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Fourier Transform–Infrared Study of the Adsorption of Unsaturated and Aromatic Hydrocarbons on the Surface of α-Fe_2O_3

I. Ethylene

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Adsorption of ethylene on α-Fe_2O_3 in the temperature range between 300 and 673 K has been studied. At room temperature π-bonded species have been detected, and their adsorption bonding is discussed on the basis of the spectroscopic features. Combustion of these species at room temperature as well as partial oxidation to formate ions at 523 K have also been observed.

INTRODUCTION

Iron(III) oxide is the main component of catalysts used for selective dehydrogenation of hydrocarbons such as butenes (*1*) and ethylbenzene (*1, 2*). However, pure α-Fe_2O_3 is active for non-selective oxidations of hydrocarbons, e.g., benzene (*3*) and propylene (*4*), mainly giving combustion products. In all these catalytic reactions an interaction of π-systems with the surface can *a priori* be reasonably proposed as the first step.

Various surface species have been observed by vibrational studies of olefin adsorption on heterogeneous catalysts. Ethylene was shown to form several different σ-bonded species on metals (*5, 6*) and on alumina (*7*). π-Bonded species are well known on cation-exchanged zeolites (*8, 9*), but only a few cases have been reported for room temperature adsorption on metals (*10*) and oxides (*11*). The one previous ir work on olefins adsorbed on ferric oxide, as on other transition metal oxides (*12*), has revealed only oxidation products on the surface.

We have carried out a Fourier transform–infrared (FT–ir) study of the adsorption of π-bond-containing hydrocarbons on haematite, in order to obtain more data on mechanisms involved in dehydrogenations on iron oxide catalysts.

EXPERIMENTAL

The samples of α-Fe_2O_3 (transmittance 10% at 4000 cm^{-1}; 24–40% at 1700 cm^{-1}; BET surface area 40 $m^2\ g^{-1}$) were obtained by decomposition of pellets (3×10^4 N cm^{-2}; 30–40 mg cm^{-2}) *of* α-FeOOH. Sample pretreatment was the same as for "oxygen-rich" surfaces of Refs. (*13,14*). Ethylene was purchased from SIO (Milano, Italy) and used without further purification.

Infrared spectra (2 cm^{-1} resolution, 20–150 sec measurement time) were obtained using a Nicolet 6000 C Fourier transform spectrometer at the Stazione Sperimentale per i Combustibili (San Donato Milanese, Italy). Subtraction of the gas phase spectrum was performed by automatic transmission ratioing.

RESULTS

Figure 1 shows the spectra of an "oxygen-rich" α-Fe_2O_3 surface at successive times under contact with 6.66×10^3 N m^{-2} of ethylene in the region 2000–1100 cm^{-1}. After a very short contact (Fig. 1a) a new band centered at 1440 cm^{-1} appears; two more bands at 1620 and 1550 cm^{-1} become clearly evident after 1 h contact (Fig. 1c), when also the 1440-cm^{-1} band is more intense. The band at 1620 cm^{-1} is characterized by a progressive growth in intensity

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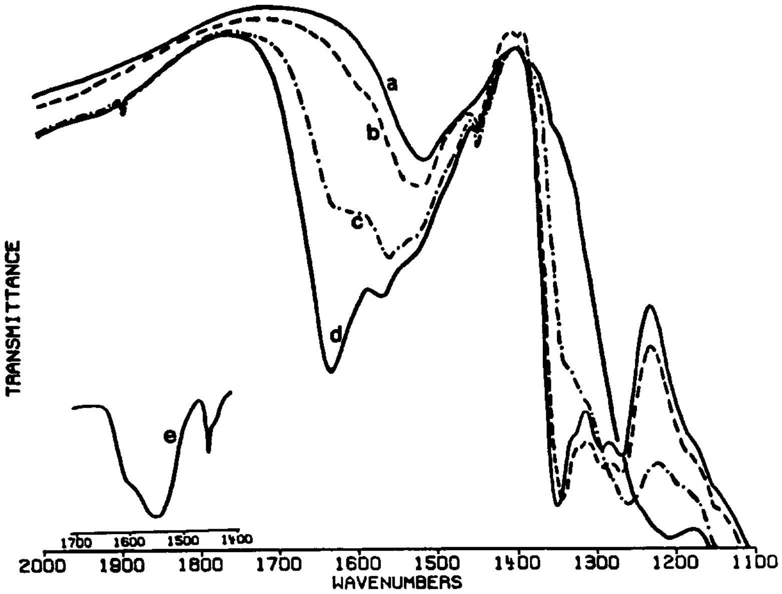

FIG. 1. Infrared spectra of ethylene adsorbed on α-Fe_2O_3 (2000–1100 cm^{-1}). (a) "Oxygen-rich" haematite disk; (b) after contact with ethylene gas 6.66×10^3 N m^{-2} at room temperature, 1 min; (c) 1 h; (d) 2 h; (e) ratio *b*/*a*.

(Fig. 1d). Simultaneous perturbation of the bands connected with surface oxygen (*13*) is detected in the region 1350–1100 cm^{-1}, as is observed when Lewis bases interact with surface cations (*13*, *14*). However, after short contact the higher frequency component appears to be unusually shifted toward lower frequencies (from 1346 to 1338 cm^{-1}).

Under the same conditions free OH's are not shifted at all by ethylene while two weak absorptions can be immediately observed at about 2980 and 2880 cm^{-1}. A broad absorption centered at about 3200 cm^{-1} progressively grows with time (Fig. 2).

The ratioed spectrum (Fig. 1e) shows that the rather broad band at 1550 cm^{-1} already exists after 1 min contact. Its intensity is lowered together with that of the 1440-cm^{-1} band, while the 1620-cm^{-1} absorption is enhanced.

Moreover, ratioed spectra more clearly show three other bands due to adsorbed ethylene at 3070, 1334 (responsible for the apparent shift of the band at 1346 cm^{-1} cited above), and 949 cm^{-1}.

On increasing the time of contact all bands at 3070, 2980, 1550, 1440, 1334, and 949 cm^{-1} are lowered in intensity, while broader bands at 3200 and 1620 cm^{-1} are progressively enhanced. This indicates that all the features cited above are connected with the same species which slowly transforms on the surface. This species is also the first one to leave the surface by degassing at room temperature. The band at 2880 cm^{-1}, for which no partner bands are clearly detected, should instead be connected with small amounts of another, more stable, species.

The strong bands at 3200 and 1620 cm^{-1} are probably connected with the formation of both water and surface carbonates by combustion of ethylene. This reaction was already observed on other surfaces where oxygen is available (*15*–*17*).

It must also be observed that ratioed spectra show some increasing of transmittance also in the region of free OH's, indi-

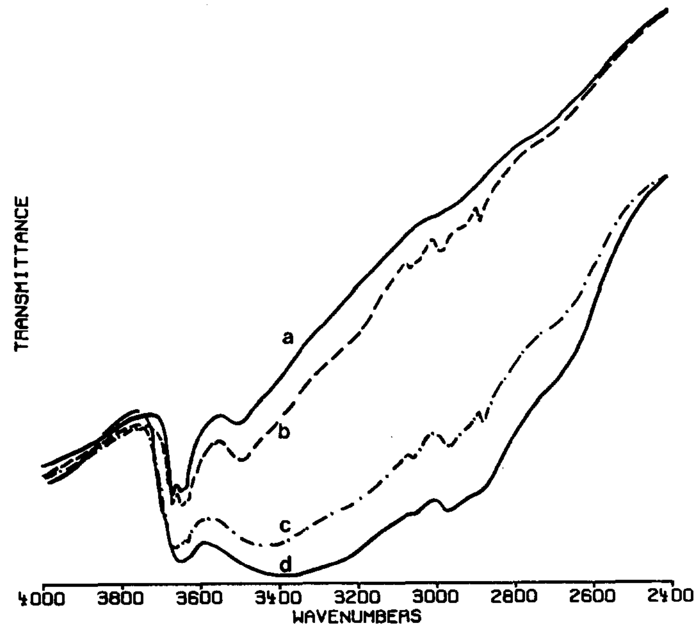

FIG. 2. Infrared spectra of ethylene adsorbed on α-Fe_2O_3 (3800–2600 cm^{-1}) (a–d) as Fig. 1.

cating that even if they are not perturbed by ethylene adsorption (being not shifted) some of them are probably involved in water formation.

At higher temperatures of contact no changes are observed until 523 K when the sectrum is substantially modified (Fig. 3b), showing two new sharp bands at 1573 (with

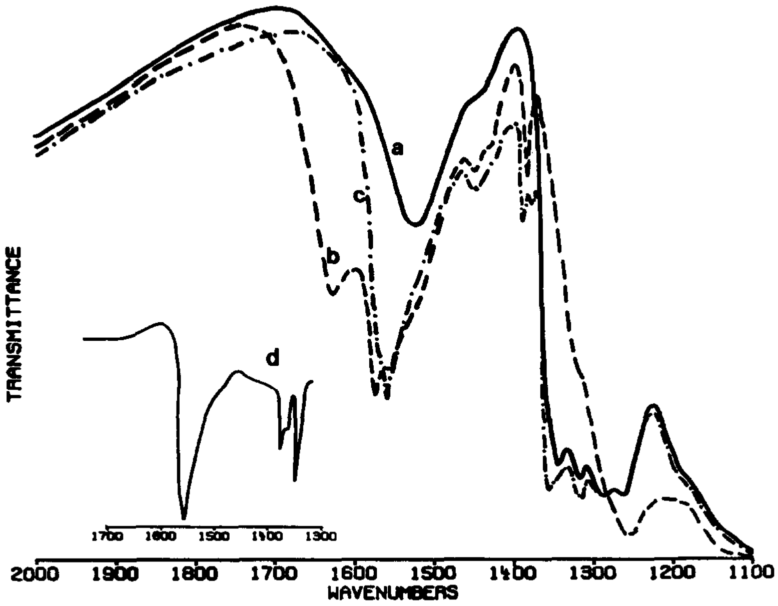

FIG. 3. Infrared spectra of ethylene adsorbed on α-Fe_2O_3. (a) "Oxygen-rich" haematite disk; (b) after contact with ethylene gas 6.66 × 10^3 N m^{-2}, 523 K, 20 min; (c) sample (b) degassed at 473 K for 20 min; (d) ratio c/a.

a shoulder at 1560 cm^{-1}) and at 1379 cm^{-1}. Two rather weak bands are also observed at 1450 and 1420 cm^{-1}, together with the 1620-cm^{-1} band already assigned to carbonates. In these conditions CO_2 is observed in the gas phase (2345 cm^{-1} PR band).

Degassing at room temperature causes the immediate disappearance of the bands at 1450 and 1420 cm^{-1}, and slowly reduces the 1620-cm^{-1} band, while by heating at 473 K (Fig. 3c) the band at 1560 cm^{-1} becomes predominant (the 1573 cm^{-1} one being now a shoulder) and the lower frequency band splits with the stronger maximum at 1382 cm^{-1}. The ratioed spectrum (Fig. 3d) shows that another maximum at 1355 cm^{-1} is superimposed on the bands in the region 1350–1250 cm^{-1}, reappearing by heat treating as is usual (*13, 14*), together with a band at higher frequencies (2891 cm^{-1}).

Three species seem to be formed by adsorption at 523 K, in addition to bidentate carbonates already cited. The first species (absorbing at 2891, 1573, 1379, and probably participating also in the 1355-cm^{-1} absorption) transforms into a more stable species (1560, 1382, and 1355 cm^{-1}). The third species, very labile, is characterized by bands at 1450 and 1420 cm^{-1}. All these bands disappear if the temperature is raised to 673 K, when CO_2 and H_2O are observed in the gas phase in great amounts.

DISCUSSION

(*a*) *Molecular Ethylene Adsorbed at Room Temperature*

Experimental results indicate that the main product of ethylene adsorption at room temperature on α-Fe_2O_3 is characterized by bands at 3070, 2980, 1550, 1440, 1334, and 949 cm^{-1}. The most relevant feature is the rather broad and intense band at 1550 cm^{-1}, which should be assigned to the ir-activated ν_2 (C=C stretching) vibration of ethylene (using the notation of Herzberg (*18*)) measured at 1623 cm^{-1} in the Raman spectrum of the gas (*18*). Infrared activation and lowering of this frequency, first observed in the ir spectrum of ethylene complexes such as Zeise's salt (*19*), should in our case be attributed to the formation of π-bonding where π-electrons of ethylene interact with surface metal centers inducing a dipole moment perpendicular to the ethylene plane and symmetry is lowered from V_h to C_{2v}. The bands at 1440, 1334, and 949 cm^{-1} are assigned to asymmetric and symmetric scissors and wagging (ν_{12}, ν_3, and ν_7) while the CH stretchings at 3070 and 2980 cm^{-1} are assigned to ν_1 and ν_9.

Following Chatt and Duncanson (*20*), π-bonding of ethylene with a transition metal is generally considered to be due to a double interaction, namely, a σ-interaction due to overlapping of the π-bonding orbital of ethylene with an empty orbital of the metal, superimposed by a π-back-donation due to overlapping of a full orbital (having a *d* character) of the transition metal to the empty π^* antibonding orbital of ethylene. The formation of both these interactions would reduce the C=C bond order, and, as a consequence, the ν_2 frequency.

It can be observed that, although π-bonding of ethylene has been considered to be the first step in its heterogeneously catalyzed hydrogenation (*21*), polymerization (*22*), and epoxidation (*23*), only in a few cases has such an interaction been found at room temperature (*10, 11*). On metals this species has been detected by EELS, but only at lower temperatures (*16, 17*), and it is stabilized by the presence of atomically adsorbed oxygen (*16, 17*). It may be also observed that stable ethylene complexes with Au, Ag, and Cu are only formed if the metal has the oxidation number +1.

Such observations support the conclusion, based on the strong lowering of ν_2 coupled with the moderate perturbations of the other frequencies, that in our case interaction takes place with a strongly oxidized metal center, where the previously cited σ-interaction is predominant.

Room temperature combustion without detectable intermediates of π-bonded ethylene of haematite parallels that detected on both Ag{110} (*16*) and Pt{111} (*17*) at 175–250 K if atomic oxygen is present. Evidence of the presence of adsorbed atomic oxygen on haematite has recently been reported (*24*).

The band detected at 2880 cm^{-1}, due to a more stable species formed by ethylene adsorption, can possibly be assigned to a di-σ-bonded species M–CH_2–CH_2–M by analogy with results obtained on several metals (*5*).

(*b*) *Products of the High Temperature Adsorption*

The spectra of adsorption products of ethylene heat-treated at 250°C are very similar to those of formate ions produced by formic acid adsorption of haematite (*25*). In fact, the bands at 2891, 1573, 1379, and 1355 cm^{-1}, characteristic of the predominant adsorbed species at 523 K, agree very well with those assigned to chemisorbed formate ions (*25*).

It is surprising that ethylene adsorption at higher temperatures produces partial oxidation species, while at room temperature combustion (albeit slow) is observed. However, this difference can be explained by considering the activity of two different oxygen species toward adsorbed ethylene.

The formate ions formed in this way, as already shown, are further oxidized to high temperature polydentate carbonates which show an exposed form (bands at 1560 and 1382 cm^{-1}) and an inner form (1560 and 1355 cm^{-1}) as already observed after adsorption of CO_2 (*26*) and formic acid (*25*).

The bands at 1450 and 1420 cm^{-1} would then be due to small amounts of monodentate carbonates (*26*).

CONCLUSIONS

The high performance of FT–ir spectroscopy has allowed a thorough study of the ir spectra of ethylene adsorbed on oxygen-rich α-Fe_2O_3 both at room and higher temperature, even for short times of contact. The main conclusions can be summarized:

(i) Formation of rather stable π-bonded species of ethylene with C_{2v} symmetry;

(ii) progressive combustion of such a π-bonded species at room temperature producing water and bidentate carbonates at the expense of surface oxygen;

(iii) partial oxidation at intermediate temperatures (523 K) to formates that further transform into polydentate carbonates;

(iv) small amounts of di-σ-bonded ethylene seem also to be present.

The possibility of formation of rather strong π-bonding between α-Fe_2O_3 surfaces and olefins has thus been confirmed and can be proposed as the first step of catalytic reactions.

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