

Infrared Study of Adsorption and Oxidation of Ammonia on Ferric Oxide

D. W. L. GRIFFITHS, H. E. HALLAM, AND W. J. THOMAS*

*Departments of Chemical Engineering and Chemistry, University College of
Swansea, Singleton Park, Swansea, Wales*

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An analysis of the background infrared spectrum of an Fe_2O_3 disc reveals a doublet at 2865 and 2630 cm^{-1} which has been tentatively assigned to the presence of a proton located near symmetrically between two surface oxide ions. When oxygen is admitted to the heated solid, the Fe_2O_3 becomes catalytically active; and when this activation process is monitored, evidence suggests the presence of adsorbed O_2^- and O_2 species. When a mixture of ammonia and oxygen is introduced into the infrared cell containing the heated activated Fe_2O_3 disc, oxidation occurs. The spectrum suggests that surface nitroxyl or nitrogen species are present during the oxidation process.

Whether nitric oxide or nitrous oxide is the main product of the catalytic oxidation of ammonia depends critically on the hydrodynamic conditions which obtain near the catalyst surface. There is ample evidence to support the contention that the distribution of products of ammonia oxidation is a function of both mass and heat transfer effects (1, 2). The relative proportion of N_2O and NO formed will thus depend on the prevailing conditions of gas flow rate and temperature in addition to the chemical composition of catalyst. It is well known that platinum gauze is widely used as a commercial catalyst for the oxidation of ammonia to nitric oxide but if the simultaneous formation of nitrous oxide is to be avoided the gas flow rate should be adjusted so that the contact time, defined as the ratio of the volume of reactor space occupied by the gauze to the actual total volumetric flow rate through the reactor, is greater than 10^{-4} sec (2, 3). The overall reaction rate is evidently mass transfer limited and a successful interpretation of

kinetic data would be exacerbated by such concomitant effects. Separation of the chemical factors operating from physical complications such as mass and heat transfer may, of course, be ameliorated by use of an infrared technique to identify chemical species existing at the catalyst surface during the oxidation reaction.

In a previous study (4), we attempted to investigate changes occurring at a supported platinum surface, which was used as a catalyst for the oxidation of NH_3 to N_2O . The mixture of oxygen and ammonia introduced to the catalyst at about 200°C was in the molar ratio 12:1 and such conditions simulate those utilized in practice when N_2O is the desired oxidation product. No surface species, other than adsorbed NH_3 and N_2O , were detected during the course of this work. The present paper describes work on a supported iron oxide catalyst which, by virtue of its electronic properties and reducibility, is a suitable material for the oxidation of NH_3 to N_2O . It is advantageous to use a heavy metal oxide such as Fe_2O_3 for infrared investigations since it absorbs in a relatively low frequency region of the spectrum and offers

*Present address: School of Chemistry and Chemical Engineering, Bath University of Technology, Claverton Down, Bath.

the possibility of scanning a fairly wide spectral region. Furthermore, iron oxide is readily dehydrated and affords a reasonably clean surface.

Zawadzki (5) showed that N_2O was the main product of ammonia oxidation when metallic oxides which readily form lower oxides are used as catalysts. Krauss (6) also reported that metallic oxides, which contain excess oxygen as lattice defects, are effective in forming N_2O and assumed that the oxygen anions within the defect lattice establish equilibrium rapidly with gas-phase oxygen and adsorbed oxygen atoms. The adsorbed oxygen was then supposed to react with ammonia from the gas phase forming NH_2OH and HNO and subsequently N_2 and N_2O . Whether or not NH_2OH and HNO are adsorbed intermediates was not established unequivocally.

Recent work on the adsorption of ammonia and water at iron oxide was reported by Blyholder and Richardson (7) who recorded the infrared spectra of the adsorbed species at a temperature of 25°C . H_2O was purported to chemisorb at the surface of this oxide by dissociating to form an OH^- ion and a proton which reacted with surface O^{2-} ions to produce another OH^- ion. NH_3 , on the other hand, was said to be chemisorbed without dissociation but occupied the same surface sites as H_2O . When ammonia and water were simultaneously chemisorbed the infrared spectra indicated two distinct, although overlapping, bands attributed to $\text{NH}_3(\text{ads})$ and $\text{OH}^-(\text{ads})$. NH_4^+ ion formation was believed to occur only when physically adsorbed H_2O and NH_3 were present. It was also found that physically adsorbed H_2O could be removed easily by heating, but there was always a vestigial trace of chemisorbed water, present as $\text{OH}^-(\text{ads})$, unless the most stringent heating and evacuation procedure is adopted. This appears to be in contrast to the work of Mapes and Eischens (8) who detected adsorption bands at 3100 and 1450 cm^{-1} , which they attributed to $\text{NH}_4^+(\text{ads})$, when NH_3 was adsorbed on a silica-alumina catalyst. In this case, NH_3 was believed to interact with residual surface water to form ammonium ions. Although this point was

not further investigated by us, since we were primarily interested in the surface interaction between NH_3 and O_2 , it must be remarked that we obtained evidence which points to the presence of strong-held surface hydroxyl groups even after prolonged heating and evacuation. However, no band at 1450 or 3120 cm^{-1} was detected and this concurs with the observations for iron oxide recorded by Blyholder and Richardson (7). The difference in behavior may be due to the higher surface concentration of OH^- in the case of silica-alumina which would meliorate the detection of NH_4^+ if interaction with NH_3 does occur.

This paper represents an attempt to identify some of the surface chemical species occurring during the oxidation of ammonia over ferric oxide and is an extension of our previous studies (4) concerning the oxidation of NH_3 over silica and silica-supported platinum.

EXPERIMENTAL METHODS

Materials

Ferric oxide (5μ particle size) was obtained from the Fisher Scientific Co. (U. S. A.). Ammonia of 99.98% purity was obtained from I. C. I. Ltd. (U. K.) and used without further purification.

Apparatus

Spectra were recorded with a single-beam S3A infrared spectrometer fitted with a sodium chloride prism. For the present work the instrument was modified to enable spectra to be recorded during the course of a high-temperature oxidation experiment. To accomplish this the infrared radiation from the Nernst filament was chopped and passed vertically downward through the sample cell containing the ferric oxide disc. Full details of the modification were given previously (4).

The cell used for studying high-temperature spectra was similar to one described earlier (4). It consisted essentially of two halves. The lower half of the cell was a tapered Pyrex socket, the end of which formed a slotted platform upon which the sample could rest. The platform could be

heated by conduction of heat from the electrically heated outside wall. The top half of the cell formed the jacket for the lower half and contained the sealed sodium chloride windows. Provision was made for cooling the windows and for measuring the temperature of the sample on the heated platform.

Sample Preparation

Ferric oxide is extremely hygroscopic and special conditions are required (4) to make satisfactory infrared transmitting discs of the material. The ferric oxide (particle size 5μ) was first heated in air to about 500°C , cooled, and then compressed to 8 tons/in.² in a 1-in. diameter die maintained at 200°C . Discs of thickness 0.03 g/cm^2 were obtained which, although brittle and fragile, could be manipulated, with care, to give adequate transmission over the frequency range 3000 to 1200 cm^{-1} . Ultra thin discs could occasionally be handled and the above range extended to higher and lower frequencies.

RESULTS AND DISCUSSION

Spectrum of Fe_2O_3 Sample

The spectrum of an Fe_2O_3 disc which has not been subjected to a degassing routine is illustrated by curve A in Fig. 1. An absorption band due to $\nu(\text{OH})$ is centered at approximately 3400 cm^{-1} which, on cell evacuation, is considerably reduced in intensity. On the other hand, prolonged pumping for 10 hr failed to remove a doublet at 2865 cm^{-1} and 2680 cm^{-1} (curve B). One

plausible assignment (Table 1) would be to attribute this doublet to a hydrogen atom vibrating against an oxygen atom. Strongly hydrogen-bonded hydroxyl groups in dimeric carboxylic acids exhibit a characteristic broad absorption centered around 3000 cm^{-1} but extending to almost 2000 cm^{-1} and containing superimposed satellite bands (9). It is quite feasible that traces of strongly adsorbed water remain on the surface after prolonged evacuation; and if this is in a chemisorbed state, then it might be possible for a proton located near symmetrically $\text{O} \dots \text{H} \dots \text{O}^-$ between two surface oxide ions to produce this feature. The band at 1265 cm^{-1} may conceivably be a bending mode associated with this structure, although it is difficult to explain why the band is so weak in the original spectrum (A) of the disc.

Admission of oxygen to Fe_2O_3

Although the sample of Fe_2O_3 was activated prior to adsorption of ammonia and oxygen in the same manner as described by Blyholder and Richardson (7), we have recorded spectra at each stage of the activation process and have also carried out oxidation studies. After evacuation for 10 hr at 25°C (curve B) the sample was then heated in oxygen (30 Torr) for 12 hr at 350°C . Curve C (Fig. 1) represents the spectrum of the solid after cooling to 25°C . A band appears to emerge at 1350 cm^{-1} but it is ill-defined because of its position in a trough within the rotational structure of the OH bending vibration of atmospheric water,

TABLE 1
SPECTRAL ASSIGNMENTS

Fe_2O_3 (cm^{-1})	Fe_2O_3 heated to 350°C in O_2 and cooled to 25°C (cm^{-1})	Fe_2O_3 heated to 350°C in presence of O_2 and NH_3 (cm^{-1})	Adsorbed species	Assignment
3400			H_2O	$\nu(\text{OH} \dots)$
2865 } 2680 }			H_2O (or H^+)	$\nu(\text{O}^- \dots \text{H} \dots \text{O}^-)$
	1350		O_2	$\nu(\text{OO})$
1265		2200	NO^+	$\delta(\text{O}^- \dots \text{H} \dots \text{O}^-)$ $\nu(\text{NO})$
	1270		O_2^-	$\nu(\text{OO}^-)$

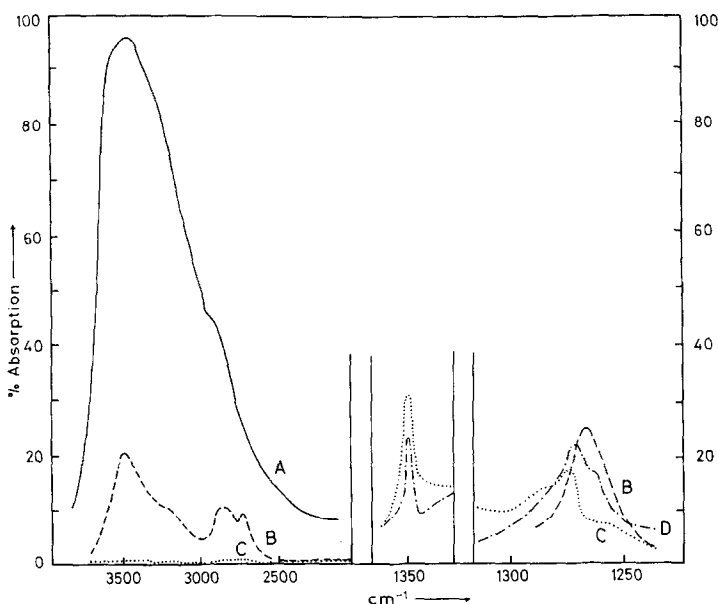


FIG. 1. Infrared spectra of iron oxide at 25°C (A); after evacuating at 25°C for 10 hr (B); after heating in oxygen at 350°C and cooling to 25°C (C); after outgassing at 350°C and cooling to 25°C (D); plotted as the ratio of $I/I(D)$ for 3600 to 2400 cm^{-1} and as $I/I(A)$ for 1400 to 2400 cm^{-1} .

which is superimposed on the whole spectrum. Simultaneously, the band at 1265 cm^{-1} and the doublet at about 2870 cm^{-1} are almost eliminated and a new feature develops at 1270 cm^{-1} . The sample was then evacuated and outgassed for 12 hr at 350°C and subsequently cooled to 25°C. Curve D (Fig. 1) represents the spectrum of the sample after cooling. The feature observed at 1270 cm^{-1} is now intensified, while the band at 1350 cm^{-1} and the shoulder at 2865 cm^{-1} remain.

These two features at 1350 and 1270 cm^{-1} , which arise when Fe_2O_3 is heated in oxygen, must be interpreted in terms of adsorbed O_2 species. A plausible interpretation would be to assign the upper band to chemisorbed O_2 and the lower one to O_2^- . A frequency lowering of 204 cm^{-1} from the Raman-active stretching frequency of gaseous O_2 at 1554 cm^{-1} (10) would seem quite reasonable for chemisorbed O_2 in a highly polar environment, the mode now becoming infrared active. The stretching frequency of O_2^- was shown recently, by Raman laser studies (11), to occur at 1141 cm^{-1} for an O_2^- ion trapped in a RbCl matrix, which on extrapolation of values in other alkali halides

yields a value of 1090 cm^{-1} for the ion in the free state. Our value of 1270 cm^{-1} for such a species in the highly polar Fe_2O_3 environment would also seem perfectly acceptable.*

Winter (12), who studied the energetics of adsorption and oxidation reactions on a variety of metal oxide surface (including Fe_2O_3), concluded that "the most probable species first formed in chemisorption of oxygen is $\text{O}_2^-(\text{ads})$." It was suggested that its existence is probably transitory and that it leads to the formation of $\text{O}^-(\text{ads})$. Our data suggest that the O_2^- species are not transient and that they are frozen into the surface on cooling to 25°C. Thus the assignment we make seems perfectly reasonable and consistent with other less direct observations.

* The authors are grateful to one of the referees for drawing our attention to the recent publication Shamir, J., Binenboym, J., and Classen, H. W., *J. Amer. Chem. Soc.* **90**, 6223 (1968), which tabulates values for the various O_2 species as O_2^+ , 1860 cm^{-1} ; O_2 , 1556 cm^{-1} ; O_2^- , 1145 cm^{-1} . Our data are in agreement with this list, although we can draw no conclusions about the possible presence of O_2^+ species since this spectral region was inaccessible.

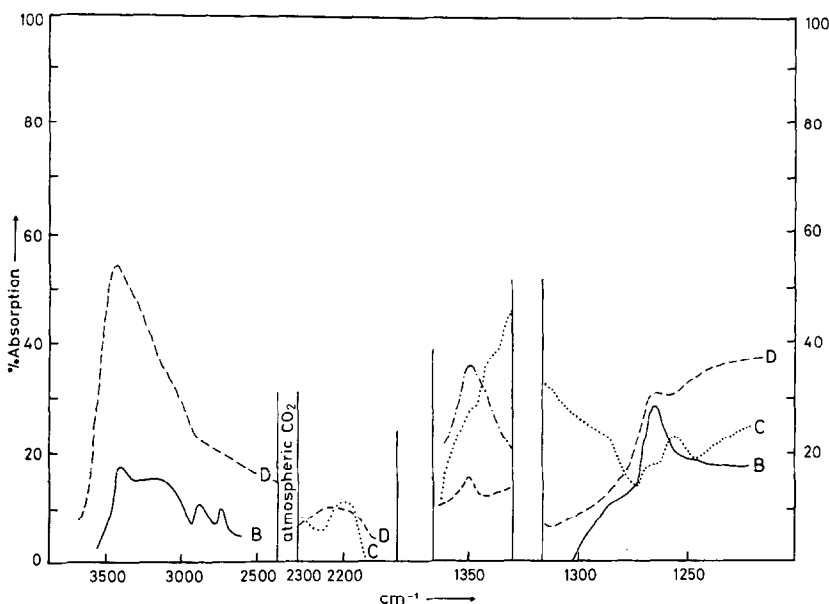


FIG. 2. Interaction of ammonia and oxygen on the surface of Fe_2O_3 : Fe_2O_3 disc after heating in O_2 at 350°C , outgassing and cooling to 25°C (A); followed by introduction of NH_3 at 25°C (B); then heated to 200°C (C); then cooled to 25°C (D); plotted as the ratio of $I/I(A)$.

Interaction of Ammonia and Oxygen over Fe_2O_3

When ammonia was introduced into the cell, a weak band was immediately produced at 3367 cm^{-1} due to νNH while the band at 1350 cm^{-1} disappeared. These events are illustrated by curve B of Fig. 2 ratioed against the background spectrum of the Fe_2O_3 disc. Addition of excess oxygen did not change the spectrum, but, when the sample was heated to 200°C , curve C shows that the feature at 1350 cm^{-1} reappeared. If the interpretation offered for the origin of this band is correct then it implies that ammonia interacts with adsorbed oxygen at the surface even at 25°C thus eliminating the band at 1350 cm^{-1} . The type of interaction envisaged is either (a) reaction of adsorbed ammonia with any surface oxygen present resulting from the activation process, or (b) weak second layer adsorption of ammonia at sites already covered with adsorbed oxygen.

Curve C also shows a well defined band at 2200 cm^{-1} and this would normally be assigned to the asymmetric stretching frequency of N_2O . The corresponding sym-

metric mode is centered at 1285 cm^{-1} in the gas phase; but, if this were present, it would be obscured by the background spectrum of the activated Fe_2O_3 disc. The spectrum recorded shows that the band at 2200 cm^{-1} has a particularly pronounced Q branch which is presumably induced by interaction with the surface. Surprisingly, however, on raising the temperature of the cell from 200 to 300°C , although the broad absorption band (attributed to adsorbed water) from 2800 to 3500 cm^{-1} appeared, the band at 2200 cm^{-1} was eliminated. On cooling to 25°C (curve D), the band did not reappear. Now one would not normally expect N_2O to be decomposed by Fe_2O_3 (13) and since separate experiments showed that it was not adsorbed, then we must reject the hypothesis that the band at 2200 cm^{-1} arises from either gaseous or adsorbed N_2O . If the disappearance of the band is not simply a spreading of the rotational envelope, then one has to invoke a species such as NO^+ or $\text{N}\equiv\text{N}=\text{X}$ to explain the presence of a fundamental band in this spectral region. If either of these species were present in sufficient amount on the surface to be detected, and both are

normal products of the oxidation reaction, on raising the temperature they would be desorbed from the surface to appear in the gas phase at a fairly low pressure (<1 Torr). This would account for the disappearance of the band at 2200 cm⁻¹ on heating the Fe₂O₃ sample after the ammonia and oxygen had reacted. Adsorbed NO is a distinct possibility, for if it were chemisorbed by the normally stable half-filled *d* orbitals of Fe³⁺ accepting an electron from the antibonding $\nu\pi$ -orbital of gaseous NO to form surface nitroxyl ions NO⁺, the band observed would fall within the range of frequencies attributed to nitroxyl salts (14). Alternatively, chemisorbed nitrogen could also account for the appearance of the band at 2200 cm⁻¹. Its Raman active frequency is at 2331 cm⁻¹ (10) and a shift of about 100 cm⁻¹ would imply some polarization on becoming attached to the surface. If chemisorbed N₂ were present, which would almost certainly be the case if the oxidation reaction proceeded by a surface mechanism, then it could be present in the undissociated state by one of the nitrogen atoms donating its lone pair orbital electrons to the half-filled *d* orbital of Fe³⁺. This, however, is rejected on the grounds that Blyholder and Richardson (15) failed to observe any adsorption of N₂ on Fe₂O₃. We thus assign the 2200 cm⁻¹ feature to adsorbed NO⁺.

From the evidence obtained in this work, it appears that ammonia interacts with surface oxygen ions to produce a surface intermediate, whose structure contains the nitroxyl group. The oxidation mechanism, formerly proposed by Krauss (6), and based on the formation of HNO as a surface intermediate, therefore, seems more plausible than the scheme, reported by Zawadzki (5), which purports the existence of NH and NH₂ surface species. Our observation con-

cerning the disappearance of the 1350 cm⁻¹ band ascribed to adsorbed O₂⁻ suggests that gaseous or weakly adsorbed NH₃ must react directly with surface oxygen to yield surface nitroxyl rather than amide or imide radicals being formed by the abstraction of hydrogen atoms from ammonia.

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