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Fourier-transform Infrared Study of the Oxidation and Oxidative Dehydrogenation of *n*-Butenes on the Surface of $FeCrO_3$

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The interaction of the three linear butene isomers and of butadiene with the surface of a well characterized $FeCrO_3$ oxidative dehydrogenation catalyst has been investigated by IR spectroscopy. Both (*Z*)- and (*E*)-but-2-enes produce well characterized molecularly adsorbed species and rapidly form *sec*-butoxides and ethyl methyl ketone at room temperature. At higher temperatures, acetates are formed by oxidative C=C bond breaking. But-1-ene gives at least two different conformeric adsorbed species and exhibits, together with the same oxidation pathway, an allylic activation pathway, with the formation of butadiene and methyl vinyl ketone. Butadiene also forms two different adsorbed species, very weakly held, and slowly transforms into crotonaldehyde, which is further oxidized at higher temperatures. These results provide evidence for different oxidative and dehydrogenative pathways at the surface and are correlated with the known behaviour of $FeCrO_3$ as an oxidative dehydrogenation catalyst for linear butenes. Its very weak interaction with butadiene explains the high selectivities obtained in oxidative dehydrogenation over this catalyst. In contrast, catalysts that are highly selective for the production of oxygenates like furan and maleic anhydride, have been found to interact very strongly with butadiene.

Butadiene is produced industrially together with butene isomers by naphtha steam cracking. Additional butadiene is obtained by heterogeneously catalysed dehydrogenation or oxidative dehydrogenation of linear butenes.[1] Dehydrogenation of butenes to butadiene is carried out industrially over iron-oxide-based or phosphate-based catalysts near 920 K in the presence of steam.[1,2] More recently, oxidative dehydrogenation processes have been developed, working at lower temperatures. Different oxidative dehydrogenation catalysts that do not need frequent regeneration, are used for these processes.[3–5] They include metal molybdates, metal antimonates and iron oxide-based compounds.

Linear butenes and butane are also raw materials for the production of oxygenated compounds by heterogeneously catalysed oxidation reactions. Maleic anhydride is produced industrially by *n*-butane or butene oxidation over vanadyl pyrophosphate catalysts,[6] while acetic acid has been produced industrially by oxidation of butane and butene over vanadia–titania catalysts.[1,7] Ethyl methyl ketone can be obtained by butene oxidation both in liquid-phase (Wacker-Hoechst process) and over heterogeneous catalysts (Pd V_2O_5–TiO_2).[8]

In previous papers the mechanisms of butene oxidation over catalysts selective for oxygenates like vanadyl pyrophosphate,[9] vanadia–titania[10] and heterogeneous Wacker-type catalysts[11] have been investigated by FTIR spectroscopy. We present here our data concerning an analogous *n*-butene oxidation study carried out over a selective oxidative dehydrogenation catalyst. The mixed oxide, $FeCrO_3$, has been chosen as the model catalyst because it can be prepared with a small particle to allow IR investigation, it is sufficiently thermally stable, allowing activation in vacuum, its catalytic behaviour in this reaction has been documented previously[12] and some data about its surface have also been published.[13] Complementary surface and bulk catalyst characterization data are also included in the text in order to indicate the active catalytic sites.

Experimental

Catalyst Preparation

A 1 : 1 molecular mixture of Cr and iron(III) nitrates was dissolved in water and precipitated at a pH of *ca.* 9 by ammonium carbonate. After ageing for three days at 330 K the precipitate was filtered, washed carefully and then dried at 390 K for 3 h. The catalyst was obtained by calcination of the precipitate at 673 K for 5 h.

Materials and Experimental Methods

Cr^{3+} and Fe^{3+} nitrates (decahydrated) and ammonium carbonate were from Carlo Erba, Milano, Italy. Pure butene isomers, butadiene and propene, were from SIO, Milano, Italy.

X-Ray diffraction (XRD) was carried out with a Philips 1130 diffractometer (Co-Kα radiation). IR spectra were recorded with a Nicolet MX1 Fourier-transform instrument, using conventional IR cells and gas-handling systems.

Results

Catalyst Characterization

The XRD patterns of the precipitate and of the calcined catalyst are reported in Fig. 1. Both are typical of crystalline compounds although amorphous material is possibly also present in the precipitate. The pattern of the precipitate corresponds to those of the two isomorphous oxyhydroxides α-FeOOH (goethite, JCPDS table 29-713) and α-CrOOH (grimaldite, JCPDS table 9-331). The peak position is, however, intermediate between those reported for these compounds: the most intense one, corresponding to the (110) planes, is found by us at 42.6 Å. The pattern of the calcined sample corresponds to that of a corundum-type structure, and again the peak position is intermediate between those of α-Fe_2O_3 (haematite, JCPDS table 33-664) and α-chromia (eskolaite, JCPDS table 38-1479). In particular, the most intense XRD peaks are observed by us at 2.512 Å [(110) planes], 2.695 Å [(104) planes] and 1.685 Å [(116) planes]. The pattern resembles that of an $(Fe_{0.6}Cr_{0.4})_2O_3$ preparation reported in the literature (JCPDS table 34-412). The IR spectrum of a KBr disk of the catalyst shows a couple of strong bands at 605 and 545 cm^{-1}, with weaker components near 680 cm^{-1} (shoulder) and 445 cm^{-1}. These frequencies are intermediate between those observed on α-Fe_2O_3 [640 cm^{-1} (shoulder, sh), 545 and 445 cm^{-1} (very strong, vs) and 385 cm^{-1}] and on α-Cr_2O_3 [700 cm^{-1} (sh), 615 and 555 cm^{-1} (vs), 442 and 410 cm^{-1}].

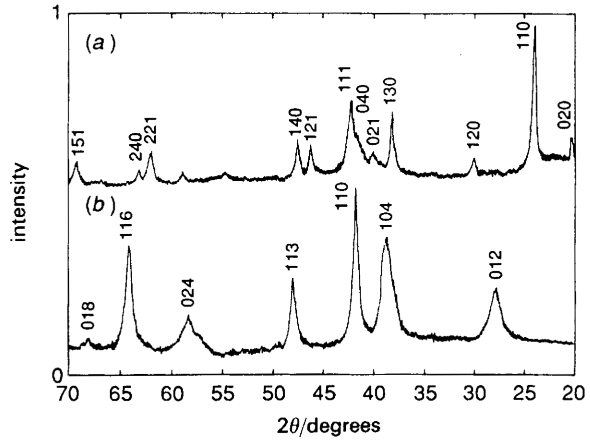

Fig. 1 XRD patterns of the precipitate (*a*) and of the calcined catalyst (*b*) and peak assignments

The spectra of α-Cr_2O_3 and of $FeCrO_3$ also present broad bands in the region near 950 cm^{-1}, due to chromate species. Consequently, our catalyst is comprised of an $FeCrO_3$ iron–chromium oxide solid solution having the corundum-type structure, although it also contains Cr^{6+}. The lineshape in the XRD pattern is not uniform, as normally found when α-FeOOH is decomposed to α-Fe_2O_3, probably owing to particle shape anistropy[14] or to the formation of slit micropores.[15] The BET surface area of the calcined material is 80 m^2 g^{-1}. The apparent crystal size measured from XRD ranges between near 60 Å [from the (012) reflection peak] and 165 Å [from the (110) reflection peak].

In Fig. 2 the FTIR spectrum of a pressed disk of pure α-$FeCrO_3$ after activation in vacuum for 1 h at 673 K is compared with those of three different powders, namely: (i) α-Cr_2O_3 activated in the same way; (ii) α-Cr_2O_3 previously reduced in hydrogen (1 atm) at 673 K for 1 h and then activated in the same way; (iii) α-Fe_2O_3 activated at the same temperature but for 10 min to avoid surface reduction. In fact, pure haematite loses its IR transmission rapidly by outgassing at 673 K:[16] according to Merchant *et al.*[17] this should occur because of surface reduction producing a surface layer of the conducting oxide, Fe_3O_4. The greater stability of $FeCrO_3$ than Fe_2O_3 with respect to reduction accords with literature data.[12,17]

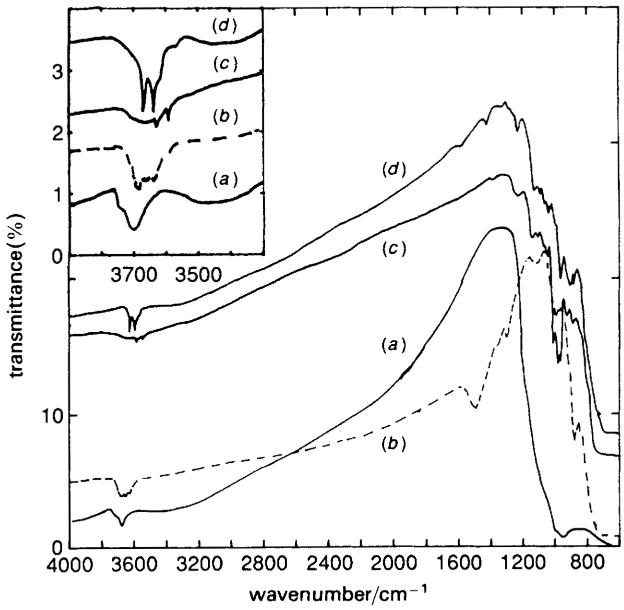

Fig. 2 FTIR spectra of pressed disks of $FeCrO_3$ (*a*), α-Fe_3O_3 (*b*), α-Cr_2O_3 (*c*) and reduced α-Cr_2O_3 (*d*). $FeCrO_3$ and unreduced α-Cr_2O_3 were simply outgassed for 1 h at 673 K, α-Fe_2O_3 was activated only for 10 min at the same temperature. Reduced α-Cr_2O_3 was first heated for 1 h in 1 atm H_2 and later outgassed for 1h at 673 K

The spectrum of $FeCrO_3$ shows a rather strong sharp band at 3690 cm^{-1} with a shoulder near 3710 cm^{-1}, certainly due to free surface hydroxy groups, and a broad band centred near 3400 cm^{-1}, due to H-bonded OHs. Similar features are also observed on reduced α-chromia (sharp bands at 3650 and 3620 cm^{-1}) as well as on α-Fe_2O_3 (3680, 3640 and 3620 cm^{-1}).[18] In contrast, in the case of unreduced α-chromia only a broad feature is observed with extremely weak and sharp features at 3650 and 3600 cm^{-1}.

On $FeCrO_3$ a prominent band is also observable centred at 950 cm^{-1}, but having a shoulder near 1000 cm^{-1}. Similarly, a strong triplet is observable in the case of unreduced chromia at 1020, 992 and 978 cm^{-1}. These prominent bands are destroyed by the reduction of chromia [Fig. 2(*c*), (*d*)], whose spectrum still contains a number of small sharp components due to overtones of bulk vibrations, and are absent on evacuated Fe_2O_3. These bands are due to surface Cr=O groups involving high-valency chromium, as elegantly demonstrated by Carrott and Sheppard for α-chromia.[19] Adsorption of different molecules shows that on $FeCrO_3$ only a sharp component, just at 1000 cm^{-1}, can be perturbed by adsorption, which is consequently thought to be due to Cr^{n+}=O (n = 5 or 6) bonds located at the surface. Most of the absorption near 950 cm^{-1} is likely to be due to chromate ions not directly exposed on the surface. The presence of Fe^{3+}, Cr^{3+} and Cr^{6+} species near the surface of $FeCrO_3$ has been reported previously by Auger electron spectroscopic analysis.[13]

The adsorption of basic molecules like pyridine allows determination of the Lewis acid sites present on the surface of $FeCrO_3$, which are similar to those also observed on pure iron and chromium sesquioxides. It is not possible to discriminate between Cr^{3+} and Fe^{3+} at the moment. Previous data reported an enrichment of Fe^{3+} at the $FeCrO_3$ surface.[13]

In summary, our catalyst is comprised of a corundum-type $FeCrO_3$ mixed oxide, at the surface of which Fe^{3+} ions, Cr^{3+} ions and Cr^{6+}=O bonds are exposed, together with surface hydroxy groups similar to those also exposed on the surface of the isomorphous pure sesquioxides.

Adsorption and Oxidation of But-2-enes on $FeCrO_3$

The spectra of the adsorbed species arising from the interaction of (*Z*)-but-2-ene with the $FeCrO_3$ surface at room temperature are shown in Fig. 3. The sharp and weak bands formed immediately at 1653, 1462, 1448, 1415 (sh), 1410 and 1380 cm^{-1} are due to molecularly adsorbed (*Z*)-but-2-ene. The band perturbation is similar to that found over other oxide surfaces.[20] In particular, the significant shift towards lower frequencies of the C=C stretching (1653 cm^{-1}, with respect to 1667 cm^{-1} for the gaseous molecule) suggests an electronic interaction of the C=C double bond with the electron-withdrawing surface centres.[21] The intensity of these bands is stable with time of contact, but they disappear immediately on pumping off the alkene, showing that the adsorptive bond is weak.

Nevertheless, some other bands rapidly grow in contact with butene gas and become progressively more intense. Their behaviour upon heating under evacuation allows them to be classified into different groups. Some bands (1160, 1128 and 1100 cm^{-1}) rapidly increase at room temperature in contact with the alkene gas (Fig. 3), are stable to outgassing

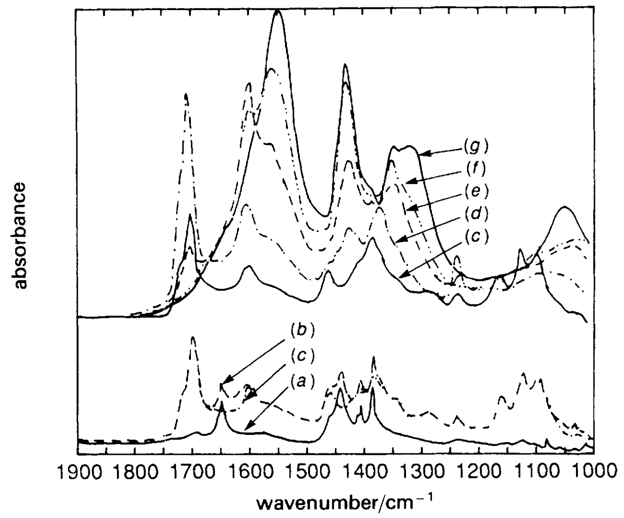

Fig. 3 FTIR spectra of the adsorbed species arising from (*Z*)-but-2-ene adsorption on $FeCrO_3$: in equilibrium with (*Z*)-but-2-ene gas (50 Torr†) immediately after contact (*a*), after 4 h (*b*), after successive outgassing at room temperature (*c*), 373 K (*d*), 423 K (*e*), 473 K (*f*) and 523 K (*g*). Spectrum (*c*) is reported twice, by shifting of the ordinate

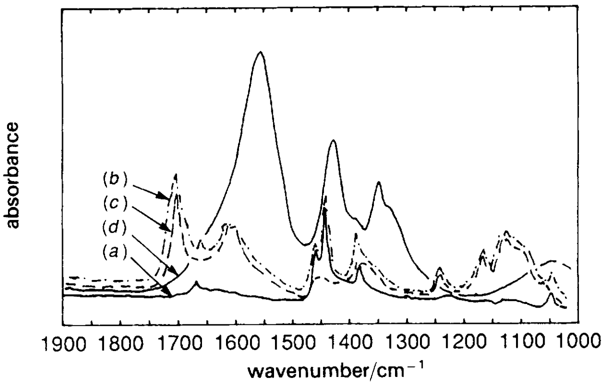

Fig. 4 FTIR spectra of the adsorbed species arising from (*E*)-but-2-ene adsorption on $FeCrO_3$: in equilibrium with (*E*)-but-2-ene gas (50 Torr) immediately after contact (*a*) and after 4 h (*b*), after successive outgassing at room temperature (*c*) and 523 K (*d*)

at room temperature, but disappear rapidly near 373 K. These can be assigned to coupled C—C and C—O stretchings of surface 2-butoxy species. In fact, they are also observed when butan-2-ol is adsorbed on the same surface. Bands first increasing (from room temperature to 373 K) and later decreasing in intensity are found at 1700 cm^{-1}, with a shoulder at higher frequencies (1715 cm^{-1}), at 1370 and at 1240 cm^{-1} and can be assigned to ethyl methyl ketone (C=O stretching, CH_3 deformation and C—C—C asymmetric stretching, respectively), slightly perturbed by adsorption.[22,23]

Other bands have a similar behaviour to those assigned to ethyl methyl ketone, but are displaced at higher temperatures. In fact, two bands at 1600 cm^{-1} and near 1350 cm^{-1} increase in intensity at their maxima near 423 K and later decrease in intensity. We have confirmed by direct ketone adsorption that these bands are due to species formed from the ketone. According to literature data,[24] these bands can be assigned to the asymmetric and symmetric stretching, respectively, of C—C—O groups of enolate anions. They can be assigned to an enolate anionic form of ethyl methyl ketone. Finally, rather broad bands grow at 1550 and 1430 cm^{-1}, typically due to O—C—O asymmetric and symmetric stretchings of carboxylate groups, where acetate ions probably predominate. This assignment is confirmed by adsorption of acetic acid.

The results obtained by adsorption of the (*E*)-but-2-ene isomer (Fig. 4) are completely analogous to those described previously for the *cis* isomer. A molecularly adsorbed form of the alkene is easily detected after room-temperature adsorption. It is characterized by the sharp CH deformation bands at 1458, 1442 and 1385–1380 (doublet) and 1305 cm^{-1} (very weak, vw).[20] The C=C stretching, which is IR inactive but Raman active (1682 cm^{-1}) in the gas because of the centrosymmetric structure of this isomer, appears very weakly activated near 1660 cm^{-1} because of the lowering of molecular symmetry upon adsorption. Again the C=C stretching is slightly shifted to lower frequency probably because of electron withdrawal by the surface cationic sites. However, a number of bands rapidly grow at room temperature. The most evident are observed at 1700, 1240, 1168, 1135 and 1050 cm^{-1}, and correspond to those assigned above to *sec*-butoxides and ethyl methyl ketone. The following evolution of the (*E*)-but-2-ene isomer is parallel to that described above for the *cis* isomer.

Adsorption and Oxidation of But-1-ene on $FeCrO_3$

A different behaviour is observed on adsorption of but-1-ene (Fig. 5 and 6) from that found with the but-2-ene isomers. Immediately after contact, molecularly adsorbed species are predominant [Fig. 5(*a*)], according to the strong and sharp band at 1632 cm^{-1} ($\nu_{C=C}$), and to the sharp CH deformation bands at 1462, 1440, 1418 and 1375 cm^{-1}. The position (1632 cm^{-1} with respect to 1643, 1647 cm^{-1} for two conformers in the gaseous phase[20]), the intensity of $\nu_{C=C}$ (stronger than that of the CH deformation modes in the region 1470–1370 cm^{-1}, while for the gas-phase molecule and for weakly adsorbed species it is weaker) and the shift of the overtone of out-of-plane CH_2 deformation (from 1833 to 1870 cm^{-1}) indicate a perturbation of the molecule owing to electron withdrawal

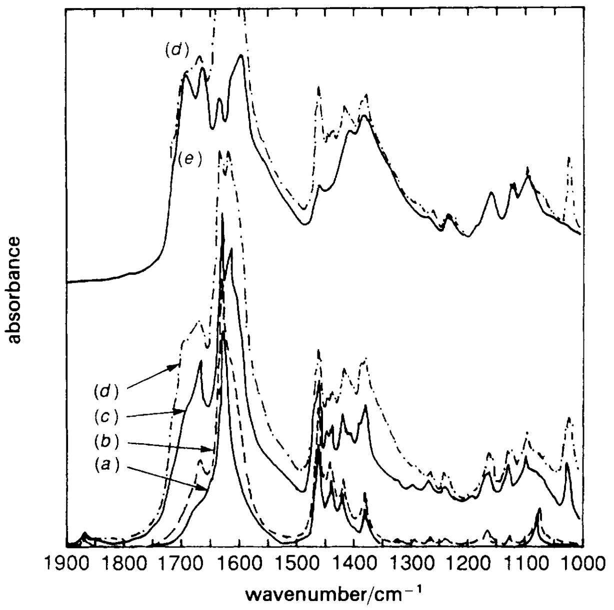

Fig. 5 FTIR spectra of the adsorbed species arising from but-1-ene adsorption on $FeCrO_3$: in equilibrium with but-1-ene gas (50 Torr) immediately after contact (*a*), after 5 min (*b*), after 30 min (*c*) and after 4 h (*d*), and after successive outgassing at room temperature (*e*); spectrum (*d*) is reported twice, by shifting of the ordinate

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† 1 Torr = (101 325/760) Pa.

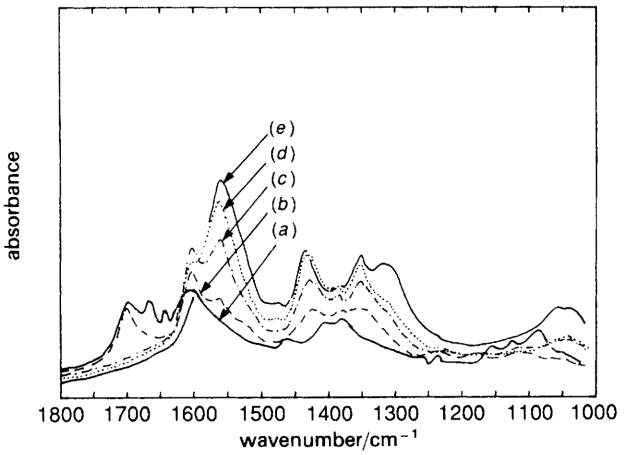


Fig. 6 FTIR spectra of the adsorbed species arising from but-1-ene adsorption on $FeCrO_3$: after contact with 50 Torr of the gas for 4 h at room temperature and after successive outgassing at room temperature (*a*), 373 K (*b*), 423 K (*c*), 473 K (*d*) and 523 K (*e*)

from the C=C double bond to the surface. These species are rapidly desorbed by outgassing. However, if the contact with but-1-ene gas is prolonged [Fig. 5(*a*), (*d*)], a number of bands appear. The absorption in the region 1750–1550 cm^{-1}, where the stretchings of the C=C and C=O double bonds fall, becomes progressively more complex. Both at the higher- and at the lower-frequency side of the C=C stretching of adsorbed but-1-ene several components become progressively more intense. At lower frequency, a second sharp component becomes very intense at 1618 cm^{-1}, while a much broader shoulder appears near 1600 cm^{-1}. At the higher-frequency side, a band first appears at 1668 cm^{-1} while a shoulder grows more slowly near 1700 cm^{-1}. On outgassing the sample, the two sharp bands at 1632 and 1618 cm^{-1} both immediately disappear, leaving four slightly broader bands, at 1700, 1668, 1638 and 1600 cm^{-1} [Fig. 5(*e*)]. Outgassing at 373 K [Fig. 6(*b*)] causes the disappearance of the bands at 1668 and 1638 cm^{-1}, while the band at 1700 cm^{-1} is stable and that near 1600 cm^{-1} slightly increases in intensity. At 423 K [Fig. 6(*c*)] the band at 1700 cm^{-1} has disappeared while that at 1600 cm^{-1} is slightly more intense. Near 523 K, no bands remain in the 1750–1580 cm^{-1} range [Fig. 6(*e*)].

Identification of the adsorbed species can be attempted by analysis of the region 1600–1000 cm^{-1}. By increasing the time of contact with but-1-ene gas at room temperature [Fig. 5(*a*)–(*d*)] the bands due to CH deformations of adsorbed but-1-ene (at 1462, 1440, 1418 and 1375 cm^{-1}) become more complex. New sharp peaks at 1466, 1447 and 1435 cm^{-1} are now apparent. These also disappear quickly upon outgassing at room temperature. These bands can be assigned to a second conformer of but-1-ene, which is also responsible for the $\nu_{C=C}$ band at 1618 cm^{-1}. It is known that different conformers of but-1-ene, distinguishable by IR, exist, namely the *s-cis* and *gauche* conformers.[25]

Another sharp and rather strong band observed at 1025 cm^{-1} increases during contact with the gas and disappears upon outgassing at room temperature. It seems unlikely that this band is due to but-1-ene conformers.[20,25] Another sharp band near 1380 cm^{-1} is likely to be associated to this band. Both are assigned to adsorbed butadiene, as shown below.

Bands growing during contact with but-1-ene at 1160, 1128 and 1100 cm^{-1} show the same behaviour described above concerning but-2-ene adsorption and can be assigned analogously to adsorbed *sec*-butoxides. A band near 1240 cm^{-1} behaves in parallel to that near 1700 cm^{-1} as discussed above for but-2-ene adsorption. They are assigned again to ethyl methyl ketone. Correspondingly, the features observed upon transformation of but-2-enes and assigned above to the enolate species of ethyl methyl ketone (1600 and 1350 cm^{-1}, growing up to 423 K and disappearing later), and those assigned to acetate species (1560, 1430 cm^{-1}, growing up to 523 K) are also found upon transformation of but-1-ene.

A few other bands are also formed upon room-temperature contact of the $FeCrO_3$ catalyst with but-1-ene. In particular, one sharp band is very evident at 1265 cm^{-1}, which is likely to be due to the C—C—O stretching of a ketone. This band behaves in parallel to those at 1668 and 1638 cm^{-1}. These bands correspond to the most intense ones of the *s-trans* conformer of methyl vinyl ketone (1690 cm^{-1}, $\nu_{C=O}$; 1620 cm^{-1}, $\nu_{C=C}$; 1250 cm^{-1}, ν_{C-C-C}; for matrix-isolated species[26,27]) slightly perturbed by coordination in the expected way.

Adsorption and Oxidation of Butadiene on $FeCrO_3$

The adsorption of butadiene over $FeCrO_3$ (Fig. 7) has a significant parallelism with that of linear butene isomers. Also, in this case, a molecularly adsorbed form is observed at room temperature, but quickly disappears on outgassing, showing that it is very weakly adsorbed. It is characterized by three sharp bands at 1588, 1381 and 1024 cm^{-1}, the last very intense. These features provide evidence that this molecule is adsorbed in the centrosymmetric *s-trans* form, with a weak vibrational perturbation (the most intense gas-phase IR frequencies: 1599 cm^{-1}, asymmetric C=C stretching; 1385 cm^{-1}, CH_2 scissoring; 1013 cm^{-1}, CH_2 twisting[28]). However, weaker bands appear and grow slightly with time, at 1638, 1458, 1439, 1430 and 1390 cm^{-1}. They all disappear quickly upon outgassing. These bands closely correspond to the non-centrosymmetric *s-cis* forms of butadiene, observed upon adsorption over some oxide surfaces.[29–31] Surprisingly, this species (certainly minor on $FeCrO_3$) is the only one observed upon butadiene adsorption on α-Fe_2O_3.[30] Butadiene adsorption on $FeCrO_3$ identifies the species responsible for the band at 1025 cm^{-1} observed after but-1-ene adsorption as butadiene produced by butene dehydrogenation.

However, if butadiene gas stays in contact with the surface for a few hours, several reaction products become observable. In particular, bands grow at 1680 and 1640 cm^{-1}, both rather broad, which are probably due to $\nu_{C=O}$ and $\nu_{C=C}$ of an

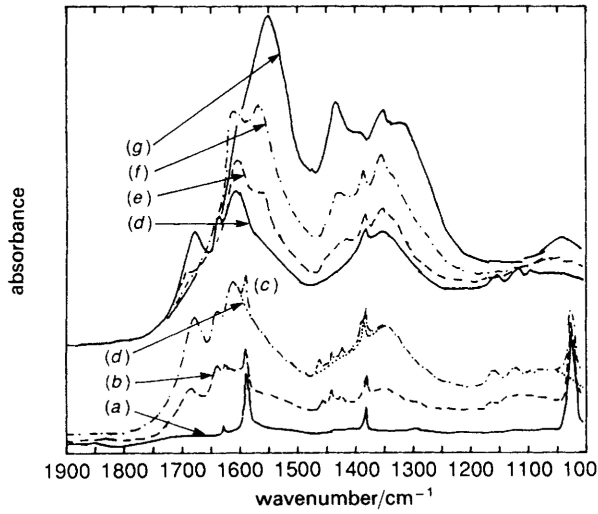


Fig. 7 FTIR spectra of the adsorbed species arising from buta-1,3-diene adsorption on $FeCrO_3$: in equilibrium with buta-1,3-diene gas (50 Torr) immediately after contact (*a*), after 30 min (*b*) and after 4 h (*c*), after successive outgassing at room temperature (*d*), 373 K (*e*), 423 K (*f*) and 523 K (*g*); spectrum (*d*) is reported twice, by shifting of the ordinate

Table 1 Observed wavenumbers (cm^{-1}) and assignments of propene adsorbed on corundum-type compounds

assign.	gas[a]	Fe_2O_3	Cr_2O_3 reduced	$FeCrO_3$
$\nu_{C=C}$	1653	1628	1620	1635
δ_{as,CH_3}	1458	1455	1454	1455
δ_{as,CH_3}	1442	1440	1436	1440
δ_{CH_2}	1414	1415	—[b]	1418
δ_{s,CH_3}	1378	1377	1373	1377
δ_{CH}	1298	—[b]	—[b]	—[b]
r_{CH_2}	1170, 1177	1178	—[b]	—[b]
r_{CH_3}	1045	1042	1050	—[b]
t_{CH_2}	990	1002	1004	—[b]
w_{CH_2}	912	940	942, 936	—[b]

[a] Ref. 32. [b] Bands not identified with certainty.

α,β-unsaturated carbonyl compound. The absence of a detectable band in the region 1270–1200 cm^{-1} indicates that this species is not a ketone. Its identification as adsorbed crotonaldehyde is supported by the detection of a second rather strong band near 1155 cm^{-1} [1146 cm^{-1} (strong's) for the free molecule in CCl_4 solution].[27] Broad bands again grow near 1600 and 1350 cm^{-1}, assigned to enolate species, probably arising from a proton abstraction in the γ position of crotonaldehyde. At higher temperatures broad bands at 1560, 1435, 1350 and 1320 cm^{-1} appear very intense, probably due to different carboxylate species including crotonate species.

Propene Adsorption on α-Fe_2O_3, α-Cr_2O_3 and α-$FeCrO_3$

It is generally recognized, in agreement with our data, that molecular adsorption is a preliminary step for alkene allylic activation. To have a more precise idea of the molecular adsorption sites for alkenes on the catalyst we have also investigated the adsorption of propene over the $FeCrO_3$ catalyst and over the isomorphous pure compounds α-Fe_2O_3 and α-Cr_2O_3. In the case of unreduced chromia we can find only traces of molecular propene adsorption. In contrast, on reduced chromia, as on Fe_2O_3 and $FeCrO_3$, we observe substantial molecular propene adsorption. The observed frequencies are given in Table 1. The vibrational perturbation undergone by propene on $FeCrO_3$ is similar, although slightly weaker, than that observed on α-Fe_2O_3, where the active sites are Fe^{3+} ions. It is definitely weaker than that undergone on the Cr^{3+} sites of α-Cr_2O_3. These data support the conclusion that the active sites for alkene adsorption on $FeCrO_3$ are Fe^{3+} ions. In an oxidizing atmosphere, chromium sites at the surface are probably essentially in the oxidized state of Cr^{6+}, and are therefore likely to be inactive for molecular alkene adsorption.

The successive evolution of propene on the surface of $FeCrO_3$ is parallel to that described for the but-2-ene isomers, *i.e.* involving formation of alkoxides (*sec*-propoxides) and of the ketone (acetone), although apparently in smaller amounts. Comparison of the evolution of propene on α-$FeCrO_3$ and α-Fe_2O_3 suggests that chromium favours the formation of the above-mentioned oxidation compounds but inhibits a direct oxidative breaking of C=C double bonds. This possibly occurs by enhancing the stability of Fe^{3+} with respect to its reduction to Fe^{2+}.

Discussion

Mechanisms of Butene Conversion at the Surface

The IR spectra demonstrate that all linear butene isomers (as well as butadiene and propene) are adsorbed in a molecular form on the surface of the catalyst $FeCrO_3$. These species are characterized by a small but significant vibrational perturbation and by complete reversibility at room temperature.

Besides molecular interaction, a number of different reactions of the butene isomers (and of propene) are also observed on the surface of the $FeCrO_3$ catalysts, and these can be related to the products of catalytic butene conversion in the presence and in the absence of oxygen. Some reactions are, in the conditions of our spectroscopic experiments, common to the three butene isomers, while others are observed only in the case of but-1-ene.

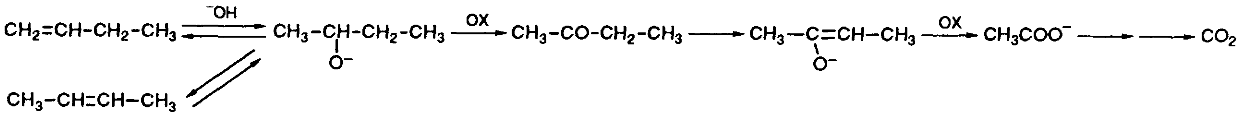
All three butene isomers are found to give *sec*-butoxide species rapidly at room temperature, which are oxidized (in part at room temperature and completely at 373 K) to the corresponding carbonyl compound, ethyl methyl ketone. *sec*-Butoxides can be considered as the adsorbed form of butan-2-ol, the product of hydration of the linear butenes. The alkoxide species can be viewed as the product of the electrophilic addition of a weakly acidic OH group on the alkene C=C bonds.[21] According to the Markovnikov rule, the three linear butenes should give the same *sec*-butoxide groups, as is indeed observed.

In agreement with the known chemistry of surface alkoxide groups,[33,34] evolution of *sec*-butoxides can follow two alternative paths: (i) elimination, giving back an OH plus one of the linear butene isomers, (ii) oxidative dehydrogenation, giving the corresponding ketone, ethyl methyl ketone. Following path (i), the *sec*-butoxide species are intermediate in double-bond isomerization of linear butenes. Accordingly, this reaction occurs over the $FeCrO_3$ catalyst in reaction conditions (near 600 K) although the rate of this reaction is reported to be lower than that of dehydrogenation.[12]

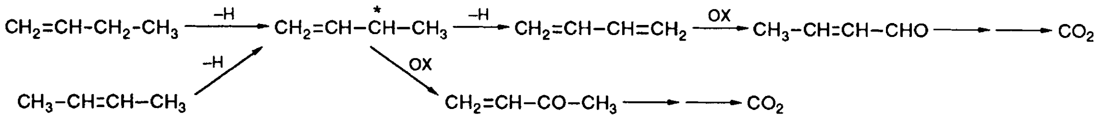
Following the second path, *sec*-butoxides are intermediate in the production of ethyl methyl ketone (EMK). Although the formation of this compound by butene oxidation over $FeCrO_3$ has not been reported, EMK is reported to be a major product of butene oxidation over Sn- and Co-based oxide catalysts.[3]

In analogy with what has been observed concerning acetone interaction with Fe_2O_3,[35] EMK is strongly adsorbed on the surface of $FeCrO_3$ and, besides being desorbed as such, it can be transformed further on the catalyst surface. Our data show that both saturated ketones evolve easily to enolate anions that can later undergo oxidative breaking of the C—C band adjacent to the carbonyl. In the case of EMK this produces an acetate species, which can later be hydrolysed in reaction conditions to give acetic acid (a product of butene oxidation on vanadia–titania).[7] These species, strongly held on the surface, are likely to undergo further oxidation giving, eventually, carbon oxides. This path (Scheme 1), observed for all three butene isomers, is a probable mechanism for their non-selective oxidation over this catalyst.

Other transformation products are observed to appear at room temperature, but only starting from but-1-ene adsorption. These have been identified above, on spectroscopic and



Scheme 1



Scheme 2

on chemical bases, as butadiene and methyl vinyl ketone. Both of these compounds derive from an activation of but-1-ene at the allylic carbon which implies that there may be a common allylic intermediate for which no direct evidence is found in our experimental conditions. Indeed, in our experience,[21] surface allyl intermediates can be formed relatively easily over strongly basic surfaces (so they are thought to be allyl anions) but they are much less easily produced on oxidation catalysts. This is probably because they are quickly oxidized by reducible cations (like Fe^{3+}) to allyl radicals or even cations that further evolve rapidly in three alternative ways: (i) by further protonic abstraction giving the corresponding diene, in this case butadiene (this obviously occurs only when the starting alkene has at least four linear carbon atoms); (ii) by reaction with surface oxide ions giving first an allyl alkoxide that can rapidly be dehydrogenated to an α,β-unsaturated carbonyl compound, in this case methyl vinyl ketone; (iii) by radical coupling resulting in hexadiene and benzene, as observed to occur when propene interacts with Fe_2O_3 in the absence of oxygen.[36]

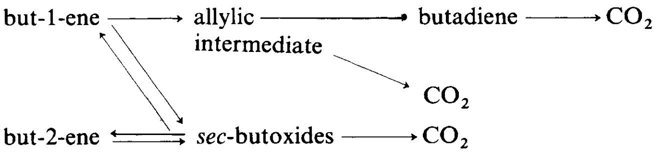
Butadiene is very weakly adsorbed on $FeCrO_3$ in a molecular form and can give only very slow further transformation, so it can leave the surface easily. In contrast, methyl vinyl ketone is, as are all carbonyl compounds, strongly adsorbed and easily undergoes further surface reactions like enolization and further oxidation. Methyl vinyl ketone probably follows an evolution similar to that described above for EMK and acetone, finally becoming a likely intermediate for a second non-selective oxidation path on our catalyst. This compound is reported to be a major butene oxidation product over catalysts like copper oxide and metal selenites.[3] Note that we cannot exclude the presence of the alternative product of butene allylic oxidation, crotonaldehyde, because of the superposition of its most intense bands with those of methyl vinyl ketone.

The detection of the allylic oxidation products while the allyl intermediate is not observed points to the high reactivity of this intermediate and, even more, to the fact that it is transformed faster than it is formed. The observation, in our experimental conditions, of allylic oxidation products only when but-1-ene is adsorbed may be due to one or both of the following reasons: (i) allylic methylene groups (those of but-1-ene) are more reactive than allylic methyl groups (those of the but-2-enes) for proton abstraction; (ii) internal C=C double bonds (those of the but-2-enes) are more reactive than terminal C=C double bonds (that of but-1-ene) for competitive electrophilic attack by OH groups. In any case, our data agree with the observation (reported for molybdate catalysts) that but-1-ene is the primary source of butadiene.[3] The formation of the allyl intermediate may certainly also occur in the case of the but-2-ene isomers, but more slowly than for but-1-ene, so it is not observed at room temperature in our experimental conditions.

As already stated, butadiene is adsorbed very weakly on the catalyst surface, probably both in *s-cis* and in *s-trans* form, and can easily leave the surface. Only very slow overoxidation of butadiene over the $FeCrO_3$ catalyst is found. As will be discussed below, this catalyst (as also Fe_2O_3) shows a completely different chemistry, compared with catalysts selective towards maleic anhydride and furan, in relation to the interaction with butadiene.[9-11] The intermediate in butadiene overoxidation is apparently crotonaldehyde, which is likely to be produced first by 1,4-addition of an OH group to butadiene, followed by dehydrogenation of the intermediate allylic alkoxide. Again, this carbonyl compound is strongly bonded and can be easily overoxidized, finally resulting in total-combustion products. The mechanisms arising from allylic activation are shown in Scheme 2.

Relation to the Kinetics and Mechanism of the Catalytic Reaction

It seems reasonable to relate the surface reactions discussed above to the mechanism of butene oxidative dehydrogenation carried out over the $FeCrO_3$ catalyst. This reaction is reported[12] to occur in the temperature range 600–650 K with an O_2 : butene ratio of 0.67 : 1 in the presence of steam. Conversions are higher than 50%, while the selectivity ranges up to 80%. According to our data and to published catalytic data, the following reaction scheme for butene oxidative dehydrogenation to butadiene over $FeCrO_3$ can be proposed:



The selective reaction implies that two protons and two electrons flow from the adsorbate to the surface at each turnover. The two protons should give water with an oxide anion while the two electrons probably reduce two Fe^{3+} ions to Fe^{2+}. Oxygen reoxidizes them, thus restoring the oxide ions.

According to our data, it seems very reasonable to propose that the slower step is the production of the allyl intermediate. This agrees with the data reported by Kung and Kung,[5] showing that the butene dehydrogenation rate over ferrite catalysts is zero order in oxygen, while nearly first order in butene. The effect of adding Cr to Fe_2O_3, *i.e.* increased activity without decreasing the selectivity, may be due to an increase in the density of active Fe^{3+} sites with respect to Fe^{2+} sites. The autoinhibition effect of butadiene agrees with the competitive molecular interaction of the alkene and the diene over the same site.

The mechanism also agrees with the observation on the $FeCrO_3$ catalyst that the butene isomerization rate is slower than the dehydrogenation rate (in fact, the alkoxides decompose more slowly with respect to butadiene formation and desorption), and it does not involve the same intermediate.[12] According to literature data which provide evidence that selective and non-selective oxidation involve separate sites, we can propose that the main combustion pathway is that involving nucleophilic attack by OH groups at the C=C bond as the first step. This is somewhat favoured by the presence of steam in the reaction mixture.

Comparison with other Catalytic Systems

As already observed, the behaviour of the $FeCrO_3$ system (and probably of other ferrite catalysts), which are highly selective for oxidative dehydrogenation of butene, differs significantly from that observed for catalysts that are highly selective for the production of oxygenated compounds, mainly furan and maleic anhydride. In fact, a striking difference is found here for butadiene adsorption compared with the behaviour observed over vanadyl pyrophosphate,[9] V_2O_5–TiO_2 [10,31] and MoO_3–TiO_2.[37] While on $FeCrO_3$, as also on pure iron oxide[30] and on other oxides like TiO_2 [31] and alumina,[29] the interaction of butadiene is very weak and gives molecular species, the interaction of butadiene with catalysts selective for maleic anhydride is strong even at room temperature and directly gives adsorbed oxygenated species similar to furan.[9,31,37] Therefore, these surfaces contain active sites that are able to bind butadiene in an *s-cis* form and to insert a surface oxygen atom rapidly at C(1)–C(4). Note that the above catalysts all contain high-oxidation-number cations characterized by very high electronegativity (the active phase is derived from metal acidic anhydrides such as MoO_3 and V_2O_5). These cations are closely associated to oxide ions giving vanadyl and molybdenyl groups and can act as strong Lewis acid sites at the surface. These characteristics are different from those of iron and chromium oxides.

Another feature of iron–chromium oxide and ferrite catalysts is the higher ionicity of the surface bonds compared with catalysts based on molybdenum and vanadium. The surface anions are, therefore, highly nucleophilic and are able to attack the carbon atoms of the oxygenated compounds. This results in their strong coordination on the surface and their subsequent overoxidaton, which accords with the combustion activity of ferrite catalysts at high temperatures.

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