

Selective oxidation of propene to acrolein on Mo-Te mixed oxides catalysts prepared from ammonium telluromolybdates

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Abstract

$(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24}\cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ telluromolybdates have been prepared by using a solution reaction and a hydrothermal synthesis, respectively. They have been decomposed in the presence of air or N_2 in order to achieve mixed metal oxides to be used as catalysts in the selective oxidation of propene. Both the characterisation and the catalytic results suggest important differences in the catalysts depending on the starting material and the calcination conditions. In this way, active and selective catalysts for the oxidation of propene to acrolein have been obtained by using $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ (prepared by hydrothermal synthesis) as starting material. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tellurium-containing catalysts are effective in the gas phase selective oxidation of hydrocarbons [1–9]. This catalytic behaviour has been related to its redox properties. The greatest drawback of using tellurium-containing catalysts is its volatility, especially in their lowest oxidation states. However, the volatility can be partially resolved by incorporating it in the lattice of the catalysts.

Several crystalline phases have been reported in the Mo–Te–O system, which depend on the chemical composition, the preparation procedure or calcination conditions [10–14].

Although they are generally obtained by solid-state reaction of mixed metal oxides [1–14], they could also be prepared by decomposition of telluromolybdates.

Thus, substitutive telluromolybdates $\text{M}^{2+}\text{Te}^{6+}_y\text{Mo}_{1-y}\text{O}_4$ and additive telluromolybdates $\text{M}^{2+}\text{Te}^{4+}\text{MoO}_6$ ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}, \text{Zn}, \text{Cu}$) can be obtained by the decomposition of the corresponding salts of the hexamolybdotelluric(VI) acid [14]. In this case, TeO_2 can be formed during the decomposition of the $\text{TeMo}_6\text{O}_{24}^{6-}$ polyanion structure with a partial or total reduction of Te^{6+} to Te^{4+} [14].

Mo-Te mixed oxides could also be obtained by the decomposition of heteropolycompounds. This is the case of Anderson-type $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24}$, a Te(VI)-containing compound [15,16], or $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ [17], a Te(IV)-containing compound. In the first case, the $(\text{TeMo}_6\text{O}_{24})^{6-}$ heteropolyanion can be described from the $(\text{Mo}_7\text{O}_{24})^{6-}$, of the C_{2v} symmetry, substituting the central Mo atom for Te(VI) in a planar configuration, leading to D_{3d} symmetry [15]. So, the TeO_6 central octahedron is surrounded by six MoO_6 octahedra (Fig. 1a) [16].

The $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ is, however, a one-dimensional structure containing linear chains of

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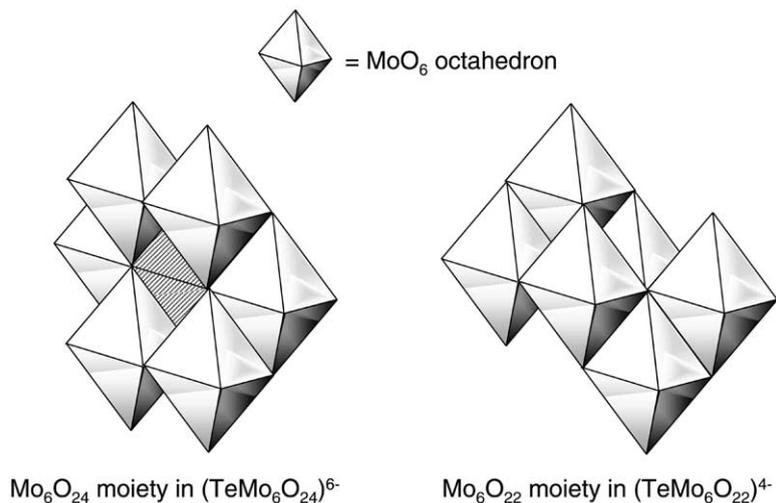


Fig. 1. Structure of telluromolybdates: (a) Mo₆O₂₄ moiety of (NH₄)₆Mo₆TeO₂₄ (the TeO₆ octahedron is shaded); (b) Mo₆O₂₂ moiety of (NH₄)₄Mo₆TeO₂₂·2H₂O (the position of the TeO₄ tetrahedron is commented in text).

(Mo₆TeO₂₂)⁴⁻ anions parallel to one other and held together by NH₄⁺. In this case, every of these (Mo₆TeO₂₂)⁴⁻ contents six fused MoO₆ octahedra connected to Te(IV) ions through O-bridges (Fig. 1b) [17].

It is clear that these heteropolyacids can be transformed into mixed metal oxides. However, the nature of crystalline phases strongly depends on the calcination conditions.

The aim of this paper is to study both the decomposition of Te(IV)- or Te(VI)-containing telluromolybdates and the catalytic behaviour of the resulting mixed metal oxides. In this way, (NH₄)₆TeMo₆O₂₄·7H₂O, prepared from solution reaction of ammonium heptamolybdate and H₆TeO₆, and (NH₄)₄TeMo₆O₂₂·2H₂O, prepared hydrothermally from aqueous solution of ammonium heptamolybdate and TeO₂, have been studied as precursors of catalysts in the gas phase partial oxidation of propene.

2. Experimental

2.1. Preparation of catalyst precursors and catalysts

Mo-Te mixed oxides catalysts have been obtained by calcination of different telluromolybdates. In this way, two telluromolybdates have been prepared by

applying a solvent evaporation or a hydrothermal method according to different procedures previously proposed. The (NH₄)₆Mo₇O₂₄·4H₂O (Merck) and Te(OH)₆ (Aldrich) or paratellurite TeO₂ (Aldrich) were used as starting materials.

(NH₄)₆TeMo₆O₂₄·nH₂O was obtained by a solution reaction of an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and H₆Te(OH)₆ (with a Mo/Te molar ratio of 6/1) at pH = 7.5 and 80 °C, according to the preparation procedure previously reported [15,18]. The mixture was left till water was completely removed. Colourless crystals were obtained after dried at 80 °C overnight. This sample will be named as SL.

(NH₄)₄TeMo₆O₂₂·2H₂O was obtained by hydrothermal synthesis with a gel having the following composition: (NH₄)₆Mo₇O₂₄·4H₂O/TeO₂/H₂O molar ratio of 1/1.6/137.32 [17]. The gel was autoclaved in a Teflon-lined stainless steel reactor at 175 °C during 4 days and then, the resulting material precursor was obtained after filtered, washed with distilled water and dried at 60 °C for 24 h. The sample will be named as HT.

The catalysts have been obtained by calcination of telluromolybdates under flowing N₂ (100 ml min⁻¹) or under flowing air (100 ml min⁻¹). The calcination was carried out with a heating rate of 3 °C min⁻¹. The final calcination temperature was 600 °C for 2 h or 500 °C for 2 h. The samples will be named as

Table 1
Preparation procedure and characteristics of telluromolybdates

Sample	Method	<i>T</i> (°C)	Time (days)	Te source	Mo/Te atomic ratio ^a	Major phase	Crystal shape (μm)	Other phases
SL	Slurry	80	–	H ₆ TeO ₆	6/1	(NH ₄) ₆ TeMo ₆ O ₂₄ ·7H ₂ O	Small blocks (0.5–1)	–
HT	Hydrothermal	175	4	TeO ₂	6/1	(NH ₄) ₄ TeMo ₆ O ₂₂ ·2H ₂ O	Needles (8–12) × (1–2)	Hexagonal

^a Nominal as-made composition.

SL-*X*-*Y* or HT-*X*-*Y* if they were prepared by slurry or hydrothermal method, respectively, in which *X* indicates the final calcination temperature (500 or 600 °C) and *Y* indicates the gas used during the calcination step (*A* = Air and *N* = N₂). In this way, the sample SL-600-N is a catalyst obtained from sample SL, (NH₄)₆TeMo₆O₂₄·7H₂O, calcined in N₂ at 600 °C. The preparation procedures and characteristics of as-synthesised telluromolybdates and calcined samples are shown in Table 1.

For comparative purpose, MoO₃ was obtained from (NH₄)₆Mo₇O₂₄·4H₂O by calcination at 500 °C for 4 h.

2.2. Catalyst characterisation

Quantitative analysis of the prepared solids was obtained by atomic absorption spectrophotometry after dissolution in an acid solution.

The specific surface areas of the catalysts were obtained in an ASAP 2000 apparatus, using the BET method from the nitrogen adsorption isotherms. The samples were previously degassed at 150 °C for 1 h.

X-ray diffraction (XRD) patterns were collected using a Phillips X'Pert-MPD diffractometer provided with a copper monochromator, operating at 40 kV and 20 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 205xB spectrophotometer, equipped with a Data Station, at a spectral resolution of 1 cm⁻¹ and accumulations of 128 scans.

Scanning electron microscopy (SEM) and EDX microanalyses were performed on a JEOL JSM 6300 link Isis Instrument. The quantitative EDX analysis was performed using an Oxford Link ISI System with the SEMQUANT program, which introduces the ZAF correction.

2.3. Catalytic tests

The catalytic test for the gas phase selective oxidation of propene have been carried out in a fixed bed quartz tubular reactor (16 mm i.d.; 500 mm length) equipped with a coaxial thermocouple for temperature profiles. All the experiments were carried out using a propene/oxygen/helium/water molar ratio of 2/8/80/10 and a total flow of 100 ml min⁻¹. On the other hand, different amounts of catalyst have been used in order to obtain different contact times, W/F (g_{cat} h mol_{C₃}⁻¹), and propene conversions. Analysis of reactants and products were carried out by gas chromatography, using two column types: (i) Porapak Q (3.0 m × 1/8 in.); (ii) molecular sieve 5A (1.5 m × 1/8 in.).

Blank runs in the temperature interval 330–450 °C were carried out substituting the catalyst by SiC, at the low total flow used (100 ml min⁻¹) in the present study. In our reaction conditions, the presence of homogeneous reaction can be neglected.

3. Results and discussion

3.1. Synthesis and characterisation of telluromolybdates

The XRD patterns of the as-synthesised samples are shown in Fig. 2. The XRD pattern of sample SL confirms the formation of (NH₄)₆TeMo₆O₂₄·7H₂O (Fig. 2a) [18]. We must point out that, in this case, the XRD pattern concerns to partially dehydrated samples, as the temperature of crystallisation is over the release of the compositional water molecules of these compounds. Moreover, a relative loss of its crystallinity can be associated with this process [18].

The XRD pattern of sample HT (Fig. 2b) confirms that Te⁴⁺ ions have been incorporated in the solid forming (NH₄)₄TeMo₆O₂₂·2H₂O, in agreement to the

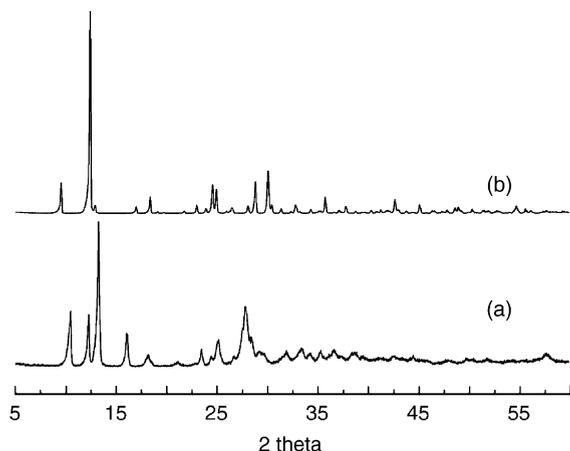


Fig. 2. XRD patterns of as-synthesised samples: (a) SL; (b) HT.

results previously reported [17]. TeO_2 is usually insoluble in water but it can be dissolved in hydrothermal conditions favouring a fast incorporation in the molybdate structure. However, the presence of a small amount of TeO_2 cannot be discarded.

Fig. 3 shows the IR spectra of as-synthesised materials. Broad bands around $3579\text{--}3417\text{ cm}^{-1}$ could be assigned to asymmetric and symmetric

O–H stretching modes of lattice water whereas the bands around $1668\text{--}1590\text{ cm}^{-1}$ can be ascribed to the H–O–H bending modes [13,17,18]. The peaks in the $3203\text{--}3011\text{ cm}^{-1}$ range and those around $1441\text{--}1393\text{ cm}^{-1}$ are due to the symmetric and asymmetric stretching vibrations of the tetrahedral ammonium cation [17,18]. The sharp peaks detected in the range $933\text{--}902$, $883\text{--}877$, $858\text{--}852$ and 557 cm^{-1} correspond to Mo–O vibrations [13,19,20], while the peaks around $753\text{--}641\text{ cm}^{-1}$ can be due to the Mo–O, Te–O and Mo–O–Te vibrations, since the different bands of these vibrations overlap in this range [13,20,21]. Finally, the band at $615\text{--}612\text{ cm}^{-1}$ observed in sample SL is assigned to the water libations [21].

Fig. 4 shows the SEM micrographs of pure telluromolybdates. Small block-like crystals, colourless, of $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24}\cdot 7\text{H}_2\text{O}$ were obtained from sample SEM micrographs of sample SL (Fig. 4a). On the other hand, colourless needle-like crystals of $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ were obtained by hydrothermal synthesis (Fig. 4b).

The results presented here clearly indicate the presence of high purity compounds in the as-synthesised samples. The different synthesis attempts let us to prepare two different telluromolybdates in which Te ions present different oxidation states. However, the

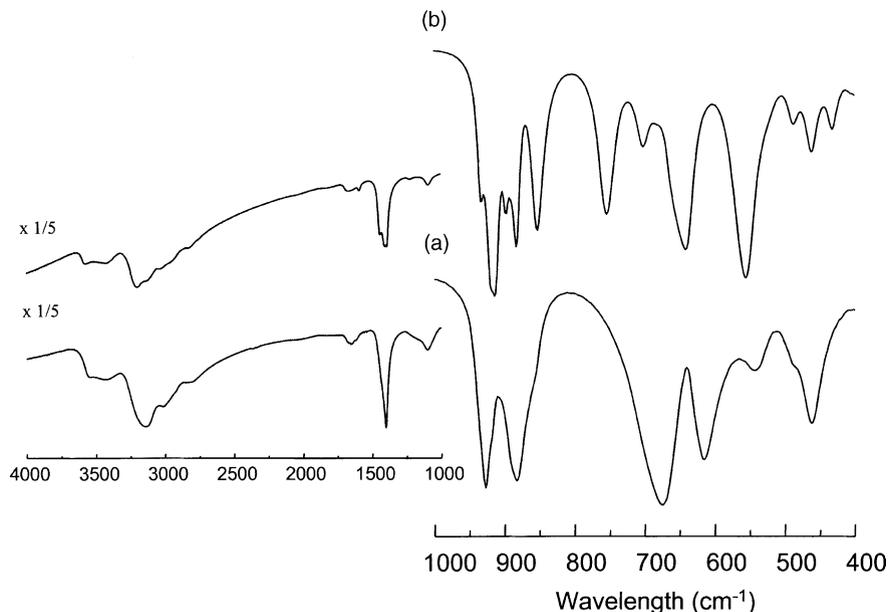


Fig. 3. IR spectra of as-synthesised samples: (a) SL; (b) HT.



Fig. 4. SEM micrographs of as-synthesised samples: (a) SL; (b) HT.

synthesis depends on the starting materials. In this way, we can inform that no telluromolybdates were achieved when the hydrothermal synthesis was carried out with telluric acid instead of tellurium dioxide.

3.2. Characterisation of samples calcined in N_2

After calcination at 600°C , the samples present surface areas of $0.7\text{--}1.0\text{ m}^2\text{ g}^{-1}$ (Table 2). On the other

hand, the Mo/Te atomic ratios change after calcination. So, if HT and SL samples present Mo/Te atomic ratios of 4.9 and 5.8, respectively, the corresponding samples calcined at 600°C present Mo/Te atomic ratios of 5.4 and 6.1, respectively. In this way, we can inform that a loss of tellurium is observed in the reactor after the calcination.

Fig. 5 presents the XRD patterns of samples calcined in N_2 at 500 or 600°C . In all cases, MoO_3

Table 2
Characteristics of Mo-Te-O mixed oxide catalysts

Sample	Calcination conditions		Mo/Te molar ratio	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Crystalline phases
	T ($^{\circ}\text{C}$)	Atmosphere			
SL-600-N	600	N_2	5.4	0.8	$\text{MoO}_3 > \text{TeMo}_5\text{O}_{16} > \alpha\text{-TeMo}_4\text{O}_{13}$
HT-600-N	600	N_2	6.1	1.0	$\text{TeMo}_5\text{O}_{16} > \alpha\text{-TeMo}_4\text{O}_{13} > \text{MoO}_3$
SL-500-A	500	Air	5.8	0.8	$\text{MoO}_3, \text{TeO}_2^{\text{a}}, \text{TeO}_2\text{-MoO}_3^{\text{a}}$
HT-500-A	500	Air	4.9	0.8	$\text{MoO}_3, \text{TeO}_2, \text{TeO}_2\text{-MoO}_3$

^a The formation of these crystalline phases was only observed in the catalyst after the catalytic test.

(JCPDS 5-508) and $\text{TeMo}_5\text{O}_{16}$ (JCPDS 31-874) have been the main crystalline phases, although the relative amount of each phase depends on the starting telluromolybdates and the calcination temperature. In addition to these, $\alpha\text{-TeMo}_4\text{O}_{13}$ (JCPDS, 31-1372 and 34-0622) is also formed.

On the other hand, small differences between the XRD patterns of samples calcined at 500 and 600 $^{\circ}\text{C}$ were observed, although those calcined at high temperature presented higher crystallinities but lower surface areas.

In order to compare the distribution of the crystalline phases in calcined samples, the $\text{TeMo}_5\text{O}_{16}/\text{MoO}_3$ ratio has tentatively been determined from the intensities to the more important reflections of each

crystalline phase, i.e. [3 0 0] in $\text{TeMo}_5\text{O}_{16}$ and [0 2 1] in the MoO_3 . The results of Fig. 5 indicate that the $\text{TeMo}_5\text{O}_{16}/\text{MoO}_3$ ratio changes from 3.5 in sample HT-600-N to 1.0 in sample SL-600-N. Smaller differences in the $\text{TeMo}_5\text{O}_{16}/\text{MoO}_3$ ratio were observed in samples calcined at 500 $^{\circ}\text{C}$. Thus, $\text{TeMo}_5\text{O}_{16}/\text{MoO}_3$ ratios of 1.3 and 1.1 were achieved for samples HT-500-N and SL-500-N, respectively.

Fig. 6 shows the IR spectra of samples calcined in N_2 . The bands at 920, 802, 704 and 640 cm^{-1} with a shoulder at 765 cm^{-1} suggest the presence of $\text{TeMo}_5\text{O}_{16}$ [15,18], while the bands at 993, 870, and 583 cm^{-1} suggest the presence of MoO_3 [12,13,19]. In addition to these, bands at 980 and 950 cm^{-1} have also been observed. They could be associated to the

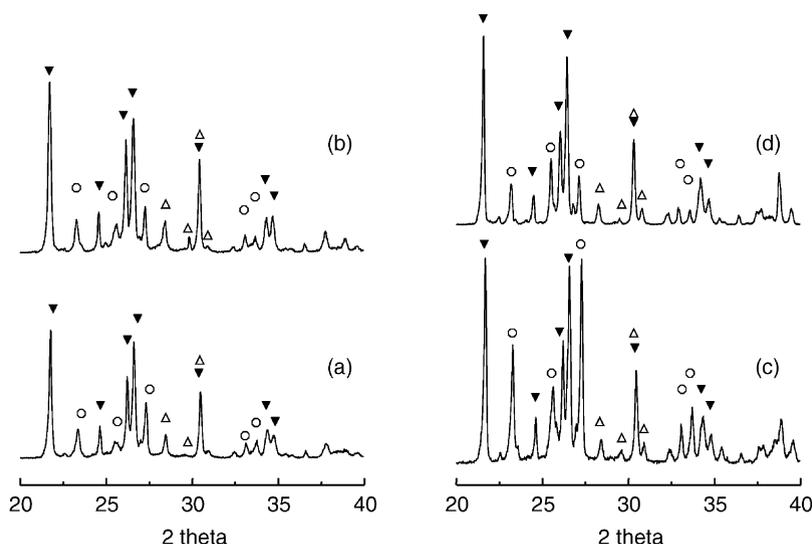


Fig. 5. XRD patterns of samples calcined in N_2 : (a) SL-500-N; (b) SL-600-N; (c) HT-600-N; (d) HT-500-N. Symbols: (○) MoO_3 ; (▼) $\text{TeMo}_5\text{O}_{16}$; (Δ) $\text{TeMo}_4\text{O}_{13}$.

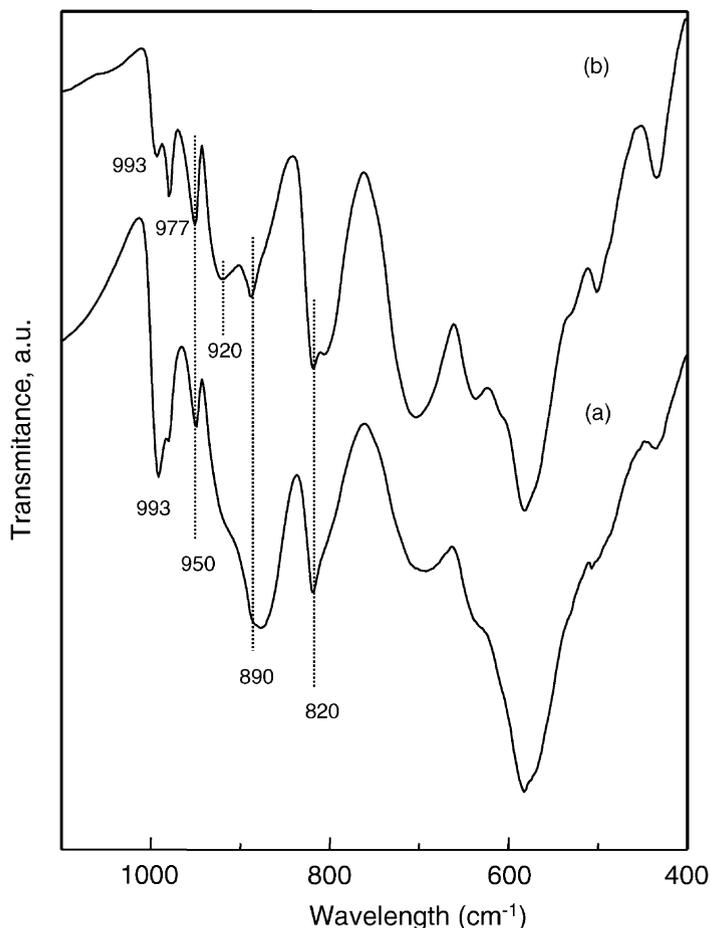


Fig. 6. IR spectra of samples calcined at 600 °C in N₂: (a) SL-600-N; (b) HT-600-N.

presence of α -TeMo₄O₁₃. In fact, the IR spectrum of α -TeMo₄O₁₃ presents two bands at 928 and 952 cm⁻¹ with two shoulders at 890 and 980 cm⁻¹ [10].

It has been proposed that Mo₄O₁₁ and/or related oxides can be formed in a first step during the decomposition of (TeMoO₂₄)⁶⁻ anions and it is stabilised at about 500 °C [18]. However, Mo₄O₁₁ was not observed by XRD in our samples.

A partial reduction of molybdenum and tellurium ions can occur during the calcination of telluromolybdates in N₂, as a consequence of different complex redox interactions in the Te–Mo–O system [10,18]. As a result of this, mixed-valence species like TeMo₅O₁₆ (with overall oxidation state of 5.6 for molybdenum) and TeMo₄O₁₃ (with overall oxidation state of 5.5 for molybdenum), in addition to Te metal, are formed

[10]. In fact, Te(VI)-containing heteropolyanions present a strong reduction of Te(VI) ions to the Te(IV) and Te⁰ [18]. However, they can react with MoO₃ or MoO₂ forming TeMo₅O₁₆. Although Te reduction should be expected to occur above 600 °C, the presence of NH₃ has a mild reducing effect decreasing the reduction temperature [22]. On the other hand, sublimation of MoO₃ occurs at temperatures about 600 °C. So, the relative amount of Mo and Te in the calcined material could be modified by the loss of Te and/or Mo metal. The results of Table 2 indicate a Mo/Te atomic ratio in calcined samples higher than those obtained in the as-synthesised samples.

Tellurite Te(IV) from sample HT decomposes also during the calcination step. In fact, although MoO₃ is mainly formed if the calcination in N₂ is carried out

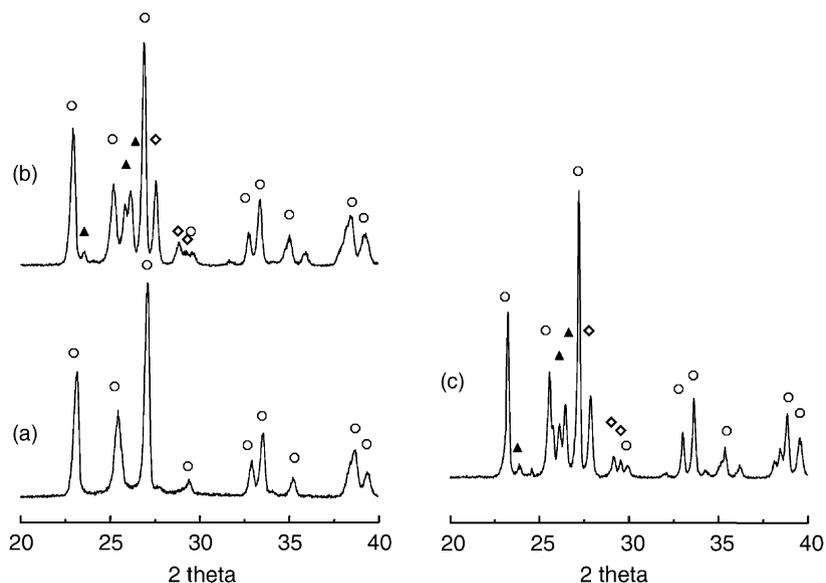


Fig. 7. XRD of samples calcined at 500 °C in air: (a) SL-500-A; (b) HT-500-A; (c) SL-500-A after its use in the catalytic tests. Symbols: (○) MoO₃; (◇) TeO₂; (▲) Te₂MoO₇.

at 400 °C [17], the results present here suggest that the formation of TeMo₅O₁₆ and/or TeMo₄O₁₃ phase could be favoured at higher reaction temperatures.

On the other hand, a partial reduction of Mo and/or Te is achieved during the calcination step of sample SL, especially in the presence of ammonia. Thus, the formation of TeMo₅O₁₆ and/or TeMo₄O₁₃ (especially α -TeMo₄O₁₃) from Te(VI)-containing compounds requires a first reduction step of Te(VI) ions, which could be carried out at about 500 °C [10,18].

3.3. Characterisation of samples calcined in air

After calcination in air, the samples presented surface areas lower than 1.0 m² g⁻¹ (Table 2). On the other hand, Mo/Te atomic ratios of 5.8 and 4.9 were obtained for samples SL-500-A and HT-500-A, respectively.

Fig. 7 shows the XRD patterns of samples calcined in air at 500 °C. The XRD pattern of sample SL-500-A indicates the presence of MoO₃ (JCPDS, 5-508) (Fig. 7a). No crystalline Te-containing phases were observed in this case. However, the XRD pattern of β -Te₂MoO₇ is characterised by the appearance of a broad peak centred at $d = 3.33$ Å ($2\theta = 26.7$)

[11]. Thus, the presence of this low-crystalline phase should also be considered.

On the other hand, MoO₃ and TeO₂ (JCPDS 41-945) have been observed in the XRD pattern of sample HT-500-A (Fig. 7b). However, the presence of Te₂MoO₇ (JCPDS 30-1339) cannot be ruled out. The different XRD patterns in Fig. 7 could be a consequence of the different initial oxidation state of Te ions in each sample.

IR spectra of samples calcined in air are shown in Fig. 8. The appearance of bands at 993, 865, 820 and 583 cm⁻¹ suggest the presence of MoO₃ in sample SL-500-A (Fig. 8a). In fact, this sample shows an IR spectrum similar than pure MoO₃ (Fig. 8b), although the bands at 865 and 583 cm⁻¹ in MoO₃ appear at 885 and 648, respectively, in sample SL-500-A. The shift of the band at 583 cm⁻¹ to higher frequencies in the spectrum of Mo-Te-O catalysts has been related to the formation of TeO₂-MoO₃ solid solutions [3].

In addition to these bands, new bands can be observed in the IR spectrum of sample HT-500-A (Fig. 8c). The bands at 760, 710 and 648 cm⁻¹ corresponds to α -TeO₂ while the bands at 945 and 900 and a broad band at 650 cm⁻¹ can tentatively be assigned to vitreous TeO₂-MoO₃ [13]. This indicates that Te

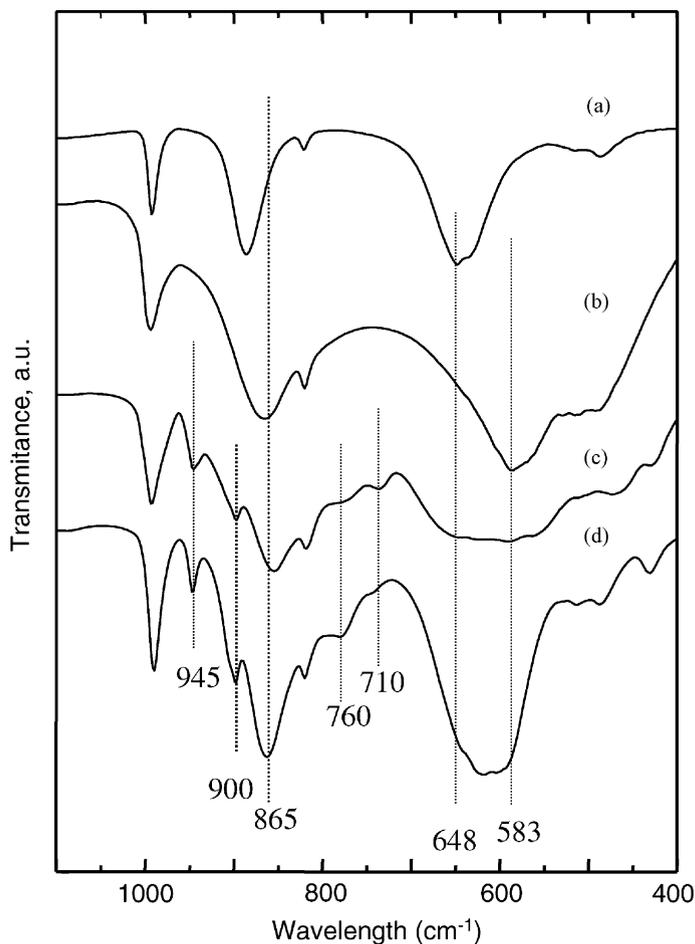


Fig. 8. IR spectra of samples calcined at 500 °C in air: (a) SL-500-A; (b) MoO₃; (c) HT-500-A; (d) SL-500-A sample after its use in the catalytic tests.

ions could be incorporated in the molybdate structure most easily than in sample SL-500-A.

Dimitriev et al. [13] report that glasses on the TeO₂–MoO₃ system are characterised by a broad maximum around 640–670 cm⁻¹ and two high frequencies in the range of 900–870 and 980–935 cm⁻¹. On the other hand, vitreous Te₂MoO₇ presents an IR spectrum with bands at 945 and 900 cm⁻¹ while they are observed at 910 and 860 cm⁻¹, respectively, in the crystalline Te₂MoO₇ phase [13]. For this reason, the presence of crystalline Te₂MoO₇, with bands at 910 and 862 cm⁻¹ cannot be discarded.

Melts of the binary TeO₂–MoO₃ system becomes to the glassy state in a wide molar ratio of both

components [11,13], while the formation of TeMo₅O₁₆ phase is inconsistent with the calcination in air [14]. Thus, it appears that the crystallisation of tellurium phases becomes harder in a large excess of molybdenum, especially if Te(VI)-containing compounds are used.

According to Bart et al. [11], it might be expected that the compound 2TeO₂·MoO₃ would be formed in the course of decomposition. The 2TeO₂·MoO₃ may exist in a glassy modification, which cannot be detected by X-ray method [11,14]. However, IR spectroscopy results indicate the presence of vitreous Te–Mo–O, as minority phase, in the sample SL-500-A only after its use in the catalytic test (Fig. 8d).

In order to determine the catalyst stability, the samples used in the catalytic tests were also studied by XRD. We must inform that no changes were observed in sample HT-500-A before and after the catalytic test. However, important differences were observed in the case of sample SL-500-A. The XRD pattern of samples SL-500-A before and after the catalytic test is presented in Fig. 7a and c, respectively. It can be seen that after the catalytic test this sample was transformed presenting a XRD pattern similar to that obtained with the sample prepared by hydrothermal synthesis (Fig. 7b).

Te^{6+} species are mainly present in sample SL while Te^{4+} species are present in sample HT. So, vitreous $\text{TeO}_2\text{-MoO}_3$ could directly be formed during the calcination if the catalysts are prepared by hydrothermal synthesis. However, a reduction of Te^{6+} ions to Te^{4+} ions is required before the formation of vitreous $\text{TeO}_2\text{-MoO}_3$ from samples obtained from $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24}\cdot n\text{H}_2\text{O}$ (samples prepared by a solution reaction). The final reduction of Te^{6+} to Te^{4+} is probably completed, in the last case, during the catalytic test.

Some transformations during the catalytic tests have also been reported in $\alpha\text{-Te}_2\text{MoO}_7$ -containing catalysts [5]. In this case, partial reduced crystalline phases, i.e. TeMo_5O_6 and Te, in addition to $\alpha\text{-Te}_2\text{MoO}_7$ were observed in tested samples. So, the high Mo/Te ratio in our case can favour the crystallisation of

tellurites phases during the cooling step. Furthermore, the re-calcination of the yellow vitreous form obtained from sample SL-500-A could regenerate a crystalline TeMoO phase [7]. This is not observed in our case, although the presence of Te_2MoO_7 cannot be completely ruled out from the IR results. However, crystalline phases with partially reduced Mo species were not observed after the catalytic tests. Probably, the high concentration of MoO_3 can stabilise the oxidation state of Te species.

3.4. Selective oxidation of propene on Mo-Te-O mixed oxide catalysts

Table 3 presents the catalytic behaviour in the selective oxidation of propene of calcined samples. From a comparative purpose, the catalytic results obtained on MoO_3 are also included. Acrolein CO and CO_2 were the main reaction products, although partial oxidation products (i.e. acetone and acrylic acid) were also observed. Acetone was observed at low reaction temperatures and low propene conversions, while acrylic acid was observed at high reaction temperature and high propene conversions. From the results of Table 3, it can be concluded that all of the catalysts are active and selective in the formation of acrolein although their catalytic behaviour depends on the catalyst precursor and the calcination procedure.

Table 3
Catalytic behaviour in the selective oxidation of propene of Mo-Te-O mixed oxides

Catalyst	W/F ^a	T (°C)	Conversion (%)	Selectivity (%) ^b					STY _{C₃H₄O} (g kg _{cat} ⁻¹ h ⁻¹) ^c
				ACROL	ACET	AA	CO	CO ₂	
SL-500-N ^d	615	380	29.3	75.3	5.6	–	5.6	13.5	20.1 ^c
SL-600-N	615	450	19.6	95.3	–	t	1.5	3.2	16.9
HT-500-N ^d	615	380	60.8	56.2	14.9	–	11.9	17.0	31.1 ^d
HT-600-N	900	450	19.8	94.8	–	t	1.4	3.8	11.7
SL-500-A	2050	400	7.6	95.8	0.6	–	1.4	2.2	
		450	10.6	91.4	–	1.1	1.9	5.6	2.9
HT-500-A	1230	400	27.8	97.0	–	t	0.9	2.1	
		425	40.3	94.9	–	1.2	1.1	2.8	18.4
MoO ₃	400	450	27.6	40.2	–	t	25.0	34.8	15.5

^a Contact time, W/F, in g_{cat} h mol_{C₃}⁻¹.

^b Selectivity to acrolein (ACROL), acetone (ACET), acrylic acid (AA), CO and CO₂; t = traces.

^c Rate of formation of acrolein per unit mass of catalyst per unit time, STY_{C₃H₄O} (space time yield) in g kg_{cat}⁻¹ h⁻¹, have been calculated at a propene conversion of about 30%.

^d The catalytic results were obtained after 2 h of time on stream (a catalyst decay was observed in this case).

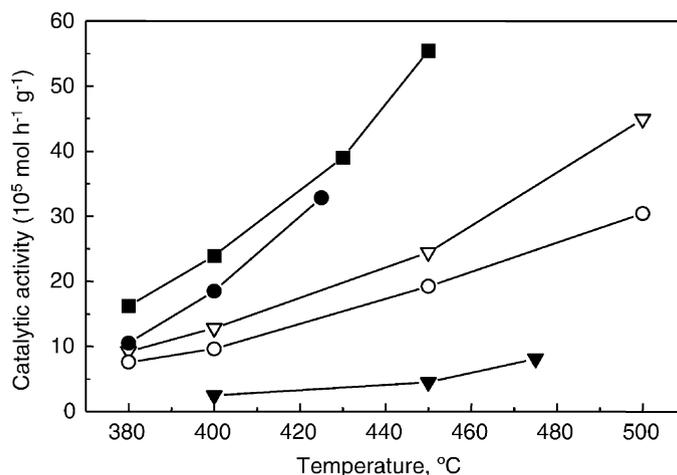


Fig. 9. Variation of the catalytic activity with the reaction temperature obtained during the oxidation of propene over Mo-Te-O mixed oxides. Experimental conditions in Table 3. Symbols: (■) MoO₃; (●) HT-500-A; (▽) SL-600-N; (○) HT-600-N; (▼) SL-500-A.

Fig. 9 shows the variation of the catalytic activity (in $10^5 \text{ mol}_{\text{C}_3} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$) with the reaction temperature. It can be seen that the catalytic activity decreases as: MoO₃ > HT-500-A > SL-600-N > HT-600-N > SL-500-A. So, the calcination procedure has a clear influence on the catalytic activity. The calcination in air favours the formation of a vitreous $x\text{TeO}_2\text{-MoO}_3$ phase, in addition to MoO₃, presenting a high activity, as occurs in sample HT-500-A. However, the

calcination in N₂ leads to catalysts with a lower catalytic activity in which TeMo₅O₆/MoO₃ are the main crystalline phases.

Fig. 10 presents the variation of the selectivity to acrolein with the propene conversion in the 400–450 °C temperature range. It can be seen that the selectivity to acrolein decreases as follow: HT-500-A > HT-600-N > SL-600-N > SL-500-A > MoO₃. The use of a hydrothermal synthesis favours the

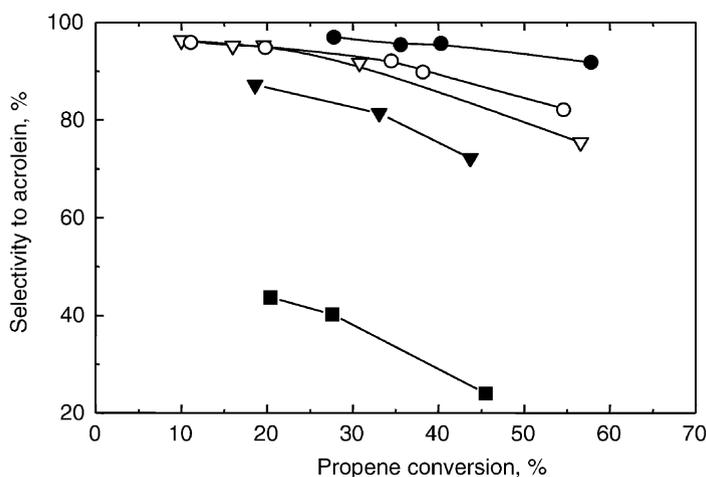


Fig. 10. Variation of the selectivity to acrolein with the propene conversion obtained during the oxidation of propene at 400–450 °C on Mo-Te-O mixed oxides. Experimental conditions as in Table 3. Symbols as in Fig. 9.

achievement of catalysts with selectivities to acrolein higher than those obtained on the catalysts prepared by slurry method.

On the other hand, the catalysts calcined in N₂ present selectivities to acrolein higher than the corresponding samples calcined in air. Since mixed TeMo₅O₆/MoO₃ are mainly observed in these catalysts, it can be concluded that TeMo₅O₆ is also a selective phase in the oxidation of propene to acrolein. However, the catalyst stability of samples calcined in N₂ depends on the calcination temperature. For this reason, these materials must be calcined at temperatures about 600 °C in order to achieve catalysts with high stability, although the catalysts present low surface areas.

An excess of MoO₃ has been observed in all samples. However, it is known that the presence of excess of MoO₃ (metal-molybdate/MoO₃) can contribute to obtain higher catalyst stability, increasing the selectivity to partial oxidation products during the oxidation of C₃–C₄ olefins [2–5,23–26]. So, telluromolybdates with high Mo/Te ratio could be used as starting materials to obtain selective catalysts in the oxidation of propene to acrolein.

4. Conclusions

From the results presented in this paper it can be concluded that telluromolybdates can be used as precursors of oxidation catalysts, especially for the partial oxidation of propene to acrolein. However, both the preparation of the telluromolybdate precursor and the calcination conditions strongly influence the nature of crystalline phases, the catalyst stability and the catalytic behaviour of these materials in the selective oxidation of propene to acrolein.

In agreement with other authors [1–6], MoO₃ is active but presents a low selectivity in the propene oxidation to acrolein. However, the incorporation of tellurium increases the selectivity to acrolein although decreases the catalytic activity. In this way, TeO₂–MoO₃ solid solution or TeMo₅O₆/MoO₃ containing catalysts appears to be selective in the oxidation of propene to acrolein. These can be prepared from telluromolybdates by calcination in air or in N₂, respectively. So, a new preparation procedure has been presented here.

On the other hand, similar rates of acrolein formation per unit mass of catalyst per unit time, STY_{C₃H₄O}, have been obtained with and without Te in the catalysts but the selectivity to acrolein increases in Te-containing catalysts.

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