IR study of alkene allylic activation on magnesium ferrite and alumina catalysts

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The interaction of propene and butenes with a butene oxydehydrogenation catalyst, $MgFe_2O_4$, and with an isomerization catalyst, γ -Al₂O₃, have been studied by FTIR spectroscopy. Allyloxy species (prop-2-en-1-oxides from propene and but-3-en-2-oxide from but-1-ene) were observed over $MgFe_2O_4$, while allyl species (prop-2-en-1-yl from propene, but-3-en-2-yl from but-1-ene and 2-methylprop-2-en-1-yl from isobutene), thought to be σ -bonded to Al³⁺ ions, were observed over γ -Al₂O₃. It is proposed that in all cases the allylic C—H bond is heterolytically broken at cation–anion couples ($M^n+O^2^-$) to give rise to anionic allyls. However, when the cation is reducible, as on the Fe³⁺ centres of magnesium ferrite, the allyl anion is further rapidly oxidized to allyloxy species that, at high temperature, can act as cationic allyls which interact weakly with oxide anions. From propene, the cationic allyls can act as symmetric species, as is expected for acrolein synthesis.

Vibrational spectroscopies allow one to gain insight into the mechanisms of several heterogeneously catalysed reactions. In particular, the interaction of alkenes with metal and metal oxide catalysts has been investigated thoroughly by Sheppard and co-workers using IR,¹ Raman² and EELS vibrational techniques.³ These studies allowed the definition of several details of the heterogeneous catalysed transformation of alkenes.

Simple and mixed metal oxides act as catalysts for several different alkene allylic oxidation reactions,⁴ such as the oxidation and ammoxidation of propene to acrolein and acrylonitrile,^{5,6} the oxidation and ammoxidation of isobutene to methacrolein and methacrylonitrile,⁷ the oxidative dehydrogenation of *n*-butenes to butadiene,⁸ the oxidation of α - and β methylstyrene to atropoaldehyde and to cinnamic aldehyde, respectively,⁹ and so on. It was recognised long ago¹⁰ that allyl species should be intermediates in this family of reactions. Starting from propene, isotopic scrambling experiments demonstrated that this intermediate must be symmetric before the insertion of oxygen, so that it is a general opinion that such ally species, to be symmetric, should be π -bonded through the delocalized electron cloud to metal sites at the surface.^{5,6} On the other hand, allyl species were also postulated to act as intermediates in double-bond isomerization reactions of *n*-butenes, occurring over ZnO¹¹ and aluminas.12-14

The IR vibrational features of allyl species, thought to be π -bonded, arising from propene and butenes were first reported by Kokes and co-workers on ZnO¹¹ which is an active catalyst for *n*-butene double-bond isomerization but is essentially poorly active and selective in alkene oxidation.¹⁵ Nguyen and Sheppard later demonstrated, using a combination of IR and Raman spectroscopies, that these species are anionic on ZnO.² On alumina the allyl species intermediates in the n-butene double-bond isomerization reaction were postulated to be σ -bonded¹²⁻¹⁴ but, to our knowledge, their IR spectra were not recorded. The IR spectra of the adsorbed species arising from propene and butenes on real allylic oxidation catalysts have been reported by other authors,16-20 some of whom assigned bands to surface allyl species,^{16,17} while others did not identify these species.¹⁸⁻²⁰ As a whole, the vibrational features of allyl species from

propene and butenes over oxidation catalysts and on alumina have not been definitely identified and the exact nature of such species is still far from clear.

In contrast, the IR detection of benzyl species arising from the oxidation of methylaromatics over real oxidation catalysts seems to be more firmly established. As reviewed recently,²¹ the spectra of such species have been detected by several authors, and quite complete band assignments have also been proposed.²² We previously reported some doubts about the real detectability of allyl species on selective oxidation catalysts and discussed possible reasons for the detection of benzyl species.²⁰

In the present paper we will summarize and compare the results of our recent investigations concerning the interaction of propene and butenes on a butene oxydehydrogenation industrial catalyst, $MgFe_2O_4$, and on an acidic isomerization catalyst, γ -Al₂O₃, with particular emphasis on our efforts in detecting allyl species intermediates.

Experimental

A commercial γ -Al₂O₃ powder (190 m² g⁻¹, pore volume 0.48 ml g⁻¹, medium pore radius 85 Å, Na < 100 ppm, Si < 0.2%; Akzo) was used as the catalyst. This material was the object of a previous characterization study.²³ The preparation of the MgFe₂O₄ aerogel was reported previously.²⁴ This material was characterized to be a crystallographically pure, partly inverted spinel (MgFe₂O₄, magnesioferrite), with a surface area of 130 m² g⁻¹.

The IR spectra were recorded by a Nicolet Magna 750 Fourier transform spectrometer. The adsorption and oxidation experiments were performed using pressed disks of the pure powders, activated by outgassing (to 10^{-4} Torr) into the IR cell. Activation of alumina was carried out for 1 h at 873 K, in order to obtain partial dehydroxylation. For magnesium ferrite, outgassing was limited to 10 min at 773 K after calcination at the same temperature for 1 h, in order to limit partial reduction upon outgassing.

Results and Discussion

Interaction of propene and butenes on γ -Al₂O₃

The IR spectrum of the activated alumina sample in the OH

stretching region is shown in Fig. 1(a). As always for thoroughly outgassed spinel-type transitional aluminas,^{25,26} the spectrum of our sample outgassed at 770 K for 1 h shows at least four bands, near 3790 (shoulder), 3775, 3730 and 3680 cm⁻¹. A fifth broader band can also be seen, after milder pretreatments, near 3590 cm⁻¹. According to a previous study,²⁷ where the model of Knözinger and Ratnasami²⁵ was partly modified, the bands at 3790 and 3775 cm⁻¹ are assigned to terminal OH groups over one tetrahedrally coordinated Al ion, either in a non-vacant environment or near a cation vacancy, respectively; the band at 3730 cm⁻¹ is assigned to a terminal OH over an octahedrally coordinated Al ion, while the bands at 3680 and 3590 cm⁻¹ (the last is broad after activation at 773 K) are assigned to bridging and triply bridging OH groups respectively.

Fig. 1(b) shows the spectrum of γ -alumina in the ν (OH) region in contact with propene. Under these conditions, the peak at 3775 cm⁻¹ disappears or decreases markedly in intensity. Moreover, a broad new component is apparent, centred near 3550 cm⁻¹. However, the subtraction spectrum shows that all ν (OH) bands are decreased in intensity. In the region 3150–2800 cm⁻¹, bands due to C—H stretchings of

Fig. 1 FTIR spectra of γ -Al₂O₃ surface hydroxy groups after activation at 873 K (a), after contact with propene gas (10 Torr) at room temperature (b) and after outgassing at room temperature for 10 min (c)

adsorbed species appear, and, correspondingly, a number of bands are also evident in the region $1900-1100 \text{ cm}^{-1}$, due to C—H deformation modes and to C—C stretchings (Fig. 2). Below 1100 cm⁻¹ the spectrum is obscured by the alumina bulk vibrations.

Outgassing (to 10^{-4} Torr) at room temperature for a few minutes causes the spectrum of the adsorbed species to decrease in intensity and to definitely change, both in the 3150-2800 cm⁻¹ region and in the 1900-1100 cm⁻¹ region. In the v(OH) region the broad band at 3550 cm⁻¹ disappears upon outgassing, showing that it is due to OH groups interacting with adsorbed species. The subtraction spectrum shows that outgassing does not restore the position of the band at 3775 cm⁻¹, which permanently shifted to 3760 cm⁻¹, and that a new weak band at 3705 cm⁻¹ is possibly formed.

The comparison of the spectra of the adsorbed species recorded in contact with the gas and before outgassing definitely shows that two kinds of species are formed [Fig. 2(a)]. The positions of the bands recorded in the presence of the gas, which disappear after a few minutes outgassing, are summarized in Table $1^{28,29}$ where they are compared with the features of gaseous propene and of propene molecularly adsorbed on other oxide surfaces. These bands correspond, with relatively small shifts and/or perturbations, with the absorption bands of molecular propene. The overall spectrum

Fig. 2 FTIR spectra of the adsorbed species arising from contact of γ -Al₂O₃ with propene gas (10 Torr) at room temperature (a) and after outgassing at room temperature for 10 min (b)

1800

wavenumber/cm -1

1600

1400

1200

Table 1 Wavenumbers (cm⁻¹) of the IR bands of propene in the gaseous state and adsorbed on various oxide surfaces

0.18

0.16

0.14

0.12 0.10 **apsorpance** 0.08

0.04

0.02

0.00

-0.02

(b)

3200 3100 3000 2900 2800 2700

vibration	assignment	symmetry	gaseous propene ^a (300 K)	SiO ₂ ^b (200 K)	γ -Al ₂ O ₃ (300 K)	MgFe ₂ O ₄ (300 K)	ZrO ₂ ^b (300 K)
V ₁	v_{as} (=CH ₂)	a′	3091	3083	3077	3079	3078
comb	43 2/			3067	3060		3050
V2	$\nu = CH -)$	a'	3017	3008	3000		3005
v3	$v_{s} = CH_{2}$	a'	2991	2979		2990	
v4	$v_{as}(CH_3)$	a'	2973	2972	2972		2975
V15	$v_{as}(CH_3)$	a″	2953	2950	2954	2956	2955
v 5	$v_{s}(CH_{3})$	a'	2932	2925	2924	2933	2923
$2 \times v_7$	$2\delta_{as}(CH_3)$		2892	2894	2894		2870
$2 \times v_{16}$	$2\delta_{as}(CH_3)$		2868	2859	2859	2858	
$2 \times v_{19}$	$2w(CH_2 -)$		1829	1832	1842		1885
v ₆	v(C=C)	a'	1653	1640	1637	1641	1630
							1621
v ₇	$\delta_{as}(CH_3)$	a'	1458	1455	1453	1466	1451
V ₁₆	$\delta_{as}(CH_3)$	a″	1442	1439	1434	1432	1432
ν ₈	$\delta(CH_2 =)$	a'	1414	1416	1416		1412
v ₉	$\delta_{s}(CH_{3})$	a'	1378	1378	1376	1390	1372
v ₁₀	$\delta(-CH=)$	a'	1298		1297		1302
v ₁₁	r(CH ₂ =)	a'	1170		1177		1172
			1177				
V ₁₇	<i>r</i> (CH ₃)	a″	1045				1050
v ₁₈	$\tau(CH_2=)$	a″	990			1002	1010
V ₁₉	w(CH ₂)	a″	912			939	950

^a From ref. 29. ^b From ref. 28.



is similar to that of propene adsorbed on hydroxylated silica, with an even more pronounced spectral perturbation with respect to the gas. In particular, the modes associated to the C=C double-bond stretching and to the asymmetric stretching of the CH₂ group are significantly, although weakly, shifted to lower frequencies, while the first overtone of the wagging CH₂ mode is shifted significantly to higher frequencies (the corresponding fundamental mode falls in the cut-off region and is consequently undetectable). According to our previous data,²⁸ these perturbations are typical of electron-withdrawing interactions from the C=C double bond by weak electron-accepting centres, such as the surface hydroxy groups. In agreement with the above perturbations of the surface hydroxy groups, we can consequently identify the species responsible for this spectrum as propene molecules hydrogen bonded to surface hydroxy groups through the C = C double bond.

The spectrum of the adsorbed species resisting outgassing to 10^{-4} Torr at room temperature [Fig. 2(b)] is definitely different from those of the free and adsorbed alkene. It contains a well defined sharp band at 1596 cm^{-1} with a component at 1606 cm^{-1} , which, for its position and sharpness, looks quite typical of a C=C double-bond stretching of a 'perturbed' alkenic entity, with the CC bond markedly weakened. Other strong bands at 1450, 1427 and 1376 cm^{-1} are certainly due to C-H bond deformations, and must consequently be associated with the corresponding stretchings at 2985, 2965 and 2923 cm^{-1} (very intense) and at 2855 cm^{-1} (broad shoulder). The spectrum in the C-H stretching region is unusual both for alkenes and for alkanes. On the other hand, the strong triplet at 2985, 2965 and 2923 cm^{-1} (with the last most intense), is strongly reminiscent of the triplet at 2999, 2967 and 2923 cm⁻¹ reported for the compound propylmagnesium bromide (H₂C=CHCH₂MgBr³⁰), containing a nearly covalently bonded, partly anionic allyl species. The spectrum also resembles that of allyl species recorded on ZnO, reported by Nguyen and Sheppard,² having two strong bands at 2970 and 2915 cm⁻¹. These species also show a C=C stretching at 1515 and 1547 cm^{-1} , respectively, *i.e.* definitely below the typical range of C=C bonds for alkenes, and the two strongest C-H deformation modes nearly coincident with those we observe here. As shown in Table 2, the overall spectrum we observe is very similar to those of the allyl species of $H_2C = CHCH_2MgBr$ and of the anionic allyls observed on ZnO, although in our case the C=C double bond is stronger, probably in association with a more covalent carbon-metal bond. It is possible that the new v(OH) band, observed at 3705 cm⁻¹ in the difference spectra (see above), is due to a new hydroxy group arising from propene dissociation.

In order to gain confirmation of this assignment, we investigated the interaction of ethene and of the three butene isomers on alumina. The interaction of ethene with alumina does not give rise to any detectable adsorbed species at room temperature, in agreement with the lower electron density at the C=C double bond, that does not allow electron withdrawal from the OH groups, and the lack of allylic hydrogens. In contrast, the adsorption of the four butene isomers all give rise to strongly adsorbed species, whose spectra are similar, but not identical, to that arising from propene. In Fig. 3(a) and (b) the spectra of the adsorbed species on γ -Al₂O₃ arising from isobutene in equilibrium with the gas and after evacuation for 10 min, respectively, are shown. The spectrum of the irreversibly adsorbed species, in particular with respect to the band positions, is very similar to that obtained from propene. However, some notable differences can be found. The peaks at 2965, 2924 and 1375 cm^{-1} are definitely stronger in the spectrum of the species arising from isobutene and additional components are observed near 2890 and 1465 cm⁻¹, with respect to that of the species arising from propene. Accordingly, these features may be due to the additional absorptions of a methyl group at 2965 (asymmetric



Fig. 3 FTIR spectra of the adsorbed species arising from isobutene adsorbed on γ -Al₂O₃ at room temperature in equilibrium with the gas (10 Torr) (a) and after evacuation at room temperature for 10 min (b)

Table 2 Wavenumbers^{*a*} (cm⁻¹) of the IR bands of the products of the reactive adsorption of butenes and propene on γ -Al₂O₃

	isobutene on γ-Al ₂ O ₃	propene on γ -Al ₂ O ₃			assignment	
on γ -Al ₂ O ₃			propene on ZnO ^b	CH ₂ =CHCH ₂ MgBr ^c	ref. 30	this work
3060 vw	3063 vw	3072 vw	3053, 3040	3038 w	$v_{as}(CH_2)$	
2982	2987	2984	3000 w	2999 m	v(CH)	
2968	2965	2965	2970 st	2967 m	$v_{s}(CH_{2})$	$\nu_{as}(CH_3)$
2925	2923	2924	2915 st	2923 st	$v_s(CH_2)$	
2895						$v_{s}(CH_{3})$
	2855	2856		2847	comb.	
(1616)		(1606)				
1586	1588	1596	1547	1515	$\int v_{as}(C=C-C)$	
(1481)						
1456	1462					$\delta_{a}(CH_3)$
1450	1445	1450		1449	$\delta_{0}(CH_{2})$	43 3/
1414		1427			0 2/	
1385	1379	1376	1390	1372	$\delta_{n}(CH_{2})$	$\delta_{s}(CH_{3})$
1300	1285	1295		1261	r(CH ₂)	5. 5,
1245		1244		1248	$r(CH_2)$	
1204		1180	1200	1228	$r(CH_2)$	
			1035	1040	$v_s(C=C-C)$	

^a vw = very weak; w = weak; m = medium; st = strong. ^b From ref. 2. ^c From ref. 30.

stretching), 2890 (symmetric stretching), 1465 (asymmetric deformation) and 1375 cm⁻¹ (symmetric deformation). Conversely, the clear, although weak, band at 1427 cm⁻¹, observed in the spectrum of the species arising from propene, is not observed in the case of the species arising from isobutene. It may in fact be due to the bending mode of the methine group, absent for isobutene and its allylic species. So, the two spectra correspond well with the spectra of allyl species and 2-methylallyl species, respectively.

In Table 2 the position of the bands due to methylallyl species produced on γ -Al₂O₃ by the interaction with but-1-ene and isobutene are also reported. A more detailed study of the interaction of the four butene isomers with γ -Al₂O₃ in relation to the catalytic activity of this material in butene isomerization will be the object of a future publication.³¹ The identification as (methyl)allyls of the species produced from propene and butenes on γ -Al₂O₃ is further supported by: (i) the formation of such species at room temperature; (ii) the lack of formation of such species starting from ethene (which does not have allylic hydrogens) and (iii) the definite difference of the observed spectra from those observed after adsorbing C₃ and C₄ oxygenates: the alcohols propan-1-ol, propan-2-ol and prop-2-en-1-ol (allyl alcohol), the four butanols, but-3-en-2-ol (methylallyl alcohol) and the corresponding carbonylic and carboxylic compounds.

Interaction of propene and *n*-butenes over magnesium ferrite oxydehydrogenation catalyst

The FTIR spectra of the surface species arising from contact of magnesium ferrite with propene gas at room temperature are shown in Fig. 4(a) and (b). Outgassing at room temperature for 5 min causes the decrease of some adsorption bands, namely at 1641, 1465 and 1433 cm⁻¹, that can be assigned to vibrational modes of molecularly adsorbed propene, as summarized in Table 1. Stronger bands resisting outgassing at room temperature cannot be assigned to molecular propene; they are certainly related to species produced by reactive adsorption. In particular, the quite strong bands near 1550 and 1465 cm⁻¹ could be due to COO⁻ stretchings of carboxylate species, while the band appearing at 1194 cm^{-1} is due to the perturbation of a mode already present in the catalyst spectrum, possibly associated with a bulk overtone or adsorbed carbonate impurities. Of particular interest are the broad complex bands observed in the region 1200-1000 cm⁻ where typically C-O stretching modes of alkoxy groups fall. In this case, we detect a maximum at 1045 cm^{-1} with shoulders near 1140 and 1100 cm⁻¹. The spectrum of the adsorbed



Fig. 4 FTIR spectra of the adsorbed species arising from propene adsorbed on $MgFe_2O_4$ at room temperature in equilibrium with the gas (50 Torr) (a), after evacuation at room temperature for 10 min (b); and after contact with propan-2-ol (c) and prop-2-en-1-ol (allyl alcohol) (d), both after outgassing at room temperature for 10 min

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species is transformed by further heating, when the low-frequency bands in the region 1200-1000 cm⁻¹ disappear while the bands in the region 1700-1300 cm⁻¹ increase in intensity.

In Fig. 5 the spectra of the adsorbed species arising from propene adsorption and heating at 523 K are compared with those arising from acrylic acid adsorption. The bands of acrylate species are present in the spectra, showing that allylic oxidation of propene to acrylate species occurs, at least in part, at 523 K on the magnesium ferrite surface.

To identify the species arising from propene responsible for the bands in the region $1200-1000 \text{ cm}^{-1}$ (very likely an alkoxide species) we investigated the adsorption of the C₃ alcohols. In Fig. 4(c) and (d), the spectra of the prop-2-oxide species and of the prop-2-en-1-oxide (allyl alkoxide) arising from the adsorption of the respective alcohols (propan-2-ol and allyl alcohol) are also reported. It is evident that the spectrum of the adsorbed allyl alcoholate species, mainly characterized by the v(C-O)/v(C-C) bands at 1120 and 1050 cm⁻¹ (Table 3), is compatible with that of the alkoxide species arising from propene while it is not compatible with those of prop-2oxides. Similarly, we verified that the spectrum is also not compatible with those of prop-1-oxides. In the spectrum of Fig. 4(d) the strong bands near 1000 and 920 cm⁻¹ arise from undissociatively adsorbed allyl alcohol (Table 3).

These data strongly suggest that propene reacts at its allylic position on the surface of magnesium ferrite giving rise to allyl alkoxides that, at higher temperatures, are further oxidized to acrylate species.

The FTIR spectra of the species arising from the contact of the MgFe₂O₄ catalyst with but-1-ene are shown in Fig. 6, where the spectrum of but-1-ene liquefied at 150 K over a KBr disk is also shown for comparison. The spectrum of the species arising from but-1-ene on magnesium ferrite at room temperature definitely contains features due to molecularly adsorbed but-1-ene. Some modes are slightly shifted by the surface interaction to lower frequencies (1635 vs. 1641 cm⁻¹, C=C stretching) or to higher frequencies (1001 vs. 994 cm⁻¹, =CH₂ twisting; 924, 912 vs. 909 cm⁻¹, =CH₂ wagging and the corresponding overtones at 1840, 1827 vs. 1825 cm⁻¹). These perturbations are typical of alkene species when they interact with the C=C alkenic double bond flat on the surface, through an interaction of the π -orbital with electronwithdrawing centres.²⁸

Additional bands appear in the range $1200-1000 \text{ cm}^{-1}$ (namely at 1189, 1153, 1089 and 1056 cm⁻¹) typically associated with C—C and C—O stretchings of alkoxide species, and do not disappear upon outgassing for a few minutes at room temperature [Fig. 6(a), (b)]. Under these conditions the C=C



Fig. 5 FTIR spectra of the adsorbed species arising from the interaction of $MgFe_2O_4$ with propene at 523 K (a), with acrylic acid at room temperature and outgassing for 10 min at 300 K (b) and at 473 K (c)

	allyl alcohol (gas)					
assignment	cis	gauche	allyl alcohol (CCl ₄ sol) ^a	allyloxy MgFe ₂ O ₄	allyloxy MgO ^b	allyloxy γ -Al ₂ O ₃
v(OH)	3675	3650	m 3620			
			p 3331			
$v_{as} = CH_2$	3102	3093	3084	3080	3088	3083
$\nu (= CH -)$			3013	3009	3008	3010
$v_s (= CH_2)$	2	995	2986	2982	2961	2981
$v_{as}(CH_2)$			2922	2915	2934	2925
$v_{s}(CH_{2})$	2	880	2867	2835	2878	2848
$2w(CH_2-)$			1847	1841	1840	1845
v(C=C)	1	654	1646	1641	1638	1643
δ(-CH ₂ -)			1453	1455	1458	1458
$\delta(CH_2 =)$	1	428	1421	1420	1420	1422
$\delta(-CH=)$	1	414	1410			
$w(-CH_2-)$	1	372	1373	1348		1374
			1339	1325		
$\delta(OH)$	1	321	m 1314			
			1290	1287	1290	1284
			1230	1247		1242
$\tau(-CH_2-)$	1	191	1199			
v(CC)/						1153
$r(CH_2 =)$	1	132	1114	1120	1121	1120, 1089
v(C-O)	1038	1110	1026	1050	1060	1022
$t(CH_2 =)$		995	992			
w(CH ₂ =)	919	930	921			

Table 3 Wavenumbers (cm⁻¹) of the IR bands of species containing the CH₂=CHCH₂O fragment (allyloxy species)

 a m = monomer; p = polymer. b Impurities are also present and cause masking of some bands.



Fig. 6 FTIR spectra of the adsorbed species arising from but-1-ene adsorbed on $MgFe_2O_4$ at room temperature in equilibrium with the gas (100 Torr) (a) and after evacuation at room temperature for 10 min (b); (c) FTIR spectrum of but-1-ene liquified at 150 K over a KBr disk



Fig. 7 FTIR spectra of the adsorbed species arising from butan-2-ol adsorbed on $MgFe_2O_4$ at room temperature and after evacuation for 10 min at room temperature (a), 423 K (b), 453 K (c) and 523 K (d)

stretching is still present, very weak and partially masked by a broad adsorption due to carboxylate species or carbonate impurities (maximum near 1580 cm⁻¹). In the C—H stretching region peaks are found under these conditions at 3082, 2973, 2935, 2905 and 2882 (shoulder) cm⁻¹, where the band at 3082 cm⁻¹ confirms the persistence of an alkenic entity (=CH₂ asymmetric stretching).

To better understand the chemistry of the C_4 linear organic compounds on the catalyst surface we investigated also the interaction of the catalyst with C_4 alcohols and carbonyl compounds. The spectra of the adsorbed species arising from butan-2-ol adsorption and the evolution upon heating under evacuation (to 10^{-4} Torr) are reported in Fig. 7. The spectrum observed upon outgassing at room temperature is characterized by a group of strong bands with maxima at 1161, 1137 and 1115 cm⁻¹, due to coupled C-C and C-O stretchings of but-2-oxide species. Heating under evacuation only causes the disappearance of all bands occurring near 473 K, without leaving significant amounts of oxidized fragments on the



Fig. 8 FTIR spectra of the adsorbed species arising from C_4 compounds adsorbed on MgFe₂O₄: but-1-ene adsorbed at room temperature and after evacuation at room temperature (a) and at 423 K (b) for 10 min; butan-2-ol adsorbed and outgassed at room temperature (c) and but-3-en-2-ol adsorbed and outgassed at room temperature for 10 min (d)

surface. This suggests that but-2-oxides decompose into gasphase butene + hydroxides (as typically occurs for such species on quite basic surfaces³¹). In fact, this can be confirmed by heating in static vacuum and monitoring the gas phase by IR spectroscopy.

The spectrum of but-2-oxides [Fig. 7(a)] is not compatible with the complex of bands due to the alkoxides arising from but-1-ene. In Fig. 8, the spectra in the C—O region of species arising from contact of the catalyst with but-1-ene at room temperature [Fig. 8(a)] and at 423 K [Fig. 8(b)], preliminarily identified as alkoxides, are compared with those of but-2oxides [Fig. 8(c)] and with the species arising from adsorption of but-3-en-2-ol (methylallyl alcohol). In effect, this alcohol gives rise to a complex of bands in the region 1200–900 cm⁻¹ which is closely similar to the spectrum of the alkoxide species arising from but-1-ene [Fig. 8(a) and (b)].

The above data strongly suggest that both but-1-ene and propene react at their allylic position with the surface of $MgFe_2O_4$ at room temperature, giving rise to the corresponding allyl alkoxides prop-2-en-1-oxides and but-3-en-2-oxides. These species are probably the first detectable species in the oxidation pathway.

Discussion

The results described above show the different behaviour of alumina and magnesium ferrite in contact with propene and butene gases, as expected. This behaviour can be discussed in relation to the catalytic activity of these two materials in the presence of these gases.

Alumina is well known to act as a catalyst for double-bond isomerization of linear butenes at low temperature.¹²⁻¹⁴ Several years ago the formation of allyl species as intermediates in these reactions was suggested but, to our knowledge, the spectral features of such intermediates were not observed. As described above, we observe that both propene and the four butene isomers give rise to surface species whose IR spectra are definitely compatible with those expected for allyl species covalently bonded to Al ions.

Magnesium ferrite is a constituent of industrial catalysts for the oxidative dehydrogenation of *n*-butenes to butadiene.⁸ Also in this case, allyl species have been invoked as likely intermediates. The IR spectra described above show that both propene and but-1-ene give rise to adsorbed species whose spectra are compatible with those of allyl alkoxide species. We previously also observed species from both propene and *n*butenes adsorbed on MgCr₂O₄ (which is also an active catalyst for butene oxydehydrogenation⁸) we tentatively assigned to allyloxy species.³²

Our previous studies concerning hydrocarbon oxidation over transition-metal oxides allowed us to conclude that most hydrocarbon molecules are activated at their weakest C—H bond by oxidation occurring at the expense of high oxidation state transition-metal cations exposed at the catalyst surface, giving rise to surface alkoxides.³² This is probably what also occurs on the surface Fe^{3+} cations on magnesium ferrite surfaces, with a mechanism that can be schematized as follows:



This mechanism implies that the two electrons of the C-H bond are assumed by the catalyst surface, where two iron(III) ions can become reduced to iron(II) ions.

From our data, it is evident that saturated alkoxides (prop-2-oxides and but-2-oxides) on the magnesium ferrite surface tend to decompose to alkenes and surface OH groups near 473 K. This does not occur with prop-2-en-1-oxide because there are no hydrogens available for the elimination reaction. This, instead, can occur with but-3-en-2-oxide, which has available hydrogens in the methyl group. The result of elimination from but-3-en-2-oxide is just buta-1,3-diene which is the main product of but-1-ene oxydehydrogenation.

It seems reasonable to propose that the primary interaction inducing the above proposed C—H activation mechanism is the interaction of the C—H bond with iron(III) ions, which are the oxidizing agents, as already proposed for the oxidation at surface chromate species of MgCr₂O₄.³² On the other hand, the same primary interaction can be proposed to occur at the surface of alumina, whose chemistry is dominated by the Lewis acidity of the coordinatively unsaturated Al³⁺ cations.²⁶ However, in this case the cations are virtually nonreducible, so that the electrons of the C—H bond must be retained by the carbon atom, giving rise to an anionic or covalently bonded allyl species. Thus, we can propose the following mechanism for C—H activation upon *n*-butene double-bond isomerization on alumina:



In this view, the activation of the allylic C—H groups on both alumina and magnesium ferrite follows the same primary step, giving rise to anionic allyls that, however, are oxidized to cationic allyls by iron(iii) ions (in general by the reducible ions at the surface of oxidation catalysts), that attach to oxide ions, finally giving rise to allyl alkoxides.

It has been mentioned already that the isotopic scrambling technique demonstrates that allyl species intermediates in propene oxidation to acrolein must be 'symmetric' before binding with oxygen atoms. However, we can recall our previous proposal³³ that alkoxide species have a more or less pronounced carbocationic nature, which becomes predominant at higher temperatures. It seems consequently very reasonable to propose that the allyl alcoholate species we observe at room temperature by propene oxidation over oxidation and oxydehydrogenation catalysts convert to symmetric allyl carbocations interacting ionically with oxide anions at higher temperature, so that, finally, the bond with oxygen can occur at either the 1 or the 3 position:

Conclusions

The main conclusions from the present work are as follows.

1. The interaction of propene and *n*-butene on the oxydehydrogenation catalyst $MgFe_2O_4$ gives rise to allylic oxidation products, the first ones being the allyl alcoholates, prop-2-en-1-oxide and but-3-en-2-oxide, respectively.

2. The interaction of propene and *n*-butene on the isomerization catalyst γ -Al₂O₃ gives rise to allyl species (prop-2-en-1-yl from propene, but-3-en-2-yl from but-1-ene and 2methylprop-2-en-1-yl from isobutene), thought to be σ -bonded to Al³⁺ ions.

3. It seems likely that, in all cases, the allylic C-H bonds are heterolytically broken at cation-anion couples $(M^{n+}O^{2-})$ to give rise first to anionic allyls.

4. The allyl anions are further rapidly oxidized to allyloxy species on the reducible Fe^{3+} centres of magnesium ferrite.

5. The observed species are likely intermediates in *n*-butene double-bond isomerization over γ -Al₂O₃ and in *n*-butene oxy-dehydrogenation to butadiene on MgFe₂O₄.

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