

Infrared Study of the Surface Reactivity of Hematite

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Infrared spectra of α -Fe₂O₃ powders (obtained by thermal decomposition of crystalline goethite α -FeOOH) and of α -Fe₂O₃ with adsorbed electron-donor organic molecules (pyridine, acetonitrile, acetamide, acetic acid, acetic anhydride, acetyl chloride, acetaldehyde and ethyl alcohol) were measured in a study of surface structure and reactivity. The experimental results give evidence that organic molecules put into contact with α -Fe₂O₃ activated in air or oxygen can generally be both physisorbed and chemisorbed on the surface. However, several molecules can also undergo chemical transformations by reaction with surface OH groups or by oxidation. Two different kinds of oxidizing sites are shown to exist on the activated surface, the first corresponding to structural oxygen atoms and the second to molecular oxygen chemisorbed on Lewis acid sites.

INTRODUCTION

The nature of active sites on α -Fe₂O₃ surfaces has been extensively investigated by various techniques (infrared spectroscopy (1-6), calorimetric measurements (7, 8), adsorption isotherms (9), dielectric measurements (10)). The existence of both hydroxyl groups and acidic Lewis sites on the surface is now well established. However, it has been observed (4) that the relative intensities of the infrared bands assigned to the OH stretching vibrations of surface hydroxyl groups are dependent on the composition of the ferrigel from which hematite is prepared by thermal activation. Infrared studies showed also that pretreatment conditions (11, 12) and interface reactions (13, 14) with external molecules can produce modifications in the surface structure of this oxide, such as partial reduction or variation of the concentration of charge carriers.

We carried out experiments on α -Fe₂O₃ obtained by thermal decomposition of goethite α -FeOOH, which undergoes a topotactic transformation (15), in order to obtain samples as structurally and morphologically well defined as possible.

Some simple C₂-chain organic molecules containing electron-donor atoms were cho-

sen as adsorbates on the basis of their ability to provide identification and characterization of the activity of the surface.

EXPERIMENTAL

Samples of hematite α -Fe₂O₃ were prepared by thermal decomposition, at 250°C in air, of self-supporting disks of pure crystalline α -FeOOH prepared by classical methods (16). The disks were obtained by compressing the α -FeOOH powder at 3 tons cm⁻². The decomposition was carried out using an external furnace on the infrared cell itself, which had a form (Pyrex glass; NaCl windows) very similar to the model described by Peri and Hannan (17).

X-Rays powder diffraction analysis confirmed that samples prepared under these conditions are pure α -Fe₂O₃; the BET surface area was measured to be 45 m² g⁻¹ using nitrogen adsorption.

Discs of between 30 and 50 mg cm⁻² were used in order to give adequate transmission over the frequency range from 4000 to 1200 cm⁻¹.

Reagent-grade organic products from Carlo Erba (Milan, Italy) were used as adsorbates, after distillation, dehydration, and degassing.

Spectra were normally recorded at beam temperature (b. t.) with a Perkin-Elmer

model 521 infrared spectrometer, but some of them were repeated at room temperature (r. t.) with a Digilab FTS-4 Fourier transform infrared interferometer.

RESULTS AND DISCUSSION

The spectrum of α -Fe₂O₃ discs between 4000 and 1800 cm⁻¹ only shows absorptions characteristic of OH stretching vibrations. These bands have been previously discussed (1, 4, 6) and assigned to both surface hydroxyls and adsorbed molecular water.

The particular activation conditions modify the infrared spectrum between 1800 and 1100 cm⁻¹ (Fig. 1) (this latter being the frequency where our samples show practical absorption blackout) as previously observed by Blyholder and Richardson (18) and by Griffiths *et al.* (3). Several bands occur in this region which are not present in the infrared spectrum of goethite before decomposition, and are therefore characteristic of α -Fe₂O₃ in different ways.

Both the activation of the 1410 cm⁻¹ band and the modifications of the higher-frequency band, which regularly grows in intensity and shifts from 1490 cm⁻¹ for the sample activated in air to 1520 cm⁻¹ for the fully degassed sample, can be assigned to a vibrational or electronic transition produced by a depletion of structural oxygen atoms from the surface, which can modify

both the oxidation and coordination conditions of surface iron atoms. Oxygen loss of α -Fe₂O₃ in analogous conditions has been previously observed (12). This deoxidation gives a surface-reduced phase containing Fe²⁺ ions, possibly magnetite, responsible for a progressive loss of transmission with increasing activation. By prolonged degassing at higher temperatures the sample can completely lose its transmission.

The reduction/enhancement of the lower-frequency absorption (1340–1320 cm⁻¹) can be reversibly obtained by adsorption/desorption of oxygen. Chemisorbed molecular oxygen could exist on the surface of α -Fe₂O₃ activated in dry air or oxygen and act as a second type of oxidation site. The existence of two oxidation sites on the α -Fe₂O₃ surface has been proposed recently by Kung *et al.* (19) on the basis of gas-chromatographic studies of the reactivity of the surface.

Adsorption of Acetonitrile and Acetamide

Spectra of CH₃CN on α -Fe₂O₃ confirm the possibility of both physisorption and chemisorption of bases on surface sites at beam temperature (Fig. 2). Interaction with electron acceptors causes an increase of the C≡N stretching frequency of acetonitrile with respect to its value (2254 cm⁻¹) in the liquid phase (20). The band at 2252 cm⁻¹ in Fig. 3a, whose frequency very nearly corresponds to that in the liquid phase and whose intensity quickly decreases with progressive degassing (Figs. 2b, c) can be assigned to physisorbed molecules. The band at 2283 cm⁻¹, whose frequency is much different from that of liquid CH₃CN and which resists degassing much better at beam temperature, corresponds to chemisorbed molecules. The component at a still higher frequency (2310 cm⁻¹) is due to Fermi resonance of the C≡N stretching vibration with the $\nu_3 + \nu_4$ combination vibration in chemisorbed molecules (21).

The frequency of the C≡N stretching vibration (2283 cm⁻¹) for acetonitrile chemisorbed on α -Fe₂O₃ corresponds quite

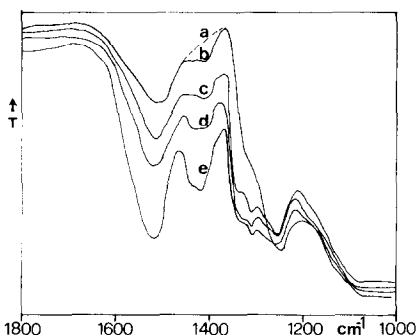


FIG. 1. Infrared spectra of α -Fe₂O₃ pressed disk (a) activated 1 h at 400°C in air and cooled under evacuation; (b–e) consecutive degassing at 150°C for: (b) 10 min, (c) 1 h, (d) 3 h, (e) 6 h.

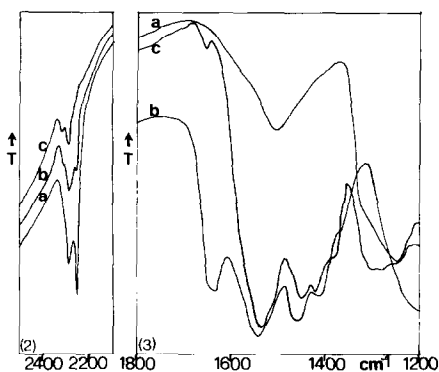


FIG. 2. Infrared spectra (2500–2100 cm^{-1}) of CH_3CN adsorbed on $\alpha\text{-Fe}_2\text{O}_3$ (a) after contact with CH_3CN vapor at b. t. (3 Torr, 10 min) and evacuation; (b, c) consecutive degassing at b. t. for: (b) 10 min, (c) 30 min.

FIG. 3. Infrared spectra (1800–1200 cm^{-1}) of CH_3CN 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) after contact with CH_3CN vapor at b. t. (3 Torr, 10 min) and evacuation, (c) after degassing for 30 min at 150°C.

well to that measured by Lavalley and Gain (22) for the same molecule chemisorbed on ZnO (2282 cm^{-1}). This result is in accordance with the same increase in frequency of the 1583 cm^{-1} band of chemisorbed pyridine on both these oxides ($\Delta\nu = 28 \text{ cm}^{-1}$) (6, 23), which indicates medium electron-acceptor ability of their nonprotonic active centers, between strong Lewis acidic surfaces like $\gamma\text{-Al}_2\text{O}_3$ ($\Delta\nu = 40 \text{ cm}^{-1}$) and silica-alumina ($\Delta\nu = 37 \text{ cm}^{-1}$), and weak acids like silica ($\Delta\nu = 12\text{--}16 \text{ cm}^{-1}$).

At frequencies below 2000 cm^{-1} several bands can be observed (Fig. 3) which cannot be assigned to physisorbed acetonitrile, but only to new species formed by its chemical transformation on the surface. After activation of the sample in air, acetonitrile was admitted into the cell at beam temperature and then eliminated by degassing. The spectrum in Fig. 3b was obtained, where the following adsorption maxima can be measured: 1640, 1560, 1470, 1450, and 1380 cm^{-1} . The band at 1410 cm^{-1} may be the same as that previously discussed and assigned to a chemical modification of the surface, connected with loss of oxygen.

By adsorption of acetamide CH_3CONH_2 a very similar spectrum is obtained (Fig. 4). Also on degassing at 150°C the spectra of both acetonitrile and acetamide undergo the same changes, the bands at 1640, 1470, and 1380 cm^{-1} strongly reducing their intensity. These bands are characteristic of chemisorbed acetamide molecules, the hydration $\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CONH}_2$ involving surface hydroxyls.

The pair of bands at 1560 and 1450 cm^{-1} which resist degassing at 150°C can be assigned to an ionic species $(\text{CH}_3\text{CONH})^-$ formed by reaction of both acetonitrile and acetamide molecules with surface OH^- groups, which was also identified by Lavalley and Gain on the surface of ZnO (22) and by Krietenbrink and Knözinger (24) on $\delta\text{-Al}_2\text{O}_3$.

Reactivity of $\alpha\text{-Fe}_2\text{O}_3$ with both acetonitrile and acetamide at temperatures higher than beam temperature was also studied. When the $\alpha\text{-Fe}_2\text{O}_3$ disc degassed at 250°C (Fig. 5a) was put into contact with acetonitrile at the same temperature, and then degassed at beam temperature, the spectrum shown in Fig. 5b was observed. The band at 2193 cm^{-1} , which disappears upon prolonged degassing at beam temperature (Fig. 5c), is completely new and can only result from a chemical transformation of

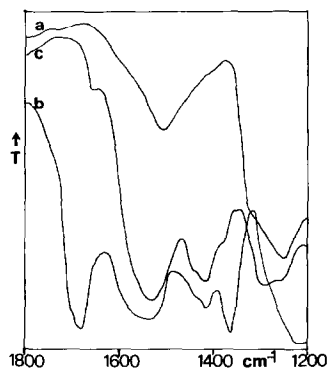


FIG. 4. Infrared spectra of CH_3CONH_2 adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) after contact with CH_3CONH_2 saturated vapor at b. t. (20 min) and evacuation, (c) after degassing for 30 min at 150°C.

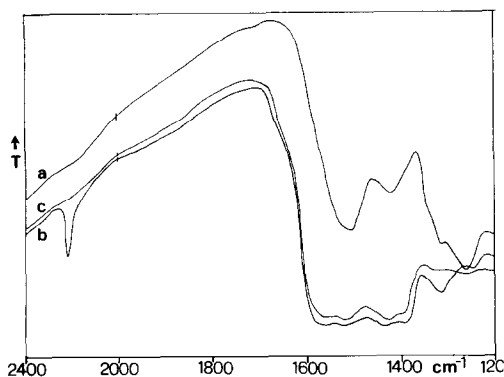


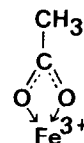
FIG. 5. Infrared spectra of CH_3CN adsorbed at 250°C on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated at 250°C under vacuum (3 h), (b) after contact with CH_3CN vapor at 250°C (3 Torr, 10 min) and cooling under evacuation, (c) after 1 h degassing at b. t.

the CH_3CN molecule. An analogous band has been observed by Krietenbrink and Knözinger (24) on $\delta\text{-Al}_2\text{O}_3$ and by Lavalley and Gain (22) on ZnO , and assigned in both cases to polymerization products. The lability of the species responsible for this band in our case seems, however, to argue against the same assignment. Bands in the same position have been also observed for CO (13) and for a species considered as NO^+ (3) adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. A complete oxidation of a part of the chemisorbed CH_3CN might then have occurred on the surface at high temperature.

Once again very strong absorptions near 1550 and 1440 cm^{-1} also appear in the spectrum (Fig. 5b), practically superimposed on the bands of the initial sample (Fig. 5a), which are not modified by subsequent degassing at 150°C (Fig. 5c). Similar absorptions (but not the band at 2193 cm^{-1} previously discussed) can be observed when the sample is put into contact with acetamide vapor in the same conditions as those for acetonitrile. In both cases a stable species has formed on the surface, which is characterized by a spectrum very similar to that obtained by adsorption of acetic acid, as described below, and can be identified as chemisorbed CH_3COO^- ions formed via a hydrolysis reaction (24).

Adsorption of Acetic Acid, Acetic Anhydride, and Acetyl Chloride

When acetic acid vapor is put into contact with $\alpha\text{-Fe}_2\text{O}_3$ at beam temperature (Fig. 6), chemisorbed species are obtained which can be identified as acetate ions through the characteristic bands centered near 1540 and 1440 cm^{-1} , which appear immediately with very strong intensity (Fig. 6b). They correspond to the antisymmetrical and symmetrical stretching vibrations of the COO^- structure, as was first shown by Lecomte *et al.* (25) on a large series of metallic acetates. Bands nearly in the same positions were observed by Paul *et al.* (26) in the spectra of $\text{Fe}(\text{CH}_3\text{CO}_2)_3$ and assigned to a chelate bidentate configuration on the basis of the frequency difference between these two bands. We can therefore propose a structure of the same type



for the acetate ions chemisorbed on the surface of $\alpha\text{-Fe}_2\text{O}_3$. A comparison of Figs. 5 and 6 clearly indicates that acetate ions are formed on the surface of $\alpha\text{-Fe}_2\text{O}_3$ also by

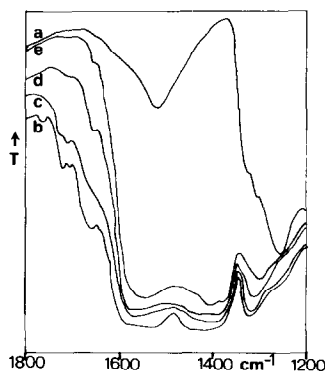
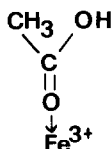


FIG. 6. Infrared spectra of CH_3COOH adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) after contact with CH_3COOH vapor at b. t. (3 Torr, 10 min) and evacuation, (c-e) consecutive degassing for: (c) 3 h at b. t., (d) 30 min at 150°C , (e) 60 min at 150°C .

heating with both CH_3CN and CH_3CONH_2 .

Molecules of acetic acid can also be both physisorbed and coordinatively liganded to Lewis acid sites at beam temperature on the surface of $\alpha\text{-Fe}_2\text{O}_3$, as can be seen by studying the region of $\text{C}=\text{O}$ stretching vibrations. The spectrum in Fig. 6b shows the presence of three bands in this region. A weak band at 1750 cm^{-1} disappears quite easily by degassing at beam temperature and may probably be assigned to physisorbed monomeric molecules (the $\text{C}=\text{O}$ stretching vibration for monomeric acetic acid was measured (27) at 1770 cm^{-1}). Of the two bands which are more resistant to degassing, one (1715 cm^{-1}) reduces its intensity first by prolonged degassing (Fig. 6c), while the other (1660 cm^{-1}) is more slowly affected. The two bands probably correspond to acetic acid molecules adsorbed in different conditions. The lower-frequency one, which can still be observed after brief degassing of the sample at 150°C (Fig. 6d), may correspond to the $\nu(\text{C}=\text{O})$ stretching vibration of molecules coordinatively bonded to Fe^{3+} ions,



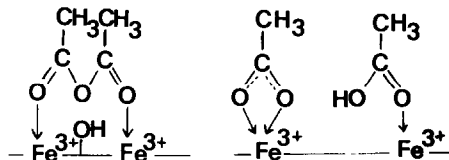
the acid hydrogen possibly also forming a hydrogen bond with surface oxygens. For the third band, which seems to be split in many of our spectra, we suggest an assignment to physisorbed cyclic dimers, as it is well established (28) that acetic acid exists predominantly as the dimer in the vapor phase at temperatures below 150°C . This assignment would be consistent with both the $\text{C}=\text{O}$ stretching frequency value (1713 cm^{-1}), very near to that of the dimeric acetic acid in vapor phase (1725 cm^{-1}) (27), and desorption characteristics.

In any case, prolonged degassing at 150°C (Fig. 6e) progressively eliminates all molecular acetic acid species bound to the surface and only bands due to coordinate

acetate ions are observed after several hours.

Acetic anhydride partly physisorbs as such on the $\alpha\text{-Fe}_2\text{O}_3$ surface and is easily eliminated by degassing. Its two characteristic $\text{C}=\text{O}$ stretching bands can be observed at 1818 and 1745 cm^{-1} (Fig. 7b), but disappear on prolonged degassing (Figs. 7c, d), before the other characteristic absorptions of adsorbed acetic acid (1715 cm^{-1} and 1660), leaving finally only the strong absorptions characteristic of coordinated acetate ions formed by chemical reaction of the anhydride with surface groups.

The fact that acetic anhydride can be detected as such only in physisorbed form could indicate that chemisorbed molecules cannot subsist on the surface at beam temperature, but are immediately transformed into coordinated acetate ions and chemisorbed acetic acid, probably via a mechanism involving one of the surface hydroxyls.



Analogous results are obtained for acetyl chloride CH_3COCl adsorption, where

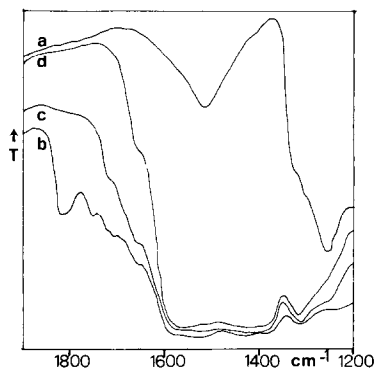


FIG. 7. Infrared spectra of $(\text{CH}_3\text{CO})_2\text{O}$ adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) after contact with $(\text{CH}_3\text{CO})_2\text{O}$ vapor at b. t. (3 Torr, 15 min), (c-d) consecutive degassing for: (c) 1 h at b. t., (d) 2 h at 150°C .

prominent bands of both adsorbed acetic acid (1715 and 1660 cm^{-1}) and coordinated acetate ions (1550 and 1440 cm^{-1}) can also be observed in the spectra (Fig. 8). No attempt was made here to identify the HCl molecules which must have been formed in the course of the surface reaction. In this case, however, the molecules can chemisorb without reaction, and the $\text{C}=\text{O}$ stretching vibrations present interesting features.

In the presence of CH_3COCl vapor a band can be measured at 1900 cm^{-1} (Fig. 8b) which is easily eliminated by degassing (Fig. 8c). This band, at higher frequency than the $\text{C}=\text{O}$ stretching vibration of the free molecule in vapor phase (1822 cm^{-1}) (29), is probably due to interactions of the CH_3COCl molecule with surface Lewis sites through the chlorine atom. An interaction which involves the chlorine atom as an electron donor can indeed reduce polarization of the $\text{C}=\text{O}$ bond and therefore enhance its stretching frequency. Thus, very strong electron acceptors like AlCl_3 were shown (29) to be able also to interact dissociatively with acetyl chloride, giving acetylium ions $(\text{CH}_3\text{CO})^+$, isoelectronic with acetonitrile CH_3CN , whose carbonylic stretching frequency is as high as 2300

cm^{-1} . On the basis of the different possibilities of interaction between acetyl chloride (two electron-donor atoms) and the $\alpha\text{-Fe}_2\text{O}_3$ surface (two electron-acceptor sites) it is possible to propose an interpretation of the other $\text{C}=\text{O}$ bands centered at 1822 , 1800 , and 1770 cm^{-1} (Figs. 8d, e), whose relative intensities seem to change during degassing. The band at 1822 cm^{-1} , whose value seems unaffected compared with the vapor phase, can be assigned to a species involving hydrogen bonding interactions $\text{C}=\text{O} \cdots \text{H}-\text{O}$ with surface hydroxyls; possibly secondary interactions of the type $\text{Cl} \cdots \text{H}-\text{O}$ counteract the frequency lowering of the $\text{C}=\text{O}$ stretching which would correspond to the first hydrogen bonding. Such a double hydrogen bonding of the CH_3COCl molecule to the surface could explain the relative difficulty in eliminating it by degassing. The two bands at 1800 and 1770 cm^{-1} might be due to weak coordination of undissociated molecules to iron ions through the $\text{C}=\text{O}$ group, involving the two orientations of the molecule with respect to the surface which are possible because of the sp^2 hybridization of the interacting oxygen atom,

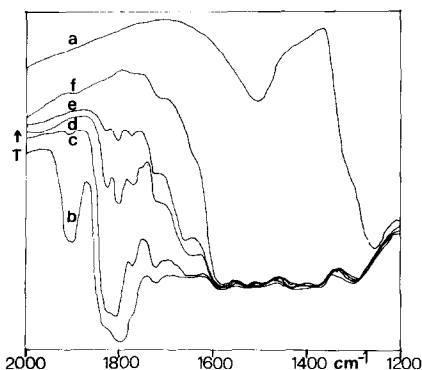
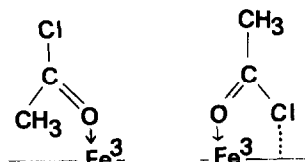


FIG. 8. Infrared spectra of CH_3COCl adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) in contact with CH_3COCl vapor at b. t. (3 Torr, 15 min), (c–f) consecutive degassing for: (c) 10 min at b. t., (d) 20 min at b. t., (e) 1 h at b. t., (f) 10 min at 150°C .



where in form (II) a secondary interaction enhancing the $\text{C}=\text{O}$ stretching frequency is sterically possible. Further experimental evidence is needed, however, in order to support this hypothesis, as the formation of different molecular species on the surface could also be considered.

Adsorption of Acetaldehyde and Ethyl Alcohol

Acetaldehyde and ethyl alcohol have been investigated in order to obtain direct confirmation of the oxidizing power of $\alpha\text{-Fe}_2\text{O}_3$ on organic molecules at room temperature. As on dispersion spectrometers

the sample temperature is definitely higher than room temperature, a Digilab Fourier transform infrared interferometer was used to perform these experiments, where the sample temperature is little affected by the beam.

The results are shown in Figs. 9 and 10. Absorption maxima in the C=O stretching region show that acetaldehyde (Fig. 9) can be both physically (1715 cm^{-1}) and chemically (1642 cm^{-1}) adsorbed on $\alpha\text{-Fe}_2\text{O}_3$ at room temperature, its C=O stretching vibration being at 1730 cm^{-1} in the gas phase (30). However, other bands in the same region indicate that acetic acid is also present in both physisorbed (1755 cm^{-1}) and chemisorbed (1670 cm^{-1}) forms; its third band previously discussed (1715 cm^{-1}) is probably superimposed on the strong absorption due to physisorbed aldehyde. Degassing at room temperature only eliminates the physisorbed molecules (Figs. 9b) of both species. As in previous cases, acetic acid forms surface acetates, identified through their strong bands at 1550 and 1440 cm^{-1} , which cannot be eliminated by degassing at 150°C : at this temperature some acetic acid, but no longer chemisorbed acetaldehyde, can still be detected. The bands at 1380 and 1340 cm^{-1} which are eliminated by degassing together with the C=O

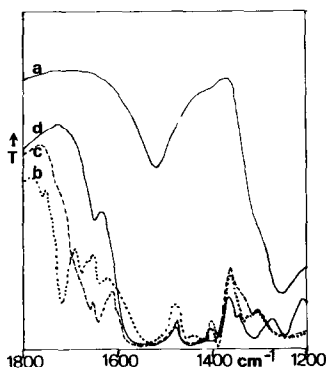


FIG. 9. Infrared spectra of CH_3CHO adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) after contact with CH_3CHO vapor at r. t. (0.5 Torr, 10 min) and evacuation, (c, d) consecutive degassing for: (c) 3 h at r. t., (d) 2 h at 150°C .

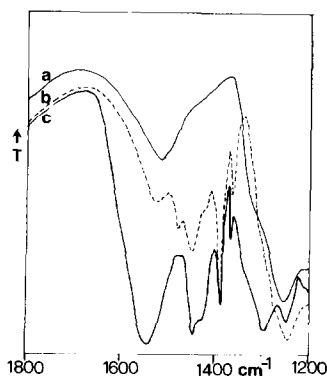


FIG. 10. Infrared spectra of $\text{CH}_3\text{CH}_2\text{OH}$ adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. (a) $\alpha\text{-Fe}_2\text{O}_3$ disk activated 1 h at 400°C in air and cooled under evacuation, (b) after contact with $\text{CH}_3\text{CH}_2\text{OH}$ vapor at r. t. (0.5 Torr, 10 min) and degassing up to 15 h at r. t., (c) after degassing 3 h at 150°C .

stretching bands are also due to internal vibrations of chemisorbed molecules.

Ethyl alcohol is strongly chemisorbed on $\alpha\text{-Fe}_2\text{O}_3$ at room temperature (Fig. 10), as thorough degassing at room temperature does not appreciably affect its CH deformation bands in the region $1300\text{--}1500\text{ cm}^{-1}$ (Fig. 10b), but no surface reaction seems to occur. Heating at 150°C (Fig. 10c) activates its direct oxidation into chemisorbed acetate ions, identified through their strong symmetric and antisymmetric stretching vibrations (Fig. 10c). No intermediate chemisorbed carbonyl compound could be detected.

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