Selective oxidation of propane to acrylic acid on MoVNbTe mixed oxides catalysts prepared by hydrothermal synthesis

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MoVNbTe mixed oxides have been prepared by both hydrothermal synthesis and slurry methods and have been tested in the selective oxidation of propane to acrylic acid. For comparative purpose, ternary metal oxides have also been prepared and tested. Characterisation results (X-ray diffraction and EPR) show important differences between the catalysts prepared hydrothermally and one prepared by a slurry method. The catalysts prepared hydrothermally show a higher activity and selectivity to acrylic acid than those prepared by slurry method. A reaction network for the partial oxidation reaction is tentatively proposed from the catalytic results obtained during the oxidation of propane and propylene on these catalysts.

KEY WORDS: oxidation of propane and propylene; acrylic acid and acrolein; molybdenum, vanadium, niobium and tellurium mixed oxides; hydrothermal synthesis; X-ray diffraction; electron paramagnetic spectroscopy

1. Introduction

Mo–V–Te–Nb mixed oxides have recently been proposed as active and selective catalysts in the oxidation of propane to acrylic acid [1–4]. These catalysts are similar to those reported for the ammoxidation of propane to acrylonitrile [5–7]. Yields of acrylic acid higher than 40% have been reported in the patent literature [1–3].

Recently, Ueda *et al.* [8] have reported the preparation of MoVMe (Me = Al, Sb, Te) catalysts by a hydrothermal synthesis. These are active and selective in the formation of acrylic acid from propane but present selectivities to acrylic acid lower than those reported in the patents.

Watanabe and Koyasu [9] compared several methods for preparing MoVNbTe mixed oxides catalysts in the ammoxidation of propane. They observed that materials prepared hydrothermally give catalyst precursors, which show twice higher activity after calcination than those prepared by the dry-up method.

In this paper we report the preparation, characterisation and catalytic behaviour in the oxidation of propane and propylene to acrylic acid of Mo–V–Nb–Te mixed oxides catalysts prepared by different methods. For comparative purposes ternary catalytic systems have also been studied. It will be shown that catalysts prepared by hydrothermal treatment present a high activity and selectivity to acrylic acid from either propane or propylene.

2. Experimental

Mo–V–Nb–Te mixed oxides and the corresponding ternary compounds (Mo–V–Te, Mo–V–Nb and Mo–Nb–Te) have been prepared by a hydrothermal method. The catalysts were prepared using vanadyl sulphate, niobium oxalate, ammonium hexamolybdotellurate (ammonium heptamolybdate was used in a Te-free catalyst) and water with a Mo/V/Te/Nb atomic ratio of 1/0.36/0.17/0.12. A MoVTe catalyst was also prepared by hydrothermal method incorporating oxalic acid in the synthesis gel (using a Mo/oxalic acid molar ratio of 1/0.7) and was named as MoVTe-OXA. The gels were autoclaved in teflon-lined stainless-steel autoclaves at 175 °C for 48 h. The resulting precursors were filtered, washed, dried at 80 °C for 16 h and calcined at 600 °C during 2 h in N_2 stream.

For comparative purpose, a MoVNbTe was prepared by the slurry method, according to the preparation procedure reported in [2] and named as MoVNbTe-SL. The characteristics of catalysts are shown in table 1.

The ammonium hexamolybdotellurate, $(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$, was prepared at 80 °C from an aqueous solution of stoichiometric ammonium heptamolybdate and telluric acid, according to a previously reported preparation procedure [6,10].

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 Cu K_α radiation ($\lambda = 0.1542$ nm).

Electron paramagnetic resonance spectra (EPR) were recorded at 77 K on a Bruker ER-200 spectrometer work-

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Table 1
Characteristics of catalysts and catalytic properties in the selective oxidation of propane at 380 °C.

Catalyst	Chemical composition[a]				S_{BET}[b]	W/F[c]	Conversion[d]	Selectivity[e] (%)						
	Mo	V	Te	Nb			(%)	AA	ACRO	ACET	AcOH	C_3H_6	CO	CO_2
MoVNbTe	1.00	0.22	0.17	0.15	24.0	409	31.1	56.5	0.1	0.4	0.7	7.1	10.8	25.8
MoVNb	1.00	0.30	0	0.12	9.2	205	14.2	0.5	0.3	0.1	1.4	12.0	35.2	50.5
MoVTe	1.00	0.15	0.19	0	6.4	614	17.5	16.3	0.1	0.4	2.1	15.1	20.5	45.6
MoNbTe	1.00	0	0.20	0.15	1.0	205	0.6	5.5	1.1	–	–	76.3	6.4	10.8
MoTe	1.00	0	0.21	0	n.d.	–	–	–	–	–	–	–	–	–
MoVTe-OXA	1.00	0.23	0.29	0	25.0	402	32.1	13.4	0.0	0.3	6.1	5.5	21.6	53.1
MoVNbTe-SL	1.00	0.30	0.23	0.12	4.0	510	18.0	7.5	0.1	0.2	0.1	17.5	43.9	30.8

[a] Chemical analysis was obtained by atomic absorption spectroscopy.
[b] S_{BET} in $m^2\,g^{-1}$; n.d. = not determined.
[c] Contact time, W/F in $g_{\mathrm{cat}}\,h\,mol_{C_3}^{-1}$.
[d] Propane conversion (%).
[e] Acrylic acid (AA), acrolein (ACRO), acetone (ACE), acetic acid (AcOH), propylene (C_3H_6) and carbon oxides (CO and CO_2).

ing at the X-band and calibrated with a DPPH standard ($g = 2.0036$). Quantitative analysis was carried out by double integration of the EPR spectra and comparison with a copper sulphate ($CuSO_4{\cdot}5H_2O$) standard. Computer simulations were employed to determine experimental parameters. Portions of *ca.* 25 mg of sample were introduced inside an EPR quartz probe cell and handled in a conventional high vacuum line for the different treatments. The samples were subjected to extensive room temperature outgassing prior to recording their spectra.

The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure. 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 200 $cm^3\,min^{-1}$) in order to achieve different propane conversion levels. The feed consisted of a mixture of propane/oxygen/water/helium with a molar ratio of 4/8/30/58. Experiments were carried out in the 350–420 °C temperature interval in order to achieve the higher selectivity to partial oxidation products. Reactants and reaction products were analysed by on-line gas chromatography, using two Hewlett–Packard apparatus equipped with three columns: (i) 23% SP-1700 Chromosorb PAW (30 m × 1/8 in) to separate hydrocarbons and CO_2; (ii) Carbosieve-S (8 m ×1/8 in) to separate O_2 and CO; (iii) Porapak Q (3.0 m × 1/8 in) to separate oxygenated products. Blank runs showed that under the experimental conditions used in this work the homogeneous reaction could be neglected.

3. Results and discussion

Figure 1 presents the XRD patterns of samples prepared hydrothermally (before the calcination step). Two intense peaks at $2\theta = 8.16°$ and 28.56° in addition to more than 25 peaks (the most intense peaks appear at $2\theta = 16.40°$, 21.75°, 22.63°, 28.03°, 28.56°, 29.8° and 31.5°) are observed in the as-synthesised MoTe (XRD pattern not shown) and MoVTe (figure 1(a)) samples. This XRD pattern is quite different from those observed in previously reported molybdotellurates (with and without V ions). However, the structure is still unknown. On the other hand, the MoVTe sample shows a crystallinity higher than that of MoTe sample.

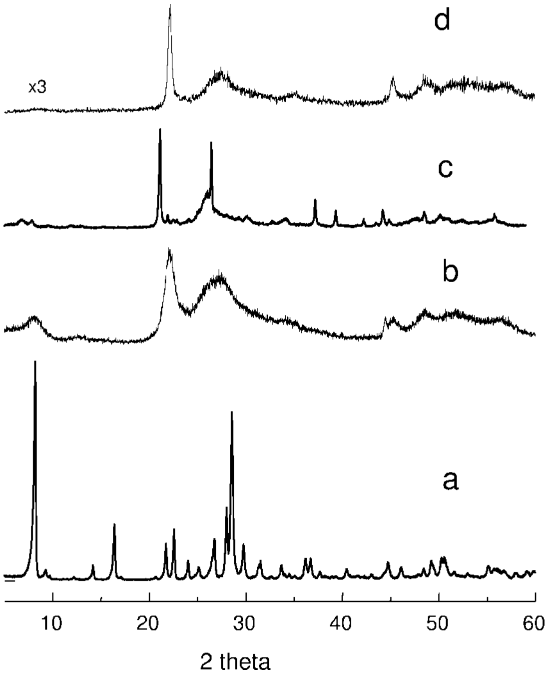


Figure 1. XRD patterns of as-synthesised catalysts: (a) MoVTe, (b) MoVNb, (c) MoVTe-OXA and (d) MoVNbTe.

Nb-containing phases, *i.e.*, MoVNb and MoVNbTe, present pseudoamorphous (or low crystalline) phases (figure 1 (b) and (d), respectively). Thus, broad peaks at $2\theta = 9.0°$, 22.2°, 27.4° and 45.4° are mainly observed in Nb-containing samples, although peaks at 14.9° and 29.87° are also observed in the MoNbTe sample (XRD not shown).

The XRD pattern of the uncalcined MoVTe-OXA sample prepared hydrothermally in the presence of oxalic acid (figure 1(c)), shows a low crystallinity intermediate between Nb-containing and Nb-free samples. Thus, it appears that Nb ions, in addition to the presence of oxalic acid during the cat-

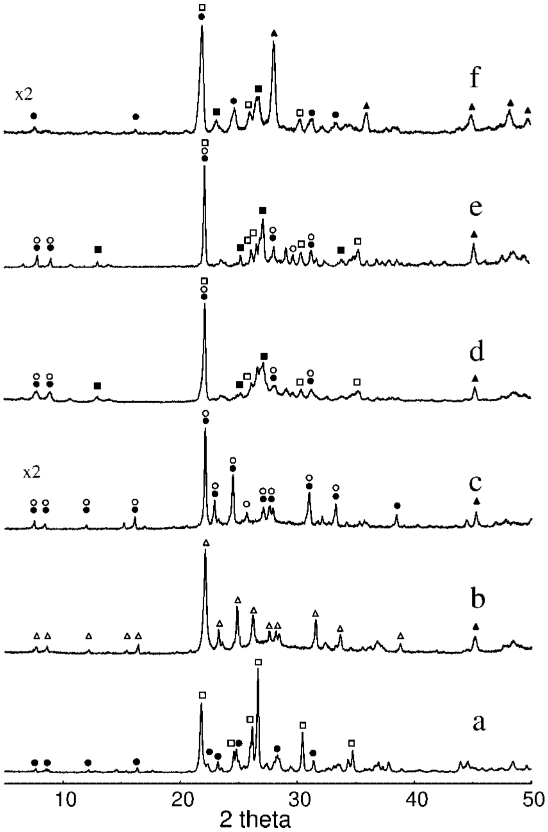


Figure 2. XRD patterns of calcined catalysts: (a) MoVTe, (b) MoTeNb, (c) MoVNb, (d) MoVTe-OXA, (e) MoVNbTe and (f) MoVNbTe-SL. (●) $(Mo_{0.93}V_{00.7})_5O_{14}$, (○) $Mo_{0.91}Nb_{00.9}O_{2.80}$, (■) MoO_3, (□) Mo_5TeO_{16}, (△) $3MoO_2{\cdot}Nb_2O_5$ and (▲) undetermined peaks.

alyst preparation, play an important role in the crystallinity of active and selective catalysts.

The XRD patterns of samples calcined in N_2 at 600 °C for 2 h show the presence of different crystalline phases, although the nature of these depends on the catalyst composition and preparation procedure (figure 2).

The XRD pattern of the calcined MoVTe sample (figure 2(a)) shows the presence of Mo_5TeO_{16} (peaks at $2\theta = 21.7°$, 24.6°, 26.2°, 26.67° and 30.5°) (JCPDS, 31-874) and $(Mo_{0.93}V_{0.07})_5O_{14}$ (peaks at $2\theta = 7.75°$, 8.86°, 12.3°, 16.46°, 22.25°, 23.4°, 24.9°, 28.1° and 31.5°) (JCPDS: 31-1437). However, the presence of $TeMo_4O_{13}$ (JCPDS: 31-1372 and 34-622) as minority crystalline phase cannot be ruled out.

The presence of the $3MoO_2Nb_2O_5$ mixed oxides crystalline phase (JCPDS:18-840) (with a peak at $2\theta = 22.20°$ in addition to peaks at 23.0°, 24.6°, 27.74°, 28.00°, 31.20°, 33.4°) can be concluded from the XRD pattern of the calcined MoNbTe sample (figure 2(b)). However, both $(V_{0.07}Mo_{0.93})_5O_{14}$ (JCPDS: 31-1437) and $Nb_{0.09}Mo_{0.91}O_{2.80}$ (JCPDS: 27-1310) are mainly presented in the calcined MoVNb sample (figure 2(c)). On the other hand, a Te-containing crystalline phase has not been observed in the calcined MoNbTe sample, suggesting that tellurium could be incorporated in an amorphous or low crystalline phase (figure 2(b)).

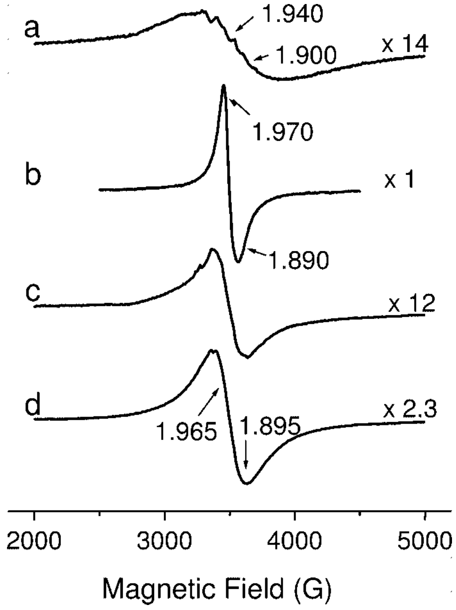


Figure 3. EPR spectra of N_2-calcined catalysts after outgassing at room temperature: (a) MoVNbTe, (b) MoVNbTe-SL, (c) MoVTe-OXA and (d) MoVTe.

Mo_5TeO_{16}, $(Mo_{0.93}V_{0.07})_5O_{14}$ and MoO_3 are observed in the XRD patterns of both MoVTe-OXA and MoVNbTe calcined samples (figure 2 (d) and (e), respectively). In addition, $3MoO_2Nb_2O_5$ crystalline phases, with low crystallinity, could also be present in the MoVNbTe catalyst.

A completely different XRD pattern is observed in the calcined MoVNbTe-SL sample (figure 2(f)). In this case, intense peaks are clearly present at $2\theta = 22.1°$, 28.2°, 36.2°, 45.2° and 50°, which have been reported in the patents as attributable to an active and selective phase in oxidation and ammoxidation of propane [5–7]. In addition, peaks at 23.1°, 24.66°, 25.98°, 26.6° and 26.8° are also observed in the range 20°–30°. A similar XRD pattern is reported by Asakura *et al.* [7] from an active and selective catalyst for the ammoxidation of propane to acrylonitrile.

EPR spectra of N_2-calcined samples subjected to extensive outgassing at room temperature are shown in figure 3 (a)–(d). The spectrum of sample MoVNbTe (figure 3(a)) is mainly constituted by a broad signal ($\langle D \rangle \approx 400$ G), which can be satisfactorily simulated by considering axial lineshape with $g_\perp = 1.940$ and $g_\parallel = 1.900$. Superimposed on that signal, the presence of sharp features can be observed, most likely arising, according to the relative magnitude of the splitting, from the hyperfine structure of minor isolated V^{4+} cations present in that sample. For sample MoVNbTe-SL, the spectrum (figure 3(b)) is formed by an axial signal, considerably narrower than that present in sample MoVNbTe, at $g_\perp = 1.970$ and $g_\parallel = 1.890$. In the case of samples MoVTe-OXA and MoVTe (figures 3 (c) and (d), respectively) the spectra are mainly constituted by axial signals with $g_\perp = 1.965$ and $g_\parallel = 1.895$, with average linewidths intermediate between those shown by the main signals in samples MoVNbTe and MoVNbTe-SL.

Overall intensities of these spectra amount to 137, 198, 102 and 286 μmol g^{-1} for, respectively, samples MoVNbTe, MoVNbTe-SL, MoVTe-OXA and MoVTe. Parameters of the main signals appearing in these spectra are consistent with the presence of Mo^{5+} cations (in the oxomolybdenum form) in distorted octahedral environments [11]. The relatively large widths of the signals with the consequent absence of a clear resolution of hyperfine features on them (*ca.* 25% of the molybdenum – ^{95}Mo and ^{97}Mo isotopes – present nuclear spin $I = 5/2$) suggest that the paramagnetic centres are immersed into magnetically active environments, of a considerably larger magnitude in the case of sample MoVNbTe (figure 3(a)).

The presence of Mo^{5+} in the EPR spectra of the N_2-calcined or oxidised samples indicates that they are partially reduced, probably due to reductive interactions with ammonia or oxalic acid (likely to be formed from components present in the metal precursors) during the preparation steps and insufficient reoxidation during the pretreatment. On this basis, the lower intensities of Mo^{5+} species in calcined MoVNbTe and MoVTe-OXA with respect to MoVNbTe-SL and MoVTe suggest that molybdenum cations are less oxidisable for the former samples. This is partially supported by the study of redox properties on samples MoVNbTe and MoVNbTe-SL, which in turn evidences the higher reducibility of those cations in the former sample [12]. These differences can be related, according to a previous XPS study [13], to the influence of vanadium promotion on molybdenum reduction–oxidation, suggesting a more efficient insertion of vanadium cations into Mo-containing phases for the MoVNbTe catalyst.

Table 1 shows the catalytic results obtained during the oxidation of propane. Partial oxidation products, *i.e.*, propylene, acrylic acid, acrolein, acetone and acetic acid, and carbon oxides have been observed, although their selectivities depend on the catalyst composition and/or the catalyst preparation procedure. The MoVNbTe catalyst, prepared by hydrothermal treatment, presents a propane conversion and selectivity to acrylic acid higher than that prepared by slurry method.

In the ternary system, MoVNb presented a high propane conversion with low selectivity to acrylic acid. However, the MoNbTe catalyst shows a very low propane conversion (propylene was the main reaction product). On the other hand, the MoVTe catalyst is active and selective to acrylic acid, although it shows a yield of acrylic acid lower than that of the MoVNbTe catalyst. When the MoVTe catalyst is prepared in the presence of oxalic acid, it presents a higher propane conversion with similar selectivity to acrylic acid than sample MoVTe. The presence of oxalic acid during the synthesis appears to be related with the surface area of this sample, favouring a higher conversion of propane.

From these results it appears that the presence of V ions plays an important role in the activation of propane, while the presence of Mo^{5+}/Mo^{6+} and Te^{4+}/Te^{6+} pairs could be related with the formation of acrylic acid. The role of Nb^{5+} ions is, at this moment, unclear but it could be related to the formation of active and/or selective crystalline phases. In this way, the presence of oxalic acid during the synthesis (which is also present when the reaction is carried out in the presence of Nb salt used in this paper) appears to be related with the increase of the surface area observed on these samples. This could favour the higher conversion on propane observed on both MoVNbTe and MoVTe-OXA samples. However, the selectivity to acrylic acid on sample MoVTe-OXA was lower than on MoVNbTe. Thus, it appears that Nb ions could also be an important promoter of these catalysts.

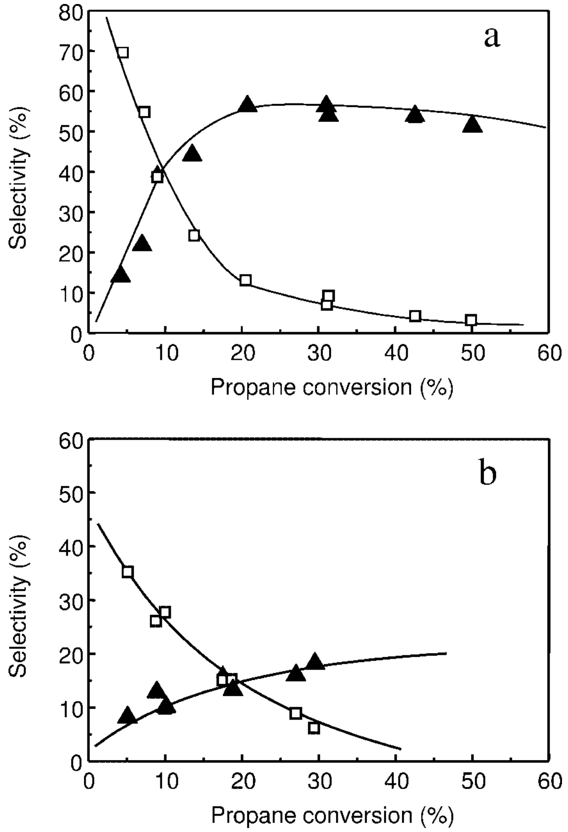


Figure 4. Variation of the selectivities to acrylic acid (▲) and propylene (□) with the propane conversion during the selective oxidation of propane at 380 °C on MoVNbTe (a) and MoVTe (b) catalysts.

Figure 4 presents the variation of the selectivity to acrylic acid and propylene with the propane conversion obtained during the oxidation of propane on both MoVNbTe and MoVTe catalysts. The selectivity to acrylic acid increases and the selectivity to propylene decreases with the propane conversion. In both cases the highest selectivities to acrylic acid are observed at propane conversions higher than 20–30% (figure 4). So, acrylic acid is mainly formed from propylene by consecutive reaction.

Figure 5 shows the variation of the selectivity to acrolein and acrylic acid with the conversion of propylene obtained during the oxidation of propylene on MoVTe and MoVNbTe catalysts. It can be seen that both acrolein and acrylic acid are primary products, although acrylic acid is also formed by consecutive oxidation of acrolein at high propylene conversions.

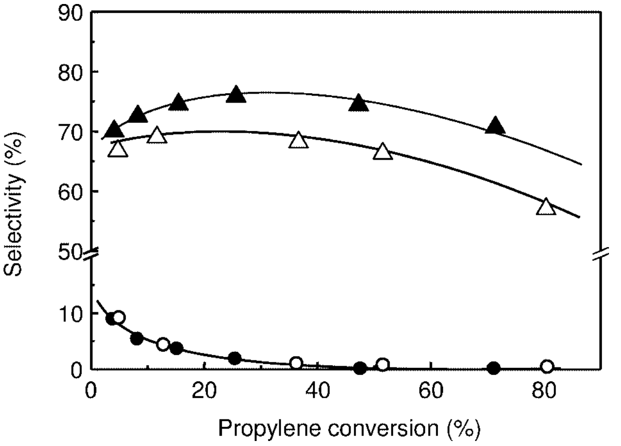


Figure 5. Variation of the selectivity to acrylic acid (▲, △) and acrolein (●, ○) with the propylene conversion during the selective oxidation of propylene at 380 °C on MoVNbTe (▲, ●) and MoVTe (△, ○) catalysts.

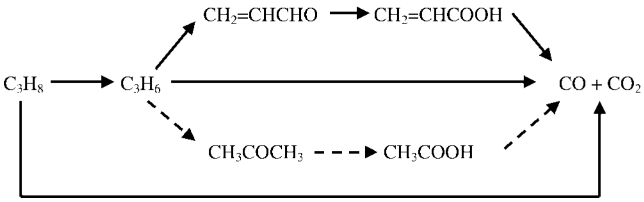
Table 2
Selective oxidation of propylene at 380 °C.

Catalyst	W/F[a]	Conversion[b] (%)	Selectivity[c] (%) AA	ACRO	ACE	AcOH	CO	CO_2
MoVNbTe	50	25.4	77.1	0.9	3.3	4.1	9.0	10.9
MoVNb	50	29.8	1.2	1.2	1.9	14.8	32.9	48.0
MoVTe	150	36.1	69.7	1.3	2.2	6.4	6.1	14.2
MoNbTe	160	1.7	0.0	91.5	–	2.1	4.3	2.1
MoTe	820	5.4	0.0	87.9	0.8	0.0	8.3	2.9
MoVTe-OXA	25	27.2	53.9	0.3	1.6	7.4	10.7	26.0
MVNbTe-SL	410	30.6	65.1	1.0	3.3	6.6	6.9	17.0

[a] Contact time, W/F in $g_{cat}\,h\,mol_{C_3}^{-1}$.
[b] Propylene conversion (%).
[c] Acrylic acid (AA), acrolein (ACRO), acetone (ACE), acetic acid (AcOH) and carbon oxides (CO and CO_2).

In the case of the MoVNb sample, acetic acid was the more important partial oxidation product from propylene while acrolein was selectively obtained with low activity on the MoNbTe sample (table 2). So, a parallelism between the catalytic performance of these catalysts in the partial oxidation of propane and propylene can be concluded, and a reaction network for the oxidation of propane on these catalysts is tentatively proposed in scheme 1. Propylene is directly formed from propane on V-containing catalysts. This should be consecutively transformed into acrolein or acrylic acid on Te-containing catalysts, depending on the catalyst composition, by an allylic mechanism. However, acetone and acetic acid are selectively formed from propylene on the MoVNb sample. In this case, a hydration mechanism could be proposed [4,14]. However, the formation of acetic acid from C_2 hydrocarbons, formed from propane, cannot be ruled out.

It can be seen that high selectivities to acrylic acid can be obtained from both propane and propylene using MoVTe-containing catalysts, although the higher activity corresponded to those containing Nb^{5+} ions. Since the higher catalytic activity corresponds to those MoVNbTe, MoVNb and MoVTe-OXA samples (which present the highest surface area), the role of Nb ions in these catalysts could be related to the formation of active phases with low crystallinity and higher surface areas.



Scheme 1. Reaction network for the selective oxidation of propane on MoVTe-based catalysts.

On the other hand, no modifications of the XRD pattern of the MoVNbTe catalyst was observed after the catalytic test indicating a relative stability of these catalysts in our reaction conditions.

In conclusion, MoVNbTe mixed oxides catalysts, active and selective in the partial oxidation of propane and propylene to acrylic acid, have been hydrothermally prepared. The catalytic behaviour can be explained by the presence of low crystalline MoVTe metal mixed oxides. The presence of Nb^{5+} ions favours the low crystallinity of active and selective phases. In addition, the MoVNbTe catalyst presents a yield and a selectivity to acrylic acid higher than that reported previously with MoVTe catalysts prepared by hydrothermal synthesis [8] or those prepared by slurry method [4].

On the other hand, the active crystalline phase (at $2\theta = 22.1°, 28.2°, 36.2°, 45.2°$ and $50°$) reported in the patents is observed in the low active MoVNbTe-SL catalyst (prepared by slurry method) but is minority in the MoVNbTe catalyst prepared by hydrothermal synthesis. Since both MoVNbTe-SL and MoVNbTe catalyst present a relatively high activity to acrylic acid from propylene, it can be concluded that more than one specific crystalline phase could be involved in the selective oxidation reaction.

In fact, more than one crystalline phase have been proposed in the ammoxidation of propane to acrylonitrile on similar metal oxides [15]. However, a higher effort will be done in order to show clearly the nature of active and selective sites in these multicomponent catalysts.

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