

Infrared Study of Methanol, Formaldehyde, and Formic Acid Adsorbed on Hematite

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This work spectroscopically confirms the oxidizing power of the α -Fe₂O₃ surface toward methanol, formaldehyde, and formic acid, at infrared-beam or higher temperatures. Oxidation reactions take place with formation of chemisorbed formate and carbonate ions and a corresponding oxygen depletion from the surface, identified through the activation of a new characteristic band of the iron oxide adsorbent. Methanol and formic acid can both physisorb via H-bonding (where they act as proton donors) and chemisorb respectively as methoxy groups (via a condensation reaction with surface hydroxyls) and formate ions (via an acid-base reaction). Formic acid molecules as well as formaldehyde molecules can also exist as such, coordinated to Lewis acid sites of the surface through their carboxylic oxygen. Formaldehyde, however, shows additional bands which can be tentatively identified as polymeric compounds.

INTRODUCTION

Iron(III) oxide is well known as a catalyst for dehydrogenation of some hydrocarbons (e.g., butene (1) and ethylbenzene (2)), and as a component of catalysts for methanol oxidation to formaldehyde (3, 4). It also catalyzes the dehydrogenation of ethyl alcohol (5) and of formic acid (6) with a good selectivity with respect to the dehydration reaction.

In a previous paper (7) we have detected a significant difference in the infrared spectra of hematite treated in oxygen (or in air) and *in vacuo*, which was assigned to modifications of the oxidation state of the surface. Our study has also shown that several organic molecules are oxidized on the surface of α -Fe₂O₃.

Nováková *et al.* (8) showed that methanol and formaldehyde are oxidized on a Fe₂O₃ surface even without gas-phase O₂.

To better understand the oxidation power of hematite surfaces and the activity of surface groups, we have carried out an infrared spectroscopic study of the adsorption of methanol, formaldehyde, and formic acid on α -Fe₂O₃ under different conditions, the results of which are presented here.

EXPERIMENTAL

The experimental conditions and the preparation of samples were the same as reported previously (7). Thin wafers of hematite were obtained from the decomposition in air (250°C) of α -FeOOH pressed disks (3 tons cm⁻²; 30-50 g cm⁻²). Their structure (α -Fe₂O₃) was confirmed by X-ray data. BET (N₂) surface area was 45.0 m² g⁻¹.

Spectra were recorded at T_b (beam temperature) with a Perkin-Elmer Model 521 infrared spectrometer. Real transmission values of the samples were a few percent in the 4000- to 3000-cm⁻¹ region and about 10-15% in the 2000- to 1200-cm⁻¹ region. The reference beam attenuation was set up in order to obtain the best apparent transmission in each region.

Formaldehyde was obtained by evaporating solid paraformaldehyde *in vacuo*. Methanol and formic acid were used after distillation, dehydration, and degassing. Methanol, formic acid, and paraformaldehyde were reagent-grade products from Carlo Erba (Milan, Italy). Perdeuteromethanol was a product for NMR spectroscopy (99.95% purity)

from E. Merck (Darmstadt, West Germany).

RESULTS AND DISCUSSION

The presentation of results will begin with the most highly oxidized compound, as the three adsorbates undergo oxidation reactions on the surface of α -Fe₂O₃ activated in air. The adsorption of CO₂, the completely oxidized C₁ compound, was reported elsewhere (9).

A. Formic Acid

In the presence of HCOOH vapor (0.1 Torr) a broad absorption appears between 3000 and 3500 cm⁻¹ centered at about 3150 cm⁻¹ near the surface OH stretching bands of α -Fe₂O₃ (10, 11) (Figs. 1a and b). An intense band at 1560 cm⁻¹, together with two shoulders at 1630 and 1720 cm⁻¹, can also be detected as well as absorptions near 1350 cm⁻¹ which are difficult to detect in these conditions, for reasons discussed elsewhere (7) (Fig. 1b). A band at 2880 cm⁻¹ is also present. After evacuation, the strong absorption centered at 3150 cm⁻¹ and the band at 1720 cm⁻¹ readily disappear, while the band at 1630 cm⁻¹ resists prolonged degassing at *T_b*, slowly lowering its intensity. If the degassing is carried out at 150°C this band also disappears, and only bands at 1555, 1376, and 1348 cm⁻¹ are detected (Fig. 1c); under these conditions,

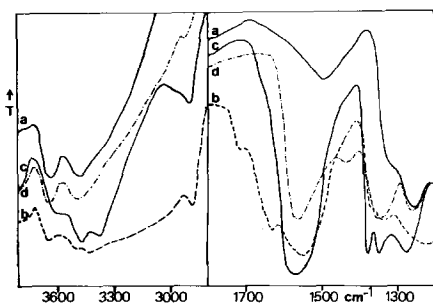
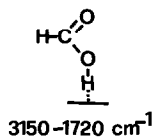


FIG. 1. Infrared spectra of HCOOH adsorbed on α -Fe₂O₃. (a) α -Fe₂O₃ disk activated 1 h at 400°C in air and cooled under evacuation; (b) in contact with HCOOH vapor (0.1 Torr; 5 min); (c) after degassing for 30 min at 150°C; (d) heated in He at 250°C for 30 min.

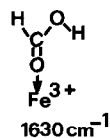
bands at higher frequencies (3460, 3380, and 2880 cm⁻¹) can be measured, the free OH band also being present as a shoulder near 3600 cm⁻¹.

If the degassing at 150°C is carried out for 5 h, the band at 3380 cm⁻¹ disappears, and the spectrum of α -Fe₂O₃ in the OH region is restored, while the new bands at lower frequencies are not affected. These bands are typical of a stable species, present on the surface after adsorption of HCOOH, which can be readily identified as formate ions, assigning the maxima at 2880, 1555, 1376, and 1348 cm⁻¹ respectively to C–H stretching, COO⁻ asymmetric stretching, C–H deformation, and COO⁻ symmetric stretching vibrations (12). Surface formates were already detected after adsorption of formic acid on Fe₂O₃ by Takezawa (13), using ir reflectance spectroscopy, as well as on a number of other oxides by different authors (14–19).

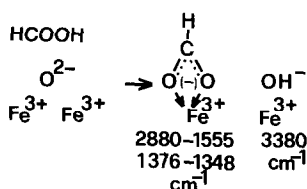
The bands due to labile species at 3150 and 1720 cm⁻¹ can be assigned to formic acid molecules physisorbed through hydrogen bonding where formic acid hydroxyls act as hydrogen donors, their stretching frequency being very strongly lowered (3150 cm⁻¹) with respect to the free molecule value (3570 cm⁻¹ (20)), while the surface free OH absorption maximum at 3640 cm⁻¹ is practically unaffected.



The band at 1630 cm⁻¹ can be assigned to a species coordinatively bonded through the carbonyl oxygen to Lewis acid sites, and which resists evacuation. Physisorbed and chemisorbed species as well as acetate ions were also detected after adsorption of acetic acid on hematite (7, 21).



The band at 3380 cm⁻¹ is still present under conditions where no physisorbed or chemisorbed molecules can exist on the surface: only formate ions, in fact, are detected in these conditions. This band can then be tentatively assigned to OH groups or H₂O molecules formed on the surface when HCOOH molecules react with surface O²⁻ or OH⁻ ions to form formate ions. This behavior would indicate a chemisorption mechanism similar to that proposed for Al₂O₃ (15) and TiO₂ (17).



If formate ions on the surface are heated *in vacuo* or in He at 250°C a progressive intensity decrease of the bands can be detected (Fig. 1d). When the bands at 2880 and 1376 cm⁻¹, corresponding respectively to C-H stretching and deformation vibrations, practically disappear, strong absorptions are still present in the spectra at 1555 and 1340 cm⁻¹ which can be assigned to bidentate carbonate ions formed on the surface (9). This will be discussed further below. Simultaneously, the enhancement of the absorption near 1410 cm⁻¹, which could correspond to oxygen depletion from the surface (7), is also detected.

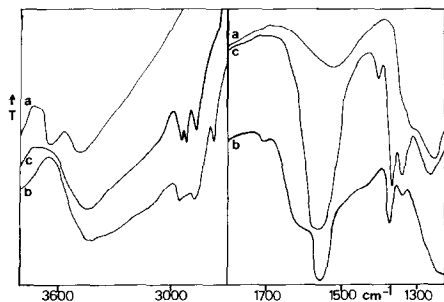


FIG. 2. Infrared spectra of CH₂O adsorbed on α -Fe₂O₃. (a) α -Fe₂O₃ disk activated 1 h at 400°C in air and cooled under evacuation; (b) in contact with CH₂O vapor (0.1 Torr; 5 min); (c) after degassing for 5 h at T_p .

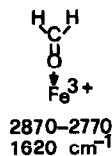
B. Formaldehyde

The contact of hematite samples with CH₂O vapor immediately causes in the OH stretching region the disappearance of the 3640-cm⁻¹ maximum and the appearance of a broad absorption toward lower frequencies (Fig. 2b). New bands are also measured in the CH stretching region at 2920, 2870, and 2770 cm⁻¹, as well as in the lower frequency region at 1710, 1620, 1560, 1375, and 1345 cm⁻¹.

Degassing at or higher than beam temperature causes the immediate disappearance of the band at 1710 cm⁻¹; the 2770- and 1620-cm⁻¹ bands are only eliminated by prolonged degassing. In these conditions the 2950-cm⁻¹ band splits into two components and a new band can be detected at 1403 cm⁻¹ (Fig. 2c). It must also be remarked that the surface free OH band at 3640 cm⁻¹ cannot be regenerated even by prolonged degassing, and the broad absorption at lower frequencies does not disappear.

Three species can be identified on the surface from the analysis of the spectra:

(a) chemisorbed molecules, via coordination bonds on Lewis acid sites, whose C=O stretching vibration is detected at 1620 cm⁻¹. The corresponding CH stretching vibrations are measured at 2870 and 2770 cm⁻¹ similar to that of gaseous formaldehyde (22).

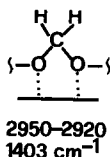


(b) formate ions, identified through their bands at 1555, 1375, and 1345 cm⁻¹, which do not disappear even by prolonged degassing. Their CH stretching band is superimposed on the asymmetric stretching of CH₂O adsorbed molecules in the spectrum of Fig. 2b, but resists evacuation (Fig. 2c).

(c) species responsible for the bands at 2950-2920 and 1403 cm⁻¹, which can be

tentatively identified as polymers of formaldehyde on the surface (23).

Species corresponding to (a) and (b) have also been detected by adsorption of acetaldehyde on $\alpha\text{-Fe}_2\text{O}_3$ (7). In the case of acetaldehyde, however, one can observe a strong carbonyl band at 1715 cm^{-1} assigned to physisorbed molecules, while in the case of formaldehyde only a weak absorption at 1710 cm^{-1} can be assigned to the corresponding monomeric carbonylic species. This experimental result, together with the fact that free OH's are not regenerated on the surface even after prolonged degassing, could be interpreted as evidence that only very few monomeric physisorbed species can exist on $\alpha\text{-Fe}_2\text{O}_3$, the predominant physisorbed species being molecules where the carbonyl group is no longer present. This could be a further confirmation that the (c) species identified above correspond to linear or cyclic polymeric compounds, whose stability on the surface even upon prolonged degassing is determined by multiple hydrogen bondings with surface OH's.



A similar assignment has already been proposed by Young and Sheppard (24) for bands of noncarbonylic compounds measured after adsorption of some aliphatic aldehydes on Cab-O-Sil.

C. Methanol and Methanol- d_4

The comparison of the spectrum of pure $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 3a) with that of the same oxide contacted with CH_3OH vapor and thoroughly degassed (Fig. 3c) indicates the complete methoxylation of the surface: methoxy groups are indeed unequivocally identified through their C-H stretching bands (2920 and 2815 cm^{-1}) and C-H bending bands (1460 and 1440 cm^{-1}), as has been done by other authors on different oxides (18, 25-28). Similar alkoxy groups have

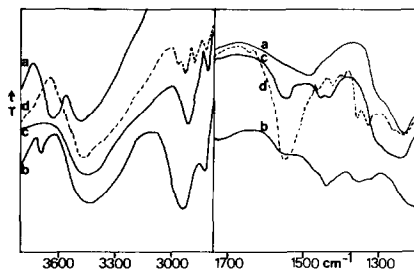


FIG. 3. Infrared spectra of CH_3OH adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation; (b) in contact with CH_3OH vapor (0.5 Torr; 5 min); (c) after degassing for 7 h at T_b ; (d) after consecutive degassing for 2 h at 150°C .

been detected after contact of hematite with ethanol vapor (7, 29). The bands at 2200 and 2060 cm^{-1} present on $\alpha\text{-Fe}_2\text{O}_3$ contacted with CD_3OD vapor under similar conditions (Fig. 4c) can by analogy be assigned to C-D stretchings of deuteromethoxy surface groups.

The mechanism of production of these species on oxide surfaces has been the object of a number of studies: in our case this mechanism must involve the reaction with the free surface hydroxyls responsible for the maximum at 3640 cm^{-1} , which irreversibly disappears. As we do not detect any new maxima in the $\nu(\text{OH})$ region, a mechanism involving the opening of oxygen Fe-O-Fe bridges on the surface is to be

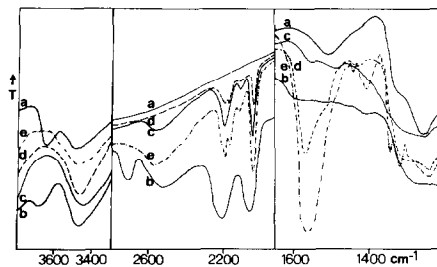
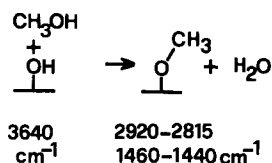


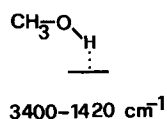
FIG. 4. Infrared of CD_3OD adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation; (b) in contact with CD_3OD vapor (0.5 Torr; 5 min); (c) after degassing for 7 h at T_b ; (d) after consecutive degassing for 2 h at 150°C ; (e) sample treated as in (a) and contacted with CD_3OD vapor at 250°C (0.5 Torr; 5 min) and then degassed for 1 h at T_b .

excluded and a condensation mechanism can be proposed:



The band at 1560 cm⁻¹ present in both these spectra (Figs. 3c and 4c) is probably to be assigned to $\nu(\text{C}=\text{O})$ in an oxidation product chemisorbed on the surface.

The spectra of both CH₃OH and CD₃OD contacted with $\alpha\text{Fe}_2\text{O}_3$ (Figs. 3b and 4b) allow us to identify the presence of molecules adsorbed without reaction in these conditions, via a hydrogen bonding where methanol acts as proton donor. This species can be identified through the absorptions near 3400 cm⁻¹ (O-H \cdots O stretching superimposed on the 3460-cm⁻¹ band of the adsorbent) and at 1420 cm⁻¹ (O-H \cdots O bending superimposed on the C-H bending bands).



Free methanol molecules seem also to exist on the surface in these conditions, identified through their bands at 3690 and 1350 cm⁻¹ (cf. vapor-phase methanol OH stretching, 3687 cm⁻¹, and OH bending, 1346 cm⁻¹ (30)). The corresponding $\nu(\text{OD})$ bands for deuterated methanol are more evident at 2540 and 2720 cm⁻¹, the OD bendings being outside the transmission region of our sample.

The presence of absorptions at 3690 and near 1400 cm⁻¹ also in the spectra of adsorbed methanol-*d*₄, as well as the persistence of a band at 2560 cm⁻¹ after degassing (Fig. 4c), can be explained on the basis of isotopic exchange between methanol-*d*₄ deuterioxylys and heavy-water molecules formed by condensation with surface OH's.

The behavior of hematite in the physi-sorption of alcohols seems therefore to be

similar to that of alumina, being namely an acceptor of hydrogen bonding (31), and different from that of silica which acts as a donor (31, 32).

If the methoxylated surface is heated at 150°C in He, in order to preserve the oxidation state of the surface, new species appear, absorbing at 2880, 1555, 1370, and 1340 cm⁻¹ (Fig. 4d). These bands correspond to those which appear after adsorption of formic acid on the same surface (see Section A) and can be assigned to surface formate ions obtained by oxidation of methoxy groups. The same reaction has already been detected on Al₂O₃ (25), MgO (33), Cr₂O₃ (27), and SnO₂ (18) surfaces. It is also known that ethanol adsorbed on hematite gives, in the same conditions, acetate ions (7). The same results are obtained by heating a *d*₃-methoxylated surface, where formate-*d* ions are characterized by bands at 2180, 1565, and 1320 cm⁻¹ (Fig. 4d); the greater difference between asymmetric and symmetric stretchings of formate-*d* ions can be foreseen on the basis of isotopic effects (25). The bands of methoxy and deuteromethoxy groups, however, do not disappear completely even after treatment at 250°C where desorption of formate ions begins. No bands due to formaldehyde-like structures can be detected.

If the adsorption of methanol is carried out at 250°C formate ions and methoxy groups are formed as on ZnO (34) and Al₂O₃ (35).

When the $\alpha\text{-Fe}_2\text{O}_3$ surface is contacted with CD₃OD vapor at 250°C, however, two new bands appear (Fig. 4e) at 1340 and 1410 cm⁻¹ together with those assigned to methoxy-*d*₃ groups (2200 and 2055 cm⁻¹) and formate-*d* ions (2180, 1560, and 1320 cm⁻¹) mentioned in the previous discussion. The 1340-cm⁻¹ band can be assigned to a vibrational mode of carbonate ions formed on the surface (9). It is known, in fact, that above 200°C the contact of methanol with Fe₂O₃ gives only carbon oxides and hydrogen (8).

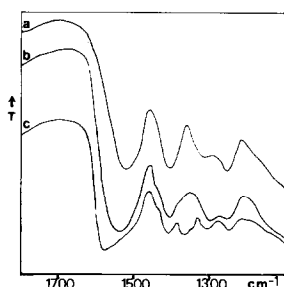


FIG. 5. Infrared spectra of CH_3OH adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 250°C under evacuation; (b) after contact with CH_3OH vapor (0.5 Torr; 5 min) and degassing for 2 h at 150°C ; (c) after consecutive degassing for 15 min at 250°C .

This band is probably present also when hematite is heated during or after contact with CH_3OH , CH_2O , and HCOOH , but it is superimposed on the symmetric stretching of formate ions. Also the other band corresponding to this carbonate structure (identified at 1560 cm^{-1} after adsorption of CO_2 (9)) is superimposed on the asymmetric stretching of formate ions. The presence on the surface of this carbonate structure has already been noted above when discussing the faster intensity decrease of the $\nu(\text{C-H})$ and $\delta(\text{C-H})$ bands (2880 and 1370 cm^{-1}) with respect to the COO^- stretchings (1555 and 1340 cm^{-1}) of formate ions if the sample is heated in the presence of adsorbed formic acid.

The band at 1410 cm^{-1} is at the same frequency at which we detected a band in samples of hematite treated at high temperature *in vacuo*, previously discussed and assigned tentatively to a vibrational or electronic transition produced by depletion of structural oxygen atoms from the surface (7). As in our conditions the oxidation of adsorbates would occur with a reduction of the surface and with depletion of oxygen atoms, as already observed by Nováková *et al.* (8); the presence of this band even under these conditions can be a confirmation of its previous assignment. The same band is also present as mentioned above after heating at 250°C the sample previously

contacted with HCOOH vapor, probably due to the oxidation of formate ions to carbonate ions. It cannot be well distinguished after adsorption and oxidation of methanol and formaldehyde because it is superimposed on C-H deformation vibrations.

The results discussed so far were all obtained on oxidized $\alpha\text{-Fe}_2\text{O}_3$ surfaces. The adsorption of the same adsorbates on a surface treated *in vacuo* at 250°C for 1 h (Fig. 5a), where our previous studies have identified a depletion of oxygen, does not show significant changes. In the case of methanol, however, the oxidation reaction (with formation of the surface formates identified by their bands at 1560 , 1370 , and 1340 cm^{-1}) seems to be activated only at higher temperature (Fig. 5).

CONCLUSIONS

This work provides spectroscopic evidence on the following different surface properties of hematite:

- (a) oxidizing power, even at ir-beam temperature, on adsorbed organic molecules;
- (b) reactivity involving basic sites, such as O^{2-} or OH^- , e.g., with HCOOH molecules;
- (c) reactivity of surface free hydroxyls (3640 cm^{-1}) with alcohols to give alkoxy groups;
- (d) proton acceptor ability in hydrogen bonding of hydroxylated species (alcohols and carboxylic acids).

The apparent lack of interaction of the OH's connected with the 3460-cm^{-1} absorption with the adsorbates used in this work is now under study.

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