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Selective oxidation of propane over alkali-doped Mo–V–Sb–O catalysts

F. Ivars [a], B. Solsona [b], P. Botella [a], M.D. Soriano [a], J.M. López Nieto [a,*]

[a] Instituto Tecnología Química, UPV-CSIC, Avda Los Naranjos s/n, 46022 Valencia, Spain
[b] Departamento de Ingeniería Química, Universidad de Valencia, Dr. Moliner 50, 46050 Valencia, Spain

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ABSTRACT

Alkali metal-doped MoVSbO catalysts have been prepared by impregnation of a MoVSbO-mixed oxide (prepared previously by a hydrothermal synthesis) and finally activated at 500 or 600 °C in N_2. The catalysts have been characterized and tested for the selective oxidation of propane and propylene. Alkali-doped catalysts improved in general the catalytic performance of MoVSbO, resulting more selective to acrylic acid and less selective to acetic acid than the corresponding alkali-free MoVSbO catalysts. However, the specific behaviour strongly depends on both the alkali metal added and/or the final activation temperature. At isoconversion conditions, catalysts activated at 600 °C present selectivity to acrylic acid higher than that achieved on those activated at 500 °C, both K-doped catalysts presenting the highest yield to acrylic acid. The changes in the number of acid sites as well as the nature of crystalline phases can explain the catalytic behaviour of alkali-doped MoVSbO catalysts.

1. Introduction

Mo–V–Sb-mixed metal oxides have been studied during the last years as catalysts for the oxidative activation of short-chain alkanes [1–3]. Although VSbO-based catalysts were initially reported [1,4,5] and Sb-rich materials have been recently proposed [6,7], MoVTe(Sb)NbO Mitsubishi-type catalysts [2,8–10] present, at the moment, the best catalytic performance. This is the case of Nb-containing [10–17] and Nb-free Mo–V–Sb–O [17–21] catalysts which show promising catalytic performance in the selective oxidation of propane to acrylic acid [7–15], the ammoxidation of propane to acrilonotrile [17] and in the oxidative dehydrogenation of ethane to ethylene [21]. However, they generally present selectivities to partial oxidation products lower than the corresponding Te-containing catalysts [8].

In the case of the propane oxidation over Mo–V–Sb catalysts, it has been observed the main formation of acetic acid rather than acrylic acid in opposite trend to that observed in selective MoVTeNbO catalysts [22]. The presence of Brönsted acid sites in the former [20,22,23], which are absent in the latter [19,20,22,23], was proposed to be responsible for the different catalytic behaviour of both catalytic systems [19,20–23]. In this way, the incorporation of potassium on the surface of a Mo–V–Sb–O catalyst modified strongly their catalytic performance favouring the formation of acrylic acid and decreasing the formation of acetic acid [19,20]. This was explained by assuming that the incorporation of potassium and the elimination of acid sites change the reaction mechanism from an oxidative scission of the olefinic intermediate to an allylic oxidation of propylene [20].

The influence of potassium on catalytic performance occurs not only by its incorporation on the catalyst surface after the catalyst activation [19,20], but also if the catalysts are prepared hydrothermally from potassium-containing synthesis gel [24]. So, an effective incorporation on the catalysts occurs independently of the catalyst preparation procedure.

In this paper, MoVSbO-mixed oxides catalysts have been promoted with different alkali metals (Li, Na, K and Cs). These catalysts have been characterized by several physico-chemical techniques and tested in the selective oxidation of both propane and propylene. In addition, the effect of heat treatment of alkali-doped samples on their catalytic behaviour has also been studied.

2. Experimental

2.1. Catalyst preparation

MoVSbO-mixed metal oxide catalyst was prepared by a hydrothermal method from a gel with vanadyl sulphate, antimony

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* Corresponding author. Fax: +34 96 3877809.
E-mail address: jmlopez@itq.upv.es (J.M. López Nieto).

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Table 1
Characteristics and catalytic properties of alkali-doped MoVSbO catalysts

Catalyst	S_{BET} ($m^2 g^{-1}$)	$TPD-NH_3$	Propane oxidation[a]				Propene oxidation[b]		
		Acid sites[c]	Conv. (%)	S_{AA} (%)	$S_{C_3H_6}$ (%)	S_{HAc} (%)	Conv. (%)	S_{AA} (%)	$S_{HAc+Acet.}$ (%)
MVS6	14.0	22.9	22.0	13.5	10.7	12.4	45.7	44.0	27.0
Li-500	11.3	7.8	19.0	24.6	15.5	7.4	43.4	48.2	17.5
K-500	10.8	8.5	22.1	35.2	13.4	6.9	30.1	56.1	13.9
Cs-500	10.7	6.1	15.0	15.4	20.2	8.6	23.3	40.0	24.4
Li-600	4.9	2.0	8.8	26.9	37.8	1.5	15.9	53.1	26.5
Na-600	6.8	10.0	13.5	46.8	23.7	2.3	18.6	58.5	20.7
K-600	10.5	10.3	20.2	55.2	15.9	4.1	26.3	62.4	18.9
Cs-600	7.5	10.3	16.5	39.8	18.5	6.0	27.4	59.0	19.4

[a] Propane conversion (Conv.) and selectivity to acrylic acid (S_{AA}), propene ($S_{C_3H_6}$), and acetic acid (S_{HAc}) at a reaction temperature of 380 °C and contact time, W/F, of 200 g_{cat} h/mol-C_3, feed detailed in text.
[b] Propylene conversion (Conv.) and selectivity to acrylic acid (S_{AA}), and acetic acid + acetone ($S_{HAc+Acet.}$) at a reaction temperature of 380 °C and a contact time, W/F, of 75 g_{cat} h $mol_{C_3}^{-1}$, feed detailed in text.
[c] Acid sites, determined by temperature-programmed desorption (TPD) of ammonia, in $\mu mol_{NH_3}/m^2$.

sulphate, ammonium heptamolybdate and water with a Mo–V–Sb atomic ratio of 1–0.18–0.15. The gel obtained was introduced in Teflon-line stainless steel autoclave at 175 °C for 48 h. The resulting mixture was filtered, washed and dried at 100 °C for 12 h. Finally, the solid was heat-treated at 600 °C for 2 h in flowing N_2 [20]. This sample will be named as MVS6.

Alkali-doped MoVSbO catalysts (alkali metal/Mo atomic ratio of 0.0025) have been obtained by "wet" impregnation of MVS6 sample with aqueous solutions of alkaline carbonates, rotaevaporated, dried overnight at 100 °C and finally activated for 1 h at 500 or 600 °C in flowing N_2. These samples will be named as X–T, where X is the impregnated cation and T is the temperature the alkali-doped solid has been finally activated. For comparison, samples treated with water in the same procedure of impregnated samples, and finally activated at 500 or 600 °C have been also prepared. These will be named as Un-500 and Un-600, respectively.

2.2. Catalyst characterization

X-ray diffraction patterns (XRD) were collected using a Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA, and employing nickel-filtered Cu Kα radiation (λ = 0.1542 nm).

Scanning electron microscopy (SEM) and EDX microanalyses were performed on a JEOL JSM 6300 LINK ISIS instrument. The quantitative EDX analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program, which introduces the ZAF correction.

Infrared spectra obtained in a Nicolet 710 FTIR spectrometer. The pellets were prepared with 20 mg of the sample mixed with 100 mg of dry KBr and pressed into a disk.

Temperature programmed desorption of ammonia (TPD) experiments were carried out on a TPD/2900 apparatus from Micromeritics. 0.30 g of sample was pre-treated in a He stream at 450 °C for 1 h. Ammonia was chemisorbed by pulses at 100 °C until equilibrium was reached. Then, the sample was fluxed with He stream for 15 min, prior to increase the temperature up to 500 °C in a helium stream of 100 ml min^{-1} and using a heating rate of 10 °C min^{-1}. The NH_3 desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer following the characteristic mass of ammonia at 15 a.m.u.

2.3. Catalytic tests

The catalytic tests were carried out in a fixed bed quartz tubular reactor (i.d. 20 mm, length, 400 mm), at atmospheric pressure, in the 340–420 °C temperature range. The feed consisted of a mixture of $C_3H_8/O_2/He/H_2O$ or $C_3H_6/O_2/He/H_2O$ with molar ratios of 4/8/58/30 or 1.7/6.8/76.5/15, respectively. Reactant and products were analysed by gas chromatography using two packed columns: (i) molecular sieve 5 Å (3 m) and ii) Porapak Q (3 m). Blank runs showed no conversion in the temperature range studied [20].

3. Results and discussion

3.1. Characterization results

Table 1 shows the main characteristics of catalysts. It can be seen that alkali-doped catalysts activated at 600 °C presented catalyst surface areas lower than the corresponding catalysts activated at 500 °C. We must notice that the EDX microanalyses of undoped and doped samples indicated Mo/V/Sb/Alkali metal atomic ratios of 1/0.26/0.16/0 (undoped) and 1/0.26/0.16/0.002 (doped), independently of the final catalyst activation temperature.

Fig. 1 shows the powder XRD patterns of undoped and alkali-doped MoVSbO catalysts heat-treated at 500 (Fig. 1A) or 600 °C (Fig. 1B). Since the diffraction peaks at 2θ = 6.6°, 7.8°, 8.9°, 10.7°, 22.2°, 27.1° and 29.2° correspond to a so-called M1 phase, $(SbO)_2M_{20}O_{56}$ (M = Mo and V) [11], and peaks observed at 2θ = 22.3°, 28.2°, 36.2°, 45.4° and 50.0° can be assigned to $(Sb_2O)M_6O_{18}$ (M = Mo and V) called M2 phase [11], it can be concluded that both $(SbO)_2M_{20}O_{56}$ and $(Sb_2O)M_6O_{18}$, are mainly observed in the catalysts heat-treated at 500 °C. In addition, no appreciable differences were observed among them regardless of the alkali metal incorporated when the catalysts were heat-treated at 500 °C (Fig. 1A).

Important differences are observed, however, between catalysts activated at 500 °C and those activated at 600 °C (Fig. 1B). Thus, the relative intensity of diffraction peaks related to $(Sb_2O)M_6O_{18}$ and $(SbO)_2M_{20}O_{56}$ phases decrease in the XRD patterns of samples heat-treated at 600 °C with the appearance of new diffraction peaks at 2θ = 22.0°, 26.4°, 26.7°, 30.6° and 34.9°, which can be related to $Sb_2Mo_{10}O_{31}$ [JCPDS: 33–105]. This partial decomposition of M1 and M2 crystalline phases increases as follows: Cs-600 < K-600 < Na-600 < Li-600; while the formation of $Sb_2Mo_{10}O_{31}$ presents an opposite trend (Fig. 1B).

TPD of ammonia has been used in order to determine the acid characteristics of the undoped and alkali-doped catalysts. Table 1 shows the amount of adsorbed ammonia obtained in undoped and alkali-doped samples. It can be seen that the incorporation of alkali metals on the surface of a MoVSbO solid favours a drastic decrease in the NH_3 adsorption suggesting an important elimination of the acid sites present on the surface of a MoVSbO catalyst. We must indicate that, the $TPD-NH_3$ pattern of sample MVS6 shows a

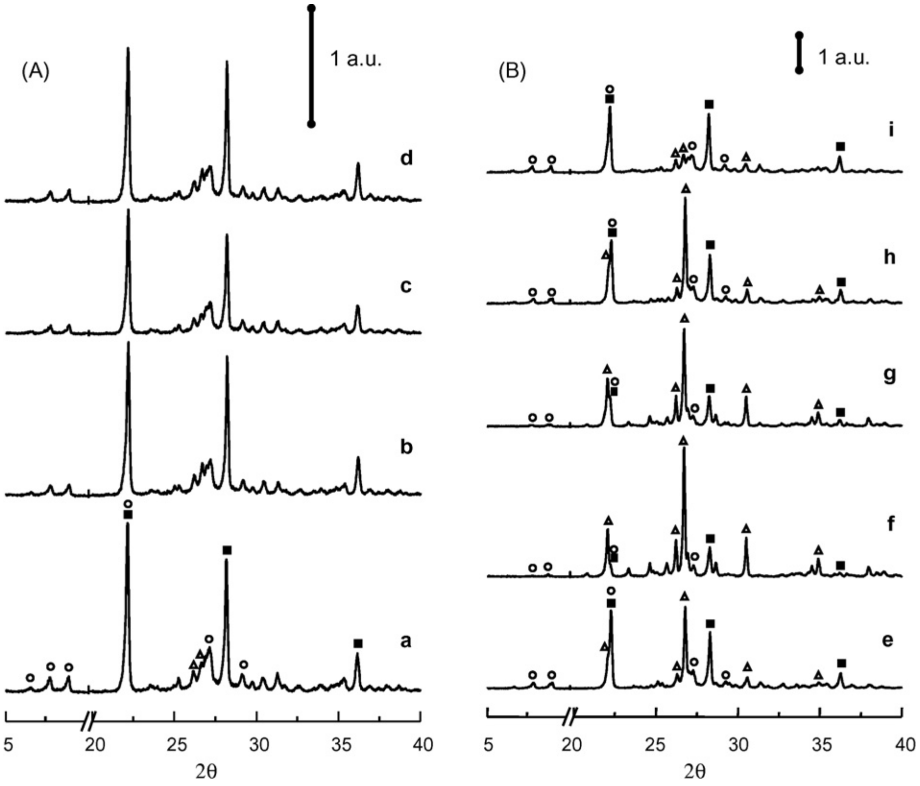

Fig. 1. XRD patterns of undoped and alkali MoVSb-doped catalysts activated at 500 °C (A) and 600 °C (B).Catalysts: (a) Un-500; (b) Li-500; (c) K-500; (d) Cs-500; (e) Un-600; (f) Li-600; (g) Na-600; (h) K-600; (i) Cs-600. Symbols: (○) $(SbO)_2M_{20}O_{56}$, (■) $(Sb_2O)M_6O_{18}$ and (Δ) $Sb_2Mo_{10}O_{31}$.

maximum observed at ca. 210 °C, indicating more acid strength than all the rest of catalysts which present no trend among them with a single peak centred at ca. 170–190 °C. These results are in good agreement to those previously reported from FTIR [20,22,23] or TPD [24] experiments of NH_3 of K-doped MoVSbO catalysts. However, no significant difference is observed among alkali-containing samples, regardless of the alkali metal added and/or the final catalyst activation temperature.

3.2. Propane and propylene oxidation on undoped and alkali-doped MoVSbO catalysts

Table 1 summarizes the catalytic results obtained during the oxidation of propane or propylene over the undoped and the alkali-doped MoVSbO catalysts. Acrylic acid, acetic acid, propylene, CO and CO_2 were the main reaction products from both hydrocarbons. Other oxygen-containing products as acrolein or acetone were also identified as minorities in propane oxidation. However, selectivity to acetone in the 10–25% range was observed during propylene oxidation over these catalysts.

In general, catalysts heat-treated at 500 °C are more active for either propane or propylene oxidation than those heat-treated at 600 °C (Table 1), being K-doped catalysts the more active ones. Moreover, while the conversion increases with the atomic number of the alkali metal added for catalysts heat-treated at 600 °C, an opposite trend can be observed in catalysts heat-treated at 500 °C. It must be indicated that no catalyst decay was observed on our catalysts after time on stream of 24 h regardless of both the heat-treatment temperature and alkali metal added.

Fig. 2 shows the variation of the selectivity to acrylic acid with the propane conversion obtained at 380 °C during the oxidation of propane over undoped and alkali-doped catalysts. An improvement in the selectivity to acrylic acid is observed in alkali-doped catalyst although this effect depends on the catalyst activation temperature and/or the nature of the alkali metal added. In this way, the selectivity to acrylic acid decreases as follows: K-600 > Na-600 > Cs-600 > Li-600 ≈ K-500 > Li-500 > Cs-500 > Un-500, Un-600, MVS6, concluding that the selectivity to acrylic acid on catalysts activated at 600 °C (Fig. 2b) is higher than on those activated at 500 °C (Fig. 2a). On the other hand, these results indicate that acrylic acid is a secondary unstable reaction product, presenting the highest selectivity to acrylic acid at propane conversions of ca. 20–30%.

Fig. 3 shows the variation of the selectivity to acrylic acid with the propylene conversion obtained during the oxidation of propylene at 380 °C. Acrylic acid can be considered in this case as a primary and unstable reaction product. The selectivity to acrylic acid depends on the alkali metal added and the final activation temperature, following a similar trend than that observed for propane oxidation. Nevertheless, the selectivity to acrylic acid from propylene was higher than from propane (see Figs. 2 and 3).

We must indicate that the selectivity to acetic acid (from propane) or acetic and acetone (from propylene) presented an opposite trend to that of the selectivity to acrylic acid, resulting to be the undoped catalysts the most selective to acetic acid. This is in agreement to previous results obtained over K-doped MoVSbO catalysts, which is related to the presence of more or less acid sites on the surface of the catalysts [19,20,24]. A similar behaviour was also observed during the olefin oxidation over Mo-based catalysts [25,26].

3.3. On the role of the presence of alkali metal on the surface of MoVSbO catalysts

It is known that alkali metals influence the catalytic behaviour of Mo-based catalysts [27–33]. Akimoto and Echigoya [27]

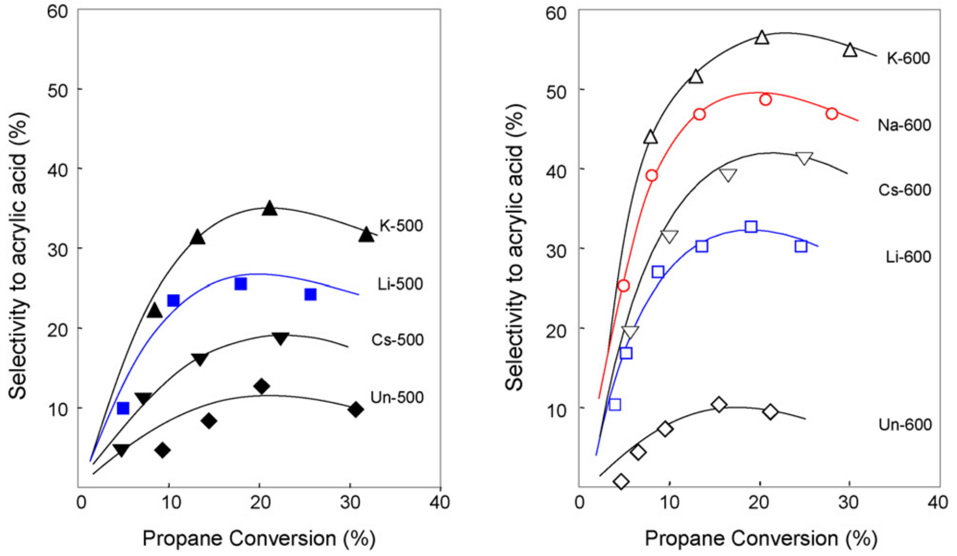

Fig. 2. Variation of the selectivity to acrylic acid with propane conversion obtained during the oxidation of propane over undoped and alkali-doped MoVSbO catalysts activated at 500 °C (full) or 600 °C (empty). Symbols: Undoped (◆ and ◇); Li- (■ and □); Na- (○); K- (▲ and Δ); Cs-doped catalysts (▼ and ▽). Experimental conditions: reaction temperature = 380 °C. Feed detailed in text.

proposed two effects of the addition of alkali metal ions on molybdenum oxide catalysts for propylene oxidation: (i) the effect of the electronegativity on the reactivity of Mo═O double bonds and (ii) the formation of inactive compounds by acid–base reaction.

In addition, it has been proposed [28] that alkali metal ions could not only affect the transformation of propylene over MoO_x catalysts, but also change the interaction of the catalyst with propane, altering propane activation step. Thus, in the case of oxidative dehydrogenation of propane, it has been proposed that the catalytic activity on alkali-doped Mo-based catalysts decreases when increasing the basicity of alkali oxide, while the selectivity to propylene shows and opposite trend [29]. This effect has been explained by the modification of the weaker Lewis acidity of Mo^{6+} cations by the presence of strongly basic alkali oxide species. Maybe, these aspects should be considered to explain the catalytic activity variation in our case depending on the alkali metal added and the final activation temperature of catalysts, along with other factors that are going to be discussed.

Fig. 4 shows comparatively the variation of the specific catalytic activity obtained during the oxidation of propane (Fig. 4a) or propylene (Fig. 4b) at 380 °C over alkali metal-doped catalysts. In general, no important differences in the specific catalytic activity between undoped and alkali metal-doped samples can be concluded, except in the case of propane oxidation over catalysts activated at 600 °C in which the specific catalytic activity increases with the atomic number of the alkali metal added. This catalytic activity trend can be explained by considering the partial destruction of crystalline phases, as observed by XRD (Fig. 1). In fact, a partial decomposition of M1 and M2 (favouring the

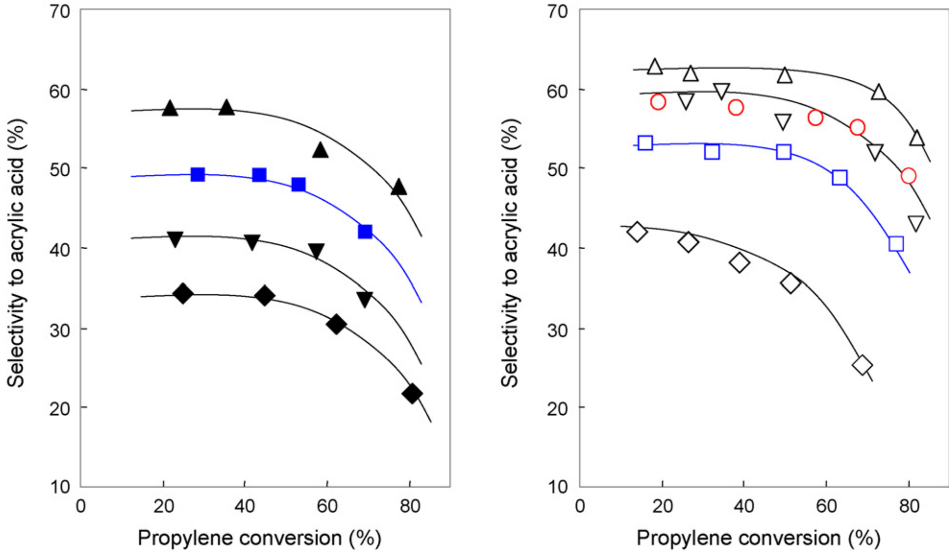

Fig. 3. Variation of the selectivity to acrylic acid with propylene conversion obtained during the oxidation of propylene over undoped and alkali-doped MoVSbO catalysts activated at 500 °C (full) or 600 °C (empty). Symbols: Undoped (◆ and ◇); Li- (■ and □); Na- (○); K- (▲ and Δ); Cs-doped catalysts (▼ and ▽). Experimental conditions: reaction temperature = 380 °C. Feed detailed in text.

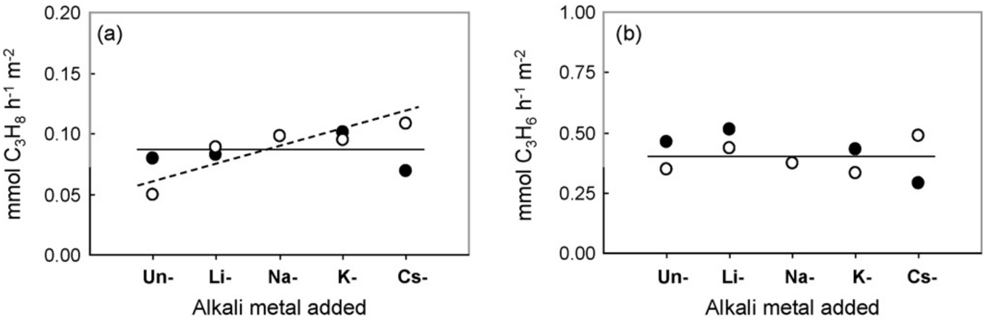

Fig. 4. Variation of specific catalytic activity (in $mol_{C_3H_8}\,h^{-1}\,m^{-2}$) for propane (a) or propylene (b) oxidation with the alkali metal added to the catalyst obtained during the oxidation of propane or propylene over catalysts heat-treated at 500 °C (●) or 600 °C (○). Reaction conditions: propane: $C_3H_8/O_2/He/H_2$ = 4/8/58/30 ($W/F = 200\,g_{cat}\,h\,mol^{-1}_{C_3H_8}$). Propylene: $C_3H_6/O_2/He/H_2$ ($W/F = 75\,g_{cat}\,h\,mol^{-1}_{C_3H_6}$). Reaction temperature = 380 °C.

formation of $Sb_2Mo_{10}O_{31}$) is observed in catalysts heat-treated at 600 °C, this effect being more important in the undoped sample and less important in the case of K- and especially in Cs-containing samples. Since M1 is the active crystalline phase for propane oxidation [34,35], and $Sb_2Mo_{10}O_{31}$ can be considered as inactive in propane oxidation, the higher or lower decomposition of M1 phase determines the lower or higher specific catalytic activity observed.

In the case of propylene oxidation (Fig. 4b), small differences in the specific catalytic activity between undoped and alkali metal-doped catalysts are apparently observed. In this case, the negative influence of the M1/M2 decomposition (in catalysts activated at 600 °C) on catalytic activity in propylene oxidation could be partially compensated by the formation of $Sb_2Mo_{10}O_{31}$, which is relatively active in partial propylene oxidation [35].

Accordingly, the different hydrocarbon conversions observed in Table 1 can be explained by the different surface areas and crystalline phases presented in the catalysts, the last strongly related to the alkali metal added.

Fig. 5 shows the variation of the selectivity to acrylic acid with the alkali metal added (for catalysts activated at 500 or 600 °C), at isoconversion conditions, obtained during the oxidation of propane (Fig. 5a) or propylene (Fig. 5b). A similar trend in the variation of selectivity to acrylic acid with the alkali metal added and/or the catalyst activation temperature is observed for propane and propylene oxidation, being the K-doped catalysts the more selective ones. On the other hand, an important improvement is also observed for catalysts heat-treated at 600 °C.

It is generally accepted that propylene is an intermediate in the selective oxidation of propane [1–24]. Our results confirm that the more important influence of the incorporation of alkali metal on the catalyst surface is the modification of the acrylic acid/acetic acid formation from propylene, indicating that this will be a key factor in the development of selective catalysts.

The undoped catalysts present a poor selectivity to acrylic acid but they are relatively selective to acetic acid (from propane) or acetone and acetic acid (from propylene). This effect has been related to the presence of acid sites on the catalysts surface, which could favour the oxyhydrative scission of propylene (forming acetic acid) rather than the allylic oxidation of the olefin (forming acrylic acid) [19,20]. In this way, the incorporation of alkali metal on the catalyst surface favours a drastic elimination of acid sites (as concluded from the TPD-NH_3 results), improving both the formation of acrylic acid by an allylic mechanism and the elimination of the actives sites for the oxidative scission. However, the catalytic performance strongly depends on the nature of the alkali metal added and the final activation temperature. For this reason, other factors must be involved in addition to the acid character of the catalysts.

However, these arguments cannot completely be used to explain the catalytic results obtained on Cs-containing samples in which $Sb_2Mo_{10}O_{31}$ is not observed and both M1 and M2 crystalline phases remain stables after heat-treatment at 600 °C (Fig. 1, pattern i).

It has been reported that the Cs-containing M1-like phase, i.e. $A_{0.5}[Mo_{5-a-b}V_aX_bO_{14}]$ exhibits low catalytic activity in the direct propane oxidation [36]. According to these authors Cs^+ ions are mainly incorporated in the heptagonal channels of M1 phase blocking the active sites for propane oxidation. Thus, this effect could explain the low catalytic activity for propane oxidation over the catalyst activated at 500 °C.

In conclusion, the incorporation of alkali metals to Mo–V–Sb–O-mixed metal oxide catalysts favours an increase in the selectivity to acrylic acid (decreasing the formation of acetic acid) during the selective oxidation of both propane and

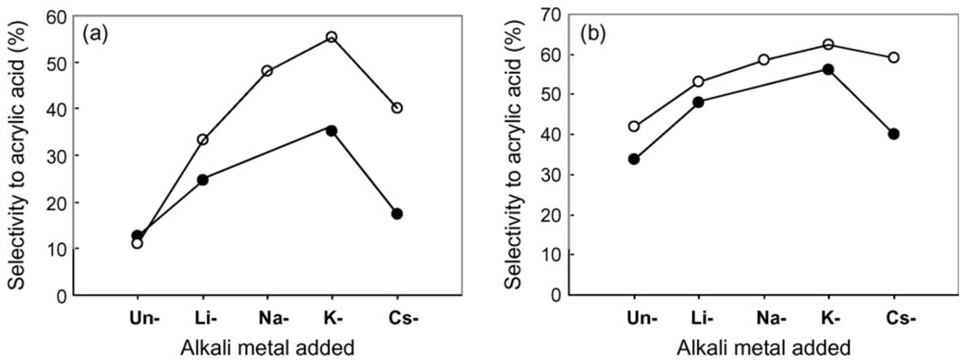

Fig. 5. Selectivity to acrylic acid obtained during the oxidation of propane (a) or propylene (b) over undoped or alkali-doped MoVSbO catalysts heat-treated at 500 °C (●) or 600 °C (○). Reaction conditions: reaction temperature = 380 °C; propane and propylene conversion = 20%, rest of reaction conditions in text.

propylene. This seems to be related to an important decrease in the number of acid sites on the catalyst surface, which favours a redox pathway (allylic oxidation) instead of an oxyhydrative scission on acid sites.

The different catalytic results achieved depending on the alkali metal added and catalyst activation temperature are not straightforward to explain. It is clear that for both kind of samples (activated at 500 or 600 °C), the incorporation of alkali metal has a promoter effect on selectivity to acrylic acid in a way that the lower the electronegativity of alkali metal added the higher is the selectivity to acrylic acid. Moreover, Cs-doped catalysts do not follow this trend, presenting lower selectivity to acrylic acid than expected. This could be related to the likely formation of Cs-containing M1 phase, which favours a partial elimination of active site for propane selective activation, as proposed by other authors [36].

On the other hand, for catalysts activated at 600 °C, two aspects must be considered a part of the changes over the redox active sites: (i) the modification of the catalyst surface area (which could depend on the alkali metal added) and (ii) the stability of crystalline phases during the catalyst activation. In this way, the stability of the phases during heat-treatment depends on the size of the incorporated cation, in a way that the higher the ionic radius the lower is the decomposition of both M1 and M2 phases into $Sb_2Mo_{10}O_{31}$. In the case of Cs-600 catalyst Cs^+ ions must be preferentially incorporated into the M1-phase framework heptagonal channels increasing its stability meanwhile $Sb_2Mo_{10}O_{31}$ is hardly formed.

Considering all these aspects the optimal catalytic behaviour has been obtained on catalysts doped with elements with intermediate electronegativity, i.e. K and Na and heat-treated at 600 °C, presenting (K-600 catalyst) a selectivity to acrylic acid about 58% at propane conversion of 30% when working at 380 °C and a contact time, W/F, of $200\,g_{cat}\,h\,mol^{-1}_{C_3H_8}$.

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