve 1). The former has been observed on NiO by Eischens and Pliskin (*5*) at 1640, and by Courtois and Teichner at 1620 together with a band at 1390 (*5*), or at 1360 (*6*). The latter authors ascribe the 1620 band to CO_2 molecules chemisorbed on the same sites (Ni^{2+}) as does CO. They assume that the configuration of the O^- ions on the surface, surrounding the chemisorbed CO and CO_2 molecules, is similar to the configuration in the CO_3^- anion. According to them this must explain the coincidence of the frequencies of the CO and CO_2 adsorbed species, i.e. the presence of a common 1620 frequency. In fact, on our samples inside the broad 1600–1700 band of adsorbed CO one can discern coalescent feeble bands at 1620 and 1670, which coincide with the peaks of adsorbed CO_2 (cf. in Fig. 1, curves 1 and 3, and in Fig. 2, curves 1 and 2). However, the stronger 1670 band, observed by us, is found neither in the samples of Courtois and Teichner, nor in the system of O'Neill and Yates, who observed for adsorbed CO a band at 1650 and ascribed it to a CO_3^- species (*7*a).

The frequencies 1620 and 1670 are in the range 1600–1700 cm^{-1}, characteristic of the carbonyl group C=O. On the basis of the infrared frequencies observed in complex compounds (*8*), we suggest that the 1620 and 1670 bands belong to the carbonyl bond in chemisorbed CO_2 in the schematic structure

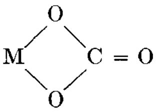


(1620, 1670 cm^{-1})

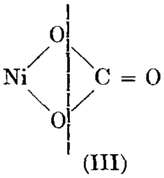
(II)

The presence in our samples of a more intense 1670 band, in addition to that at 1620 observed by all the authors (*6, 7*) might be ascribed to a difference in the distance between the Ni and O adsorption sites, for different crystalline planes.

The group



(e.g., $M = Co^{3+}$) in the complexes exhibit frequencies in the range 1640–1590 cm^{-1} (*8*). The broad 1600–1700 band of chemisorbed CO can thus be assigned to the following structure in which two surface O atoms are involved:



(1600–1700 cm^{-1})

(III)

The difference between structures (III) and (II) is that in the former both O atoms belong to the surface, whereas in structure (II) only one of them does. The coincidence of the frequencies of adsorbed CO_2 and CO on NiO is thus easier to understand.

When NO was adsorbed on NiO we observed in the range 1500–2200 cm^{-1} only a single intense band at 1805, which has been ascribed in the work of Roev and Terenin (*1*) to NO molecules coordinatively bound to surface Ni^{2+} cations (the absorption band of gaseous NO is at 1876 cm^{-1}).*

For NO adsorbed on our NiO samples we observed a band at 1215 which is ascribed to NO_2 (possibly NO_2^-), resulting from a reaction of NO with the oxygen in NiO. In fact, the nitrite anion has a strong band at 1250–1230 (*11*).

For synthetic zeolites we did not observe the band of adsorbed NO, but only bands belonging to N_2O and NO_2, as reaction products (*9*).

B. Successive Adsorption of Different Gases

When NO is admitted to NiO with preadsorbed CO, the bands of the latter disappear rapidly (in a time less than 1 min) and the strong band of NO appears at 1805 (Fig. 1, curve 2). When the experiment is carried out in the reverse sequence, *viz.* first, NO adsorption, and then CO admitted, the NO band at 1805 is not removed. This conspicuously shows that NO molecules are bound to the NiO surface more strongly, in comparison to CO.

When CO_2 is admitted *in vacuo* to the sample with chemisorbed NO, bands of the former appear at 1620 and 1670, but the NO band at 1805 does not show any change (Fig. 1, curve 3).

When the experiment is carried out in the reverse sequence, viz., when CO_2 is preadsorbed (Fig. 3, curve 1) and then NO

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*According to these authors several feeble bands (intensities less than 1–3%) were also observed at 1625, 1660, 1695, and 1735 cm^{-1}. These bands, ascribed to covalent bonds of NO with O atoms of the adsorbent, disappeared under evacuation at temperatures from 150° to 350°C.

These four bands were not confirmed by the present investigation. Our experiments showed that if careful vacuum treatment of the samples and desiccation of the spectrometer is achieved, bands in the range 1600–1800 cm^{-1} are not observed, when NO is adsorbed on NiO, or on supported Ni metal.

The discrepancy can be ascribed to transmittance changes of the sample after the NO adsorption and during the evacuation process. This could lead to false maxima in the final curve (giving the ratio of the transmittance before and after gas adsorption), owing to the presence of bands, due to atmospheric H_2O. Moreover it may be remarked that the vacuum treatment of the samples in previous work (*1*) was carried out at 150°C, which was insufficient for complete removal of adsorbed water from the adsorbent.

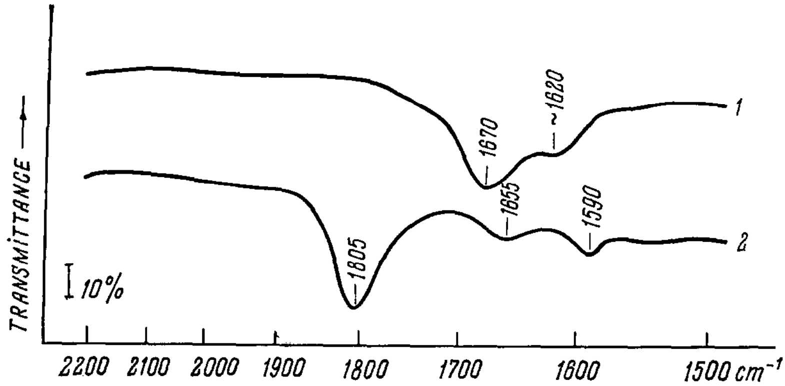

FIG. 3. Infrared spectra of CO_2 (curve 1) and NO (curve 2), adsorbed in succession on NiO. Pressures of the admitted gases 20 mm Hg. Spectral slitwidth 25 cm^{-1}. Sample thickness 38 mg/cm^2.

admitted to NiO with evacuation at 20°C between, the 1805 band of adsorbed NO is seen as previously, but the usual 1670 and 1620 bands of adsorbed CO_2 are distinctly shifted to 1655 and 1590, respectively, i.e. to lower frequencies (Fig. 3, curve 2). These CO_2 bands disappear completely on prolonged staying in the presence of NO in excess.

This interesting finding of a frequency change in the preadsorbed molecule without a change of that in the second one, shows that the preadsorbed molecules (CO_2) are being removed from their sites by the more strongly adsorbed NO molecules. As the latter are evidently localized on Ni sites, but not on the O ones, we can assume, using the scheme (II), that in the bridge structure of chemisorbed CO_2 the Ni site is occupied by a NO molecule.

Similarly to Courtois and Teichner (*6*), we also carried out the CO adsorption on preadsorbed CO_2. In accordance with these authors, it has been found that CO admitted to NiO with preadsorbed CO_2 does not remove the latter. However, when in the reverse sequence CO_2 is admitted to NiO with preadsorbed CO, the bands 2050, 1985, and 1925 of the latter disappear immediately. At the same time the wide 1600–1700 cm^{-1} band of chemisorbed CO is enhanced and there appears on it an absorption maximum at 1670, belonging to adsorbed CO_2 (Fig. 2, curve 1).

CONCLUSIONS

The spectral findings described above allow the following inferences to be made:

1. NO being adsorbed on NiO rapidly removes preadsorbed CO.
2. CO does not remove neither preadsorbed NO, nor CO_2.
3. CO_2 displaces preadsorbed CO.
4. NO and CO_2 adsorbed in succession can coexist for some time being adsorbed in close proximity, as revealed by a marked shift of the CO_2 frequencies.

Thus qualitatively the sequence of the adsorption strengths is

$$NO > CO_2 > CO,$$

i.e., NO is a more effective "poison" for NiO than CO_2.

The results reported here are preliminary ones and are to be extended to other oxides.

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