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IR studies on the activation of C–H hydrocarbon bonds on oxidation catalysts

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Abstract

The total oxidation of propane and its oxy-dehydrogenation to propene have been studied on spinel-type catalysts Mn_3O_4, Co_3O_4 and $MgCr_2O_4$ in a flow reactor and in an IR cell. Analogous studies have been performed on the oxy-dehydrogenation of *n*-butenes to 1,3-butadiene over $MgFe_2O_4$. Information on the reaction mechanism have been reached. The activation of the hydrocarbons is thought to occur by abstraction of a hydrogen from the weakest C–H bond, with a simultaneous reduction of a surface site and with the formation of a surface alkoxy-group. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: C–H hydrocarbon bond; Oxy-dehydrogenation; *n*-Butenes

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1. Introduction

The IR spectroscopic methods are among the oldest instrumental techniques applied to surface chemistry and heterogeneous catalysis [1–4]. The very first beginnings of their use have been reviewed recently by Sheppard [5] and by Tsyganenko [6]. On the other hand, these techniques underwent further developments (e.g. with the developments of Fourier transform instruments and of diffuse reflectance attachments) and are among the most widely applied nowadays. This is because:

1. IR spectrometers are relatively cheap;
2. the fundamentals of IR spectroscopy are well known and completely established;
3. the apparatuses necessary to study catalyst surfaces and catalytic reactions are also easily available.

The successful application of this technique for the characterization of solid surfaces is beyond any doubt. In their books, both Tamaru [7] and Davydov [8] also devoted a chapter to the application of spectroscopic techniques to mechanistic studies of heterogeneous catalytic reactions, where this technique was found to be quite successful. In the issues on "Identification of intermediate species in catalytic reactions", edited by Quinn [9], and "In situ methods in catalysis", edited by Burch [10], some additional successful applications of IR spectroscopic methods were described. Recent review papers published by Tamaru [11], Matyshak and Krylov [12–14] and Busca [15] also showed some successes in the identification of surface intermediate species involved in heterogeneously catalyzed reactions.

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On the contrary, some authors express some doubts on the usefulness of this technique in providing data for determining the mechanisms of heterogeneously catalyzed reactions. In a recent review paper on the methods for the determination of the mechanisms in heterogeneous catalysis [16], Burwell stated that "IR has not been particularly helpful in mechanistic studies of reactions of hydrocarbons on metals" but also concluded that "the application of transient techniques to a combined study of rate and the IR spectrum (...) provide excellent opportunities". In 1984, when FT instruments were at an early stage of development, in a review on "Infrared spectroscopy in catalytic research", Peri [17] stated that "rather limited real success has been achieved to date (...) in the search for active intermediates on catalyst surfaces" by IR methods. His conclusion was "it is very unlikely that activated complexes will be found at significant concentrations on any active catalyst" [17].

We will present here some new results obtained in our laboratory concerning studies of the mechanisms of activation of C–H bonds over oxide surfaces, using joint IR and flow-reactor experiments. We will also summarize our view on the use of different IR spectroscopic methods in the studies of reaction mechanisms in heterogeneous catalysis.

2. Experimental

The IR spectra were recorded on a Nicolet Magna 750 Fourier transform instrument, using pressed disks of pure catalysts powders. Before experiments, the samples were activated by outgassing and by calcination in oxygen or in air at 573–773 K into the IR cell. After the admission of the reactant gases in the IR cell, the temperature was raised step-by-step and both the gas-phase spectra and the catalyst spectra were recorded in static conditions for each step.

Catalytic tests of propane oxidation were carried out at atmospheric pressure in a continuous flow tubular glass reactor with an internal chamber where the catalyst is packed, and an external co-axial tube filled with glass spheres to have a pre-heated homogeneous gas phase. The effects of feed gas composition, contact times, and reaction temperatures have been investigated. Hydrocarbons, oxygenates and permanent gases were analyzed among the products by two on-line gas chromatographs (HP5890).

The preparation and the solid state and surface characterization of Mn_3O_4 (24 m^2/g) [18], $MgCr_2O_4$ (53 m^2/g) [19–22], Co_3O_4 (15 m^2/g) [23] and $MgFe_2O_4$ (110 m^2/g) [24] have been described previously. XRD and FT-FIR analyses show that the samples consist of the spinel-type phases, very well crystallized.

3. Results and discussion

3.1. *Propane oxidation over spinel-type metal oxides*

3.1.1. *Propane oxidation over Mn_3O_4*

The results of some experiments concerning propane oxidation on Mn_3O_4 are reported in Fig. 1.

In excess of oxygen (right), propane completely burns above 600 K giving CO_2 selectivity very near to 100%. At lower temperatures conversion is incomplete and propene is produced with greater selectivity, the lower is the temperature. In excess of propane (left), oxygen is totally consumed at 570 K, and again CO_2 and propane are largely the predominant products. However, propene selectivity is higher than in excess of oxygen and is still relatively high (>25%) at total oxygen consumption.

Propane oxidation experiments in the presence of oxygen have also been performed in the IR cell. We find propene (sharp weak bands at 990 and 912 cm^{-1}, twisting and wagging modes, of the terminal $=CH_2$ group [25]) and CO_2 (bands with the typical roto-vibrational contours at 2340 and 667 cm^{-1}, asymmetric stretching and deformation [26]) as the main gas-phase products. The effect of temperature on the absolute intensities of these IR bands is compared in Fig. 2 with the effect of temperature on the molar amounts of the reactants and products found at the exit of the flow reactor. The two trends are parallel.

Looking at the catalyst surface, no evidence for adsorbed species can be found by IR until above 400 K. At 433 K (Fig. 3) bands begin to be formed at 1570, 1540, 1430, 1376 and 1350 cm^{-1}, that can be assigned to a mixture of acetate ions (1540 cm^{-1}, COO asymmetric stretching; 1430 cm^{-1}, COO symmetric stretching) and formate ions (1570 cm^{-1}, COO asymmetric stretching; 1376 cm^{-1}, CH deformation; 1350 cm^{-1}, COO symmetric stretching) [27]. A weak

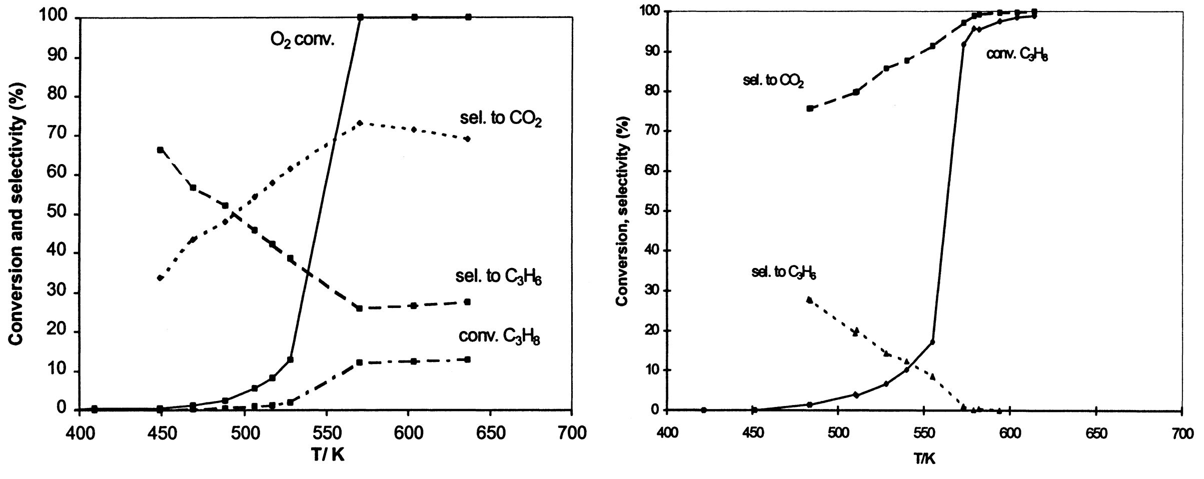


Fig. 1. Flow reactor experiments: conversion of propane and oxygen and product selectivities on Mn_3O_4 in oxygen defect (stoichiometric to oxydehydrogenation) (left); and in oxygen excess (combustion) (right).

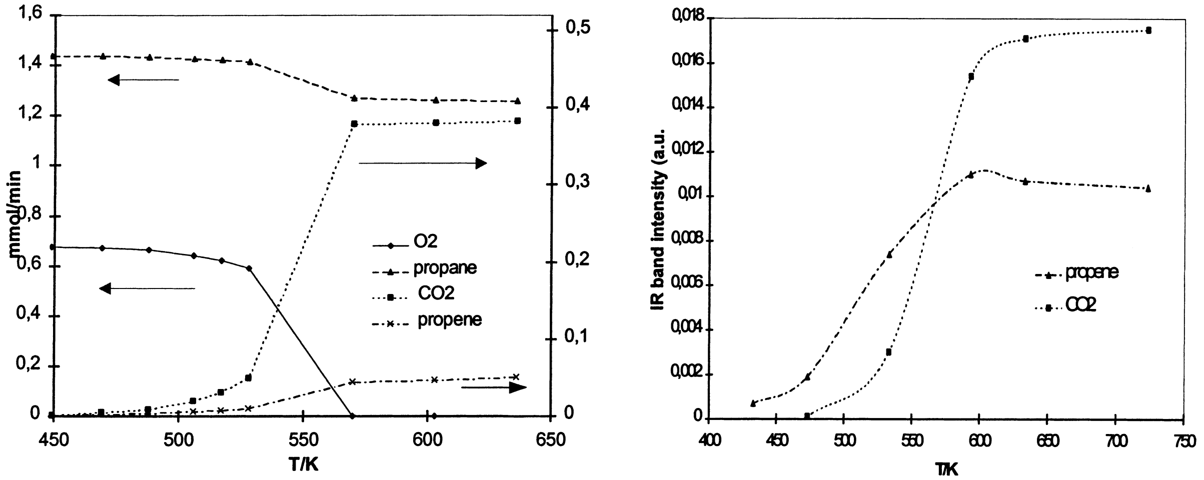


Fig. 2. Conversion of propane and oxygen and products formation (expressed in mmol/min) on Mn_3O_4 (flow reactor experiment) (left) and formation of the same reaction products in the IR cell, related to the intensity of the IR bands (right).

band is also observed at 2862 cm^{-1}, due to a C–H stretching. These bands are stable up to 523 K, when they almost disappear with the formation of bands at 1550 and 1400 cm^{-1}, assigned to carbonate species [28].

The analysis of both surface and gas-phase species in the IR cell strongly suggests that CO_2 arises from the combustion of the carboxylate species (acetates and formates) formed by the reactive adsorption of propane. On the contrary, we did not find any evidence of intermediate species in propene formation from propane.

3.1.2. *Propane oxidation over $MgCr_2O_4$ and Co_3O_4*

The results of studies of propane oxidation over spinel-type Co_3O_4 and $MgCr_2O_4$ have been previously published [21,22]. Cobalt oxide gives rise to substantial conversion of propane starting from near 523 K while on Mg chromite, propane conversion becomes significant above 600 K.

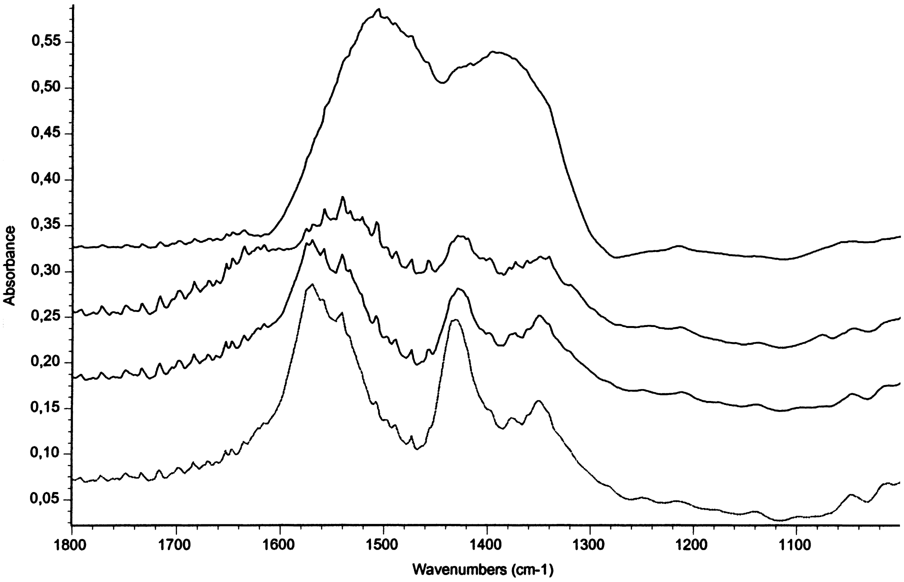


Fig. 3. FT-IR surface species arising from propane oxidation over Mn_3O_4, from bottom: after evacuation at 433, 473, 523, and 573 K.

IR studies [19,20] showed that the interaction of propane with $MgCr_2O_4$ in the range 373–423 K gives rise to strong bands at 1590, 1440, 1385 and 1355 cm^{-1}, due to a mixture of acetate and formate species, and to weaker but well resolved bands near 1700, 1240 and 1095 cm^{-1}, due to adsorbed acetone. This assignment was based on the comparison of these spectral features with those of any hydrocarbon or oxygenate adsorbed species that could be formed by propane oxidation, and in particular, of adsorbed acetone. The data supported the idea that acetone is the primary detectable oxidation product of propane on the $MgCr_2O_4$ surface: acetone is later oxidized at C_1–C_2 giving rise to a mixture of formates and acetates that later burn to carbon oxides as final products.

On Co_3O_4 [23], propane is activated at a very low temperature, apparently both at C_1 and C_2, giving rise to mixtures of acetate, formate, propanoate and acrylate species. This suggests that on Co_3O_4 the same reactivity found also on Mn_3O_4 and $MgCr_2O_4$ takes place, with additional activation of propane at C_1.

3.1.3. *Other light alkane oxidation over $MgCr_2O_4$*

We investigated by IR spectroscopy the interaction of several other hydrocarbons with $MgCr_2O_4$. When the oxidized catalyst disk is put into contact with methane gas, the spectrum of the catalyst is not modified at all up to 773 K, showing that reaction did not occur below this temperature. At 773 K an interaction occurs, as evidenced by the detection of gas-phase CO_2 and by the detection of new absorption bands at 1630, 1520, 1405 and 1222 cm^{-1}, the last very weak, due to water and surface carbonate and bicarbonate species. From these data we conclude that methane molecules burn by reaction with the oxidized catalyst surface at 773 K, and in these conditions, only the final products of these reactions are observed, i.e. CO_2, carbonates, water and the reduced catalyst.

If contact of the activated catalyst with ethane gas is carried out, the reaction is observed at much lower temperature, i.e. already at 423 K. The most intense bands due to adsorbed species are observed at 1600 and 1440 cm^{-1}, due to acetate species. A weak band at 1385 cm^{-1} and a shoulder near 1580 cm^{-1} could be associated to traces of formate ions produced by deeper oxidation. Other sharp peaks at 1470 and 1304 cm^{-1}, together with broad and stronger absorptions centered near 1180 and 1060 cm^{-1}, can tentatively be assigned to dioxy-ethylydene species –O–(CH_3)CH–O–, an adsorbed form of acetaldehyde similar to dioxy-methylene –O–CH_2–O– species produced by formaldehyde adsorption and widely described previously [29]. Heating to 573–773 K gives rise to gas-phase CO_2 and water, surface carbonates and completely reduce the catalyst surface.

Interaction between the $MgCr_2O_4$ catalyst surface and *n*-butane and isobutane is observed to occur, like for propane, in the temperature range 373–423 K. Starting from *n*-butane, the strongest bands are due to surface acetate species. However, sharper bands near 1690, 1475 (very weak), 1385 (sharp and rather strong) and 1175 cm^{-1} are also found and all correspond to evident features in the spectrum of adsorbed methyl–ethyl ketone (C=O stretching, asymmetric and symmetric CH_3 bendings, and C–C–C asymmetric stretching, respectively). A further sharp band at 1025 cm^{-1} could be associated, together with a broader absorption in the range 1150–1100 cm^{-1} to C–O and C–C stretchings of 2-butoxy species, by comparison with the spectrum of adsorbed 2-butanol.

Upon the interaction of isobutane with the surface of $MgCr_2O_4$ at 373 K, formates (relatively more intense than in the previous cases) and acetate species (relatively less intense than in previous cases) are formed again. This provides evidence of the oxidative breaking of two C–C bonds of isobutane, giving rise to two C_1 fragments (formates) and one C_2 fragment (acetates). However, weak but evident bands are also observed at 1245 and 1190 cm^{-1}. These bands are associated to C–C and C–O stretchings of ter-butoxide species, and closely correspond to the bands produced by ter-butanol dissociative adsorption. It is remarkable that ter-butanol oxidation on our catalyst gives rise to the same bands produced also by isobutane, and assigned to acetate and formate species, with the same intensity ratios. This indicates that the C–H bond of isobutane is first broken and a C–O bond is formed, giving rise to ter-butoxide species. These species evolve by breaking of a C–C bond to formate and acetone, that in the same condition, fast transforms to acetate and formates. So, each isobutane molecule gives rise to two formate and one acetate species, while propane oxidation forms one formate and one acetate species and *n*-butane oxidation only forms (at first) acetate species.

These data strongly support the idea that the alkane/$MgCr_2O_4$ interaction occurs by extraction of a hydrogen from the weakest C–H bond of the hydrocarbon, giving rise, as the first intermediate, to the corresponding alkoxide species. However, the less reactive is the alkane, the higher is the temperature needed for activation ($(CH_3)_3CH < CH_3CH_2CH_3 < CH_3{-}CH_3 < CH_4$). On the other hand, the higher is the temperature needed for activation, the deeper is the oxidation of the first detectable surface species (alkoxides→ carbonyls→carboxylates→carbonates). However, this sequence occurs in all cases upon total oxidation. At the conditions in which the reaction actually occurs and CO_2 is formed in the gas phase, only the last species (carboxylates and cabonates) can be found at the catalyst surface.

3.1.4. Oxidation of 2-propanol and acetone over Mn_3O_4

To have information on the possible intermediacy of 2-propoxide species and of acetone in the oxidation of propane on the above spinel-type oxide catalysts, we have investigated also the oxidation of 2-propanol and of acetone. The molar amounts of 2-propanol and of acetone, CO_2 and propene upon 2-propanol oxidation on Mn_3O_4 are reported in Fig. 4 as investigated in the flow reactor (left) and in the IR cell (right). In the flow reactor, 2-propanol starts to be detectable above 323 K giving rise to acetone with nearly 98% selectivity. The conversion grows progressively up to near 85% at 500 K without substantial change in product selectivities. Further increase of reaction temperatures causes conversion to approach 100%, but selectivity to acetone suddenly falls to zero at 535 K when CO_2 selectivity suddenly grows to above 90%. Propene and acetaldehyde (not shown in the figure) and traces of acetic acid are also formed. In agreement with these data, the oxidation of acetone on Mn_3O_4 starts near 473 K, with significant selectivities to acetaldehyde (30%) and traces of acetic acid; conversion rises very high values in the range 510–563 K where only CO_2 is produced.

The results of the IR analysis of the gas-phase species upon a similar experiment performed in the IR cell is shown in Fig. 4, right. The results are well consistent with those found in the flow reactor although the curves appear to be displaced towards the higher temperatures. In fact, the analysis of the gas phase shows that acetone (1738, 1365 and 1216 cm^{-1} with typical roto-vibrational contours, C=O stretching, CH_3 deformation and C–C–C asymmetric stretching, respectively [30]) is the main product of isopropanol oxidation in the range 423–523 K. Above 523 K propene in small amounts (not shown in the

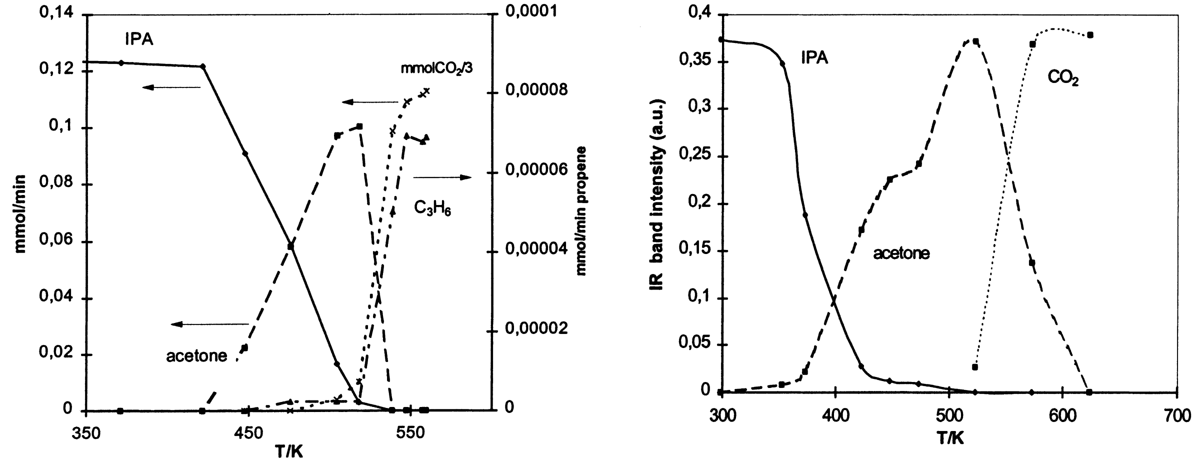


Fig. 4. Conversion in flow reactor of 2-propanol (mmol/min) and products formation (left) on Mn_3O_4 (in oxygen excess) and formation of the same reaction products in the IR cell, following the relative intensity of the IR bands (right).

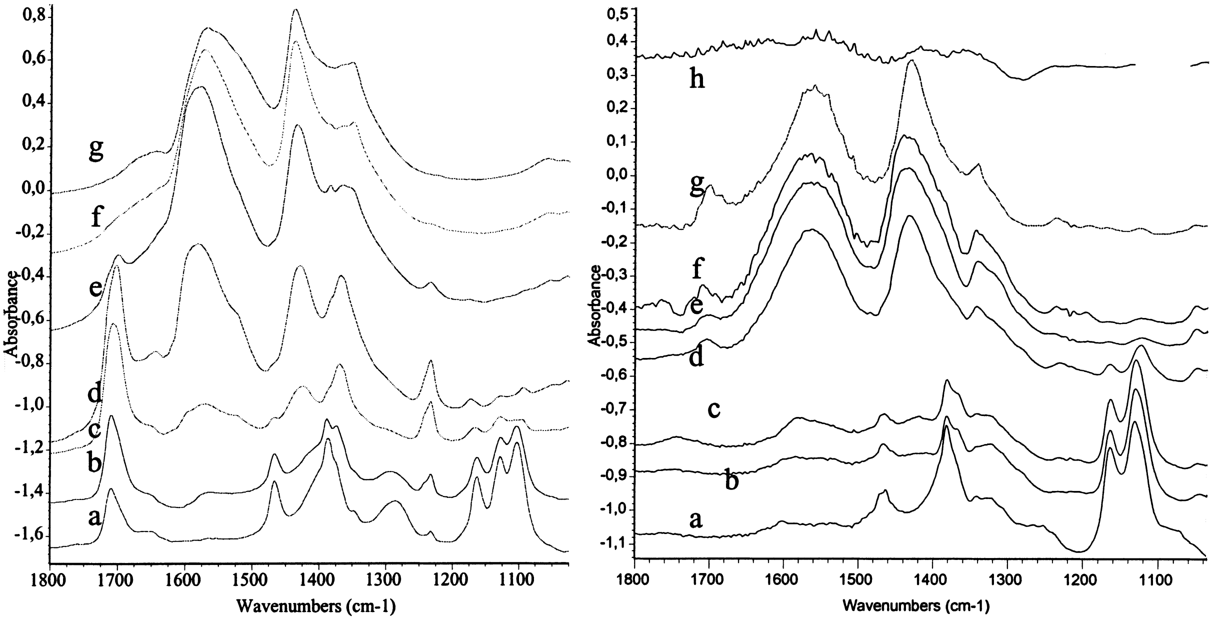


Fig. 5. FT-IR subtraction spectra of the surface species arising from isopropanol adsorption over $MgCr_2O_4$ (A) and Mn_3O_4 (B). (A) spectra recorded at: room temperature for 30 min (a), after evacuation at 373 (b), 423 (c), 473 (d), 523 (e), 573 (f), and 623 K (g). (B) Spectra recorded at: room temperature (a), after evacuation at 353 (b), 373 (c), 423 (d), 448 (e), 473 (f), 523 (g), and 573 K (h).

figure) and CO_2 are mainly observed in the gas phase, while the bands of gas-phase isopropanol and acetone completely disappeared. Working without gas-phase oxygen strongly increases the amount of propene formed.

The analysis of the surface species (Fig. 5, left) shows the predominance at temperatures below 423 K of strong bands at 1462 (methyl asymmetric deformation), 1382 (methyl symmetric deformation), 1340 (methyne in-plane deformation), 1164 and

1129 cm^{-1}, very strong (C–O/C–C coupled stretchings), typical of isopropoxide groups [31]. A weak band at 1690 cm^{-1} observed in the range 273–423 K can be assigned to C=O stretching of adsorbed acetone.

In the range above 373 K such bands begin to disappear while bands at 1570, 1430 and 1379 cm^{-1} grow progressively. These bands, assigned again to a mixture of carboxylate species, disappear progressively above 473 K and bands due to surface carbonates appear at 1550 and 1400 cm^{-1}, very broad.

These data show that isopropoxides formed by isopropanol dissociative adsorption give rise, in excess of oxygen, mainly to acetone, by oxidative dehydrogenation, and that acetone is overoxidized to CO_2, with the intermediacy of acetates and formate species. However, acetone (both gas-phase and adsorbed) and surface 2-propoxides can only be found at $T<373$ K, i.e. well below the temperature at which propane activation is ever detectable. This allows us to propose that adsorbed acetone and adsorbed 2-propanol (i.e. 2-propoxide species) may act as intermediates in propane total oxidation on Mn_3O_4, although they have not been observed spectroscopically from propane. On the other hand, IR studies show that in the absence (or defect) of oxygen, 2-propoxides decomposition gives rise to propene. This strongly suggests that the evolution of 2-propoxides represent a cross-road between the total oxidation way and the selective oxy-dehydrogenation way over Mn_3O_4.

3.1.5. Oxidation of 2-propanol and acetone over $MgCr_2O_4$ and Co_3O_4

Co_3O_4 and $MgCr_2O_4$ behave in the oxidation of isopropanol and acetone in a similar way as Mn_3O_4. In all cases, high selectivities to acetone are found at low isopropanol conversions [21]. The curve of acetone selectivity upon isopropanol oxidation falls down at the same temperature at which the conversion of acetone grows up in acetone oxidation experiments. This suggests that acetone is overoxidized to CO_x at high temperature upon isopropanol oxidation experiments. In all cases, acetone and 2-propanol combustion are found at lower temperatures than propane combustion. This allows us to propose that adsorbed acetone and adsorbed 2-propanol (i.e. 2-propoxide species) may act as intermediates in propane oxidation in all cases.

To obtain indication on this, the adsorption of 2-propanol has been also studied by IR (Fig. 5, left). The main results are the following: 2-propanol is adsorbed in part dissociatively giving rise to 2-propoxide species, as well as adsorbed undissociated alcohol. 2-Propoxide species are oxidized in part at r.t. and completely at 473 K, giving rise to acetone, and later, to acetates and formates that finally give rise to CO_2. This means that at the temperature at which propane starts to be oxidized (i.e. 423 K), isopropoxides, if formed, are already unstable and give rise rapidly to acetone.

3.1.6. Oxidation of propene over Mn_3O_4, $MgCr_2O_4$ and Co_3O_4

The oxidation of propene on the three catalysts is faster than that of propane and even more selective to CO_2. Reactive adsorption of propene on Mn_3O_4 is already found by IR spectroscopy at 373 K, when bands are formed at 2862, 1575, 1425, 1375 and 1350 cm^{-1}. The overall spectrum actually seems closely similar to that described above, arising from the reactive adsorption of propane above 430 K, so that we can assign the observed bands again to a mixture of formate and acetate species. Again these bands disappear near 523 K and CO_2 is observed concomitantly in the gas phase. These data agree with flow reactor experiments that show propene combustion over this catalyst with a light-off just near 540 K.

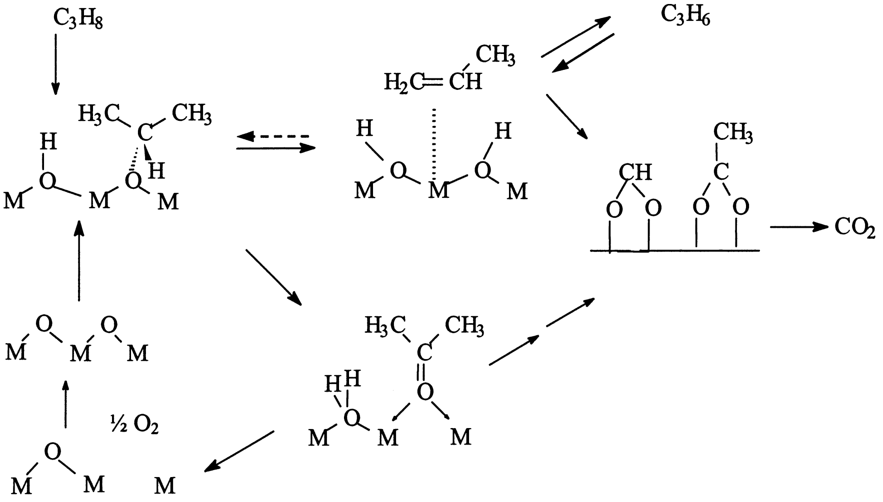
3.1.7. Proposal of a generalized mechanism for propane activation and oxidation over metal oxide catalysts

The data reported above strongly suggest that the oxidation of propane occurs on the spinel-type catalysts investigated here through the formation of a surface 2-propoxide species. The evolution of these 2-propoxide species is a selectivity-determining step through two competitive ways:

1. the elimination reaction that gives rise to propene, which is an acid-basic step;
2. the over-oxidation through acetone, which is a purely redox step.

Accordingly, the way of direct combustion of propane via 2-propoxide–acetone is the main one over Mn oxides in excess of oxygen, but it is strongly reduced in rate by decreasing the oxygen to propane ratio down to below the stoichiometry for combustion. When the catalyst is in a less oxidized state the acid-basic elimination predominates and propene is formed. However, propene too is overoxidized to CO_2 the more, the higher is the contact time. On $MgCr_2O_4$ the oxidation way through 2-propoxide and acetone is clearly observed by IR and is thought to be the dominant one at least in excess of oxygen, starting from both propane and propene. This way is apparently active also on cobalt oxide, although in this case, according to the apparently very high surface reactivity, activation at C_1 seems to occur too.

Consequently, we can propose the following as a generalized scheme for propane oxidation pathway over spinel type catalysts:



Proposed generalized reaction pathway for propane oxidation over spinel-type oxide catalysts.

3.2. Oxy-dehydrogenation of *n*-butanes on $MgFe_2O_4$

The oxy-dehydrogenation of *n*-butenes is carried out industrially over $MgFe_2O_4$ spinel-type catalysts [32–34] to produce 1,3-butadiene. This reaction belongs to the "allylic oxidation" reaction class, and should have, from the mechanistic point of view, features in common with other allylic oxidation reactions such as the synthesis of acrolein from propene. We present here our results on an FT-IR study of the interaction and oxidative conversion of *n*-butenes over a home made active catalyst composed by $MgFe_2O_4$.

3.2.1. Interaction of *n*-butenes on $MgFe_2O_4$

In Fig. 6 the results of the IR analysis of the gas-phase species observed in our IR cell upon experiments at constant temperature (right) and at variable temperature (left) with *n*-butenes are reported. The identification of the hydrocarbons is made by using either the very strong CH out of plane deformation modes or the C=C stretching modes. These data, in agreement with literature data, show the formation of butadiene from *n*-butenes at temperatures near 600 K and no *n*-butene isomerization. CO_2 and CO are also found as the products.

The FT-IR spectra of the species arising from the contact of the $MgFe_2O_4$ catalyst with the three *n*-butene isomers at r.t. are shown in Fig. 7, where the spectrum of 1-butene liquefied at 150 K over a KBr disk and the spectrum of the adsorbed species arising from but-3-en-2-ol on the same catalyst are also shown for comparison. The spectra of the surface species formed at r.t. certainly contain features due to molecularly adsorbed *n*-butenes with additional features. Strong bands appear in fact in the range 1200–1000 cm^{-1}, namely at 1189, 1153, 1089 and

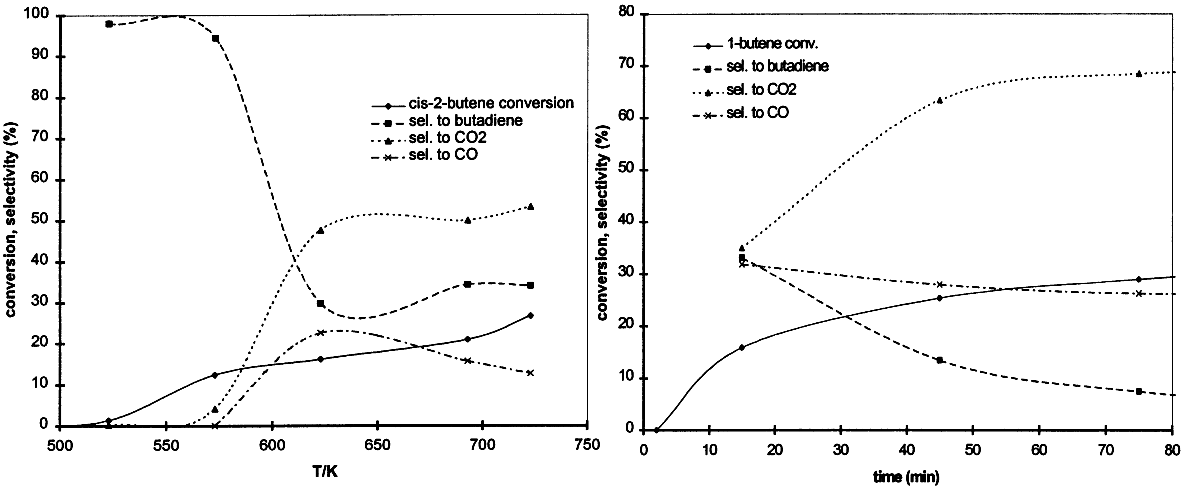


Fig. 6. Conversion and selectivity of *cis*-2-butene at increasing temperatures (left) and 1-butene at increasing time and constant temperature (right) on $MgFe_2O_4$, in the IR cell, following the relative intensity of the IR bands.

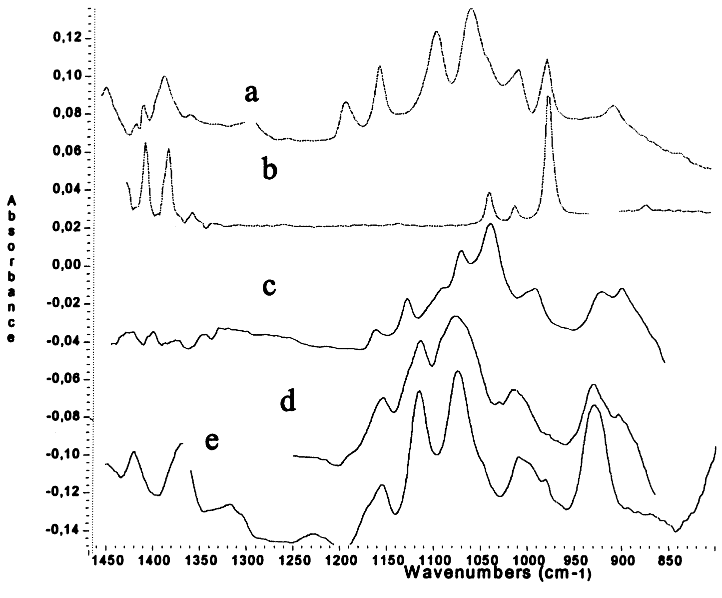


Fig. 7. FT-IR spectra of surface species arising from *cis*-2-butene adsorption on $MgFe_2O_4$ at room temperature (a), and liquid *cis*-2-butene (b), spectra of the surface species arising from reactive adsorption of 1-butene (c), of *trans*-2-butene (d) and spectrum of the products of the irreversible adsorption of but-3-en-2-ol (methyl-allylalcohol) over the same surface (e).

1056 cm^{-1}, and do not disappear upon outgassing at room temperature. These bands closely correspond to those arising from but-3-en-2-ol adsorbed species, typically due C–O and C–C stretchings of alkoxide species. It is straightforward to conclude that but-3-en-2-oxide species (or their isomeric forms but-2-en-1-olate) are formed on the catalyst from both the corresponding alcohol and all three *n*-butenes.

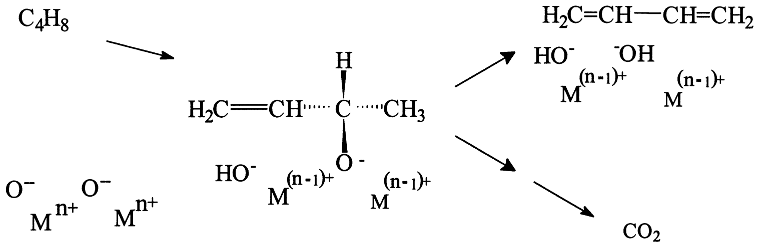
In all cases, heating at 200°C and above causes the progressive disappearance of these bands, while very strong absorptions grow near 1605, 1590, 1435, 1390, 1370 and 1355 cm^{-1}. These bands are typically due to asymmetric stretchings (1605 and 1590 cm^{-1}), symmetric COO stretchings (1435 and 1370 cm^{-1}) and C–H deformations (1355 and 1390 cm^{-1}) of acetate (1605, 1435 and 1355 cm^{-1}) and formate species (1590, 1390 and 1370 cm^{-1}). Also these bands later decrease in intensity down to disappear by heating, while butadiene and CO_x are formed in the gas phase.

The spectra obtained upon adsorption of 1,3-butadiene over the Mg ferrite catalyst show that the molecule is weakly adsorbed either in the non-centrosymmetric s-*cis* configuration, or its symmetry is strongly lowered by interaction with the surface. Outgassing at r.t. causes the complete disappearance of 1,3-butadiene adsorbed as such, but weak bands due to species produced by reactive adsorption are still at the surface. By increasing temperature, weak bands become detectable that can be associated to carboxylate species. This shows that the interaction of butadiene with the catalyst is weak. Its formation from surface butenoxide species can be consequently thought to be irreversible.

3.2.2. *On the mechanism of n-butenes oxy-dehydrogenation to 1,3-butadiene*

The data reported above show that butenoxides are formed by the interaction of *n*-butenes over Mg ferrite catalysts. These species decompose by elimination giving rise to gas-phase butadiene. According to the weak interaction of butadiene with the surface (likely associated to the lower nucleophilic character of the delocalized π-type electron cloud with respect to that of the localized cloud of *n*-butenes), this step is mainly an irreversible one.

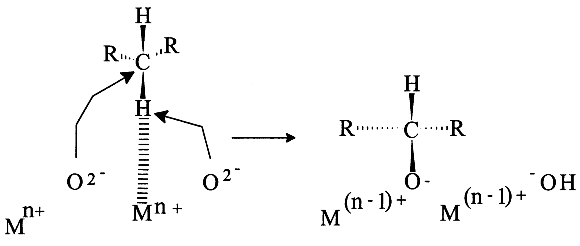
Alternatively, oxidation of butenoxides is also found at the surface, giving rise to carboxylate species that could be the precursors for CO_x. Consequently, our data, in parallelism with the data arising from oxidation of propane through 2-propoxides, discussed above, strongly suggest the following pathway for butene oxy-dehydrogenation:



Proposed reaction pathway for *n*-buteneoxidation over spinel-type Mg ferrite catalysts.

3.3. *On the activation of C–H hydrocarbon bonds on metal oxide catalysts*

The data summarized above support the idea that alkoxide species are the first adsorbed intermediate upon hydrocarbon activation on metal oxide catalysts. It seems reasonable to propose that the primary interaction inducing the proposed C–H activation mechanism consists in the interaction of the C–H σ-type orbital of the weakest C–H bond with surface high-oxidation-state metal ions, which are the oxidizing agents, according to a Mars–van Krevelen redox type reaction scheme. This mechanism implies that the two electrons of the C–H bond are assumed by the catalyst surface, where one or two metal ions are reduced. Consequently, the hydrogen atom is bonded to a surface oxide ion to give an hydroxide species while the alkyl moiety interacts with another surface oxide species giving rise to an alkoxide:



Proposed mechanism for C–H bond activation over metal oxide catalysts.

The C–H activation step to give the alkoxide is irreversible, and this accounts for the isomerization of *n*-butenes either not occurring (as we observe here) or occurring in a separate path [32–34], with a different C–H activation mechanism.

The following evolution of the alkoxide is by elimination to an olefin from a paraffin and a diene from an olefin or by oxidation to a carbonyl compound. These species, however, if enolizable undergo, further transformation (probably through their enolate ions [35]) so that they remain strongly bonded to the surface and finally burn. The former is the way to oxy-dehydrogenation, the latter to total oxidation.

4. On the use of IR spectroscopic technique for the study of the mechanisms of heterogeneous catalytic reactions

In Section 3, it has been shown that information can be reached on the mechanisms of the selective oxy-dehydrogenations of propane to propene and of *n*-butene to butadiene over oxide catalysts, as well as on their total oxidations. In particular, evidence has been provided for a role of surface alkoxide species in all these reactions. By using our IR cell as a static ''batch'' gas-phase catalytic reactor, it has been shown that these species can be formed from the reactants (propane and *n*-butenes) and can give rise to the products (propene, butadiene and CO_x). However, the alkoxide species are only detectable when the overall reaction is actually not occurring. When the reaction actually runs (and the products become detectable in the gas phase), alkoxide species suddenly disappear.

It can be taken as obvious that under reaction conditions the concentration at the surface of most or all surface intermediate species is expected to be very low, if any. In particular, this is expected to be true for species involved in steps successive to the slowest one. In hydrocarbon oxidations (including propane and *n*-butene oxy-dehydrogenations [32–34] and total oxidation) it has most frequently been concluded that the slowest step is the very first C–H activation step. Our data (in particular, those arising from the activation of different hydrocarbons on Mg chromite) confirm this, showing that the C–H activation rate depends on the strength of the weakest C–H bond of the hydrocarbon. In this case the surface intermediate species we deal with (i.e. alkoxides, carbonyl compounds, etc.) should not be (and actually are not) detected upon in situ experiments.

To slow down the evolution of the surface intermediates and allow their detection, the temperature can be lowered, and the gas-phase oxygen concentration lowered down to zero. In fact, the elimination of the alkoxides to the corresponding olefin and diene is certainly an endothermic phenomenon, and is consequently very unfavored (for both kinetic and thermodynamic reasons) at lower temperatures. By lowering the temperature, some reaction steps (e.g. the alkoxide evolution) can be slowed down much more than others (e.g. the alkoxide formation), depending from their activation energy. On the other hand, the further oxidation of such species needs reducible species that can be no more available if reoxidation of the surface cannot occur. These are the reasons why working below the reaction temperature and without gas-phase oxygen, the intermediate species in oxidation reaction can sometimes be detected.

On the other hand, the concentration of a true intermediate species should be very sensitive to changes of temperature and gas-phase composition just below the reaction temperature, and is expected to become zero when the reaction runs. Consequently, one should search the conditions where the expected product forms, to determine whether this occurs at the expense of the supposed intermediate. Only in this case the mechanism implying this intermediate can be considered ascertained. In the case of alkoxide species we just confirmed that they evolve to the desired species (propene from propane and butadiene from butene) or to CO_x approaching reaction conditions.

The conclusion is that, in general, the in situ studies in actual industrial conditions are certainly very useful to monitor the state of the working catalyst, in particular, in relation to the presence on its surface during reaction of strongly adsorbed species. However, they cannot give information on the reaction mechanism if the rate determining step is a very early one (i.e. the first one as in the case of alkane oxidation). To have useful information on the mechanism, the intermediates must be ''caught'' in the conditions where they can be ''isolated'' or ''frozen in'' and their evolution to the products followed by analyzing both the surface species and the gas-phase molecules.

Indeed, an analysis of the IR studies aimed at the determination of the reaction mechanisms indicate that in most cases (in spite of the title of the paper that frequently refers to the study as an in situ investigation) they are not performed in situ (i.e. in conditions where the catalytic reaction actually occurs, and conversion, selectivities and yields can be and are measured), just because in situ nothing good is observed. Most of the spectra are recorded in conditions where the overall catalytic reaction does not actually run. These studies should be both referred to as ''studies under controlled atmospheres'' or with equivalent notations.

Certainly, for experiments that are not performed under reaction conditions, the doubt concerning the actual relation between the phenomena observed during the experiments and what occurs in the industrial reactor can persist. However, the analysis of the gas-phase concentrations in contact with the catalyst in different conditions should allow to reveal (as already said) whether the products are formed (in case in different conditions) from the species detected.

Finally, we can note that our studies have been performed using the transmission–absorption technique and very conventional ''static'' IR cells. According to our experience, the use of the transmission–absorption technique, sometimes in spite of big troubles due to the catalyst disk preparation, allows better experimental conditions for recording the IR spectra with respect to the diffuse reflectance technique. The possibility of outgassing the cell (just due to the use of catalysts in a pressed form) allows to perform experiments in actually dry atmospheres. Few advantages can be found in the detection of the overall catalytic reaction by using flow rather than static conditions. In fact the use of flow cells allows to obtain data on kinetics of intermediate species (when detectable) during in situ experiment. In any case we disagree with a quite diffuse opinion that, to perform studies of the mechanisms of heterogeneously catalyzed reactions, they must be only performed in situ using diffuse reflectance attachment (quite expensive) and flow cells (quite expensive too). In our experience, such studies can be performed using conventional ''static'' IR cells using the transmission–absorption technique, and to have better information, the spectra recorded just when the products are formed (i.e. in situ) must be compared with those recorded at lower temperature and with different gas-phase compositions, i.e. when the reactions does not actually run.

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