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Infrared Evidence for the Formation of Oxidised Species from N_2 Adsorbed on α-Fe_2O_3 Surfaces

We have recently been concerned with infrared studies of the adsorption of simple gases on hematite (*1*, *2*). With nitrous oxide (*1*), only physically adsorbed N_2O molecules could be observed on newly prepared "oxygen-rich" surfaces exhibiting absorptions from adsorbed oxygen between 1350 and 1300 cm^{-1}. However, on evacuated surfaces which did not show the above bands, a new chemisorbed species was formed. This was identified as a N_2O^- ion, such as is usually considered as an intermediate in the N_2O-decomposition mechanism which produces N_2 (*3*, *4*). It was therefore of interest to investigate the interaction of N_2 with the same surfaces.

It is known that N_2 frequently chemisorbs on the surfaces of transition metals, where its stretching vibration becomes ir active and is lowered in frequency with respect to that of the free molecule (*5*, *6*). For oxides, previous ir and Raman studies have only found very weakly perturbed N_2 molecules on ZnO (*7*) and NaA and NaCaA zeolites (*8*, *9*), while no adsorbed species have been detected on CuO (*10*).

The experimental techniques used, as well as the preparation and pretreatment conditions of the α-Fe_2O_3 samples, are described elsewhere (*1*, *2*). High-purity commercial N_2 was used after drying with molecular sieves and dry-ice/acetone traps.

The spectra of the samples were recorded both at beam temperature (b.t.), using a dispersion-type Perkin–Elmer model 521 infrared spectrophotometer, and nearer room temperature (r.t.) using a Digilab FTS 14 interferometer.

No changes are detected in the ir spectra after admission of N_2 between room temperature and 400°C to the "oxygen-rich" hematite surface which exhibits 1350- to 1300-cm^{-1} absorption bands. Figure 1b shows the spectrum, obtained with the Perkin–Elmer spectrometer, in a nitrogen flow at beam temperature over an evacuated α-Fe_2O_3 sample which did not show the above bands. Even in this case no bands could be detected due to molecularly adsorbed nitrogen. However, strong bands appeared at 1570 cm^{-1}, with an unresolved component near 1540 cm^{-1}, and at 1380 and 1350 cm^{-1}. These bands were also detected after contact with N_2 at higher temperatures up to 200°C (Fig. 1c). The wavenumbers and relative intensities of these bands are very close to those obtained for samples exposed to N_2O under similar conditions (*1*). It seems reasonable, on the basis of the spectroscopic and chemical considerations previously discussed (*1*), to assign these bands once again to surface N_2O^- species. The fact that the same species can be detected after contact of both N_2O or N_2 with evacuated hematite surfaces that do not exhibit the 1350- to 1300-cm^{-1} bands supports the above assignment. Mass spectrometric data (*11*) showed that N_2O can be detected in pure nitrogen that has flowed over α-Fe_2O_3 at 300°C. It seems therefore that the N_2-forming step of the usually proposed mechanism of N_2O decomposition on oxides such as α-Fe_2O_3 (*3*, *4*) is reversible according to the equilibrium:

$$N_2O^- \text{ (ads)} \rightleftharpoons N_2 \text{ (g)} + O^- \text{ (ads)}.$$

This involves O^- ions, which Bielanski and Haber (*12*) have reported to be formed on the surface, as the possible reactive oxygen species.

The 1350- to 1300-cm^{-1} bands are thought to arise from perturbed O_2^- ions

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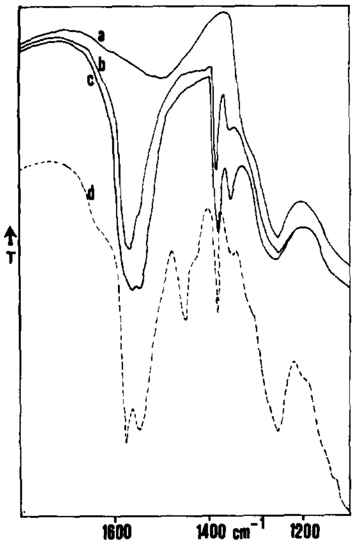

FIG. 1. Infrared spectra of N_2 adsorbed on a previously evacuated α-Fe_2O_3 sample (see text). (a) Initial α-Fe_2O_3 surface, using the Perkin–Elmer spectrometer; (b) after exposure to pure N_2 flow at b.t. (20 min); (c) after exposure to pure N_2 flow at 200°C (1 hr); (d) same conditions as (c) but the spectrum was measured at r.t. using the Digilab FTS 14 interferometer.

adsorbed on Lewis-acid sites on the surface (*2*). The fact that no interaction can be observed with an oxygen-rich surface which exhibits these bands indicates that:

(i) the reaction does not involve those oxygen species;

(ii) the formation of N_2O^- species requires previous interaction of N_2 molecules with Lewis-acid sites. Nitrogen is probably unable to replace the perturbed O_2^- species on these cationic sites because of its lower basicity. The same behaviour was already observed for N_2O on the same surface (*1*).

The presence of two different but related species (1570 and 1380 cm^{-1} and 1540 and 1350 cm^{-1}) with similar behaviour and characteristic infrared absorptions can be taken as a confirmation of the existence of two different coordination sites of somewhat different acid strength, as is also indicated by the ir spectra of chemisorbed pyridine (*13*). The proposed mechanism, involving N_2 interaction with bare cationic sites as the first step, is supported by the fact that N_2O^- species form on a water-precovered surface only after contact with N_2 at 150–200°C, under which conditions water desorbs from the same sites (*11*). The spectrum reported in Fig. 1d was recorded with a Digilab FTS 14 interferometer at r.t. It shows a better resolution of the components of the higher-frequency band and an additional double band at 1450–1425 cm^{-1} which is not present in the spectra recorded at b.t. using the dispersive spectrophotometer (Figs. 1b and c). This experimental result seems to indicate that a different species, thermally or photochemically unstable in the beam of the dispersive spectrophotometer, is present on the surface exposed to the colder beam of the interferometer.

It is unlikely that the strong N≡N bond can be broken under these mild conditions: the new species is therefore tentatively identified as a $N_2O_2^{2-}$ hyponitrite ion, which is known to have a band near 1400 cm^{-1} (*14*). Other characteristic vibrations of the latter ion fall in the lower-frequency region where strong background absorptions from Fe_2O_3 do not allow their observation. The species identified as $N_2O_2^{2-}$ seems also to be present on two slightly different sites.

It is interesting to observe that the formation of both N_2O^- and $N_2O_2^{2-}$ species only involves the reaction of N_2 with surface oxygen ions

$$N_2 + O^- = N_2O^-,$$
$$N_2 + 2O^- = N_2O_2^{2-}$$

although the latter product could in principle be obtained via the O_2^{2-} (peroxide) ion. All the previously discussed bands disappear by heating above 250°C and only a transient absorption near 1600 cm^{-1} can then be detected, as after contact of the surface with N_2O at 400°C. This band may be connected with a reaction intermediate for N_2 desorption from chemisorbed N_2O^- (*1*).

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