Preparation, characterisation and catalytic behaviour of a new TeVMoO crystalline phase

P. Botella, J.M. López Nieto *, and B. Solsona
Instituto de Tecnología Química, UPV-CSIC, Avenida de los Naranjos s/n, 46022-Valencia, Spain

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$TeM_xMo_{1.7}O$ mixed oxides (M = V and/or Nb; $x = 0$–1.7) have been prepared by calcination of the corresponding salts at 600 °C in an atmosphere of N_2. A new crystalline phase, with a Te/V/Mo atomic ratio of 1/0.2–1.5/1.7, has been isolated and characterised by XRD and IR spectroscopy. This phase is observed in the TeVMo or TeVNbMo mixed oxide but not in the TeNbMo mixed oxide. The new crystalline phase shows an XRD pattern similar to $Sb_4Mo_{10}O_{31}$ and probably corresponds to the M1 phase recently proposed by Aouine *et al.* (Chem. Commun. 1180, 2001) to be present in the active and selective MoVTeNbO catalysts. Although these catalysts present a very low activity in the propane oxidation, they are active and selective in the oxidation of propene to acrolein and/or acrylic acid. However, the product distribution depends on the catalyst composition. Acrolein or acrylic acid can be selectively obtained from propene on Nb-free or Nb-containing TeVMo catalysts, respectively. The presence of both V and Nb, in addition to Mo and Te, appears to be important in the formation of acrylic acid from propene.

KEY WORDS: oxidation; propane; propene; acrolein; acrylic acid; molybdenum, vanadium, niobium and tellurium mixed oxides; MoVTeNb; X-ray diffraction; infrared spectroscopy

1. Introduction

MoVTeNbO mixed oxides have been shown to be active and selective catalysts in both the selective oxidation of propane to acrylic acid [1–5] and in the ammoxidation of propane to acrylonitrile [6–8]. These materials probably represent one of the most interesting catalytic systems developed in the last decade for the gas phase selective oxidation of hydrocarbons.

The catalyst preparation, the optimal chemical composition as well as the nature of the active and selective sites are still under discussion. Most papers and patents published in recent years indicate the presence of two or more crystalline phases [5,8–10]. One of them, named M1 [8], is characterised by the presence of peaks at $2\theta = 9.0°$, 22.1°, 27.3°, 29.2°, and 35.4° in the XRD pattern, and a second phase, named M2, gives diffraction peaks at $2\theta = 22.1°$, 28.2°, 36.2°, 45.2°, and 50.0° [1–5,9].

Recently, it has been proposed that the selective MoVTeNb catalysts present two crystalline phases (M1 and M2) with stoichiometries of $Te_{0.33}MO_3$ and $Te_{0.2}MO_{3.2}$ (M = Mo, V and/or Nb), respectively [10]. The former structure is isomorphous with $Sb_4Mo_{10}O_{31}$, and the latter is probably similar to that of $TeMo_5O_{16}$ and $Sb_2Mo_{10}O_{31}$.

Several crystalline phases have been observed to be present in binary and ternary mixed metal oxides [11–13], especially Mo-V-Te-O [13]. However, none corresponds to those reported in the patent literature on MoVTeNb catalysts.

In this paper we report for the first time the preparation of a new TeVMoO crystalline phase, which is probably related to one of those recently proposed to be present in active and selective MoVTeNb-based catalysts. It will be shown that this crystalline phase is inactive for the selective oxidation of propane, but it is active and selective in the oxidation of propene to acrolein and/or acrylic acid. The importance of the incorporation of V and Nb in these catalytic systems is also discussed.

2. Experimental

2.1. Catalyst preparation

TeVMo samples of different chemical composition have been prepared by the slurry method. An aqueous suspension of $Te(OH)_6$ and ammonium heptamolybdate in the molar ratio of 1/1.8 was heated at 60 °C and adjusted to pH 7.5 by dropwise addition of aqueous NH_3 (25 wt%). Vanadyl sulfate was then incorporated. The solution with the three elements was finally evaporated and the resulting solid dried at 90 °C overnight. The samples were finally calcined at 600 °C in N_2 for 2 h.

For comparative purposes, TeNbMo- and TeVNbMo-containing catalysts have also been prepared by the same procedure using niobium oxalate as starting material. The characteristics of these catalysts are shown in table 1.

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* To whom correspondence should be addressed.
E-mail: jmlopez@itq.upv.es

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Table 1
Characteristics of TeXMoO (X = V and/or Nb) mixed oxides

Sample	**X** in TeXMo	Chemical composition [a]	XRD crystalline phases [b]
TM-0.5	—	Te/Mo = 1 : 1.7	$MoO_3 \gg TeMo_5O_{16}$
TVM-1	V	Te/V/Mo = 1 : 0.13 : 1.7	$TeMo_5O_{16}$
TVM-2	V	Te/V/Mo = 1 : 0.64 : 1.7	**TeVMoO** > $TeMo_5O_{16}$
TVM-3	V	Te/V/Mo = 1 : 0.61 : 1.7	**TeVMoO** $\gg TeMo_5O_{16}$
TVM-4	V	Te/V/Mo = 1 : 0.92 : 1.7	**TeVMoO**
TVM-5	V	Te/V/Mo = 1 : 1.36 : 1.7	**TeVMoO** $\gg MoO_3$
TNbM-1	Nb	Te/Nb/Mo = 1 : 1.30 : 1.7	$3MoO_2{\cdot}Nb_2O_5$
TVNbM-1	V and Nb	Te/V/Nb/Mo = 1 : 1.36 : 0.30 : 1.7	**TeVMoO**

[a] Chemical analysis was performed by atomic absorption spectrophotometry (Mo, V, Te) and ICP (Nb).
[b] **TeVMoO** a new crystalline phase with an XRD patttern similar to $Sb_4Mo_{10}O_{31}$.

2.2. Catalyst characterisation

The surface areas of the catalysts were measured on a Micromeritics ASAP 2000 instrument by adsorption of krypton. X-ray diffraction patterns (XRD) were collected using a Philips X'Pert diffractrometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm). Infrared spectra were recorded at room temperature in the 300–3900 cm^{-1} region with a Nicolet 205 × B spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

2.3. Catalytic test

The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure [5]. The flow rate and the amount of catalyst were varied (from 50 to 200 cm^3 min^{-1}) in order to achieve different hydrocarbon conversion levels. The feed consisted of a mixture of propane/oxygen/water/helium (with a molar ratio of 4/8/30/58) or propene/oxygen/water/helium (with a molar ratio of 2/8/10/80) [5]. Experiments were carried out in the 350–420 °C temperature interval in order to achieve high selectivities 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

3.1. Catalyst characterisation

Surface areas lower than 1 and 2 m^2 g^{-1} have been obtained in Nb-free and in Nb-containing TeVMo samples, respectively.

The XRD patterns of TeVMo samples with different V contents are shown in figure 1. For a comparative purpose, a MoTeO mixed-oxide (sample TM-0.5) is also included. The XRD pattern of this sample indicates the presence of MoO_3 (JCPDS, 5-508) and $TeMo_5O_{16}$ (JCPDS, 31-874), the first one appearing to be predominant (figure 1(a)), while other Te-containing crystalline phases are not observed. The relative intensity of the most intense reflections of MoO_3 is different from that previously reported. Thus, the peak at $2\theta = 25.7°$ (related to the [040] face) is more intense than that at $2\theta = 27.3°$ (related to the [021] face). This modification could be related to the presence of Te^{4+} ions on the catalyst.

The introduction of small amounts of vanadium (sample TVM-1) favours the disappearance of MoO_3 and the crystallisation of a $TeMo_5O_{16}$ phase (figure 1(b)). However, new peaks are observed at $2\theta = 22.1°$,

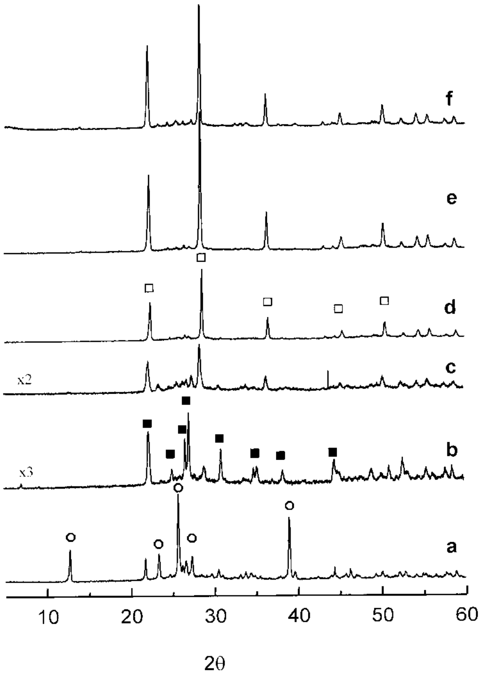

Figure 1. XRD patterns of TeVMoO catalysts: (a) TM-0.5; (b) TVM-1; (c) TVM-2; (d) TVM-3; (e) TVM-4; (f) TVM-5. Symbols: (○) MoO_3; (■) $TeMo_5O_{16}$; (□) new TeVMo phase.

28.2°, 36.2°, 45.2° and 50.0°, corresponding to a new TeVMoO crystalline phase, arising when the amount of vanadium increases (figure 1, spectra c–f). Other weak reflections, probably due to the presence of some impurities, are also detected. Indeed, $TeMo_5O_{16}$ or MoO_3 are observed as minor components, in samples with low (figure 1(c)) or high V-content (figure 1(f)), respectively.

The new TeVMoO crystalline phase (figure 1(d)–(f)) presents an XRD pattern similar to $Sb_4Mo_{10}O_{31}$ (JCPDS: 33-0104) and is formed at TeVMo atomic ratios of $1/x/1.7$ (with $x = 0.2$–1.5).

This new phase could correspond to one of the crystalline phases recently reported to be present in MoVTeNb catalysts. According to Aouine *et al.* [10], MoVTeNb catalysts are formed by two crystalline phases: (i) phase M1, isomorphous with $Sb_4Mo_{10}O_{31}$, of a stoichiometry of $Te_{0.33}MO_3$ (M = Mo, V, Nb); and (ii) phase M2, with a structure similar to that of $TeMo_5O_{16}$ or $Sb_2Mo_{10}O_{31}$, and a stoichiometry of $Te_{0.2}MO_{3.2}$ (M = Mo, V, Nb). According to our results, this new TeVMo phase, with a stoichiometry $Te_2V_xMo_{5-x}O_z$ [14], must be equivalent to the phase M1 [10], which probably crystallises in the hexagonal system with possible space groups P6mm, P6m2, P622 or P6/mmm.

In order to determine if Nb^{5+} ions can be involved in the formation of this new crystalline phase, TeNbMo (sample TNbM-1) and TeVNbMo (sample TVNbM-1) mixed oxides have been prepared by total and partial substitution of V by Nb. Figure 2 shows the XRD pattern of calcined Nb-containing samples.

The most intense peaks in the XRD pattern of sample TNbM-1, appearing at $2\theta = 22.2°$, 23.0°, 24.6°, 25.9°, 26.2, 27.5°, 30.2°, and 31.0°, indicate the formation of $3MoO_2{\cdot}Nb_2O_5$ (JCPDS18–840) (figure 2(a)), although the presence of minor amounts of $TeMo_4O_{13}$ (JCPDS, 34–622) cannot be completely ruled out. Therefore, it seems that Nb^{5+} ions are not directly involved in the formation of a TeNbMoO crystalline phase similar to that obtained in TeVMoO samples, probably because of the different size of V^{5+} and Nb^{5+} ions (0.54 and 0.64 Å, respectively).

The XRD pattern of sample TVNbM-1 (figure 2(b)) shows peaks at $2\theta = 22.1°$, 28.2°, 36.2°, 45.2° and 50.0°, characterizing the new TeVMoO crystalline phase described above. At this moment, it is difficult to establish if Nb^{5+} is incorporated, besides V^{5+}, in the M1-like phase. However, our results suggest that the incorporation of Nb^{5+} ions in the new structure, if it occurs, must be accompanied by the incorporation of V ions (probably occupying the same crystallographic positions) without apparent changes in the crystal structure.

Figure 3 shows the IR spectra of the calcined samples. The V-free sample (TM-0.5) shows bands at 991, 946, 900, 870, 775, 580 and 428 cm^{-1} (figure 3(a)). The bands at 991, 870, 813 and 583 cm^{-1} suggest the presence of MoO_3 [12–14]. The bands at 945 and 900 and a broad band at 650 cm^{-1} can tentatively be assigned to vitreous TeO_2-MoO_3 [13] which can explain the changes in the relative intensities of the XRD pattern of MoO_3.

The incorporation of vanadium modifies the IR spectra of the calcined samples. In catalysts with low V-content, *i.e.*, TVM-1 (figure 3(b)), bands centred at 920, 801, 710, 635, 578 and 435 cm^{-1} are observed. The bands at 920, 802, 704 and 640 cm^{-1} suggest the presence of $TeMo_5O_{16}$ [15] in agreement with the XRD results. The shift of some bands can tentatively be explained by the incorporation of V-atoms into the crystals.

New bands centred at 925–920, 848, 801, 778, 721, 580 and 450 cm^{-1} are observed in samples with higher V-content. The band at 848 cm^{-1}, whose intensity increases with the V-content, is probably related to the

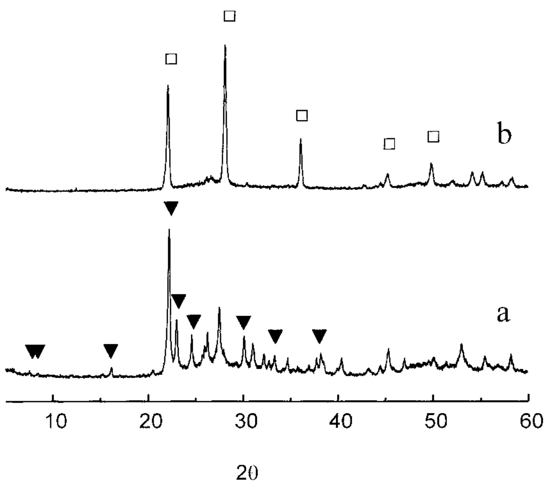

Figure 2. XRD patterns of Nb-containing catalysts: (a) TNbM-1; (b) TVNbM-1. Symbols: (▼) $3MoO_2{\cdot}Nb_2O_5$; (□) new TeVMo phase.

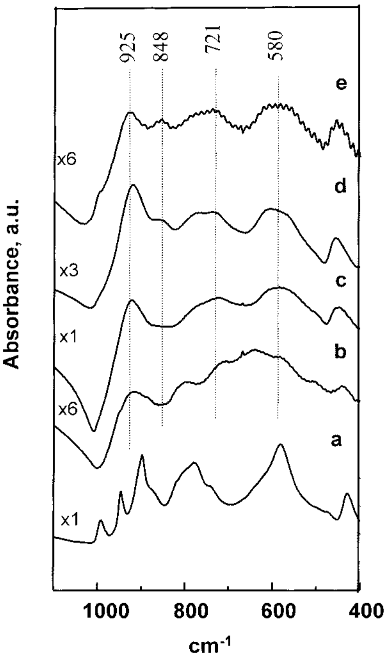

Figure 3. IR spectra of TeVMoO catalysts: (a) TM-0.5; (b) TVM-1; (c) TVM-2; (d) TVM-3; (e) TVM-4.

Table 2
Catalytic behaviour of TeVMoO-based catalysts during the selective oxidation of propene

Sample	T (°C)	W/F[a]	Conv., %	Selectivity, %				$\mathrm{STY}_{\mathrm{POP}}$[b]
				Acrolein	Acrylic acid	CO	CO_2	
TM-0.5	420	1640	1.9	89.9	—	2.3	6.3	58.3
TVM-1	420	1640	2.3	91.5	—	2.5	4.2	71.9
TVM-2	380	820	5.3	93.0	—	1.6	3.3	337
TVM-3	380	820	8.3	94.2	—	1.3	3.3	534
TVM-4	380	820	18.3	94.4	1.1	1.6	4.0	1198
TVM-5	380	820	8.7	92.0	1.8	1.7	4.5	561
TNbM-1	380	820	12.0	90.3	4.2	1.2	4.0	784
TVNbM-1	380	820	13.7	13.6	65.9	4.7	14.0	920
		1640	22.4	4.5	65.6	5.8	18.9	

[a] Contact time, W/F, in g_{cat} h $(\mathrm{mol}_{\mathrm{C3H6}})^{-1}$.

[b] Rate of formation of partial oxidation products (acrolein and/or acrylic acid) per unit mass of catalyst per unit time, $\mathrm{STY}_{\mathrm{POP}}$ (space time yield) in $g_{\mathrm{POP}}\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{h}^{-1}$, have been calculated at propene conversions <15%.

incorporation of V atoms into the crystals of the new M1-like structure. The shift of the other bands could be related to the distortion of the corresponding M–O bonds, after the incorporation of vanadium.

Besides the bands characteristic of the new phase, a shoulder at 990 cm^{-1} is also observed in sample TVM-5 (figure 3(e)) which must be associated with the formation of MoO_3. The segregation of MoO_3 at high V-content, suggests that this new crystalline phase is formed for a range of Mo/V atomic ratios.

3.2. Selective oxidation reactions

These materials were studied as catalysts in the selective oxidation of propane and propene. No propane transformation over TVM-series and TNbM-1 catalyst was observed during the oxidation of propane in the 380–420 °C temperature range and a contact time, W/F, of 2000 g_{cat} h $(\mathrm{mol}_{\mathrm{C3H8}})^{-1}$. For sample TVNbM-1, a propane conversion of 4.6% with a selectivity to propene of 65.7% was obtained at 420 °C and a W/F = 1640 g_{cat} h $(\mathrm{mol}_{\mathrm{C3H8}})^{-1}$. So, this new crystalline phase appears to have a very low activity in the propane activation.

Previously reported effective MoVTeNbO catalysts possess, generally, a Mo/Te atomic ratio higher than 4 [1–9], while the samples studied here have a Mo/Te atomic ratio of 2 (table 1). The lower Mo/Te atomic ratio, and the absence of other Mo-containing crystalline phases observed in active catalysts [1–9], may be the origin of the low paraffin activation power of the catalysts studied here.

Table 2 presents the catalytic behaviour of these materials in the selective oxidation of propene. Acrolein and/or acrylic acid, in addition to CO and CO_2, were mainly observed. However, both the catalytic activity and the selectivity to partial oxidation products depend on the catalyst composition. In fact, the incorporation of small amounts of vanadium to the TM-0.5 sample increases both the catalytic activity and the selectivity to acrolein, while acrylic acid was only observed on the catalyst with high V-content and at high propene conversions (figure 4).

Nb-containing samples, *i.e.*, TNbM-1 and TVNbM-1, are also active and selective in the oxidation of propene (table 1), although the formation of acrylic acid from propene is mainly observed on the TVNbM-1 catalyst. The importance of Nb^{5+} ions in the formation of acrylic acid during the oxidation of propane and propene on MoVTeNb catalysts has been recently proposed [5], but this effect appears to be important only if V is also present.

The formation rates of partial oxidation products (acrolein and/or acrylic acid) per unit mass of catalyst per unit time, $\mathrm{STY}_{\mathrm{POP}}$, are comparatively shown in table 2. Formation rates of partial oxidation products over 1200 $g_{\mathrm{POP}}\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{h}^{-1}$ keeping selectivities to acrolein close to 95% can be obtained in TeVMo catalysts (table 2). On the other hand, formation rates of partial oxidation products over 920 $g_{\mathrm{POP}}\,\mathrm{kg}_{\mathrm{cat}}^{-1}\,\mathrm{h}^{-1}$ keeping selectivities to acrylic acid close to 70% can be obtained in Nb-containing TeVMo catalyst.

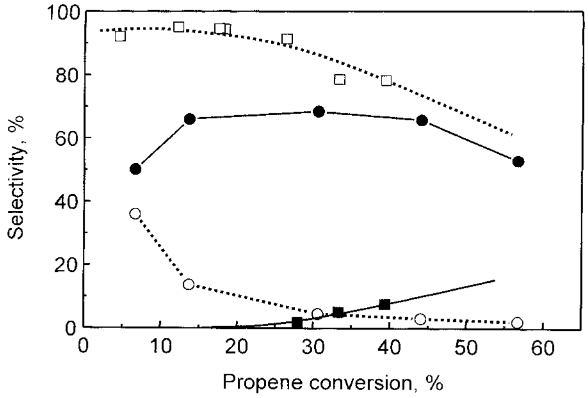

Figure 4. Variation of the selectivities to acrolein (○, □) and acrylic acid (●, ■) obtained during the oxidation of propene on TVM-4 (□, ■) or TVNbM-1 (●, ○) catalysts. Experimental conditions in table 2.

According to these results, acrolein is selectively formed from propene on the new TeVMoO crystalline phase. This reaction probably occurs on Mo-sites, although the selectivity to acrolein is enhanced by the presence of Te ions [16–18]. Moreover, the incorporation of V ions in the TeVMoO phase strongly increases the formation rate of acrolein (table 2). So, the catalytic behaviour of TeVMoO phases could be related to the changes in the crystalline structure but also to the acid and/or redox properties of the Mo-Te-O catalyst in a similar way as in $Bi_{1-x/3}V_{1-x}Mo_xO_4$ catalysts [19]. In this way, a cooperation of diverse active sites (site cooperation) should be considered [20].

Ushikubo *et al.* [9] proposed that the oxidation and ammoxidation of propane could be explained by the presence of two phases: one active in the propane activation (forming propene) (named M1) and other active and selective in the formation of acrylic acid or acrylonitrile (named M2) [9]. According to this mechanism proposed by Ushikubo *et al.* [9], our new TeVMo crystalline phase should be related to phase M2. However, the stoichiometry of this TeVMo crystalline phase corresponds to that of phase M1 ($Te_{0.33}MO_3$) proposed by Aouine *et al.* [10]. So, a revision of the assignment of the crystalline phases in MoVTeNb catalysts appears to be necessary.

In conclusion, a new ternary TeVMo oxide crystalline phase has been synthesised, for the first time, by calcination at 600 °C in N_2 of solids with Mo/Te/V atomic ratios of $2/1/x$ ($x = 0.5$–2.0). This crystalline phase presents an XRD pattern similar to $Sb_4Mo_{10}O_{31}$ and corresponds probably to the M1 phase recently proposed by Aouine *et al.* [10] in MoVTeNbO catalysts. Accordingly, a tentative stoichiometry can be proposed: $Te_2V_xMo_{5-x}O_z$.

The catalytic tests indicate that these catalysts are not active in the oxidation of propane but they are active and selective in the oxidation of propene to acrolein and/or acrylic acid, giving a product distribution which depends on the composition of the catalysts. Acrolein is mainly formed in TeVMoO (and also on TeNbMoO) catalysts while acrylic acid is selectively formed, at relatively low propene conversion, on the multicomponent Te-V-Nb-Mo-containing catalysts. Although both the TeVMo- and the TeVNbMo-containing catalysts presented here show a similar crystalline structure, the different catalytic behaviour in the formation of acrylic acid could be related to the simultaneous presence of both Nb and V ions.

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