

Reactivity of Keggin-type heteropolycompounds in the oxidation of isobutane to methacrolein and methacrylic acid: Reaction mechanism

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Abstract

The oxidation of isobutane to methacrolein and methacrylic acid over a Keggin-type heteropolycompound of composition $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ was studied in both flow reactor studies and with FT-IR spectroscopy of species which develop at the surface. In both cases either isobutane or possible reaction intermediates were used as probe molecules. It is proposed that the activation of the isobutane at the tertiary C–H bond leads to the formation of an alkoxy species, which is then converted to an allylic alkoxy species, precursor for the formation of methacrolein and methacrylic acid. The mechanism proposed explains the experimental evidence relative to the absence of isobutene among the reaction products, and the parallel pathways to the two products. Competitive pathways are the formation of acetic acid, maleic anhydride and carbon oxides.

Keywords: Keggin heteropolycompounds; 12-molybdophosphates; Isobutane oxidation; Methacrylic acid; Methacrolein; Mechanism of isobutane selective oxidation

1. Introduction

The synthesis of methylmethacrylate is presently carried out through the well-known acetone–cyanohydrin process, while minor amounts are produced by oxidation of isobutene to methacrolein and then to methacrylic acid. The acetone–cyanohydrin process suffers from a number of drawbacks, which make it environmentally unfriendly: (i) the use of a toxic reagent, cyanohydrin acid, and intermediate, the

cyanohydrin, and (ii) the coproduction of ammonium sulphate, which is contaminated by organic compounds and cannot be used as a fertilizer; therefore it has to be discharged in spoil banks, or pyrolyzed to recover sulphuric acid.

Among the different alternative pathways which have been proposed in the literature [1,2], the most fascinating is the one-step oxidation of isobutane to methacrolein and methacrylic acid. This process, if developed at an industrial level, would have the advantages of simplicity, low environmental impact and low cost of the raw

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material [3–5]. From a mechanistic point of view, the reaction looks rather complex, and in some ways it recalls the transformation of *n*-butane to maleic anhydride [6]. Indeed, both transformations are multi-electron oxidations, where the catalyst needs different properties in order to perform the various kinds of oxidizing attacks required to functionalize the molecule: acid properties to activate the C–H bond of the saturated substrate, oxidehydrogenation properties and oxygen insertion properties.

In previous papers [7,8], we have reported about the use of Keggin-type heteropolycompounds for the reaction of isobutane oxidation. Mixed ammonium/potassium salts of 12-molybdophosphoric acid, doped with iron, were found to be effective for the reaction. In the present paper we describe the catalytic performance of the catalyst with composition $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$, and we make an analysis of the reactivity of possible reaction intermediates in the transformation of isobutane to oxygenated compounds. In addition, an FT-IR study of the organic species which develop on the catalyst surface at increasing temperatures when isobutane and isobutene are put in contact with the catalyst was carried out. The combination of the results from the flow reactor and spectroscopic studies can provide information on the reaction mechanism.

2. Experimental

Preparation of the heteropolycompounds was carried out according to the following procedure: $(NH_4)_3Mo_7O_{24}$ is dissolved together with H_3PO_4 and KNO_3 in water, at the desired stoichiometric ratio, and then HNO_3 is poured into the solution in order to reach pH values lower than 1.0. Under these conditions the primary Keggin structure is developed, which precipitates in the presence of potassium and ammonium, since the corresponding salts are insoluble. Doping with iron is obtained by addition of a $Fe(NO_3)_3$ solution to the slurry. The solid

is separated by solvent evaporation, and is then dried and calcined in air at 350°C for 6 h, following a stepwise temperature gradient. The development of the Keggin structure was confirmed by means of FT-infrared spectroscopy and X-ray diffraction analysis [7,8].

The IR spectra were recorded using a Nicolet Magna 750 Fourier transform instrument, with a heatable cell connected to a conventional gas-handling system. The catalyst powder was pressed in self-supporting discs calcined in air or in pure oxygen at 300°C and outgassed at the same temperature before being put in contact with the reaction gas.

Catalytic tests were carried out in a continuous flow reactor at atmospheric pressure, with total volume 10 ml, and diameter 1 cm. The catalyst was used in the form of granulated particles ranging from 0.3 to 0.6 mm in size; 3 ml of catalyst was loaded (residence time was calculated with respect to this value), and the remaining void space was filled with inert material, steatite, in order to minimize homogeneous reactions. All reaction products were analyzed by gas chromatography. A 70 cm column of 10% SP-1200 + 1% H_3PO_4 on Chromosorb WAW connected to a FID detector was used to separate isobutane, methacrolein, acetic acid, maleic anhydride and methacrylic acid; other by-products formed in minor amounts were acrylic acid and isobutyric acid. The oven temperature was programmed to rise from 40 to 100°C at a rate of 16°C/min. The isobutane/isobutene separation was carried out using a 5 m column of 23% SP-1700 on Chromosorb PAW, at room temperature, connected to an FID detector. The analysis of carbon oxides and oxygen was carried out using two packed columns connected to a TCD detector in isothermal conditions: a 4 m column of Porapak QS for CO_2 and a 2 m column of Carbosieve S for CO and oxygen.

The catalytic performance was rather unstable in the first 10–20 h time-on-stream, during which a progressive decrease of activity and increase in selectivity was observed. After this

initial period the performance stabilized and was maintained constant during the catalytic experiments; no decline in activity or selectivity was observed for more than 100 h time-on-stream, provided reaction temperatures lower than 400°C were used.

3. Results and discussion

Most catalytic tests and spectroscopic measurements were carried out with the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst [7,8], which in previous studies was found to give the best yield of methacrylic acid. Some catalytic tests were also done, for comparison, on the undoped $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst. Tests were carried out using fuel-rich conditions, thus under conditions at which oxygen is the limiting reactant. The standard composition of the feedstock was the following: 26 mol% isobutane, 13 mol% oxygen, 12 mol% water, balance helium. When other organic compounds were fed in order to study the reaction pattern, the amount of reactant used was much lower. This was done in order to operate under conditions as close as possible to those used under tests of isobutane oxidation, during which the amount of possible reaction intermediates produced is very low.

3.1. The reactivity of the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst

3.1.1. Oxidation of isobutane

The effect of residence time on reactant conversion and product distribution is illustrated in Fig. 1. The main products obtained were methacrolein, methacrylic acid, acetic acid, maleic anhydride, CO and CO_2 . Although the presence of low amounts of acetone is likely, none could be detected with our chromatographic analysis in the contemporaneous presence of unconverted isobutane or isobutene. Isobutene formed always in very low amount, with a selectivity lower than 1–2%. The selec-

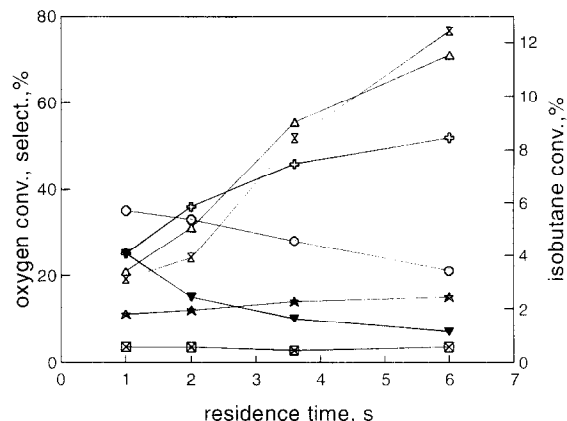
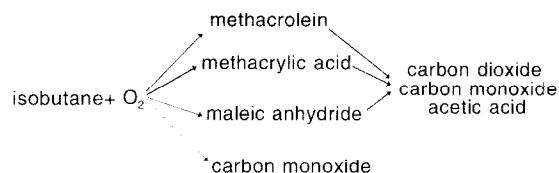


Fig. 1. Catalytic performance as a function of the residence time in isobutane oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst. Temperature 350°C; feedstock composition: 26% isobutane, 13% oxygen, 12% water, balance helium. Symbols: hydrocarbon conversion (Δ), oxygen conversion (hourglass), selectivity to methacrylic acid (○), to methacrolein (▼), to acetic acid (⋈), to maleic anhydride (square with diagonal cross), to carbon oxides (×), and to acetone (◆).

tivity trend of maleic anhydride, methacrolein and methacrylic acid is typical for primary products formation, thus indicating the presence of parallel reactions; however, the selectivity rapidly decreases with increasing isobutane conversion. The selectivity to acetic acid, to CO and to CO_2 seems instead to be nil or in any case very low at low conversion.

These data indicate that the reaction network is constituted of the primary, parallel reactions of isobutane transformation to maleic anhydride, methacrolein and methacrylic acid, with also a likely contribution of direct combustion to CO. Consecutive reactions of oxidative degradation to acetic acid, CO and CO_2 are responsible for the decrease in the selectivity to



Scheme 1. Reaction network for the oxidation of isobutane at 350°C over $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst.

the desired products. The reaction network is summarized in Scheme 1.

It is worth mentioning that the amount of isobutene formed was in any case very low. The absence of isobutene among the reaction products may be due to two different reasons:

(1) The isobutane, once activated, is directly transformed to methacrolein and methacrylic acid by contemporaneous attack of different oxidizing centers. Therefore, an adsorbed olefinic-like species is not an intermediate in the transformation of isobutane to unsaturated oxygenated compounds.

(2) The isobutane adsorbed and activated is first transformed to an olefinic species, but the latter is quickly oxidized by allylic oxidation to the oxygenated compounds before it may desorb as isobutene.

3.1.2. Oxidation of isobutene, methacrolein and methacrylic acid

Tests were done which involved feeding isobutene at 2.6 mol%, while keeping the other conditions the same as those used in the oxidation of isobutane. These tests were intended to compare the performance of isobutene with that of isobutane, in order to define whether isobutene may be a reaction intermediate in the transformation of isobutane.

Fig. 2 shows that isobutene reached very high conversion already at low residence time. The olefin was approximately 2–3 times more reactive than isobutane (under the hypothesis of a first order reaction with respect to the hydrocarbons). It was converted mainly to methacrolein, the selectivity of which however rapidly declined as the olefin conversion increased. The selectivity to methacrylic acid was instead lower at low residence time, but remained approximately constant in the range examined. The observed trend would suggest that methacrolein and methacrylic acid are primary products of isobutene oxidation. The acetic acid is clearly formed by consecutive reaction. CO and CO₂ are likely primary products, and their selectivity only slightly increased with increasing conver-

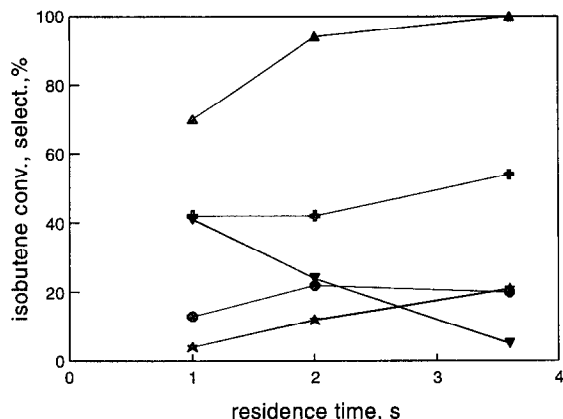
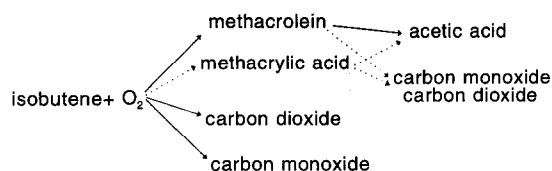


Fig. 2. Catalytic performance as a function of the residence time in isobutene oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst. Temperature 350°C; feedstock composition: 2.6% isobutene, 13% oxygen, 12% water, balance helium. Symbols as in Fig. 1.

sion. The network for the isobutene oxidation, illustrated in Scheme 2, therefore comprises the direct reactions of olefin transformation to methacrolein, methacrylic acid and carbon oxides, and the consecutive reactions undergone by methacrolein with formation of mainly acetic acid and CO. Methacrylic acid likely also undergoes consecutive reactions of oxidative degradation, but to a much lesser extent than the methacrolein.

Except for the presence of maleic anhydride, which is obtained only from the isobutane, the nature of the products obtained from the isobutane and from the isobutene, as well as the reaction networks, are therefore similar. The only remarkable difference concerns the selectivity to methacrolein and methacrylic acid. From isobutane the acid is the preferred product, while from the olefin methacrolein prevails at low residence time. At total olefin conversion



Scheme 2. Reaction network for the oxidation of isobutene at 350°C over $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst.

methacrylic acid is the prevailing selective product, and the methacrolein is very low.

The conversion of methacrolein and the product distribution as functions of residence time are illustrated in Fig. 3. The amount of methacrolein fed was 2%, the other conditions being the same as for the isobutane oxidation. Methacrolein mainly yields CO, CO₂ and acetic acid, with only minor amounts of methacrylic acid (selectivity less than 10%) even at low residence time. This confirms that with these catalysts methacrylic acid is not formed by consecutive reaction of methacrolein transformation.

The oxidation of methacrylic acid is shown in Fig. 4. CO, acetic acid and CO₂ are formed in comparable selectivities, while acetone is formed to a lesser extent. Methacrolein and methacrylic acid exhibit similar reactivity, since they reach similar conversion at the same residence time.

These data provide further indications on the reaction pattern in isobutane oxidation. Both methacrolein and methacrylic acid are very reactive under the conditions employed for the activation of isobutane, and are readily transformed to acetic acid and carbon oxides. Therefore, operation in isobutane oxidation should be

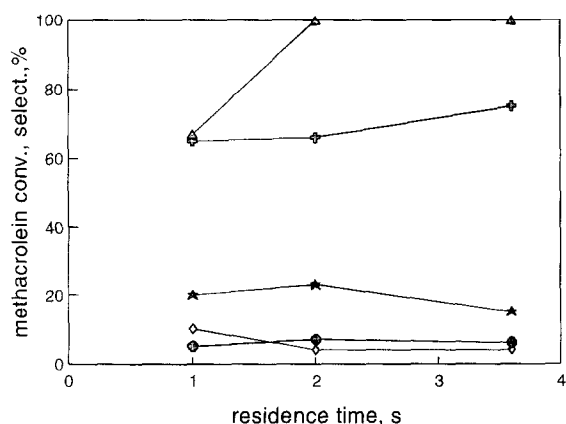


Fig. 3. Catalytic performance as a function of the residence time in methacrolein oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst. Temperature 350°C; feedstock composition: 2.0% methacrolein, 13% oxygen, 12% water, balance helium. Symbols as in Fig. 1.

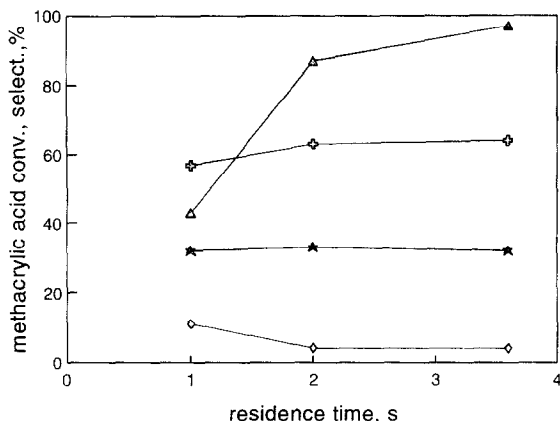


Fig. 4. Catalytic performance as a function of the residence time in methacrylic acid oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst. Temperature 350°C; feedstock composition: 2.0% methacrylic acid, 13% oxygen, 12% water, balance helium. Symbols as in Fig. 1.

conducted at lower temperatures, in order to allow the selectivity to the desired products to be maintained high.

A proof for the intermediate formation of an olefinic-like compound has not been obtained, but it cannot be definitely excluded. In any case, the absence of isobutene among the reaction products in the oxidation of isobutane indicates that, even if it is formed, the olefin is quickly transformed to the consecutive products. It is worth mentioning that the data reported demonstrate that isobutene, methacrolein and methacrylic acid have comparable reactivity under these conditions and over this catalyst. Therefore, if we assume that isobutene is not obtained as a product in the oxidation of isobutane due to its very high reactivity in the adsorbed state, for the same reason we should expect that neither methacrolein nor methacrylic acid are formed when isobutane is oxidized, since they should be readily converted to acetic acid and carbon oxides before they can desorb. On the contrary, since the two oxygenated compounds are major products in the oxidation of isobutane, these arguments do not support the formation of an intermediate olefinic-like species in isobutane oxidation.

3.2. Reactivity of the $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst

It is worth comparing the reactivity of the iron-doped catalyst with that of the undoped $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst. Fig. 5 reports the effect of the residence time on the catalytic performance in isobutane oxidation (in this case tests were done at 370°C, other conditions being the same as those in Fig. 1), while Fig. 6 shows the results obtained in the oxidation of isobutene at 350°C (same conditions as in Fig. 2). The absence of iron leads to a remarkable decrease in the activity with respect to the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst. The selectivity to methacrolein and methacrylic acid was the same in the two catalysts for the same isobutane conversion. This leads therefore to a remarkably improved yield to the oxygenated products on the iron-doped catalyst with respect to the undoped one. The selectivity to methacrolein decreases with increasing conversion in both catalysts. The selectivity to methacrylic acid in undoped catalyst was approximately constant, while in the iron-doped catalyst it rapidly decreased. This difference may be due to both the higher isobutane conversion achieved with the latter catalyst, and to an enhanced reactivity of the methacrylic acid.

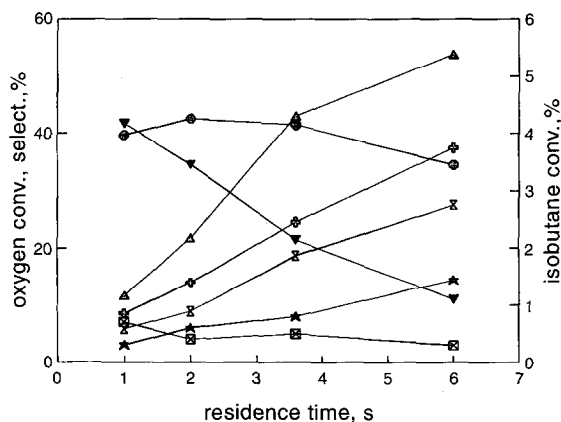


Fig. 5. Catalytic performance as a function of the residence time in isobutane oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst. Temperature 370°C; feedstock composition: 26% isobutane, 13% oxygen, 12% water, balance helium. Symbols as in Fig. 1.

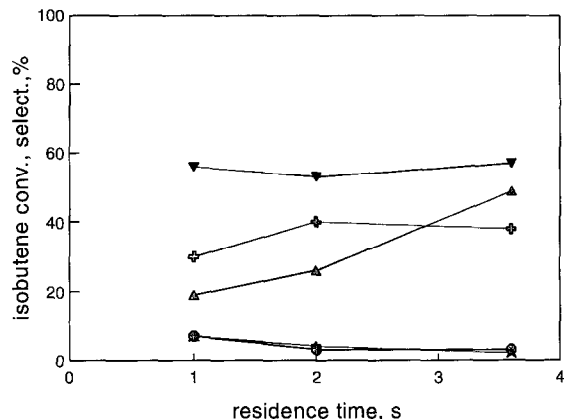


Fig. 6. Catalytic performance as a function of the residence time in isobutene oxidation for the $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst. Temperature 350°C; feedstock composition: 2.6% isobutene, 13% oxygen, 12% water, balance helium. Symbols as in Fig. 1.

In the case of isobutene oxidation, the main differences concern (i) the lower conversion of isobutene, analogous to that observed from isobutane, in undoped catalyst, (ii) the lower selectivity to methacrylic acid in the undoped catalyst (less than 8% with respect to approximately 20% in iron-doped catalyst), (iii) the higher selectivity to methacrolein (approximately 50% against less than 40% in the iron-doped sample), which moreover remains approximately constant in the range examined, and (iv) the corresponding lower formation of CO, CO₂ and acetic acid. In this case, therefore, if we compare the selectivities to the products for similar values of isobutene conversion, a different product distribution is obtained. Other tests were done at 300°C, which did not yield methacrylic acid at all, thus confirming the results obtained at 350°C, that is, the substantial inability of the undoped catalyst to produce methacrylic acid from isobutene.

Since the formation of methacrolein and methacrylic acid is through parallel reactions, these data indicate that in the case of isobutane oxidation the presence of iron modifies the catalyst activity, but does not substantially modify the product distribution with respect to the undoped catalyst. On the contrary, in the case of isobutene oxidation, a modification in both ac-

tivity and product distribution is obtained. This argument is again not in favor of the formation of intermediate isobutene in the oxidation of isobutane.

3.3. FT-IR study of adsorbed species over the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst

3.3.1. Interaction of the catalyst with isobutane

The FT-IR spectra of the species arising from contact of the catalyst with isobutane are shown in Figs. 7 and 8. Fig. 7b shows the spectrum recorded at room temperature in the presence of 150 Torr of isobutane, after a long contact time; the spectrum of the gas (given in Fig. 7a) has been subtracted. The spectrum is assigned to molecularly adsorbed isobutane, as deduced by comparison with the spectrum of gaseous isobutane. The bands at 1473, 1364 and 1327 cm^{-1} are due to different C–H deformation modes, while the band at 1171 cm^{-1} is due to C–C

stretching [9], also showing a small vibrational perturbation to lower frequencies. Molecularly adsorbed isobutane is desorbed by outgassing at room temperature.

Prolonged heating of the catalyst in isobutane at 70°C causes the formation of a new feature, a broad absorption band centered near 1175 cm^{-1} , with also a component centered at 1245 cm^{-1} (Fig. 8a). After further heating at 100°C (Fig. 8b) this feature disappears, but some new ones appear. In particular, a weak sharp band at 1626 cm^{-1} is formed, together with a component growing near 1350 cm^{-1} and a very weak band at 1537 cm^{-1} . The band at 1626 cm^{-1} disappears upon outgassing and could be associated with the C=C stretching of an olefinic compound. Further heating in isobutane at 150°C (Fig. 8c) and above causes the growth of the absorption band in the range 1550–1300 cm^{-1} . This range is disturbed by the presence of the strong band centered at 1425 cm^{-1} , which is in

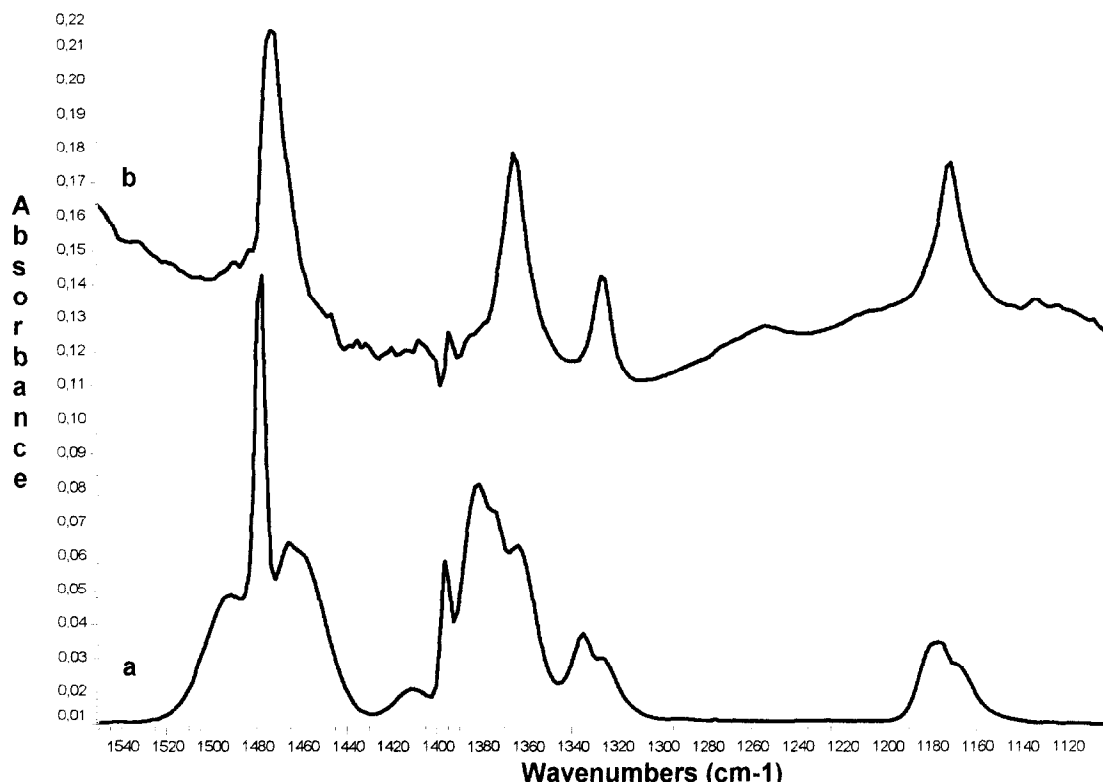


Fig. 7. FT-IR spectra of isobutane gas (a) compared with isobutane molecularly adsorbed over the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_1O_{1.5}$ catalyst at room temperature (b).

the spectrum of the catalyst and almost obscures the region $1460\text{--}1380\text{ cm}^{-1}$. This band is due to the asymmetric deformation of the NH_4^+ species which is present in the cationic position of the heteropolycompound. However, bands at 1470 and 1370 cm^{-1} can be distinguished in this region, which are associated with CH_3 bending modes.

Additional bands grow from the interaction of isobutane with the surface at 200 and 250°C (Fig. 8d and e), with maxima at 1737 and 1779 cm^{-1} and a shoulder at 1842 cm^{-1} . The position of these bands implies their assignment to C=O stretching modes characterized by very high bond order. The band at 1779 cm^{-1} and the shoulder at 1842 cm^{-1} are typical features of cyclic anhydrides [10]; the appearance of cyclic anhydrides necessarily implies at least four carbon atoms in a straight chain, and is therefore in agreement with the formation of

maleic anhydride as one of the most relevant by-products. The additional band at 1737 cm^{-1} can be assigned to the C=O stretching of a carbonyl compound. Upon contact at temperatures higher than 200°C the features typical of adsorbed CO_2 appear.

These data indicate that isobutane reacts with the catalyst surface already at low temperatures (70°C), giving rise to adsorbed species characterized by bands at 1245 and 1175 cm^{-1} that further evolve into an adsorbed olefinic compound characterized by a band at 1626 cm^{-1} . At higher temperatures, a cyclic anhydride and a carbonyl compound are found, and CO_2 also appears.

3.3.2. Interaction of the catalyst with isobutene

The subtraction spectrum of the species arising from isobutene adsorbed reversibly at room temperature (it could be desorbed by simple

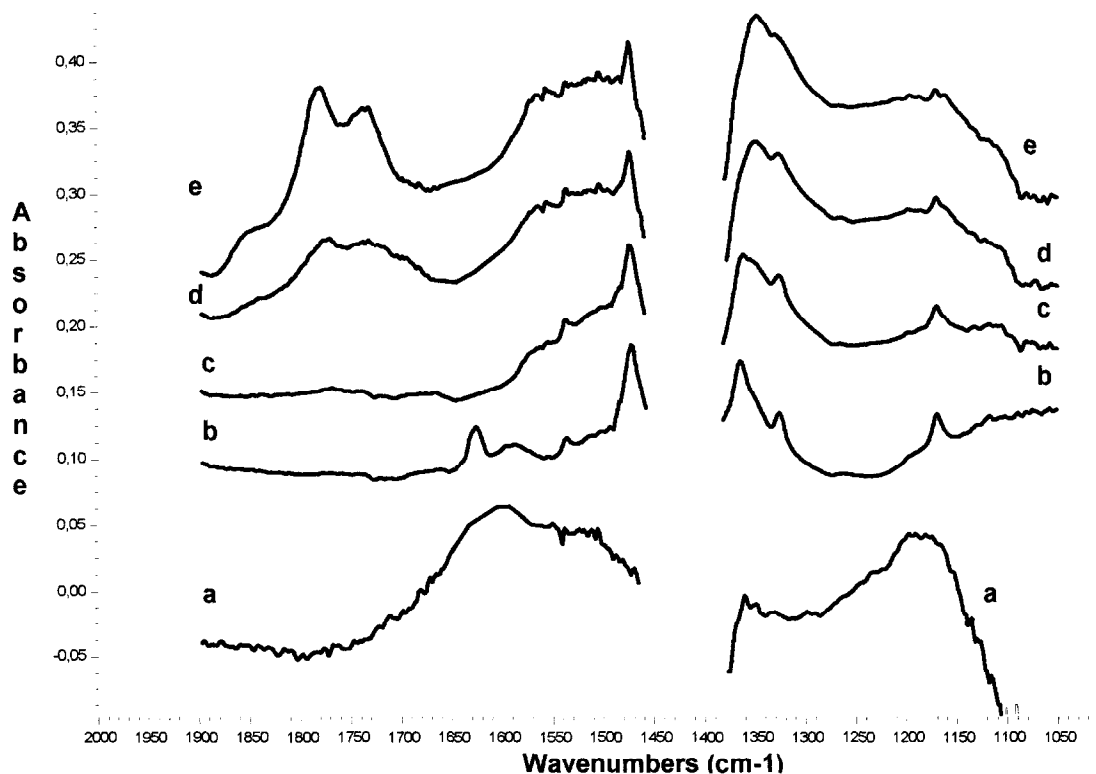


Fig. 8. FT-IR spectra of the surface species arising from heating the $\text{K}_1(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}/\text{Fe}_1\text{O}_{1.5}$ catalyst in the presence of isobutane gas, at 70°C (a), 100°C (b), 150°C (c), 200°C (d) and 250°C (e). The region $1470\text{--}1350\text{ cm}^{-1}$ was cut because it is obscured by the asymmetric deformation mode of the NH_4^+ species adsorbed on the catalyst.

outgassing) is shown in Fig. 9a. Many features of this spectrum are very similar to those in Fig. 8b, and can be attributed to molecularly adsorbed isobutene [11]. The sharp band at 1635 cm^{-1} , due to the C=C stretching, and the bands at 1478, 1460, 1430 and 1370 cm^{-1} , with a shoulder at 1280 cm^{-1} , are all assigned to CH deformation modes. The different position of the band due to the C=C stretching in Fig. 9a and in Fig. 8b (1635 versus 1626 cm^{-1}) can be due to the adsorption of the olefin in sites with different degrees of reduction. On the other hand, very strong new bands appear at 1235 and 1201 cm^{-1} , which are not due to adsorbed intact isobutene. Similar bands have been previously detected in the spectra of adsorbed species arising from contact with TiO_2 and ZrO_2 [11], and have been assigned to the dimeric species 2,4,4-trimethyl-pent-1-ene. Part of these

molecules desorb at room temperature by outgassing.

Fig. 10 shows the spectrum of the irreversibly adsorbed species arising from contact with isobutene at room temperature (Fig. 10a), and after outgassing at 100°C (Fig. 10b). A sharp band at 1245 cm^{-1} and a broad one centered near 1177 cm^{-1} , both strong, are observed together with the usual bands near 1470 and 1370 cm^{-1} , associated with CH_3 bending modes. The above strong bands closely resemble, for position and shape, those formed by isobutane contact shown in Fig. 8a. These bands disappear after heating at 100°C (Fig. 10b), as also observed for isobutane, leaving the bands at 1233 and 1200 cm^{-1} , assigned above to the isobutene dimer.

Spectra obtained when the contact between isobutene and the catalyst took place at 150 ,

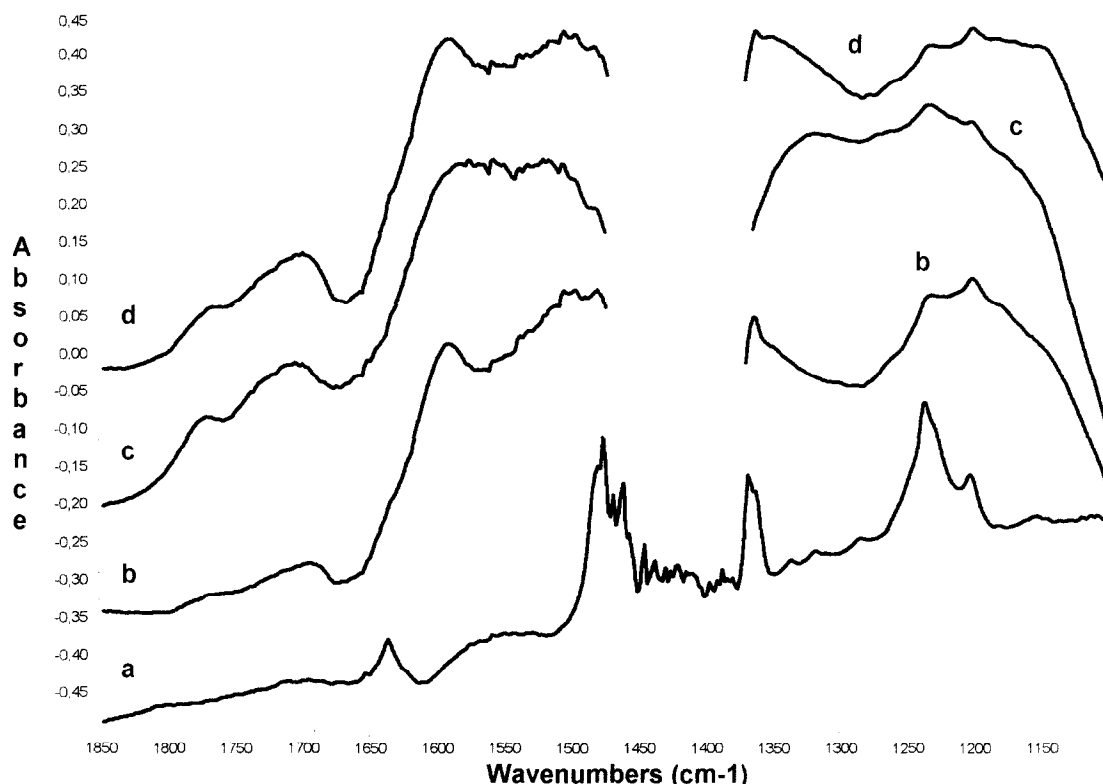


Fig. 9. FT-IR spectra of the surface species arising from: isobutene adsorption at room temperature over the $\text{K}_1(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}/\text{Fe}_1\text{O}_{1.5}$ catalyst followed by outgassing at room temperature (a); isobutene adsorption at 150°C (b), 200°C (c) and 250°C (d).

200 and 250°C are shown in Fig. 9b, c and d, respectively. A complex strong absorption band appears in the range 1600–1100 cm^{-1} , where a sharper component centered near 1600 cm^{-1} , and a new peak at 1240 cm^{-1} can be identified. In the middle of this absorption band, a negative band near 1430 cm^{-1} also appears, due to the subtraction of the deformation band of the NH_4^+ ion, possibly in part released from the structure during this treatment. Additional absorption bands are also found in the region 1900–1680

cm^{-1} , with the main maximum near 1690 cm^{-1} and weak components at 1770 and 1840 cm^{-1} . The last features correspond to those also observed after isobutane interaction, and should be assigned again to cyclic anhydrides.

Common aspects are found for isobutane and isobutene:

(1) The formation at room temperature from isobutene and at 70°C from isobutane of a species characterized by the broad absorption at around 1180 cm^{-1} , which is removed only by

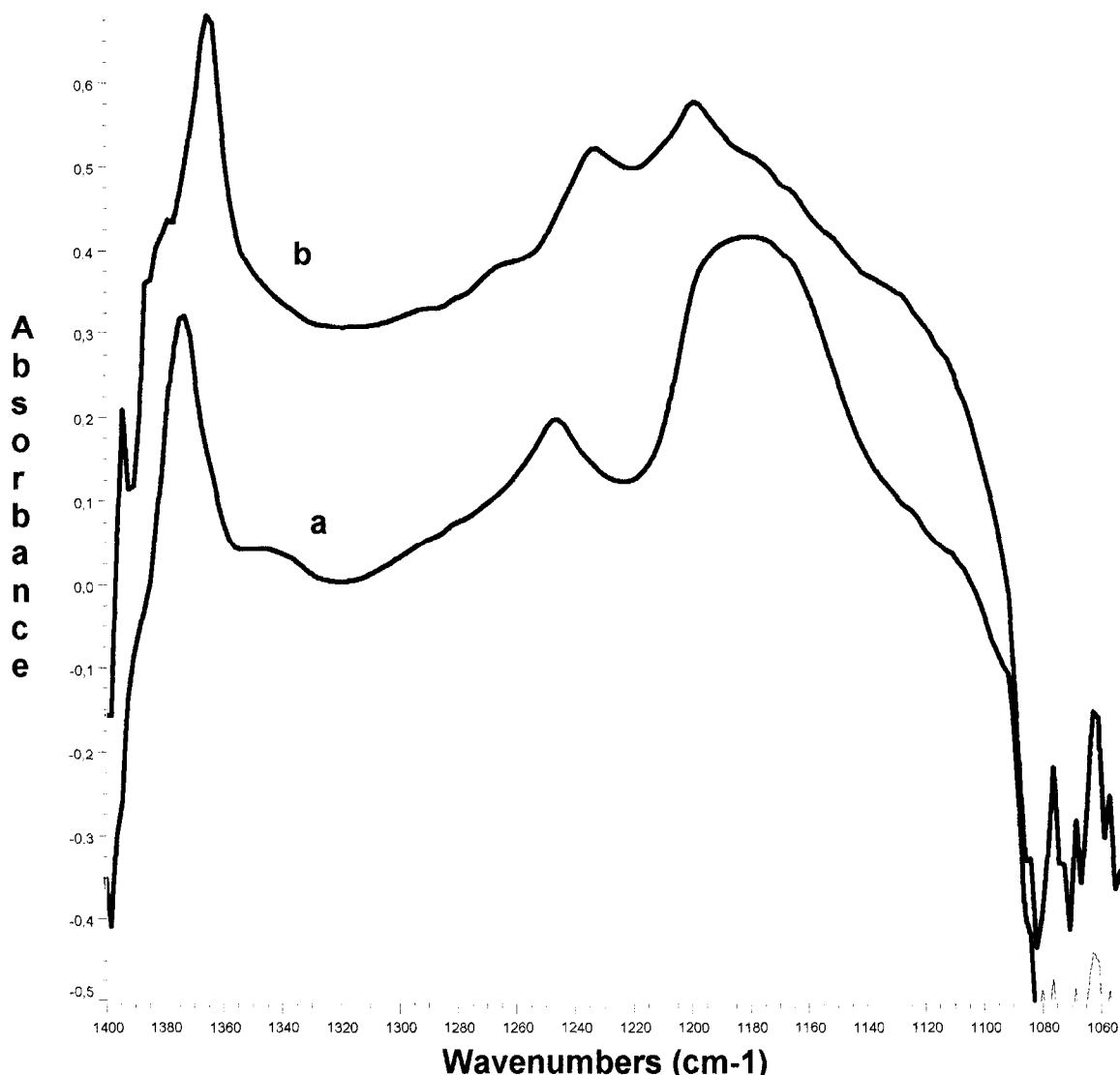


Fig. 10. FT-IR spectra of the surface species arising from isobutene adsorption at room temperature over the $\text{K}_1(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}/\text{Fe}_1\text{O}_{1.5}$ catalyst (a) and after outgassing at 100°C (b).

outgassing at 100°C, and therefore does not derive from a simple physical absorption. Identification of this species will be dealt with in the following sections.

(2) The formation of a cyclic anhydride at temperatures above 150–200°C. This suggests that under the conditions used for the tests (i.e., very long contact time), the isoolefin and the isoparaffin undergo skeletal isomerization and can be oxidized to form the very stable cyclic maleic anhydride. The driving force for the

isomerization at this relatively low temperature (possibly catalyzed by the strong acidity of heteropolycompounds) therefore may be the oxidation to the anhydride. The high stability of the maleic anhydride allows its detection even at the long residence times which are typical of these experiments. Maleic anhydride is one of the main by-products in the oxidation of isobutane in the flow reactor, while it was not detected in the case of isobutene oxidation. On the contrary, the methacrylic acid and methacrolein

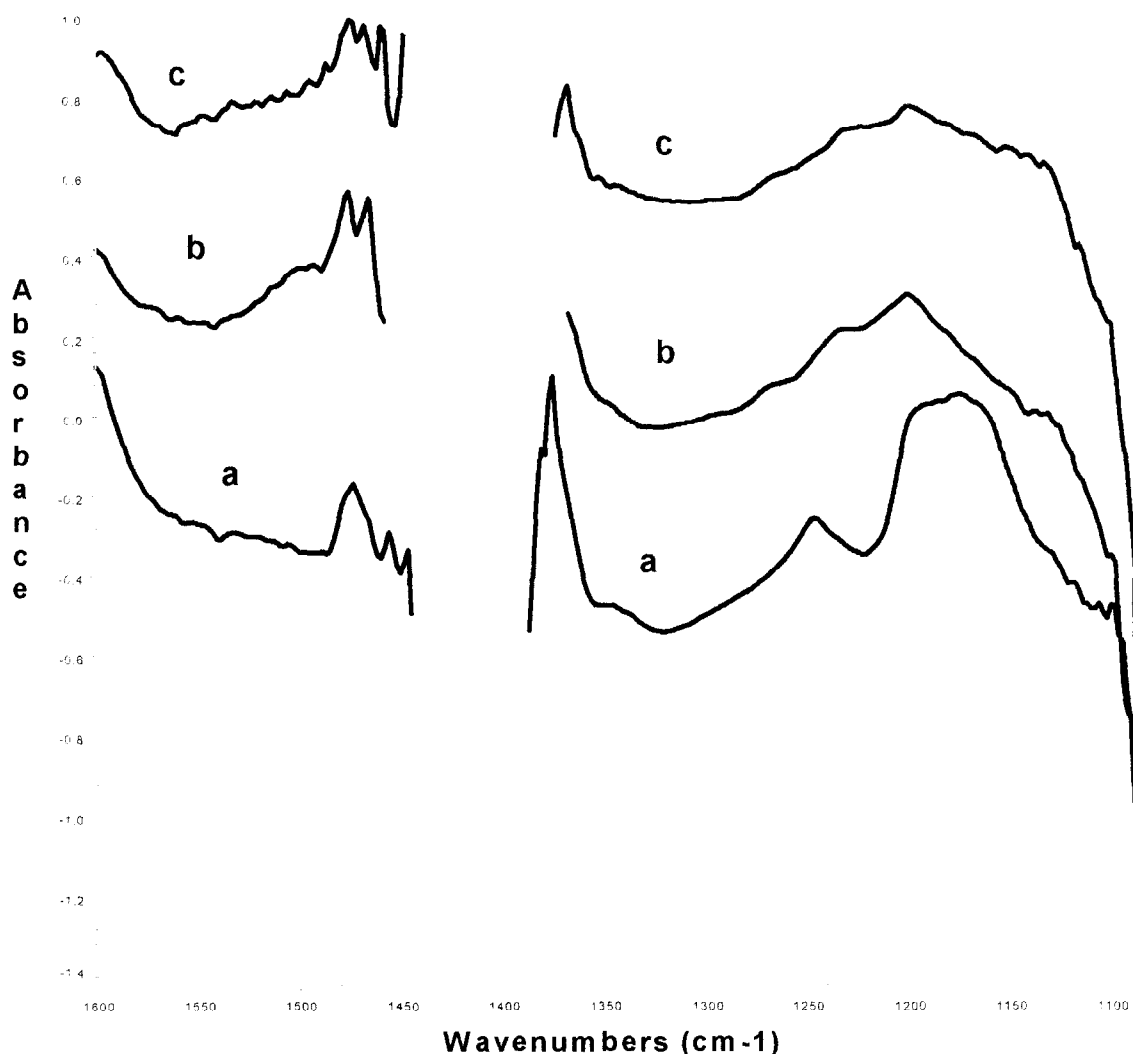


Fig. 11. FT-IR spectra of the surface species arising from tertbutanol adsorption at room temperature over the $K_1(NH_4)_2PMo_{12}O_{40}/Fe_{1.5}O_3$ catalyst (a), and after outgassing at 100°C (b) and 150°C (c).

are not detected, likely due to the fact that under the conditions of the FT-IR study they are transformed to carbon oxides.

Spectrum b in Fig. 8 clearly indicates that at 100°C an isobutene species is developed at the catalyst surface by contact with the paraffin. This species disappears at higher temperatures, and might possibly be the precursor of other species (CO₂ or cyclic anhydrides).

A difference between the paraffin and the olefin concerns the dimeric species which form by contact with the olefin, and which are not observed from the isobutane under our conditions. Only when high partial pressures of isobutane were used, was the formation of dimeric species observed.

3.3.3. Interaction of the catalyst with terbutanol

The interaction of terbutanol with the catalyst surface at room temperature yielded the spectrum shown in Fig. 11a. The bands at 1473, 1375 and 1245 cm⁻¹ and a complex, broad band near 1175 cm⁻¹ are assigned according to previous studies [12,13] to the terbutyl alkoxide, the first ones corresponding to the asymmetric and symmetric methyl deformations, respectively, and the last two to C–C and C–O coupled stretchings. These bands correspond to those observed from isobutane interaction at 70°C and from isobutene at room temperature. So, it is possible to conclude that terbutoxy species are formed very easily from isobutene adsorption and with more difficulty from isobutane adsorption. The production of the terbutoxy species from the olefin can be the result of an electrophilic addition of a weakly acidic OH group to the olefin. This reaction is in fact typical of catalyst surfaces showing medium-strong Brønsted acidity [14]. It is worth mentioning that heteropolycompounds exhibit protonic acidity even when they are formally completely neutralized [15]. The formation of terbutoxy species from isobutane, instead, necessarily implies the oxidation of the molecule by a surface site. Terbutoxy species have already been detected after isobutane oxidation over the

combustion catalyst MgCr₂O_{4+x} at room temperature [13], and a similar C–H bond activation mechanism can be postulated in our case.

The evolution of the terbutoxy species with temperature is the same as that observed with isobutane and isobutene, and this supports the assignment to the same species. At 100°C (Fig. 11b) these bands disappear, leaving only two very weak bands at 1230 and 1199 cm⁻¹, and a peak at 1367 cm⁻¹, which can be assigned, as above, to the isobutene dimer.

Under these conditions an evident band is formed at 1595 cm⁻¹, stable to outgassing, which is similar to the one which was also observed for isobutene oxidation at relatively high temperatures. A possible attribution of this band is, according to the spectra of adsorbed acetic acid, to the asymmetric COO stretching mode of acetate species; however, certain attribution can not be made, since the spectra of acetate may overlap with those of acrylates as well as other species. Unfortunately, the corresponding symmetric stretching mode of COO falls in the region obscured by the ammonium band. Previous studies showed that over oxidation catalysts terbutoxy species can in part evolve by C–C bond breaking to a mixture of formates and acetates [13]. However, formates are much less stable than acetates and can decompose easily. Isopropoxide evolves by oxidative breaking of the C–C bond, giving rise to two formate species and an acetate species; the former are decomposed, while the latter can desorb as acetic acid in the presence of water [13]. Overoxidation of these fragments can be one way to the formation of carbon oxides. The detection of acetate species is in agreement with the products obtained under flow reaction studies. The correspondence with steady state tests in a flow reactor is in this case possible due to the stability of the acetic acid, which is a final product of oxidative degradation.

The activation of isobutane at C₁ is excluded because of the lack of bands assignable to isobutoxy species after isobutane interaction. This is concluded by the comparison of the spectra

arising from isobutane, isobutene and terbutanol adsorption with that one arising from interaction of the catalyst with isobutanol. In the latter case, a band at 1045 cm^{-1} is observed, attributable to the C–O stretching band originated by adsorption at the primary carbon atom, which was not observed in the former cases.

3.3.4. Interaction of the catalyst with methacrolein

The spectrum relative to the interaction with methacrolein is shown in Fig. 12. The adsorption of methacrolein causes the formation of a very strong absorption in the region $1800\text{--}1500\text{ cm}^{-1}$. The spectrum obtained after adsorption at room temperature shows a sharp band at 1695 cm^{-1} , certainly due to the C=O stretching of a liquid-like molecule that accordingly disappears by outgassing at 100°C . The broader band centered near 1650 cm^{-1} is likely associated with the C=O stretching and C=C stretching modes of coordinated species. The subtraction spec-

trum shows that this band is associated with a sharp band at 1316 cm^{-1} , typical of the deformation mode of the aldehydic C–H bond. With further heating, these bands decrease in intensity while a sharper one appears near 1580 cm^{-1} , but distinct shoulders also appear near 1730 and 1780 cm^{-1} . The latter features resemble those already observed from both isobutane and isobutene and assigned in part to a cyclic anhydride.

3.3.5. Interaction of the catalyst with methacrylic acid

The spectra of the species arising from the adsorption of methacrylic acid are shown in Fig. 13. Several bands in the $1800\text{--}1500\text{ cm}^{-1}$ range are observed, and a typical sharp band at 1245 cm^{-1} , with components at 1300 and 1205 cm^{-1} . After outgassing at room temperature the main maximum is found at 1620 cm^{-1} , but after outgassing at higher temperatures several components are clearly evident at 1770 , 1712 , 1674 ,

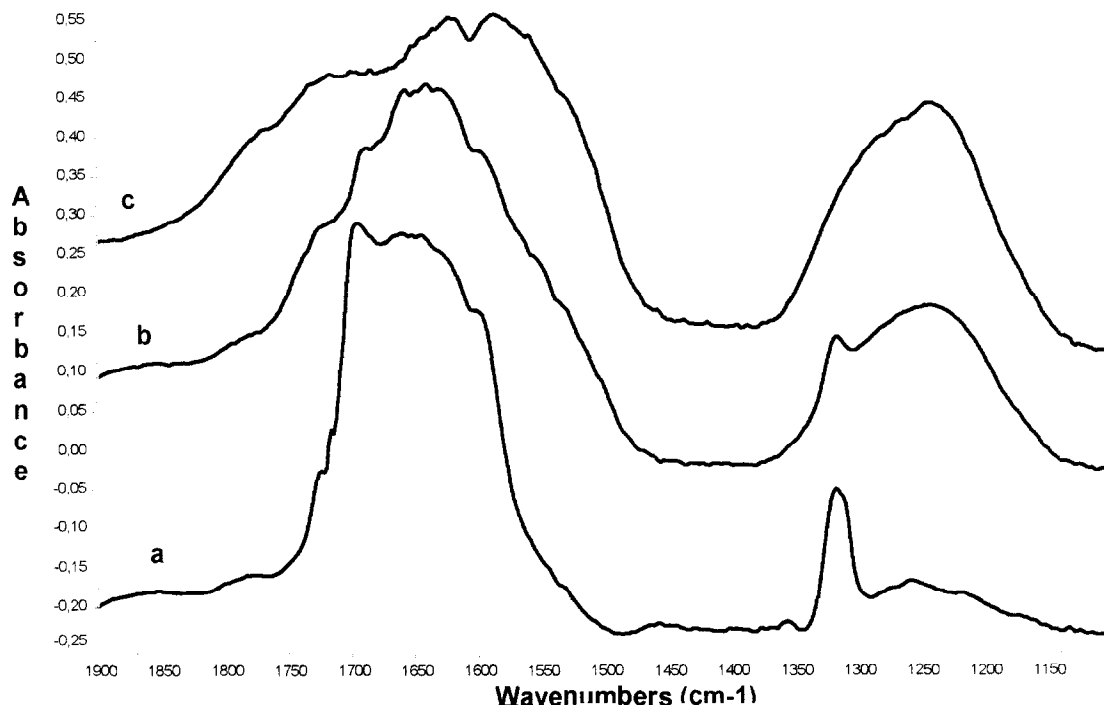


Fig. 12. FT-IR spectra of the surface species arising from methacrolein adsorption at room temperature over the $\text{K}_1(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}/\text{Fe}_1\text{O}_{1.5}$ catalyst (a), and after outgassing at 100°C (b) and 150°C (c).

1634, 1575 and 1543 cm^{-1} . The bands at 1575 and 1543 cm^{-1} can be assigned, together with that at 1245 cm^{-1} , to acrylate species (COO asymmetric stretching of two different forms, and C–C stretching, respectively). The bands near 1675, 1300 and 1205 cm^{-1} are instead associated with adsorbed undissociated methacrylic acid. The component near 1635 cm^{-1} is due to the C=C stretching of all species. The main maximum near 1620 cm^{-1} cannot be assigned with certainty to a dissociated or an undissociated methacrylic acid form. It seems likely that the bands at 1717 and 1770 cm^{-1} are due to the C=O stretching mode of species arising from the overoxidation of methacrylic acid, and could correspond to those found in the same region after oxidation of all the above adsorbates.

These spectra allow a more clear assignment of the bands developed by isobutene interaction with the catalyst. Indeed, there are several com-

mon aspects with the spectra obtained by contact with methacrolein and methacrylic acid. Bands in the region 1600–1450 cm^{-1} developed by isobutene oxidation at 150–250°C can be with certainty attributed to the presence of methacrylates, while methacrolein adsorbed as such is not found (absence of the band at 1316 cm^{-1}). On the other hand this agrees with the observation that methacrolein is totally converted to methacrylates by direct interaction at 200°C. The band observed near 1580 cm^{-1} can be alternatively assigned to acetates or to methacrylates.

The consecutive transformation of methacrolein to methacrylates does not find confirmation in the flow reactor tests. In fact, the formation of methacrolein and methacrylic acid was found to follow two parallel pathways, rather than a consecutive mechanism. However, the reaction conditions can play a fundamental role in this reaction. In previous studies it was

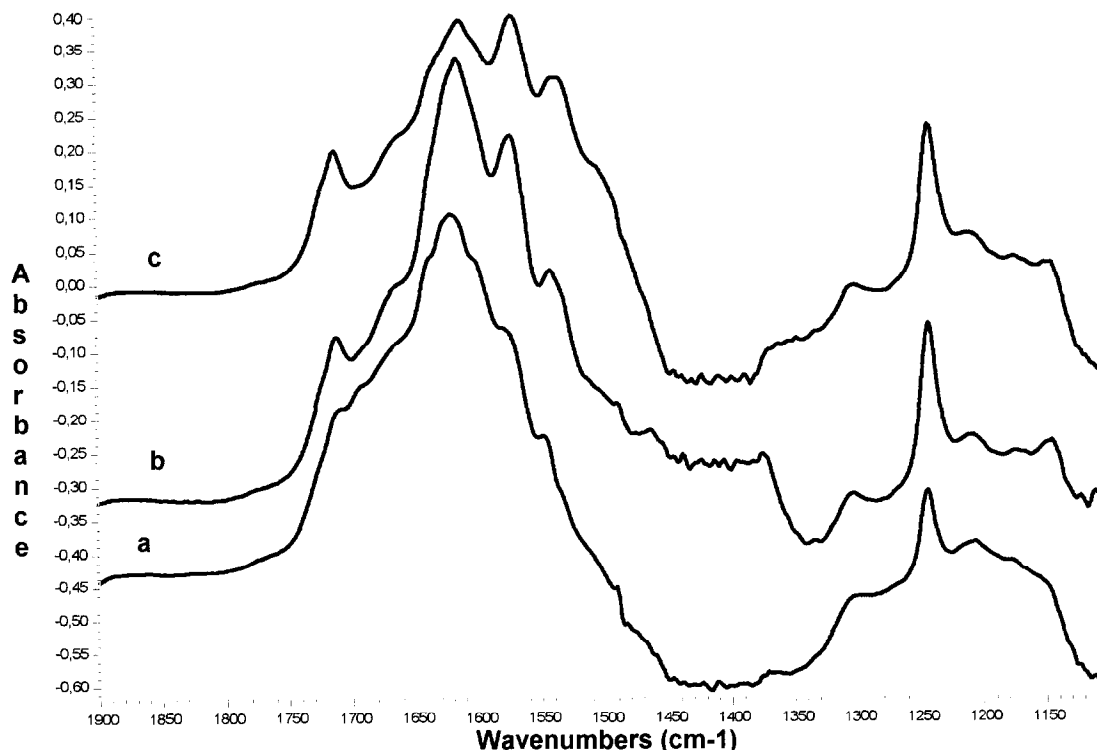


Fig. 13. FT-IR spectra of the surface species arising from methacrylic acid adsorption at room temperature over the $\text{K}_1(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}/\text{Fe}_1\text{O}_{1.5}$ catalyst (a), and after outgassing at 100°C (b) and 150°C (c).

found that the consecutive transformation of methacrolein to methacrylic acid is non-negligible at reaction temperatures lower than 350°C. Alternatively, it can be postulated that both methacrolein and methacrylic acid have a common intermediate. This intermediate therefore can either desorb, yielding methacrolein, or be converted to the carboxylate and thus to methacrylic acid. This would be in agreement with a parallel reaction network, provided further readsorption of methacrolein and transformation to methacrylic acid is not favored.

In regards to isobutane oxidation, common features in the 1700–1450 cm^{-1} range are less relevant. Similar bands in the 1900–1700 cm^{-1} region are found in all spectra, but those from isobutane are relatively more intense than those from other adsorbates. However, it must be remarked that the intensity of the bands of all adsorbed species is by far weaker (in absolute) for isobutane than for the other adsorbates.

4. Conclusions: the mechanism of isobutane oxidation

The results obtained allow some conclusions to be drawn about the mechanism of isobutane oxidation and the reaction network for its transformation to methacrolein and methacrylic acid:

(1) Isobutane can be activated by the catalyst surface already at relatively low temperatures at the tertiary carbon by oxidative breaking of the weakest C–H bond. This produces an alkoxide and a hydroxy group, with two electrons being assumed by the oxidized surface that is consequently reduced.

(2) This species can evolve towards the formation of adsorbed isobutene, so completing an oxidehydrogenation step. This evolution is typical of very acidic and very basic surfaces, where alkoxides tend to dehydroxylate, giving rise to the olefins.

Under steady state conditions in a flow reactor, no indication about the formation of an olefinic intermediate was obtained. It is likely

that at 350°C and the contact times used in a flow reactor, the formation of the carbonylic or carboxylic group is contemporaneous to the double bond introduction or that, in any case, it occurs before desorption of the olefinic intermediate can occur.

The results of spectroscopic measurements indicate the formation of a *tert*-butoxy species at the catalyst surface. It can be hypothesized that the nature of this adsorbed species may be a function of the operating conditions. In fact, the C–O bond of the alkoxy species can exhibit a certain extent of polarization, and its ionic character may be a function of the temperature, as well as of the acidity of the OH which is correspondingly formed. On the other hand, a partial positive charge localized on the tertiary carbon atom necessarily involves a partial double bond character for the neighboring C–C. This olefinic character may be enough to favor the allylic oxidation, but not enough to favor desorption of isobutene. On the other hand, when isobutene is directly put in contact with the catalyst surface, the *tert*-butoxy species can be formed by simple electrophilic addition of a M–OH group. In this case, the *tert*-butoxy species which develops is obviously characterized by a more ionic character, and can easily reversibly turn back to the olefin. This also implies that the two *tert*-butoxy species developed from the paraffin and from the gaseous olefin are probably different, or that in any case it is likely that they are formed at different active sites.

(3) The formation of methacrolein may occur through the intermediate development of an allylic alkoxide, thus with formation of a C–O bond at the primary carbon atom. The latter may be formed from the previous alkoxy species, by oxidation of the allylic C–H bond. An hydroxy group is also formed, and the reduction of the catalyst surface by two electrons occurs. The allylic alkoxide can evolve to the formation of methacrolein. Alternatively, a common intermediate can be hypothesized for methacrolein and methacrylic acid that is a dioxyalkylidene species where the primary carbon atom is con-

nected to the catalyst surface via two C–O–Mo bridges.

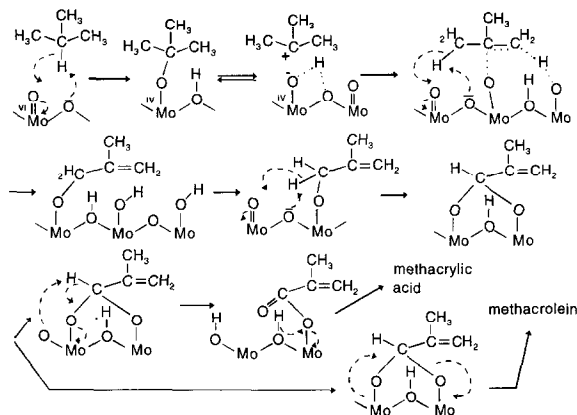
(4) The dioxyalkylidene species can evolve either to the formation of methacrolein, through dissociation of a C–O bond, or to a carboxylate species, via oxidation on a Mo–O bond, which is the precursor for methacrylic acid formation. The parallel formation of the two products, as suggested by flow reactor tests, indeed indicates the possibility of a common reaction intermediate.

(5) One competitive pathway is constituted by the dimerization or polymerization of the isobutene. Indeed, a dimeric species is observed that, however, may be formed easily at low temperatures and relatively high olefin pressure, but likely is much less favored under flow reactor conditions of isobutane oxidation. The absence of tars in spent catalysts confirms that this pathway is not favored under reaction conditions, since these oligomers can be reasonably expected to be precursors for the formation of heavy compounds.

(6) The formation of maleic anhydride, one of the primary products of isobutane oxidation, indicates that the skeletal isomerization of isobutane occurs, likely due to the acid properties of the catalyst [7], even though a contribution due to the presence of *n*-butane impurities in the feedstock can not be excluded.

(7) Other undesired side-reactions are the formation of acetic acid and of carbon oxides. Spectroscopic measurements did not give definite evidence for the formation of acetate species, since the spectra of acetate are partially superimposed on those of acrylates and other species.

The mechanism proposed is illustrated in Scheme 3. For the purpose of simplicity, the mechanism is referred to molybdenum sites, and thus to the undoped $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst, since the described phenomena occur in both doped and undoped catalysts. The addition of iron improves the catalytic activity, likely by affecting the Mo ion redox properties, even though a direct participation of iron in the reac-



Scheme 3. Proposed reaction mechanism for the oxidation of isobutane over $K_1(NH_4)_2PMo_{12}O_{40}$ catalyst.

tion mechanism can not be excluded. A more detailed study of the role of iron in Keggin-type 12-molybdophosphates is now in progress.

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References

- [1] F. Cavani and F. Trifirò, *Appl. Catal. A: General* 88 (1992) 115.
- [2] R.V. Porcelli and B. Juran, *Hydrocarbon Process.* 65(3) (1986) 37.
- [3] F. Cavani and F. Trifirò, in: *Catalysis*, Vol. 11 (R. Soc. Chem., Cambridge, 1994) p. 246.
- [4] S. Yamamatsu and T. Yamaguchi, *Eur. Patent* 425,666 A1 (1989), assigned to Asahi Chem. Co.
- [5] N. Mizuno, M. Tateishi and M. Iwamoto, *J. Chem. Soc. Chem. Commun.* (1994) 1411.
- [6] F. Cavani and F. Trifirò, *Chemtech* 24 (1994) 18.
- [7] F. Cavani, E. Etienne, M. Favaro, A. Galli, F. Trifirò and G. Hecquet, *Catal. Lett.* 32 (1995) 215.
- [8] F. Cavani, E. Etienne, M. Favaro, A. Galli, G. Sella and F. Trifirò, in: *Environmental Catalysis*, G. Centi, C. Cristiani, P. Forzatti and S. Perathoner (Eds.) (Società Chimica Italiana, Roma, 1995) p. 439.
- [9] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* (Academic Press, San Diego, 1991).

- [10] L.J. Bellamy, B.R. Connelly, A.R. Philpotts and R.L.Z. Williams, *J. Electrochem. Soc.* 64 (1960) 563.
- [11] G. Busca, G. Ramis and V. Lorenzelli, *J. Chem. Soc. Faraday Trans. I* 85 (1989) 137.
- [12] G. Ramis, G. Busca and V. Lorenzelli, *J. Chem. Soc. Faraday Trans. I* 83 (1987) 1591.
- [13] E. Finocchio, G. Busca, V. Lorenzelli and R.J. Willey, *J. Catal.* 151 (1995) 204.
- [14] G. Busca, V. Lorenzelli, G. Ramis and V. Sanchez Escribano, *Mater. Chem. Phys.* 29 (1991) 175.
- [15] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269.