



Reflux method as a novel route for the synthesis of MoVTeNbO_x catalysts for selective oxidation of propane to acrylic acid

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ABSTRACT

This work reports the applicability of reflux to the synthesis of Mo–V–Te–Nb–O metal oxide catalysts for the first time. The well-formed and defined orthorhombic M1 phase, i.e. Te₂M₂₀O₅₇ (M = Mo, V, Nb), was found to be better developed when a longer time was used to reflux the mixed metal clusters. The catalysts efficient for propane selective oxidation to acrylic acid, reaching ca. 60% of selectivity to acrylic acid at propane conversion of ca. 50% and at a reaction temperature of 693 K. In addition, a parallel between catalytic activity and catalyst reducibility is also concluded.

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1. Introduction

MoVTeNbO_x mixed oxide is reportedly the most promising catalyst system for the selective oxidation of propane to acrylic acid. These catalysts were developed and patented by Mitsubishi Chemicals [1], who reports the highest acrylic acid yield (ca. 50%) up until today. Academic and industrial communities in the area of partial oxidation are enthusiastic about improving its catalyst performance. This is easily evidenced by a significant amount of work on these materials [1–24]. It is debatably suggested that their unique catalytic properties are due to the presence of two major structures, termed as orthorhombic M1 phase, Te₂M₂₀O₅₇ (M = Mo, V, Nb), and hexagonal M2 phase, Te_{0.33}MO_{3.33} (M = Mo, V, Nb) [9]. Other phases such as (Mo_{0.93}V_{0.07})₅O₁₄, MoO₃, and TeMo₅O₁₆ can also be present depending on the preparation and activation [18,19]. The M1 phase alone can activate propane and selectively convert it to acrylic acid [18,20]. On the contrary, the M2 phase is inactive for propane oxidation, but selectively oxidizes free intermediately formed propylene to desired products [11,19]. Two additional topics have been stressed in the literature: the cooperation of phases

[11–23] and the isolation of the active sites [11,15–18,20,21,23]. In the former, different authors have concluded that at least in the case of the (amm)oxidation of propane, the performance of the M1 phase could be improved by cooperation of the pseudo-hexagonal Te_{0.33}MO_{3.33} phase (M = Mo, V, Nb) [11,16–18,20,21,23].

Despite the effort expended in synthesizing and characterizing mixed metal oxides, only a few methods have been used to synthesize these catalysts. Although Slurry [1,4,7,11,12] and hydrothermal [3,4,6,11,13,23,24] methods are the most common options, microwave-assisted hydrothermal synthesis has been also proposed [24]. Undoubtedly, these methods have produced the desired catalysts. This is especially true for the hydrothermal method, through which it is possible to obtain, in the appropriate conditions, the monophasic MoVTeNbO material with M1-like crystalline structures. The hydrothermal synthesis of these materials is usually performed at 448 K in a nitrogen atmosphere with a synthesis time of 48 h [11,23,24] and is mainly characterized by its high solvent effect and equilibrium conditions, which lead to the formation of the most favored crystalline phase. On the contrary, the slurry method uses a non-solution precursor, which implies a complexity in the formation of the active phase. For this reason, the slurry method contributes to the multiphase MoVTeNbO system in which the species is always present in different valence states due to its non-equilibrium state [1,4,7,11,12].

In the present work, a reflux method has been developed for the synthesis of MoVTeNbO_x catalysts. The catalysts were prepared by refluxing the aqueous synthesis gel with a mixture of metals.

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This method has the advantage of allowing intimate mixing of corresponding species in a homogeneous state under atmospheric pressure and at the solvent's boiling point. This is the first reported work on the utilization of this method in synthesizing MoVTeNbO_x catalysts for propane selective oxidation. The method has been found successful for the synthesis of (VO)₂P₂O₇ [25] based catalyst employed in the transformation of butane to maleic anhydride. The effect of the reflux period on the catalyst structural development was also studied. The activity of these catalysts in the propane conversion to acrylic acid was studied.

2. Experimental

2.1. Catalyst preparation

Commercial chemicals of ammonium heptamolybdate, AHM, (NH₄)₆Mo₇O₂₄·4H₂O (Merck), vanadyl sulphate, VOSO₄ (Aldrich), telluric acid, Te(OH)₆ (Aldrich), and ammonium niobium oxalate, (NH₄)₂Nb₂(C₂O₄)₅ (CBMM), were used as the metal sources for Mo, V, Te and Nb respectively. The gel presented a Mo/V/Te/Nb atomic ratio of 1/0.3/0.17/0.12. The preparation process begins by dissolving AHM in deionized water, heated at 353 K and was followed by the addition of telluric acid to form the first solution. In another beaker, a second solution was prepared by dissolving VOSO₄ in deionized water heated at 353 K, and then added to the first solution, producing a dark green solution. A third solution was obtained by dissolving niobium oxalate in deionized water solution, which was added to the former mixture. The resulting dirty green mixture was left to stir for 10 min before being refluxed. The effect of reflux time was studied by conducting reflux for 1, 4, 7, and 14 days. Following the reflux, the solid phase was filtrated and a purplish-black solid was obtained which was then dried overnight in an oven at 373 K. The dried samples were heat-treated in flowing N₂ at 873 K for 2 h. The corresponding materials were denoted as A-1, A-4, A-7, and A-14 (Table 1).

2.2. Catalyst characterization

BET specific surface area measurements were performed using a ThermoFinnigan Sorptomatic apparatus, with adsorption of N₂ at 77 K. Bulk composition of the catalyst was determined by inductive coupled plasma-atomic emission spectrometer (ICP-AES).

Powder XRD patterns were collected by employing a Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 30 mA and using Ni filtered CuK_α radiation with wavelength, λ = 0.1542 nm. Samples were ground and put on a horizontal sample holder and XRD patterns were recorded in the 5–60° range.

Infrared spectra were recorded at room temperature in the 300–3900 cm⁻¹ region with a Nicolet 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm⁻¹ with an accumulation of 128 scans. The pellets were prepared with 20 mg of sample mixed with 100 mg of dry KBr and pressed into disks.

Raman spectra were obtained with an "in via" Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 785 nm from a Renishaw HPNIR laser with a power of ca. 15 mW on the sample.

Scanning electron microscopy (SEM) was performed using JEOL Model JSM 6400 to record the image at an accelerating voltage of 15 kV.

Temperature programmed reduction of hydrogen (H₂-TPR) was achieved by using a ThermoFinnigan TPDRO1110 apparatus, utilizing a thermal conductivity detector (TCD). Hydrogen (5% in Ar, 1 bar, 25 ml/min) flowed over the samples at temperatures ranging

from room temperature to 1250 K following the evolution of water continuously on a mass spectrometer. The temperature was increased linearly at 10 K/min.

2.3. Catalytic test

Propane selective oxidation was carried out at atmospheric pressure in a fixed bed quartz tubular reactor (i.d. 12 mm, length 400 mm). The weight of the catalyst (with homogeneous particle size in the 0.3–0.5 mm range) was varied in order to achieve different contact times, Silicon carbide was added in order to keep a constant volume in the catalytic bed. The gas feed consisting of C₃H₈:O₂:H₂O:He with a 4:8:30:58 (%) molar composition was supplied at flow rates of 30–100 ml/min. Experiments were carried out in the 613–693 K range. Reactants and products were analyzed by online gas chromatography using two packed columns: (i) molecular sieve 5 Å (3 m); and (ii) Porapak Q (3 m).

3. Results and discussion

Table 1 summarizes some of the main characteristics of MoVTeNbO_x catalysts. No significant differences in the chemical composition can be seen in the activated samples, which are close to the atomic ratios used in the synthesis gel. On the other hand, heat-treated samples present BET surface areas ranging from 1.9 to 9.3 m² g⁻¹ (Table 1), within the range of those previously described for similar materials [21,26,34]. A correlation between surface area and reflux time is observed, in that the longest reflux time is obtained by the highest surface area.

3.1. Characterization of as-synthesized samples

XRD patterns of the as-synthesized samples (before heat treatment) are displayed in Fig. 1A. The reflections set with a peak at 2θ = 22°, and two broad peaks at 2θ < 10° (low intense) and at 2θ = 27° are similar to those found in the precursor of the Mo/W orthorhombic and tetragonal phases [11,29,30]. The peak appeared at 2θ of ca. 22° is related to a kind of Mo-based oxides with layer-type structures closely related to the ReO₃-family [27,28]. Overlapping another set of reflections are observed only in the XRD patterns of as-synthesized samples prepared from 1 to 7 days, which indicate the presence of heteropoly-compounds (HPC) with Anderson-type structure (NH₄)₆TeMo₆O₂₄·7H₂O [11], (NH₄)₇TeMo₅VO₂₄·8H₂O [12], and/or (NH₄)₈(V₁₉O₄₁(OH)₉)(H₂O)₁₁ [ICSD 063213]. The narrow diffractions become broad bands during the reflux, which means that HPCs slowly turn into pseudo-crystallines with increasing time of up to 14 days' synthesis resulting in a homogeneous distribution of crystalline nano-domains without a trace of heteropoly-compound reflections (Fig. 1A, d).

Raman spectra of as-synthesized samples, before the heat-treatment, are shown in Fig. 2A. The A-1 sample presents a homogeneous composition with practically identical Raman spectra obtained at different discrete points of the sample, characterized by the presence of a band at ca. 950 cm⁻¹. This band is related to Mo–O_t stretching vibration from Anderson-type HPC structures (more or less shifted depending on hydration), in agreement with XRD results [31,32]. On the other hand, the sample obtained at 4 days of reflux (A-4 sample) presents a heterogeneous composition with different Raman spectra at different selected areas of the sample (Fig. 2A, spectra b1–b3), similar to spectra of samples prepared in 1 day (indicating the presence of Anderson HPC). However, there is also a new Raman spectrum at 874 cm⁻¹, which can be associated with the presence of pentagonal [M₆O₂₁]⁶⁻ (M = Mo, V, Nb) units [33]. In the case of the sample A-14 (Fig. 2A, spectrum c), only one type of Raman spectrum is observed with a wide band centered

Table 1
General characteristics of MoVTeNbO_x catalysts prepared by reflux.

Catalysts	Reflux time (days)	Bulk composition ^a	BET surface area (m ² g ⁻¹)	TPR results		
				T _{max} (K)	E _r (kJ mol ⁻¹) ^b	O ₂ (atom g ⁻¹)
A-1	1	Mo ₁ V _{0.22} Te _{0.17} Nb _{0.08}	1.9	941 ^c	157	2.5 × 10 ²¹ 2.5 × 10 ²¹
A-4	4	Mo ₁ V _{0.25} Te _{0.11} Nb _{0.10}	4.5	911 ^d	152	3.2 × 10 ²¹ 3.2 × 10 ²¹
A-7	7	Mo ₁ V _{0.27} Te _{0.12} Nb _{0.11}	4.7	824 883	138 148	1.7 × 10 ²¹ 1.7 × 10 ²¹ 3.4 × 10 ²¹
A-14	14	Mo ₁ V _{0.28} Te _{0.14} Nb _{0.11}	9.3	839 887	140 148	1.8 × 10 ²¹ 1.1 × 10 ²¹ 2.9 × 10 ²¹

^a Chemical composition determined by ICP-AES. In all cases, the atomic ratio in the synthesis gel was Mo/V/Te/Nb = 1/0.3/0.17/0.12.

^b Reduction activation energies in H₂-TPR experiments.

^c A shoulder at 890 K is also observed.

^d Shoulders at 820 and 890 K are also observed.

at 850 cm⁻¹, which is formed by at least two bands overlapping with maximum peaks at 840 and 875 cm⁻¹, the latter related to the structural pentagonal units [33], and a shoulder at 930 cm⁻¹.

Fig. 3A shows the IR spectra of as-synthesized samples in the range of 500–1800 cm⁻¹. All of these spectra show two bands at ca. 1600 and 1400 cm⁻¹, associated with the presence of H₂O and ammonium ions respectively [34], forming part of the solids. On the other hand, the sample prepared in 1 day shows IR bands at ca. 620, 670, 800, 890, 937 cm⁻¹ which is related to the presence of a tellurium molybdate with Anderson-type structures [31], in accordance with XRD and Raman results.

The most highlighted difference among IR spectra of as-synthesized samples is an intensity increase of the bands at 858 and 890 cm⁻¹. The intensity of bands centered at ca. 800 and 820 cm⁻¹ reduces as reflux time increases and as a consequence, the resolution of IR spectra becomes lower in A-4 and is practically indistinguishable in the A-7 sample. The band at 937 cm⁻¹ also decreases with the reflux time until it is practically absent in

the A-14 solid IR spectrum. In contrast with the others, the latter spectrum is quite similar to those obtained after heat treatment at 873 K in N₂ (Fig. 3B, d) with slight differences due to improved crystallization and a different level of hydration, as indicated by the peak at 1600 cm⁻¹ which is also present in the latter sample but with a lower intensity. This peak associated to H–O–H bending modes also is present in the remaining heat-treated samples.

3.2. Characterization of catalysts

As a consequence of the different as-synthesized solids, several crystalline phases are observed by XRD in catalysts, i.e. materials heat-treated at 873 K in N₂ (Fig. 1B), depending on time of reflux. Thus, the TeM₅O₁₆ (M = Mo, V, Nb) phase is mainly observed in the case of A-1 catalysts (Fig. 1B, pattern a), although the presence of M₅O₁₄ cannot be completely ruled out. However, new peaks begin to appear at 2θ = 6.6, 7.9, 9.0, 22.1, and 27.2°, characteristic of orthorhombic M1 phase [26], Te₂M₂₀O₅₇ (M = Mo, V, Nb), in

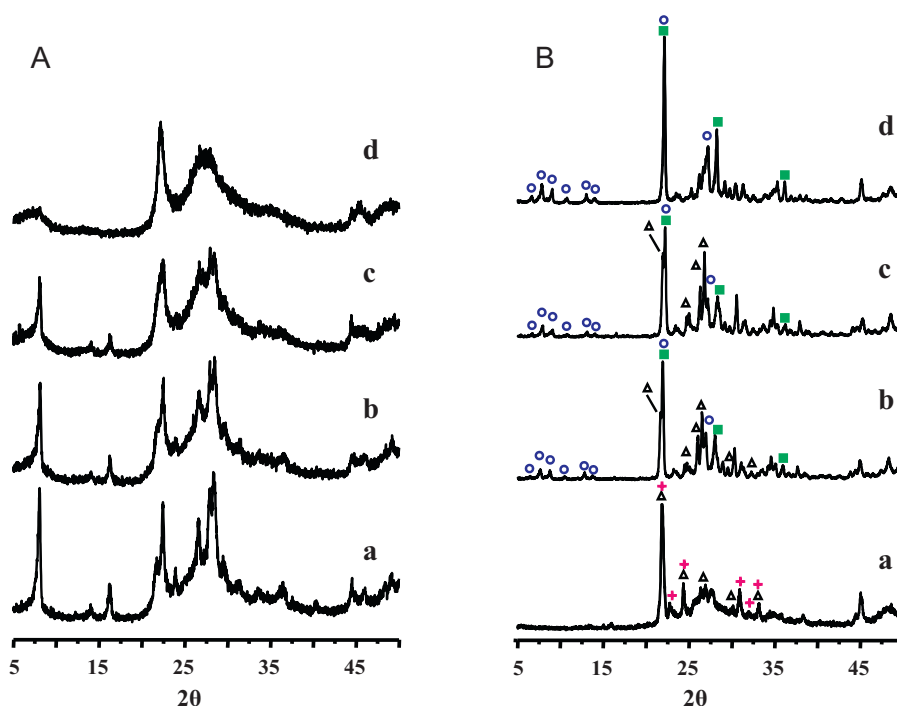


Fig. 1. XRD patterns of as-synthesized (A) and heat-treated (B) MoVTeNbO_x materials from solids prepared by reflux during: 1 (a), 4 (b), 7 (c), or 14 (d) days. Symbols: (○) M1 phase (Te₂M₂₀O₅₇), (■) M2 phase (Te_{0.33}MO_{3.33}), (△) TeM₅O₁₆, (+) M₅O₁₄. (M = Mo, V, Nb).

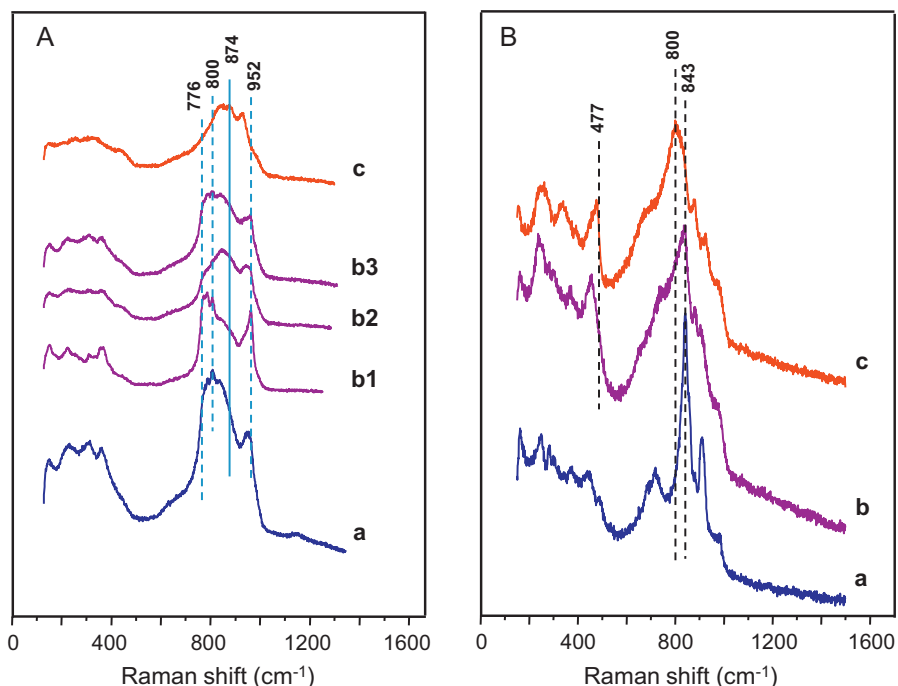


Fig. 2. Raman spectra of as-synthesized (A) and heat-treated (B) MoVTeNbO_x materials prepared by reflux during 1 day (a), 4 days (b), or 14 days (c). b1, b2, b3 indicate Raman spectra at different selected particles in the same sample.

catalysts achieved from precursors with refluxing time of 4 days (Fig. 1B, patterns c–e, respectively). In addition to these, peaks at $2\theta = 22.3, 25.8, 28.3, 36.3, 45.0,$ and 50.0° , related to M2 phase, Te_{0.33}MO_{3.33} ($M = \text{Mo}, \text{V}, \text{Nb}$), were also observed to a minor extent. It should be noted that TeM₅O₁₆ was not observed in A-14 catalyst, which is mainly of the M1 phase with the minority presence of M2 phase (Fig. 1B, pattern d). Additionally, it must be noted that the longest reflux time during the preparation of catalyst precursor provides the best scenario for the M1 phase crystallization at a high temperature during activation (Fig. 1B).

Fig. 2B shows the Raman spectra of heat-treated samples. The Raman spectrum of the A-1 catalyst presents two main peaks at 843 and 910 cm⁻¹ with shoulders at 680, 720, 880 and 980 cm⁻¹

of low intensity. The intensity of the latter Raman peaks increases for the rest of catalysts, overlapping and forming a wide Raman band with maxima and shoulders at *ca.* similar wave numbers, save the maximum at 843 cm⁻¹ (in A-1 catalyst) which shifts to lower energies with increasing days in reflux, up to 800 cm⁻¹ in the A-14 catalyst. Regarding the zone of less absorption, the presence of 477 cm⁻¹ in A-14 sample suggests the main presence of M1 phase [35], in agreement with XRD results.

Fig. 3B shows the IR spectra of catalysts. In the case of the A-1 catalyst (Fig. 3B, spectrum a), the IR spectrum shows bands at 904, 727, 650 and 540 cm⁻¹ which are similar to those described for the TeMo₅O₁₆ phase [36]. In addition to these, a shoulder at 950 cm⁻¹, associated with stretching Mo–O frequencies in the

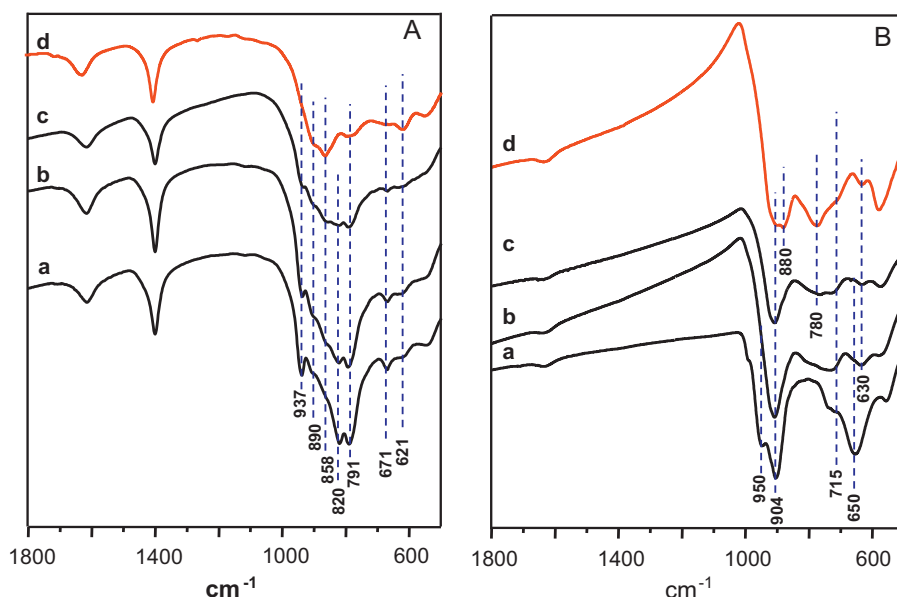


Fig. 3. IR spectra of as-synthesized (A) and heat-treated (B) MoVTeNbO_x materials prepared by reflux during 1 day (a), 4 days (b), 7 days (c) or 14 days (d).

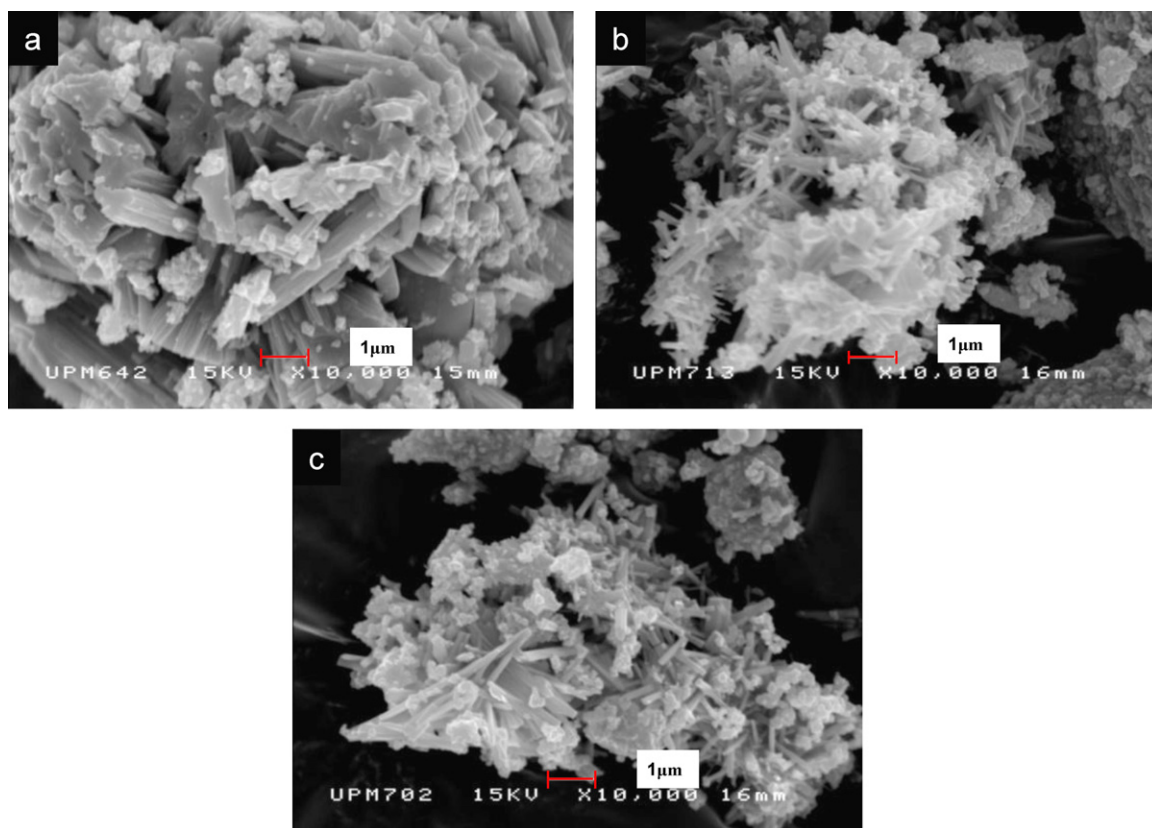


Fig. 4. SEM micrography of MoVTeNbO_x catalysts (heat-treated at 873 K in N_2) achieved from solid prepared by reflux during 1 day (a), 4 days (b) or 14 days (c).

Mo_5O_{14} phase [37], is also observed. We must indicate that the shoulder at 950 cm^{-1} is not present in catalysts prepared from 4 to 14 days in reflux, for which Mo_5O_{14} was not observed by XRD. However, the intensity of IR bands in the $700\text{--}900\text{ cm}^{-1}$ range increases with reflux time. In this way, the IR spectrum of the A-14 catalyst presents a set of bands at $905, 880, 775, 715, 630$ and 575 cm^{-1} , characteristic of the crystalline M1 phase [19]. The presence of the M2 phase cannot be completely ruled out, as suggested by the hinted shoulders at 924 and 750 cm^{-1} [11a].

The catalysts were studied by scanning electron microscopy (SEM). In general, the heat-treated catalysts obtained from materials prepared with four or more days of reflux showed crystals with pointed corners and sharp edges, which indicate highly crystalline materials. This is in good agreement with XRD results, which showed highly intense and sharp diffraction peaks. A-14 catalyst is presented in Fig. 4c as rod-shape crystals, commonly observed for M1 phase crystals [11b,38], with a rather homogeneous size, along with more particles in an apparent quasi-amorphous state. In contrast, the sample prepared in one day contains larger crystals (Fig. 4a). According to Ueda and Oshikara [14], the catalytic properties are derived from the cross-sections of the rods. Therefore, materials were ground before being tested in catalyst reaction in order to enhance their catalytic performance.

Fig. 5 shows the temperature programmed reduction profiles (H_2 -TPR) of heat-treated samples. The catalysts display changes in the TPR patterns depending on the synthesis time. At low synthesis time, i.e. 1 day, the catalyst mainly shows two reduction peaks at 890 and 940 K (Fig. 5a). Moreover, a new reduction peak at $824\text{--}841\text{ K}$ increases and the reduction peaks at 940 K shift to lower temperatures when reflux time is increased during catalyst synthesis. This is in accordance with the presence of crystalline phases which are octahedrally more distorted as shown by XRD results (Fig. 1). Although resolution is low due to the wide and overlap-

ping TPR signals, the TPR patterns of samples prepared at synthesis times of 7 and 14 days have two maximum peaks at 820 and 890 K (Fig. 5, patterns c and d), similar to previous results for hydrothermally prepared MoVTeNb catalysts containing M1 and M2 phases [39,40]. Note that the reduction of both Mo^{6+} and V^{5+} which are octahedrally coordinated in our catalysts are reduced more easily than in pure MoO_3 and V_2O_5 [41]. However, for the 1-day refluxed sample, the maximum peak happens at 941 K with a shoulder at 883 K (Fig. 5a). This reduction peak is higher than that of other catalysts and is probably due to the reduction of $\text{TeMo}_5\text{O}_{16}$ and/or M_5O_{14} phases ($M = \text{Mo}, \text{V}, \text{Nb}$) [40].

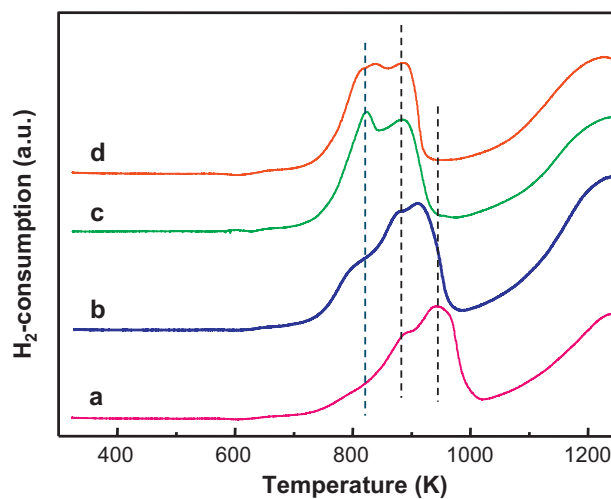


Fig. 5. H_2 -TPR profiles of MoVTeNbO_x catalysts (heat-treated at 873 K in N_2) achieved from solid prepared by reflux method during 1 day (a), 4 days (b), 7 days (c) or 14 days (d).

Table 2

Catalytic results obtained during propane oxidation at 673 K.

Catalysts	Conv. (%) ^a	Selectivity (%)					
		AA ^b	Propene	Acrolein ^c	HAc ^b	CO	CO ₂
A-1	2.5	0.0	77.3	0.4	0.0	11.2	11.1
A-4	8.5	12.8	39.8	t	0.2	24.4	22.8
A-7	14.6	31.1	38.9	t	0.2	15.5	14.3
A-14	28.9	56.2	11.3	t	0.6	15.4	16.5

^a Propane conversion at 673 K and a contact time, W/F, of 200 g_{cat} h mol_{C₃H₈}⁻¹.^b Selectivity to acrylic acid (AA) and acetic acid (HAc).^c Traces.

The onset of reduction reaction occurs at ~ 650 K, which is the same for all catalysts. This onset temperature coincides approximately with the temperature for propane activation. Therefore, it is suggested that the oxygen removed in the anaerobic H₂-TPR could be the same lattice oxygen species for the selective oxidation of propane. In this way, a rough estimation on the amount of oxygen removed was made by deconvoluting the H₂-TPR curves (Table 1). All of the samples released roughly the same number of oxygen atoms by reduction, i.e. $\sim 3.0 \times 10^{21}$ atom g⁻¹. However, the maximum for H₂-uptake change depends on the synthesis time or, in other words, on the nature of crystalline phases. Thus, samples A-7 and A-14 presented the higher numbers of oxygen atoms reduced at low temperature (Table 1) with a maximum peak at 820 K.

On the other hand, monolayer surface oxygen species accounted for roughly 1.0×10^{15} atom g⁻¹ cm⁻², according to the Arrhenius law, so lattice oxygen species are also involved in H₂-TPR results. All of the samples showed rather high reduction activation energy ($E_r > 100$ kJ mol⁻¹).

In the catalysts with M1 and M2 phases, Mo and V ions may undergo charge transfer on the Mo and V sites: $V^{5+}O^{2-} \rightleftharpoons V^{4+}O^-$ and $Mo^{5+}O^- \rightleftharpoons Mo^{6+}O^{2-}$. The lattice oxygen species O²⁻ could be involved in the α -H abstraction in propane (V-sites) and with the insertion into the allylic intermediate (Mo-sites). Some studies revealed an association between the V=O activity and the dehydrogenation of propane [40–42], whereas Mo=O is involved in selective oxidation of propylene [16,43–44].

3.3. Catalytic test

Results obtained during propane oxidation with the prepared catalysts are summarized in Table 2. The main reaction products were acrylic acid, propylene and CO_x, though acrolein and acetic acid were also detected as minority compounds. Catalytic results show that A-4, A-7 and A-14 catalysts are active and selective for propane selective oxidation to acrylic acid, with a catalytic behavior improving with refluxing time during catalyst synthesis. However, the catalytic properties drastically change for A-1 catalyst, which presents an extremely low propane conversion.

Fig. 6 shows the variation in both the catalytic activity (Fig. 6A) and the selectivity to acrylic acid (Fig. 6B) with the reaction temperature achieved during the propane oxidation on catalysts prepared by reflux. In general, it is observed that the refluxing time during catalyst synthesis exerts an important influence on the catalytic activity of the final catalyst, so that the propane conversion is progressively higher with reflux time. The highest gap is observed for the catalyst prepared with 14 days in reflux, which is the most active one. It is important to note that the catalyst with only 1 day in reflux (sample A-1) is practically inactive for propane conversion in all the range of temperatures tested, in that only traces of acrylic acid were found during propane oxidation with this material.

A similar trend was observed in the selectivity to acrylic acid, whereby the catalysts prepared from 4 days in reflux presented significant acrylic acid selectivity. The selectivity to acrylic acid slightly increased from A-4 to A-7 catalyst (from 4 to 7 days in

reflux, respectively), but selectivity improved greatly with the A-14 catalyst. A-14 catalyst was the most active and selective in propane partial oxidation to acrylic acid. The selectivity towards propylene also followed a similar trend, while an inverse tendency was observed for the selectivity to both acetic acid and CO_x.

Characterization and catalytic reaction results confirm that it is necessary for the presence of the M1 phase to obtain active and selective catalysts for propane oxidation to acrylic acid, as was previously reported [1,14,22,23]. In this way, the materials prepared from 4 to 14 days of reflux present mainly M1 crystalline phase, with small differences in the phases distribution among them, though important differences in the catalytic behavior are observed. Therefore, there seems to be a strong dependence between catalytic behavior and the crystallization of the M1 phase [23]. Reflux time improves the crystalline growth of the M1 phase but also minimizes the presence of other undesired crystalline phases that are inactive for propane oxidation and/or unselective for acrylic acid in consecutive oxidation of reaction intermediates.

Poor activity for the propane oxidation of A-1 is due to the absence of M1 phase, which may be a consequence of the presence of the samples' disordered structure since the reflux time employed for its synthesis was insufficient to develop the appropriate solid precursor, which leads to the crystallization of the active and selective M1 phase.

On the other hand, the catalytic activity is clearly related to the behavior of catalysts in the TPR experiments. Thus, the higher catalytic activity was observed in samples prepared at high synthesis times, which presented a first reduction peak at 820 K (Fig. 5). Moreover, the samples prepared with a lower synthesis time show the same number of oxygen atoms in the 600–1000 K range, but with lower reducibility, presenting the maximum H₂-uptake in the 900–940 K range.

4. General remarks

According to characterization results, as reflux time increases, the as-synthesized solid gradually transforms into a precursor with similar characteristics to that obtained by employing a similar synthesis gel composition through hydrothermal synthesis, according to XRD [11], IR [11b] and Raman [35] results. In this way, reflux provides an excellent opportunity to study in detail, the formation of the different phases during the synthesis of MoVTeNb mixed metal oxides, which will contribute to an improved understanding of the molecular processes that lead to the formation of an optimal precursor. Additionally, reflux provides the advantage of interactions at the desired moment in order to incorporate changes and modifications at a time that could lead to new materials with improved catalytic properties.

It must be taken into account that hydrothermal and slurry syntheses are the methods most often used to prepare these kinds of catalysts. So the procedures involving them have been widely studied and optimized for more than a decade [1].

According to XRD results (Fig. 1B), the nature of crystalline phases in catalysts is a consequence of the transformation of the

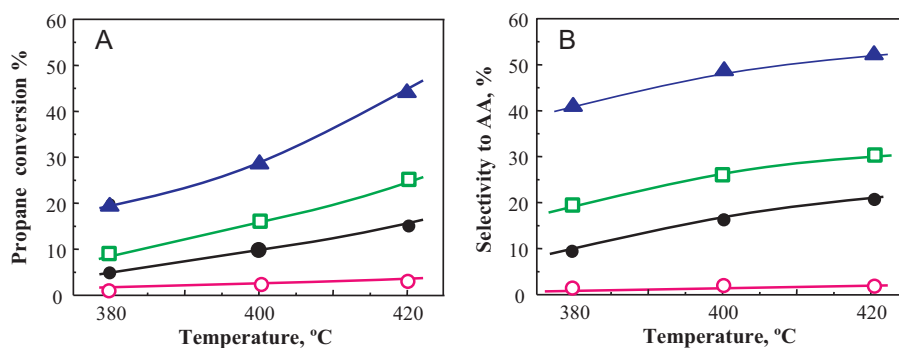


Fig. 6. Variation of propane conversion (A) and selectivity to acrylic acid (B), during partial oxidation of propane at different temperatures over MoVTeNbO_x catalysts prepared by reflux: A-1 (○); A-4 (●); A-7 (□); A-14 (▲). Contact time, W/F, of 200 g_{cat} h mol_{C₃}⁻¹. Molar ratio fed of C₃H₈/O₂/He/H₂O = 4/8/58/30.

different as-synthesized solids (Fig. 1A), which strongly depends on refluxing time. The presence of hexagonal domains of Anderson-type HPC led to the formation of TeMo₅O₁₆ (presenting hexagonal channels), while the presence of both hexagonal domains and pentagonal [M₆O₂₁]⁶⁻ (M = Mo, V, Nb) units allow for the formation of M1 crystalline phase, which is characterized by its pentagonal rings which join with the hexagonal ones and allows for the arrangement of octahedral-forming heptagonal channels [33].

The XRD pattern of as-synthesized samples prepared by reflux at 80 °C for 14 days (i.e. the precursor of A-14 catalyst) suggests the presence of pseudo-amorphous materials (Fig. 1A, d). This is quite similar to as-synthesized MoVTeNb materials prepared hydrothermally at 175 °C (48 h), with a low intense broad peak at 10°, a peak at 22° and a broad peak at around 27° [11,38]. However, it is different from those obtained by the slurry method, which had only two broad and low intense peaks at 2θ around 10° and 27° [34].

On the other hand, the XRD pattern of as-synthesized samples prepared by reflux at 80 °C and for 1 day, i.e. the precursor of A-1, is quite similar to precursor materials of TeMo₅O₁₆-containing solids prepared by slurry [34], presenting crystalline heteropoly-compounds (HPC).

Similar conclusions can be suggested from the IR results. Thus, Anderson type-HPC are clearly observed in the as-synthesized A-1 sample (Fig. 3A, spectrum a) as well as in the precursors of TeMo₅O₁₆-containing materials [31,34]. It must be indicated that IR [45] and Raman [46] spectra similar to those of as-synthesized A-1 samples are observed by other authors by drying or filtrating the synthesis gel prior to hydrothermal synthesis.

On the contrary, the IR spectrum of precursors obtained after 14 days in reflux (the precursor of A-14 catalyst) is quite similar to those obtained for well-crystallized M1 phase containing solids prepared by other methods such as hydrothermal [11b,19] or slurry [34] and are characterized by the presence of mixed metal oxides.

Refluxing for one day was not enough to form the desired precursor, with a poorly formed final activated material. A minimum of four days of reflux was needed for the correct arrangement of molecular building blocks in aqueous solution to enable M1 phase crystallization during heat-treatment. We must indicate that the XRD pattern of A-14 catalyst, achieved after heat-treatment of as-synthesized sample prepared by reflux at 80 °C for 14 days, is quite similar and presents catalytic behavior comparable to those achieved for heat-treated samples prepared from hydrothermal synthesis (at 175 °C, 2 days) [3,4,6,11,13,23,24], or microwave-assisted hydrothermal synthesis (175 °C, 2 h) [24].

5. Conclusions

Synthesis of highly active and selective Mo–V–Te–Nb–O catalysts for propane oxidation to acrylic acid was successfully

performed through reflux. This is the first ever report on the application of reflux to synthesize these mixed metal oxide catalysts. The M1 orthorhombic phase, active and selective to acrylic acid had significant results when the initial synthesis gel was refluxed for at least 4 days, and was optimum for a reflux synthesis for 14 days.

Through reflux, it is possible to combine the advantages of both the slurry and hydrothermal methods, the most commonly employed methods to prepare these kinds of MoVTeNbO catalysts. Reflux favors solvent power and chemical transport, and provides a controlled synthesis ambience for the steady oxidation states of the different metal elements. All these factors lead to the formation of meta-stable crystalline phases with higher purity and homogeneous crystal size. The latter feature is similar to the results obtained in the hydrothermal method, but without the inconvenience a closed system. Accordingly, reflux could be a promising method to prepare this kind of catalyst, since it offers the possibility for observation and involvement, allowing interaction and more thorough inspection of the reaction medium, whose chemical and physical properties may change over the course of the reaction. The method also favors solubility and provides the conditions and controlled synthesis that welcomes steady oxidation states of the different metals, which allows for the formation and stabilization of meta-stable phases (in pseudo-minimum energy state) as is the case of the M1 phase.

There is a clear parallel between redox and catalytic properties, suggesting that the reducibility of crystalline phases is a key factor in the partial oxidation of propane. In this way, the M1 phase is an active and selective crystalline phase.

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