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Reaction products and pathways in the selective oxidation of C_2–C_4 alkanes on MoVTeNb mixed oxide catalysts

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ABSTRACT

The catalytic properties of MoVTeNbO catalysts during the selective oxidation of short chain alkanes and olefins (C_2–C_4) have been comparatively studied. The main reaction products have been: ethylene from ethane, acrylic acid from propane, maleic anhydride from n-butane and methacrolein from isobutane. FTIR studies of the adsorption of the main reaction products, i.e. olefins and aldehydes, over MoVTeNbO catalyst has been carried out. Accordingly, the reaction pathway is explained on the basis of the characteristics of the alkane fed, the stability and reactivity of both the intermediates and the reaction products, and the nature of the catalytic sites involved in each reaction.

1. Introduction

Lower alkanes are interesting raw materials in the production of olefin and/or oxygen containing products by partial oxidation reactions [1–10]. However, at the present, only the partial oxidation of n-butane to maleic anhydride over VPO catalysts has achieved commercial operation [5].

On the other hand, the comparison of the catalytic behaviour of different alkanes can contribute to the understanding of the catalytic performance of catalysts. This is the case of comparative studies on the partial oxidation of lower alkanes over VPO [6], niobium and pyridine-exchanged heteropolyacids [7] catalysts, but also on the oxidative dehydrogenation of C_2–C_4 alkanes over V-containing catalysts [8–10].

However, Mo-V-O based catalysts appear as the most important catalysts in alkane activation [11–26]. MoVNbO catalysts were reported as active and selective in the ODH of ethane [11], although they show a poor selectivity in the ODH of C_3–C_4 alkanes [12]. However, Te- or Sb-containing Mo-V-O catalysts, prepared hydrothermally, were reported as active and relatively selective in both the ODH of ethane and the partial oxidation of propane [13,14].

Ushikubo et al. proposed in the early 1990s that MoVTe(Sb)NbO mixed metal oxides could be an extremely efficient catalytic system for the selective oxidation of propane to acrylic acid [15]. More recently, these multicomponent catalysts have been reported to be very selective in the oxidative dehydrogenation of ethane to ethylene [16], relatively selective in the oxidation of *n*-butane to maleic anhydride [17] but presenting a low selectivity in the partial oxidation of isobutane [18].

Typically, the most efficient MoVTe(Sb)NbO catalysts present generally two crystalline phases [14–26]: (i) an orthorhombic $(AO)_{2-2x}(A_2O)_xM_{20}O_{56}$ (A = Te or Sb and M = Mo, V, Nb; with $0 < x < 1$), the so-called M1 phase; and (ii) an orthorhombically distorted $(A_2O)M_6O_{19}$ phase (A = Te or Sb and M = Mo, V, Nb), the so-called M2 phase. In addition, $TeMo_5O_{16}$ (or $Sb_4Mo_{10}O_x$), $(V,Nb)_xMo_{5-x}O_{14}$ and/or tetragonal bronzes can be also present depending on the catalyst preparation procedure [22]. Pure M1 phase based catalysts can be obtained by hydrothermal synthesis [13,14,16,22–25] or by using post-synthesis treatment [26].

In this paper it will be presented a comparative study on the partial oxidation of C_2–C_4 alkanes over a MoVTeNbO mixed metal oxide catalyst, prepared hydrothermally, and presenting the M1 phase. It will be shown that the nature of the reaction products and the corresponding intermediates are very different depending on the alkane fed. According to these results different reaction pathways will be proposed.

2. Experimental

MoVTeNb oxidic bronze catalyst, with a Mo/V/Te/Nb atomic ratio of 1/0.24/0.24/0.13, was prepared hydrothermally from an aqueous solution containing ammonium heptamolybdate tetrahydrate, vanadyl sulphate, telluric acid and niobium oxalate, according to the procedure previously proposed [22]. The solid obtained was then heat-treated in flowing N_2 at 600 °C for 2 h.

Chemical analyses of the catalysts were carried out by atomic absorption spectroscopy (in the case of Mo, V and Te elements) or

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inductively coupled plasma atomic emission spectroscopy, ICP (for Nb element). X-ray diffraction patterns (XRD) were collected using a Phillips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA, and employing nickel-filtered CuKα radiation (λ = 0.1542 nm).

IR spectra of adsorbed olefins have been recorded with a Nicolet Nexus spectrometer using a conventional quartz IR cell connected to a vacuum dosing system. Prior to olefin adsorption the sample was evacuated at 250 °C for 2 h and cooled down to room temperature (r.t.) in vacuum (10^{-6} mbar). Olefins (30 mbar) have been adsorbed at 25 °C and IR spectra have been collected at r.t. and increasing temperatures. In the co-adsorption experiments, 20 mbar of O_2 has been co-adsorbed on the previous evacuated samples.

The catalytic experiments were performed in a fixed-bed quartz tubular reactor (i.d. 12 mm; length 400 mm) under atmospheric pressure. The reaction temperature studied was in the 360–400 °C range. The feed consisted of a mixture of alkane, oxygen, and helium with a molar ratio of 4/8/88. The amount of catalyst was varied from 0.1 to 3 g in order to obtain several contact times. Reactant and products were analyzed by gas chromatography using two packed columns: (i) molecular sieve 5 Å (2.5 m) and (ii) PorapackQ (3 m). Blank runs showed no conversion in the temperature range studied.

3. Results and discussion

The XRD pattern of the catalyst is characterized by Bragg reflections at $2\theta = 6.6, 7.7, 8.9, 10.7, 22.1, 27.2, 29.2, 35.4^\circ$, indicating the presence of M1 phase [22]. However, the presence of M2 as a minority phase cannot be ruled out. On the other hand, we must indicate that no changes in the XRD patterns of catalyst after the catalytic tests were observed.

3.1. Catalytic properties in the partial oxidation of C_2–C_4 alkanes and olefins

Firstly, it must be mentioned that the catalytic activity for the alkane conversion depends on the nature of the alkane and, as expected, the larger is the alkane the higher is the reactivity, with ethane and propane being the less reactive alkanes. Regarding the selectivity to reaction products, very different patterns have been observed. Fig. 1 shows the selectivity to the main partial oxidation products achieved during the partial oxidation of the C_2–C_4 alkanes at 400 °C and an alkane conversion of ca. 25%. In the oxidation of ethane, ethylene was the only partial oxidation product, with a selectivity to ethylene of ca. 95%, meanwhile no aldehydes or acids were observed. However, in the case of C_3–C_4 alkanes, the nature of the main partial oxidation products changes depending on the alkane fed. Thus, acrylic acid and propene (from propane), maleic anhydride and butadiene (from *n*-butane) and methacrolein (from isobutane) were mainly observed (Fig. 1). We must notice that the sum of the selectivities to the main partial oxidation products (i.e. olefin and O-containing products) strongly depends on the alkane fed and decreases according to the following trend (Fig. 1): ethane > propane > *n*-butane > isobutane. On the other hand, the presence of olefins in the reaction products decreases also from ethane to isobutane. In this way, isobutene was practically not observed during the oxidation of isobutane in all the isobutane conversion range studied (from 5% to 25% isobutane conversion).

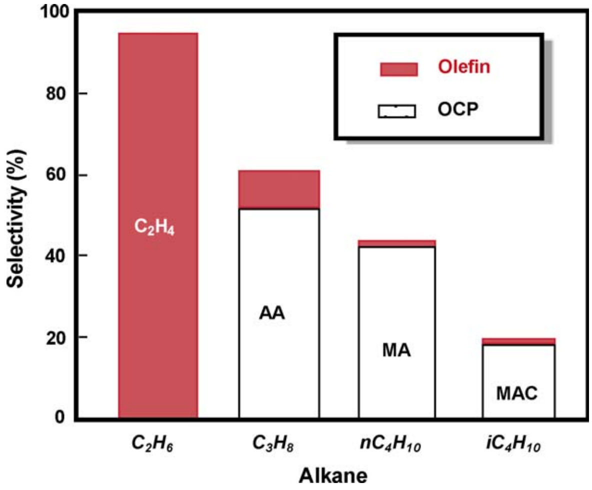

Fig. 1. Variation of the selectivity to the main reaction products, i.e. olefin and O-containing products (OCP), achieved during the oxidation of C_2–C_4 alkanes over a MoVTeNbO catalyst at 400 °C and an alkane conversion of ca. 25%. O-containing products: acrylic acid (AA); maleic anhydride (MA); methacrolein (MAC).

Fig. 2 shows the variation of the yield to the main reaction products achieved during the oxidation of C_2–C_4 olefins at 380 °C and a contact time, *W*/*F*, of 75 g_{cat} h $mol_{olefin}{}^{-1}$ (Fig. 2 a) and the variation of the selectivity to the partial oxidation products achieved during the oxidation of C_2–C_4 olefins at 380 °C and an olefin isoconversion of 20% (Fig. 2b). According to these results, it can be concluded that the same O-containing products were achieved from alkanes (Fig. 1) and from the corresponding olefins (Fig. 2a), although the selectivity to the main partial oxidation products observed during the partial oxidation of olefins was higher than those achieved from the corresponding alkanes.

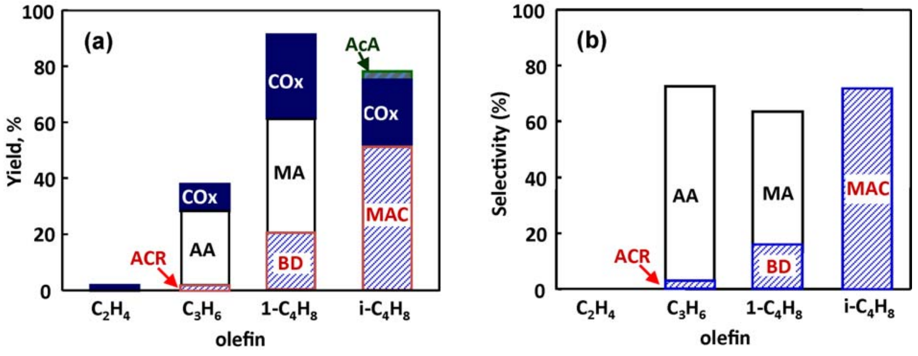

Fig. 2. (a) Variation of the yield of the main reaction products achieved during the oxidation of C_2–C_4 olefins over a MoVTeNbO catalyst at 380 °C and a contact time, *W*/*F*, of 75 g_{cat} h $mol_{olefin}{}^{-1}$. (b) Variation of the selectivity to the main partial oxidation products achieved during the oxidation of C_2–C_4 olefins over a MoVTeNbO catalyst at 380 °C and an olefin conversion of ca. 20% (different contact times were employed). Reaction products: acrolein (ACR); acrylic acid (AA); butadiene (BD); maleic anhydride (MA); methacrolein (MAC); acetic acid (AcA).

In the case of ethylene no oxygen containing products different from CO_x were observed. In addition, we must inform that the catalyst studied here presents a very low conversion in ethylene oxidation (Fig. 2a), which explains the high selectivity to ethylene observed during the oxidation of ethane. In this way we have calculated the ratio between the reaction rates of the olefin and alkane oxidation. Meanwhile the reaction rate for ethane is much higher than the rate for ethylene ($r_{C_2=}/r_{C_2} < 0.1$). In the case of the C_3–C_4 hydrocarbons, the reactivity of the olefins is remarkably higher than that of the alkanes, with $r_{\text{olefin}}/r_{\text{alkane}}$ of ca. 24 ($r_{C_3H_6}/r_{C_3H_8}$), 31 ($r_{1C_4H_8}/r_{nC_4H_{10}}$) and 38 ($r_{iC_4H_8}/r_{iC_4H_{10}}$).

Finally, we must indicate that there is a correlation between the nature of partial oxidation products and the reactivity of the olefin. Thus, the higher is the amount of the products directly formed by an allylic mechanism (i.e. acrolein, butadiene and methacrolein) the lower is the amount of acid and anhydrides. An increase in the reactivity of the olefin has been reported to favour a higher reduction of the catalyst surface [27]. Thus, one could expect that the reduction degree of the catalysts during the oxidation of isobutene [28] must be higher than during the propene oxidation [29,30] favouring a lower extension of the consecutive conversion to acid or anhydrides.

3.2. FTIR study on the adsorption of olefins and aldehydes

Fig. 3 shows the main adsorbed species observed by FTIR of propene (Fig. 3A), isobutene (Fig. 3B) or ethylene (Fig. 3C) adsorbed over the MoVTeNbO catalyst. The appearance of bands at 1493 cm^{-1} (at 100 °C) and 1292 cm^{-1} (at 150 °C) after adsorption of propene can be related to π-allylic intermediate and acrylate species respectively, which can be considered as intermediates in the formation of acrolein and acrylic acid [31,32]. In addition to these, it is also observed the presence of bands at 1554 and 1194 cm^{-1} (at 100 °C, related to propene interacting with Lewis acid sites via enolate species) and at 1482 and 1436 cm^{-1} (at 150 and 200 °C related to carboxylate species), which are the precursors of the formation of carbon oxides [32].

The IR spectra of isobutene adsorbed on the MoVTeNbO catalyst does not show any IR band in the temperature interval between 25 and 250 °C (Fig. 3B, spectrum d). However after O_2 co-adsorption at 250 °C the appearance of broad IR bands at 1780, 1593 and 1413 cm^{-1} are evident (Fig. 3B, spectrum e). These bands involves species with a carbonyl group (IR band at 1780 cm^{-1}), and because of the very high ν(C=O) frequency it could be assigned to an adsorbed lactone like specie or cyclic anhydride compound, formed by over-oxidation of surface species [32].

The absence of IR bands after isobutene adsorption could tentatively be explained by the formation of a carbocation type intermediate specie weakly adsorbed on the catalyst surface. In fact, a high reactivity of isobutene and its tendency to cationic polymerization catalyzed by Lewis or Brönsted acid sites has been previously reported [33].

The adsorption of ethylene on MoVTeNbO catalyst is shown in Fig. 3C. Ethoxy species are formed at 25 °C as evidenced by the IR band at 1057 cm^{-1} (Fig. 3C, spectrum g). Increasing the temperature no IR bands are observed until 250 °C, probably due to the desorption of adsorbed species. However, a broad IR band at 1550 cm^{-1} starts to appear together with another band at 1789 cm^{-1} (Fig. 3C, spectrum h) at 250 °C. Both bands increase in intensity at 250 °C after O_2 co-adsorption and could be assigned to oxalate species formed due to the oxidation of re-adsorbed species (Fig. 3C, spectrum i). However, no bands related to carboxylate and formiate species were observed.

Fig. 4 shows the spectra of acrolein (Fig. 4A) and methacrolein (Fig. 4B) adsorption on MoVTeNbO catalyst at increasing evacuation temperature. IR bands at 1721, 1605, 1460, 1441 and 1198 cm^{-1} are observed after evacuation at 25 °C (Fig. 4A, spectrum b), which are related to adsorbed acrolein species. Increasing the temperature to 60 °C and 150 °C a new broad band at 1545 cm^{-1} is evidenced. This band can be assigned to acrylate species [34], which are considered as precursors of acrylic acid.

In the case of methacrolein adsorption at 25 °C, IR bands at 1708, 1606, 1460 and 1382 cm^{-1} are observed associated to adsorbed methacrolein species (Fig. 4B, spectrum b). These bands remain after heating at 100 °C, though less intense, and disappear completely at 150 °C due to the desorption of the adsorbed surface species (methacrolein is already detected in the gas phase). Increasing temperature to 250-300 °C new IR bands at 1784, 1606, 1549 cm^{-1} are observed. These bands are due to over-oxidation products: cyclic anhydride type species (IR band at 1784 cm^{-1}), and carboxylates (IR band at 1549 cm^{-1}). The formation of cyclic anhydride species has been also observed by other authors after

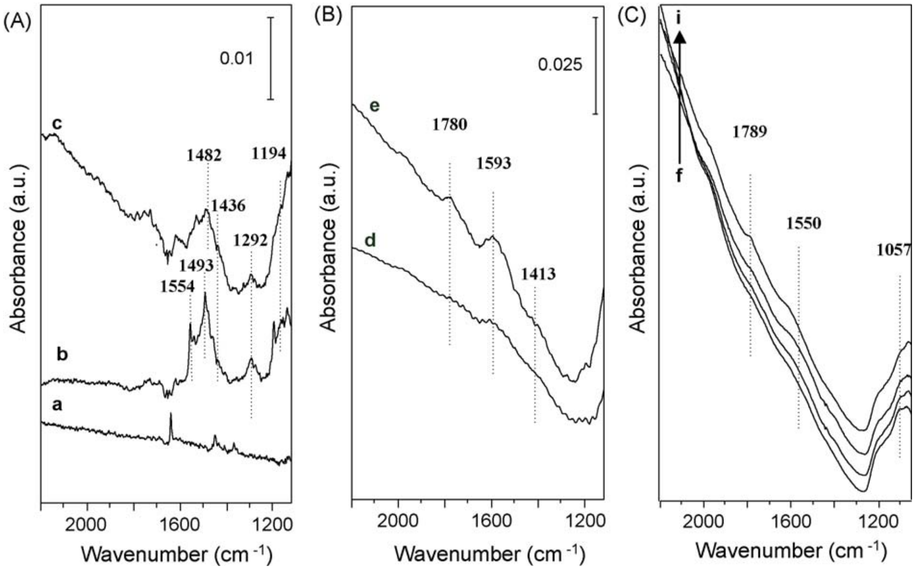

Fig. 3. Main adsorbed intermediates observed by FTIR of propene, isobutene or ethylene adsorbed over MoVTeNbO catalyst: (A) propene adsorption: (a, b and c) after adsorption and evacuated at 25 °C, 100 °C and 250 °C, respectively. (B) Isobutene adsorption: (d) after adsorption and evacuated at 250 °C, (e) after co-adsorption of O_2 at 300 °C. (C) Ethylene adsorption: (f) prior to adsorption, (g and h) after adsorption and evacuated at 25 °C and 250 °C, respectively, (i) after co-adsorption of O_2 at 250 °C.

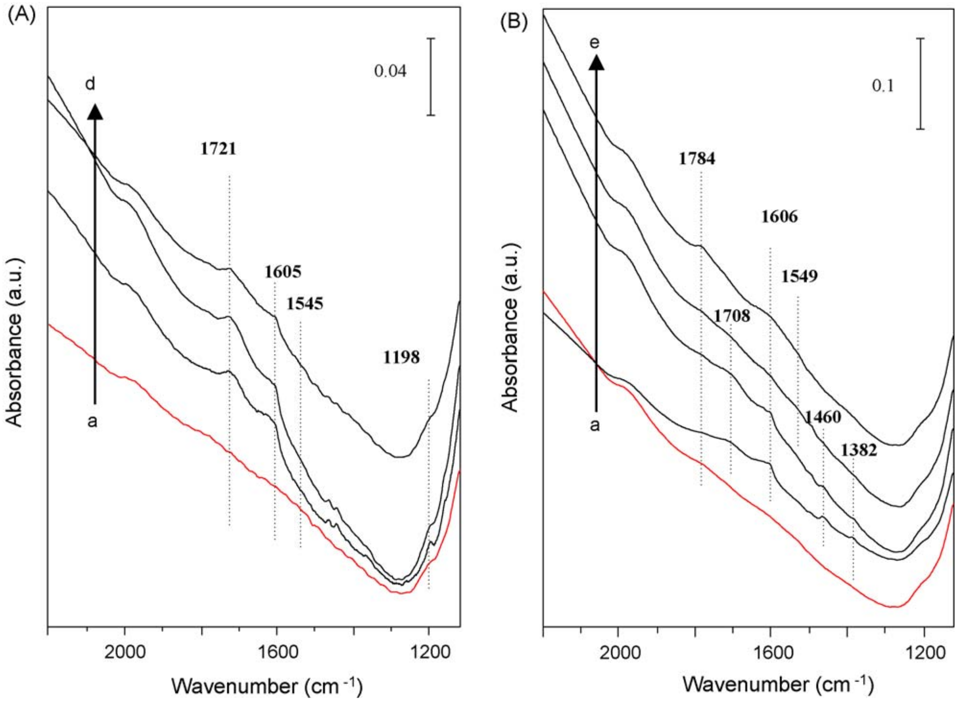

Fig. 4. Main adsorbed intermediates observed by FTIR of acrolein and methacrolein adsorbed over MoVTeNbO catalyst: (A) acrolein and O_2 co-adsorption: (a) prior to adsorption, (b, c and d) after adsorption, evacuated at 25 °C, 60 °C and 150 °C, respectively. Methacrolein and O_2 co-adsorption: (a) prior to adsorption, (b, c, d and e) after adsorption at 25 °C, 100 °C, 150 °C and 250 °C, respectively.

methacrolein adsorption on Mo-based heteropolycompounds [35]. Thus, in agreement to previous results [36], from the IR spectra desorption of methacrolein to the gas phase is evidenced hindering further oxidation to methacrylic acid.

Accordingly, partial oxidation of acrolein to acrylic acid is favoured even at low temperature on MoVTeNbO catalysts, while the partial oxidation of methacrolein to the corresponding methacrylic acid is not favoured, which is in good agreement to catalytic results.

3.3. General remarks

The results presented here show that C_2–C_4 alkanes can be selectively activated over a MoVTeNbO catalyst. In all cases, the formation of the corresponding olefin seems to be the first step in the selective oxidative activation of lower alkanes. However, the adsorption/desorption behaviour of the olefinic intermediates and also the amount of olefin observed during the catalytic oxidation of lower alkanes change depending on the length of the alkane. In addition, the FTIR spectra of C_2–C_4 olefins show that the activation mechanism and the nature of the intermediates change. Thus, low interaction is observed when ethylene is adsorbed over MoVTeNbO catalyst, while the rest of olefins present a low interaction with the catalyst.

In the case of ethane, ethylene has been the main partial oxidation product (with a selectivity higher than 90% at an ethane conversion of 50%). Since no adsorbed species have been observed during the adsorption/desorption experiments, it has been concluded that this catalyst is very effective in the transformation of ethane to ethylene. This is also in agreement to the low reactivity of ethylene over this catalyst.

Propene is mainly formed at low propane conversion and then is selectively transformed to acrylic acid at higher propane conversion. Thus, consecutive reactions (two steps) on the catalysts surface can be proposed in agreement to previously reported mechanisms [3,14,15b,31,37] (Fig. 5a). Propene is initially formed in one type of active sites (probably V–O–Mo pairs in the heptagonal channels), then is desorbed and subsequently adsorbed in a second type of sites (probably Te–O–Mo pairs in hexagonal channels]) and finally transformed into acrylic acid in Mo–O–V(Nb) pairs [37,3]. The adsorption/desorption experiments of propene indicate the formation of an allylic intermediate from propene, which is finally transformed to acrylic acid. However, acrolein is not observed in our catalytic tests, suggesting that it is easily transformed during the reaction without any apparent desorption in agreement to the adsorption/desorption experiments carried out feeding acrolein. On the other hand, we must indicate that propene has been proposed as the first reaction product, although the efficiency of these type of catalysts changes clearly depending on the catalyst composition and the crystalline phases present [3,14,15b,37].

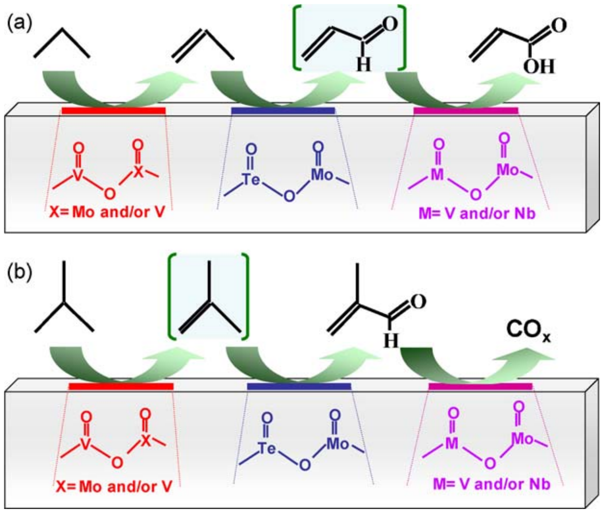

Fig. 5. Reaction steps in the propane (a) and isobutane (b) oxidation.

In the case of C_4-alkanes the formation of olefins at low alkane conversion is low for n-butane and very low in the case of isobutane (Fig. 1), indicating that other aspects must be considered in these two cases.

It has been observed that 2-butene and butadiene are the primary partial oxidation products observed during the 1-butene oxidation on a MoVTeNbO catalyst [17]. This suggests that, both acid (isomerisation of monoolefins) and redox (oxidative dehydrogenation of monoolefins to butadiene) sites are present in the catalyst. Since butadiene is formed from monoolefins by an allylic mechanism, a similar reaction network than that suggested for propane oxidation can be proposed for *n*-butane oxidation (Fig. 5b), although maleic anhydride rather than acrylic acid is the main partial oxidation product. Indeed, the adsorption of 1-butene on a similar catalyst leads to the appearance of IR bands related to butadiene (band at 1568 cm^{-1}) and enolic type species (bands at 1521, 1176, 1168 cm^{-1}) at an adsorption temperature of 100 °C, while furan species (IR band at 1527, 1472, 1442, 1294, 1125 and 1091 cm^{-1}) are observed by increasing adsorption temperature [17]. However, O_2 co-adsorption at this temperature (150 °C) has no effect on the spectra.

In the case of isobutane oxidation, isobutene is practically not observed even at low isobutane conversion. This suggests that isobutene, if formed, is rapidly transformed into adsorbed species which should be then transformed into methacrolein. However, a fast combustion is observed at high isobutane conversion rather than the formation of methacrylic acid (Fig. 5b). The absence of IR bands after isobutene adsorption could tentatively be explained by the formation of a carbocation type intermediate species weakly adsorbed on the catalysts surface as a consequence of the high reactivity of isobutene [33].

We must indicate that a different behaviour has been observed after isobutene adsorption on VPO [32]. Accordingly, different reaction mechanism and therefore selectivity to the main reaction products can be proposed for VPO and MoVTeNbO-based catalysts due to the different acid characteristics of catalysts.

On the other hand, the nature of the partial oxidation products depends also on the length of alkanes and olefins as reported on other catalytic systems [5–26]. These results are in good agreement to those previously proposed by Costine and Hodnett [38], in which ethylene, acrylic acid and maleic anhydride/butadiene are the most favoured reaction products during the oxidation of ethane, propane and n-butane, respectively. In the case of the isobutane oxidation, methacrolein and methacrylic acid are not apparently stable reaction products although higher selectivity to the aldehyde than to the acid is expected. In fact, the oxidation of isobutane leads to the lowest yields to partial oxidation products in comparison with the oxidation of other light alkanes.

In our case, acrylic acid and methacrolein are the main partial oxidation products achieved during the partial oxidation of propane and isobutane, respectively. The absence of IR bands associated to adsorbed methacrolein could be related to a fast surface desorption avoiding secondary oxidation toward methacrylic acid. Moreover, the mechanism and characteristics of industrial catalysts used in the partial oxidation of corresponding aldehydes could help to understand the differences observed in the nature of O-containing partial oxidation products during the oxidation of propane or isobutane. Thus, different catalysts are used industrially for the oxidation of acrolein ($(MoVW)_5O_{14}$-type oxides) [39] or methacrolein (heteropolyacid based catalysts) [40] to the corresponding unsaturated carboxylic acid, while similar catalysts can be used for the partial oxidation of propene or isobutene to the corresponding unsaturated aldehydes [41]. The use of different types of catalysts for the partial oxidation of C_3–C_4 aldehydes to the corresponding acids has been explained on the basis of the different stability of the corresponding acids during the reaction depending on the characteristics of catalysts [42]. Thus, it has been noticed that while the oxidation of acrolein on mixed oxide (Mo, V, W) catalysts shows an exceptionally high selectivity with respect to acrylic acid, the selectivity of the analogous oxidation of methacrolein is only moderate [43]. This has been explained due to a considerably lower oxidation rate of methacrolein compared to that of acrolein, while in the undesired subsequent oxidation of carboxylic acids, methacrylic acid is of the same order of magnitude as the oxidation of acrylic acid [43a]. However, it has been proposed that a moderate increase of methacrylic acid selectivity could be reached over MoVW-based catalysts by optimizing the Mo/V ratio and/or the incorporation of promoters [43,44].

As in Mo_5O_{14} [39], the M1 phase in MoVTeNbO catalysts is built from center-occupied pentagonal rings that are linked together by corner-sharing octahedral sites [19,25]. Thus, one could expect to have a similar behavior in the oxidation of acrolein to acrylic acid on $(MoVW)_5O_{14}$-based catalysts and on M1-containing MoVTeNbO catalysts. In this way, the results presented here confirm the relatively low consecutive reaction of acrylic acid to carbons oxides [15–26] and the higher degradation of methacrolein [18] over MoVTe-based catalysts.

Finally, a low reactivity of ethylene on MoVTeNbO catalyst is observed, which is an anomalous behaviour if compared to the other olefins studied. However, the low reactivity of ethylene is probably due to the fact that vinyl hydrogen rather than allyl hydrogen is only present. So, the MoVTeNbO catalyst has a high facility to abstract allyl hydrogen (as in C_3–C_4 olefins forming partial reaction products by an allylic oxidation mechanism) but no to abstract vinyl hydrogen (favouring no consecutive transformation of ethylene). This favours the achievement of high yield to ethylene during the oxidation of ethane.

4. Conclusions

MoVTeNbO mixed metal oxides present interesting catalytic properties in the oxidation of ethane, propane, *n*-butane and isobutane, yielding valuable reaction products. However the nature of the reaction products obtained strongly depends on the alkane fed. These results can be explained on the basis of (i) the characteristics of the active sites of MoVTeNb catalysts, (ii) the nature of the alkane fed and (iii) the stability of the intermediate and reaction products obtained.

MoVTeNbO-based catalysts present active sites of different nature in a single matrix [11–26]. They have active sites for the selective oxidative activation of C_2–C_4 alkanes. In addition, they have active and relatively selective sites for partial oxidation of olefins (except in the case of ethylene, in which a very low activity was observed). However, different reaction products are observed during the partial oxidation of C_2–C_4 alkanes, which can be explained by the presence of different intermediates depending on the number of carbon atoms in the alkanes/olefins. Thus, propene is clearly observed as a primary product during the oxidation of propane [14,15,31,36,37], although it is then selectively transformed to acrylic acid via the formation of acrolein as an intermediate. Moreover, butenes or isobutene are only observed as traces during the oxidation of *n*-butane or isobutane, respectively. This suggests that these C_4-olefins easily react to form partial oxidation products (butadiene and methacrolein) by an allylic mechanism. However, due to the different reactivity of the hydrocarbons fed, the nature of the partial oxidation products is quite different. Butadiene is selectively transformed to maleic anhydride (from both butane and 1-butene), while deep oxidation of methacrolein is favoured at high conversion from isobutane although it is relatively stable from isobutene.

According to this, a reaction network for propane and isobutane oxidation can be proposed (Fig. 5) in which the detection of reaction intermediates and the nature of the final reaction products depends on the more or less facility in the desorption of the corresponding reaction intermediates. It is clear that these aspects are clearly related to the nature and number of active sites in the catalyst. In addition, the different facility in the desorption of intermediates could determine the nature of the final reaction products, which is related to the structure of catalyst.

Acknowledgements

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