



# Understanding effects of activation-treatments in K-free and K-MoVSbO bronze catalysts for propane partial oxidation

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## ABSTRACT

The effect of activation treatments of K-free and K-MoVSbO bronzes on either their physico-chemical characteristics or catalytic properties for propane partial oxidation have been studied. The as-synthesized materials, hydrothermally prepared and presenting  $(\text{SbO})_2\text{M}_{20}\text{O}_{56}$  type structure (the so called M1-phase), were activated by different heat-treatments, characterized (XRD, SEM-EDS, HRTEM, V K-edge, Sb L<sub>1</sub>- and K-edges XANES, EPR, XPS, NH<sub>3</sub>-TPD) and tested in propane partial oxidation. In general, the selectivity to acrylic acid (the most valuable product) was higher in K-containing MoVSbO catalysts. In addition, different trend in the catalytic behavior was found between K-free and K-containing MoVSbO series, mostly related to different changes in crystalline phases distribution and catalysts surface characteristics (composition and acid properties) induced by the several activation treatments which also modified the average Sb oxidation state.

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## 1. Introduction

MoVTe(Sb)NbO mixed oxides have been proposed as the most effective catalysts in selective (amm)oxidation of propane [1–6] and oxidative dehydrogenation of ethane [7,8], and present as well relatively high selectivity to partial oxidation products in the oxidation of *n*-butane [9]. Two crystalline phases are mainly observed in these catalysts [1–20]: the orthorhombic  $(\text{XO})_2\text{M}_{20}\text{O}_{56}$  (X = Te or Sb; M = Mo, V, Nb) known as M1 phase [5,20–25], and an orthorhombically distorted HTB-type phase  $(\text{X}_2\text{O})\text{M}_6\text{O}_{19}$  (X = Te or Sb; M = Mo, V, Nb), named as M2 phase [25,26]. Although the M1 crystalline phase is the responsible for the selective oxidation of propane into acrylic acid, it has been suggested that the presence of the M2 phase has a positive synergetic effect in Te-containing materials [25,27–29]. Unlike, the presence of M2 phase in Sb-containing MoVO catalysts has apparently a negative effect on the yield to acrylic acid in partial oxidation of propane [28–30]. Besides the crystalline phases present in MoVTe(Sb) mixed oxides, the catalytic performance for propane partial oxidation also depends on the

chemical composition [31,32], crystallinity [32], crystal orientation [32–36] and surface acid/base properties [14,16], among others. Therefore, the only presence of the M1 phase is not enough to get an adequate catalyst [24].

Regarding the chemical composition, the addition of promoters to the mixed metal oxide has a strong influence on their catalytic behavior in the propane oxidation reaction. Thus, the presence of niobium in MoVTeNbO mixed oxides is a key factor to achieve high selectivity to acrylic acid [4,5,10–12], which has been related to the modification of the acid sites [14,15] and/or to the stabilization of the acrylic acid formed, avoiding further oxidation [13,19]. However, the presence of Nb in the corresponding Sb-containing oxides has a less-pronounced effect on this reaction, and so other promoters have been investigated, finding that potassium or other alkali metals strongly increase the selectivity to acrylic acid [16–18]. Anyway, the best catalytic results, so far, are those reported for MoVTeNbO catalysts [1–5].

Besides the composition, also the activation procedure used to transform the as-synthesized mixed metal oxides into effective catalysts (usually treatment at ca. 600 °C upon relatively inert conditions, preceded or not by a treatment in air at lower temperatures [16,37–39]) will determine the physico-chemical properties and catalytic performance of these materials [13,19,40]. Thus, although tellurium has been mainly found as Te<sup>4+</sup>, different ratios of redox pairs Mo<sup>6+</sup>/Mo<sup>5+</sup>, V<sup>5+</sup>/V<sup>4+</sup> and Sb<sup>3+</sup>/Sb<sup>5+</sup> have

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**Table 1**  
Characteristics of K-free and K-MoVSb mixed oxides.

Sample <sup>a</sup>	Activation procedure	$S_{\text{BET}}$ m <sup>2</sup> g <sup>-1</sup>	Acidity $\mu\text{mol}_{\text{NH}_3}$ m <sup>-2</sup> (°C) <sup>b</sup>	Bulk			Crystalline phases <sup>f</sup>
				Mo <sup>5+</sup> /Mo <sub>total</sub> (%) <sup>c</sup>	V <sup>4+</sup> /V <sub>total</sub> (%) <sup>d</sup>	Sb <sup>3+</sup> /Sb <sub>total</sub> (%) <sup>e</sup>	
f-AS	Untreated	n.d.	n.d.	n.d.	n.d.	n.d.	M1
f-T0	280 °C/air	n.d.	n.d.	<1.0	91	4	M1
f-T1	450 °C/air	30.2	n.d.	10.0	<1	<1	MoO <sub>3</sub> » M1
f-T2	280 °C/air; 600 °C/N <sub>2</sub>	14.6	45.5 (230)	<1.0	98	19	M1, MoO <sub>3</sub> > M2
f-T3	600 °C/N <sub>2</sub>	13.2	24.3 (214)	1.1	95	>99	M1, M2
f-T4	600 °C/N <sub>2</sub> ; 280 °C/air	11.0	10.2 (180)	<1.0	94	37	M1, M2 » MoO <sub>3</sub>
K-AS	Untreated	n.d.	n.d.	n.d.	n.d.	n.d.	M1
K-T0	280 °C/air	n.d.	n.d.	1.3	91	2	M1
K-T1	450 °C/air	14.7	n.d.	8.9	<1	<1	MoO <sub>3</sub>
K-T2	280 °C/air; 600 °C/N <sub>2</sub>	13.4	12.3 (180)	<1.0	93	19	M1, MoO <sub>3</sub> > M2
K-T3	600 °C/N <sub>2</sub>	8.6	9.4 (190)	4.4	96	>99	M1, M2
K-T4	600 °C/N <sub>2</sub> ; 280 °C/air	4.7	12.2 (180)	2.3	98	95	M1, M2, Sb <sub>2</sub> Mo <sub>10</sub> O <sub>31</sub>

<sup>a</sup> The samples after the thermal activation step presented a Mo/V/Sb/K ratio of 1.00/0.27/0.15/0.00 (f-series) or 1.00/0.29/0.11/0.02 (K-series) determined by ICP.

<sup>b</sup> In parenthesis, temperature of maximum desorption during NH<sub>3</sub>-TPD experiment.

<sup>c</sup> Determined by EPR, XANES and ICP.

<sup>d</sup> Determined by V K-edge XANES.

<sup>e</sup> Determined from Sb L-edge and/or Sb K-edge XANES (Sb<sub>total</sub> = Sb<sup>3+</sup> + Sb<sup>5+</sup>).

<sup>f</sup> Determined by XRD.

n.d.: not determined.

been revealed by XANES and/or XPS, depending on the composition and the activation treatment of the MoVTe(Sb)NbO mixed oxides [16,21,23,39,41]. Further, in-situ and operando studies on M1-type MoVTe(Sb)NbO mixed oxide catalysts showed small and reproducible changes in the average oxidation state of V (Te-containing ones) and of V and Sb simultaneously (Sb-containing ones) under reaction conditions, suggesting that those species are strongly involved in redox and catalytic reactions, while no important variation was detected in Nb, Te or Mo cations [39,42].

In the present work we have studied the influence of different activating heat-treatments on the evolution of physico-chemical and catalytic properties of hydrothermally prepared K-free and K-containing MoVSbO mixed oxide materials. Several characterization techniques, as well as catalytic tests in propane selective oxidation have been employed, and correlations among the metal oxidation states, nature of crystalline phases, characteristics of catalyst surface and catalytic behavior of these materials are discussed.

## 2. Experimental methods

### 2.1. Catalysts preparation

K-free and K-containing MoVSbO mixed oxides precursors were hydrothermally prepared from aqueous gels containing vanadyl sulfate, antimony sulfate and ammonium heptamolybdate, with a Mo/V/Sb/K atomic ratio of 1/0.25/0.15/ $x$  ( $x=0$  or 0.04) [16]. The K-free and K-containing precursors (named f-AS and K-AS, respectively) were then subjected to different heat-treatments: (T0) at 280 °C for 1 h in air; (T1) at 450 °C for 1 h in air; (T2) at 280 °C for 1 h in air and then at 600 °C for 2 h in N<sub>2</sub> stream; (T3) at 600 °C for 2 h in N<sub>2</sub> stream; and (T4) at 600 °C for 2 h in N<sub>2</sub> stream and then at 280 °C for 1 h in air. The samples were named as f-Tn (K-free) or K-Tn (K-containing) in which Tn is the abbreviation previously used to describe the corresponding heat-treatment (T1–T4). Table 1 shows the main characteristics of the prepared catalysts.

### 2.2. Catalyst characterization

The catalysts chemical composition was determined by inductively coupled plasma atomic emission spectroscopy. BET specific surface areas were measured on a Micromeritics TriStar 3000 instrument, with adsorption of N<sub>2</sub> at –76 °C.

X-ray diffraction patterns (XRD) were collected using a Philips XíPert diffractometer equipped with a graphite monochromator,

operating at 40 kV and 45 mA and employing nickel-filtered CuK $\alpha$  radiation ( $\lambda=0.1542$  nm).

Sb L<sub>1</sub>-edge and V K-edge XANES spectra of MoVSb oxides were acquired at room temperature using a double crystal Si (3 1 1) monochromator detuned until 50% [16]. The Sb L<sub>1</sub>-edge data were acquired using energy steps of 0.5 eV s<sup>-1</sup> and 0.2 eV s<sup>-1</sup> in the 4650–4680 eV and the 4680–4735 eV ranges, respectively; and of 0.4 eV s<sup>-1</sup> in the region 4735–4780 eV. The V K-edge spectra were measured in the 5400–5600 eV range, with an energy step of 3 eV s<sup>-1</sup> in the 5400–5460 eV region, and of 0.3 eV s<sup>-1</sup> and 1.5 eV s<sup>-1</sup> in the 5460–5500 eV and 5500–5600 eV ranges, respectively.

Sb K-edge and V K-edge XANES spectra of K-containing MoVSbO catalysts were acquired at the BM31 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble using a Si (1 1 1) monochromator, and were recorded in the 30,300–30,652 eV and 5420–5560 eV ranges, respectively, with an energy step of 1 eV s<sup>-1</sup>. Antimony or vanadium metal foils were used as references to calibrate the pre-edge absorption energy of the Sb and V spectra to 30,491 eV and 5468 eV, respectively. Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>5</sub>, FeSbO<sub>4</sub>, and VOMoO<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, MgV<sub>2</sub>O<sub>6</sub> were used as standard patterns to calculate Sb and V oxidation states, respectively, as previously reported for V K-edge [41,42], Sb L<sub>1</sub>-edge [16,21,23], and Sb K-edge [43] XANES spectra, processing the data using the free software *Dactyloscope* [44].

Electron paramagnetic resonance (EPR) spectra were collected at –173.15 °C with a Bruker Elexsys spectrometer working in the X-band (9 GHz) at 100 K, using a receiver gain of 60 dB, attenuation of 15 dB (20 mW) and modulation amplitude of 1 G. Vanadyl acetylacetonate was used as g factor standard to calibrate magnetic fields. Quantitative analyses of spins were carried out by double integration of the EPR spectra and using the linear range of a calibrating curve made using copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O) standards [16]. Since V<sup>4+</sup> and Mo<sup>5+</sup> were the only paramagnetic species, the content of Mo<sup>5+</sup> was determined by subtracting the amount of V<sup>4+</sup> measured by XANES spectroscopy to the total paramagnetic species concentration (Table 1).

X-ray photoelectron spectra (XPS) have been acquired at room temperature and base pressure of  $2 \times 10^{-10}$  mbar in the analysis chamber, using a pass energy of 50 eV with a SPECS spectrometer equipped with a PHOIBOS 150 9 MCD detector, and monochromated Al K $\alpha$  ( $h\nu=1486.6$  eV) X-ray radiation operating at 300 W. Binding energy of C1s (284.5 eV) has been used as internal reference, and the peak intensity was estimated integrating individual components obtained by subtracting a S-shape background and

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