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Infrared Study of the Adsorption of Nitrogen Dioxide, Nitric Oxide and Nitrous Oxide on Hematite

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An infrared spectroscopic study of the adsorption of NO_2, NO, and N_2O on α-Fe_2O_3 was carried out in order to identify chemisorbed species which could act as catalytic intermediates. Presorptions of pyridine and water were used in addition to usual pretreatments of the surface, in order to identify and discuss adsorption sites and mechanisms. Stable nitrate ions are formed on the surface, starting at beam temperature (b.t.) with NO and are predominant at 150°C with NO_2. Between b.t. and 150°C, NO_2 mainly chemisorbs as such or as its dimer N_2O_4. Depending on the pressure, NO chemisorbs at b.t. also as is or as NO^- ions, as well as in the form of its dimer N_2O_2. N_2O merely physisorbs on an "oxygen-rich" surface, but it strongly chemisorbs on an "evacuated" surface producing species which can be identified as N_2O^-.

INTRODUCTION

Iron(III) oxide is well known to be a good catalyst for NO reduction by CO (*1, 2*), H_2 and NH_3 (*2*). Mechanisms proposed for these reactions on other oxides usually consider NO chemisorption as the first step of the catalytic reaction (*3, 4*). However, literature data on adsorption of NO on Fe_2O_3 largely disagree: while some authors have not found any NO adsorption on α-Fe_2O_3 by ir spectroscopy (*5, 6*) and XPS (*7*), others have identified a number of adsorbed species from ir spectra (*8, 9*), quantitative adsorption (*10*), isotopic exchange (*11*), electrical conductivity, and work function measurements (*12*). Therefore, we have carried out a new detailed ir spectroscopic study of the adsorption of NO on well-defined samples of α-Fe_2O_3.

Previous studies have demonstrated the high oxidizing power of hematite (*13, 14*) and the possibility of different oxidizing species on its surface (*13, 15*), as well as the role of more-oxidized species as intermediates in mechanisms of catalytic reduction of NO (*4, 16*). Consequently, our study was extended to the adsorption of the higher oxide NO_2 in order to identify possible oxidation compounds already observed on other oxides (*17*).

As N_2O is a product of NO reduction on iron(III) oxide catalysts (*18*), infrared spectra of this molecule adsorbed on α-Fe_2O_3 are also described and discussed. Previous ir spectroscopic studies have shown that N_2O can physisorb (*3, 19–22*) or chemisorb (*23–26*) on several oxide systems. Negatively charged forms were identified by Cunningham *et al.* (*27*) and by Sazonova *et al.* (*12*) on Fe_2O_3 using electrical conductivity and electron work function measurements. The same species appear in a proposed mechanism of nitrous oxide dissociation on heterogeneous catalysts, used for testing the activity of oxide systems (*28–31*).

EXPERIMENTAL

Experimental conditions were similar to those previously reported (*13–15*). The double-beam infrared cell (NaCl windows), with an external furnace out of the ir beam was purchased from Glass Emery (Genoa). NO and NO_2 were taken from commercial cylinders (Baker, USA) and purified by multiple distillation under vacuum. N_2O

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was a hyperpure product from SIO (Milan) and was used without further purification.

The samples of α-Fe_2O_3 were obtained by vacuum decomposition of pellets of α-FeOOH (3 tons/cm^2; 30–50 mg/cm^2) in the ir cell. The BET surface area of the resulting hematite samples was 45.0 m^2/g using N_2 adsorption. Following previous procedures (*15*), two standard α-Fe_2O_3 surfaces can be obtained using different pretreatments:

"Oxygen-rich" surface. The pressed α-FeOOH sample is decomposed to α-Fe_2O_3 by heating under degassing at 250°C for 3 h, then treated in flowing dry oxygen for 1 h at 400°C and cooled in oxygen. Under these conditions four infrared bands are detected in the region 1340–1250 cm^{-1}, assigned to chemisorbed molecular oxygen.

"Evacuated" surface. The oxygen-rich surface, obtained as above, was exposed to water vapour and then degassed at 100°C for 1 h; under these conditions only one band at 1250 cm^{-1}, assigned to chemisorbed molecular oxygen, can be detected. Spectra were recorded at b.t. between 4000 and 1100 cm^{-1} with a Perkin-Elmer model 521 ir spectrophotometer. Reference beam attenuation was set up in order to obtain the best apparent transmission in each region. However, the ν_{OH} region of the spectra will only be reported when significant for our discussion.

RESULTS AND DISCUSSION

Nitrogen Dioxide

Contact of an oxygen-rich surface with NO_2 in the gas phase causes the progressive formation of an absorption at 1605 cm^{-1} Fig. 1b), already observed on other oxides (Table 1), very near to the symmetric

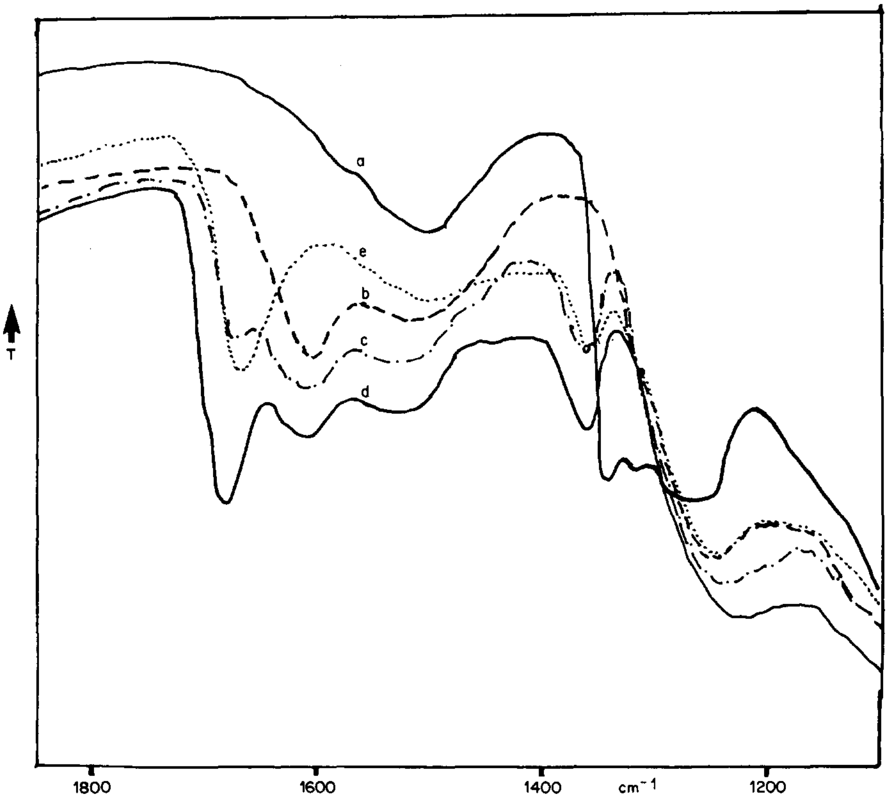


FIG. 1. Infrared spectra of NO_2 adsorbed on α-Fe_2O_3: (a) oxygen-rich α-Fe_2O_3 surface; (b–d) after contact with NO_2 (2 Torr at b.t.): (b) 30 min; (c) 2 h; (d) 4 h; (e) after degassing at b.t. for 30 min.

TABLE 1

Infrared Bands Assigned to N_xO_y Adsorbed Species

Species (ads)	Frequencies (cm^{-1})	Adsorbate	Adsorbent	References
N_2	2260–2180	N_2	Metals	(*33*)
N_2O	2305–2220, 1339–1195	N_2O, NO	Oxides	(*3, 19–26*)
$N_2O_2^{2-}$	1384, 1190, 1150, 830	NO	MgO	(*34*)
trans-N_2O_2	1750–1730	NO	Y-Zeolites	(*20*)
cis-N_2O_2	1902–1840, 1795–1735	NO	Oxides	(*20, 22, 35–37*)
NO^-	1820–1103	NO	Oxides	(*20, 34, 38*)
NO	1980–1720	NO	Oxides	(*8, 17, 22*)
NO^+	2260–1830	NO, NO_2	Oxides	(*8, 17, 20, 38*)
NO_2^-	1330–1208, 1230–1180, 900–850	NO	Oxides	(*17, 20, 34, 38*)
ONO^-	1470–1400, 1185–1120	NO	Oxides	(*20, 34, 39*)
N_2O_3	1920, 1555, 1305	NO	Y-Zeolites	(*20*)
NO_2	1632, (1320)	NO + O_2	V_2O_5/Al_2O_3	(*4*)
N_2O_4	1740, (1380)	NO_2	CuO	(*21*)
NO_2^+	2200–1980	NO, NO_2	Oxides	(*20, 40*)
NO_3^-	monodentate: 1570–1458, 1331–1250, 1035–970	NO, NO_2	Oxides	(*17, 38–40*)
	bidentate : 1600–1500, 1310–1225, 1040–1003	NO, NO_2	Oxides	(*17, 21, 38–41*)
	bridging : 1660–1590, 1260–1225, 1030–1000	NO_2	Oxides	(*39, 40*)

stretching frequency $\nu_3(B_1)$ of gaseous NO_2 (1610 cm^{-1}) (*32*). The simultaneous disappearance of the bands between 1340 and 1300 cm^{-1}, due to the more labile chemisorbed oxygen species coordinated on Lewis acid sites (*15*) can be interpreted as evidence that NO_2, because of its higher basicity, replaces these oxygen species on the same sites. A confirmation is given by the fact that no adsorption of NO_2 can be detected on surfaces where those sites have been previously poisoned with stronger bases such as pyridine or water. By increasing the time of contact, a new species is progressively formed on the surface, which is responsible for two intense bands at 1680 and 1380 cm^{-1} (Fig. 1c,d). Successive degassing at beam temperature (b.t.) removes the 1605-cm^{-1} band rather easily, while the pair of bands at 1680 and 1380 cm^{-1} only slowly decrease. This behaviour supports the assignment of the latter bands to N_2O_4 molecules, the corresponding bands having been measured at 1712 and 1380 cm^{-1} for N_2O_4 in the solid phase (*42*). Also the N_2O_4 dimers are probably chemisorbed on Lewis acid sites, as their bands, like that at 1605 cm^{-1} previously assigned to chemisorbed NO_2, cannot be observed after contact of NO_2 with samples whose cationic sites have been previously poisoned by pyridine or water.

However, these bands also disappear very quickly by degassing at 150°C and two new bands appear at 1540 cm^{-1} and near 1200 cm^{-1}. The latter are predominant also when contact of an evacuated α-Fe_2O_3 surface with NO_2 is carried out directly at 150°C (Fig. 2b). We propose that these two bands, which resist evacuation at 150°C (Fig. 2c) (only the higher frequency one slightly shifting towards lower frequencies), can be assigned to nitrate ions, formed by both NO_2 and N_2O_4 by reaction with surface oxygen ions. Their position and their frequency difference ($\Delta\nu \approx 340$ cm^{-1}) seem consistent with a bidentate structure (Table 1).

The same spectra as those obtained for NO_2 in contact with an oxygen-rich suface can be reproduced starting from an evacuated surface. This result implies that chemisorbed molecular oxygen responsible for the bands between 1340 and 1300 cm^{-1} is

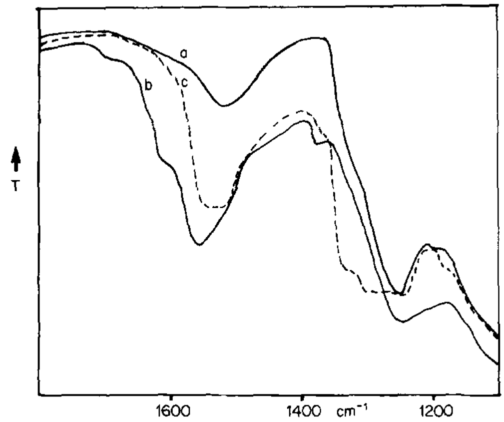


FIG. 2. Infrared spectra of NO_2 adsorbed on α-Fe_2O_3: (a) evacuated α-Fe_2O_3 surface; (b) after contact with NO_2 (2 Torr at 150°C; 30 min); (c) after degassing at 150°C for 15 min.

not involved in chemisorption or reaction of NO_2 on the α-Fe_2O_3 surface.

Nitric Oxide

Contact of NO (5 Torr) with an oxygen-rich surface of α-Fe_2O_3 immediately causes the disappearance of the bands due to adsorbed oxygen species (*15*) in the region 1340–1300 cm^{-1}. Strong bands, increasing with NO pressure, with main maxima at 1540 and 1220 cm^{-1} (Fig. 3b) are simultaneously generated. They can also be assigned to nitrate structures (Table 1), similar to the ones discussed above for NO_2 adsorption (Fig. 2). Their features will be discussed below.

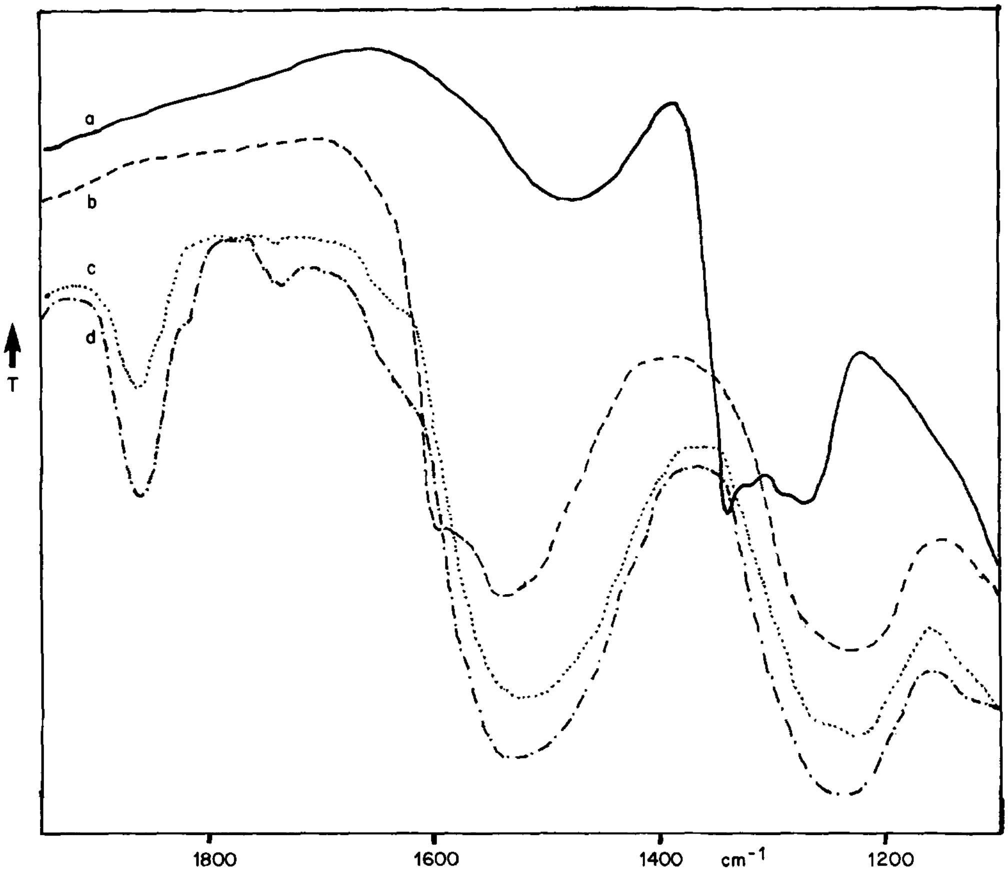


FIG. 3. Infrared spectra of NO adsorbed on α-Fe_2O_3: (a) oxygen-rich α-Fe_2O_3 surface; (b–d) after contact with NO (30 min at b.t.): (b) 5 Torr; (c) 200 Torr; (d) 300 Torr.

Further increase of NO pressures up to 200 Torr (Fig. 3c) causes the progressive appearance of an intense band at 1858 cm^{-1} and the simultaneous disappearance of the shoulder at 1595 cm^{-1} on the higher-frequency side of the 1540-cm^{-1} nitrate band. At 300 Torr (Fig. 3d) a weak band at 1735 cm^{-1} and a new component at 1830 cm^{-1} can also be detected. A shoulder at 1620 cm^{-1} may indicate the presence of some adsorbed NO_2 (see above) formed by NO oxidation on the surface.

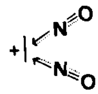
All the new bands, which occur only at high NO pressures, are reversibly eliminated by evacuation at b.t. with simultaneous reappearance of the 1595-cm^{-1} absorption. Their frequencies are not very different from those measured by other authors for reversibly adsorbed NO species on iron-containing oxides, summarized in Table 2. The band at 1595 cm^{-1}, which immediately appears in the spectrum upon NO adsorption (Fig. 3b), together with the strong bands attributed to chemisorbed nitrates, is unlikely to correspond to a second nitrate structure. If it did, the relatively high stretching frequency would correspond to NO_3^- species more strongly bonded to the surface, as a bridged species. However, the strong nitrate bands at 1540 and 1220 cm^{-1} are much more stable to degassing (Fig. 4c). The position of the 1595-cm^{-1} band, together with the fact that it does not appear to have a partner band at lower frequencies, would be consistent with its assignment to a NO^- species (Table 1), bonded through a highly ionic interaction with surface cationic sites. The presence of negatively charged species on Fe_2O_3 surfaces up to 150–160°C was previously identified after NO adsorption by Sazonova *et al.* (*12*) using electrical conductivity and electron work function measurements.

The bands at 1858 cm^{-1}, whose frequency is somewhat lower than that of gaseous NO (1880 cm^{-1} (*43*)), can be assigned to slightly perturbed NO molecules. As a purely coordinative bond, giving partially positive NO species, would be expected to increase the stretching frequency, this is likely to come from an adsorbed species where NO acts both as a σ donor and a π acceptor (*33*). However, as this species only appears at rather high NO pressures, with simultaneous disappearance of the 1595-cm^{-1} band, its identification with slightly perturbed NO molecules formed by interaction of a second NO molecule with a further coordinative site of iron ions already bonded to a NO^- species, is proposed (Table 2).

The bands at 1830 and 1735 cm^{-1}, which only appear at high NO pressures, increasing with time of contact, can possibly be assigned to adsorbed *cis*-N_2O_2 species (Tables 1 and 2). The corresponding bands were measured at 1862 and 1768 cm^{-1} by Fateley *et al.* (*44*) at −190°C in CO_2.

TABLE 2

Position (cm^{-1}) and Assignments of ν_{NO} Bands for NO Adsorbed on Fe-Containing Oxide Systems

Fe_2O_3 (gel) (Ref. *8*)	Fe_2O_3 (Ref. *9*)	Fe^{III} on SnO_2		α-Fe_2O_3 (This work)
		O_2 pretreatment (Ref. *22*)	CO pretreatment (Ref. *22*)	
1927]:N=O^+				1858 
1805]:NO	1810 NO on Fe^{2+}	1832 $Fe^{3+} \leftarrow$:NO	1770 $Fe^{3+} \leftarrow$:NO	1830 ν_{asym} NO } *cis*-N_2O_2
1735]-NO			1720 $Fe^{2+} \leftarrow$:NO	1735 ν_{sym} NO } *cis*-N_2O_2
				1620 NO_2(ads)
				1595 +|···NO^-

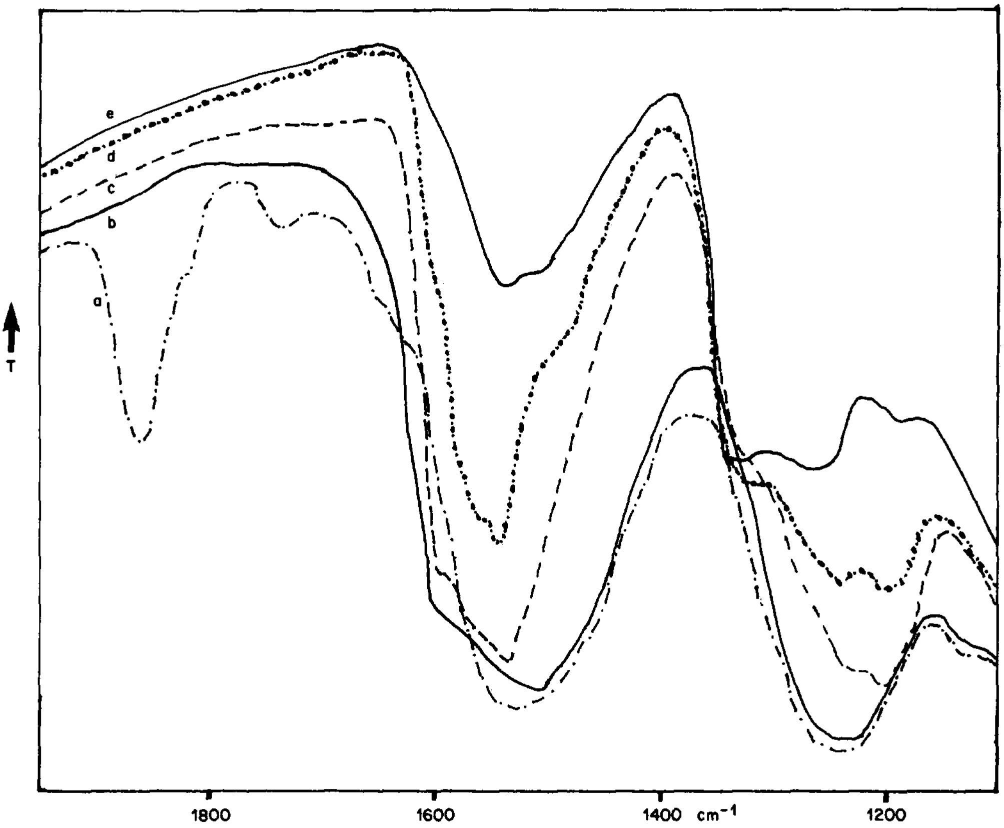


FIG. 4. Infrared spectra of NO adsorbed on α-Fe_2O_3: (a) same as Fig. 3d; (b) after evacuation at b.t.; (c–e) after degassing: (c) at 150°C for 15 min; (d) at 150°C for 1 h; (e) at 250°C for 30 min.

As noted above, evacuation at b.t. completely eliminates the bands assigned to NO, NO_2, and N_2O_2 chemisorbed species and restores the 1595-cm^{-1} band, previously assigned to NO^-, which only disappears completely by degassing at 150°C (Fig. 4d), in agreement with results of Sazonova *et al.* (*12*).

Degassing at increasing temperatures (Fig. 4d,e) provides evidence for the existence of some components in the intense and broad absorptions centered at 1540 and 1220 cm^{-1}, already assigned to chemisorbed NO_3^- ions. The species most resistant to degassing shows two bands at 1540 and 1190 cm^{-1} (Fig. 4e), and can be identified from its relative stability and from its stretching frequencies as a bidentate nitrate structure (Table 1). After only partial degassing (Fig. 4d) both bands show unresolved components towards higher frequencies (1560 and 1200 cm^{-1}), which could correspond to bidentate NO_3^- ions on different sites.

Species very weakly bonded to the surface can also be identified as monodentate nitrate ions both from their lability to degassing and from their vibration frequencies, which are measured at about 1480, 1270, and ca. 1130 cm^{-1} by comparison of spectra b and c in Fig. 4 (Table 1).

The formation of nitrates on the α-Fe_2O_3 surface after contact with NO is consistent with many literature data showing that nitrates are usually present on transition metal oxides, such as ZrO_2 (*17*), NiO (*17*), CuO (*21*), and TiO_2 (*41*), under similar conditions. Nitrite, nitro, and hyponitrite ions are, on the contrary, predominant after NO adsorption at beam or room temperature on non-transition-metal oxides, such as Al_2O_3 (*17*), MgO (*17, 34*), and CaO (*38*).

The decomposition of chemisorbed nitrate species with desorption of nitrogen oxides could be responsible for the electron acceptor effect, which was shown to become important at 237°C and above by Sazonova *et al.* (*12*), on the basis of their temperature dependence study of the electrical conductivity of Fe_2O_3 on NO. The progressive appearance of the oxygen absorptions in the 1300-cm^{-1} region, observed in our spectra (Figs. 2c and 4 c–e) at temperatures above 150°C, has already been discussed (*15*). The formation of O_2^- (and eventually O_2^{2-} species from structural oxygen ions and their desorption as O_2 molecules can be responsible for the trend of electrical conductivity reported by Sazonova *et al.* (*12*) by evacuation at temperatures above 300°C.

It has been observed above that the bands at 1340–1300 cm^{-1}, due to O_2^- species chemisorbed on Lewis acid sites (*15*), immediately disappear after contact with NO (Fig. 3b). This disappearance could be due either to a rearrangement of the O_2^- species due to NO^- or NO_3^- chemisorption, as already observed with water (*15*), or to a reaction between the same O_2^- species and NO to give nitrates. However, this second possibility cannot be predominant in nitrate formation as we have detected identical NO_3^- bands on evacuated surfaces. Nitrate ions must therefore be formed mainly by reaction of NO with surface structural oxygen ions.

In order to establish whether nitrate formation from NO necessarily involves its previous coordination on Lewis acid sites, we have also carried out the adsorption of NO on pyridine (*45*) and water-covered α-Fe_2O_3 surfaces. As identical nitrate structures are formed in both conditions it is evident that coordination of NO on cationic sites is not the first step in nitrate formation; therefore, direct reaction should occur with surface oxygen ions. Chemisorption of NO^- species is likely to be responsible for the displacement of the more labile O_2^- from Lewis acid sites. Our spectroscopic results agree with those reported for NO adsorption on the same oxide by Glazneva *et al.* (*9*) and on α-FeOOH by Rochester and Topham (*39*). They are also consistent with the high isotopic exchange rate between NO and the surface oxygen of hematite (*11*).

Nitrous Oxide

The spectra obtained for N_2O in contact with an oxygen-rich surface at beam or higher temperatures (up to 400°C) are shown in Fig. 5b: absorptions are detected near 2200 cm^{-1} (two components at 2250 and 2190 cm^{-1}, respectively) and at 1240 cm^{-1}. Simultaneously, a slight decrease in intensity of the ν_{OH} bands due to surface OH groups (3670 and 3640 cm^{-1} (*46*)) and a broadening of the 3460-cm^{-1} band assigned to hydrogen bonded OHs (*46*) can be observed, as well as a decrease in intensity of the band at 1340 cm^{-1}, due to the more weakly bonded molecular oxygen species (*15*). Degassing immediately restores the spectrum of the original surface.

These features indicate that two physisorbed species are formed on the oxygen-rich hematite surface. A species physisorbed on surface OHs through either N or O terminal atoms, with bands at 2250 and 1240 cm^{-1}, is consistent with analogous physisorbed species observed on several oxides (*3, 19–22*). This interaction would enhance the splitting between the ν_3 and ν_1 vibrations, with respect to the gaseous species (ν_3 = 2224 cm^{-1}; ν_1 = 1285 cm^{-1} (*32*)). On the contrary, an interaction of the central N atom with surface oxygens, which is likely to induce a slight bending of the linear molecule, could justify the existence of the second weakly adsorbed species, whose asymmetric stretching is shifted to-

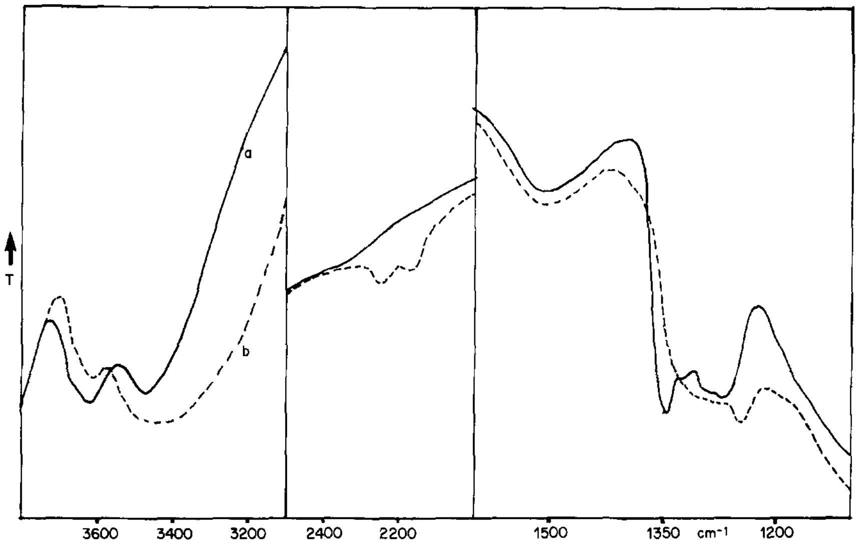


FIG. 5. Infrared spectra of N_2O adsorbed on α-Fe_2O_3: (a) oxygen-rich α-Fe_2O_3 surface; (b) after contact with N_2O (300 Torr at b.t. for 1 h).

wards lower frequencies (2190 cm^{-1}) with respect the gaseous phase.

A completely different situation is obtained with N_2O on an evacuated surface (Fig. 6). After a few minutes of contact at b.t. (Fig. 6b) bands at 1560, 1375, and 1350 cm^{-1} can be clearly measured whose intensity grows with time of contact and temperature (up to 200°C; Fig. 6d), the band at 1560 cm^{-1} developing also a component at 1540 cm^{-1}. These bands resist prolonged evacuation (Fig. 6c) at temperatures below 250°C.

Previous ir studies of the adsorption of N_2O on oxides have identified N_2O linear species chemisorbed on cationic sites of Na-A-zeolites (*23*), α-Cr_2O_3 (*24*, *25*), and η-Al_2O_3 (*26*). Such species, even if more perturbed than the physisorbed ones, show two stretching vibrations (ν_3 and ν_1) not very far from those measured in the gas phase. It is clear that the bands measured in our spectra cannot be assigned to analogous species. Interaction of N_2O on oxide systems was studied by various techniques in order to explain its catalytic decomposition mechanism. The steps usually accepted on oxides (*28–31*), including Fe_2O_3 (*27*), are the following:

$$N_2O(g) \rightarrow N_2O(ads),$$
$$N_2O(ads) + e^- \rightarrow N_2O^-(ads),$$
$$N_2O^-(ads) \rightarrow N_2(g) + O^-(ads),$$
$$O^-(ads) \rightarrow \tfrac{1}{2}O_2(g) + e^-,$$

or

$$O^-(ads) + N_2O(g) \rightarrow N_2(g) + O_2(g) + e^{-1}$$

Experimental evidence for the existence of negatively charged species on Fe_2O_3 after N_2O adsorption, identified as N_2O^-(ads), were obtained by Cunningham *et al.* (*27*) and, more recently, by Sazonova *et al.* (*12*). The bands measured in our spectra at 1560 and 1540 cm^{-1} and at 1375 and 1350 cm^{-1} cannot be easily assigned to N_xO_y adsorbed species (Table 1). However, they are not very far from the characteristic frequencies of the NO_2 molecule (ν_3 = 1610 cm^{-1}; ν_1 = 1318 cm^{-1} (*32*)). An assignment of these bands to adsorbed NO_2 is very unlikely due to the difficulty in envisaging the formation of such a species and to the completely different results obtained by direct adsorption of this molecule (see above).

On the contrary, an assignment to the

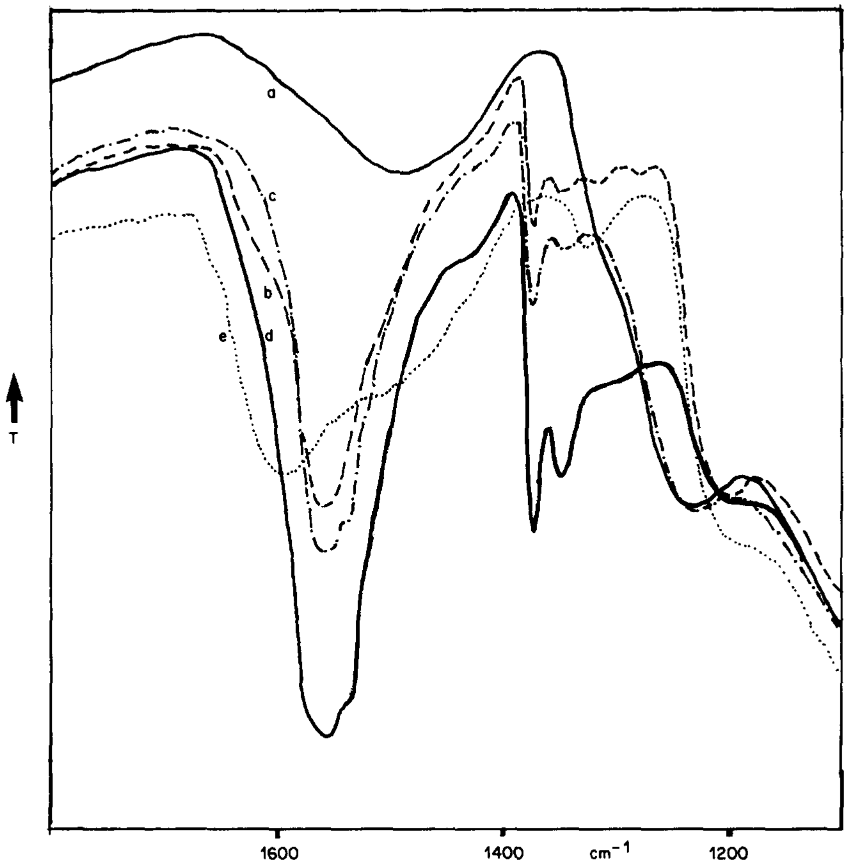


FIG. 6. Infrared spectra of N_2O adsorbed on α-Fe_2O_3: (a) evacuated α-Fe_2O_3 surface; (b) after contact with N_2O (300 Torr at b.t. for 1 h); (c) evacuated at b.t.; (d,e) after new contact with N_2O 300 Torr: (d) 1 h at 200°C; (e) 15 min at 400°C

asymmetric and symmetric stretching vibrations of chemisorbed N_2O^- species, isoelectronic with NO_2 as well as with the so-called "carboxylate" CO_2^- species, produced by adsorption of CO_2 on metals, absorbing in the regions 1575–1510 cm^{-1} and 1410–1330 cm^{-1} (*47*), can be proposed.

The experimental result, that this negatively charged species cannot be detected on the oxygen-rich surface or on water-covered surfaces, can be taken as evidence that the formation of this species requires an interaction with Lewis acid sites which N_2O cannot reach on such "poisoned" surfaces because of its poor basicity. N_2O, first chemisorbed on Lewis acid sites, could react with an electron from the n-type semiconducting oxide to form a nonlinear N_2O^- species, chemisorbed in two slightly different conditions as indicated by the splitting of both bands.

These chemisorbed species are stable until 250°C; at higher temperature they progressively transform into a third species, predominant after contact at 400°C (Fig. 6e), characterized by bands at 1600 and 1320 cm^{-1}, which could be the intermediate for the desorption of N_2. It is in fact known that N_2O decomposition on Fe_2O_3 starts before 500°C (*29*).

The reversible shift towards lower frequencies of the band at 1250 cm^{-1} (*15*), when N_2O is present in gas phase over an evacuated surface (Fig. 6), can be connected with a perturbation of the species responsible for this band by weakly adsorbed N_2O molecules; previous results have shown analogous shifts upon physisorption of water and other electron acceptor molecules on α-Fe_2O_3 (*13, 15*). This interpretation is supported by very weak bands of weakly adsorbed N_2O near 2200 and 1300 cm^{-1}, easily eliminated by evacuation.

CONCLUSIONS

This work has shown that NO_2, NO, and N_2O can all adsorb and react with the hematite surface, depending on the experimental conditions. Nitrogen dioxide chemisorbs at b.t. on Lewis acid sites of the hematite surface very quickly as NO_2 and, more slowly, as N_2O_4. At 150°C nitrate ions become predominant.

Nitric oxide reacts at b.t. with the hematite surface to give three types of nitrate ions with different thermal stability and coordination state. It also chemisorbs at low pressures on Lewis acid sites possibly as NO^-, replacing O_2^- species on oxygen-rich surfaces. At higher NO pressures, slightly perturbed NO species are formed on the same sites, together with N_2O_2 dimeric molecules.

Nitrous oxide reacts with an evacuated α-Fe_2O_3 surface to give species which can be identified as chemisorbed N_2O^-, and which are intermediates for its catalytic decomposition. It merely physisorbs in two different forms on an oxygen-rich surface, being unable to replace the oxygen molecules on the Lewis acid sites. Water and pyridine poison these sites for all three nitrogen oxides.

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