FTIR Studies on the Selective Oxidation and Combustion of Light Hydrocarbons at Metal Oxide Surfaces

Propane and Propene Oxidation on MgCr₂O₄

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The interaction of propene and propane with the surface of the oxidized spinel $MgCr_2O_{4+x}$ has been studied in the temperature range 300–773 K by FTIR spectroscopy. This solid is reduced reversibly by reaction with these organic compounds in the temperature range 300–673 K, giving rise to stoichiometric $MgCr_2O_4$ and more oxidized organic species that finally produce CO_2 . Comparison with the results of adsorption and oxidation of C_3 oxygenates (propan-1-ol, propan-2-ol, allyl alcohol, propionaldehyde, acetone, acrolein, propionic acid and acrylic acid) as well as of C_2 and C_1 oxygenates showed that the predominant oxidation pathways for the two molecules are different. Oxidation of propene occurs predominantly through its previous activation at C_1 to give strongly adsorbed acrolein and acrylate species. These species later burn. Acetone is the primary oxidation product of propane at the surface, at 423 K. Acetone is later oxidized to formate species (which rapidly decompose) and to acetate species that burn at higher temperatures (573–773 K). The different observed paths are rationalized by taking into account the lower C—H dissociation energy at the methylene group in the case of propane and at the allylic methyl group in the case of propene. The data reported here are consistent with the data available on catalytic alkane oxidation over this and similar catalysts. A comparison is made with the behaviour observed with more selective oxidation catalysts like $Mg_3(VO_4)_2$, V_2O_5 –TiO₂ and MoO_3 –TiO₂. A mechanism for propene and propane catalytic combustion is proposed.

The production of oxygenates via catalytic partial oxidation of hydrocarbons can be achieved with high selectivities using light alkenes as the reactants. Accordingly, the selective oxidation of alkenes constitutes a prominent area of industrial petrochemistry.¹⁻³ However, several potentially useful oxidations of alkenes, e.g. acetaldehyde and acetone production from ethene and propene and the one-step propylene oxide synthesis, still cannot be achieved effeciently in the gas phase. Moreover, efforts are focused today on the use of light alkanes arising from natural gas as raw materials in petrochemistry. Nevertheless, the partial oxidation of alkanes is far more difficult than that of alkenes and is at present limited, at the industrial scale, to butane oxidation to maleic anhydride.⁴ Other processes, like the direct ammoxidation of propane to acrylonitrile⁵ and the oxidative dehydrogenation of propane and butane to the corresponding alkenes⁶ are now under promising development.

On the other hand, the hydrocarbon catalytic combustion is also of great interest at present to limit pollutant emissions of waste gases.^{7–9} In particular, the replacement of noble metal-based catalysts with the less expensive transition-metal oxide-based catalysts has been attempted. In order to develop new, more efficient and more convenient processes based on hydrocarbon catalytic oxidation, detailed mechanisms for these reactions are required. However, the factors affecting the selectivities in hydrocarbon oxidations are still far from clear.² Moreover, according to Spivey,¹⁰ a general theory of catalytic combustion on metal oxides still does not exist.

In our laboratory, FTIR spectroscopy has been recently applied to the study of some oxidation and oxidative dehydrogenation reactions on selective catalysts.¹¹⁻¹⁴ We recently undertook more systematic studies on selective and unselective oxidation of light hydrocarbons at catalyst surfaces. As a first step, we report here studies on propene and propane oxidation on MgCr₂O₄.

This material was chosen because it is recognized as a good combustion catalyst for alkanes and alkenes,^{15,16} like

chromia and other chromites.^{17,18} MgCr₂O₄ was found to be more active than chromia in methanol oxidation,¹⁹ and is more stable than chromia.¹⁶ Moreover, it displays significant selectivity in some oxidative dehydrogenation reactions.²⁰ It is a typical p-type semiconductor, and this property is associated with its activity both as an oxidation catalyst and as an oxygen²¹ and ethanol²² sensor. Finally, it can be prepared as an aerogel and it displays excellent optical properties for IR spectroscopic studies.²³

Experimental

The preparation of the MgCr₂O₄ aerogel has been described previously.²³ A mixture of Mg acetate and Cr acetylacetonate was dissolved in methanol and hydrolysed with the stoichiometric amount of water. The resulting gel was dried under supercritical conditions in an autoclave (524 K, 127.5 bar), *i.e.* above the critical point of methanol (512.6 K, 80.9 bar). The powder was then calcined for 6 h at 973 K. The resulting surface area was 53 m² g⁻¹. FTIR spectra have been recorded with a Nicolet Magna 750 instrument, using conventional IR cells connected to an evacuation–gas manipulation apparatus. The catalyst powder was pressed into self-supporting discs, calcined in air at 723 K for 1 h and outgassed at 723 K for 20 min before use in the interaction experiments.

Liquid adsorbates were from Carlo Erba (Milano, Italy), while gases were purchased from SIO (Milano, Italy). The chemicals used in the catalyst preparation were from Aldrich.

Results

Catalyst Characterization

The X-ray diffraction (XRD) pattern of the catalyst shows all of the diffraction peaks typical of the spinel MgCr₂O₄ only (JCPDS table 10-351). The FTIR–FT-FIR spectrum (Fig. 1) also shows the typical features of the spinel MgCr₂O₄²⁴ with





Fig. 1 FTIR spectra of MgCr₂O₄: (a) FTIR spectrum (1200-400 cm⁻¹) of a KBr pressed disc; (b) FT-FIR spectrum (500-50 cm⁻¹) of the powder deposited on a polyethylene disc; (c) FTIR spectrum of a pressed disc of the pure powder after outgassing at 723 K; (d) after (c) and following an interaction with hydrocarbon in the temperature range 573-773 K

the four IR-active modes at 630, 480, 415 and 250 cm⁻¹. However, the IR spectrum, which is also sensitive to noncrystalline and surface species, shows an additional weak complex band in the region 1000-800 cm⁻¹, typically associated with Cr=O stretchings involving high-valency Cr. Although it seems reasonable to identify these species as involving hexavalent Cr⁶⁺ species, according to Klissurski *et al.*²⁵ it cannot be excluded that Cr⁵⁺ is involved. The above spectral features indeed roughly correspond to the most intense bands of Mg chromate(vi), MgCrO₄.²⁶ However, the IR spectra of metal chromate(v) species are characterized by Cr=O stretching bands (900-800 cm^{-1 27}) at frequencies only slightly lower than, or superimposed upon, those of the chromate(vi) species.

The FTIR spectra of pressed discs of the pure catalyst powder show, as usual, a transmission window above 800 cm⁻¹, with maximum transmittance at 1300 cm⁻¹ and a progressive decrease in transmission towards higher frequencies due to the wavelength dependence of radiation scattering. Also these samples show the above-cited absorption in the region 1050–800 cm⁻¹, clearly structured into one sharp band at 1002 cm⁻¹, and components at 975, 940, 920 and 840 cm⁻¹. A broad absorption is also found near 3500 cm⁻¹, due to H-bonded surface hydroxy groups (Fig. 2).

The IR spectra of the pure catalyst disc after interaction with hydrocarbons or oxygenated organic compounds in the temperature range 573–773 K are different [Fig. 1(*d*) and Fig. 2(*b*)]. The absorption in the region 1050–800 cm⁻¹ is either decreased strongly in intensity or disappears completely, leaving weaker harmonic bands of the skeletal vibrations of MgCr₂O₄. However, if oxygen or air are admitted into the cell in the same temperature range the absorptions in the 1000–800 cm⁻¹ range reappear quickly.

This behaviour agrees with the known p-type semiconducting behaviour of $MgCr_2O_4$.^{21,22,28,29} In fact, $MgCr_2O_4$ in oxidizing atmospheres is partly oxidized mainly at the surface²⁹ giving rise to $MgCr_2O_{4+x}$, and is associated with the appearance of Cr=O stretching bands of high-valency chromium in the region 1050–800 cm⁻¹. On the other hand, interaction with reducing agents, like hydrocarbons, oxygenated compounds and hydrogen,²³ causes the nonstoichiometric oxygen to be destroyed, producing nearly stoichiometric MgCr₂O₄.

Our data show that redox cycles are relatively fast in the temperature range 573-773 K, *i.e.* in the range where this



Fig. 2 FTIR spectra (OH-stretching region) of $MgCr_2O_4$ disc outgassed at 723 K: (a) oxidized sample; (b) sample previously reduced in hydrocarbon atmosphere (673 K, 150 Torr)

compound is active as an oxidation catalyst^{15,16,19,20} and that the analysis of the IR spectrum in the region 1050–800 cm^{-1} allows the oxidation state of the catalyst to be monitored.

Reduction also causes the growth of a band near 3750– 3650 cm⁻¹, due to free surface hydroxy groups [Fig. 2(b)], while bands due to adsorbed hydrocarbon residues may also be present in the region $1800-1200 \text{ cm}^{-1}$ [Fig. 1(d)].

As discussed recently,¹⁴ the surface acidity may have a relevant role in the catalyst oxidation activity and selectivity. Therefore, we tested the surface acidity of oxdized $MgCr_2O_{4+x}$ and of nearly stoichiometric $MgCr_2O_4$ via adsorption of pyridine as probe (Fig. 3). The spectrum of pyridine on the 'reduced' nearly stoichiometric catalyst shows sharp bands at 1607, 1576, 1488, 1443, 1219, 1148, 1068 and 1042 cm^{-1} , associated with pyridine coordinated over Lewis acidic Cr³⁺ sites.³⁰ The spectrum of pyridine adsorbed on the oxidized sample shows the same pattern but with additional bands. Sharp peaks at 1593 and 1033 cm⁻¹ persist after outgassing at room temperature (RT) and are associated either with physisorbed pyridine or with species bonded to OH groups. This species is not so evident on the reduced sample, which might suggest the presence of Hbonding with the hydroxy groups that are responsible, in the



Fig. 3 FTIR spectra of pyridine adsorbed on oxidized $MgCr_2O_4$ at room temperature (a), and after successive outgassing for 30 min at room temperature (b), 373 K (c) and 423 K (d); (e) as (b) but on a pre-reduced sample

activated oxidized sample, for the broad band near 3500 cm^{-1} [Fig. 2(*a*)].

Additionally, two other weak bands at 1640 and 1538 cm^{-1} are also evident and persist after outgassing at 373 K; these bands are associated typically with pyridinium cations, produced by protonation of pyridine by hydroxy groups of sufficient Brønsted acid strength.

These data show that the oxidized catalyst $MgCr_2O_{4+x}$ has medium Lewis acidity, similar to that of the reduced one, but is also a weak Brønsted acid, having active hydroxy groups able to interact with pyridine by H-bonding and by protonation. Behaviour similar to the above was found in the case of oxidized and reduced Cr_2O_3 (using ammonia as the basic probe molecule³¹) and is ascribed to the greater covalency of the Cr^{n+} —O bond (n = 6 or 5) compared with the Cr^{3+} —O bonds, resulting in a stronger acidity of the OH bonded to the high-valency Cr than that bonded to Cr^{3+} .

The subtraction spectra relative to pyridine adsorbed on the oxidized sample also show a negative sharp band at 1003 cm^{-1} . This band has been assigned above to Cr=O stretching of a chromate species. Its disappearance upon pyridine adsorption provides evidence for the ability of the corresponding species to interact with pyridine. It seems reasonable that the band at 1003 cm^{-1} is due to the Cr=O stretching of a surface chromyl group having one coordinative unsaturation, which can consequently coordinate one pyridine molecule, resulting in a weakening of the Cr=O bond and a decrease of the stretching frequency. Surface chromyl species perturbed by adsorbed pyridine were also observed on oxidized chromia.³²

Interaction with Propene Gas

The FTIR spectrum of the adsorbed species arising from contact of the activated $MgCr_2O_4$ with propene gas at RT is reported in Fig. 4(*a*). Most bands are assigned to molecularly adsorbed propene as deduced from a comparison with the spectra of propene in the gas-phase and adsorbed on other oxide surfaces.^{33,34} The sharp band at 1638 cm⁻¹ is due to the C=C stretching (1653 cm⁻¹ in the gas phase), while those at 1454, 1440, 1420, 1377, 1178 and 1048 cm⁻¹ are associated with different CH deformations, as dicussed previously.^{33,34} The vibrational perturbation is small and does not give a precise indication of the adsorption mode. However, the fact

Fig. 4 FTIR spectra of the adsorbed species arising from propene adsorption over $MgCr_2O_{4+x}$ at room temperature (a), after 30 min at room temperature (b), heating in propene at 373 K (c), and after outgassing at 373 K (d), 432 K (e), 473 K (f) 523 K (g)

that the spectrum is detectable and that the C=C stretching is definitely shifted to lower frequencies show that the interaction strength is non-negligible and probably implies electron withdrawal from the C=C double bond. The vibrational perturbation is weaker than that previously observed on reduced α -Cr₂O₃, but is similar to that occurring on the unreduced FeCrO₃ dehydrogenation catalyst,¹³ whose surface is also 'covered' by chromate species. We can suppose that chromate species, more than reduced Cr³⁺ centres, are involved in propene molecular adsorption. Molecularly adsorbed propene is desorbed by outgassing at RT.

However, other small absorptions that cannot be assigned to adsorbed propene are observed in the spectrum. These bands include a definite peak at 1675 cm⁻¹, almost certainly due to the C=O stretching of an adsorbed carbonyl compound, a broad band near 1600 cm⁻¹ [possibly due to the v_{as} (COO) of a carboxylate species, whose symmetric counterpart is masked by the CH deformations] and sharp peaks at 1350 and 1256 cm⁻¹.

Heating the sample in propene at 373 K causes the formation of stronger bands certainly due to transformation products [Fig. 4(c) and (d)]. The carbonyl band at 1680 cm⁻¹ is now more evident and exhibits a shoulder at 1647 cm⁻¹. The region 1600–1300 cm⁻¹ presents several peaks [1595, 1562, 1452, 1435, 1424, 1382, 1372 (very weak), 1356 and 1330 cm⁻¹], which are associated with COO stretchings of different carboxylate species and CH deformations of several adsorbed species. Weak bands are also observed at 1255 and 1241 cm⁻¹, while below 1200 cm⁻¹ we find peaks at 1180, 1160 (weak), 1115, 1090 and 1030 cm⁻¹, (very strong). The features in the 1200–1000 cm⁻¹ region are assigned to C—C stretchings and/or C—C/C—O coupled stretchings of alcoholate species.

The bands below 1300 cm⁻¹ completely disappear upon further heating at 473 K [Fig. 4(f)], when the components near 1680 and 1640 cm⁻¹ also decrease in intensity at different rates, thus demonstrating that they are not due to the same species. Instead, heating causes a further growth of the absorption in the region 1600–1300 cm⁻¹, which finally exhibits peaks at 1596, 1560, 1500, 1435, 1385 and 1355 cm⁻¹.

Above 523 K all bands decrease in intensity and CO_2 is found in the gas phase. Moreover, Cr=O stretching bands are substantially eroded, providing evidence for the reduction of the oxidized catalyst surface according to the oxidation of the adsorbed organic species.

This behaviour indicates that propene oxidation at the $MgCr_2O_4$ surface gives rise above 373 K to alcoholate and carbonyl species that later transform upon heating to carboxylate species and finally burn above 523 K. The experiments described below are aimed at the individual identification of these oxygen-containing species.

Interaction with Propane Gas

The interaction of the activated oxidized catalyst with 50–150 Torr of pure propane gas has also been investigated in the temperature range 300–773 K. Below 373 K, the interaction does not give any appreciable effect. Above 373 K, instead, this interaction gives rise to new absorption bands (Fig. 5) associated with adsorbed species. Simultaneously, the Cr=O stretching bands at 1000–900 cm⁻¹, typical of the oxidized catalyst, decrease in intensity, and corresponding negative bands appear in the subtraction spectra. The interaction at 423 K produces two broad and rather strong bands at 1600 and 1440 cm⁻¹ and weaker components at 1380 and 1350 cm⁻¹. Together with these absorptions, a pronounced band split at 1702 and 1692 cm⁻¹ and weaker bands at 1245, 1176





Fig. 5 FTIR spectra of the adsorbed species arising from propane adsorption over $MgCr_2O_4$ and successive evacuation at 423 K (*a*), 453 K (*b*), 473 K (*c*), 523 K (*d*) and 573 K (*e*)

and 1094 cm⁻¹ are found. The features at 1702, 1692, 1245 and 1094 cm⁻¹ disappear progressively upon further heating in vacuum, while the other bands grow and shift slightly to 1595, 1439, 1385 and 1356 cm⁻¹ after heating to 473 K, but later decrease in intensity and disappear above 573 K. Under these conditions, CO₂ is detected in the gas phase. In the CH-stretching region one weak band is observable at 2880 cm⁻¹ after interaction in the 423–573 K range.

A rough assignment of these bands can be proposed at this stage, and will be refined below. The strongest bands at 1595 and 1400 cm⁻¹ are typical of CO₂ asymmetric and symmetric stretchings of carboxylate anions, while the split band at 1702, 1692 cm^{-1} is clear evidence of the formation of a carbonyl compound (C=O stretching). The bands at lower frequencies are associated with CH deformations and/or C-C stretchings. The spectra show that propane interacts with the surface in the temperature range 373-573 K and undergoes paritial oxidation with a consequent reduction of the catalyst surface. Oxygenate species are produced, whose exact structure will be investigated by comparison with the spectra of any conceivable oxidation product of propane directly adsorbed onto the catalyst surface. These oxygenated species underwent further oxidation and burned in the temperature range 573-773 K, with production of gas-phase CO₂.

On the basis of these observations we can conclude that oxidation of propane and propene produces adsorbed species with clearly different IR spectra (cf. Fig. 4 and 5). This suggests that two different oxidation paths operate for the two molecules.

Identification of the Adsorbed Oxygenate Species and of the Oxidation Pathways

The above data showed that partial oxidation products are formed from propene and propane at the surface of our catalyst. The gas-phase partial oxidation of propene is carried out industrially to produce acrolein³⁵ or acrylic acid.³⁶ Other products can be obtained in non-negligible yields over oxide catalysts, *i.e.* acetone,^{2,37–39} propionaldehyde,^{38,39} acetaldehyde,³⁹ acetic acid and C₆ hydrocarbons (hexa-1,5-diene and benzene).^{35,39} Propane catalytic oxidation also gives rise to acrolein,⁴⁰ acrylic acid⁴¹ and propene,⁴² but acetone and acetic acid were also mentioned as by-products. To determine the nature of the adsorbed oxygenate species observed upon propene and propane oxidation over $MgCr_2O_4$, we produced them *via* adsorption of the corresponding carbonyl compounds, carboxylic acids and alcohols.

In Fig. 6 the spectra of the species arising from the adsorption at room temperature of acrolein, acetone, propionaldehyde and acetaldehyde are reported. The bands assigned to the molecular adsorbed species are summarized in Table 1. In the case of acetaldehyde, strong bands of acetate species (1560, 1435 and 1350 cm⁻¹) are already observed, showing its very fast oxidation. Bands arising from oxidized species are also evident, but weak in the cases of acrolein and propionaldehyde. In contrast the only ketone studied, acetone, is apparently almost stable under these conditions.

The spectra of carboxylate species produced by adsorption on MgCr₂O₄ of formic, acetic and propionic acids are shown in Fig. 7. The spectrum of formate species [Fig. 7(*a*)] is characterized by bands at 2975, 2880, 1602, 1390 and 1360 cm⁻¹. The four lower-frequency bands are due to CH stretching, asymmetric COO stretching, CH deformation and symmetric COO stretching, respectively.⁴⁷ The highest-frequency band is due to the combination $v_{as}(COO) + \delta(CH)$.⁴⁷ The band due to the asymmetric COO stretching actually exhibits shoulders on both sides, probably due to the presence of species adsorbed differently or on different sites.



Fig. 6 FTIR spectra of the adsorbed species arising from contact of $MgCr_2O_{4+x}$ with acrolein (a), acetone (b), propionaldehyde (c), acetaldehyde (d), all after adsorption and outgassing at RT



Fig. 7 FTIR spectra of the adsorbed species arising from the adsorption of formic acid (a), acetic acid (b) and propionic acid (c) at RT and after outgassing at RT over $MgCr_2O_4$

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Table 1 Position of the IR absorption bands of adsorbed and pure carbonyl compounds

acrolein ⁴		acetone ^b		propionaldehyde		acetaldehyded					
ads.	gas	ass.	ads.	gas	ass.	ads.	gas	ass.	ads.	gas	ass.
$\frac{1691}{-\epsilon}$	1724	v(C=O)	$\frac{1710}{-1695}$	1731	v(C=O)	$\frac{1721}{-e}{1710}$	1754	v(C=O)	$\frac{1711}{-e}$	1743	v(C=O)
1613	1625	v(C=C)	,			.,			,		
1427	1420	$\delta(\mathrm{CH}_2)^f$	1435	1454 1435	$\delta_{as}(CH_3)$ $\delta_{as}(CH_3)$	1467	1468	$\delta_{as}(CH_3)$			
1366	1360	δ[CH(O)] ^ƒ	1422 1369	1410 1363	$\delta_{as}(CH_3)$ $\delta_{s}(CH_3)$	1413 1395 1347	1423 1395 1340	$\delta(CH_2)$ $\delta[CH(O)]$ w(CH_1)	 1395 1346	1433 1395 1352	$\delta_{as}(CH_3)$ $\delta[CH(O)]$ $\delta(CH_2)$
1281 1176	1275	δ(CH=)	1240			1253	1254	$t(CH_2)$	1540	1552	v _s (C113)
4 1170	1158	v(C-C)	$\frac{-e}{1232}$	1215	$v_{as}(CCC)$	1178	1138	v(C-C)	1179	1114	v(C-C), r(CH ₃)
			1094	1090	w(CH ₃)	1096	1100	v(C-C)	1102	1107	γ(CH ₃), r(CH ₃)

^a Ref. 43. ^b Ref. 44. ^c Ref. 45. ^d Ref. 46. ^e Splittings due to the presence of different sites. ^f Coupled modes.

The spectrum of acetate species [Fig. 7(b)] is characterized by strong bands at 1560 and 1435 cm⁻¹, the latter being more intense and sharper than the former, assigned to the asymmetric and symmetric COO stretchings. At the lowerfrequency side a sharp peak at 1350 cm⁻¹ is observed, assigned to the symmetric CH₃ deformation, while a very weak band is found near 1055 cm⁻¹, probably due to methyl rocking.⁴⁸ Acetate species are characterized by extremely weak CH stretchings, with a sharp band at 2935 cm⁻¹ and broader ones at 3015 and 2990 cm⁻¹.

The spectra of propanoate species are, as expected, more complex. In the v(CH) region three sharp and rather strong bands are observed at 2978, 2944 and 2886 cm⁻¹. In the lower-frequency region, the strong and broad bands at 1560 and 1425 cm⁻¹ are associated, as always, with the asymmetric and symmetric COO stretchings. Additional sharp but strong peaks are found at 1471, 1380 (shoulder), 1301 and 1080 cm⁻¹, which can be assigned to CH₃ asymmetric and symmetric bending, CH₂ deformation (probably a rocking mode) and C—C stretching.⁴⁹

The adsorption and oxidation of C1, C2 and C3 alcohols has also been investigated; some of these experiments gave valuable information for the identification of propane and propene oxidation pathways. The spectra of the adsorbed species arising from allyl alcohol adsorption on MgCr₂O₄ are shown in Fig. 8. Most features correspond closely with the spectrum of adsorbed acrolein [Fig. 6(a)], *i.e.* strong C=O stretching at 1690 cm⁻¹ (moving to lower wavenumbers with decreasing coverage), weak C=C stretching 1613 cm⁻¹, sharp CH deformations at 1427, 1366 and 1281 cm⁻¹ (the last weak) and sharp C-C stretching at 1176 cm^{-1,12,43} The additional bands at 1640 and 1021 cm⁻¹ can be assigned¹² to C=C and C-O stretching of allyl alcoholate species. So allyl alcohol is partly oxidatively dehydrogenated to acrolein at RT. Further oxidation of acrolein gives rise to carboxylate species from RT to 423 K, when the aldehyde has almost disappeared. In the complex spectrum of the carboxylate species arising from allyl alcohol oxidation, features assignable⁴⁵ to formate species (1600, 1390 and 1360 cm⁻¹) and acetate species (1560, 1435 and 1350 cm⁻¹) are certainly present. However, additional components like the sharp shoulder at 1640 cm⁻¹ [v(C=C)], the bands near 1500 and 1440 cm^{-1} (COO stretchings) and the bands near 1370 and 1270 cm⁻¹ (the last a shoulder, CH deformations) correspond to those reported for acrylate species.12,50,51

The spectra of the adsorbed species arising from contact of propan-2-ol with the catalyst are shown in Fig. 9. According to previous studies, $^{12.52}$ the three bands at 1163, 1128 and



Fig. 8 FTIR spectra of the adsorbed species arising from allyl alcohol adsorption over $MgCr_2O_{4-x}$ at RT (*a*), and after successive outgassing for 30 min at RT (*b*), 373 K (*c*), 423 K (*d*), 473 K (*e*), 523 K (*f*), 573 K (*g*)



Fig. 9 FTIR spectra of the adsorbed species arising from propan-2ol adsorption over $MgCr_2O_{4+x}$ at RT (a), and after successive outgassing at 373 K (b), 423 K (c), 473 K (d), 523 K (e), 573 K (f) and 623 K (g)

1103 cm⁻¹ characterize the 2-propoxy species (coupled C-C and C-O stretchings) produced by propan-2-ol dissociation, while the broad band at 1284 cm⁻¹ characterizes the undissociated adsorbed propan-2-ol (COH in-plane deformation). However, the sharp bands at 1710 and 1235 cm^{-1} , due to C=O stretching and C-C-C asymmetric stretching of adsorbed acetone [Fig. 6(b) and Table 1], show that propan-2-ol is oxidatively dehydrogenated at RT on the catalyst surface. The bands at 1467, 1385 and 1347 cm⁻¹ are associated with CH deformations of the three species. After the sample is heated, the 2-propoxy bands disappear near 420 K when the acetone bands rise to their maximum intensity. Later, acetone bands also decrease in intensity and disappear, while the bands at 1580, 1435, 1385 and 1350 cm^{-1} grow. These bands are due to a mixture of formate and acetate species [Fig. 7(a) and (b)].

The most intense bands, assigned here to 2-propoxy groups and acetone, are also observed (with small shifts) in the spectrum of the species arising from propene transformation (Fig. 4); however, they are in this case very weak. In contrast, the strong bands at 1680, 1640 and 1030 cm⁻¹ observed there cannot be assigned to these C₃ species containing oxygen at C₂. Finally, the complex spectrum of the carboxylate species arising from propene oxidation is definitely different from that of the species arising from propan-2-ol oxidation. This allows us to conclude that the pathway involving oxygen insertion at C₂, definitely predominant on V_2O_5 —TiO₂ oxidation catalysts,¹² is of only minor importance for MgCr₂O₄. However, the most prominent features of the spectra of the adsorbed species arising from propene oxidation (Fig. 4) are definitely similar to those of the species arising from allyl alcohol oxidation (Fig. 8).

The spectral region 1200-1000 cm⁻¹ is dominated by C-O or coupled C-C/C-O stretchings of alcoholate-like species. The spectra obtained after propene interaction at 373 K with the catalyst surface show a prominent sharp band at 1020 cm⁻¹, and a complex pattern in the region 1150–1090 cm⁻¹. Comparison with the spectra of the surface species arising from ethanol and propan-1-ol adsorption (Fig. 10) allows us to exclude the formation of ethoxy and 1-propoxy species from propene in significant amounts. In fact, both these species are characterized by a main sharp band near 1040 cm⁻¹ and other components in the range 1120-1040 cm⁻¹. In contrast, the bands of alkoxy groups arising from propene are those typical of allyl alcoholate species [1020 cm^{-1} , Fig. 7(a)] and 2-proposy species [1150-1090 cm⁻¹ Fig. 6(a)]. Analogously, no evidence is found for adsorbed acetaldehyde and propionaldehyde in the spectra of the species arising from propene adsorption. In conclusion, comparison of the spectrum of the adsorbed species arising from propene oxidation with those arising from allyl alcohol oxidation shows that the same species are formed and dominate the spectra in both cases, although 2-propoxy species and adsorbed acetone can also be found, in small amounts.

In the spectra of the species arising from propane oxidation (Fig. 5), bands due to acetone (near 1700 and 1240 cm⁻¹) can be found. For this reason acetone adsorption and oxidation has been studied in detail (Fig. 11). At room temperature, adsorbed acetone gives rise to sharp and intense bands, as summarized in Table 1. In the temperature range 423-573 K acetone is converted to carboxylate species. Comparison of the spectra in Fig. 11(*d*) and (*e*) with those reported in Fig. 7 shows that the former are due to a mixture of acetates and formates. At this temperature ketone species are no longer observed: the typical bands at 1710 and 1233 cm⁻¹ have disappeared. Obviously, the spectra of the species arising from acetone and propan-2-ol transformation are very similar (*cf.* Fig. 8 and 11).



Fig. 10 FTIR spectra of the adsorbed species arising from contact of $MgCr_2O_{4+x}$ with ethanol (a) and propan-1-ol (b) at room temperature

Comparison of the spectra of the adsorbed species arising from oxidation of propane with those due to species arising from adsorption and oxidation of acetone strongly supports the assignment of the carbonyl species formed by propane oxidation as acetone. This is due to the close correspondence of most band positions, as well as of the further oxidation products of both molecules.

The absence of the strong bands at 1470, 1300 and 1080 cm^{-1} in the spectra of the adsorbed species arising from propane oxidation on the MgCr₂O₄ surface clearly argues against the presence of propanoate species. On the other



Fig. 11 FTIR spectra of the adsorbed species arising from acetone adsorption at room temperature over $MgCr_2O_4$ and following evacuation at RT (a), 423 K (b), 473 K (c), 523 K (d), 573 K (e), 623 K (f), 673 K (g)

(h)

(C

1600

1400

wavenumber/cm⁻¹

Fig. 12 FTIR spectra of adsorbed species arising from formic acid

adsorption over MgCr₂O₄ at 373 K (a) and following decomposition

hand, the absence of a sharp v(C=C) band in the region near

1635 cm⁻¹ and of a COO asymmetric stretching component

near 1500 cm⁻¹, characterizing adsorbed acrylate species (see

above), precludes the presence of acrylate and, consequently, C3 carboxylate species are apparently not formed at all. Similarly, no trace is found of the C₃ aldehydes acrolein and pro-

pionaldehyde (cf. Fig. 5 and 6). In contrast, the spectra of

carboxylate species arising from both propane and acetone oxidation can easily be obtained from a sum of the spectra of

acetate and formate species. From this analysis we conclude

that carboxylate species are obtained by the oxidative cleav-

The study of the species arising from adsorption of $C_1 - C_3$

acids as well as of the corresponding aldehydes and alcohols

allowed us to determine the stability range of these adsorbed

species on MgCr₂O₄. For completeness, we also studied the

stabilities of the carboxylate species produced by propane

oxidation, i.e. formates and acetates. As mentioned above, the

age of the C(1)-C(2) bond of acetone and propane.

Thermal Evolution of Carboxylate Species

1200

1000

(a)

1800

3.4

3.2

3.0

2.8

2.6

2.4

2.2

2.0

1.8

2000

at 473 K (b) and 573 (c)

absorbance

The evolution of acetate species with temperature is shown in Fig. 13. Acetates, characterized by bands at 1560, 1435, 1350 and 1055 cm^{-1} (see above), are substantially stable up to 573 K, while they progressively disappear in the range 573-773 K, giving rise to bands due to carbonate species and to gas-phase carbon oxides. However, their disappearance is accompanied by a strong decrease of the Cr=O stretching bands in the region 1000-800 cm⁻¹. This provides evidence that the disappearance of these species is due to their overoxidation to carbon oxides, with a parallel reduction of the catalyst surface.

Our data show that formate species undergo decomposition below 573 K, so they are very unstable at the temperature at which propane begins to be oxidized. Acetate species, instead, burn at higher temperatures with a consequent reduction of the catalyst; they are almost stable up to above 573 K.

Discussion

Mechanism of Propene Oxidation at the MgCr₂O₄ Surface

The present results show that propene reacts with the surface of oxidized MgCr₂O₄ at room temperature, but this reaction becomes more evident near 373 K when adsorbed acrolein and allyl alcoholate species are observed, although acrylate species (and perhaps other carboxylate species) have already appeared. However, acrolein and allyl alcohol in the temperature range 373-473 K are rapidly oxidized, giving rise to acrylate species as the predominant products, which become unstable above 523 K, being burnt. Thus, we have provided evidence for the main oxidation pathway of propene on $MgCr_2O_4$ (Scheme 1).

This pathway implies the breaking of the allylic C-Hbond with a subsequent oxygen insertion to give allyl alcoholate species, which are, in fact, observed via the detection of

CH3-CH2-CH3 CH2=CH-CH2 CH₃· -СН₃ =CH-CH2 CH-CH2=CH CH=O CH₃--CH₃ c CH2=CH -C=C à н CH₃ ₀^{,c}≈ہ م^{ج, C} جرم

Scheme 1 Propane and propene oxidation pathways and their connection at the surface of the oxidized MgCr₂O₄ catalyst

co

- CO2



Fig. 13 FTIR spectra of adsorbed species arising from acetic acid adsorption over MgCr₂O₄ at 473 K (a), 573 K (b), 673 K (c), 773 K

(d)



the typical sharp C-O stretching band at 1020 cm⁻¹. Further evolution strictly parallels allyl alcohol oxidation. The key step in this mechanism is the breaking of the allylic C-H bond. The active site in our case is identified as a $C_{\Gamma}^{n+} = O$ site (n = 5 or 6), which should be reduced to $Cr^{(n-2)+}$. A likely intermediate in this process is the formation of an allyl species, either anionic or radical, as proposed for the selective oxidation of propene to acrolein.² However, such an intermediate can be observed only if its formation is faster than its further reaction with surface oxide species to give allyl alcoholate. Anionic allyl species have been unequivocally identified on ZnO_{2}^{53} and ZrO_{2}^{34} which are not active allylic oxidation catalysts (so the subsequent oxygen insertion should be slow or may not occur at all) and have a strong basic character. On true allylic oxidation catalysts such as uranyl antimonate,⁵⁴ acrolein was found upon propene adsorption, but neither the allyl intermedite nor allyl alcoholate were detected spectroscopically. This is probably because anionic or radical-like allyl species are oxidized so rapidly to allyl alcoholate species that they cannot be observed. This implies that the rate-determining step is the first hydrogen abstraction from the methyl group. Also allyl alcoholates can be rapidly dehydrogenated to acrolein at the temperature at which they form, so their detection can be difficult too. This situation differs from that found in the case of toluene oxidation to benzaldehyde on vanadia-titania.55 In this case, the rate-determining step is probably the reaction of the intermediate benzyl species with surface oxygen to give benzyl alcoholates, which are later rapidly dehydrogenated. For this reason benzyl species are observed while benzyl alcoholates are not.55 The reverse is observed here for allyl and allyl alcoholate species.

Besides the allylic oxidation pathway at C(1), another propene oxidation pathway is evident on MgCr₂O₄ (although it is definitely of minor importance) with the production of species oxidized at C(2) (Scheme 1). According to our previous data,¹²⁻¹⁴ this pathway is associated with the electrophilic attack of weakly Brønsted acidic OH groups of the alkene double bond, according to the Markovnikov rule, giving rise to secondary propoxy species that are later oxidized to acetone, and finally undergo oxidative breaking of the C(2)—C(3) bond leading to acetate and formate species. This pathway (called oxidative hydration²) was shown to be predominant on vanadia–titania,¹² which is less active as an oxidation catalyst and gives mixtures of acetone and acrolein upon propene oxidation.⁵⁶

Mechanism of Propane Oxidation at the MgCr₂O₄ Surface

The present data show that propane gas interacts with the surface of oxidized MgCr₂O₄ starting from above 373 K giving rise to adsorbed oxygen-containing species that can further be oxidized to carbon oxides. Complete burning of hydrocarbon and oxygenated organic compounds by the oxidized MgCr₂O₄ catalyst is observed at 773 K. The data presented here also give a relatively simple picture of the propane combustion pathway on this surface. In fact, the first detectable adsorbed oxidation product is acetone, which is later converted into a mixture of formate and acetate species, by oxidative cleavage of the C(1)-C(2) bond. Formate species rapidly decompose while acetate species burn only near 773 K (Scheme 1, left-hand side). Surprisingly, compounds oxidized at C(1) like acrolein and acrylate species are very evident upon popene oxidation under the same conditions, but are not found at all with propane. So, the pathways of propane and propene oxidation (Scheme 1, right-hand side) are considerably different. This supports the data reported several years ago by Yao⁵⁷ which showed that the

oxidation pathways of alkanes and alkenes are different on α -Cr₂O₃.

The formation of acetone from propane implies propane activation at C(2). This agrees with the lower dissociation energy of C—H at secondary carbons (—CH₂— methylene groups, 94 kcal mol⁻¹) with respect to C—H at primary carbon atoms (methyls, 99 kcal mol⁻¹²). Accordingly, also the C—H bond dissociation energy at the primary carbon in the case of propene is in agreement with the lower energy for C—H bond cleavage at an allylic methyl group (77 kcal mol⁻¹) with respect to that of a vinylic group (105 kcal mol⁻¹). The lower temperature at which propene oxidation to acrolein is observed, with respect to propane oxidation to acetone, is justified by the lower C—H bond dissociation energies of allylic methyls with respect to alkane methylenes.

It seems reasonable, although it is not strictly proved here, that cleavage of the first C—H bond of propane is followed by insertion of an oxygen before the second C—H bond at C(2) is broken. This hypothesis is confirmed by the detection of allyl alcoholates from propene, as well as by studies which are now in progress⁵⁸ concerning the oxidation of other hydrocarbons. Therefore, 2-propoxy species should be the first intermediates in propane oxidation, although they cannot be observed easily because at the temperature at which their formation is sufficiently fast, their further transformation to acetone is even faster, making their concentration zero.

The active site for C—H bond scission is certainly associated with the high-valency Cr ions responsible for the Cr=O stretching bands in the region 1000-800 cm⁻¹. It is not excluded that the sites active for propane activation do not entirely coincide with those active for propene oxidation. In fact, it is possible that only the most active sites can attack both molecules, the least active ones being able to attack propene only. On the other hand, sites able to break the C—H bonds of the propene methyl groups can cooperate with sites able to interact with the alkene double bond.

Acetone is a rather reactive molecule, and this causes its strong adsorption and further oxidation at the C(2)-C(3) bond to formate and acetate species. The last stages in propane combustion correspond to the evolution of acetate and formate species. However, the behaviour of these two species is different. Formates decompose rapidly, giving CO, while acetates need further oxidation to give finally CO_2 .

Comparison with Other Catalytic Systems: Activity–Selectivity in Heterogeneously Catalysed Oxidation of Propene and Propane

The data reported above concern surface reactions observed to take place from an oxidized $MgCr_2O_4$ catalyst surface with propane and propene. However, they do allow a development of the theory of catalytic hydrocarbon combustion mechanisms on metal oxides. The conditions under which these interactions are observed (373–773 K) agree roughly with those at which this compound was found to act efficiently as a combustion catalyst for propene and light alkanes.^{15,58} Our data show that propene combustion can be obtained in the absence of gaseous oxygen, totally at the expense of the Cr=O oxidized sites of the catalyst, which in the 573–773 K range are quickly reoxidized by gas-phase oxygen. This strongly supports the idea that catalytic combustion of propene and propane over this catalyst can occur completely with a Mars–Van Krevelen type mechanism.⁵⁹

Our data also show that adsorbed partial oxidation products are formed upon propene and propane oxidation at the surface of $MgCr_2O_4$, well known to be essentially a nonselective combustion catalyst. These adsorbed partial oxidation products are intermediates in the formation of carboxylate species, already recognized as intermediates of propene combustion over chromia-based catalysts.^{51,60}

The data concerning propene oxidation on this combustion catalyst can be discussed in relation to previous data obtained on selective oxidation catalysts.¹¹⁻¹⁴ Similar surface reaction pathways are observed for selective and nonselective oxidation catalysts. However, important differences can be found in the temperature at which the same steps occur on different catalysts. Propene activation is observed to commence on $MgCr_2O_4$ at 373 K, while on $Mg_3(VO_4)_2$ it starts at near 523 K.^{14,61} The much lower reactivity of Mg vanadate with respect to Mg chromite with propene explains why the former acts as a selective catalyst for propane oxidative dehydrogenation to propene,⁴² while the latter is a nonselective combustion catalyst for both propane and propene.¹⁵ Acrolein is also definitely oxidized on MgCr₂O₄ at 373 K, while it is much more stable on the surfaces of V_2O_5 -Ti O_2 ¹² and MoO₃-Ti O_2 .⁶² This could explain why these catalysts are rather selective in the oxidation of propene to $\operatorname{acrolein}^{63}$ while MgCr₂O₄ is not.

The reaction pathway proposed in Scheme 1 implying propane activation at C(2) on $MgCr_2O_4$ also agrees with the behaviour reported for another chromite, $ZnCr_2O_4$, as a catalyst for *n*-butane oxidation. In fact, over this catalyst complete butane combustion has been observed at 623 K, while at 493 K butane oxidation gives acetic acid and methyl vinyl ketone [*i.e.* compounds functionalized at C(2)] with rather high selectivity.⁶⁴ On the other hand, acetic acid is frequently reported as a product of propane oxidation over oxide catalysts:⁶⁵ this could be the result of activation at C(2) and agrees with the stability of acetate species to overoxidation, evidenced above, allowing desorption of acetic acid.

According to Scheme 1, propene is not an intermediate in the main propane oxidation path, so that propene and propane oxidation follow predominantly two different pathways on the MgCr₂O₄ surface. On the other hand, our data suggest that decomposition of 2-propoxide groups (the first intermediate starting from propane) to propene and an OH group is competitive with its oxidative dehydrogenation giving rise to acetone (Scheme 1). This competition could provide a 'cross-roads' between alkane oxidative dehydrogenation and oxidation at C(2). On $MgCr_2O_4$, the dehydrogenation of 2-propoxy groups to acetone is much faster than their decomposition to propene, which is consequently not an intermediate for further oxidation. This makes $MgCr_2O_4$ an oxidation (combustion) catalyst rather than an oxidative dehydrogenation catalyst for propane. This picture finds support in the comparison between the behaviour of MgCr₂O₄ and Mg vanadate catalysts, which are completely opposite. On Mg vanadates, in fact, alcoholate species decompose quickly at very low temperature, giving only traces of oxidized species.^{14,61} Therefore, the equilibrium propene \rightleftharpoons 2-proposide is displaced left (towards the alkene) on Mg vanadates, in contrast to Mg chromite where it is shifted to the right (towards the alkoxide). This agrees with the behaviour of Mg vanadates as oxidative dehydrogenation catalysts for production of propene from propane.⁴²

Comparison of the behaviour of the different metal oxide catalysts allows us to apply the generalization of the mechanism of Scheme 1 to all of them. The behaviour of an oxidation catalyst is strongly influenced by its acid-base properties. In fact, the decomposition of the alcoholate species giving rise to the alkene is a purely acid-base reaction. According to our data, the equilibrium propene $\rightleftharpoons 2$ propoxide is displaced left (towards the alkene) on both very basic and very acidic catalysts (in fact, alcohol dehydration is either acid- or base-catalysed⁶⁶), while it is shifted right (towards the alkoxide) for catalysts with medium Brønsted acidity. In fact, Mg chromite shows Brønsted acidity while Mg vanadate does not.⁶¹

The propane oxidative dehydrogenation pathway (through propene) can be followed by allylic oxidation, giving rise to acrolein and/or acrylic acid. Therefore, catalysts with no Brønsted acidity but strong Lewis acidity (allowing decomposition of 2-propoxy groups to propene) and very active allylic activation centres are the best candidates for propane oxidation to acrolein. These data support the idea that the main difference between a selective and a non-selective oxidation catalyst is in its ability to overoxidize selected products. This leads us to propose that a combustion catalyst is one that is able to perform selective oxidation, but from which the partial oxidation product is unable to be desorbed without further oxidation. This is supported by two observations: (i) Efficient partial oxidation processes from hydrocarbons are limited to the production of compounds such as acrolein, acrylonitrile, maleic and phthalic anhydrides, which have intrinsic chemical stability owing to their ability to delocalize ionic charges. Compounds whose ionic charges are more localized (like acetone or the non-conjugated aldehydes, with respect to acrolein) are more reactive towards the oxide catalyst surface (which always contains electrophilic and nucleophilic sites) and are desorbed less easily. (ii) Basic dopants frequently increase the selectivity but decrease the activity of partial oxidation catalysts, becase they lower the adsorption strength of the oxygenate compounds (which are always Lewis bases) on the surface (which always contains Lewis acid sites), but this tends to limit the activity for C-H bond scission (which needs Lewis acidity¹⁴).

Therefore, the main requirement of a partial oxidation catalyst is inactivity towards overoxidation of the desired product, in spite of being a poorly active catalyst. This is the case for V_2O_5 - and MoO_3 -based catalysts, which are generally much less active than typical combustion catalysts, like, among others, those based on Cr_2O_3 .

This view is only partially in disagreement with that of Haber^{2.67} which associates selective oxidation with nucleophilic oxygen species (O_2^- lattic oxide ions) and combustion with electrophilic oxygen (O_2 , O_2^- and $O_2^{2^-}$). Our study confirms that lattice oxygen performs selective oxidation, but suggests that it may also be involved in non-selective combustion pathways. This does not preclude the involvement of electrophilic oxygen (together with nucleophilic oxygen) in a different combustion pathway.

Conclusions

The FTIR study of propene interaction with the surface of oxidized MgCr₂O₄ shows that the alkene is totally oxidized in the temperature range 573-773 K at the expense of surface $Cr^{n+}=O$ (n = 5 or 6) species. However, this occurs through two different 'selective oxidation' pathways at the surface, one of which involves activation at C(1) via allyl alcoholate species, and the other activation at C(1) via 2-propoxy species. Combustion seems to involve essentially successive overoxidation of the partial oxidation products.

Propane is oxidized at the same surface to acetone, which further transforms into acetates and formates and, finally, into carbon oxides; this occurs in the 573–773 K range. This oxidation pathway is completely different from the main one undergone by propene. The surface reactions observed allow us to propose a detailed reaction pathway for both selective and unselective oxidation of propane and propene. On the basis of the comparison of these data with data available for

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other catalytic systems we propose this pathway as a general mechanism for alkane and alkene catalytic oxidation.

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