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Infrared studies of the reactive adsorption of organic molecules over metal oxides and of the mechanisms of their heterogeneously-catalyzed oxidation

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Abstract

The use of IR spectroscopic techniques to provide information on the mechanisms of catalytic oxidation over metal oxide catalysts is briefly discussed. The data published on studies of the catalytic oxidation of methanol, of linear C_4 hydrocarbons and of methylaromatics over different metal oxide surfaces are reviewed and discussed. Lattice oxygen appears to act as the active oxygen species in both selective and total oxidation. Generalized mechanisms of these complex oxidation reactions are proposed and the catalyst features affecting selectivities in these reactions are discussed. The reaction network is apparently essentially governed by the organic chemistry of the reacting molecule (thus being substantially the same over the different oxide catalysts). However, the catalyst surface governs the rate of the different steps, favoring some paths over others. Thus, selectivity is determined by the catalyst chemical behavior and by the reaction variables (contact time, temperature, gas-phase composition, presence of steam, etc.). IR studies, if performed under conditions where some intermediates are actually detectable and jointly with other techniques, can give valuable information on the catalysis mechanisms. On the other hand, it has been concluded that in situ studies frequently do not give reliable information on reaction mechanisms, because under reaction conditions spectators rather than intermediates are detected.

Keywords: Infrared spectrometry; Metal oxides; Oxidation

1. Introduction

In the report 'Opportunities in Chemistry' (known as the 'Pimentel Report' [1]) published in 1985 as the result of a study of a United States National Research Council committee 'to survey the chemical science' under the chairmanship of professor George C. Pimentel, priority was recommended for five research frontiers. The first was 'Understanding Chemical Reactivity: (...) to apply the full power of modern instrumental techniques (...) to the clarification of factors that control the rates of reaction'. The second one was 'Chemical Catalysis: (...) to obtain a molecular-level and coherent understanding of catalysis'. Although the understanding of the chemical reactivity and catalysis certainly further improved in the last decade, the priorities indicated by the Pimentel report appear to be still actual.

A relevant fraction of the industrial chemical processes are carried out in conditions of heterogeneous catalysis or, more specifically, in gas-phase in the presence of solid catalysts. For most of them a molecular-level understanding of the catalytic act has still not been achieved, the details of the mechanism being still not unanimously recognized.

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It is clear that surface chemistry techniques had and have an important role in the development of the understanding of heterogeneous catalysis as well as in the development of new catalysts. A complete review of the methods for the determination of the mechanism in heterogeneous catalysis has been recently published by Burwell [2], where a chapter was devoted to infrared spectroscopy. This technique is perhaps one of the oldest instrumental techniques that can be applied to surface chemistry studies. However, it also underwent further developments and is now one of the most widely applied. This is because IR instruments are relatively cheap with respect to other surface techniques, the fundamentals of IR spectroscopy are well known and completely established and do not require highly specialized scientific background for interpretation (at least in routine use), the apparatuses necessary to study catalyst surfaces and catalytic reactions are also easily available.

A first requirement in determining the mechanism of a heterogeneous catalytic reaction is a model of the catalyst surface. As shown in other chapters of this issue, IR spectroscopy is today one of the preferred techniques for characterization of the nature of the Brønsted and Lewis acid sites and of the basic or nucleophilic sites on an oxide surface, as well as for determining the oxidation state of surface cationic centers and the structure of the surface hydroxy groups and of some metal-oxygen species. Infrared data, coupled with those from other surface techniques, permit obtaining a rather precise idea of the structure of the catalyst surface and, consequently, its behavior in contact with reagents can be forecast or understood. In fact, the presence of different surface sites determines the *functionalities* of the catalyst surface, that are responsible for its catalytic behavior.

The second and main step in the molecular-level understanding of heterogeneous catalytic reactions is to address the *reaction pathway* and, thirdly, the *mechanisms* of the individual steps. Indeed, since the first developments of IR spectroscopy in the surface chemistry (see first chapter in this issue), this technique has been applied to study the interaction of vapor- or gas-phase reactants with solid catalyst surfaces in, near or out of reaction conditions. The reliability of the results of IR spectroscopy with respect to the reaction mechanisms is still a matter of some controversy, because, as we will point out below, data from IR spectroscopy cannot be ordinarily taken just in reaction conditions. So, a gap between the conditions of IR studies and the real catalyst working conditions generally remains, but this gap can be very small and could be overcome by extrapolation, with the aid of parallel techniques.

Another approach that, in the opinion of the present author, can provide deeper insight on the molecular level bases of heterogeneous catalysis is to consider *the catalyst as a variable*, i.e., to investigate the changes in the product distribution and in the reaction mechanism as a function of the catalyst composition and of the catalyst nature (acidity, basicity and redox properties). In the present paper results mainly arising from our laboratory concerning few catalytic reactions performed on different metal oxide catalysts will be reviewed. Data from other laboratories on the same topics will also be discussed in parallel. The discussion will emphasize the idea that, mutatis mutandis, the reaction pathways for oxidation reactions can often be generalized to many different oxide catalysts and essentially depend on the chemical nature of the reactants. The role of the catalyst is to determine the relative rates of the different steps, so governing overall activity and selectivities.

2. Methodological problems

2.1. Relation between surface reactions and heterogeneous catalysis: in situ studies and studies under controlled atmospheres

From the first applications of the IR technique for surface studies and heterogeneous catalysis (see first chapter of this issue) it was recognized that this technique can be useful not only for the characterization of the surface structure of catalysts by the detection of the spectra of the adsorbed probe-molecules but can also give almost direct information on the mechanisms of heterogeneous catalysis. This is because the spectra of adsorbed species can provide information on the chemistry occurring at the surface.

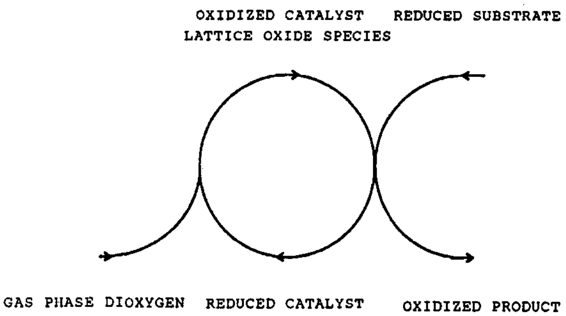
However, in his review on 'Infrared Spectroscopy in Catalytic Research', published in 1984 [3], Peri, one of the pioneers of IR spectroscopy in catalysis, after reviewing the successful application of this technique for the characterization of solid surfaces, stated that 'rather limited real success has been achieved to date (...) in the search for active intermediates on catalyst surfaces' by IR methods. Among the few successes in this search Peri cited the identification of π-allyl species upon butene double bond isomerization on ZnO by Kokes and coworkers [4,5] and stated that 'attempts to find and identify intermediates in more practical catalytic systems have been unsuccessful to date'. Peri at that time believed that 'the best chances for success lie in studies of catalyzed reactions of CO'. His pessimistic conclusion was 'it is very unlikely that activated complexes will be found at significant concentrations on any active catalyst' [3].

Similarly, also Burwell in his already cited recent work [2] was not very optimistic and stated that 'IR has not been particularly helpful in mechanistic studies 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'.

Several years before (in 1978) Tamaru published his book on 'Dynamic Heterogenous Catalysis' [6] where a chapter was devoted to the 'application of spectroscopic techniques to the dynamic treatment of adsorbed species under reaction conditions' where this technique was found to be quite successful in providing data on the mechanisms of some simple catalytic reactions such as: (i) the olefin isomerization and hydrogenation over ZnO; (ii) the decomposition of formic acid; (iii) the water–gas shift reaction over ZnO and MgO; (iv) the decomposition of methanol over ZnO; (v) the oxidation of CO on Pd.

Also Davydov, in his book on 'Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides' (published in his English edition in 1990, but previously in Russian in 1984) [7] devoted a chapter on 'Application of Infrared Spectroscopy to Mechanistic Studies of Heterogeneous Catalytic Reactions' where he took into account nearly the same reactions considered by Tamaru, with the addition of the NO reduction by CO and the oxidations of propene, acrolein and methanol. In the issues on 'Identification of Intermediate Species in Catalytic Reactions', edited recently by Quinn [8] and 'In-Situ Methods in Catalysis', edited by Burch [9], some applications of IR spectroscopic methods were described and found to be successful.

We believe that the pessimistic conclusion of Peri, cited above, is not unreasonable, but could partly be corrected. As it is well-known, two main types of mechanisms are usually assumed for heterogeneous catalytic reactions, i.e., the so-called Langmuir–Hinshelwood mechanism and the so-called Rideal-type (or Rideal–Eley-type) mechanism [10]. In the first case the reaction is assumed to occur between adsorbed reactant molecules on the catalyst, while in the second one, a reactant molecule reacts from the gas phase with another in the adsorbed state. Obviously, in the case of complex reactions, several successive steps necessarily occur, with one or the other mechanism, giving rise to a complex reaction pathway. In the case of the selective oxidation reactions over metal oxide catalysts, the so-called Mars–van Krevelen or redox mechanism [10,11] is widely accepted to occur where the oxidized catalyst surface oxidizes the reactant and is reoxidized by gas phase O_2 in a separate step. Also in this case, several



Scheme 1. The Mars–Van Krevelen reaction scheme for selective oxidation.

successive steps can follow, while parallel ways can give rise to byproducts. In various cases rake-type pathways have been proposed, where the main way to the final product is constituted by successive steps at the surface, the desorption of intermediates representing secondary competitive routes [10] (Scheme 1).

In any case, adsorbed intermediates must be present at the catalyst surface during the catalytic reaction and, in principle, they should be detectable by IR. However, most of reactions of interest are performed at relatively high temperature, e.g., 473–773 K. Molecular adsorption processes are exothermic, so that the adsorption equilibria are definitely shifted towards the gas-phase species, the more the higher the temperature. So, the concentration of the adsorbed species is, mainly for volatile compounds, very small in reaction conditions while it can be very large at room or lower temperatures. So, the detectability of the adsorbed species (in particular for the weakly adsorbed species) is very difficult, if even possible, at high temperatures but is much easier at room temperature or, e.g., at liquid nitrogen temperature. This is more or less true, in principle, for reactants, products, stable intermediates, as well as for by-products, adsorbed diluents, etc.. So when all of these species are present, the detectability of the different species depends on their volatility as well as on their chemical stability in the given conditions.

It seems obvious that under reaction conditions, when the reactants adsorb on the surface, and they transform to intermediates and to the products, that finally desorb rapidly, the concentration at the surface of most or all these species is expected to be very low. In particular, this is expected to be true for species involved in steps successive to the slowest one so that, in principle, these species cannot be observed. However, in some simple cases, like those studied under dynamic conditions by Tamaru [6,12], it is evident that the concentration of the surface species was sufficiently high to detect them and the real 'activity' of these species was demonstrated by the 'isotope jump method'. It is likely that also in these cases the catalytic reaction conditions used during IR experiments were not those allowing best productivities. So also in these cases one could wonder whether the conditions of the IR experiments were really reflecting those of the industrial process.

In less simple or less fortunate cases, in reaction conditions the actual intermediates were not found. On the contrary, heavy adsorbed species that are not involved in the main reaction concentrate at the catalyst surface can be easily detected. It is possible to forecast that, if a species is detected to be highly concentrated and stable in reaction conditions, it either is *the true catalyst* (like sometimes surface carbonaceous materials deposed at the surface during the induction period [13]), or *a poison* (like coke that is a main cause of deactivation of acidic catalysts [14]) or finally, is *a spectator* species. On the contrary, it seems reasonable that *a true intermediate* species should be not highly concentrated in reaction conditions and its concentration should be very sensitive to changes of temperature and gas-phase composition just below the reaction temperature. If possible, 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.

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 most frequently do not give information on the reaction mechanism. This just corresponds to the pessimistic conclusion of Peri, cited above.

Nevertheless, if the temperature is more or less lowered, the rates of the different steps in the reaction will slow down (even to zero). According to the Arrhenius law, the dependency of the reaction rate on the temperature is exponential and essentially (if not entirely) dependent on the activation energy E_a, that is generally positive and differs from step to step. So, by lowering the temperature some steps can be slowed down much more than others and the concentration of the adsorbed species before the slower steps can increase. Moreover, as a consequence, the location of the rate-determining step can also change. On the other hand, the rates of the different steps can also be modified by modifying more or less drastically the gas-phase compositions. As for example, in the case of oxidation reactions, the two fundamental steps (oxidation of the organic substrate, reoxidation of the catalyst) can be separated. Finally, also the equilibria between surface and gas-phase species are shifted towards the adsorbed species by lowering the temperature.

As for example, in the case of n-butane selective oxidation to maleic anhydride over vanadyl phosphate (VPO) catalysts butene, butadiene and furan can be considered as intermediates [15]. According to the data presented by Zhang-Lin et al. [16] the intrinsic rate of maleic anhydride formation above 673 K is highest from furan, medium from butadiene and smallest from butane. Accordingly, the step butane-to-butadiene is assumed to be rate-determining in the overall reaction. However, the apparent activation energies of maleic anhydride formation are 109 kJ/mol from furan, 125 kJ/mol from butadiene and 67 kJ/mol from butane and the activation energy for the overall furan conversion was 132 kJ/mol. This means that, by decreasing the reaction temperature, butane oxidation could become faster than butadiene and furan oxidation. For the same reason, if we follow butane oxidation over VPO catalysts under reaction conditions, we cannot detect furan at the surface (just like it occurred to Wenig and Schrader [17]), because it is further oxidized more rapidly than it is formed. However, if we adsorb butane at lower temperatures on the oxidized catalyst in the absence of gas-phase oxygen (even if in these conditions the overall reaction rate is zero) we can observe furan as a product at the surface [18]. This is mainly because at lower temperatures the rate of furan oxidation decreased more than that of butane oxidation and because in these conditions furan adsorption equilibrium is displaced towards the adsorbed species. So, under these conditions adsorbed furan is formed faster than it is oxidized and is quite stable in the adsorbed state.

In several cases it is consequently possible to ‘freeze in’ at least some reaction steps and *some intermediate reactant species can be found*, at least if they occur before some slow steps. Moreover, the study of the evolution of the molecules that could be formed after the slowest step in the overall reaction, directly put into contact with the catalyst, provides information on possible reaction ways and on those that can be ruled out. This is possible in particular when at least one of the reactants reacts from a strongly adsorbed state and in particular it occurs in many selective and unselective oxidation reactions occurring with the Mars–van Krevelen mechanism, with the participation of lattice oxygen. In this case, in fact, the two steps (oxidation of the reactant and reoxidation of the catalyst by oxygen) can be separated and the oxidation of the organic molecule by the oxidized surface can be studied. Being most of the oxidation reactions performed at 1 atm in air (i.e., in oxygen/hydrocarbon mixtures diluted by nitrogen) and at temperature not exceeding 873 K, this situation can be easily simulated or, better, progressively approached from milder conditions. 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 were the overall catalytic reaction does not actually run. In the opinion of this author, these studies should be referred to as 'studies under controlled atmospheres' or with equivalent notations.

On the other hand, when complex reactions occur, i.e., when strongly adsorbed species form upon reaction conditions and have an important role (either positive, with a participation to the catalytic cycles, or negative, as poisons) or when the catalyst itself changes significantly its structure under reaction conditions before to reaching a steady state, to obtain reliable information by IR spectroscopy these induction processes must be performed or at least simulated before IR experiments.

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. To be confident on this, parallel experiments with other techniques that allow the analysis of the gas-phase concentrations in contact with the catalyst in different conditions, like temperature programmed desorption, temperature programmed surface reaction, pulse catalytic reaction techniques, appear to be very useful. In other words, one should approach the reaction conditions from milder conditions with techniques that reveal (in closely parallel conditions) the surface species (i.e., IR spectroscopy) and the gas phase species in equilibrium with them (TPD, TPSR).

2.2. Infrared techniques aimed at the investigation of reaction mechanisms

Among the different techniques available for IR studies at solid-gas interface (see first chapter in this issue) two of them are most frequently used, i.e., the transmission/absorption technique and the diffuse reflectance technique. The already cited review of Peri [3] exhaustively summarizes several experimental details concerning transmission/absorption studies, including sample preparation, cell design and gas-handling apparatuses. Additional data can be found in a more recent review by Bell [19]. Some additional problems arise for an apparatuses allowing to investigate in situ the catalyst under reaction conditions, particularly at high pressures. A number of cell designs have been published [20–29]. However, information on the mechanisms of surface reactions and of heterogeneous catalytic reactions can also be obtained with simpler cell designs, as those of any adsorption system. Of particular interest, at least for some experiments, are the cells built to record spectra below room temperature, like those described by Zecchina and coworkers [30].

The development of the diffuse reflectance technique for reaction mechanism studies started after the work of Niwa and coworkers [31–33] and particularly after those of Griffiths and coworkers [34,35] that proposed new solutions for a reflectometer as well as cells for in situ measurements. Similar cells are available commercially since several years.

As discussed in the first chapter of this issue, the performances obtained using the transmission/absorption technique and those with the diffuse reflectance technique are today quite comparable. This has been demonstrated, among others, by the work done in the frame of the Eurocat-oxide group under the chairmanship of Vedrine and Bond [36], where the same vanadia-titania catalytic materials have been investigated by several different laboratories. The analysis of the IR data [37] showed that those arising from transmission/absorption experiments done in some laboratories were perfectly comparable with those obtained by diffuse reflectance experiments in others.

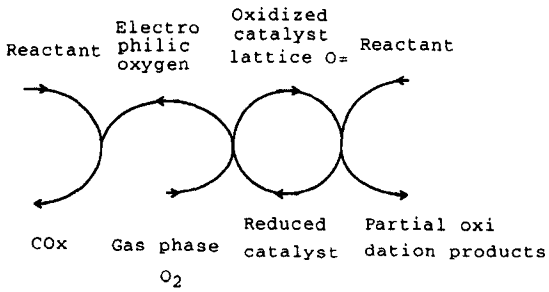
3. What are the active oxygen species in oxidation over metal oxide catalysts? Data arising from ir studies

In the cases of the selective oxidation reactions over metal oxide catalysts the so-called Mars–van Krevelen or redox mechanism [11] (Scheme 1) is widely accepted, where the oxidized catalyst surface oxidizes the reactant and is reoxidized by gas phase O_2 in a separate step. Although in the redox model the 'oxidized catalyst surface' could be constituted by the catalyst surface covered by adsorbed oxygen, this mechanism looks particularly successful if the active oxygen species are assumed to be lattice oxide O^{2-} species [10], whose behavior is, as pointed out by Haber [38] and Bielanski and Haber [39], nucleophilic.

According to Spivey [40], instead, a general theory of catalytic total oxidation over metal oxide still does not exist. A possible role of adsorbed electrophilic oxygen (molecularly adsorbed O_2 and partially reduced oxygen species like O_2^-, O_2^{2-} or O^-) in complete oxidation has been proposed by Haber [38] and Bielanski and Haber [39]. Recently some authors have advanced the hypothesis of a role of adsorbed oxygen also in selective oxidation, like in the cases of maleic anhydride synthesis from n-butane over VPO systems [41,15] and from benzene over vanadia-based catalysts [42,43]. However, Satterfield [10] is still wondering 'whether surface chemisorbed oxygen plays any role' in catalytic oxidation.

In effect, partially reduced oxygen species can be produced at the surface of some transition metal oxides active in oxidation, like supported vanadium, chromium, molybdenum and tungsten oxides, at least at low temperatures [44] and, when produced, they were found to be very active in total oxidation [44,39]. However, as noticed by Sokolovskii [45], these reactions occur at temperatures significantly lower than combustion catalysis so that their relevance with respect to catalysis is unclear. On the other hand, it should be noted that the difference between adsorbed and lattice oxygen can become very slight. In fact, the catalysts work necessarily in conditions where the stabilities of two different oxidation states of their cations are very similar. Suppose the catalyst oxidation step is near equilibrium and the 'electrophilic' oxygen species O_2^-, O_2^{2-} and O^- are intermediates in the reduction of O_2 to O^{2-} and in the oxidation of the cation between its lowest and highest oxidation state. The question then arises whether the reduction of O_2 by the reduced catalyst surface is complete and fast or, in the presence of the organic reactant, it can be incomplete thus allowing the intermediate electrophilic oxygen species to have sufficient lifetime to react with the organic reactant, e.g., with a Rideal-type mechanism. A possible picture for the involvement of electrophilic oxygen in oxidation is shown in Scheme 2.

The metal oxides active in catalytic oxidation are almost invariably semiconductor transition metal oxides. The only relevant exceptions are most of the catalysts used for the oxidative coupling of methane [46] occurring at very high temperature, whose mechanism is certainly not of the redox type and involves in part gas-phase radicals [47]. As pointed out by Bond in his handbook [48], part of the semiconducting ox-



Scheme 2. A possible reaction scheme involving catalyst lattice oxygen in selective oxidation and electrophilic oxygen in non-selective oxidation.

ides tend to be n-type semiconducting and part tend to be p-type semiconducting. n-Type semiconducting oxides tend to be non-stoichiometric because of oxygen defect. This is due to the fact that the cations involved are in their highest oxidation state but tend to be reduced into a lower one. This is the case of CuO, Fe_2O_3, TiO_2, ZnO, V_2O_5, MoO_3, WO_3. p-Type semiconducting oxides instead tend to be non-stoichiometric because of an oxygen excess, due to the fact that their cations are in a stable relatively low oxidation state but they can in part be oxidized to higher oxidation states. This is the case with CoO, Co_3O_4, Cu_2O, Cr_2O_3, NiO.

According to Bond [48] p-type semiconducting oxides are generally better combustion catalysts than n-type semiconducting oxides. However, in several cases it is difficult to determine whether the real working catalyst is in an n-type or in an p-type form, like, for example, copper oxides (CuO and Cu_2O) as well as vanadium oxides (see below). However, it seems useful to underline that the order of the two steps in the redox-type mechanism is reversed in the two types of catalysts. In fact, over n-type semiconductor oxides the catalyst (thought to be stoichiometric at first) is first reduced by the hydrocarbon and later reoxidized by oxygen, so it actually works in a partly reduced state. On the contrary over p-type semiconductor oxides the catalyst is first oxidized by oxygen and later re-reduced by the hydrocarbon, so it actually works in a partly oxidized state.

IR spectroscopy is able, at least in some cases, to give an indication of the redox state of an oxidation catalyst. The use of CO as an adsorbed probe-molecule permits to distinguish the oxidation state of cations like, for example, Cu^{2+} and Cu^{+} [49,50], Ti^{4+} and Ti^{3+} [51], Cr^{3+} and Cr^{2+} [52]. Moreover, IR spectra can give an even more direct evidence concerning the state of oxygen on these oxides. In fact, oxides that tend to be n-type semiconductors generally transmit IR radiation well when they are nearly stoichiometric, but they tend to become opaque when highly non-stoichiometric, even due to simple outgassing at high tempera-

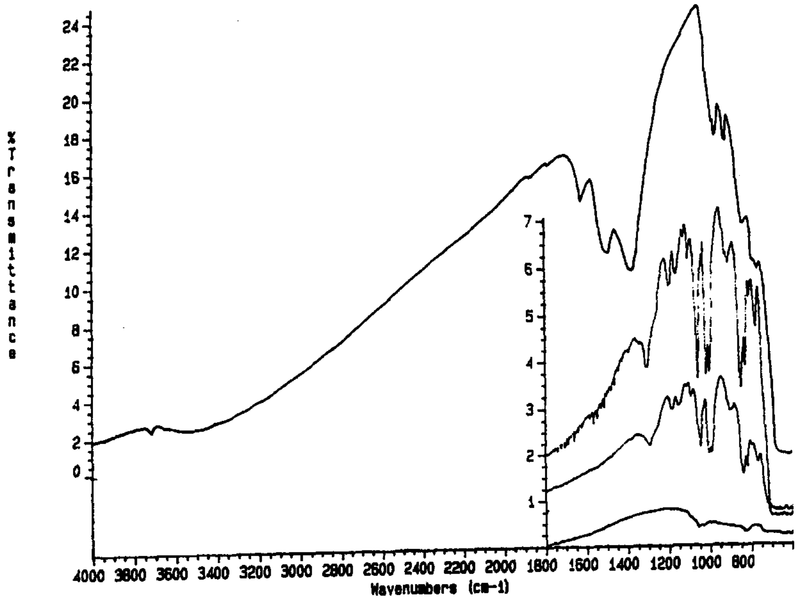


Fig. 1. FT-IR spectra of Co_3O_4 activated in oxygen at 573 K (a), under outgassing at 573 K for 2 h (b) and (c) and after treating with methane at 610 K for few minutes (d). Spectra (a), (b) and (d) have been recorded at 300 K, while spectrum (c) has been recorded at 150 K. Spectra are numbered (a) to (d) from bottom to top.

ture, as has been shown for Fe_2O_3 [53,54], TiO_2 [55], ZnO [56], V_2O_5 [57] and WO_3 [58]. The optical behavior of these slightly reduced oxides can be attributed to the absorption of electrons that at room temperature in part already lie in the conduction band and are, consequently, delocalized into the entire solid particle.

Oxides that tend to be p-type semiconducting can show just the reverse behavior. This can be observed in the case of Co_3O_4 that, when fully oxidized (although outgassed), is almost completely opaque to the IR radiation (Fig. 1a), but becomes very transmitting by reduction with hydrogen [59] or with methane (Fig. 1d) [60]. This can be due to the fact that part of Co^{2+} in stoichiometric Co_3O_4 loses one electron in the presence of oxygen, so being oxidized to Co^{3+}, whose empty orbitals can act as acceptor levels and consequently holes in the valency band are easily generated. Excess Co^{3+} are associated to excess oxygen in the form of additional interstitial oxide ions. This picture finds support in the strong effect of the temperature in varying the IR light transmission by the sample (Fig. 1b and Fig. 1c). Chromia and chromites apparently behave differently. When they are non-stoichiometric the oxygen excess is essentially located at the surface, where high valency cations, essentially Cr^{6+} [61,62] but possibly also Cr^{5+} [63], give rise to chromate species. As shown in Fig. 2, these species are very evident in IR spectra, because they are responsible for typical Cr=O stretching bands in the region 1020–800 cm^{-1}. So, in both cases IR spectroscopy permits to distinguish the nearly stoichiometric surface from that of the p-type semiconducting form. IR studies showed that the features associated to the oxidized states disappear or weaken upon reaction with organic molecules in conditions approaching those of the catalytic oxidation.

Moreover, IR spectra can also detect some adsorbed dioxygen species, like nearly neutral O_2, surface superoxides O_2^- and surface peroxides O_2^{2-} [7,64]. Similar species have been found by IR to be actually active in oxidation of, e.g., ammonia [65].

A number of IR studies (most of which will be cited below) showed that n-type metal oxides that are nearly stoichiometric or even slightly reduced by outgassing, are able to oxidize, at least partially, organic molecules to selective products. This is a further confirmation that, at least in the case of n-type semiconducting ox-

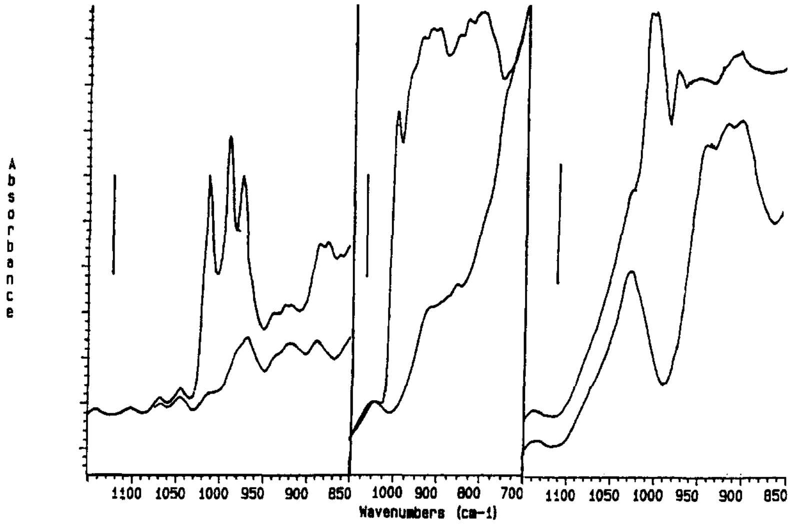


Fig. 2. FT-IR spectra of α-Cr_2O_3 (left), $MgCr_2O_4$ (middle) and $CoCr_2O_4$ (right) in the oxidized state (upper spectra) and in the nearly stoichiometric state (lower spectra).

ides, selective oxidation occurs at the expense of lattice oxygen. However, we observed that slightly reduced n-type semiconductor surfaces (like Fe_2O_3 and CuO, but also TiO_2) are also undoubtedly able to cause burning of several molecules, like methanol (see below). As for p-type semiconducting oxides, we have found that chromate species are responsible for burning of light hydrocarbons over the oxidized surface of $MgCr_2O_4$ [66,67] and that the Co^{3+} species responsible for obscuring the IR spectrum of oxidized Co_3O_4 disappear upon total oxidation of methane (Fig. 1a and Fig. 1d) [59]. These reactions occur on $MgCr_2O_4$ at temperatures definitely lower than those needed to decompose thermally the excess oxygen, so they should be direct redox reactions, without the participation of intermediate oxygen species. This implies that oxide ions with highly reducible cations can behave as active sites for total oxidation, without the intermediacy of electrophilic oxygen.

A typical and very actual case-study, from this point of view, is that of the so-called VPO catalysts for n-butane selective oxidation to maleic anhydride. It seems established that the best catalysts contain almost a pure $(VO)_2P_2O_7$ phase, with tetravalent vanadium [15,16], but the copresence of $VOPO_4$, with pentavalent vanadium, was found to enhance catalytic activity [68]. In any case, authors agree that the presence of some amounts of pentavalent vanadium is essential, in particular, for the butadiene-to-maleic anhydride step [15,16,68]. So, the vanadyl-pyrophosphate catalyst (based on tetravalent vanadium) probably behaves like a p-type semiconductor, in contrast to pentavalent vanadium phases (V_2O_5 and $VOPO_4$) that behave as an n-type semiconductor [69].

TAP experiments of n-butane oxidation over this catalyst suggested that a labile 'activated' oxygen species can be responsible for the last step, furan to maleic anhydride [41]. However, it seems likely that this activated oxygen species simply corresponds to the additional oxide species stoichiometrically necessary to convert V^{4+} into V^{5+} [16]. This agrees with the conclusions we reached from our IR studies, that showed that maleic anhydride can be formed directly from n-butane in the absence of gas-phase oxygen over VPO catalysts that have been oxidized in oxygen and outgassed at 620 K and that are apparently constituted exclusively by the $(VO)_2P_2O_7$ phase [18]. After these pretreatments, in our opinion, the oxidized sites should be constituted by pentavalent vanadium either present as undetected $VOPO_4$ or located at the surface of the $(VO)_2P_2O_7$ phase, according also to very recent ^{31}P NMR data [70]. On the other hand, the Dupont process consisting of the butane oxidation to maleic anhydride in a transport bed reactor (where the hydrocarbon–catalyst reaction is separated from the molecular oxygen–catalyst reoxidation [71]) confirms that gas-phase dioxygen is not necessary.

If this picture is true, the VPO catalysts could work in two oxidation ranges, with the $V^{4+} \Leftrightarrow V^{3+}$ redox couple active for the butane-to-butadiene steps (so as an n-type semiconductor) and with the $V^{4+} \Leftrightarrow V^{5+}$ cycle for the butadiene-to-maleic anhydride step (so as a p-type semiconductor). This is associated to the extreme complexity of this reaction (see below).

In conclusion, IR studies strongly support the idea that lattice oxygen is the active species in both partial and total oxidation catalysis over metal oxides, although a role of adsorbed oxygen in some particular cases cannot, obviously, be ruled out.

4. Case studies

4.1. *The selective and non-selective catalytic oxidation of methanol*

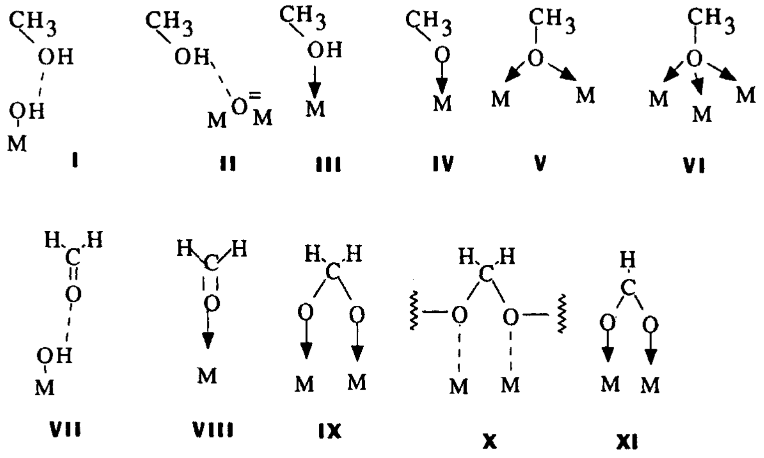
Methanol is a primary intermediate in industrial chemistry [72,73]. The catalytic oxidation of methanol is carried out industrially for the production of formaldehyde. Two types of processes have been developed [10,73], one essentially based on a dehydrogenation over silver catalysts working with a methanol-rich feed and the other consisting in a oxidative dehydrogenation route carried out at 620–720 K over ferric molybdate catalysts, working with methanol-lean feed with yields above 95%. Other catalysts, like pure and silica-supported molybdena and vanadia and different molybdates and tungstates behave in appropriate conditions as highly selective catalysts for formaldehyde production by oxy-dehydrogenation [73–76] with yields well above 90%. In most cases (like for tungstates and molybdates) the main parallel by-reaction is the methanol dehydration, a typically acid catalyzed reaction. This reaction is performed as an industrial process over acid catalysts like aluminas, silica-aluminas and protonic zeolites for the production of dimethylether [72,77].

Recently it has been shown that other catalysts such as molydenum-tin-oxides [78] and vanadium-titanium-oxides [79,80] are useful for the selective oxidation of methanol to methylformate with high yields. Transition metal oxides such as cobalt or copper oxides as well as noble metals are the most effective catalysts for methanol and other alcohol catalytic combustion [81] investigated in the frame of studies aimed at the abatement of poisonous VOC compounds [82].

To obtain a complete picture of the oxide-catalyzed chemical transformations of methanol we have investigated its interaction with acidic catalysts (alumina and titania), as well as with different metal oxides that are very active in its catalytic combustion (Fe_2O_3, CuO, Co_3O_4) and in its selective oxidation to formaldehyde (pure and silica-supported vanadia) and to methylformate (vanadia-titania).

4.1.1. IR spectroscopic characterization of the adsorbed species arising from C_1 oxygenated compounds

The structure of the surface species which can be involved in methanol oxidation are summarized in Scheme 3. Methoxy groups (IV to VI in Scheme 3) are generally the most abundant methanol adsorbed forms. They are characterized by a couple of strong bands in the CH stretching region, that are frequently incorrectly assigned to the asymmetric and symmetric stretching modes. Instead, these bands are actually associated only to the symmetric CH_3 stretching mode split due to its Fermi resonance with the first overtone of the corresponding symmetric deformation [83]. The asymmetric stretching mode gives rise to a weak band at higher frequencies. The two methyl deformation modes give rise to a couple of sharp bands in the region 1455–1440 cm^{-1}, while the C–O stretching mode is associated to a strong band in



Scheme 3. Structure of adsorbed species involved in methanol transformations.

the region 1200–1000 cm^{-1} at the higher frequency side of which a methyl rocking mode can be found. The relative intensity of stretching and deformation modes depend on the covalency/ionicity of the CH_3O–metal bond, being the stretchings by far relatively more intense on covalently bonded methoxide groups than on ionic methoxides [80]. According to Lamotte et al. [84] the position of the C–O stretching mode is sensitive to the coordination state of the methoxy groups, either terminal (IV), bridging (V) or triply-bridging (VI): this mode can be multiple due to the presence of differently coordinated methoxides, whose multiplicity parallels that of the surface hydroxy-groups found on the clean surface [84,85].

Undissociated adsorbed forms of methanol (I to III) are characterized by rather broad νOH (3600–3000 cm^{-1}) and δOH modes (1480–1300 cm^{-1}), by the $\nu_{sym}CH_3$ couple at slightly higher frequencies than methoxy-groups and, finally, by νC–O, sharp, not far from 1030 cm^{-1}.

The molecular adsorbed forms of formaldehyde (VII and VIII) are mainly characterized by its C=O stretching mode in the region 1750–1650 cm^{-1} depending upon adsorption mode (H-bonding or coordination on Lewis sites) and by two stretchings and three deformation modes of the CH_2 group [86]. Nevertheless, molecularly adsorbed formaldehyde species can be found only in traces at room or higher temperatures, while they can be more easily observed at very low temperatures. It has been shown [86] that formaldehyde adsorbs on ionic metal oxides mostly in the form of dioxymethylene species (IX), whose spectra are mainly characterized by at least two strong C–O stretching bands in the region 1200–1000 cm^{-1}, to which two stretchings and several deformation modes of the CH_2 group are added. Polymeric species (X) can also be observed when relatively high formaldehyde pressures are put into contact with the catalyst.

Formate groups (XI) are characterized by a single weak CH stretching band that however frequently appears to be multiple due to Fermi resonances with overtone modes [86]. At lower frequencies formate species give rise to a typical strong triplet, due to the asymmetric COO stretching (1600–1550 cm^{-1}), CH bending (1390–1370 cm^{-1}, sharp) and symmetrical COO stretching modes (1380–1300 cm^{-1}).

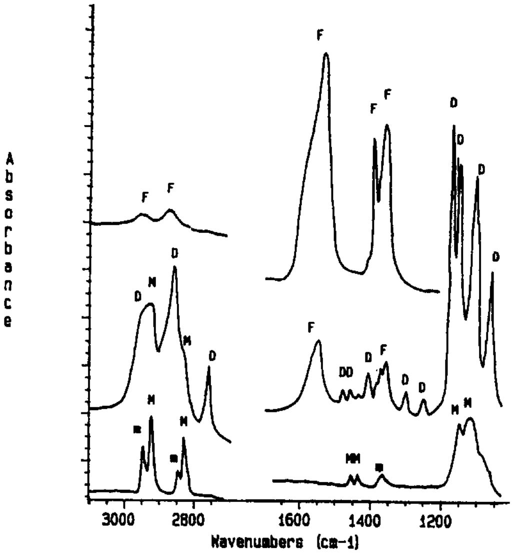


Fig. 3. FT-IR spectra of the adsorbed species arising from adsorption of methanol (a), formaldehyde (b) and formic acid (c) on TiO_2 (anatase), after outgassing at rt for methanol and formaldehyde and at 473 K after formic acid adsorption. Bands due to (M) methoxy-groups, (m) undissociated methanol, (D) dioxy-methylene, (F) formate species.

Typical spectra are reported in Fig. 3, these are relative to the more strongly held species obtained by methanol, formaldehyde and formic acid adsorption on TiO_2 (anatase). Over this surface methanol adsorption gives rise to mixtures of dissociated and undissociated methanol species [87–89], while formaldehyde gives mainly rise to dioxymethylene species that, however, undergoes partial disproportionation already at room temperature (rt) to methoxy and formate species [86,90].

4.1.2. The catalytic dehydration of methanol to dimethylether and methanol decomposition and dehydrogenation

Non-transition metal oxides, according to their composition with non-reducible cations, are poorly active in oxidation catalysis for methanol. However they can be active either in the presence or in the absence of oxygen in the dehydration of methanol to dimethyl ether (in methanol-rich feeds) or in its decompostion:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (1)$$

$$CH_3OH \rightarrow CO + 2H_2 \quad (2)$$

Besides being a reaction of industrial interest for the synthesis of dimethylether, reaction (1) is relevant with respect to the oxidation of methanol because dimethylether can be a main by-product in the processes for the formaldehyde synthesis [74–76]. Reactions (1) and (2) occur over alumina that is an excellent catalyst for the synthesis of dimethyl-ether [91–94] but also catalyzes the methanol decompostion to CO [92]. The most active catalysts in methanol decomposition are also active in methanol synthesis that is just the reverse of reaction (2), like Cu-based catalysts [95] and, among oxides, ZnO [6] and $ZnCr_2O_4$ [96]. Working at low methanol conversion, over these systems methylformate can also be synthesized efficiently with a dehydrogenative route through reaction (3):

$$2CH_3OH \rightarrow HCOOCH_3 + 2H_2 \quad (3)$$

The mechanism of methanol dehydration has been studied by several authors on both Lewis acidic catalysts as aluminas and Brønsted and Lewis acidic catalysts as silica-alumina. Our studies on the interaction of methanol [97–99] and formaldehyde and formic acid [86] with transitional aluminas gave an indication on the mechanisms of both dehydration and decomposition reaction.

Based on the adsorption of different isotopic forms of methanol like CH_3OH, CD_3OH and CHD_2OH and on both calorimetric and IR spectroscopic experiments, four different adsorbed methanol species were observed [97]. The more strongly bonded one was identified as a bridging methoxide (called I′), obtained by the activated dissociation of an undissociatively adsorbed species (type I) coordinated, through the oxygen lone pair, to tetrahedral Al ions acting as Lewis acid sites. Other two undissociated adsorbed forms were found, one of which is primarily Lewis bonded to octahedral Al cations (II) and the other H-bonded over surface oxide anions (III). The identification of three different undissociated forms of methanol was made on the basis of the analysis of the δOH mode, observed at 1420 cm^{-1}, sharp, for species I and at 1440 cm^{-1}, broad, for species III. In the case of species II this mode appeared to have a transmission window at 1455 cm^{-1} and this was interpreted as an evidence of a Fermi resonance of this mode with the first overtone of the γOH mode [97].

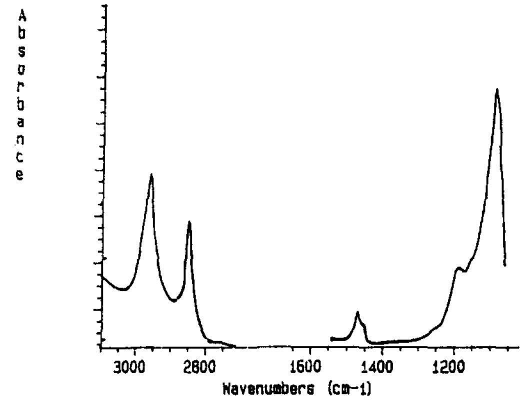
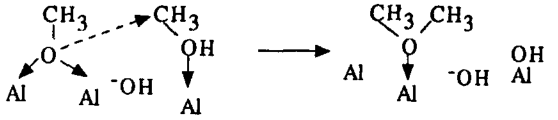


Fig. 4. FT-IR spectra of the adsorbed species arising from adsorption of methanol on alumina at 473 K.

By increasing the adsorption temperature [98] species III disappears first or is converted into the other ones and later also species II desorbs. At 473 K only bridging methoxides are adsorbed stable (Fig. 4), characterized by the bands at 2970, shoulder, 2955 and 2844 cm^{-1} (CH_3 stretchings, see above), 1472 and 1458 cm^{-1} (CH_3 bendings), 1200 cm^{-1} (CH_3 rocking) and at 1098 cm^{-1} (C–O stretching). These data agree with the observation that the catalytic activity of aluminas in methanol dehydration increases with crystallization of the spinel type structure typical of transitional aluminas [93], that also increases the number and strength of Lewis sites identified as highly coordinatively unsaturated Al^{3+} cations.

Further studies of methanol/CO_2 coadsorption on alumina showed that (in spite of the



Scheme 4. Reaction scheme for methanol dehydration to dimethyl ether over alumina.

strong adsorption over the surface) adsorbed methoxy-groups act as nucleophilic species, rapidly giving rise at rt to the following reaction:

$$CH_3O^- + CO_2 \rightarrow CH_3\text{-}O\text{-}COO^- \quad (4)$$

with the production of strong bands due to monomethylcarbonate species [99]. So, the observation of the nucleophilic methoxide species together with undissociated methanol coordinated over strong Lewis acid sites (whose carbon atom is certainly strongly electrophilic) gives rise to a very reasonable mechanism for methanol dehydration reaction (Scheme 4). This scheme is consistent with the mechanism proposed by Knözinger in 1968 [91] and represents one of the two alternative pathways proposed recently to occur by Schiffino and Merrill [94] based on our IR study and their own catalytic data. These authors proposed that a second mechanism can derive from the reaction between two methoxy-groups.

However, on very strong Brønsted acidic surfaces, like protonic zeolites, an alternative mechanism similar to that observed in the liquid phase sulphuric acid catalyzed dehydration may also be proposed. In such a case, protonation of an alcohol molecule favors the following nucleophilic substitution.

In agreement with the previous data of Greenler [100], who performed a detailed study of methanol adsorption over alumina in 1962, heating of adsorbed methanol at 473 K or above gives rise to formate species that are likely intermediates in the methanol decomposition (reaction (2)). In fact formate ions rather easily decompose over metal oxides following the reversible reaction:

$$H\text{-}COO^- \Leftrightarrow CO + OH^- \quad (5)$$

as observed by IR. What is not definitely established is how formate ions are formed from methanol over a non-transition non-oxidizing metal oxide catalyst like alumina. A plausible answer to this question arises from our study on formaldehyde adsorption on alumina [86]. It has in fact been shown that adsorption of formaldehyde on alumina gives rise reversibly to dioxymethylene species that later undergo a Cannizzaro-type disproportionation giving rise to methoxy groups and formate species.

$$CH_2O + O^{2-} \Leftrightarrow [O\text{-}CH_2\text{-}O]^{2-} \quad (6)$$

$$2[O\text{-}CH_2\text{-}O]^{2-} \rightarrow CH_3O\text{-} + HCOO^- + O^{2-} \quad (7)$$

Thus dioxymethylene (or adsorbed formaldehyde) can be produced by methanol dehydrogenation over alumina (reaction (8)) and a cycle can follow (reactions (7) and (8)) producing formates that finally decompose (reaction (5)) so giving rise to the methanol decomposition via formate intermediates.

$$CH_3\text{-}O\text{-} + OH\text{-} \rightarrow \text{-}O\text{-}CH_2\text{-}O\text{-} + H_2 \quad (8)$$

IR studies have shown that this mechanism occurs more efficiently over hydrogenation–dehydrogenation catalysts, like those active in methanol synthesis and decomposition. Besides those based on copper, methanol decomposition has been investigated by IR spectroscopy over metal oxides like ZnO [6,101], $ZnCr_2O_4$ [102], $ZnAl_2O_4$ [103] and ZrO_2 [104]. Over ZnO [105] and ZrO_2 [106] also monocrystal EELS studies of methanol decomposition have been published. In these cases, as we observed over Zn-chromites [102], when methanol is present in sufficient amounts (like at low conversion), methylformate can be obtained instead of methanol decomposition, because reaction (9) becomes preferential with respect to reaction (5).

$$HCOO^- + CH_3OH \rightarrow HCOOCH_3 + OH^- \quad (9)$$

Methanol decompostion has also been studied over TiO_2 anatase [87,107] and rutile monocrystals [108] from where formaldehyde is produced through reaction (8) and the reverse of equilibrium (6).

4.1.3. The catalytic combustion of methanol over oxide catalysts

The catalytic combustion of methanol:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad (10)$$

has been investigated by our group over a number of combustion catalysts like Fe_2O_3 [109], CuO [49] and Co_3O_4 [59]. Similar experiments have been performed by Davydov over CuO, Fe_2O_3 and Cr_2O_3, with similar results [7]. According to Boreskov et al. [81] CuO and Co_3O_4 are, among binary metal oxides, the most active catalysts for methanol combustion. In both cases, we found that oxidation of methanol already occurs at rt. Over CuO [7,49] methoxy groups are formed by methanol dissociation already in the range of 250–273 K but at 273 K methanol oxidation by CuO already gives rise to formate ions. Methoxy-species are no more detectable over the CuO surface at 420 K but at this temperature also formate species decompose and only carbonate species can be found on the surface of CuO. Similarly, methanol adsorption on Co_3O_4 [59] gives rise even at rt to a mixture of methoxy-, formate- and dioxy-methylene species. Previous reduction of Co_3O_4 to give CoO causes the surface to be much less reactive. In this case methoxy-species are stable at rt and oxidized only at higher temperatures.

Experiments have also been carried out by our group over $MgCr_2O_4$, which shows very poor selectivity with respect to formaldehyde production at 470 K [110]. The spectra reported in Fig. 5 show that over this catalyst methanol is adsorbed at rt essentially in the form of methoxy-groups, characterized by the couple of sharp bands at 1470 and 1450 cm^{-1}, methyl bending modes, by the weak band near 1110 cm^{-1}, methyl rocking and mainly by the strong C–O stretching at 1020 cm^{-1}, together with some undissociated methanol, mainly characterized by the broad COH deformation mode centered near 1380 cm^{-1}. These absorptions decrease in intensity on outgassing at 373 K, when bands due to two different types of formate species grow at 1620 and 1600 cm^{-1} (asymmetric COO stretching) and at 1385 and 1360 cm^{-1}

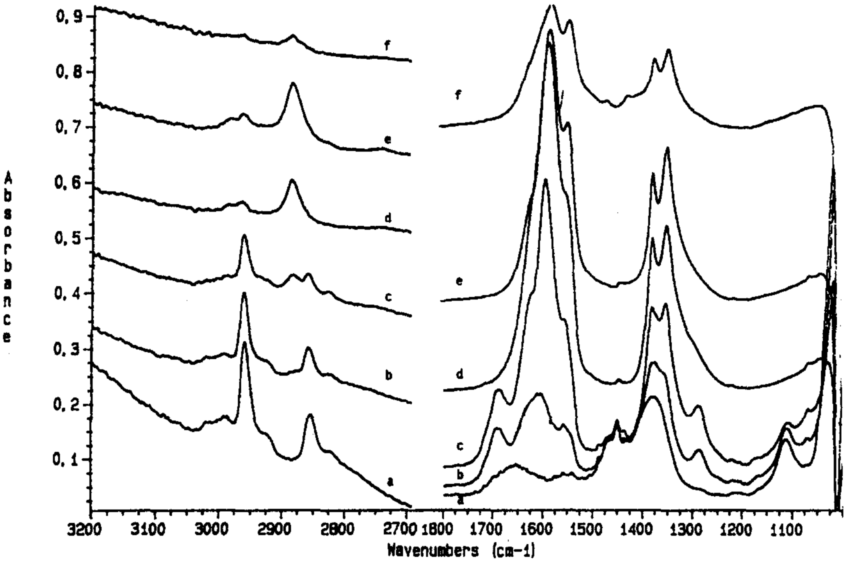


Fig. 5. FT-IR spectra of the adsorbed species arising from adsorption of methanol on $MgCr_2O_{4+x}$ at rt (a) and after outgassing at 373 K (b), 423 K (c), 473 K (d), 523 K (e) and 573 K (f). The negative band at 1010 cm^{-1} is due to the surface chromate species that are reduced upon methanol oxidation.

(CH bending and symmetric COO stretching, respectively). However, in the range 373–450 K bands are also evident at 1695, 1490 (sharp and weak) and 1280 cm^{-1}, typically due to adsorbed formaldehyde (CO stretching, CH_2 scissoring and wagging [86]) that can in fact be found among reaction products just at 473 K, although with very poor selectivity [110]. This species is clearly an intermediate in formate formation because they disappear at 473 K when formate bands are no longer growing and the bands of methoxy-groups have already disappeared.

4.1.4. *The selective oxidative dehydrogenation of methanol to formaldehyde*

Literature data show that pure vanadia [74,75,92] and vanadia-silica [111,112] act as selective catalysts in methanol oxidative dehydrogenation to formaldehyde. Other compounds such as the dehydration product dimethylether and the oxidation products dimethoxymethane (the ketal of formaldehyde), methylformate and CO are obtained as by-products [74–76,92,111,112].

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \qquad (11)$$

The behavior of the C_1 molecules methanol, formaldehyde and formic acid on the surfaces of pure vanadia and vanadia-silica [113] is rather parallel, considering that in the latter case the silica surface is exposed in part and also acts in adsorption and in catalysis. Over pure vanadia methanol adsorption gives rise to methoxy-groups that are stable up to ca. 450 K (Fig. 6). Above this temperature the features of methoxy groups start to decrease in intensity, while new bands grow that are typical of dioxy-methylene species. However, above 500 K all bands disappear, the surface being totally cleaned. These data agree with those from formaldehyde adsorption on the same vanadia surface, that gives rise, in the temperature range 170–300 K to a mixture of adsorbed dioxy-methylene and of the linear polymer polyoxymethylene. However, at rt, or just above it, these species desorb, so formaldehyde adsorption and reactivity over vanadia is almost undetectable. This is in spite of the significant reactivity observed in the case of formic acid, that is adsorbed in the form of rather stable formate species.

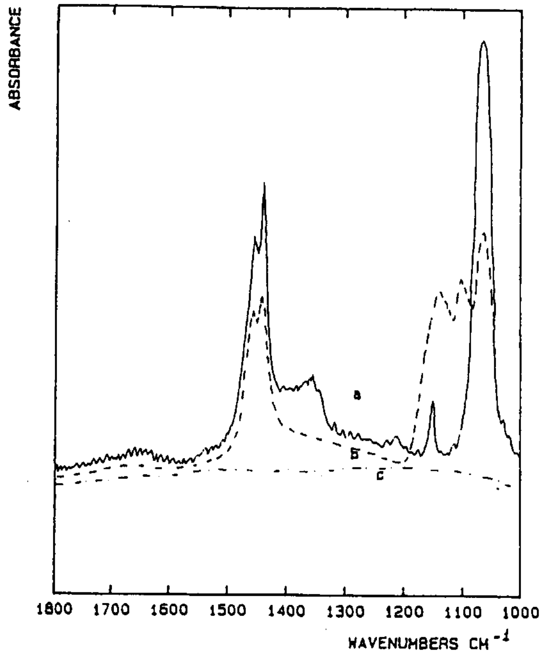


Fig. 6. FT-IR spectra of the adsorbed species arising from adsorption of methanol on pure vanadia at rt and after outgassing at rt (a), at 490 K (b) and at 520 K (c). Reprinted with permission from ref. [113].

These data indicate that methoxy-groups undergo nucleophilic attack by surface oxygen species giving rise to dioxy-methylene species that easily desorb as formaldehyde immediately after their formation. Our data agree nicely with those arising from methanol oxidation experiments over pure vanadia [92] that show that methanol conversion and formaldehyde selectivity become very high near 473 K. Above ca. 520 K, formaldehyde selectivity decreases and selectivity to CO (formed by formates decomposition, reaction (5)) strongly increases.

The high selectivity in formaldehyde synthesis on vanadia is associated with the almost undetectable reactivity of vanadia towards formaldehyde. This lack of reactivity is associated with the covalency of the V–O oxygen bonds, while over ionic oxides formaldehyde reacts strongly, its more stable adsorbed species being dioxy-methylene. Similar behavior has been observed by Chung et al. [114], by Groff [115] and by Davydov [7] over MoO_3, that is even more efficient in formaldehyde production than vanadia, where also methoxy species have been detected but their evolution was found to produce no detectable adsorbed species [114,115] or only adsorbed formaldehyde in a molecular form [7], without further evolution to formates.

4.1.5. *The selective oxidative dehydrogenation of methanol to methylformate*

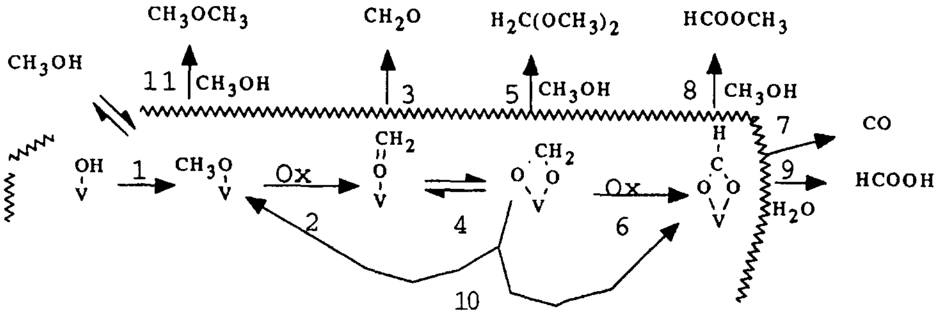
Methanol oxidation over vanadia-titania gives product selectivities very different from pure vanadia and vanadia silica. Over this catalyst very high yields of methyl-formate can be obtained [79,80], as previously observed over other mixed oxide catalysts like, among others, Sn-Mo- and Sn-W-oxides [78].

$$2CH_3OH + O_2 \rightarrow HCOOCH_3 + 2H_2O \qquad (12)$$

This reaction has been investigated in our laboratory as well as by Feil et al. [116] over different vanadia-titania systems. Methanol adsorption gives rise to methoxy-groups that start to be oxidized above 400 K. At this temperature formate species and adsorbed formaldehyde are found. Formate species are stable in the adsorbed form up to near 490 K but later tend to decompose to CO_x. If formaldehyde is directly adsorbed at rt on vanadia-titania, dioxymethylene species appears to be the key adsorbed form of formaldehyde. This species is stable up to 370 K and, in any case, is strongly bonded giving rise, upon heating, to both methoxy- and formate-groups via reaction (7) by disproportionation or, by oxidation, to formate-groups only. This behavior may be interpreted assuming that the desorption of formaldehyde from dioxymethylene species is on vanadia-titania, as on many other oxides, slow and oxidation or disproportionation may occur. In the presence of methanol at relatively low temperature dioxy-methylene reacts with methanol giving rise to dimethoxy-methane, that in fact is produced with high selectivity at low conversion. Formate species are also quite stable so that their reaction with methanol gives rise to methylformate.

4.1.6. *A generalized mechanism for methanol oxidation and transformation over oxide catalysts*

The data discussed above allowed us to propose the generalized reaction Scheme 5 for methanol oxidation over metal oxides. From this mechanism it is evident that the products formaldehyde, dimethoxy-methane, methylformate and CO are substantially successive oxidation products, being their adsorbed forms converted one into the other, giving rise to a so-called *rake-type mechanism.* So, on active and selective oxidation catalysts, the selectivity to these products does depend strongly on experimental conditions like contact time or space velocity in relation to the catalyst surface area. Over pure vanadia [74] and vanadia-titania



Scheme 5. Generalized reaction scheme for oxide-catalyzed methanol transformation.

[79,80] all products can be produced with high selectivities at different conversion degrees. Methylformate and dimethoxy-methane are evidently formed by reaction of an oxidized adsorbed species with unreacted methanol, so their production necessarily occurs at incomplete methanol conversion.

On the other hand, the different catalysts also certainly differ in their ability to favor the production of one particular oxidation product. Thus, we can discuss the catalyst requirements needed to shift the selectivity towards formaldehyde or, alternatively, towards methylformate or, eventually, towards carbon oxides. Among very active catalysts, where methoxy groups oxidation (reaction 2) starts at sufficiently low temperatures to avoid substantial condensation to dimethylether (reaction 11), catalysts selective towards formaldehyde must allow desorption of this molecule (reaction 3) before its further oxidation (reaction 6) or disproportionation (reaction 10). They then must be poorly nucleophilic, so inducing a sufficient thermal lability of dioxymethylene with respect to its desorption as formaldehyde (reactions 3 and 4). As has been found here, this is the case for pure vanadia and vanadia-silica, that, accordingly, allow very high selectivities in formaldehyde even at almost total conversion [74]. This is also true for bulk molybdena, where formate ions have not been detected during heat treatment of adsorbed methanol and for the industrial ferric molybdate catalysts, for which a similar mechanism has been proposed [76]. This agrees with the fact that the catalysts that allow the production of formaldehyde by methanol oxidation with very high yields are very poorly active in the Tischenko dimerization of formaldehyde to methylformate [117], for which the equilibrium 4 is certainly necessarily shifted towards dioxymethylene.

On the contrary catalysts selective towards methylformate must block formaldehyde as dioxymethylene allowing a further oxidation to formate ions. However, it is also necessary for these catalysts that formate ions were not so labile, allowing the reaction of these species with unreacted methanol giving methylformate (reaction 8) before formates were decomposed into CO (reaction 7).

According to several studies [10,39] the rate determining step in methanol oxidative dehydrogenation is the breaking of the C–H bond of the methoxy-groups. So all successive steps are more or less faster. This is why the adsorbed forms of formaldehyde can only be observed at relatively low temperature, not only over catalysts selective to formaldehyde but also over catalysts allowing high methylformate selectivities.

The same scheme can also apply to methanol decomposition and dehydrogenation, if we substitute the oxidation steps (denoted as ox in Scheme 2) with dehydrogenation steps. The difference is the following: in the oxidative dehydrogenation upon these steps a C–H bond is broken in such a way that the hydrogen is adsorbed as H^+ and the two electrons are assumed by the catalyst that becomes reduced. In the pure dehydrogenation the electrons stay with the hydrogen atom giving rise to an adsorbed hydride species H^- that together a proton H^+ (produced previously by dissociation of methanol or later from the OH^- given by the formate decomposition) gives rise to dihydrogen.

It is obvious that the driving force for the oxidation steps is in the tendency of the oxidized catalyst center to be reduced. The driving force for the dehydrogenation steps could be associated to the ‘affinity’ of the corresponding catalyst surfaces towards hydride species, like that found by several ZnO-based surfaces as well as, obviously, by the thermodynamic instability of the alcohols towards dehydrogenation.

4.2. The catalytic oxidation of linear C_4 hydrocarbons

The increased availability of light alkanes from natural gas makes their use as the feedstocks for the synthesis of chemicals very attractive [73,118]. For this reason, the partial oxidation and oxy-dehydrogenation of light alkanes is the object of increasing interest. Since several years n-butane is used for the synthesis of maleic anhydride over VPO catalysts. This reaction has been the object of several papers and reviews [15,119,120]. Recently, the V-Mg-O system (V_2O_5-MgO) has been proposed as a promising one for the oxidative dehydrogenation of alkanes like butane to butene or butadiene [121,122] and propane to propylene [123]. The alkane oxy-dehydrogenation reaction has also been reported to occur promisingly over supported vanadias [121,124] as well as on VO_2-SnO_2 solid solutions [125]. On the other hand, n-butane partial oxidation can also give rise to other products. According to the literature, acetic acid has been produced industrially by n-butane oxidation over V_2O_5-TiO_2 catalysts [118] but also tetrahydrofuran [126] has been produced with interesting selectivities over VPO catalysts and methyl-vinylketone, methyl-ethylketone and crotonaldehyde can or could be produced by selective oxidation of butane [15].

Obviously, the catalytic combustion to CO_x is the main competitive reaction to be avoided in all partial oxidation processes. However, n-butane combustion is of interest today as a test reaction in catalytic combustion studies, i.e., in the field of the abatement of volatile organic compounds (VOC) [127] and in that of automotive catalytic converters [128].

Another possibility for use of n-butane as a raw material for organic chemicals is the pure dehydrogenation route, carried out over chromia-alumina catalysts [129] where new reactor solutions have been proposed to overcome the problems arising from catalyst deactivation [130]. Industrial processes using K_2CO_3-Fe_2O_3-based catalysts are also available [118].

On the other hand, the butenes, produced by cracking of oil fractions, have been used for decades as the feedstock for the production of C_4 organic compounds. Butadiene is produced industrially by oxy-dehydrogenation over ferrite-based [118,131] or molybdate-based catalysts [39], while n-butene oxidation also allows the production of maleic anhydride over VPO [15], V_2O_5-TiO_2 [132], MoO_3-TiO_2 [133] and bulk molybdate catalysts [134]. Acetic acid is produced from butenes by oxidation in the presence of steam over V_2O_5-TiO_2 [135] while cro-

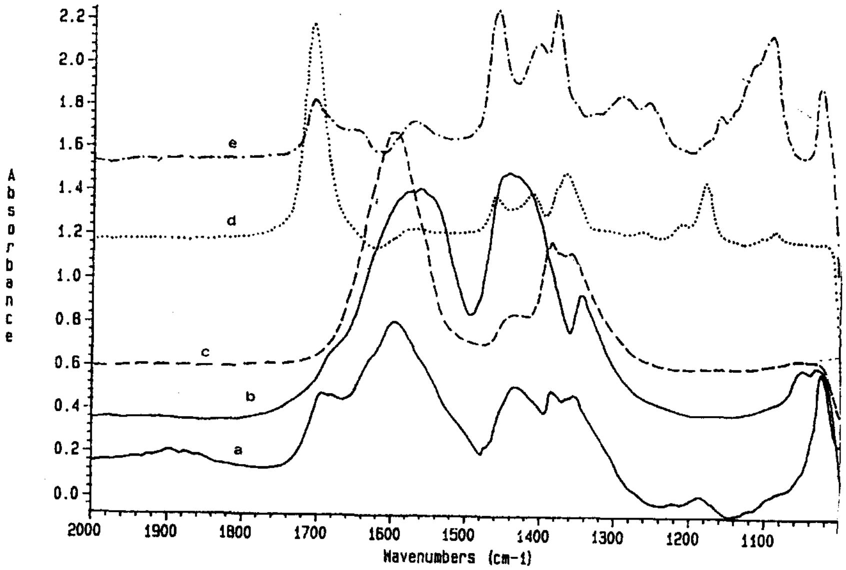


Fig. 7. FT-IR spectrum of the surface species arising from the interaction of the Mg-chromite catalyst with n-butane at 423 K (a), compared with the spectra of adsorbed acetates (b), formates (c), 2-butanone (d) and 2-butanol (e) over the same surface.

tonaldehyde, methyl-vinylketone and methyl-ethylketone can or could also be produced [39].

4.2.1. The n-butane and n-butene catalytic combustion over $MgCr_2O_4$

Mg-chromite, like chromia [136,140] and most chromites, has been reported to be efficient transition metal based catalysts for hydrocarbon combustion, but it is more active and more stable than pure chromia [137,138]. We confirmed this [67] and studied with IR spectroscopy the interaction of several light hydrocarbons with particular emphasis on propane and propene [66] as well as butane and butenes [139].

$$n\text{-}C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O \qquad (13)$$

The IR spectrum of the adsorbed species formed upon the interaction of n-butane with the surface of oxidized $MgCr_2O_{4+x}$ are shown in Fig. 7. The reaction is observed starting from 423 K. At this temperature the strongest bands are observed near 1590 and 1440 cm^{-1} and can be assigned, together with a weaker band at 1355 cm^{-1}, to acetate species (COO^- asymmetric and symmetric stretching and CH_3 symmetric bending, respectively), in agreement with the spectra obtained upon the dissociative adsorption of acetic acid (Fig. 7b). However, the sharp doublet at 1385 and 1355 cm^{-1} suggest that formate species are also present (CH deformation and COO^- symmetric stretching); they participate also to the band near 1590 cm^{-1} (COO^- asymmetric stretching). These species are again identified in comparison with the spectra of formates obtained by formic acid adsorption (Fig. 7c). Moreover, 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-ethylketone (C=O stretching, asymmetric and symmetric CH_3 bendings and C–C–C asymmetric stretching, respectively), that has also been adsorbed over the same surface, as shown in Fig. 7d. A further sharp band at 1025 cm^{-1} is assigned, 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 (Fig. 7e). The above assignment finds support on the evolution of the spectra upon further heating. In fact, the bands

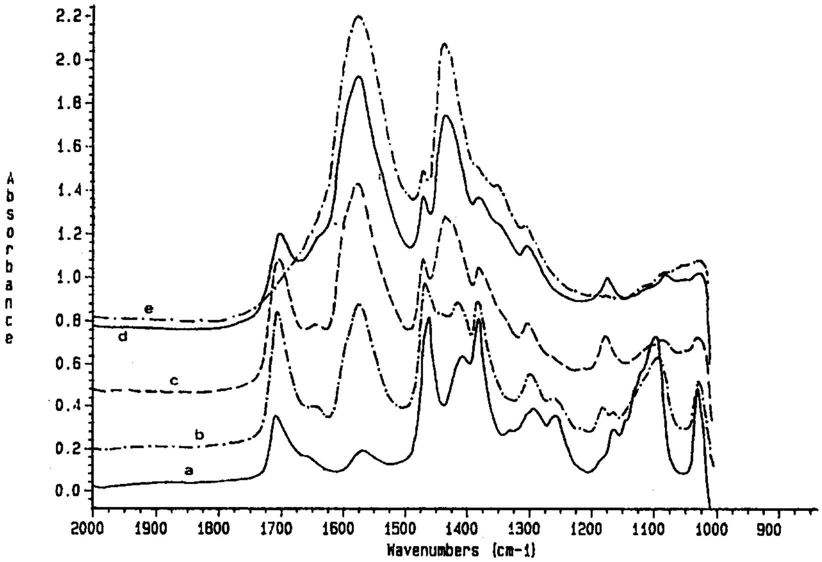


Fig. 8. FT-IR spectra of the surface species arising from the adsorption and oxidation of 2-butanol over the Mg-chromite catalyst at increasing temperature: outgassed at room temperature (a), 373 K (b), 423 K (c), 473 K (d) and 523 K (e).

assigned above to the ketone and to the alkoxide disappear by heating at near 473 K, while those associated to acetate species grow in intensity. The formation of sec-butoxy-species and of 2-butanone from n-butane oxidation is also substantiated by the observation that very similar spectra (but not identical) are found upon oxidation of 2-butanol (Fig. 8), 2-butanone and n-butane on this surface. Starting from the alcohol, the bands assigned to the 2-butoxy-species decrease, although they are still visible, at 423 K when the bands due to adsorbed 2-butanone rise to their maximum and those due to acetate species are already evident. Both starting from n-butane and from 2-butanol at 473 K the bands of adsorbed 2-butanone are still present, rather weak, while those due to acetate species increase at least up to 573 K, but later decrease with the appearance of water and CO_x in the gas phase and of water and carbonates on the surface. This behavior agrees with the catalytic behavior of Mg chromite, that is an effective combustion catalyst for several light alkanes in the range 620–770 K.

To verify the mechanism of n-butane oxidation, we also compared the spectra of C_4 oxygenates functionalyzed at C(1) (1-butanol, butyraldehyde and butyric acid) and of C_3 oxygenates functionalyzed at C(1) (1-propanol, propionaldehyde and propionic acid) and we did not find evidence of their presence among n-butane oxidation products.

On the other hand, the main difference between the spectra obtained upon n-butane oxidation and those obtained upon oxidation of 2-butanol and 2-butanone is the detection, starting from butane only, of formate ions. These species are not detected from C_4 oxygenates functionalized at C(2). The presence of this C_1 fragment (only from n-butane), without a corresponding C_3 fragment, can only be interpreted assuming that something occurs during the C–H activation step at C(2) (so before the production of the 2-butoxide from butane) that gives rise to a parallel path that can produce C_1 fragments.

In our studies [66,67,139] we have proposed that C–H activation over Mg chromite occurs at surface O^{2-}--Cr^{6+}--O^{2-} oxidized centers with a 'concerted' mechanism giving rise to the oxidative breaking of the C–H bond with the consequent production of an OH and an alkoxide and the assumption of two electrons by the cation, so reduced (formally) to Cr^{4+}. CH activation occurs at C(2) in the case of n-butane because the C–H's at C(2) are those associated to the smaller dissociation energy.

The results discussed above (in particular the observation of formates upon n-butane oxidation) can be rationalized assuming that the mechanism is not a concerted one, but interaction of the alkane with the oxidizing centers can give rise first to the formation of a 'quasi free' carbenium ion that only later approaches an oxide anion to produce the alkoxide. So, the 2-butyl cation produced by n-butane oxidation can isomerize in part to the ter-butyl cation before giving rise to the alkoxide. The ter-butoxy species have been found to give rise, by oxidation, to two formate and one acetate species [67], so justifying the formation of formate species from n-butane too.

We have also investigated the interaction of 1-butene and butadiene over the same surface, but the observed spectra are very different from those recorded upon interaction with butane. In fact, the spectra obtained from 1-butene contain bands that should be assigned to 1-butene-2-oxide species (C–O stretching at 1019 cm^{-1}) and to methyl-vinylketone (bands at 1667, 1634 and 1173 cm^{-1}, C=O, C=C and C–C stretchings, respectively). This can be interpreted as an evidence of the allylic oxidation mechanism occurring, as always, with the breaking of the weakest C–H bond (the allylic ones, in this case) and the formation of the corresponding allylic alkoxide species. This species can later be oxidatively dehydrogenated to the corresponding carbonyl compound, methyl-vinylketone. This strongly implies that olefins are not intermediates in the combustion route of n-butane, because adsorbed allylic species are not found upon n-butane oxidation.

4.2.2. *The n-butane oxy-dehydrogenation over Mg-vanadates*

Mg-vanadates are active catalysts for the oxy-dehydrogenation of butane to butene and butadiene [121,122]. It is still not clear what is the most active phase among Mg ortho-, pyro- and meta-vanadates [141] for this reaction, but it is certain that even catalysts where the only detectable crystalline phase is MgO can be efficient for butadiene production [122].

$$\text{n-}C_4H_{10} + 1/2O_2 \rightarrow \text{n-}C_4H_8 + H_2O \qquad (14)$$

$$\text{n-}C_4H_{10} + O_2 \rightarrow \text{n-}C_4H_6 + 2H_2O \qquad (15)$$

The interaction of Mg-vanadates with propane and butane [139,142] does not give any detectable adsorbed species, although it is certainly effective above near 623 K according to the formation of gas-phase carbon oxides and to the decrease of transmittance of the sample likely due to reduction. However, the surface of this catalyst is reactive towards oxygenate compounds even at very low temperatures. The spectra of sec-butanol adsorbed on Mg vanadate show that the adsorption is almost completely dissociative, as deduced by the almost complete absence of the OH deformation mode and by the observation of the strong C–O/C–C modes of alkoxides near 1100 cm^{-1}. The alkoxides are progressively destroyed with the appearance of small amounts of methyl-ethylketone near 450 K, evidenced by the sharp band C=O stretching near 1700 cm^{-1}, but disappear completely at near 523 K. Above this temperature, no adsorbed species can be found.

On the other hand, also the interaction of 1-butene and of butadiene over Mg vanadate is extremely weak. The interaction with 1-butene is observed only near 523 K, with the formation of carboxylate species, characterized by bands at 1590 and 1420 cm^{-1}, due to the asymmetric and symmetric $-COO^-$ stretchings. However, these adsorbed carboxylate species disappear on further heating at 673 K, due their complete combustion and/or desorption of partly oxidized fragments. The same bands observed after contact with 1-butene are also found after contact with 1,3-butadiene but at significantly lower temperatures (473 K).

These results show that polar molecules like alcohols do react with the surface of Mg vanadates, giving raise to dissociative adsorption, while further dehydrogenation also can occur (although perhaps to a limited extent). However, the reactivity of this surface is by far weaker than that of Mg-chromite where the alcohols are partially oxidized to ketones even at room temperature, ketones are very strongly bonded and further transform to carboxylate species and finally completely decompose.

The behavior observed upon butane interaction with Mg-vanadate (no detectable intermediates) is understandable because at the temperature at which the interaction really occurs (above 623 K) the resulting partially oxidized surface species (likely 2-butoxide species) further transform very fast. Accordingly, 2-butanol adsorbed as 2-butoxide species dehydrates to n-butene gas and adsorbed water at much lower temperature (523 K). This agrees with the very weak reactivity of Mg-vanadate with butene and butadiene, that do not give rise to any detectable reactive adsorption up to 470–550 K. Therefore, over Mg-vanadate the butane activation could occur just with the same mechanism as on the Mg-chromite, although the alkoxide forms slowly and very rapidly dehydrates to the olefin n-butene, that can be recovered as the main useful product. However in part they produce CO_x, likely via ketone-acetates. The key step determining selectivity is, consequently, the evolution of the alkoxides that over the vanadate can in part decompose to the olefin while over the chromite are strongly bonded to the surface and are mainly oxy-dehydrogenated to the ketone and, eventually, burn totally.

4.2.3. *The n-butane and n-butene oxidation to acetic acid over vanadia-titania*

According to the literature [118] acetic acid has been produced in the past by n-butane selective oxidation over vanadia-titania catalysts. The production of acetic acid from n-butenes over similar catalysts has been the object of a more recent investigation [135].

$$n\text{-}C_4H_{10} + 5/2O_2 \rightarrow 2CH_3\text{-}COOH + H_2O \quad (16)$$

$$n\text{-}C_4H_8 + 5/2O_2 \rightarrow 2CH_3\text{-}COOH \quad (17)$$

The interaction of the three linear butene isomers with the surface of vanadia-titania oxidation catalysts is simpler than those discussed above for the combustion catalyst. Over this catalyst in fact, 2-butoxide species are observed largely predominant after rt contact (see Fig. 10 for 1-butene adsorption) and their evolution to methyl-ethylketone follows rapidly at slightly higher temperatures [143]. The ketone starting from 423 K undergoes C–C bond breaking at C(2)–C(3) giving rise to acetate species. Allylic oxidation species are observed only in small amounts, if any, and need low temperature adsorption to be evident. The interaction of n-butane is molecular and very weak at rt while at higher temperatures acetate species are the main observed n-butane oxidation products. This means that the spectra arising from butane and butene oxidation at temperatures near 570 K are the same (Fig. 9) while they differ from those that are observed by butadiene oxidation (Fig. 10, see below). This contrasts with what is observed with Mg-chromite, where different species are obtained by butane and butene oxidation at high temperature (see above) and with VPO catalysts, where the same species are found from butane, butene and butadiene oxidation, but they are not acetates (see below).

These data agree with the activity of vanadia-titania to give acetic acid by n-butane

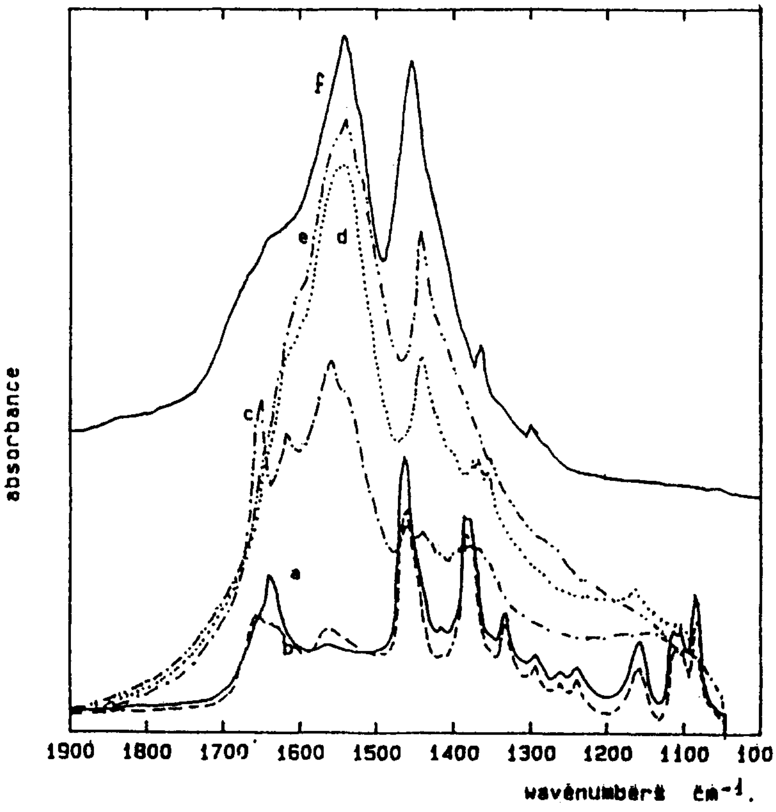


Fig. 9. FT-IR spectra of the adsorbed species arising from 1-butene and butane adsorption over V_2O_5-TiO_2. Butene adsorption at rt (a), after outgassing at rt (b) and after heating at 423 K (c), 473 K (d) and 573 k (e). Butane adsorption at 573 K (f).

and n-butene oxidation. This kind of catalysts is reported to give rise to mixtures of allylic oxidation products and of 'Wacker' type products upon olefin oxidation (i.e., acetone and acrolein from propene [144]), always with big amounts of acetic acid. Water certainly facilitates the desorption of acetate ions in the form of acetic acid (instead of burning), thus allowing to interrupt the most usual combustion way at an intermediate step. Moreover, water certainly increases the number of weakly Brønsted acid sites that electrophilically attack the olefin, so favoring the production of Wacker-type compounds (methyl-ethylketone) with respect to allylic oxidation products. It is obvious that selectivity can be greatly influenced by the modulation of the amount of steam in the feed.

The studies of olefin oxidation we performed over vanadia-titania [143,145,146] gave similar results with respect to those reported by Miyata and coworkers over vanadia-titania [147] and vanadia-zirconia [148] and by Davidov and Budneva over vanadia-alumina [149]. The medium Brønsted acidity of supported vanadia seems to be a key factor favoring the reactivity of this surface towards olefinic double bonds and tending to stabilize the alkoxide intermediates, thus decreasing selectivity towards oxy-dehydrogenation products as well as allylic oxidation. However, the milder oxidizing character of V^{5+} with respect to Cr^{6+} allows selective oxidation and, finally, acetic acid production from n-butane and n-butene.

Over vanadia-titania, while butene oxidation gives mainly rise to acetic acid, butadiene oxidation gives rise to maleic anhydride with appriciable selectivities [132]. Butadiene, due to the delocalization of its π-type electrons is less susceptible to electrophilic attack. On the other hand, according to our experiments [150], particular sites are present on vanadia-titania that are able to insert oxygen atoms in the 1,4-

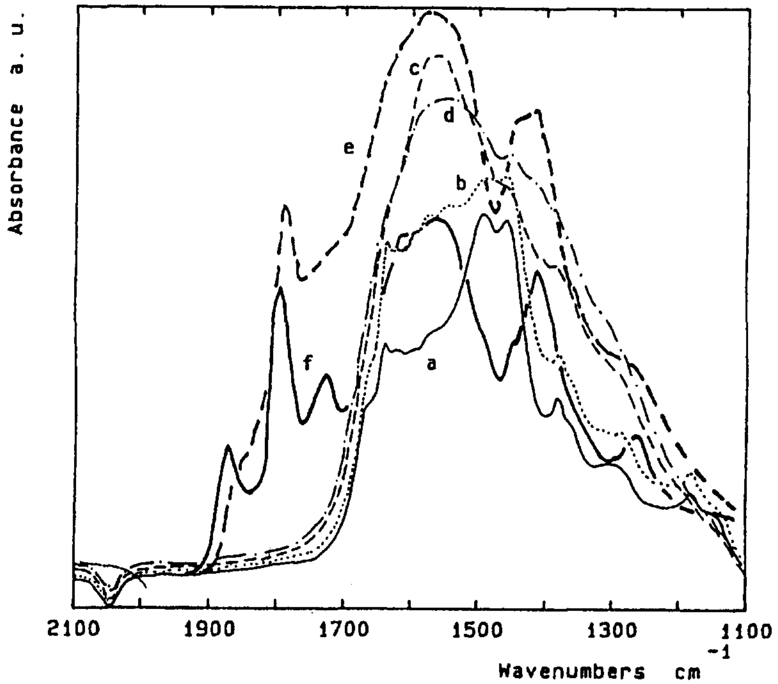


Fig. 10. FT-IR spectra of the adsorbed species arising from butadiene adsorption over V_2O_5-TiO_2. (a) adsorption at rt; after heating under outgassing at 373 K (b), 473 K (c) and 523 K (d); after adsorption at rt and heating in oxygen at 473 K (e) and at 523 K (f).

position of butadiene giving rise to maleic anhydride (reaction 18). This will be discussed in the next paragraph.

$$\text{n-}C_4H_6 + 5/2O_2 \rightarrow C_4H_2O_3 + 2H_2O \qquad (18)$$

4.2.4. The n-butane and n-butene oxidation to maleic anhydride over vanadia-based catalysts

VPO catalysts, mainly constituted of the pyrophosphate $(VO)_2P_2O_7$, are used industrially for the production of maleic anhydride ($C_4H_2O_3$) from n-butane oxidation [15,119,120]. They also allow the synthesis of maleic anhydride from n-butene as well as from 1,3-butadiene, but with lower selectivities.

$$\text{n-}C_4H_{10} + 7/2O_2 \rightarrow C_4H_2O_3 + 4H_2O \qquad (19)$$

$$\text{n-}C_4H_8 + 3O_2 \rightarrow C_4H_2O_3 + 3H_2O \qquad (20)$$

The oxidation of n-butane and n-butenes over VPO based catalysts has been investigated by IR spectroscopy by several authors [17,18,142,151–159]. The interaction of n-butane with a very active and selective $(VO)_2P_2O_7$ catalyst has been reported to be molecular, weak and reversible at temperatures up to 520 K. Above this temperature a reactive adsorption becomes evident, giving rise to a strongly adsorbed species responsible for a broad band at 1620 with a shoulder near 1710 cm^{-1} and a weaker maximum at 1780 cm^{-1}. The same spectrum of adsorbed species can be found if the catalyst is put into contact with 1-butene and 1,3-butadiene, but the temperature at which this spectrum appears differs significantly: 450 K for butene, 300 K for butadiene [18,142].

If the sample has been previously oxidized, the component at 1780 cm^{-1} is much stronger and shows a pronounced shoulder at 1850 cm^{-1}. In all cases, if oxygen is later added the spectrum transforms with the growth of the band at 1780 and its shoulder at 1850 cm^{-1} and the decrease of that at 1620 cm^{-1}, while a sharp band near 1715 cm^{-1} can reach strong intensities in intermediate conditions. The bands at 1780 and 1850 cm^{-1} are very typical of cyclic anhydrides like maleic anhydride (symmetric and asymmetric C=O stretchings, respectively) while the bands at 1715 and 1620 cm^{-1} could be due to intermediate species in the oxidation of butadiene to maleic anhydride.

The study of the adsorption of furan and 2,5-dihydrofuran support the identification of the species responsible for the band at 1620 cm^{-1} as an adsorbed form of furan, while the band at 1715 cm^{-1} has been assigned to the unsaturated lactone oxacyclopent-2-en-3-one, that would also be an intermediate in the maleic anhydride synthesis.

This picture has been supported by parallel studies of butene and butadiene oxidation over other less performing catalysts that, however, also give rise to high selectivities to maleic anhydride, like V_2O_5-TiO_2 [150] and MoO_3-TiO_2 [160]. Very similar spectra have been in fact observed in interaction of butadiene on these three catalysts, showing that all three have particular sites able to insert an oxygen atom in the 1,4-position of butadiene, giving rise to furan-like cyclic compounds.

The ability to interact strongly with butadiene to give rise to furan and maleic anhydride is limited to few oxide catalysts, likely those have active vanadyl and molybdenyl species. As for example, while on catalysts like Mg vanadates and ferrite materials (typically active in dehydrogenation) react weakly with butadiene and give rise mainly to crotonaldehyde species, VPO's [18], V_2O_5-TiO_2 [150] and MoO_3-TiO_2 [160] react strongly with butadiene at rt. The spectra obtained over V_2O_5-TiO_2 are shown in Fig. 10. Butadiene at rt gives rise to strongly adsorbed species characterized by a couple of bands at 1490 and 1455 cm^{-1}. On heating this species transforms into another characterized by a very strong and broad band centered at 1565 cm^{-1}. These two species have been identified as two different forms of adsorbed furan [150]. In the presence of oxygen, maleic anhydride (strong bands at 1870 and 1790 cm^{-1}) and maleate species (1560 and 1430 cm^{-1}) grow. The behavior of VPO in the step butadiene → maleic anhydride looks very similar to that of V_2O_5-TiO_2.

The picture we propose indicates that VPO is substantially an oxidative dehydrogenation catalyst that, however, also contains active sites to insert oxygen in 1,4-positions of butadiene, giving rise to cyclic compounds (furan and maleic anhydride). According to the mechanism discussed above, an oxy-dehydrogenation catalyst should necessarily be characterized either by a strong basicity or by a strong acidity. As studied in detail, a very active VPO catalyst is indeed strongly acidic [161,162] and this allows the alkoxy-intermediate to evolve very rapidly to the olefin. Interestingly, it has been shown that when the acidity of VPO is lowered by potassium doping, not only the n-butane conversion activity is strongly decreased, but, more precisely, the selective way is stopped and VPO becomes a poorly active combustion catalyst for n-butane [159]. This could be due to slower butene evolution from butoxide, with a consequent favored competitive combustion, likely again via adsorbed ketone and acetates.

The data reported in our studies do not disagree with those reported by several other authors. The spectra observed by Wenig and Schrader [17,156,157] at 373 K are roughly similar to those we have reported, while the same authors emphasized the presence under in situ conditions of a band at 1715 cm^{-1} that they assigned to adsorbed maleic acid. In effect, maleic acid can be in dynamic equilibrium with the anhydride under reaction conditions, where water is present in significant amounts. However, these authors proposed that the reactions occur over this catalyst through activation of butadiene by reaction with dioxygen to give a peroxidic species [157]. This does not agree with our conclusions.

Puttock and Rochester [153] also observed spectra similar to ours but assigned the band found from furan at 1615 cm^{-1} to carboxylate species, as also suggested previously by Gerei et al. [151] and Rozhkova et al. [152]. Ramstetter and Baerns [154] and Do and Baerns [155] studied the n-butane oxidation over oxide-supported VPO catalysts. The main difference between the species identified by these authors and ours concerns the identification of a 1,4-'addition' complex of butadiene to which a band at 1650 cm^{-1} was assigned, in spite to its broadness, unusual for C=C olefin stretchings that are typically sharp. These authors also speculated that furan should be adsorbed at 2-position in a cationic form.

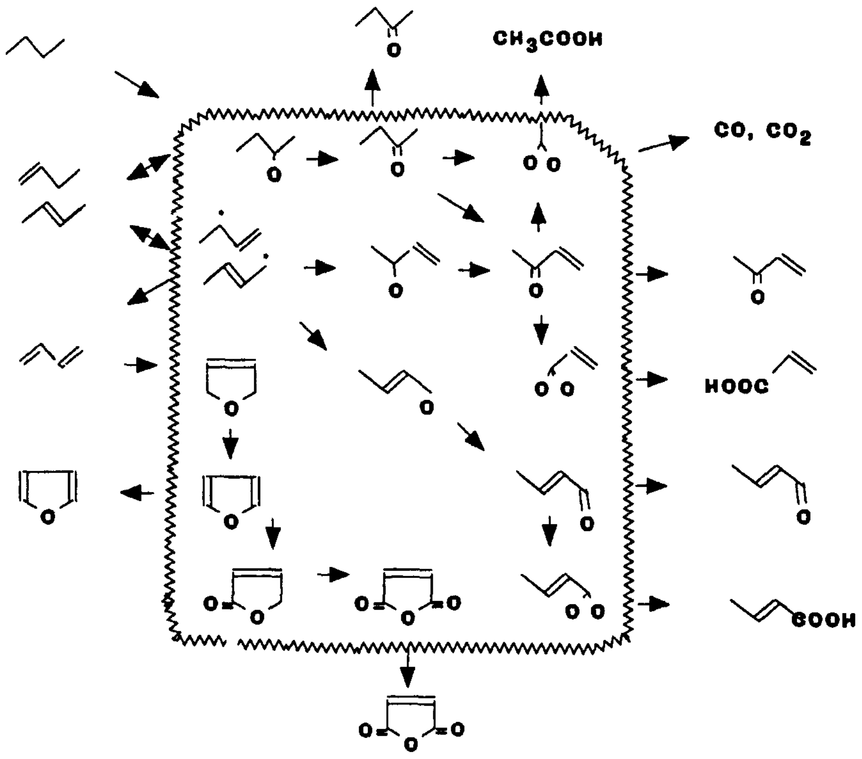
4.2.5. The n-butene oxy-dehydrogenation and oxidation over ferrite and chromite catalysts

The molecular interaction of n-butenes is stronger with oxy-dehydrogenation catalysts like ferrites than with the above vanadia-based catalysts, showing the role of full or partly full d-orbitals of Fe^{3+} and/or Cr^{3+} in interacting with π-orbitals of the olefins [163]. The interactions of 1-butene with typical olefin oxy-dehydrogenation catalysts [164,139] show the path observed also on the Mg-chromite and vanadia-titania catalysts to 2-butoxy-species, 2-butanone and acetates, together with a different path with formation of methyl-vinylketone and butadiene. On the other hand, perhaps the most typical characteristic of this kind of catalysts is the poor reactivity towards butadiene. 1,3-butadiene is in fact adsorbed molecularly too and no evidence of reaction is found at rt, in contrast to, for example, vanadia-titania and molybdena-titania, where butadiene strongly reacts already at rt. This behavior is probably associated with very weak Brønsted acidity, if any, but no strong basic character. Thus, this kind of catalyst is not very aggressive towards olefinic double bonds, although weak electronic interaction can occur with transition metal cations. This allows an attack on the C–H bonds in allylic position. It seems very interesting that this reaction is observed at rt for the 1-butene isomer, while it is not for the 2-butene isomers. This agrees with the weaker dissociation energy of allylic methylene groups with respect to allylic methyl groups, as discussed elsewhere [164]. So, it seems very likely that 1-butene is the reactive intermediate in allylic oxidation or oxy-dehydrogenation of butenes.

4.2.6. A generalized mechanism for the heterogeneously-catalyzed oxidative conversion of n-C_4 hydrocarbons

In Scheme 6 we propose a generalized pathway for n-butane and n-butene oxidation over oxide catalysts. Again, the selectivity is not only governed by the chemical nature of the catalyst, that in part determines the relative rates of the different steps. In fact, as underlined by Cavani and coworkers [165,166] the reaction conditions influence the product distribution both directly and indirectly, by causing modifications on the oxidation state of the catalyst.

According to (i) our results obtained over combustion catalysts; (ii) the known relative rate of reaction of different C–H bonds on hydrocarbons; and (iii) the results of isotopic labeling experiments of butane oxidation over VPO catalysts by Papera et al. [167], n-butane is activated at C(2) over oxidized M^{n+}--O^{2-} centers, giving rise to sec-butoxy species. This species provides the main selectivity determining step (using a concept proposed by Michalakos et al. [121]). In fact, over very active oxidation catalysts the alkoxy-groups are rapidly dehydrogenated oxidatively to the ketone that rapidly undergoes C(2)–C(3) bond breaking to acetate species. In the presence of water, acetic acid can be produced, but usually carbon oxides are the main result of this path. Over catalysts that have low oxidizing activity but very pronounced acidic or basic character the alkoxide decomposes rapidly, giving rise to the mixture of n-butenes, that can be evolved in the gas phase only over surfaces that are very unreactive towards olefins, like Mg-vanadates. Over catalysts very active in allylic attacks, the n-butenes give rise to allylic species that very rapidly result in allyl-alkoxides, either but-1-en-3-oxide or but-3-en-1-oxide. The former is the main precursor for the methyl-vinylketone (that can also evolve later to acetates) while the latter is the precursor for crotonaldehyde that can later give rise to crotonates. Both these ways can



Scheme 6. Reaction pathways for butane oxidation.

give rise to selective oxidation products (methyl-vinylketone or crotonaldehyde) but could also result predominantly in total oxidation.

Both allyl alkoxides (but-1-en-3-oxide and but-3-en-1-oxide) by elimination give rise to butadiene that is again free to live the surface over catalysts that are very unreactive towards dienes. Only over some particular catalysts butadiene undergoes 1,4-oxidation to give dihydrofuran, furan and later maleic anhydride, with a possible intermediacy of the butenolactone.

As discussed above this scheme seems to explain the activity of catalyst for butane catalytic combustion, for partial oxidation to acetic acid, methyl-ethylketone and methyl-vinylketone and for oxidative dehydrogenation to butene and butadiene.

As for the case of VPO catalysts active for maleic anhydride production, a further discussion is possible, because of the large amount of data available. According to Centi et al. [15] and to Zhang-Lin et al. [16,168], some of the more typical features of the VPO catalytic system are the following: (i) butene and butadiene are produced from butane only in excess of butane; (ii) butene oxidation to maleic anhydride is by far faster but much less selective than butane oxidation to maleic anhydride and results in rapid deactivation; (iii) butadiene is oxidized even more rapidly; (iv) the reduced phase $(VO)_2P_2O_7$ is more active than the oxidized phase $VOPO_4$ in the butane selective oxidation, while the reverse is found for butadiene and furan oxidation to maleic anhydride. These data can be interpreted on the basis of the Scheme 6 and of the idea, discussed above, that this catalytic system works with three types of functionalities: (i) oxy-dehydrogenation functionality, working for the step butane → butadiene; (ii) functionality for oxygen insertion to butadiene, to give furan; (iii) sites for oxidation of furan to give maleic anhydride. According to the above discussion, for the oxy-dehydrogenation step this catalyst probably works as an n-type semiconductor (i.e., the active species is associated to tetravalent vanadium); for the step from butadiene to furan it should act as a p-type semiconductor (i.e., the active species is associated to pentavalent vanadium). Therefore, butane should be activated over tetravalent vanadyls of $(VO)_2P_2O_7$ and there it undergoes the selective way up to butadiene, almost without desorbing (or being readsorbed very fast in a reduced environment). The main path for unselective oxidation upon maleic anhydride synthesis is through butoxy- and acetate species (starting from butene) and this is confirmed by the detection of acetic and acrylic acids as by-products also in industrial conditions. If butenes are directly fed, they can interact with pentavalent vanadium species (and over P-OH Brønsted acid sites) and this results in a very fast oxidation to CO_x via butoxide-acetate. This explains why the oxidation of butenes is much less selective than the oxidation of butane. Butadiene undergoes a very rapid oxygen insertion, likely over pentavalent vanadium, and, on similar sites, furan is further oxidized to maleic anhydride. This view is in agreement with the proposal of Volta and coworkers [16,68,168], that the best VPO catalysts contain the oxidized phase $VOPO_4(VPO_5)$ together with the predominant reduced one, $(VO)_2P_2O_7(V_2P_2O_9)$, although it is not excluded that the best formulation for the active phase is $V_2P_2O_{9+\delta}$, with small oxygen excess and vanadium partially pentavalent, in better agreement with the view of Centi et al. [15]. The difference between the two models can be very labile.

The most likely path to tetrahydrofuran, produced with very low O_2/C_4H_{10} feeds [126] could be associated with hydrogenation of dihydrofuran by surface carbonaceous materials, probably formed in big amounts in those conditions.

4.3. The selective oxidation of methylaromatics

The gas-phase selective oxidation of o-xylene to phthalic anhydride is carried out industrially over vanadia-titania-based catalysts [169–171].

The main by-products are maleic anhydride and carbon oxides. Minor by-products are o-tolualdehyde, o-toluic acid, phtalide, benzoic acid, toluene, benzene and citraconic anhydride. Vanadia-based catalysts can also be used for the gas-phase selective oxidation of toluene [172,173] and para-xylene [174] to the corresponding aromatic aldehydes and/or carboxylic acids. According to Huuhtanen et al. [173] vanadia-titania is the best catalyst also for the benzaldehyde synthesis. Vanadia-based catalysts, among which vanadia-titania [169,175], are also used industrially for the production of aromatic nitriles by gas-phase ammoxidation of toluene and of the three xylene isomers: alumina-supported V-Sb-based oxides seem to be the best catalysts.

The mechanisms of such methyl-aromatic oxidation reactions are obviously strongly correlated, due to the similarity of the most active catalysts and of the reactants. Correspondingly, the activation mode of the hydrocarbons is expected to be in all cases the same.

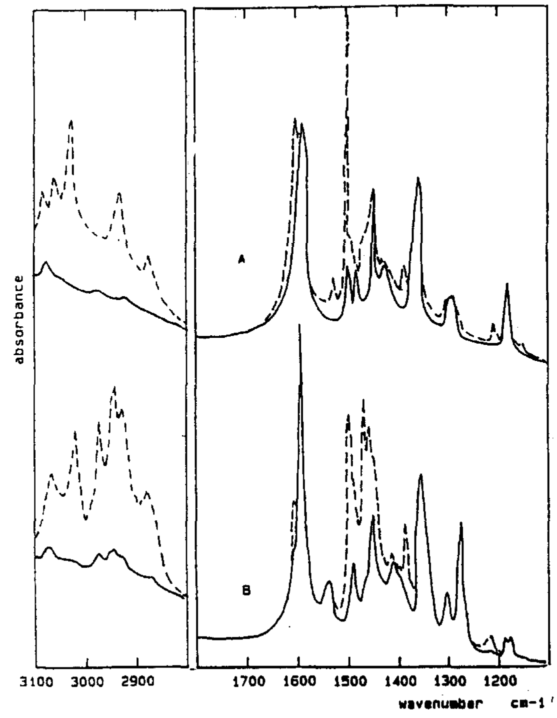


Fig. 11. FT-IR spectra of the adsorbed species arising from adsorption of toluene (A) and o-xylene (B) over V_2O_5-TiO_2. Broken lines, in contact with the vapors at rt; full lines: after outgassing at 350 K.

Several years ago Sachtler et al. reported IR data on toluene oxidation [176]. More recently several IR studies have been devoted to the mechanisms of these reactions. Niwa et al. [31–33] first studied by the in situ diffuse reflectance technique the ammoxidation of methylaromatics over vanadia-alumina. More recently van Hengstum et al. [177] reported a transmission FT-IR study of the oxidation of toluene and o-xylene over vanadia-titania. The ammoxidation of toluene was later studied by us [178–180] over vanadia-titania (anatase), by Azimov et al. over V-Sb catalysts [181] and by Lee et al. over V-Bi catalysts [182] using the transmission technique and by Sanati and Anderson [183] over vanadia-TiO_2(B) using the DRIFT technique. The oxidation of toluene has been investigated over different supported vanadias by Busca et al. [178–180], by Miyata et al. [184,185], by Davydov [186] and by Woiciechowska et al. [187] while that of o-xylene has been studied by Busca [179,180] and by Nobbenhuis et al. [188].

4.3.1. *IR studies on the activation of alkylaromatics over vanadia-based catalysts*

The activation of toluene and of the three xylene isomers over vanadia-titania occurs even at room temperature, giving rise to adsorbed species that are certainly already transformation products [179]. In fact the spectra show that weakly perturbed toluene and xylenes are desorbed by outgassing in the temperature range of 300–373 K, leaving adsorbed more strongly bonded species that are stable up to near 373 K (see Fig. 11 for toluene and o-xylene). The IR spectra of these species have a number of similarities in the cases of all methylaromatics showing that they are due to closely related species. They show in all cases in the region 1650–1100 cm^{-1} the typical ring vibration modes of mono- and/or di-substituted aromatics. The spectra do not show bands that can be assigned to C=O or C–O stretching modes. Moreover, the spectra are definitely different from those of any conceivable oxygen-containing species, directly adsorbed on the catalyst surface. Nevertheless, the evolution of the spectra by heating in the presence and/or in the absence of oxygen demonstrate that these species transform into side-chain oxidized species like benzaldehyde, the tolualdehydes, benzoate and toluate species and phthalic anhydride from o-xylene. Both the simplicity of the IR spectra and the experimental conditions imply that they are due to mononuclear aromatic species, the formation of coupling products being excluded. Spectroscopic and chemical considerations strongly support the conclusion that the spectra are due to hydrocarbon entities that have one intact aromatic ring. Reaction, if occurred, took place at the methyl groups.

The particular spectroscopic features of these spectra, including a band in the region 1370–1340 cm^{-1}, strong in all cases and generally not found in aromatic hydrocarbons, assigned to a CH_2 deformation mode, can be interpreted as due to benzyl species, as discussed in Ref. [179].

Very similar spectra have been observed by Davydov [186] for toluene over vanadia-alumina and by Azimov et al. [181] over V-Sb catalysts. However, these authors assigned them to the cationic form of toluene, formed by protonation of the aromatic ring by a very strong Brønsted acid site. This assignment contradicts the experimental result showing that toluene interaction with much stronger Brønsted acids like the superacid sulphated titania and some zeolites do not give rise to the same species. Miyata et al. [184,185] and Sanati and Andersson [183] observed similar spectra for toluene over supported vanadia and also assigned them to the benzyl species. Miyata et al. [184] based this assumption on comparison with the spectra obtained by adsorption of toluene-d_3. On the other hand, the features of the same species are probably present in the spectra recorded in situ by van Hengstum et al. [177] but, due to the copresence of several other species, the presence of benzyl species could not be recognized by these authors. Finally, the quality of the spectra reported by Nobbenhuis et al. [188] is so poor that they do not allow a clear identification of the less stable adsorbed species.

In a following paper, Finocchio et al. [66] discussed the fact that over vanadia-titania toluene and xylene selective oxidation catalysts the benzyl species is easily observed while on catalysts active and selective for propene oxidation, the corresponding allyl species cannot be found. In fact, according to the kinetic measurements of Sanati and Andersson [189] the rate determining step in toluene oxidation is the interaction of the benzyl species with surface oxide species. On the contrary, in the case of propene selective oxidation the rate determining step is the hydrogen abstraction from the methyl group of propene to give the allyl intermediate [190]. This means that the lifetime of allyl species is expected to be so short that it cannot be detected over real oxidation catalysts, in contrast to the lifetime of the benzyl species that is very long at low temperature. This can be associated to the very extensive delocalization of the charge (if any) or the radical center in the case of benzyl species.

Adsorbed toluene species with similar spectroscopic features, acting as intermediates in toluene oxidation, have been also observed over the combustion catalyst α-Fe_2O_3 [191] and were also assigned to benzyl species. A similar intermediate was previously found over ZnO [192] and was assumed to be an anionic benzyl intermediate. This seems to indicate that activation of methyl-aromatics over these oxide catalysts follow a similar mechanism.

As for the mechanism of the hydrogen abstraction, Mamedov et al. [193] proposed that it occurs over the basic sites of V-Sb-based ammoxidation catalysts with abstraction of an H^+. This fully contrasts with the conclusion of the same authors that toluene would be adsorbed on the same catalysts in a protonated form [181]. We disagree with both ideas (i.e., protonation of toluene and hydrogen abstraction over basic sites). We suggested that activation of alkylaromatics at the methyl groups occurs over oxidizing sites by hydrogen abstraction in the form of an H^- (i.e., $H^+ + 2\ e^-$) or $H^\cdot$ [178–190]. In a more recent study, Meijers et al. [194] showed that the parent molecule allyl-benzene (even more active at the benzylic C–H than methylaromatics) reacts far more strongly with oxidation catalysts like vanadia-titania (characterized by medium-high surface acidity) than with magnesia and that purely Lewis acid catalysts like pure titania also show some reactivity. This has been interpreted as a further support to the idea that basicity has nothing to do with methyl aromatic activation over oxidation catalysts.

4.3.2. The synthesis of the aromatic aldehydes

After the hydrocarbon activation, the mechanism of the oxygen atom insertion and of the aldehyde production by alkylaromatic oxidation over vanadia-titania should be clarified. The results of the oxidation experiments of toluene, para- and meta-xylene parallel each other. In Fig. 12 the spectra relative to meta-xylene oxidation are reported. As already cited, near 373 K the spectrum of the adsorbed intact hydrocarbon disappears while the bands due to the m-methyl-benzyl species are predominant, although a new band is also observed near 1635 cm^{-1}, weak. A band at 1635 cm^{-1} grows in the temperature range 373–473 K and later disappears, both in the presence and in the absence of gas phase oxygen, starting both from toluene and from the three xylene isomers. It coincides with the C=O stretching of adsorbed benzaldehyde and tolualdehydes [178,180,187] and can be assigned to adsorbed benzaldehyde and the three tolualdehydes (m-tolualdehyde in Fig. 11) produced by oxidation of the benzyl species.

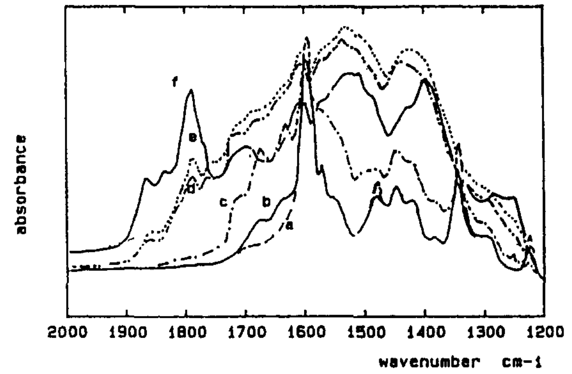


Fig. 12. FT-IR spectra of the adsorbed species arising from m-xylene adsorption over V_2O_5-TiO_2: adsorption at rt; (a) and treatment in oxygen at 373 K (b), 423 K (c), 473 K (d), 523 K (e) and 573 K (f).

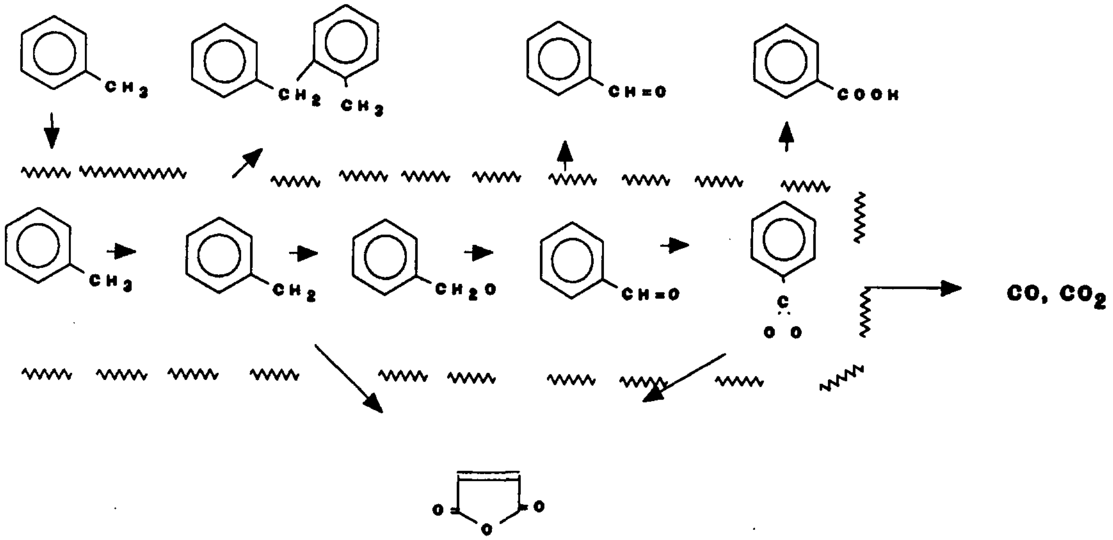
Upon m-xylene oxidation, near 523 K the above band of m-tolualdehyde disappears, while a couple of strong and broad bands grow near 1530 and 1430 cm^{-1}. These bands are typical of carboxylates and are again observed, with very weak band shifts, upon oxidation of all methyl-benzenes, as well as of the corresponding aromatic aldehydes. They can be assigned predominantly (if not entirely) to benzoate and toluate anions (in Fig. 11, meta-toluate anions). These bands show their maxima near 523 K in all cases and suddenly disappear above 673 K, when gas-phase CO_2 begins to be detectable.

These features provide evidence for a reaction path, common to the four methyl-aromatics under study, that involves the following steps: (i) activation of the methyl-aromatic in the form of a benzyl species; (ii) reaction of such species with the catalyst surface giving the corresponding aldehyde, very likely with the intermediacy of benzyloxy-species [178]; (iii) oxidation of the aldehyde by the catalyst surface to give the carboxylate species; (iv) decarboxylation of the carboxylate species giving CO_2 and, likely, a demethylated hydrocarbon (toluene from xylenes and benzene from toluene). All these successive processes occur both with and without gas phase oxygen, that, consequently, is thought to be not active in them.

However, features belonging to other species not involved in this path are also observed upon m-xylene oxidation. Near 433 K two other bands are clearly observed at 1710 and 1670 cm^{-1}. A feature near 1700 cm^{-1} persists also near 673 K when a very strong and complex absorption pattern becomes detectable in the 1900–1700 cm^{-1} region. In this region the couples of bands due to symmetric and asymmetric C=O stretchings of the O=C–O–C=O system of cyclic anhydrides typically fall. The IR spectra of the different cyclic anhydrides differ slightly for the position of these bands, as well as for the position and intensities of the C–O–C stretchings, observed in the 1300–1200 cm^{-1} region. The complexity of the spectra observed when m-xylene is oxidized on the vanadia-titania surface (distinct bands are observed at 1870, 1840, 1800, 1790 cm^{-1} and at 1290 and 1260 cm^{-1}) suggest that we are dealing with a mixture of maleic and citraconic anhydrides. Very similar spectra are observed when starting with p-xylene, while only maleic anhydride is observed upon toluene oxidation (bands at 1870, 1790, 1290 and 1260 cm^{-1}). Being maleic and citraconic anhydrides main by-products in toluene and xylenes oxidation, their origin has been investigated further.

Experiments involving toluene, meta- and para-xylene oxidation by the catalyst surface in the absence of gas-phase oxygen show the oxidation path at the methyl group, as already cited; however, neither the bands of cyclic anhydrides nor those at 1720 and 1670 cm^{-1} (found in intermediate conditions in O_2) are observed. This suggests that species responsible for these bands are intermediates in the formation of maleic and citraconic anhydrides. A similar situation has been observed by studying the oxidation of benzene over vanadia-titania [195], where phenate species where though to give rise to quinone species, responsible for a band at 1670 cm^{-1}, successively giving maleic anhydride.

The spectra relative to adsorption and heating of benzaldehyde over vanadia-titania in the presence of gas-phase oxygen fully confirm the data discussed above. Adsorbed benzaldehyde (mainly characterized by its C=O stretching at 1635 cm^{-1}, but also by features at 1600, 1582, 1494, 1461 cm^{-1}, ring vibrations, at 1395 cm^{-1}, CHO deformation cm^{-1} and at 1325, 1238 and 1175 cm^{-1}, ring vibrations) transforms into benzoate species (more intense bands at 1500 and 1430 cm^{-1}) in the 423–473 K range. Benzoates later decarboxylate giving CO_2 near 573 K. No bands of maleic anhydride where found starting from the aldehyde. In our experimental conditions benzene is likely formed upon decarboxylation and desorbed as such. However, benzene, if formed, can be oxidized above 573 K over the vanadia-titania surface, giving benzoquinone, maleic anhydride and carbon oxides [196]. We believe that this consecutive path is the main one for carbon oxide production and a



Scheme 7. Reaction pathways for toluene oxidation.

secondary one for maleic anhydride production. The main way to maleic anhydride should involve the attack of gaseous oxygen to an adsorbed hydrocarbon species, very likely the benzyl species. Accordingly, we propose the reaction Scheme 7 for the oxidation of toluene, meta- and para-xylenes to the corresponding aldehydes on surface of vanadia-based catalysts.

This picture is supported by an excellent correlation between the temperature at which the maximum concentration of the different surface species (aldehydes, carboxylate species, cyclic anhydrides) is observed and those at which selectivity in the corresponding gas-phase products (aldehydes, carboxylic acids and cyclic anhydrides) raises the maximum. As for example, the main products in toluene oxidation over vanadia-titania catalysts are reported to be benzoic acid and benzaldehyde, with maximum selectivity near 540 K and maleic anhydride with maximum selectivity near 573 K [172], in good agreement with our data. In particular, our data definitely support that side chain oxidation (giving the aldehyde, carboxylic acids and finally CO_2) and ring oxidative opening (giving maleic and citraconic anhydrides) are mainly competitive paths, probably both starting from adsorbed benzyl species reacting either with the catalyst surface at the side chain or with gas-phase oxygen at the aromatic ring.

The spectra reported by Busca et al. [178,180] are similar to those previously published by van Hengstum et al. [177] concerning toluene oxidation over the same catalyst. Also the interpretation of the results does not differ very much, although in some details on the assignments of the C=O stretching bands significant differences can be found.

The results of IR studies of toluene oxidation over vanadia-titania can be compared with those observed over Fe_2O_3 [191], $MgCr_2O_4$ [67] and over CuO [186]. All these systems are essentially combustion catalysts for toluene [197], although all of them show give rise to traces of selective oxidation products (benzaldehyde and benzoic acid). Over Fe_2O_3 after toluene interaction the benzyl species are detected at rt (as on vanadia-titania) and was observed to convert into benzoate species near 523 K [191]. The aldehyde was not observed. On the contrary, over the chromite the benzyl species was not detected, but features associated with adsorbed benzaldehyde were found at 423 K that convert to benzoates at 423 K [67]. Over CuO the spectrum of benzoate species appeared at rt [186] in agreement with the extremely high activity of this material as a toluene combustion catalyst [197]. These data suggest that the scheme reported above can be generalized to toluene combustion catalysts.

4.3.3. The synthesis of phthalic anhydride

The spectra of the adsorbed species arising from interaction of ortho-xylene with the surface of the vanadia-titania catalyst in the presence of oxygen show some parallel features with respect to those discussed above concerning the oxidation of toluene and meta- and para-xylene. Also in this case the o-methylbenzyl species begins to transform above 373 K (Fig. 13), with production of adsorbed o-tolualdehyde (band at 1635 cm^{-1}) and of a quinone derivative (band at 1670 cm^{-1}). Successively bands likely due to o-toluate species (1530, 1420 cm^{-1}) grow first and decrease later with production of gas-phase CO_2.

However, already near 473 K (Fig. 13c) two strong bands predominate, centered at 1860 and 1790 cm^{-1}, associated to a single band at 1255

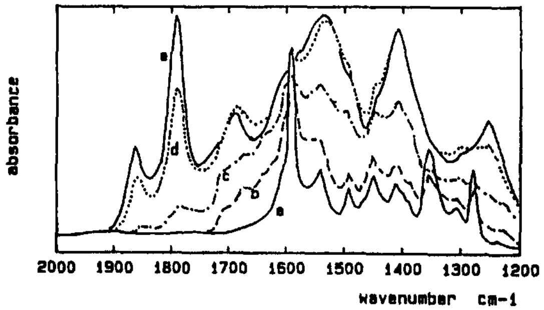


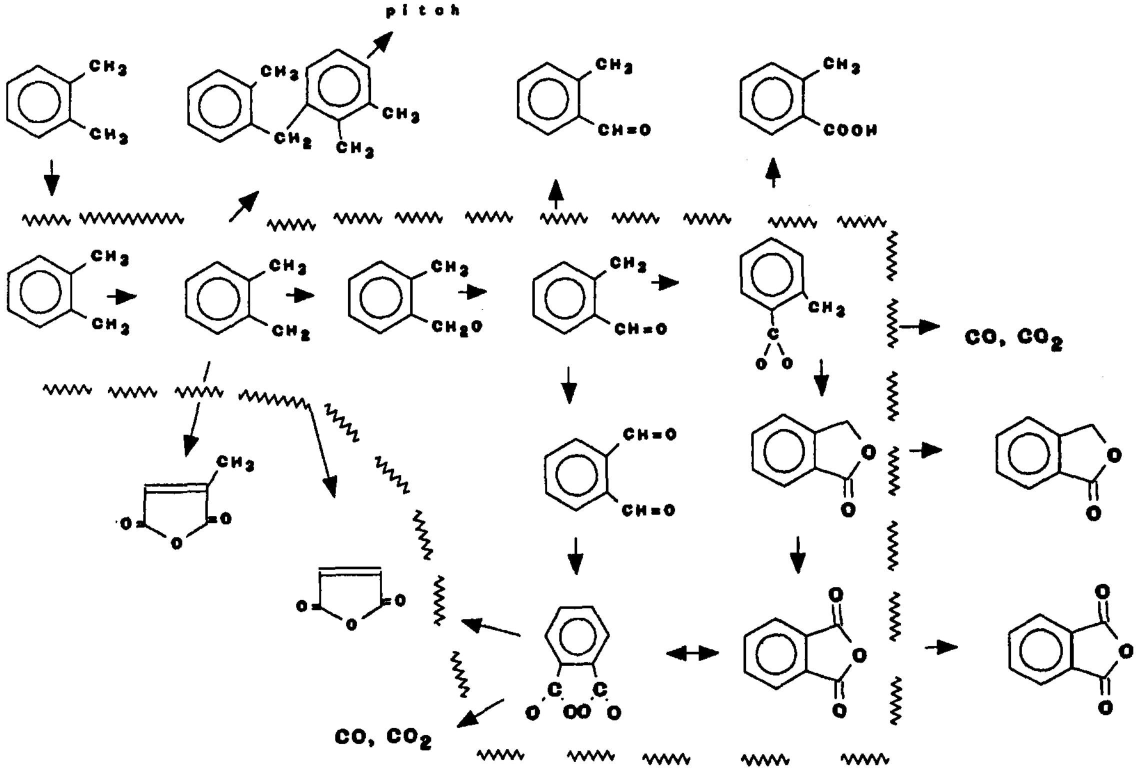
Fig. 13. FT-IR spectra of the adsorbed species arising from o-xylene adsorption over V_2O_5-TiO_2: adsorption at rt; (a) and treatment in oxygen at 373 K (b), 423 K (c), 473 K (d), 523 K (e).

cm^{-1}. These features are typical of phthalic anhydride, as confirmed by the direct adsorption of this compound on the catalyst. Another strong band appears in the same conditions at 1690 cm^{-1}, certainly due to a compound containing a carbonyl or a carboxyl group. This band is not observed so evident with m- and p-xylene. It very likely corresponds to adsorbed phthalide. The bands due to phthalic anhydride further grow up to 573 K, while that at 1690 cm^{-1} decreases in intensity. At 593 K all these bands decrease strongly although a more complex weak pattern remains in the 1900–1700 cm^{-1} range, probably due to a mixture of maleic and citraconic anhydrides [180].

Experiments carried out in the absence of oxygen show that the bands due to phthalic anhydride are detectable, although much weaker, also in the absence of gas-phase oxygen. This suggests that the formation of this compound does not involve O_2, but oxidized catalyst surface sites.

In conclusion, the reaction Scheme 8 is proposed for the oxidation of ortho-xylene on vanadia-titania catalysts. This scheme and our data agree with the product distribution in o-xylene oxidation reported by many authors [169–171,198–202], as well as with experiments of oxidation of intermediates [203]: o-tolualdehyde and phthalide are observed as the main intermediates in the 523–573 K temperature range, while phthalic anhydride selectivity grows in the 473–573 K range and later slightly decreases above 573 K due to the formation of carbon oxides and maleic and citraconic anhydrides.

One relevant feature concerns the main route to maleic anhydride. In fact, different authors disagree on this subject: Wainwright and Foster [170] and Wachs et al. [199] believe that maleic



Scheme 8. Reaction pathway for o-xylene oxidation.

anhydride is mainly formed from phthalic anhydride successive oxidation, while following Bond and Bruckman [200] it is formed from 'one of the last adsorbed intermediates in the reaction sequence'; finally, in the reaction scheme proposed by Bielanski and Haber [39] it is formed in a competitive way. Our data provide evidence for the formation of maleic anhydride near 573 K from all alkyl aromatics. This supports the idea that the main paths producing maleic and phthalic anhydrides are competitive and that side-chain oxidation products have a minor role in maleic anhydride production. Our data provide also evidence for the competitivity of the main route to carbon oxides, essentially due to decarbonylation of o-toluate anions and combustion of the aryl species, with respect to the selective route to phthalic anhydride. The mechanism we propose looks quite similar to that which has been employed recently by Papageorgiou et al. [202] in a kinetic modelling of this reaction.

Again the spectra we found do not differ substantially from those published previously by van Hengstum et al. [177] although these authors emphasized a likely role of carboxylate species we tend to exclude, in spite of the evident formation of these species. Again the spectra published by Nobbenhuis et al. [188], due to their poor quality, do not allow a comparison with the spectra published by other authors.

5. Conclusive comments

5.1. *On the use of IR spectroscopy in the identification of surface intermediates and of surface reaction pathways*

The data discussed above show that IR spectroscopy allows to give a contribution to the identification of the reaction mechanisms and surface reaction pathways, in oxide-catalyzed oxidations. However, the conditions of the experiments are sometimes critical and the best experimental conditions must be chosen from case to case. In the opinion of the present author, the use of IR spectroscopy in the field of catalysis research suffers nowadays of the excessive availability and use of this technique versus a sometimes insufficient experience in analyzing IR spectra as well as in mechanistic studies. In fact, almost any laboratory has available the apparatuses for IR studies. This sometimes results in the publication of spectra that are not understood sufficiently well and are only used to support arbitrarily conclusions arising from other experimental data or pure theories.

So, to gain much from these studies it is imperative to have a deep knowledge of the spectroscopic features of the species involved. One of the most elegant examples of good use of IR spectroscopy in catalysis over oxides is the identification of adsorbed formyl species (H–C=O) as an intermediate of the synthesis of methanol from CO + H_2 over ZnO, reported by Saussey et al. several years ago [204]. The identification of this species was obtained through the observation, upon CO + H_2 coadsorption, of two CH stretching bands at very low frequencies (2770, 2661 cm^{-1}) that convert into one only C–D stretching band (2020 cm^{-1}) by isotopic scrambling. The doublet in the CH region is due to the Fermi resonance of the CH stretching with the first overtone of the deformation mode (found at 1370 cm^{-1}) of an aldehyde-type CH bond. This Fermi resonance does not occur in the case of D–C=O (deuteroformyl) species. This identification is clearly due to the coupling of very good experiments with a deep knowledge of spectroscopy. This species would not be recognized by inexpert spectroscopists.

5.2. *On the usefulness of IR spectroscopy and the factors determining the selectivities in the catalytic oxidation over metal oxides*

The analysis of the results of the infrared studies on the oxidation of methanol, C_4 hydrocarbons and methylaromatics, over a number of metal oxide surfaces, discussed in the context of the known data arising from catalytic experiments and from other techniques, allowed us to propose generalized reaction networks for most of them. These schemes seem to correctly interpret the published conversion and selectivity data and can be the bases of *kinetic modelling*.

The possibility to propose generalized reaction networks emphasizes the role of the organic chemistry of the reactant in determining the catalytic reaction mechanism. This concept should be underlined, because it indicates that, in general, *the chemistry of organic molecules at metal oxide surfaces is a chapter of organic chemistry* and essentially follows the basic principles of the classical organic chemistry, with few exceptions (like, for example, the aldolic condensation of carbonyls with oxygen retention reversal [205,206]). This should be taken into account when the mechanisms and kinetics of the heterogeneously-catalyzed transformation of organic compounds are addressed. This is also an useful concept, because the mechanisms of several organic reactions in solutions are well-known and they can be a model, mutatis mutandis, for corresponding heterogeneously-catalyzed reactions.

However, the catalyst surfaces influences the rates of the different steps, thus favoring one way with respect to the others. The chemical behavior of the catalyst surface and the reaction conditions concur in determining the product selectivities. The schemes shown above contain typical redox steps together with steps that are acido-basic. Although redox and acido-basic properties of the metal oxide surfaces are not independent properties, both being the result of the chemical composition and of the (crystalline) structure of the catalyst, it is evident that activities and selectivities in oxidation reactions are deeply influenced by the acido-basic properties [207]. This concept has been evidenced in several papers (like for example the many ones reported by M. Ai [75]) and is certainly a useful concept. However, just because *acid-base properties are not independent from redox properties*, it is impossible to modify only one of them. So, it should be recognized that *every catalyst has his individual properties*. For these reasons mechanistic studies should be always preceded by a deep characterization of the catalyst.

We hope that the above data and these concepts, although not really new, will contribute to the *catalyst design* for new oxidation reactions or for the improvement of already well-known reactions still not sufficiently performing.

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