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Reactions of Gaseous Pollutants with Solids

V. Infrared Study of the Sorption of NO on CaO*

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A Fourier transform spectrometer was used to record spectra of the surface layer formed on CaO by sorbed NO, and during the conversion and destruction of the layer by degassing and treatments with oxygen. NO was taken up at pressures in the low micro-Torr range, most of the surface layer being relatively firmly bound. Numerous infrared bands were observed, pointing to the existence of at least a dozen distinct surface species. Tentative band assignments suggest the formation of NO^-, NO_2^-, NO_3^-, NO^+, and monodentate and bidentate nitrato complexes. At least six other species are unidentified, so that the mechanisms cannot be considered. The extreme complexity of the system and the numerous surface species found with CaO lead to the speculation that on other adsorbents, on which quite few NO_x species have been found, there may also exist numerous NO_x species.

The interactions of NO and solid surfaces have been extensively studied, most of the adsorbents used being transition metals and their oxides. Most of the infrared spectroscopic data in this area were reviewed by Little (*1*) and more recently by Shelef and Kummer (*2*); a wide variety of surface species has been described. Not much seems to be known about the reactions of NO_x with Group II oxides or carbonates, however. As such materials may find use as adsorbents in aircleaning, and NO_x reactions per se are of wide interest, we have begun work in that area and presently report some work results of an infrared study of the sorption of NO on CaO.

EXPERIMENTAL METHODS

Most experimental procedures have already been described (*3*, *4*). Commercial NO was purified by a method (*5*) similar to that described by Yates and Madey (*6*). The adsorbent was CP CaO powder pressed at 20 tons/in.^{2} to form self-sustaining sample pellets containing about 40 mg/cm^2. Spectra of the adsorbents recorded after 800°C degassings showed the samples to be dehydroxylated. As only the N–O compounds were of interest, only the 2300–600 cm^{-1} region was studied.

Infrared spectra were recorded with a Digilab Inc. Model FTS-14 Fourier transform spectrometer which had been modified (*7*) and fitted with a magnetic disc recorder. Each single-beam spectrum was obtained by summing 300 interferograms. The resolution was constant throughout the spectral range at 4 cm^{-1}. Series of spectra were recorded as follows. Each time a fresh adsorbent sample was used, its single-beam spectrum was measured and stored in the disc memory. That spectrum, e.g., A, (Fig. 1,) was used as "background" for a series of spectra. After the sample had been exposed to NO or subjected to some other treatment, another single-beam spectrum, e.g., B, Fig. 1, was recorded and stored. A ratioed spectrum (Figs. 2, 3), equivalent to one obtained by double-beam operation, was produced by digital computation using the instrument's computer. The ratioed

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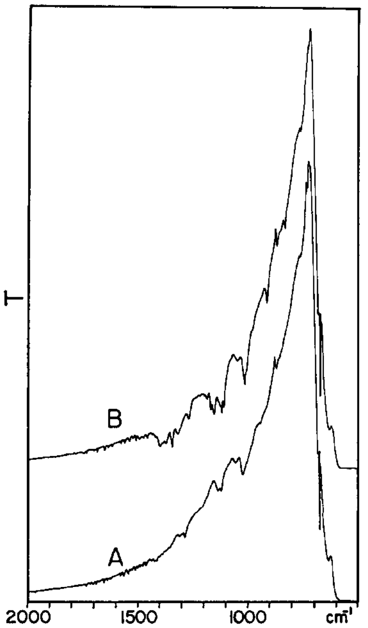


FIG. 1. Single-beam spectra. (A) CaO, after degassing. (B) after exposure to 150 μm of NO at 25°C. Each spectrum was obtained by summing 300 scans; the resolution was 4 cm^{-1}.

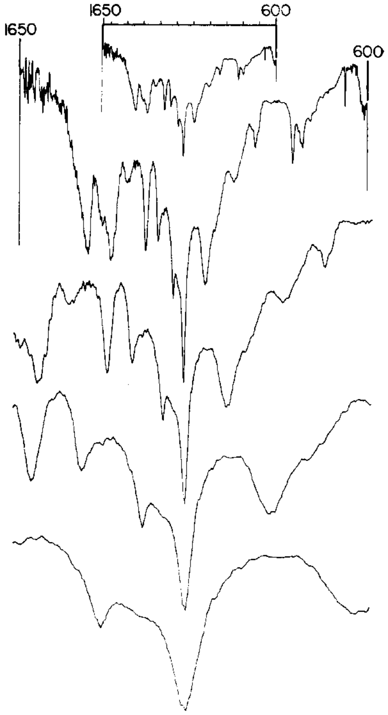


FIG. 2. Scale expansion of spectra. The top trace is a segment of a ratioed spectrum of CaO which had been exposed to 1.1 Torr of NO at 25°C and degassed at 98°C. The second trace shows the same segment with the ordinate expanded and the abscissa doubled; further abscissa expansions resulted in the other traces. In descending order, the abscissa was expanded by a factor of 1, 2, 4, 8, and 16 (the latter corresponded to a plot of 12.5 cm^{-1} $in.^{-1}$).

spectra had flat backgrounds so that bands and their changes could be well defined. Ordinate and abscissa expansions of selected portions of all spectra were produced routinely as required by digital computation; an example is shown in Fig. 2. As the transmittance of the samples rose steeply below 2000 cm^{-1} (this was caused by a decrease of scattering of radiation by the samples, and is characteristic of our CaO samples) and declined abruptly below 700 cm^{-1} (caused by absorption of radiation by the adsorbent), the high- and low-frequency portions of the various spectra were noisier than the central portions; the 600–400 cm^{-1} region was so noisy that, although it was always measured, it was not used.

EXPERIMENTS AND RESULTS

NO Sorption at 25°C. A small amount of NO was placed in a cell containing freshly degassed CaO sample, and the pressure within the cell was monitored with a Pirani gauge. NO was taken up at even quite low pressures. When the pressure within the cell had fallen to a steady value (this usually required a few minutes), a spectrum was recorded. Additional NO was then introduced so that a new, higher "equilibrium" pressure was reached, another spectrum was recorded, and so on. A series of measurements at incrementally increasing final NO pressures was obtained in that fashion.

Some segments of some of the spectra of such a series are shown in Figs. 2 and 3. New infrared bands caused by adsorbed species (*8*) were observed at quite low pressures, and the number of bands and their intensities changed progressively as more NO became bound. The results thus differ significantly from those reported by

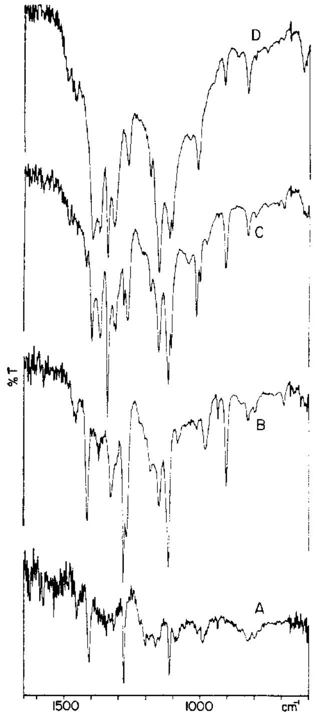


FIG. 3. NO sorption at 25°C. A few segments of a series of spectra recorded after exposing CaO to NO at 25°C. The pressures (μm) were: (A) 1.5; (B) 6; (C) 95; (D) 1100.

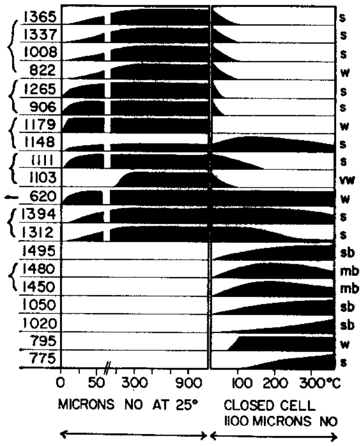


FIG. 4. Band relations for NO sorption.

Kortüm and Quabeck (*9*). Using reflection spectroscopy, they found one band at 2248 cm^{-1} when CaO was exposed to NO; the band was easily removed by pumping at 20°C, and they concluded that CaO had no adsorption sites which could bind NO more strongly. A 2248 cm^{-1} band was not observed in the present work; possibly an artifact was involved (*10*).

It does not seem feasible to describe verbally the complex spectral behavior encountered, or the even more complex results considered later, in an efficient and concise manner. Consequently, in order to avoid excessively long verbal descriptions, the data are summarized in Fig. 4. The latter lists the band positions and indicates changes in the intensities of individual bands. In many cases there was severe band overlapping, so that precise band intensities could not be obtained. However, the graphs of Fig. 4 serve qualitatively to show changes in the bands and relations between them. Not shown are the changes for three quite weak bands at 1408, 1280, and 980 cm^{-1}. These bands appeared immediately upon exposing a sample to NO, reached their maximum intensities at about 10 μm, and then declined in intensity and disappeared in the 80–100 μm range.

Desorption. In order to obtain information about the stability of the sorbed layer, experiments were made in which the adsorbent was exposed to NO at 25°C and then degassed at progressively increasing temperatures. A few spectra from such a series are shown in Fig. 5. It is apparent that degassing caused the adsorbed layer to change: new bands appeared and ex-

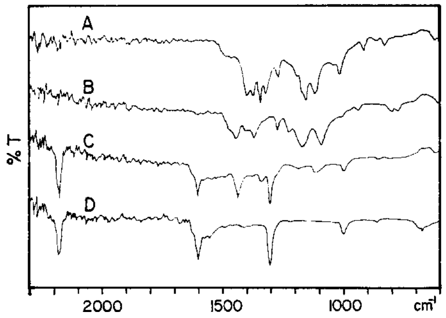


FIG. 5. NO desorption. After a CaO sample had been exposed to 1.1 Torr of NO at 25°C (A), the sample was degassed at successively higher temperatures. For the traces shown, the temperatures (°C) were (B) 155; (C) 394; (D) 515.

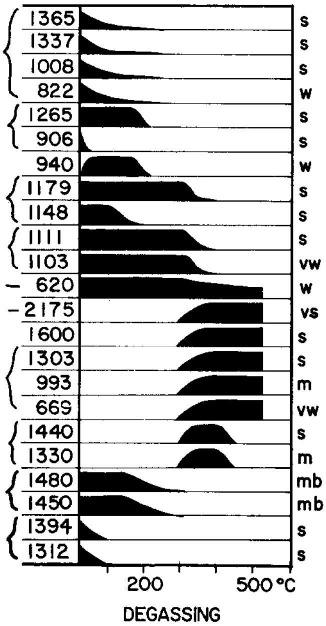


FIG. 6. Band relations for NO desorption.

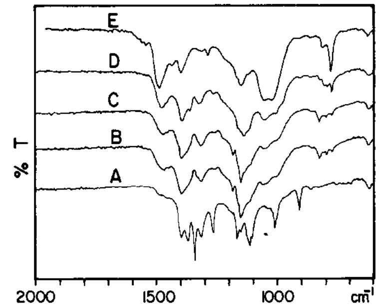


FIG. 7. NO sorption at elevated temperatures. A CaO sample was exposed to 1100 μm of NO at 25°C (A). The cell was then closed off, and the sample was heated in the residual gas at 110°C for 0.5 hr (B); at 190°C for 0.5 hr (C); at 190°C for 1 hr (D); and at 355°C for 0.5 hr (E). The band relations are shown on the right position of Fig. 4.

isting ones changed in intensity. The complex behavior is summarized in Fig. 6.

NO Sorption, 25–400°C. In order to obtain information about the uptake of NO at temperatures above 25°C, experiments were made in which CaO was heated in NO. The gas was placed in the cell and, after a steady pressure had been reached, a spectrum was recorded. The sample was then heated, the cell containing the sample and NO remaining closed, cooled to 25°C, another spectrum was recorded, the sample was heated in the closed cell at a higher temperature, and so on. A few spectra obtained under such conditions are shown in Fig. 7; the spectral behavior is summarized by the right portions of Fig. 4.

Reaction of the sorbed layer with oxygen. A series of measurements were carried out to test the susceptibility of the sorbed layer to oxidation. A fresh CaO sample was exposed to NO at 25°C and, when the pressure was steady at 700 μm, the residual NO was removed by pumping at 25°C. Oxygen was then introduced so that the pressure was 700 μm, and a spectrum was recorded, the cell remaining closed. Additional spectra were recorded after heating the sample in the residual gas for 30–40 min at each of progressively increasing temperatures (105–545°C); segments of some of these are shown in Fig. 8.

In order to test the stability of the oxidized surface layer, the sample was degassed at progressively increasing temperatures. Segments of spectra of a degassing sequence are shown in Fig. 9.

It is apparent that the surface layer suffered pronounced, complex changes during the oxidation and subsequent degassing. The results are summarized by Fig. 10.

DISCUSSION

The initial and obvious observation to be made is that the present results are intricate and complex, especially in comparison to the quite simple data observed during earlier studies of NO sorption. NO sorption on various metals and oxides (*1*, *2*, *5*, e.g., *9–18*) has led to the formation of only very few infrared bands with each adsorbent, and the band frequencies are in most cases rather high. In the present case, the bands are numerous and the frequencies of many of them are rather low. The bonding within the NO-produced surface layer on CaO is thus generally of a different character than thought to exist previously, and there exist many NO_x forms on CaO. Identifying them all, i.e.,

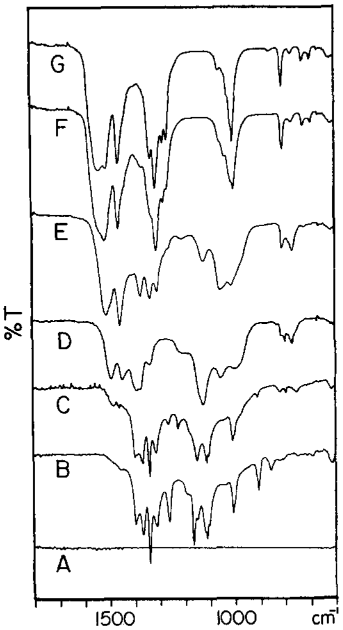


FIG. 8. O_2-Treatment of Sorbed NO. (A) The "base line," i.e., a ratioed spectrum obtained by recording a single beam spectrum *x* of the degassed CaO and storing *x*, recording another spectrum *y*, and then ratioing *x* and *y*. (B) Recorded after the CaO sample had been exposed to 700 μm of NO at 25°C. After degassing at 25°C to remove residual NO, the sample was exposed to 700 μm O_2 for 34–40 min at the following temperatures (°C): (C) 25; (D) 105; (E) 205; (F) 305; (G) 410. The sequence is continued in Fig. 9, with (H) 410; (J) 545.

making unequivocal band assignments, seems a task of monumental proportions and one which is probably impossible. However, by closely observing the intensity changes of the bands and the intensity relations between the bands it is possible to bring about some order and to group the bands. That has been done to some extent in the data summaries of Figs. 4, 6, and 10. Comparison of bands and groups of bands with the spectra of known compounds then becomes feasible but, because of the numerous potential structures, it is likely that band assignments can be made which cannot be accepted without reserve and in some cases without great doubt. Such band grouping and comparisons have led us to the tentative assignments outlined

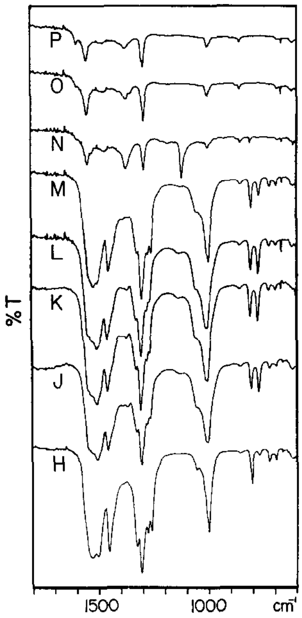


FIG. 9. O_2-Treatment of sorbed NO. Continuation of the sequence of Fig. 8. For (H, J) see legend of Fig. 8. The sample was degassed at 25°C for 11 hr (K) and then for 30 min at the following temperatures (°C): (L) 200; (M) 340; (N) 515; (O) 590; (P) 640.

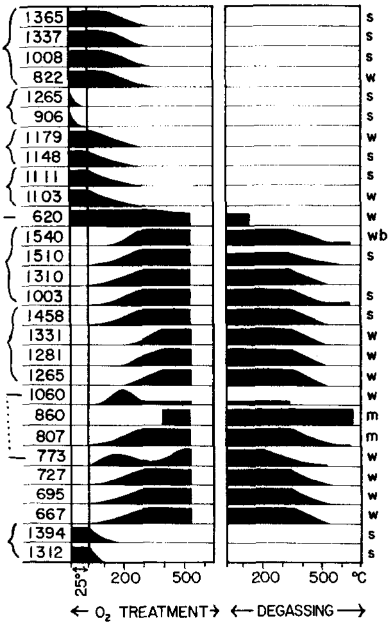


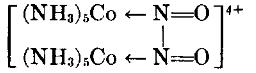
FIG. 10. Band relations of the spectra of Figs. 8 and 9.

below; they seem to be reasonable ones. Alternative assignments might be possible in some cases, but these, and partial assignments, and assignments for which the arguments are excessively speculative and the polemics interminable, have been omitted.

Adsorbed NO forming NO^-. The N–O stretching frequency, which is at 1876 cm^{-1} for gaseous NO, can shift markedly depending on the type of bonding. If an electron is lost and nitrosonium ion, NO^+, is formed, the frequency rises; it is in the 2300–2200 cm^{-1} range for NO^+ salts, and in the 2000–1700 cm^{-1} range for coordinated nitrosonium ions. Electron gain leads to a decrease, nitrosyl (NO^-) salts absorbing near 1100–1000 cm^{-1}, the coordinated nitrosyl frequency being in the same range. For adsorbed NO, the frequency and intensity of the N–O band have also varied drastically, falling in or near the 2200–1500 cm^{-1} range, and a variety of bonding, e.g., "double bond ionic," or "coordinative ionic," has been proposed for adsorbed NO. As pointed out by Shelef and Kummer (*2*), every transition metal ion has its own predominant mode of bonding with NO, the formation of negative ions is absent, and the covalent mode of bonding is relatively unimportant.

In distinct contrast to all except one of the earlier studies, the spectra of NO sorbed on CaO (Fig. 4) show no bands above 1500 cm^{-1} but show numerous bands at lower frequencies. The formation of NO_x species would thus seem to be indicated. However, four bands were formed which could not be grouped with other bands as progressive changes occurred in series of spectra (Figs. 2, 3, 4). The bands at 1111 and 1179 cm^{-1} were formed at very low NO pressure of $\sim$1.5 μm. The 1148 cm^{-1} band formed at 4 μm. The 1179 cm^{-1} band was "saturated," i.e., did not appear to increase in intensity with increasing gas pressure, at about 10 μm while the 1148 cm^{-1} band grew until 240 μm was reached, when it exceeded the 1179 cm^{-1} band in intensity. The 1111 cm^{-1} band also became saturated at rather low pressure and another band at 1103 cm^{-1} appeared at 200 μm pressure. The changes suggest that two related pairs of bands were formed.

The spectra of transition metal NO^- complexes were studied by Griffith, Lewis and Wilkinson (*19*). Dimeric complexes, e.g.,



$$\left[\begin{array}{l}(NH_3)_5Co \leftarrow N{=}O \\ \qquad\qquad\qquad\ | \\ (NH_3)_5Co \leftarrow N{=}O\end{array}\right]^{4+}$$

gave rise to N–O frequencies in the 1195–1045 cm^{-1} range, the frequency depending on the anions attached to the complex. The monomeric complex, $[(NH_3)_5\,Co \leftarrow N{=}O]^{2+}$, also had the N–O frequency in the same region, but generally at lower frequency than the dimeric complex. Also, the infrared spectra of sodium, silver, and mercuric hyponitrites show peaks at 1035, 1058, and 1138 cm^{-1}, respectively, attributed to the N–O stretching vibration of the coordinated NO^- ion (*20*).

It consequently seems reasonable to attribute the 1179 cm^{-1} band to a dimeric $(NO^-)_2$ structure containing a hyponitro-type bridge (*19*), bound to surface calcium atoms. The fact that such a structure was formed first and saturated early, i.e., at quite low NO pressures, would indicate that the surface species was bound to adsorption sites on the surfaces of high index, these being energetically high, and that such facets comprised only a small fraction of the total crystal surface area. The 1148 cm^{-1} band is attributed to a similar dimeric structure bound to sites on lower index facets. The fact that the 1148 cm^{-1} band was formed when the 1179 cm^{-1} band was saturated and achieved high intensity at higher pressures would support the suggestion that lower index facets were in the majority and the bonding to sites located on them was weaker. The assignments are consistent with the observations that, during desorption at elevated temperatures, the 1148 cm^{-1} band was the first to diminish.

Similarly, the bands at 1111 and 1103 cm^{-1} can reasonably be assigned to adsorbed monomeric NO^-. The 1103 cm^{-1} band was formed only after the 1111 cm^{-1} band had stopped increasing in intensity, so that it would seem that the 1111 cm^{-1}

species was the stronger and the 1104 cm^{-1} species was the weaker-bound to the surface.

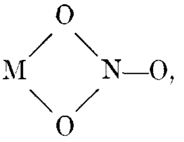
Adsorbed NO forming NO$^+$. The highest frequency band was at 2175 cm^{-1} and was observed only after degassing at and above 300°C. The 2175 cm^{-1} band seems to be related to bands at 1600, 1303, 993, and 669 cm^{-1} (Fig. 6) which formed at the same time and exhibited similar behavior. However, these five bands do not match the band patterns of known compounds; and it is probable that more than one surface species is responsible for these absorptions. The simplest assignment is to attribute the 2175 cm^{-1} band to NO$^+$ on Cr_2O_3 (*1, 12*). Brunner (*21*) has found that a number of NO$^+$ complexes, such as $NO^+(Bu_3P)_2NiCl_2^-$, have the N–O absorption near 2220 cm^{-1}; that would tend to support the assignment of the 2175 cm^{-1} band to a surface NO$^+$ structure.

A nitronium (NO_2^+) would also absorb at high frequency; ν_3 of the nitronium ion in concentrated HNO_3 is at 2360 cm^{-1}, ν_1 being at 1400 cm^{-1} and ν_2 at 667 cm^{-1} (*22*). However, the observed bands do not fit that pattern. Also, the 2175 cm^{-1} band was observed only during degassing; it was not observed during the oxidation and subsequent degassing, when the formation of an oxygen-rich species might be more plausible. It thus does not seem likely that a nitronium species was detected.

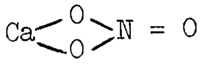
Adsorbed NO forming NO_2^-. The bands at 1265 and 906 cm^{-1} are grouped, and are attributed to adsorbed nitrite ion, $-NO_2^-$. Nitrite ions of metal salts normally absorb at 1400–1300 cm^{-1} (ν_1), near 1250 cm^{-1} (ν_3), and near 830 cm^{-1} (ν_2) (*23*). Although both ν_1 and ν_3 are infrared active for the C_{2v} symmetry of NO_2^-, ν_3 is normally much weaker in intensity than ν_1 and appears as a weak shoulder of the ν_3 band (*24–26*) Anbar, Halman and Pinchas (*24*) observed ν_1 at 1374 cm^{-1} with $AgNO_2$, but Weston and Brodansky (*27*) observed only two bands for $AgNO_2$ at 1250 and 846 cm^{-1}, taken to be ν_3 and ν_2, respectively. The absence of ν_1 was also reported by James and Leong (*28*). In our case, the ν_1 band of NO_2^- might not be observable because it might be quite weak and be overpowered by the strong bands in its vicinity.

The assignment seems plausible. However, it is pertinent to note while the 1265 and 906 cm^{-1} bands showed generally similar behavior (Figs. 4 and 6), the 906 cm^{-1} band shifted on degassing the specimen (Fig. 6). The 906 cm^{-1} band declined, while another grew at 940 cm^{-1}. The 1265 and 940 cm^{-1} bands then declined together. The behavior suggests that two pairs of bands existed, one structure giving rise to the 1265, 906 cm^{-1} pair being transformed to another giving rise to a second pair absorbing at 1265 and 940 cm^{-1}.

Adsorbed NO forming NO_3^-. The group of bands at 1365, 1337, 1008, and 822 cm^{-1} appeared and disappeared in concert during all of the experiments, and resemble the bands of the ionic nitrate ion in $Ca(NO_3)_2$. They are assigned to surface NO_3^- groups: ν_3 = 1365, 1337 cm^{-1}; ν_1 = 1008 cm^{-1}; ν_2 = 822 cm^{-1} (*29, 30*). The splitting of ν_3 has been observed for the alkaline earth metal nitrates and was thought to be caused by a lowering of symmetry from point group D_{3h} to C_{2v} (*30*). Ferraro (*30*) also attributed the dissymmetry of these nitrates to the higher ionic potential of the cations. Accordingly, the splitting of ν_3 of the surface NO_3^- would imply that the NO_3^- is firmly bound to the surface Ca^{2+}, the ionic radius of Ca^{2+} being small relative to that of the bound NO_3, yielding a high ionic potential (*31*).

Covalent NO_x. On adsorbing NO_2 on Fe, Blyholder and Allen (*32*) observed bands at 1550, 1290, 1020, 804, and 765 cm^{-1} which were attributed to a bidentate nitrate species,  apparently covalently bonded to the surface iron atoms, in analogy to bidentate nitrato complexes (*33*). Monodentate nitrato complexes are known, and absorb at frequencies somewhat lower than bidentate complexes (*34*). It seems that similar structures were formed on CaO.

Two groups of bands appeared and disappeared during the oxidation and subsequent degassing experiments (Fig. 10). The group at higher frequencies (1540, 1510, 1310 and 1003 cm^{-1}) is similar to the bands of the covalent bidentate nitrato species (*32*); the group at lower frequencies (1458, 1331, 1281 and 1265 cm^{-1}) shows a similar band pattern and bears resemblance to that of monodentate complexes. It thus seems reasonable to make the following assignments:



Covalent bidentate

ν_3 = 1540, 1510 cm^{-1}

ν_1 = 1310 cm^{-1}

(N=O) stretch = 1003 cm^{-1}

Covalent monodentate

ν_3 = 1458 cm^{-1}

ν_1 = 1331, 1281, 1265 cm^{-1}

There are weak bands at 807, 727, 773, 727, 695, and 667 cm^{-1} which seem to appear and disappear along with the more prominent bands listed above. These weaker bands may be caused by the bending modes of the mono- and bidentate nitrate species.

The 620 cm^{-1} band. Many of the spectra show a band at 620 cm^{-1}. It appears to be unrelated to any other individual band or small group of bands, but seems to appear whenever what have been taken to be the ionic NO_x species are on the surface. The band declines and disappears when the ionic NO_x species disappear and the covalent species appear during the oxygen treatment and subsequent degassing (Fig. 10). The 620 cm^{-1} band is attributed to the Ca–N stretching mode, presumably that of $Ca^{2+} \ldots NO_x^-$ structures.

Spectra of NO adsorbed on transition metals led Alekseev and Terenin (*35*) to conclude that the transition metal ions were the adsorption sites. Similarly, Poling and Eischens (*15*) thought NO to be bound to surface ferric ions on iron oxide, and in general, based on Shelef and Kummer's (*2*) review and analysis, cations appear to be the adsorption sites for NO. Also, Blyholder and Allen (*16*) observed bands at 650 and 625 cm^{-1} for NO adsorbed on Ni, and attributed the 650 cm^{-1} band to Ni–N stretching and the 625 cm^{-1} band to Ni–N–O bending modes. The Zn–N stretching frequencies for a series of Zn complexes containing amine ligands were reported to be near 450 cm^{-1} (*36*). The Fe–N stretching frequency of $Na_2FeNO(CN)_5 \cdot 2H_2O$ were found to be at 652 and 662 cm^{-1} (*37*). There is thus reasonable support for the assignment of the 620 cm^{-1} band.

Other bands. Two relatively strong bands at 1394 and 1312 cm^{-1} appear to be related and to be caused by a weakly bound species. The band frequencies are similar to those of nitrates and nitrites, but possibly a nitro complex (*38*) could be involved. Similarly, the group of weak bands at 1408, 1280, and 980 cm^{-1}, which are the first observed on exposing a fresh sample to NO, show similarity to nitrate or nitrite bands, but also fall near the 1419, 1121, and 1031 cm^{-1} bands of $N_2O_2^{2-}$ (*39*).

The cause of a group of bands at 1600, 1303, 993 and 669 cm^{-1} is also uncertain (Fig. 6). The 2175 cm^{-1} band (which has been tentatively attributed to NO^+) together with the 1303 and 669 cm^{-1} bands are similar to the bands of solid N_2O (*23*) leading to the suggestion that N_2O had formed via disproportionation. Roev and Alekseev (*14*) assumed N_2O to be formed on adsorbing NO on CoO/Al_2O_3, but found that the adsorbed material could be removed at room temperature. In contrast, tightly bound material was formed in the present experiments, the bands remaining at 500°C (Fig. 6), so that it seems unlikely that those bands were caused by an N_2O species.

A transient species having bands at 1440 and 1330 cm^{-1} was formed during degassing over the 200–450°C range. Apparently, another transient species having bands at 1060 and 773 cm^{-1} was formed during the oxygen treatment over the 50–300°C range; the bands are superimposed on others at the same frequencies (Fig. 10).

The cause of the various bands is not known. A large number of possible structures, including those postulated by Chao and Lunsford (*40*) can be invoked.

SUMMARY AND CONCLUSIONS

The various results suggest that at least a dozen surface species were formed, the tentative assignments pointing to the existence of ionic species as well as covalent NO_x groupings. The NO^- species seems particularly interesting, as a quite substantial change in the N–O bond is implied. Low-frequency bands corresponding to such species do not seem to have been observed previously, although Chao and Lunsford (*41*) suggested that formation of NO^- occurred on Y-type zeolites; they attributed bands in the 1820–1850 cm^{-1} region (depending on the zeolite and temperature) to such species, but the rather high frequencies suggest that it seems more likely that an NO_x^+ species was responsible. However, there seems little point in discussing the NO–CaO mechanisms, because the nature of so many of the surface species is unknown and a variety of steps is possible, including NO decomposition and disproportionation with subsequent reaction of the products, nitrite and nitrate decomposition, nitro to nitrito isomerization, and the like. Little more can be deduced than that the layers on CaO are multicomponent mixtures of variable composition. The deduction of the bewildering variety of species on CaO can, however, have a more useful function than confirming Shelef and Kummer (*2*) that ". . . detailed information concerning the catalytic chemistry of NO is still in a rudimentary state."

One is first led to suspect that some NO_x species on other adsorbents may have remained undetected because infrared studies may have been carried out under conditions of insufficient resolution and sensitivity: there seem no compelling chemical reasons to account for the large differences between NO layers on CaO and other adsorbents. Particularly, there seems little reason to expect large differences between CaO and MgO adsorbents, yet it was reported that NO sorbed on MgO gave rise to only four bands at 1420 and 1390 cm^{-1} (attributed to an NO_2 species bonded to two calciums through one oxygen and the nitrogen) and 1220 and 1180 cm^{-1} (attributed to a bidentate NO_2 or to Ca^+ NO_2^-) (*42*). If other NO_x species exist, it is conceivable that one of them is important in catalytic NO conversion processes, either directly as reaction intermediate, or as "poison" for some suitable catalytic site. One is then led to wonder about the involvement of some undetected but possibly detectable species in disproportionation (*40, 43*), decomposition (*44*), and conversion (*2*) mechanisms, and to question the utility of NO as "molecular probe" in infrared (*45, 46*), ESR (*47*), and physical adsorption (*48*) studies. The implications are obvious.

It seems pertinent to note, also, that NO was taken up by CaO at quite low pressures, most of the surface layer being relatively firmly bound. The surface melange precludes computing precise surface coverage. Crude estimates, e.g., that there is one adsorbed structure of unknown structure and unknown cross-sectional area per surface calcium atom, and the like, suggest that multilayers were not formed and that the "coverage" was less than complete for the various spectra shown. The sorption isotherms rose steeply in the 1–20 μm range and rose only slightly above 50 μm, suggesting that much of the reaction of NO with the surface occurred at quite low pressure. The low micrometer range is equivalent to the low ppm range in terms of NO concentration in gas at atmospheric pressure. CaO, or CaO-containing adsorbents or catalysts, or others containing MgO, might thus be useful in removing NO. Possibly, the low pressure sorption might be important in the interaction of NO with airborne aerosols.

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