Preparation, characterization and catalytic behavior for propane partial oxidation of Ga-promoted MoVTeO catalysts

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Abstract

Two sets of Ga-promoted MoVTeO catalysts were synthesized hydrothermally and heat-treated at 600ºC in N_2: i) materials prepared from gels with Mo/V/Te/Ga atomic ratios of 1/0.60/0.17/x (x = 0 - 0.12) (**A**-series); and ii) materials prepared from gels with Mo/V/Te/Ga atomic ratios of 1/0.60-x/0.17/x (x = 0.15 or 0.25) (**B**-series). In addition, a Ga-containing MoVTeO catalyst was also prepared from M1-containing MoVTeO material by impregnation with aqueous solution of gallium and heat-treated at 450ºC in N_2. Catalysts were characterized by means of powder XRD, TEM, Raman spectroscopy, NH_3-TPD and XPS and tested in the partial oxidation of propane. The results showed that the addition of small amount of gallium significantly increase the selectivity to acrylic acid (**AA**) at low propane conversion. However, at high propane conversion, the selectivity to **AA** strongly depends on both the catalyst composition and the gallium incorporation method. The higher selectivity to acrylic acid over Ga-containing MoVTeO catalysts has been related to: i) structural changes in the M1 phase by the incorporation of Ga^{3+} into the octahedral structural framework, and/or ii) incorporation of Ga^{3+} species on the catalyst surface thus modifying catalysts acid properties.

Key words: Gallium, Mo-V-Te oxide catalysts, M1 phase, partial oxidation of propane, acrylic acid.

1. INTRODUCTION

Multicomponent MoVTe(Sb)NbO mixed metal oxides are an interesting catalytic system for (amm)oxidation of propane to acrylic acid and acrylonitrile [1-3] and for the oxidative dehydrogenation of ethane to ethylene [4,5]. Their catalytic performance has been related to the presence of the orthorhombic M1 phase (active and selective by itself), which strongly depend on the chemical composition [4, 6-17]. In this way, the presence of Nb^{5+} species is a key factor of their catalytic performance [4, 6-17]. The incorporation of Nb^{5+} favors both a higher thermal stability of M1 phase and a lower presence of Brönsted and Lewis acid sites on the catalyst surface [9, 10], improving the yield to acrylic acid and acrylonitrile during propane (amm)oxidation. It has been proposed that Nb occupied the same structural position of V and the resulting catalyst improved the selectively to acrylic acid (particularly at high conversion region) due to the further oxidation of acrylic acid to COx was suppressed [8].

In an attempt to improve catalytic performance, the use of metal promoters is a common practice. The incorporation of metal promoter by impregnation modifies the surface properties of the catalysts, which can change both catalytic activity and selectivity of materials. Moreover, the incorporation of metal promoters into the synthesis gel may also affect the distribution of crystalline phases, and therefore, their catalytic properties. However, except in the case of Nb-promoted MoVTeO, the incorporation of promoters other than Nb^{5+} have had little impact on catalytic performance of these catalysts [18-25].

Pd, W, Ru and Au promoted MoVTeNbO catalysts, incorporated by impregnation, have been studied [18-20]. The presence of Pd and W on catalyst surface seems to increase slightly the catalytic activity depending on the amount of metal promoter incorporated [18,

19]. However, Au or Ru-containing catalysts are less active and selective than undoped catalysts due to the formation of Au and RuO_2 nanoparticles on catalyst surface [20].

W, P, B, Cu, Ti, Sn, Ge, Re or Mn promoted MoVTeNbO catalysts have been studied by the incorporation of these metals in the synthesis gel [21, 22]. If P, B and Cu slightly improve the catalytic performance of M1 phase [21], the incorporation of W, Ti or Sn has a negative effect on the catalytic behavior of M1 phase [21]. On the other hand, incorporation of Re or Mn in the synthesis gel seems to favor the formation of other crystalline phases (as M2 phase, MoO_3 and Mo_5O_{14}) instead of the active M1 phase, whereas the incorporation of Ge at M1 phase is not observed.

The partial substitution of cations in the octahedral network of the M1 phase has been usually considered when studying the incorporation of promoters. Thus, it has been reported the synthesis of Mo-V-M-O (M = Te, Sb, Bi, Fe, W, Ga, Cs) metal oxides [23-25]. However, M1 phase was only obtained in the presence of Te [23], Sb [23] or Cs [25] in the synthesis gel. While, both Te- and Sb- containing catalysts were active and selective in partial oxidation of propane [23], Cs-containing M1 phase is not able to activate propane, possibly due to the occupancy of the heptagonal channels [25].

The partial incorporation of alkali [26-29], alkali earth [30] and rare earth metals (i.e. La, Ce, Nd and Sm) [31] in MoVSbO catalysts have been also investigated. Moreover, at this moment, only alkali-promoted MoVSbO catalysts are actives for propane oxidation due to the presence of M1 phase. But the catalytic properties of these alkali-doped materials depend on the alkali metal incorporated. Na, K and Rb-containing catalysts improve the selectivity to acrylic acid, being K-containing catalysts the most selective one. The incorporation of potassium in K-MoVSbO catalyst has a similar effect that niobium in MoVTeNbO, since both elements promote the disappearance of Brönsted acid sites on the catalyst surface. This effect

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has been observed when potassium is incorporated by impregnation on a heat-treated MoVSbO catalyst [26-28] or when it is directly incorporated into the synthesis gel [29].

Although most of the studies are devoted to the M1 phase, some authors have studied also the role of promoters in the so-called M2 phase, i.e $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb), which is active and selective for the (amm)oxidation of propylene. Thus, partial substitutions of W for Mo; Ti, Fe for V; Nb for Mo and V; and Ce for Te in M2- phase MoVTeNbO have been achieved and tested in propene ammoxidation [32-34]. An improvement in both catalytic activity and selectivity to acrylonitrile was observed over W and Ce-containing catalysts [33].

On the other hand, few results for promoted Nb-free MoVTeO catalysts have been published. Ce, Cu and Co-containing MoVTeO catalysts show low activity in propane oxidation [35], due to the formation of M2 as main phase. M1 phase formation on Fe-containing MoVTeO is possible when Fe^{2+} species are incorporated in the catalyst precursor but the activity and selectivity is lower than on MoVTeNbO catalysts [36].

Ga_2O_3-based catalysts have been proved to be active in dehydrogenation [37] or dehydrogenation/ aromatization of light alkanes [38-40], but also in the oxidative dehydrogenation of light alkanes [41], the ammoxidation of propane [42], or in the production of renewable aromatic compounds by catalytic fast pyrolysis of lignocellulosic biomass [43]. Provided that the catalytic performances of Ga-containing catalysts are related to their acid/redox properties [37-43], Ga species seem to be attractive as promoter in partial oxidation catalysts.

Ueda et al. [23] studied Mo-V-M-O (M = Al, Ga, Bi, Sb and Te) oxides prepared hydrothermally for ODH of ethane and partial oxidation of propane. They concluded that all the synthesized solids were rod-shaped and relatively effective in ODH of ethane, although only Te- and Sb containing catalysts seem to be selective in partial propane oxidation.

Guliants et al. [24] studied the incorporation of Ga, Fe, and W, in a Mo-V-M-O M1 phase in order to improve the stability of catalyst under propane ammoxidation conditions. The Mo–V–M–O (M = W, Fe, Ga) M1 phases displayed improved stability as compared to the parent Mo–V–Te–O M1 phase but present a lower production of acrylonitrile.

In this paper, we present a comparative study on the catalytic behavior of Ga-promoted MoVTeO catalysts. It will be shown that their catalytic performance strongly depends on catalyst compositions but also on the gallium incorporation procedure. According to the characterization results, it will be presented that the promoter effect of Ga^{3+} species in these catalysts is related not only to a small incorporation of Ga^{3+}-species into the M1 phase but especially to changes occurring on the catalyst surface. This has been confirmed by preparing an active and selective catalyst by impregnating heat-treated MoVTeO samples with an aqueous solution of gallium sulfate.

2. EXPERIMENTAL

2.1. Catalyst preparation

Ga-containing MoVTeO catalysts were synthesized hydrothermally from aqueous solution of ammonium heptamolybdate, tellurium oxide, vanadium sulfate and gallium sulfate, according to a procedure similar to that previously reported [11]. The gels were autoclaved in teflon-lined stainless steel autoclaves at 175 ºC for 48 h.

Two sets of MoVTeGaO catalysts were prepared by hydrothermal synthesis: i) catalysts with Mo/V/Te/Ga molar ratios of 1/0.60/0.17/x (x = 0.04- 0.12) (**A**-series); and ii) considering a partial substitution of V for Ga in the synthesis gel, i.e. with Mo/V/Te/Ga molar ratios of 1/0.60-x/0.17/x (x = 0.15 or 0.25) (**B**-series). These catalysts will be referred in the text as A-*n* and B-*n*, where *n* is the Ga/Mo molar ratio in the synthesis gel. For comparison,

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MoVTeO with high and low V-content (i.e. Mo/V/Te molar ratio of 1/0.60/0.17 and1/0.35/0.17, respectively) as well as Te-free MoVGa samples have been also prepared (**A-0**, **B-0** and **C-1** catalysts, respectively). In all cases, the resulting solids were filtered, washed and dried at 100ºC for 16 h, and then heat-treated at 600ºC during 2h in N_2-stream.

On the other hand, a Ga-doped catalyst (**Ga/B-0** sample) was prepared by "wet" impregnation of sample **B-0** with an aqueous solution of gallium sulfate (Ga/Mo atomic ratio of 0.0025), dried at 100ºC for 16 h, and finally activated for 2h at 450ºC in N_2-stream. The characteristics of catalysts are shown in Table 1.

2.2. Catalyst Characterization

The surface areas of catalysts were determined by multipoint N_2 adsorption (77 K) on a Micromeritics TriStar 3000 apparatus, and data were treated in accordance with the BET method.

Powder X-ray diffraction patterns (XRD) were collected in a PANalytical CUBIX diffractometer equipped with a graphite monochromator, operating at 45 kV and 40 mA and employing nickel-filtered Cu K_α radiation ($\lambda = 0.1542$ nm). Phase composition of the catalysts was analyzed with X'Pert High Score Plus software. The amount of amorphous phases in the samples was determined by adding 20 wt% V_2O_5 [JCPS: 77-2418] as internal standard.

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

Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were carried out on a JEOL JEM300FEG electron microscope. Crystal

by crystal XEDS microanalysis to determine the Mo/V/Te/Ga cationic ratio was performed by using the same microscope JEOL 300FEG equipped with an X-ray microanalysis ISIS 300 (Oxford Instruments) with a detector model LINK "Pentafet" (resolution 135 eV). Samples for transmission electron microscopy (TEM) were ultrasonically dispersed in n-butanol and transferred to carbon coated copper grids.

Raman spectra were recorded with an "in via" Renishaw spectrometer, equipped with a microscope (Olympus). The samples were excited by the 785 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 20 s 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 by using AlK_α radiation (AlK_α=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.

Temperature programmed desorption of ammonia (NH_3-TPD) experiments were carried out on a TPD/2900 apparatus from Micromeritics. 0.30 g of sample were 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 helium 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.

2.3. Catalytic tests

The catalytic experiments for partial oxidation of propane were carried out in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm), working at atmospheric pressure [11]. Catalyst samples (0.2-0.4 mm particle size) were 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 25 to 100 cm^3 min^{-1} and from 0.3 to 3.0 g, respectively) in order to achieve different propane conversion levels. The feed consisted of a mixture of propane/oxygen/water/helium with 4/8/30/58 molar ratio. 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 [11].

3. RESULTS

3.1. Catalyst characterization

In all the studied MoVTeGaO samples, the chemical analysis indicated the incorporation of gallium in the materials, and no significant variation of V- and Te-contents with the Ga-content was observed in each series (Table 1).

Figure 1 shows the XRD patterns of the heat-treated samples (the XRD patterns of as-synthesized samples have been included as supplementary information, Fig. *S-1*). In the case of A-series, diffraction patterns indicate the presence of M1 phase as main crystalline phase and variable small amounts of M2, but also TeMo$_5$O$_{16}$ [JCPDS: 31-0874], VOMoO$_4$ [JCPDS: 18-1454], and MoO$_3$ [JCPDS: 05-0508] can be observed. The presence of both M2 and

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TeMo$_5$O$_{16}$ crystalline phases decreases when increasing the Ga/Mo ratio (Fig. 1, patterns c and d). For the B-series, patterns show also the presence of M1 as main phase and variable amounts of M2 except in the case of the **B-0.30** sample where M1 is absent.

On the other hand, the XRD pattern of MoVGaO catalyst (**C-1** sample) suggests the presence of an amorphous layered material with a diffraction peak at $2\theta= 22.2°$ (i.e. ca. 4Å), similar to that previously observed [23-24].

Figure 2 displays the crystalline phase composition of the materials with presence of M1 phase. The percent of M1 phase in the heat-treated catalysts depends on both the Ga/Mo and V/Mo ratio in the synthesis gel. In the case of Ga-free catalysts (**A-0** and **B-0** samples), a lower V/Mo ratio favors a less complex phase distribution, mainly M1 and M2 phase, and higher amount of M1 phase. In addition, when Ga is incorporated in the synthesis gel, the amount of M1 phase in the material increases with Ga/Mo ratio, while the presence of other crystalline (as M2 phase) and amorphous phases decreases. Additionally, B-series prepared by impregnation (**Ga/B-0**) shows similar phase distribution compared with the parent sample (**B-0**).

We should notice that M1, M2 and TeMo$_5$O$_{16}$ are observed in both Ga-free sample (Fig. 1, pattern e) and the corresponding Ga-doped sample prepared by impregnation (Fig. 1, pattern h). Thus, the formation of TeMo$_5$O$_{16}$ decreases with the incorporation of Ga^{3+} in the synthesis gel, but it does not change when Ga^{3+} species are incorporated on the catalyst surface by impregnation of a MoVTeO catalyst. Accordingly, the differences observed in heat-treated samples must be a consequence of the solid state reaction occurring between M1 phase and other crystalline phases [45].

Raman spectra of A- and B-series are shown in Figure 3. For comparison the spectra of Ga-free samples have been also included. All catalysts exhibit similar spectra to those

previously reported by other authors [11, 46-48]. The bands at higher frequency (960‑980 cm^{-1}) can be assigned to stretching vibrations of terminal Mo=O and V=O bonds, while the bands at 770‑880 cm^{-1} and at around 470 cm^{-1} can be related to asymmetric and symmetric M‑O‑M bridge stretching modes, respectively [46-49].

Ga-free MoVTeO catalysts exhibit an intense Raman band at 872 cm^{-1} with a broad shoulder toward lower frequencies, at around 840 cm^{-1}, and a weak shoulder to higher frequencies, in the 900-930 cm^{-1} Raman region (Fig. 3, spectra a and e). Spectra of Ga-promoted catalysts present some differences depending on the Ga-content (Fig. 3, spectra b - d). The relative intensity of the band at 872 cm^{-1} decreases and band at 840 cm^{-1} is more clearly defined when increasing the amount of Ga. Furthermore, the band at 915 cm^{-1} shift to 936 cm^{-1} in Ga-containing samples, whereas a new band at lower frequencies (ca. 470 cm^{-1}) is also observed.

The **B-0.15** sample presents a homogeneous composition (Fig. 3, spectrum f), with practically identical Raman spectra obtained at different discrete points of the sample, and characterized by the presence of bands at 840 and 870 cm^{-1} similar to those observed for Ga-promoted catalysts (**A**-series). However, in the case of **B-0.30**, a heterogeneous composition with different Raman spectra at different selected areas of the sample has been observed (Fig. 3, spectra g1-g3). Both, **B-015** and **B-0.30** catalysts show more defined bands at 936 and 963 cm^{-1} than that observed for the rest of catalysts (Fig. 3, spectra f and g). These bands can be assigned to stretching vibrations of terminal Mo=O [50, 51] and are more difficult to relate to a particular crystalline phase. In this way, Keggin-type [GaMo$_{12}$O$_{40}$]$^{n-}$ complex are characterized by the presence of four bands at 963, 936, 872 and 642 cm^{-1} [52]. However, our Raman results cannot confirm the presence of this phase. On the other hand, bands at 766,

653, 416 and 346 cm^{-1} characteristics of Ga_2O_3 [53] are not observed in any sample, suggesting that gallium is mainly incorporated in the framework of crystalline phases.

Raman spectra of **Ga/B-0** sample (Fig. 3, spectrum h) shows bands very similar to that observed in the corresponding Ga-free material (Fig. 3, spectrum e), with a broad band around 818 cm^{-1}. In addition, a less intense band at 870 cm^{-1} is also observed.

The differences among Ga-containing samples under study were further analyzed in detail by transmission electron microscopy, a unique tool to elucidate where and at which crystal phase has been gallium incorporated. The analysis of the present crystal phases is in agreement with what we observed from powder X-ray diffraction data: **A-0.08**, **B-0.15** and **Ga/B-0** catalysts are constituted by M1 as main phase. Cationic ratio Mo/V/Te/Ga on each crystal was determined by XEDS (Table 2). The microanalysis performed shows that there occurs no formation of secondary phase which is constituted by gallium as a major component. Moreover, gallium is only incorporated in the crystals of M1. The atomic compositions of the M1 phase diverge in a narrow fringe regardless the Ga/Mo ratio in the synthesis gel (see Table 2) giving rise to an average stoichiometry $Te_{0.5}(Mo_{0.65}V_{0.24}Ga_{0.02})_5O_{14}$ (calculated on the basis of the M1, $Te_2M_{20}O_{57}$, framework). At this point it is important to mention that the microanalysis performed on the **Ga/B-0** sample did not show the presence of gallium, probably because gallium concentration in this catalyst is close to the limit imposed by the technic (i.e. below 1.5 %).

Figure 4 shows the high resolution images of three different crystals of M1 in the **B-0.15** catalyst projected along the [100] (a), [1$\bar{1}$0] (b) and [001] (c) directions. The corresponding electron diffraction patterns have been also included.

Crystals in the images contain variable gallium atomic percentages in the range 2.5 – 4.5 as determined from the XEDS microanalysis performed. Images contrasts can be easily

identified in the three crystal projections and the corresponding *d* spacing have been labelled for clarity. There are no differences between the contrasts observed for these crystals and that previously observed in M1 crystals of catalysts that do not contain gallium, the contrast being in all cases sharp and clear along the observed directions. It allows us to suggest that the incorporated gallium becomes part of the structural framework and it is not just on the catalysts crystal surface as a spurious phase. The ability of gallium (III) to adopt tetrahedral [54] as well as octahedral [55] coordination facilitates its incorporation into the skeleton of the structure. Its ionic size in both IV and VI coordination is suitable to replace Mo (VI) or vanadium (V) [56] and too small to compete with tellurium and being placed in the hexagonal tunnels. Furthermore, the compositional flexibility in the structure of M1 phase [57] enables its introduction that can be accompanied by a partial reduction of the oxygen content without crumbling the basic structure. All the above facts enable us to assume the introduction of gallium (III) in the M1 structure by partially replacing the species V^{n+}/Mo^{n+}.

An important aspect of the M1 phase refers to the crystal morphology. Independently on the sample considered, they exhibit a characteristic rod-like shape with lengths varying between 0.5 and 2 microns, which is associated to their preferential growth parallel to the *c* axis of the structure. Thus, images like those shown in Figures 4a and 4b are routinely found for this crystalline phase. On the contrary, crystals oriented in the *ab* plane (Figure 4c) are scarce and present very small crystal size. The same structural features are observed along the different compositions in the series in spite of the diverse gallium content (Table 2), thus reinforcing our hypothesis that gallium is incorporated to the structural frame.

The oxidation states of the elements at the surface of catalysts have been studied by XPS spectroscopy. Table 3 presents the surface composition obtained by XPS for

characteristics Ga-free (**A-0** and **B-0** samples) and Ga-containing catalysts (**A-0.08**, **B-0.15**, **Ga/B-0** and **C-1** samples) and Figure 5 shows the corresponding XPS spectra.

Mo 3d core-level spectra show that only Mo^{6+} species (BE= 232.8eV, [11, 59-61]) are present in both Ga-free and Ga-promoted catalysts, while Mo^{5+} species (BE = 231.7 eV, [11, 59-61]), has not been observed in any sample. An additional band at 233.4 eV (which will be named as Mo_B^{6+}) is also observed for sample **C-1**. This band can be related to the presence of Mo^{6+} species in a different environment to those observed for the rest of catalysts.

In addition, a deficiency of vanadium in the surface is observed in all the samples except in the case of Te-free catalyst (**C-1**) when compared to bulk composition (Table 3). The V 2p3/2 core level spectra of these materials shows the presence of components at 516.2 and 517.3 eV, which are related, respectively, to V^{4+} and V^{5+} species [11, 59-61]. A similar distribution of V^{4+} and V^{5+} species is observed for Ga-free and Ga-promoted catalysts, although the amount of V^{5+} species in **C-1** catalysts is higher than in the rest of samples.

The Te core-level spectra of the catalysts indicate that the binding energy of the Te 3d5/2 changes depending on the catalyst composition. Thus, a band at 576.2 eV is mainly observed (Fig. 5). Moreover, and in addition to this, a second band at 577.6 eV is also observed for samples **B-0.15** and **Ga/B-0**. The BE corresponding to Te^{4+} is reported at 576.2 eV, while Te^{6+} is observed at 577.3 eV [11, 61]. Accordingly, it can be concluded that Te^{4+} is the main tellurium species in both Ga-free and Ga-containing MoVTe catalysts. Moreover, Te^{6+} species were also observed in Ga-containing samples prepared from gels with low V/Mo ratio (B-series). Te^0 (binding energy at 573.0 eV) was not observed in any case.

The core Ga 2p3/2 spectra show a band at ca. 1118.2 eV, which can be related to the presence of Ga^{3+} species as in Ga_2O_3 [62]. In addition to this, a second component is also

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observed at 1120.2 eV for **B-0.15** sample (Fig. 5) due to the presence of Ga^{3+} species in different environment.

As a general trend, no significant variation of Te or Ga content on the catalyst surface has been observed in respect to the bulk composition except in the case of **B-0.15**, where the tellurium surface content is higher than in the catalyst bulk. It must be noted, however, the similarity in gallium content in all studied sample. On the other hand, the Ga/Mo ratio observed for **Ga/B-0** sample suggests that the incorporation of gallium occurs mainly on the monolayer of catalyst.

TPD of ammonia was used in order to determine the distribution of surface acidity and acid strength of catalysts. NH_3-TPD patterns obtained over Ga-free and Ga-containing samples, normalized to sample mass, have been included as supplementary information, Fig. *S-2*, and the values of NH_3 adsortion on the catalyst surface are listed in Table 1. According to that, Ga-containing samples present a number of acid sites lower than the Ga-free samples. In the case of A-series catalysts, the amount of acid sites decreases when increasing the Ga-content in the synthesis gel. In the case of samples **B-0.15** and **Ga/B-0**, the amount of acid sites was lower to those observed for A-series catalysts.

The above results suggest that part of the acid sites disappear with the incorporation of gallium to the catalyst, independently of catalyst preparation procedure. A similar effect was observed when alkali metal were incorporated on the catalyst surface of heat-treated MoVSbO catalysts [29] or when niobium [10] was incorporated in the synthesis gel for the preparation of modified MoVTeO catalysts.

3.2. Catalytic results for partial propane oxidation

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Table 4 presents the catalytic results obtained in propane conversion and selectivity to reaction products achieved during the propane oxidation at 380ºC and a contact time, W/F, of 400 g_{cat} h mol^{-1}_{C3H8} over Ga-free and Ga-containing MoVTeO samples. Acrylic acid, acetic acid, propylene and carbon oxides were the main reaction products detected in the oxidation of propane. Traces of acrolein, acetaldehyde and acetone were also identified.

The overall trend shows that Ga-containing catalysts present lower catalytic activity but higher selectivity to acrylic acid than those observed for MoVTeO samples, with **A-0.08**, **B-0.15** and **Ga/B-0** catalysts presenting the higher selectivity to acrylic acid. In addition, lower selectivity to acetic acid (and an important reduction of the formation of CO and CO_2) is observed on the last catalysts. However, extremely low propane conversion was observed for both **B-0.30** and **C-1** catalyst (**Table 2**). The absence of M1 phase in both samples can explain the low catalytic activity observed during propane oxidation over these catalysts.

Since the selectivity to acrylic acid strongly depends on the propane conversion, Figure 6 shows the variation of the selectivity to acrylic acid with the propane conversion obtained during the propane oxidation at 380ºC over Ga-containing catalyst. The catalytic results achieved on the corresponding Ga-free MoVTeO catalysts (i.e. **A-0** and **B-0** samples) and on the Ga-doped MoVTeO (i.e. **Ga/B-0** sample) have been also included for comparison. In both series, selectivity to acrylic acid increases with Ga-content until a maximum is obtained (Ga/Mo = 0.08 in A-series and Ga/Mo= 0.15 in **B**-series) and then decreases for further Ga-content increment.

On the other hand, Ga-doped MoVTeO (i.e. **Ga/B-0** sample) presents high selectivity to AA (50%) at propane conversion of 50%, resulting in a yield of 25%. This value is higher than those previously reported for Mo-V-Te-O [11, 23, 45, 47] or Mo-V-Ga-O catalysts [24].

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In addition, B-**0.15** catalyst presents high formation of acrylic acid with selectivity to AA of 41% at a propane conversion of 58%. Accordingly Ga^{3+} has a promoter effect in this type of catalysts. In addition, and although this promoter effect is lower to those generally reported for Nb-containing Mo-V-Te-O samples [6-17], the promoter effect is higher to those reported for other modified catalysts [32-33]. Thus, optimizing both V- and Ga-content, it is possible to increases the selectivity to AA.

In this way, **B-0.15** sample seems to be the most effective catalysts from all materials prepared hydrothermally with Ga^{3+} in the synthesis gel. Thus, selectivity to acrylic acid of *ca*. 55% at a propane conversion of 40% (at reaction temperature of 380ºC and contact time, W/F, of 400 $g_{cat,}$ h mol_{C3H8}^{-1}) is observed for this catalyst. Similar catalytic behavior to those achieved over **B-0.15** sample is also observed over the Ga-doped MoVTeO catalyst (**Ga/B-0** sample), which suggests that the changes occurring on the catalyst surface by the incorporation of Ga^{3+} species can be by it-self responsible of the higher production of acrylic acid.

4. DISCUSSION

Except samples **B-0.30** and **C-1** (which do not show the presence of M1 in their corresponding XRD patterns), Ga-containing catalysts are less active but more selective than Ga-free MoVTeO catalysts, presenting space time yields of acrylic acid, STY_{AA} (Table 4), higher than those achieved in Ga-free catalysts. Accordingly, the improvement of the selectivity to acrylic acid during the partial oxidation of propane over Ga-containing catalysts should be related to the incorporation of gallium in these materials.

When comparing the catalytic performance of Ga-containing catalysts prepared from gels with a V/Mo ratio of 0.60 (A-series) with those achieved over Ga-containing catalysts

prepared from gels with a V/Mo ratio of 0.45 (B-series), it can be concluded that the former present lower selectivity to acrylic acid. This behavior can also be deduced when comparing the corresponding Ga-free catalysts, i.e A-0 and B-0, although their selectivity to acrylic acid is lower than that achieved over Ga-doped ones.

The characterization results of these catalysts show important differences between both series and the catalytic performance can be partially explained by considering the nature of the present crystal phases.

The XRD patterns of A-series catalysts indicate the presence of several crystalline phases, i.e. M1, M2, $VOMO_4$, $TeMo_5O_{16}$ and MoO_3, although M1 is the main phase and the presence of both M2 and $TeMo_5O_{16}$ crystalline phases decreases when increasing the Ga/Mo ratio. For B-series catalysts, the main presence of M1 is accompanied by M2, although at high Ga/V ratios $TeMo_5O_{16}$ is also detected. Thus, high vanadium content in the synthesis gel seems to favor the formation of $VOMoO_4$, which could be responsible for the lower selectivity in A-series catalysts.

In this sense, it has been proposed that the orthorhombic M1 phase $Te_2M_{20}O_{57}$ (M = Mo,V) contains Mo^{6+}/Mo^{5+}, V^{5+}/V^{4+} and Te^{4+} species which are active and selective for partial oxidation of propane to acrylic acid [60, 62]. The presence of M2 and/or $TeMo_5O_{16}$ could have a positive effect on selectivity to partial oxidation products, since both crystalline phases are active and selective in partial oxidation of propene (the first intermediate products in partial oxidation of propane) [9, 13]. However, $VOMoO_4$ is not selective in partial oxidation of hydrocarbons [47] and MoO_3 is inactive in propane oxidation [47, 63]. Thus, and according to the results of Table 4, the V-content in both Ga-free and Ga-containing the Mo–V–Te–O catalysts has an impact on product distribution and it must be optimized in order to improved both activity and selectivity.

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In both series, Mo-V-Te-Ga catalysts show an increase in selectivity to acrylic acid (at low propane conversion) followed by a decrease in the selectivity to acrylic acid (at high propane conversion), both depending on the Ga/Mo ratio in the synthesis gel. This suggests that Ga^{3+} incorporated in the material could participate as an active site in the partial oxidation of propane, by both favoring the oxidation of propylene to acrylic acid and modifying the decomposition of acrylic acid at high propane conversion.

Gallium has been reported as active and selective component in the dehydrogenation and aromatization of small alkanes in the absence or in the presence of air [37-42]. Thus, it is generally accepted that the role of gallium sites in the dehydrogenation (or aromatization) reactions on Ga-containing catalysts is the activation of C–H bond in alkanes [37-40] but also in the ODH [41, 64] and in the ammoxidation of propane [42].

Ga^{3+} sites could activate the C-H bond of propane. In fact, it is known that the first step of propane oxidation is the formation of propene by oxidative dehydrogenation. Then, activation of propene could take place in Ga^{3+}-sites on the M1 phase, favoring their partial oxidation to acrylic acid. However, Ga^{3+}- sites could interact with the acrylic acid formed and oxidize it to combustion products (CO and CO_2) at high propane conversion. However, an increase of the catalytic activity is not observed during the partial oxidation of propane over Ga-containing catalysts.

HREM results show that the incorporation of Ga into the octahedral network of the M1 phase is likely to occur. Moreover, in all cases, the amount of Ga incorporated into the M1 phase structure is similar, with an atomic percent of 2.5-5% (Table 3). Additionally, there is no evidence about the presence of any secondary or spurious phase containing Ga in these samples. Accordingly, it could be tentatively proposed that the incorporation of Ga^{3+} in the framework of phase M1 is directly responsible of the higher yield of acrylic acid with respect

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to the corresponding Ga-free samples. However, this cannot explain completely the different behavior observed in catalysts with different Ga-content in the synthesis gel.

In fact, Ga-containing MoVTe catalysts prepared hydrothermally (**A** and **B** series) show differences in their catalytic properties at high propane conversion. A higher selectivity to acrylic acid at propane conversion of 40% has been observed for **B-0.15** catalyst (prepared with a Ga/Mo ratio of 0.15 and V/Mo ratio of 0.45), while the maximum selectivity to acrylic acid for A-**0.08** sample (prepared with Ga/Mo = 0.08 and V/Mo = 0.60) is achieved at propane conversion of 25%. These differences cannot be related to the incorporation of Ga into the network of the M1 phase provided the similar atomic percentage found in both samples (Table 2). Thus, if the Ga amount incorporated in M1 is similar in all Ga-containing catalysts, the different catalytic observed with both the Ga/Mo ratio in the synthesis gel and the catalyst preparation procedure behavior should be related to other changes probably occurring on the catalyst surface.

Additionally, XPS results indicate the presence of Ga^{3+} species on the catalysts surface, with no significant variation between bulk and surface composition (Table 4). Thus, it can be suggested that Ga^{3+} could be located partially on the surface of the material. But they must be interacting with the M1 phase, since extraframework Ga^{3+} species in the form of a secondary phase have not been detected according to XRD, Raman or HREM results.

The incorporation of a small amount of Ga on the catalyst surface significantly increases the selectivity to acrylic acid, as in the case of **Ga/B-0** catalyst (prepared by impregnation) (Figure 6). In addition, NH_3-TPD results confirm that the initial incorporation of Ga^{3+} on the catalyst surface favors a decrease of the number of acid sites of the catalyst. Thus, the presence of Ga^{3+} on the catalysts surface seems to decrease the number and strength of acid sites favoring the selective propane oxidation to acrylic acid. This effect is similar to

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those previously reported by the incorporation of niobium to MoVTeNbO [6-17] or potassium to MoVSbO [26-29], where a parallelism between the decrease of the number and strength of acid sites on the catalysts surface and the increase of the selectivity to acrylic acid has been shown.

The catalytic performance achieved during the partial oxidation of propane over sample **Ga/B-0** illustrates very well this fact and Ga^{3+} must be mainly incorporated on the catalyst surface. In fact, sample **Ga/B-0** shows activity and selectivity similar to those achieved over sample **B-0.15** (2.5 - 5% Ga in M1). Therefore, the catalytic behavior can be related to bulk changes related to the composition of M1 but also to changes in surface features.

It has been reported in the case of phosphorous-promoted MoVTeNbO catalysts that P doping leads to an improved selectivity to AA and also a much higher activity of propane conversion. It allows authors to believe that P could be located on the M1 surface in the vicinity of $V^{5+} = O \longleftrightarrow \bullet V^{4+} - O\bullet$ sites [21]. In our case, the incorporation of Gallium on the surface of catalyst is mainly related to a decrease in the formation of carbons oxides (improving selectivity to acrylic acid). Accordingly, we believe there are two effects: **i**) Ga^{3+} can be incorporated in the structural framework of the M1 phase, thus facilitating an increase in selectivity to acrylic acid at low propane conversions, and **ii**) Ga^{3+} can be incorporated on the catalyst surface, decreasing the number of acid sites and facilitating a higher selectivity to acrylic acid at high propane conversion.

On the other hand, the variation of selectivity to acrylic acid with propane conversion could be used by determining both the initial formation of acrylic acid (when comparing the selectivity to acrylic acid at low conversion of propane) and the acrylic acid stability (when comparing the selectivity to acrylic acid at high propane conversion) [6-17].

From the results of Figure 6, it can be concluded that the formation of acrylic acid at low propane conversion (< 10%) is favored on Ga-containing catalysts, even when a small amount of gallium is incorporated (Ga/Mo = 0.0025) by impregnation (**Ga/B-0** sample). This behavior suggests that the incorporation of gallium could favor a faster transformation from propane to acrylic acid than over the corresponding MoVTeO catalysts. The selectivity to acrylic acid obtained over Ga-containing catalysts is slightly lower to that reported over Nb-promoted MoVTe [9-13].

However, the acrylic acid stability (determined by the comparison of the selectivity to acrylic acid at higher propane conversion) depends strongly on Ga/Mo ratio (Fig. 6). It achieves a maximum value for **A-0.08** in A-series (Figure 6a) and for **B-0.15** and **Ga/B-0** in B-series (Figure 6b). The different nature of the present crystal phases could be related to this fact, but it also exists when comparing **A-0** and **B-0** samples and their catalytic performance is very similar. Nevertheless, the presence of gallium species on the crystals surface can have a positive effect. Accordingly, the results suggest that small Ga-loading tends to diminish degradation of acrylic acid (consecutive reaction), this being lower in the case of **A-0.08** , B-**0.15** and **Ga/B-0** catalyst. Excess of gallium, however, leads to lower selectivity to acrylic acid at high propane conversion

5. CONCLUSIONS

In summary, Ga-containing Mo–V–Te–O catalysts with different Ga content and/or V/Mo ratio were synthesized hydrothermally. Catalysts were constituted by M1 phase as major component although M2, $TeMo_5O_{16}$, $VOMO_4$ and MoO_3 were also observed in variable amounts depending on the composition of the synthesis gel.

Doping MoVTeO catalysts with Ga^{3+} significantly enhances the desired selectivity to acrylic acid at any propane conversion during the partial oxidation process. This effect strongly depends on Ga^{3+} loading, V/Mo ratio in the synthesis gel and the gallium incorporation method used. In this way, Ga-containing catalysts prepared from gels with a V/Mo ratio of 0.45 (B-series) present selectivity to acrylic acid higher to those achieved over Ga-containing catalysts prepared from gels with a V/Mo ratio of 0.60 (A-series). The catalytic performance can partially be explained by considering the nature of crystalline phases. Thus, an excess of vanadium in the synthesis gel seems to favor the formation of $VOMoO_4$, which could be responsible of the lower selectivity in A-series catalysts.

The characterization performed on these catalysts showed the partial incorporation of Ga^{3+} in the structural framework of the M1 phase in 2.5-5 atomic %. However, the different catalytic behavior observed over Ga-containing catalysts with different Ga-content in the synthesis gel should not be only related with the presence of Ga in the M1 phase. Both XPS and NH_3-TPD results also suggest that the incorporation of Ga on the surface of catalysts could have an important role on the selectivity to acrylic acid. Thus, good selectivity (and high productivity) to acrylic acid can also be achieved by impregnating a MoVTeO catalyst a Ga^{3+}-containing aqueous solution, dispersing Ga^{3+}-species on the catalysts surface. Accordingly, gallium has demonstrated to be an interesting promoter for MoVTeO materials.

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