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Additional Information

On the nature of active sites in MoVTeO and MoVTeNbO catalysts. The influence of catalyst activation temperature

P. Concepción, S. Hernández, J.M. López Nieto *

Instituto de Tecnología Química, UPV-CSIC, Campus de la Universidad Politécnica de Valencia, Valencia (Spain)

* To whom correspondence: Fax: +34963877809; email: jmlopez@itq.upv.es

Abstract

MoVTeO and MoVTeNbO catalysts have been prepared, characterized (by XRD, Raman, IR, XPS, oxygen isotopic-exchange and IR of adsorbed methanol) and tested in the partial oxidation of propane to acrylic acid. The catalysts have been prepared hydrothermally and heat-treated at 500, 550 or 600ºC in a N_2 atmosphere. The heat-treatment has a different influence on the formation and stability of M1, the surface characteristics of catalysts and the catalytic behavior of MoVTeO and MoVTeNbO catalysts. The more selective catalyst was the MoVTeNbO sample heat-treated at 600ºC, which present relatively high oxygen isotopic-exchange, the lower onset temperature of $^{18}O_2$-consumption and a very low number of acid sites. In addition, it is characterized by the presence of only a type of Mo^{6+} species and the absence of Te^{6+} species (only Te^{4+} is observed) on the catalyst surface. The characteristics of active and selective catalysts are also discussed.

1. INTRODUCTION

Multicomponent MoVTeNbO mixed metal oxides are an interesting catalytic system since they show high activity and selectivity in the (amm)oxidation of propane to acrylic acid and acrylonitrile [1-4] and in the oxidative dehydrogenation of ethane to ethylene [5, 6]. After the publication of the first patents by Mitsubishi researchers [1, 2], many groups have worked in the last ten years on the synthesis and characterization of this type of catalysts [3-33].

Although MoVTeO are active and relatively selective in partial oxidation of propane to acrylic acid [7-10], the Nb-containing materials show at present the best catalytic behavior [1-6, 8, 9, 11-22]. In general two crystalline phases, the so-called M1 and M2 phases, have been proposed to be present in active and selective catalysts, although their proportions strongly depend on catalyst preparation, i.e. procedure, composition, etc [3,4, 8,9, 11-29]. However, the catalytic behavior of these catalysts is strongly related to the presence of M1 phase [18, 22, 23], although the presence of M2, in some case, could have a synergic effect [17-19]. This is so, because M2 phase is active and selective in propylene oxidation to acrylic acid [8, 28].

These crystalline phases can be directly obtained by hydrothermal synthesis [7-15], while a catalyst precursor is only achieved when using a slurry method [1-4, 11]. Moreover, independently of the catalyst preparation procedure, the active and selective catalyst are obtained when the catalyst precursors are heat-treated at high temperature [1-27], generally about 600ºC in an inert atmosphere. However, there is not a clear explanation about the changes occurring in the catalyst during the heat-treatment. Ueda and co-workers [7] observed that both the catalytic behavior and the characteristics of the catalyst surface of MoVTeO materials change depending on the catalyst activation procedure. Schlögl et al. [24] observed an anisotropic growth of the needle-like M1 phase during the heat-treatment. Accordingly, changes in the catalyst surface could occur during the catalyst activation, especially in Nb-containing catalysts. Thus, it has been proposed that the incorporation of Nb^{5+} cations decreases the number of acid sites [16], stabilizes the crystalline structure [25], and could facilitate a less degradation of acrylic acid to carbon oxides [26].

Bulk oxidation state of different cationic element of MoVTeNbO catalysts have been studied by XANES [12, 21, 27] and Mössbauer spectroscopies [12]. In this way,

tellurium has a role not only on catalyst structure but also as bulk component to storage oxygen in the hexagonal channels [28].

XPS results have suggested some differences between bulk and surface [8b, 12, 17, 28], although the modifications in the oxidation state of elements could also be related to the catalyst activation procedure [7]. However, more important changes could occur on the surface of catalysts, which cannot be completely followed by XPS. Thus, it has been suggested that the zone of dynamics in these types of catalysts could be limited to a thickness of about 1 nm [29]. Accordingly, other characterization techniques should be used to determine changes in the surface of catalysts.

Methanol temperature programmed surface reaction (TPSR) spectroscopy has been also employed to determine the nature of active surface sites for MoVTeNbO catalysts [30], concluding that that V^{5+} (redox) and Mo^{6+} (acid) cations are the more active surface sites while Nb^{5+} and Te^{4+} cations could be promoter ligands. On MoVO or MoVTeO catalysts, formaldehyde was only observed while both formaldehyde (on VOx sites) and dimethyl ether (on MoOx sites) are observed over MoVTeNbO catalyst. This suggests modifications in both redox and acid sites depending on catalyst composition.

Guliants et al. studied the role of surface cations in propane oxidation in orthorhombic MoVMe (M= Te, Nb and Sb) catalysts using low-energy ion scattering (LEIS) [31], suggesting that the Nb cations were preferentially located at the topmost surface, while subsurface Te or Sb concentrations declined gradually into the bulk. More recently, this group has studied the methanol and allyl alcohol chemisorptions and surface reaction in combination with LEIS in order to investigate the surface compositions and chemical nature of active phase in these catalysts [32]. Methanol species were preferentially adsorbed at the surface VO_x and MoO_x sites. In addition, they conclude that the topmost surface of catalyst shows a lower V- and Mo-content and an enriched Nb and Te with respect to both subsurface and the bulk composition, suggesting that the bulk of catalyst acts as a support.

In this work, we present a comparative study on the catalytic behavior of MoVTe(Nb)O catalyst, heat-treated at 500, 550 and 600ºC. In addition, a comparative study of the surface characteristics of materials followed by XPS, FTIR studies of adsorption of methanol as well as exchange isotopic reaction of O^{18} will be provided. Strong differences in the catalytic behavior are observed, depending on the catalyst

composition and the activation temperature, which can be explained by changes in the surface of the catalysts.

2. EXPERIMENTAL

2.1. Catalyst preparation

MoVTeO and MoVTeNbO catalysts have been prepared hydrothermally according to a procedure previously reported [15]. The gels, prepared from aqueous solutions of the corresponding salts, presented Mo/V/Te or Mo/V/Te/Nb molar ratios of 1/0.50/0.17 or 1/0.25/0.17/0.17, respectively [8]. Ammonium heptamolybdate, telluric acid or tellurium oxide, vanadium sulphate, niobium acid and oxalic acid were used, respectively, as Mo-, Te-, V-, Nb and oxalate sources. The gels were autoclaved in teflon-lined stainless steel autoclaves at 175 ºC for 48 h. The resulting solids were filtered, washed, dried at 80ºC for 16 h. The Nb-free and Nb-containing catalyst precursors will be named **A-as** and **B-as**, respectively.

The catalyst precursors have been heat-treated in the 500-600 ºC interval during 2 h in N_2-stream. The Nb-free and Nb-containing catalyst were named as **A-x** and **B-x**, respectively, where x is the catalyst activation temperature (x= 500, 550 or 600ºC).

2.2. Catalytic tests

The catalytic experiments were carried out in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm), working at atmospheric pressure [15]. Catalyst samples (0.3-0.5 mm particle size) were introduced in the reactor and diluted with 2-4 g of silicon carbide (0.5-0.75 mm particle size) in order to keep a constant volume in the catalyst bed. The flow rate and the amount of catalyst were varied (from 50 to 100 cm^3 min^{-1} and from 1.0 to 2.0 g, respectively) in order to achieve different propane conversion levels. The feed consisted of mixture of propane/oxygen/water/helium (4/8/30/58).

Experiments were carried out in the 340-420ºC temperature range in order to achieve the highest selectivity to partial oxidation products. Reactants and reaction products were analyzed by on-line gas chromatography [15].

2.3. Catalyst Characterization

The chemical composition was determined by atomic absorption spectroscopy. BET specific surface areas were measured on a Micromeritics ASAP 2000 instrument (adsorption of krypton) and on a Micromeritics Flowsorb (adsorption of N_2).

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 CuKa radiation (k = 0.1542 nm).

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

Infrared spectra were recorded at room temperature in the 300 to 3900 cm^{-1} region with a Nicolet 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

Raman spectra were recorded with an "in via" Renishaw spectrometer, equipped with a microscope (Olympus). The samples were excited by the 514.5 nm line of an Ar^+ laser (Spectra Physics Model 171) with a laser power of 2.5 mW. The following spectrometer characteristics were used: microscope objective, 50 x; spectral resolution, 2.5 cm^{-1}; integration time 20s per spectrum and number of scans 50, while the spatial resolution of each analysis is about 0.4 μm.

Photoelectron spectra (XPS) were recorded on a SPECS spectrometer using Al Kα radiation (Al Kα=1486.6 eV) of a twin anode in the constant analyser energy mode, with a pass energy of 50 eV. Samples were previously outgassed in the preparation chamber of the spectrometer and subsequently transferred to the analysis chamber. The pressure of the main chamber was maintained at ca. $5x10^{-10}$ mbar. The binding energy (BE) scale was regulated by setting the C_{1s} transition at 284.6 eV. The accuracy of the BE was ±0.1 eV. Spectra analysis has been performed using the CASA software.

IR spectra of adsorbed methanol were recorded at room temperature with a Nexus 8700 FTIR spectrometer using a DTGS detector and acquiring at 4cm^{-1} resolution. For IR studies the samples were pressed into self-supported wafers and activated at 150ºC in vacuum ($1x10^{-4}$ mbar) for 2h prior to the adsorption experiments. Methanol has been adsorbed at room temperature at increasing pressure (1-6 mbar). The

spectra shown are difference spectra between absorbances of the sample after and before adsorption of methanol.

Oxygen isotopic-exchange experiments have been performed using a quartz flow reactor equipped with mass flow controllers and an electrically heated oven. The reactor exit was connected by a heat inlet capillary system to a quadrupole mass analyser (Omnistar, Balzers) for on-line monitoring of the exit gas composition. The concentration profiles were obtained by acquiring the signals relative to the following mass-to-charge (m/z) values: 32 ($^{16}O_2$), 34 ($^{18}O^{16}O$), 36 ($^{18}O_2$). Before each experiment the sample (40 mg) were pre-treated at 250ºC in 20%O_2/argon for 2h followed by argon flow 1h at the same temperature and subsequent cooling of the sample to room temperature in argon flow. For the isotopic experiments the catalyst was subjected to 5% $^{18}O_2$/argon flow (15 ml min^{-1}) and the temperature was raised from 25ºC to 420ºC at a heating rate 10ºC min^{-1}. The system was maintained isothermally at 420ºC for 20 minutes under the $^{18}O_2$ gas mixture.

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 an Ar stream at 450ºC for 1 h. Ammonia was chemisorbed by pulses at 100ºC until equilibrium was reached. Then, the sample was fluxed with He stream for 15 minutes, prior to increase the temperature up to 500ºC in a helium stream of 100 ml min^{-1} and using a heating rate of 10 ºC min^{-1}. The NH_3 desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer.

3. RESULTS

3.1. Catalytic results for partial propane oxidation.

Table 1 shows the catalytic behavior in the partial oxidation of propane of MoVTe and MoVTeNbO catalysts heat-treated at different temperatures. Propene, acrylic acid, acetic acid and carbon oxides (CO and CO_2) are mainly observed, with traces of acetone. Propane conversion on MoVTeO catalysts decreases when increasing the activation temperature. Moreover, a different trend is observed for MoVTeNbO catalysts in which the higher the activation temperature the higher the propane conversion is.

On the other hand, the selectivity to acrylic acid increases when increasing the activation temperature, although MoVTeO catalysts are less selective to acrylic acid than the corresponding MoVTeNbO catalysts (Table 1). We must indicate that samples **B-550** and **B-600** are the most selective ones presenting space time yields at 380ºC of ca. 76.3 and 82.8 g_{AA} kg_{cat}^{-1} h^{-1}, respectively (Table 2). In the case of Nb-free catalysts only the sample heat-treated at 600ºC (**A-600**) appeared as relatively selective in the partial oxidation of propane to acrylic acid, showing a space time yield at 380ºC of ca. 17.3 g_{AA} kg_{cat}^{-1} h^{-1}.

On the other hand, the as-synthesized samples activated at 400ºC in reaction conditions (see results over samples **A-500** and **A-550** in Table 1), resulted active in propane oxidation but unselective for acrylic acid formation. In addition, no apparent changes in the catalytic performance with the time on stream were observed during their corresponding catalytic tests.

Figure 1 shows the variation of the catalytic activity (Fig. 1a) and the specific catalytic activity (Fig. 1b) with the catalyst activation temperature for Nb-free and Nb-containing catalysts. The catalytic activity for propane oxidation in MoVTeO catalysts decreases when increasing the catalyst activation temperature (Fig. 1a). Moreover, an opposite trend is observed for MoVTeNbO catalysts in which the catalytic activity increases when increasing the catalyst activation temperature.

However a different performance is observed when considering the surface area of catalysts. Thus, no variation in the specific catalytic activity with the catalyst activation temperature id observed for MoVTeO catalysts, while the specific catalytic activity increases with the catalyst activation temperature over MoVTeNbO catalyst (Fig. 1b).

3. 2. Catalyst Characterization

In order to explain the catalytic behavior of these catalysts, bulk and surface characterization of samples heat-treated in the 500-600ºC temperature interval has been studied. For comparison, the corresponding as-synthesized samples have been also studied. The characteristics of catalysts are shown in Table 2.

XRD patterns of as-synthesized and heat-treated samples are comparatively shown in Figure 2. In the case of Nb-free series, the as-synthesized samples (Fig.2.a) and samples heat-treated at 500 or 550 ºC (Fig. 2, patterns b and c) suggest the main presence of M1 phase. However, the XRD pattern of the sample heat-treated at 600ºC (A-**600**) suggests the presence of $TeMo_5O_{16}$ and MoO_3 in addition to M1 and M2 phases (Fig. 2, pattern d).

In the case of Nb-containing series, amorphous layered material with a diffraction peak at ca. $2\theta = 22.2º$ (i.e. ca. 4Å) is only observed in both the as-synthesized sample (Fig. 2, pattern e) and in the sample heat treated at 500ºC (Fig. 2, pattern f). However M1 phase is mainly observed for samples heat-treated at 550 or 600ºC, although with the minority presence of M2 phase (Fig. 2, patterns g and h).

The SEM images of Nb-free catalysts (the as-synthesized and samples heat-treated at 500 or 600ºC) presents long rod-shape crystallites oriented in no particular direction with lengths of about 2-10 μm (Fig. 3, at the top). In the case of Nb-containing samples the SEM micrographs shows the presence of small slabs and rods of low diameter (ca. 1 μm) (Fig. 3, below), presenting high homogeneity in their composition according to EDX.

Figure 4 shows the infrared spectra of catalysts in the low-frequency region (1100-400 cm^{-1}). The as-synthesized MoVTeO samples (Fig. 4, spectrum a) shows bands at 918, 870, 807, 715, 650 and 605 cm^{-1}, which can be related to the presence of M1 phase [33]. Similar spectra have been also observed in samples heat-treated at 500 (Fig. 4, spectrum b) or 550ºC (Fig. 4, spectrum c), although with additional bands at 924 and 895 cm^{-1} (related to $TeMo_5O_{16}$ [34]) and at 990 and 820 cm^{-1} (related to MoO_3 [34]). Accordingly, it can be concluded that M1 phase in addition to MoO_3 and $TeMo_5O_{16}$ are present in the sample heat-treated at 600ºC. However, the presence of M2 as minority cannot be completely ruled out.

In the case of Nb-containing MoVTeO catalysts important differences are observed depending on the activation temperature. Thus, bands at 895, 860, 765, 620 and 554 have been observed in the as-synthesized MoVTeNbO sample (Fig. 4, spectrum e), while bands at 895, 880, 765, 630, 580 and 455 cm^{-1} can be observed in samples heat treated at 500, 550 or 600ºC (Fig. 4, spectra f to h). M1 phase is proposed to show band at 918, 870, 807, 715, 650 and 605 cm^{-1} [33], while M2 phase shows

characteristics bands at 924, 750, 560 and 455 cm^{-1} [33]. Accordingly, M1 phase, is mainly observed in the samples heat-treated at 550 and 600 ºC (M2 phase is also observed as minority in both catalysts). Additional bands are observed for the as-synthesized sample and the heat-treated at 500ºC, which could be related to the presence of amorphous materials as suggested by XRD. Since M2 phase is not observed by XRD, small crystals sizes should be considered for M2 phase.

Figure 5 shows the Raman spectra of MoVTeO and MoVTeNbO catalysts. MoVTeO catalysts exhibit an intense Raman band at 874 cm^{-1} with a broad shoulder towards lower frequencies, in the 770-840 cm^{-1} Raman region, and a weak shoulder to higher frequencies, at around 970 cm^{-1}. In addition to these, bands at lower frequencies, 437 and 470 cm^{-1} are also observed. These spectra are similar to those previously reported by other authors [3, 23, 30, 35]. The shoulder at 970-980 cm^{-1} can be assigned to stretching vibrations of terminal Mo=O and V=O bonds [36], while the bands at 770-880 cm^{-1} and at around 470 cm^{-1} can be related to asymmetric and symmetric Me-O-Me bridge stretching modes, respectively. In the case of the sample heat-treated at 600ºC, it can be seen an additional band at 964 cm^{-1} which can be related to the presence of TeMo$_5$O$_{16}$ [23].

Important differences are observed for MoVTeNbO catalysts (Fig. 5, spectra e to h). A broad band centred at 840 (for the as-synthesized sample, Fig. 5, spectrum e) which shifts to 800-817 cm^{-1} (for heat-treated samples, Fig. 5, spectra f to h) can be clearly observed. These spectra are similar to those previously reported by other authors [37]. The broad band at 817 cm^{-1} together with the 650 cm^{-1} band has been assigned to the formation of Nb-O-Nb bonds [38], while the symmetric vibration of isolated NbO$_6$ octahedra has been assigned at 907 cm^{-1}. Bands at 470, 870, 922 and 982 cm^{-1} assigned to Me-O-Me bridge stretching modes and Me=O bonds are also observed.

Table 3 summarizes the XPS results of samples heat-treated at 500 and 600ºC., while Figure 6 shows the Mo 3d$_{5/2}$ and 3d$_{3/2}$ (Fig. 6a), Te 3d$_{5/2}$ (Fig. 6b) and O$_{1s}$ (Fig. 6c) core-level spectra of MoVTeO and MoVTeNbO samples heat-treated at 500 and 600ºC, respectively, which show mainly M1 phase. According to the XPS results a deficient vanadium surface versus bulk composition is observed in all samples. Moreover, on the samples heat-treated at high temperature (600ºC), it can be observed a decreases in the vanadium surface concentration and a partial reduction of V^{5+} cations increasing the amount of V^{4+} species (Table 3). On the other hand, differences in the

surface composition and oxidation states of the elements are observed, which should be interpreted with caution in those samples presenting different crystalline phases and/or amorphous materials, i.e sample **A-600** and **B-500**.

The Mo 3d core-level spectra of catalysts show that the binding energy of the Mo $3d_{5/2}$ changes depending on the composition and heat-treatment of catalysts (Fig. 6a). Thus, two types of Mo^{6+} species, i.e. Mo_A^{6+} (BE= 232.8eV) and Mo_B^{6+} (BE= 233.8eV), in different coordination environments, are observed in all cases, except for sample B-600 in which only one type of Mo-species (Mo_A^{6+}) is only observed. Mo^{5+} species, with BE at 231.7 eV [39], has been not observed in any sample.

On the other hand, the Te core-level spectra of the catalysts indicate that the binding energy of the Te $3d_{5/2}$ changes from 577.9 to 576.4 eV (Table 3). The BE corresponding to Te^{4+} is 576.2 eV, while H_6TeO_6 is observed at 577.3 eV [40]. According to this, it can be proposed that both Te^{6+} and Te^{4+} are observed on the main of studied samples, with $Te^{6+}/(Te^{6+}+Te^{4+})$ ratios between 15 to 25%. However, only Te^{4+} is detected in the **B-600** sample (Fig. 6b). On the other hand, Te^0 (binding energy at 573.0 eV) was not observed in any case.

The Nb3d core-level spectra of Nb-containing samples present one component assigned to Nb^{5+} species (BE= 207.0 eV). Moreover, the V2p core-level spectra shows the presence of two components assigned to V^{4+} (BE= 516.6 eV) and V^{5+} (BE= 517.67 eV) (Table 3). V^{4+} is mainly observed in all catalysts (from 60 to 80% depending on catalyst composition and activation temperature). In addition, and as indicated above, the heat-treatment of the samples decreases the V^{5+} surface concentration on all samples.

Finally, two types of oxygen surface species with BE at 530.6 eV and 532.3 eV (named as O_A and O_B, respectively) are observed on all samples (Fig. 6 c, Table 3), which can be assigned to oxygen species with different electrophilic properties. The $O_B/(O_A+O_B)$ ratio in Nb-containing catalysts was lower than those observed in the corresponding Nb-free catalysts (and it decreases when increasing the activation temperature.)

According to the results in Table 3, a high amount of Mo_B^{6+} species and a Te^{6+}-enrichment is observed for **A-600** sample, which could be related to the presence of MoO_3 and $TeMo_5O_{16}$ crystalline phases. On the other hand, the presence of an amorphous phase on the **B-500** sample could also modify their surface composition as already observed in Table 3. However, the differences observed by XPS in the surface

composition of both **A-500** and **B-600** samples cannot be explained by the presence of other crystalline and/or amorphous phase since only M1 (and the presence of M2 phase as minority) has been detected by XRD, IR and Raman.

As indicated previously, one type of Mo^{6+} surface specie (Mo_A^{6+}, BE= 232.8 eV) and one type of tellurium species (Te^{4+} are only detected) as well as a lower surface concentration of oxygen species, with the higher basicity, are observed mainly in the **B-600** sample (see Figure 6). Thus, the different surface composition detected by XPS in the **B-600** sample could explain partially the different catalytic behavior observed over this catalyst.

However, the use of conventional XPS spectroscopy facilitates the analysis of about 50 monolayers of the catalysts surface. Thus, the information obtained is not strictly related to the surface of the catalysts. In order to evaluate changes on the catalyst surface other characterization techniques such as FTIR of adsorption of methanol and Oxygen isotope experiments have been employed.

IR spectroscopy of methanol adsorption has been performed in order to evaluate the nature of Lewis acid sites located on the catalyst surface. Methanol adsorption on metal oxides at room temperature may be either molecular (physical adsorption) or dissociative. Dissociative adsorption of methanol involves acid/base Lewis pairs on the metal oxide surface, with the formation of metal-methoxy ($M-OCH_3$) groups and surface hydroxy groups (OH). It has been shown that the $\nu(OC)$ mode of methoxy surface groups is cationic adsorption site depended [41]. Thus valuable information about the nature of surface sites can be obtained from the $\nu(OC)$ stretching frequency of adsorbed methoxy species. On the other hand, surface methoxy species can be susceptible to further oxidation reaction with the production of partially oxygenated reaction products (formaldehyde and methylformate).

The IR spectra in the 2000-1000 cm^{-1} region of methanol adsorbed on the Nb-free and Nb-containing MoVTe catalysts are shown in Figure 7. A broad IR adsorption in the 1182-1041 cm^{-1} range is observed on both (Nb-free and Nb-containing) samples heat treated at 500ºC (Fig. 7, a and c), while IR bands at lower frequencies (1031, 1091 and 1006 cm^{-1}) are observed on all samples. The IR bands at high frequencies (maxima at 1148 and 1078 cm^{-1}) are assigned to the OC stretching frequency of metal-methoxy species while the IR bands at lower frequencies should be assigned to weakly adsorbed methanol species (gas phase methanol shows IR bands at 1058, 1034 and 1014 cm^{-1}).

Thus, methanol dissociation with the formation of metal-methoxy species is mainly observed on samples activated at 500ºC (Fig. 7, a and c). This account for the presence of certain type of surface acid/base Lewis pairs on the samples treated at 500ºC, which seems to be absent on the same samples treated at higher temperature, i.e. 600ºC (Fig. 7, b and d). On the other hand, IR band at 1453 cm^{-1} due to $\delta(CH_3)$ bending vibrations of adsorbed methanol species and at 1361 cm^{-1} due to OH bending mode are also observed on all samples. Additional bands at 1564, 1607, and 1355 cm^{-1} due to formate species and 1710 (1774 cm^{-1}) due to methylformate are observed on samples treated at 500ºC revealing a higher reactivity of the adsorbed methoxy species toward oxidation products.

Similar conclusions can be obtained from the $\nu(CH)$ IR region. While no IR bands are observed on the samples treated at 600ºC, IR bands at 2953 and 2845cm^{-1}, due to undissociated Lewis bonded methanol species, at 2926 and 2832 cm^{-1}, due to dissociated surface methoxy species and at 2947 and 2880 cm^{-1} associated to formate species are observed on both (Nb-free and Nb-containing) samples treated at 500ºC. The lack of IR bands in this region on the samples treated at 600ºC is due to the low surface concentration of adsorbed species of these samples.

Thus a different reactivity and nature of the catalyst surface can be inferred depending on the heat-treatment conditions. These results are also in agreement to those achieved by TPD experiments of NH$_3$. In fact NH$_3$-TPD results presented in Table 2 show a concentration of acid sites on samples heat-treated at 500ºC higher to those heat-treated at 600ºC.

In order to obtain further information about the nature and/or reactivity of oxygen species participating in the oxidation of propane oxygen isotopic-exchange experiment with $^{18}O_2$ have been performed. Oxygen isotope exchange is a common method for studding the participation of oxygen form the catalysts in oxidation reaction [42, 43]. The temperature programmed oxygen isotopic-exchange profiles in the 25-420ºC temperature range is shown in Figure 8. In all cases consumption of $^{18}O_2$ and release of $^{16}O_2$ and $^{16}O^{18}O$ is observed. The onset temperature of $^{18}O_2$-consumption increases in the following trend: 310ºC (**A-500**), 333ºC (**B-500**), 382ºC (**A-600**) or 399ºC (**B-600**). Thus, the onset temperature of $^{18}O_2$-consumption is lower on the samples heat-treated at 500ºC. These results suggest higher oxygen mobility in the

samples heat-treated at 500ºC, i.e. **A-500** and **B-500**. This agrees with the lower selectivity in the propane oxidation observed for these catalysts as presented in Table 1. On the other hand, the amount of exchangeable oxygen species decreases in the following trend (Fig. 8): 0.269×10^{-10} A/m^2 (**B-500**) > 0.140×10^{-10} A/m^2 (**B-600**) > 0.053×10^{-10} A/m^2 (**A-600**) > 0.016×10^{-10} A/m^2 (**A-500**). Accordingly, the amount of exchangeable oxygen species in the Nb-containing catalysts is higher than in the corresponding Nb-free catalysts.

4. DISCUSSION

According to the characterization results (XRD, FTIR and Raman) the catalyst activation temperature has a different influence in Nb-free and Nb-containing catalysts. For Nb-free catalysts, M1 is mainly formed in the as-synthesized sample (**A-as** sample) but also in samples heat-treated at 500 or 550ºC. Moreover, it decomposes partially to MoO_3 and $TeMo_5O_{16}$ at a catalyst activation temperature higher than 600ºC (**A-600** sample). In a different trend, an amorphous material is only observed in the as-synthesized Nb-containing material (**B-as** sample), which is also mainly observed in samples heat-treated at activation temperatures of about 500ºC (**B-500** sample). However, this amorphous material is selectively transformed into M1 phase for samples heat-treated at activation temperatures higher than 550ºC, i.e. **B-550** and **B-600** samples.

When comparing the catalytic results for propane oxidation over MVTeO and MoVTeNbO catalysts (Table 1), an important influence of the catalyst activation temperature on the catalytic behavior can be concluded. Thus, the higher the catalyst activation temperature the higher is the selectivity to acrylic acid, although Nb-containing catalysts presented the higher selectivity to partial oxidation products. This is in agreement to previous results [1-6, 8, 9, 11-22]. However, there is not a clear correlation between bulk characteristics of these catalysts, with and without niobium, and their catalytic activity. For this reason, the catalytic behavior cannot be completely explained in terms of the presence/absence of M1 phase but also as a consequence of modifications of the surface of catalysts during the catalyst activation step.

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The catalytic activity for propane oxidation over Nb-free catalysts decreases when increasing the catalyst activation temperature. Moreover, an opposite trend can be proposed over Nb-containing catalysts (Fig. 1a). According to the bulk phase characterization of catalysts, this catalytic performance could be related to the presence of M1 phase.

However, when considering the specific catalytic activity (i.e. the catalytic activity per surface area of catalysts) (Fig. 1b), it can be concluded that it increases with the catalyst activation temperature for MoVTeNbO catalysts (and with the main presence of M1 phase in the catalyst). Moreover, no modification of the specific catalytic activity with the catalyst activation temperature is observed for Nb-free MoVTeO catalysts. It is clear that the partial decomposition of M1 phase and the formation of other crystalline phases can modify the effective surface area of M1 phase in these catalysts (the presence of small crystals of MoO_3 and $TeMo_5O_{16}$ could mask a the real surface area of M1 phase increasing the surface area of catalysts and decreasing the specific catalytic activity). This has been recently observed in M1 catalysts prepared by post-synthesis procedure [22, 33].

Moreover, the most significant difference among these catalysts is related to the formation of acrylic acid. According to the catalytic results in Tables 1 and 2, M1 phase in MoVTeO catalysts (**A-500** sample) presents a very low selectivity to acrylic acid, while M1 phase in MoVTeNbO catalyst (**B-600** sample) is very active and selective in the partial oxidation of propane to acrylic acid.

It has been proposed that catalysts with and without niobium present a completely different morphology [8, 9]. This is in part as a consequence of the presence of oxalate anions which modify not only the oxidation state of each element [8] but also prevents the formation of long and large needles during the hydrotermal synthesis by slowing down the crystallization in the [001] axis of the particles [24]. However, the more important factor to be considered is the fact that the incorporation of niobium in the framework of M1 phase facilitates an important decrease in the number of acid sites in this type of catalysts [16], but also changes in the reaction mechanism [16, 44, 45]. On the other hand, the presence of niobium in the framework of M1 phase improves the stability of this crystalline structure [25], and facilitates a less degradation of acrylic acid to carbon oxides [26].

In fact, it is know that not only MoVTeO [7, 8, 10] but also MoVSbO catalysts [7, 44-46], obtained hydrothermally and presenting pure M1 phase show low selectivity to acrylic acid, although the selectivity can be improved by using post-synthesis treatments [33, 44]. The low selectivity to acrylic acid in MoVTeO and MoVSbO has been related to the presence of Brönsted and Lewis acid sites, which are not observed in the corresponding Nb- or K-containing catalysts [16, 33, 44, 46].

However, and in addition to the existence of M1 phase, other factors should be considered in order to explain the changes observed in the formation of acrylic acid over these catalysts. In this way, important differences have been observed when comparing the surface characteristics of catalysts (Table 3), especially related to the nature of Mo^{6+} species, the absence of Te^{6+} and the nature of oxygen species on the catalyst surface of the more selective catalyst, i.e. the MoVTeNbO sample heat-treated at 600ºC. In this way, the presence of a second Mo^{6+} species in Nb-free samples (Mo_B^{6+}, BE= 233.8 eV) can be related to the appearance of other crystalline phases as MoO_3 or $TeMo_5O_{16}$. However, the absence of Te^{6+} in B-600 sample should be related to the formation of M1 (and M2 as minority) as a consequence of the incorporation of Nb^{5+} in the framework of M1 phase.

On the other hand, changes in the acid characteristics of catalysts have been also observed by IR of adsorbed methanol (Fig. 7) and NH_3-TPD (Table 2). The IR results of adsorbed methanol indicate the existence of acid sites in samples heat-treated at 500ºC, while they practically disappear when the samples are heat-treated at 600ºC. It is clear that in the case of MoVTeO samples heat-treated at 500ºC, in which M1 is mainly observed, the acid sites must be related to surface species on M1 phase. However, the heat-treatment facilitate the partial decomposition M1 and the formation of non-acidic crystalline phases such as MoO_3 and $TeMo_5O_{16}$ favoring an important decease of the number of acid sites. In addition, some contamination of the surface of M1 crystals during the heat-treatment cannot completely ruled out.

In the case of MoVTeNbO samples heat-treated at 500ºC, the presence of acid sites must be related to the presence of amorphous material, while the acid sites disappear when the amorphous is transformed into M1 phase. According to this, the incorporation of Nb^{5+} cations in M1 phase favors a strong decrease of acidity of these catalysts during the heat-treatment. This is in agreement to previous results in which the

presence of Nb^{5+} facilitate a drastic reduction of the number of acid sites [16]. However, this could be not only a consequence of the presence of Nb cations but also, by the presence of oxalate anions during the preparation. In fact, some improvement in the selectivity to acrylic acid has been also observed for MoVTeO catalysts prepared hydrothermally in the presence of oxalate anions in the synthesis gel [8, 47].

In addition to the changes in the acid character of catalysts with the heat-treatment, the nature of oxygen species on the catalyst surface also change as determined by oxygen isotopic exchange experiments (Fig. 8). In fact, a different reactivity of the catalysts surface is observed after heat-treatment of the catalyst depending on the activation temperature. Heat-treatment at 500ºC leads to the presence of Lewis acid sites and a higher mobility of surface oxygen species which could be responsible for the low selectivity to acrylic acid observed during the oxidation of propane on this catalyst. Moreover, the results achieved on samples heat-treated at higher temperatures, especially in the case of **B-600** sample, suggest some "blockage" of the Lewis acid sites and the most reactive oxygen species favoring a higher selectivity to acrylic acid.

These results indicate that although the presence of M1 phase is necessary to increase the oxidative propane conversion, the surface characteristics of catalyst must be tailored in order to improve the selectivity to acrylic acid. The elimination of acid sites and some decrease of the most reactive oxygen species on the catalyst surface seem to have a positive effect on the selectivity to acrylic acid. In other words, and as suggested by other authors [29-32], only the surface of M1 phase seems to be directly involved in the catalytic behavior of these materials: the bulk of M1 phase could act as a support while modifications in the monolayer of these crystals could be directly involved in their catalytic performance. In this way, and in addition to the formation of M1 phase (in the case of Nb-containing catalysts), the heat-treatment could optimize the surface composition and the oxidation state of each element modifying the nature of surface oxygen species. Thus, the bulk of the catalyst could be considered as a support in which the M1 phase easily favors the adequate distribution of active sites in environments with appropriate chemical characteristics, i.e. low acidity and oxygen surface species with relatively low mobility, in which the participation of adsorbed oxygen species is low. If this is so, it is clear that post-synthesis treatments as recently suggested [22, 33] and/or

adequate catalyst activation procedures can provide adequate improvements in the catalytic behavior of these catalysts.

Conclusions

In conclusion, a strong influence of the catalyst activation temperature on catalytic behavior of MoVTeO and MoVTeNbO catalysts has been observed. However, this influence depends on the catalyst composition.

In the case of MoVTeO catalysts, which present M1 phase, low selectivity to acrylic acid is observed. The catalytic activity for propane oxidation decreases and the selectivity to acrylic acid increases when increasing the catalyst activation temperature. M1 phase is mainly observed at low catalyst activation temperatures, while a partial decomposition of M1 phase into M2, MoO_3 and $TeMo_5O_{16}$ in the sample heat-treated at 600ºC. Accordingly, the catalytic results can be explained by considering the M1 phase in Mo-V-Te catalysts as very active but unselective for the partial oxidation of propane to acrylic acid. However, an important improvement in the selectivity to acrylic acid has been observed for MoVTeO sample heat-treated at 600ºC, in which a partial decomposition of M1 phase. Maybe some contamination on the catalyst surface can provide some modification of non-selective sites in these catalysts.

In the case of MoVTeNbO catalysts, it has been observed the presence of amorphous phases at low catalyst activation temperatures and M1 phase at high activation temperatures. Since both the catalytic activity for propane oxidation and the selectivity to acrylic acid increase when increasing the catalyst activation temperature, it can be concluded that Nb-containing M1 phase, with Nb cations incorporated in the framework, could be proposed as active and selective for partial oxidation of propane.

The comparative study by XPS, infrared spectroscopy of adsorbed methanol and $^{18}O_2$ isotopic exchange, of MoVTeO and MoVTeNbO catalysts suggests that the catalytic behavior of these materials could be more easily explained by considering the characteristics of the surface of the catalysts, which change in a different manner depending on the catalyst composition and activation temperature. Thus, in addition to the positive effect of the presence of Nb on the stability of M1 phase, the elimination of the acid character of catalysts, the presence of some element in a lower oxidation state

(especially the presence of Te^{4+} and the elimination of Te^{6+}) and a better homogeneous distribution of molybdenum cations (the presence of Mo_A^{6+} species as indicated in Table 3) can explain the high selectivity to acrylic acid of Nb-containing MoVTeO catalysts heat-treated at 550-600ºC temperature range. We must indicate that these catalysts present also surface oxygen species with reactivity lower to that observed in the corresponding Nb-feee catalysts.

Acknowledgment

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Table 1. Catalytic results in the partial oxidation of propane on MoVTeNbO catalyst at 400ºC.

Catalyst	Activation procedure	Conv. (%) [a]	Selectivity (%) [b]				
			AA	C_3H_6	AcA	CO	CO_2
A-as	-	48.1 [c]	T	2	t	48	47
A500	500ºC/N_2	49.8 [d]	2	3	10	38	47
A550	550ºC/N_2	45.2	5	4	8	38	45
A600	600ºC/N_2	27.6	27	9	12	24	28
B-as	-	23.3 [c]	1	6	2	44	46
B500	500ºC/N_2	19.4	12	9	3	38	38
B550	550ºC/N_2	42.4	73	5	3	9	10
B600	600ºC/N_2	44.2	74	5	3	10	8

a) Conversion of propane at 400ºC and a contact time, W/F, of 200 g_{cat} h $(mol_{C3H8})^{-1}$; propane/oxygen/water/helium molar ratio of 4/8/30/58; and a total flow of 50 ml min^{-1}; b) Selectivity to acrylic acid (AA); propylene (C_3H_6); acetic acid (AcA); and carbon oxides (CO and CO_2). Acetone was observed as minority; c) Activated in reaction conditions at 400ºC, after a time on stream of ca. 180 (**A-as**) and 300 min (**B-As**); d) At a reaction temperature of 380ºC.

Table 2. Characteristics of MoVTe(Nb)O materials.

Catalyst	Heat-treatment	Catalyst Composition[a] Mo/V/Te/Nb	Surface area (m^2g^{-1})	XRD and IR [b]	NH$_3$-TPD $(mol_{NH3}\ g^{-1})$	Catalytic results in propane oxidation at 380°C [d]	
						STY$_{AA}$	S$_{AA}$ (%)
A-as	-	1/0.47/0.18/0	n.d.	M1		0	t
A-500	500°C/N$_2$	1/0.48/0.15/0	16.3	M1	4.10	3.6	2.2
A-550	550°C/N$_2$	1/0.50/0.15/0	15.7	M1		10.8	7.7
A-600	600°C/N$_2$	1/0.46/0.13/0	5.9	M1, MoO$_3$, TeMo$_5$O$_{16}$	2.27	17.3	25.1
B-as	-	1/0.24/0.25/0.25	n.d.	A		0	t
B-500	500°C/N$_2$	1/0.21/0.22/0.22	19.5	A	3.05	8.6	18.4
B-550	550°C/N$_2$	1/0.23/0.21/0.22	11.7	M1, M2		76.3	75.2
B-600	600°C/N$_2$	1/0.22/0.26/0.23	7.0	M1, M2	1.36	82.8	75.7

a) Catalyst after activation done by EDX ; b) Main crystalline phases detected by XRD: A= amorphous; c) Amount of NH$_3$ adsorbed in the TPD experiments; d) Space time yield (STY$_{AA}$, in g_{AA} kg$_{cat}^{-1}$ h^{-1}) and selectivity to acrylic acid (S$_{AA}$, in %) at 380°C and a contact time, W/F of 200 g$_{cat}$ h (mol$_{C3H8}$)$^{-1}$, i.e. a weight of catalyst of g and a total flow of 50 ml min^{-1}.

Table 3. XPS results of MoVTe y MoVTeNbO catalysts.

Sample	Bulk composition [a]	Surface composition [b]				
	Mo/V/Te/Nb	Mo/V/Te/Nb/O	$Mo_A^{6+}/(Mo_A^{6+}+Mo_B^{6+})$ ratio (%) [c]	$V^{5+}/(V^{5+}+V^{4+})$ ratio (%) [d]	$Te^{6+}/(Te^{6+}+Te^{4+})$ ratio (%) [e]	$O_B/(O_B+O_A)$ ratio (%) [f]
A-500	1/0.48/0.15/0	1/0.30/0.14/0.0/4.04	88.5	25.8	21.6	21.2
A-600	1/0.46/0.13/0	1/0.25/0.16/0.0/5.22	72.2	20.4	23.3	20.5
B-500	1/0.21/0.22/0.22	1/0.12/0.28/0.21/4.23	93.0	38.1	17.1	16.5
B-600	1/0.22/0.26/0.23	1/0.10/0.29/0.25/3.52	100	28.9	0	14.2

a) Bulk composition determined by EDX; b) surface composition determined by XPS ; c) Mo_A^{6+} (BE= 232.8 eV), Mo_B^{6+} (BE= 233.8 eV); d) V^{5+} (BE= 517.67 eV), V^{4+} (BE= 516.65 eV); e) Te^{6+} (BE= 577.7 eV), Te^{4+} (BE= 576.4 eV); f) O_A (BE= 530.6 eV), O_B (BE= 532.3 eV).

Caption to Figures

Fig. 1. Catalytic activity (10^{-3} mol_{C3H8} h^{-1} g^{-1}) (a) and Specific catalytic activity (in 10^{-4} mol_{C3H8} h^{-1} m^{-2}) (b) achieved during propane oxidation on MoVTeO (□) and MoVTeNbO (●) catalysts heat-treated at 500, 550 and 600ºC (2h in a N_2 stream). Reaction conditions: reaction temperature: 380ºC; contact time, W/F, of 200g_{cat} h (mol_{C3H8})$^{-1}$ and propane/oxygen/water/helium molar ratio of 4/8/30/58 (total flow of 50 ml min^{-1}).

Fig.2. XRD patterns of MoVTeO (A-series) and MoVTeNbO (B-series): a) **A-as**; b) **A-500**; c) **A-550**; d) **A-600**; e) **B-as**; f) **B-500**; g) **B-550**; h) B-600. Symbols: M1 (○); M2 (■); $TeMo_5O_{16}$ (●); MoO_3 (Δ).

Fig. 3 SEM micrographies of MoVTe(Nb)O samples: a) **A-as**; b) **A-500**; c) **A-600**; d) **B-as**; e) **B-500**; f) **B-600**.

Fig.4. IR spectra of MoVTeO (A-series) and MoVTeNbO (B-series): a) **A-as**; b) **A-500**; c) **A-550**; d) **A-600**; e) **B-as**; f) **B-500**; g) **B-550**; h) **B-600**.

Fig.5. Raman spectra of MoVTeO (A-series) and MoVTeNbO (B-series): a) **A-as**; b) **A-500**; c) **A-550**; d) **A-600**; e) **B-as**; f) **B-500**; g) **B-550**; h) **B-600**.

Fig. 6. Deconvolution of the Mo $3d_{5/2}$ and $3d_{3/2}$ (a), the Te $3d_{5/2}$ (b), and the O_{1s} (c) peaks for MoVTeO (**A-500**) and MoVTeNbO (**B-600**) catalysts. (Solid line) Observed data; (broken lines) deconvoluted peaks.

Fig. 7. FTIR spectra of adsorbed methanol at 25ºC on MoVTe(Nb)O catalysts: a) **A-500**, b) **A-600**, c) **B-500** and d) **B-600** samples.

Fig.8 Temperature-programmed oxygen isotopic-exchange over MoVTe(Nb)O catalysts: a) **A-500**, b) **A-600**, c) **B-500** and d) **B-600** samples.