Effect of potassium doping on the catalytic behavior of Mo–V–Sb mixed oxide catalysts in the oxidation of propane to acrylic acid

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Small addition of potassium to a Mo–V–Sb mixed oxide catalyst (previously prepared by hydrothermal synthesis) strongly modifies its catalytic behavior. Thus, while acetic acid is mainly observed in the K-free catalysts, acrylic acid is selectively obtained in K-doped catalysts. In this case, a selectivity to acrylic acid of about 30% is achieved at propane conversions of 30%. This catalytic behavior is apparently not due to modification of the crystalline phases in the K-doped catalysts but to the elimination of the acid sites of the undoped Mo–V–Sb mixed oxide catalyst.

KEY WORDS: propane oxidation; acrylic acid; acetic acid; molybdenum; vanadium; antimony; potassium; hydrothermal synthesis; Lewis and Brønsted acid sites.

1. Introduction

The investigation of new catalytic systems for the gas-phase selective oxidation of propane to acrylic acid has special interest from both industrial and fundamental point of view. In this way, Mo–V–Te–Nb–O catalysts seem to be the most active and selective at relatively moderate temperatures [1,2].

Mo–V–Sb–O mixed oxide catalysts have been proposed as active and selective in the oxidation of propane to acrylic acid [3]. Despite this interest, relatively few fundamental studies on the nature of Mo–V–Sb-based catalysts and their catalytic behavior [4–7] have been published. Recently, it has been proposed that the calcination conditions strongly influence the catalytic behavior of Mo–V–Sb–Nb–O catalysts [4], but relatively low selectivities to acrylic acid were reported [4–6].

Hydrothermal synthesis has also been proposed as an interesting alternative synthetic route in the preparation of Mo–V–Sb–O-based catalysts [7]. At this moment, low selectivities to acrylic acid (ca. 6%) have been reported over hydrothermally synthesized Mo–V–Sb–O catalysts, although the selectivity to acrylic acid was increased from 6 to 20% by grinding the samples before the calcination step [7].

In this paper, we present how the incorporation of potassium to Mo–V–Sb–O catalysts (previously synthesized by a hydrothermal synthesis) has a promoter effect on their catalytic performance for the selective oxidation of propane. In addition, the characterization results suggest that the higher selectivity to acrylic acid observed in K-doped catalysts could be related to elimination of acid sites on the catalyst surface, which could favor a higher formation of propylene and/or a selective transformation of propylene to acrylic acid.

2. Experimental

2.1. Catalyst preparation

Mo–V–Sb mixed oxide catalyst has been prepared by a hydrothermal method. The catalyst was prepared using vanadyl sulphate, antimony (III) sulphate, ammonium heptamolybdate and water with a Mo/V/Sb atomic ratio of 1/0.18/0.15. The gel was autoclaved in teflon-lined stainless-steel autoclaves at 448 K for 48 h. The resulting precursor was filtered, washed, dried at 353 K for 16 h and heat-treated at 873 K during 2 h in N_2 stream. It was named **MVS** sample. K-doped catalysts (with K/Mo atomic ratios of 0.005 and 0.02) have been prepared by "wet" impregnation of the **MVS** sample with an aqueous solution of potassium nitrate with the corresponding K/Mo atomic ratio. The resulting powders were dried overnight at 373 K and finally heat-treated at 773 K for 1 h in a N_2 stream. The samples were named ***K-x***, in which x is the K/Mo atomic ratio.

From a comparative purpose, the **MVS** sample was also treated with water in the same way as that described for ***K-x*** samples and with a final heat-treatment at 773 K for 1 h in a N_2 stream. This sample was named **MVS-m**. The characteristics of catalysts are shown in table 1.

2.2. Catalyst characterization

X-ray diffraction patterns (XRD) were collected using a Philips X'Pert diffractometer equipped with a

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Table 1
Characteristics of catalysts and catalytic properties in the selective oxidation of propane at 653 K[a]

Catalyst	K/Mo atomic ratio[b]	S_{BET} (m^2/g^{-1})	Conversion (%)	Selectivity (%)[c]						
				AA	C_3H_6	ACRO	ACET	AcOH	CO	CO_2
MVS	0	8.4	18.1[d]	8.6	11.3	–	1.9	17.7	22.1	38.4
			39.7	2.0	3.6	–	1.4	17.7	24.7	50.7
MVS-m	0	8.0	38.2	11.3	4.3	t	1.1	20.6	22.5	40.1
K–0.005	0.005	8.2	13.5[d]	34.4	27.1	0.1	2.1	5.1	11.0	20.3
			27.3	30.8	9.1	0.1	1.1	11.3	16.9	30.7
K–0.02	0.02	8.0	19.7	33.2	13.0	0.2	1.8	10.5	14.9	26.4

[a] Reaction conditions: $C_3H_8/O_2/H_2O/He$ molar ratio of 4/8/30/58; Contact time, $W/F = 500\,g_{cat}\,h^{-1}\,(mol_{C_3H_8})^{-1}$.

[b] Chemical analysis was obtained by atomic absorption spectroscopy. In all cases, the heat-treated samples presented a Mo/V/Sb atomic ratio of 1/0.18/0.15.

[c] Acrylic acid (AA); propylene (C_3H_6); acrolein (ACRO); acetone (ACET); acetic acid (AcOH), and carbon oxides (CO and CO_2); t = traces.

[d] Contact time, $W/F = 250\,g_{cat}\,h^{-1}\,(mol_{C_3H_8})^{-1}$.

graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm). Infrared spectra of the solid catalysts have been recorded with a BioRad instrument using KBr pellets containing a 1 wt% catalyst (total weight of pellet, 120 mg). Infrared spectra of adsorbed NH_3 on catalyst surfaces have been recorded using conventional IR cells connected to a vacuum-dosing system. The catalyst powder was pressed into a self-supporting disc and activated at 473 K in vacuum (10^{-2} Pa) for 1 h, before adsorption experiments. Adsorption of NH_3 (31.8 mmol/g) has been performed at room temperature (RT), followed by evacuation at the same temperature in order to remove the physisorbed NH_3. Under these conditions, spectra at 298 K and after increasing the temperature to 373 K have been collected.

2.3. Catalytic tests

The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure [8,9]. The feed consisted of a mixture of propane/oxygen/water/helium with a molar ratio of 4/8/30/58. Experiments were carried out in the 613–693 K temperature interval in order to achieve the highest selectivity to partial oxidation products. Reactants and reaction products were analyzed by on-line gas chromatography using two Hewlett-Packard apparatus equipped with three columns: (i) 23% SP-1700 Chromosorb PAW (30 m × 1/8 in) to separate hydrocarbons and CO_2; (ii) Carbosieve-S (8 m × 1/8 in) to separate O_2 and CO; (iii) Porapak Q (3.0 m × 1/8 in) to separate oxygenated products. Blank runs showed that under the experimental conditions used in this work, the homogeneous reaction could be neglected.

3. Results and discussion

The propane oxidation results at 653 K are shown in table 1. Partial oxidation products, i.e., propylene, acrylic acid, acrolein, acetone and acetic acid and carbon oxides, have been observed. The **MVS** sample presents a very low selectivity to acrylic acid but an important selectivity to acetic acid. A relatively higher selectivity to acids (acrylic and acetic acids) was obtained over the **MVS-m** without apparent changes in the propane conversion. These results are similar to that reported by Ueda *et al.* [7], in which the selectivity to acrylic acid was increased from 6 to 20% by grinding the samples before the calcination step.

The catalytic behavior is completely modified after the incorporation of potassium on the surface of the catalyst. The incorporation of small amounts of potassium (K/Mo atomic ratio of 0.005) notably increases the selectivity to acrylic acid, decreasing the selectivity to both acetic acid and carbon oxides. Although the propane conversion decreases when the K-content increases, the sum of organic acids initially increases with the K-content (figure 1). Thus, and at the same reaction conditions, the yield of acrylic acid obtained on K-doped catalysts is higher than that of undoped Mo–V–Sb samples (figure 1). We must inform that the yield of acrylic acid obtained here is also higher than those previously reported in literature on Mo–V–Sb–O [7] or on Mo–V–Sb–Nb–O [4–6] catalysts.

Higher amount of potassium has a negative effect on the propane conversion, indicating a probable interaction between the active sites for propane oxidation and the potassium ions.

XRD patterns on K-free and K-doped Mo–V–Sb catalysts are shown in figure 2. Similar patterns are shown in both cases. The appearance of peaks at $2\theta = 22.1$, 28.2, 36.2, 45.2, and 50.0 could apparently be related to the presence of $Sb_4M_{10}O_{31}$ [5] and/or $Sb_2M_6O_{19}$ (with M = Mo and V) [10], while the

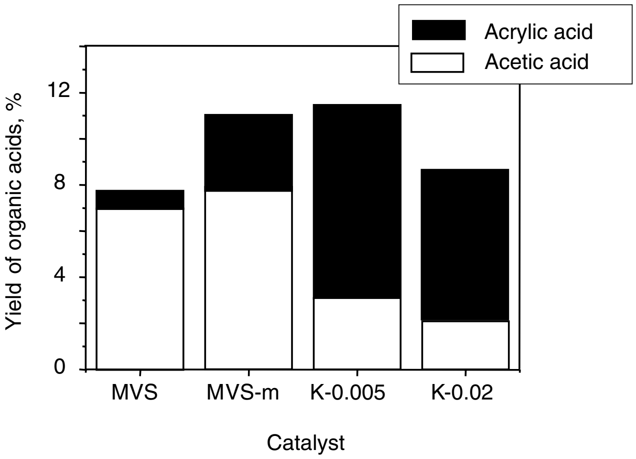


Figure 1. Variation of the yield of organic acids, i.e., acetic and acrylic acid, obtained during the oxidation of propane at 653 K on undoped and K-doped catalysts. Experimental conditions as in table 1.

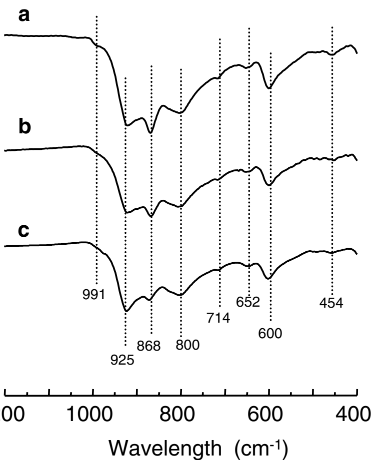


Figure 3. FTIR spectra of undoped and K-doped sample: (a) **MVS**, (b) **K–0.005** and (c) **K–0.02**.

presence of peaks at $2\theta = 6.6$, 7.8, 8.9, 12.1, 26.2, 26.7 and 29.3 could be related to the formation of $\mathrm{Sb}_2M_{10}\mathrm{O}_{31}$ [5] and/or $\mathrm{Sb}_2M_{20}\mathrm{O}_{58}$ (with M = Mo and V) [10]. In addition to these, the presence of peaks at $2\theta = 12.9$, 25.4, and 27.2 could be related to the formation, as minority, of MoO_3.

The infrared spectra of the calcined catalysts are shown in figure 3. The band at 991 and the shoulder at 868 cm^{-1} correspond to symmetric stretching vibrations of Mo = O cis-dioxo groups in MoO_3, while those detected at 800, 714 and 650 cm^{-1} are due to antisymmetric vibrations of Mo–O–Me (Me = Mo, Sb) bridging bonds [7,9]. All of these bands can be shifted from their original positions because of the incorporation of V atoms to the network. Moreover, bands at ca. 925, 600, and 454 cm^{-1} are probably related to V = O groups and V–O–Me bonds [7,9]. Since no differences are found among the samples with variable K-content, it can be concluded that the incorporation of potassium in the Mo–V–Sb catalyst does not produce any significant change in the bulk of the catalyst.

The IR spectra recorded after NH_3 adsorption at 298 K on undoped and K-doped samples and subsequent evacuation at 373 K are shown in figure 4. Adsorption of NH_3 on the undoped **MVS** sample (figure 4(a)) leads to the appearance of a broadband at 1423 cm^{-1}, assigned to an asymmetric deformation vibration (δas) of the ammonium ions (NH_4^+) [11]. The broadening of this band could be related to a nonhomogeneity of Brønsted acid sites, or due to a splitting of the δas vibration due to the adsorption symmetry of the NH_4^+ molecule with the catalyst surface. On the other hand, the band at 1608 cm^{-1} is due to the asymmetric bending vibration for ammonia adsorbed on Lewis acid sites [11].

The addition of potassium on the MVS samples (sample K–0.02) leads to a partial elimination of Lewis acid sites, in addition to a drastic decrease of the number of Brønsted acid sites (figure 4(b)). Thus, a blockage of acid sites due to the presence of potassium can be

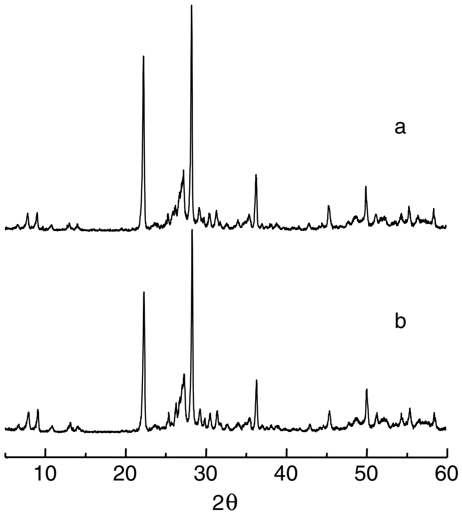


Figure 2. XRD patterns of undoped and K-doped catalysts (a) **MVS** and (b) **K–0.02**.

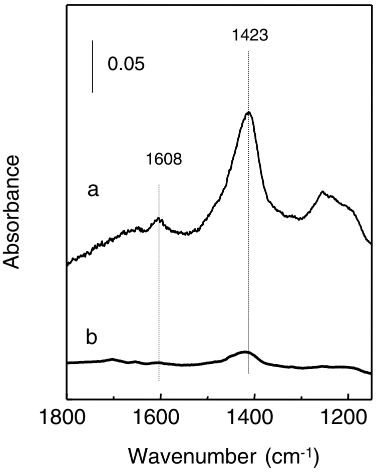


Figure 4. FTIR spectra of NH_3 adsorbed after evacuation at 373 K: (a) **MVS** and (b) **K-0.005**.

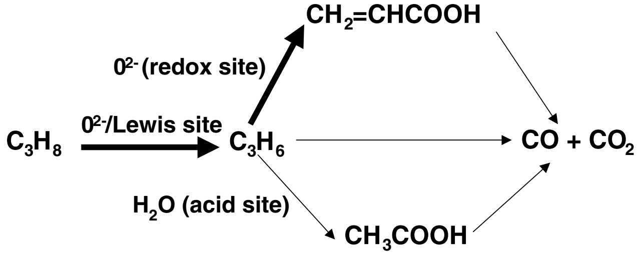
inferred, in analogy to that observed in other catalytic systems [12–16].

It is generally accepted that the oxidative dehydrogenation of propane to propylene is the first step in the selective oxidation of propane to acrylic acid on Mo–V–Sb–O-based catalysts [5,17]. This is initiated via H-abstraction from propane by concerted mechanism over acid-base pairs: the Lewis acid site (V cation) and the basic oxygen (O^{2-}) interact with the α- and β-hydrogen of propane, respectively, to form propylene [17,18]. In this way, it has been observed that the incorporation of small amounts of pyridine in the feed decreases the catalytic activity of active catalysts in propane oxidation [18]. These results were explained considering a blockage of the active sites with the pyridine. So, the lower catalytic activity of K-doped catalysts could be related to the decrease of the number of acid sites observed in our catalysts.

Higher selectivities to propylene, especially at low propane conversions, can be seen on K-doped catalysts (table 1). It is known that the addition of potassium to V- [12,15,16] or Mo-based [17,18] catalysts favors the formation of propylene from propane. In these cases, the incorporation of potassium favors a decrease of the number of acid sites, which are responsible of the deep oxidation of hydrocarbons. For this reason, the presence of potassium in K-doped Mo–V–Sb–O catalysts could also favor the oxidative dehydrogenation decreasing the deep oxidation reactions.

In addition to this, the consecutive transformation of propylene to acrylic acid and/or acetone/acetic acid changes also with the presence of potassium as a consequence of changes in the acid character of the catalyst.

It is known that V_2O_5–MoO_3-based catalysts are active and selective in the oxidative scission of propylene in the presence of water vapor to form acetone/acetic acid [19]. As observed in other V-based catalysts, the reaction could be carried out by the propylene hydration on acid sites [20,21]. So, the elimination of the Brønsted acid sites in Mo–V–Sb–O catalysts by the incorporation of potassium could also favor the allylic oxidation rather than the oxidative scission of propylene. So, a reaction network can be proposed for undoped and K-doped Mo–V–Sb–O catalysts (scheme 1), in agreement with previous results obtained on other V-containing catalysts [5,9,22]. However, at this moment, it is difficult to propose the nature of reaction intermediates involved in these reactions or the location of potassium atoms on the surface of the catalysts. So, a greater effort should be made in order to clarify the nature of active sites in each reaction step (oxidative dehydrogenation, O-insertion or oxidative scission) as well as the sites in which potassium cations are incorporated.



Scheme 1. Reaction network in propane oxidation over undoped and K-doped Mo–V–Sb–O catalysts.

4. Conclusions

Doping of the Mo–V–Sb–O catalysts by potassium strongly modify their catalytic behavior favoring the selective oxidation of propane to acrylic acid. The presence of Brønsted acid sites in the undoped Mo–V–Sb–O catalysts could favor both the deep oxidation of propane and the oxidative scission of propylene to acetic acid. The incorporation of potassium leads to a partial elimination of acid sites and a partial loss of the catalytic activity. However, the changes in the acid character in the K-doped catalyst favor a higher oxidative dehydrogenation of propane to propylene and a higher selective oxidation of propylene to acrylic acid.

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