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Selective oxidation of propane and propene on MoVNbTeO catalysts Effect of chemical composition in catalysts prepared by slurry

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Abstract

Mo-V-Te and Mo-V-Te-Nb mixed oxide catalysts, with different Mo/Te, Mo/V and Mo/Nb atomic ratios have been prepared from aqueous solutions of the corresponding salts, dried at 120 °C and heat-treated at 600 °C for 2 h in a N_2 stream. They have been characterised by several physico-chemical techniques (AAS, S_{BET}, XRD, DRS-UV-Vis) and tested in the selective oxidation of both propane and propene. Low specific surface areas have been obtained in all cases. However, both the nature of crystalline phases and the catalytic performance depend strongly on the catalyst composition. All the catalysts were active in propene oxidation but only some of the Mo-V-Te-Nb-O catalysts were also active and selective in the oxidation of propane to acrylic acid. The nature of active and selective Mo-V-Te-Nb-O crystalline phases is also discussed.

Keywords: Mo-V-Te-Nb-O metal oxide catalysts; Catalyst preparation; Catalyst characterisation; Selective oxidation of propane and propene; Acrolein and acrylic acid

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1. Introduction

Acrylic acid is an important intermediate for the preparation of fibres, synthetic rubbers, synthetic resins, etc. [1]. It is currently produced by a two-step gas phase oxidation of propene. Increasing research effort is being directed towards the study of the possibilities for direct oxidation (one stage) of propane since it is a lower-cost feedstock than propene [2,3].

Mo-V-Te-Nb catalysts seem to be one of the most promising catalytic systems in the direct oxidation of propane to acrylic acid [3–12]. Generally, they are prepared from aqueous slurries [4,6–8], although they can also be obtained by hydrothermal synthesis [5,6]. The improvement of their catalytic performance goes through a better knowledge of the structural aspects of the catalyst that characterise its specific ability in the selective transformation of propane. In this way, one of the main questions to be resolved is the nature of active and selective sites (and the crystalline phases involved in the reaction) and the optimal preparation conditions of catalysts.

In this paper we present a comparative study of the influence of the chemical composition of catalysts on both physico-chemical and catalytic properties. The catalysts have been prepared from slurries of different composition. The results presented here show how the composition is a key element in the preparation of these catalysts. In addition, the nature of active and selective sites for the oxidation of propane and propene to acrylic acid is tentatively proposed.

2. Experimental

Mo-V-Te, Mo-Te-Nb and Mo-V-Te-Nb mixed oxide catalysts have been prepared according to a previously described method [4]. The aqueous solutions comprising the corresponding metal ions, i.e. ammonium heptamolybdate, ammonium metavanadate, telluric acid, and niobium oxalate, in the appropriate atomic ratios, were rotaevaporated until complete dryness. The resulting solids were dried at 120 °C overnight. Finally, the solids were heat-treated at 600 °C for 2 h in a N_2-stream. The resulting catalysts were pressed and sized to 0.42–0.59 mm for testing.

Elemental analyses of mixed metal oxides were obtained by atomic absorption spectrophotometry after dissolution in an acid solution. X-ray diffraction patterns (XRD) were

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collected using a Phillips X'Pert-MPD diffractometer provided with a copper monochromator, operating at 40 kV and 20 mÅ and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm). Diffuse reflectance UV-Vis spectra (DRS) were collected on a Cary 5 equipped with a 'Payting Mantis' attachment from Harric under ambient conditions.

The catalytic activity tests were performed in a fixed bed quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure, in the range of 340–420 °C, with mixtures of propane (propene)/oxygen/water/helium with molar ratios of 4/8/30/58 (2/8/30/58), and a total flow of 50 to 200 $cm^3 min^{-1}$. Reactants and reaction products were analysed, on-line, by gas chromatography [5].

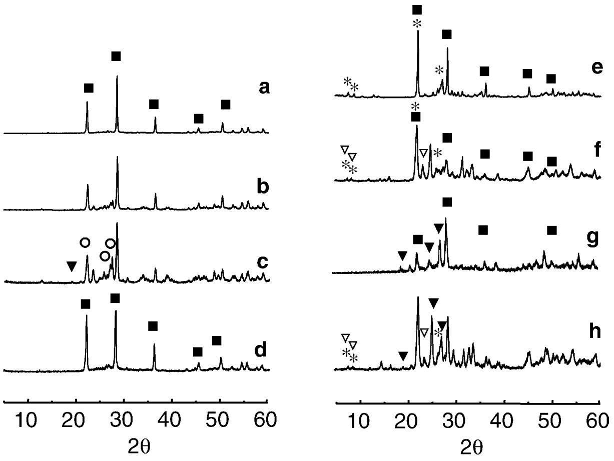

Fig. 1. XRD patterns of Nb-free and Nb-containing Mo-V-Te mixed oxide catalysts: (a) Cat-1; (b) Cat-3; (c) Cat-5; (d) Cat-6; (e) Cat-7; (f) Cat-8; (g) Cat-9; (h) Cat-11: (■) $Te_{0.33}MO_{3.33}$ (M = Mo/V or Mo/V/Nb); (*) $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb); (▼) $VOMoO_4$; (○) $TeMo_5O_{16}$; $Mo_{5-x}(V/Nb)_xO_{14}$ (▽).

3. Results and discussion

3.1. Catalyst characterisation

The characteristics of the catalysts are comparatively shown in Table 1. In all cases, this preparation method provides materials with a low specific surface area ($<6\ m^2/g$).

The XRD patterns of catalysts are shown in Fig. 1 (Table 1). Mo-Te-V series is characterised by the presence of peaks at $2\theta = 22.1°$, 28.2°, 36.2°, 44.7° and 50.0°, suggesting the presence of a $Te_{0.33}MO_{3.33}$ (M = Mo and V) bronze phase [9–11]. $TeMo_5O_{16}$ (JCPDS, 31-874) in samples with high Mo/Te ratios and $VOMoO_4$ (JCPDS, 18-1454) in samples with high V/Mo ratios were also observed.

$Te_{0.33}MO_{3.33}$ (M = Mo, V, and Nb) bronze phases have also been detected in the XRD pattern of Mo-Te-V-Nb-O catalysts, especially in those with low Mo/Te atomic ratio, although the intensity of the most important peak (at $2\theta = 28.1$) decreases when the Mo/Te ratio increases. In addition to this, new crystalline phases have been observed depending on the catalyst composition. $Te_{0.33}MO_{3.33}$ and $Te_2M_{20}O_{57}$ phases (M = Mo, V, and Nb) are observed in the XRD pattern of sample Cat-7, in agreement to previous results [6–8,10]. However, the presence of $(Mo_{0.93}V_{0.07})_5O_{14}$ (JCPDS, 31-1437) and/or $Mo_{0.91}Nb_{0.09}O_{2.80}$ (JCPDS, 27-1310) cannot be ruled out, especially for catalysts with both high Mo/Te ratio and high V-content. On the other hand, $VOMoO_4$ was also observed on some Mo-V-Te-Nb-O catalysts (Cat-8 to Cat-11). We must indicate that the XRD patterns of V-free MoTeNb catalyst (sample Cat-12)

Table 1
Characteristics of catalysts prepared by a slurry method

Sample	Chemical composition		S_{BET} (m^2/g)	Catalytic activity[a]		Crystalline phases detected by XRD[b]
	Mo/Te	Mo + Te/V/Nb		Propene oxidation	Propane oxidation	
Cat-1	2	1.2/0.3/0	<1	0.8	0	$Te_{0.33}(Mo/V)O_{3.33}$
Cat-2	4	1.2/0.3/0	<1	1.3	0	$Te_{0.33}(Mo/V)O_{3.33}$; $TeMo_5O_{16}$
Cat-3	2	1.2/0.6/0	<1	3.5	0	$Te_{0.33}(Mo/V)O_{3.33}$; $TeMo_5O_{16}$; $VOMoO_4$
Cat-4	4	1.2/0.6/0	<1	8.2	0	$Te_{0.33}(Mo/V)O_{3.33}$; $TeMo_5O_{16}$; $VOMoO_4$
Cat-5	6	1.2/0.6/0	3.5	9.3	0	$Te_{0.33}(Mo/V)O_{3.33}$; $TeMo_5O_{16}$; $VOMoO_4$
Cat-6	2	1.2/0.3/0.12	1.3	0.5	0.29	$Te_{0.33}(Mo/V/Nb)O_{3.33}$
Cat-7	4	1.2/0.3/0.12	5.4	6.4	1.40	$Te_2M_{20}O_{57}$ + $Te_{0.33}(Mo/V/Nb)O_{3.33}$
Cat-8	6	1.2/0.3/0.12	5.0	26	0.96	$Te_{0.33}(Mo/V/Nb)O_{3.33}$; $Mo_{5-x}(V/Nb)_xO_{14}$; $Te_2M_{20}O_{57}$; $VOMoO_4$
Cat-9	2	1.2/0.6/0.12	2.4	3.7	0.08	$Te_{0.33}(Mo/V/Nb)O_{3.33}$; $VOMoO_4$
Cat-10	4	1.2/0.6/0.12	Nd[c]	14	0.48	$Te_{0.33}(Mo/V/Nb)O_{3.33}$; $VOMoO_4$; $Te_2M_{20}O_{57}$
Cat-11	6	1.2/0.6/0.12	Nd[c]	37	0.14	$Te_{0.33}(Mo/V/Nb)O_{3.33}$; $VOMoO_4$; $Mo_{5-x}(V/Nb)_x\ O_{14}$; $Te_2M_{20}O_{57}$
Cat-12	2	1.2/0/0.42	2.0	7.4	–	$3MoO_2{\cdot}Nb_2O_5$

[a] Catalytic activity in ($10^4\ mol\,g\,h^{-1}$) (reaction conditions in text).

[b] $Te_2M_{20}O_{57}$ (with M = Mo, V, and Nb); $Mo_{5-x}(V/Nb)_xO_{14}$ is $(Mo_{0.93}V_{0.07})_5O_{14}$ and/or $Mo_{0.91}Nb_{0.09}O_{2.80}$.

[c] Not determined.

presented only the corresponding peaks of $3MoO_2 \cdot Nb_2O_5$ (JCPDS, 18-840) [5,6], suggesting that the formation of $Te_{0.33}MO_{3.33}$ bronzes is only carried out in the presence of V ions.

The DRS spectra of Mo-V-Te-O samples (not shown here) presents three broad bands at about 300, 350 and 580 nm. The bands at 300 and 350 nm could be related to the presence of Mo^{6+} and V^{5+}, respectively, in octahedral coordination, while the band at 580 nm is related to the presence of Mo^{6+}/Mo^{5+} species [9]. In addition to these, a band is also observed at 420 nm in Mo-V-Te-Nb-O catalysts which can be assigned to octahedral V^{5+} species in a different environment than that in Mo-V-Te-O catalysts. According to the DRS results presented here, and in agreement to previous EPR results [6], it can be concluded that Mo^{6+}/Mo^{5+}, V^{5+}, Nb^{5+} and Te^{4+} (formed during the heat-treatment) are mainly present in our catalysts.

3.2. Catalytic results and nature of active sites

Table 1 shows the catalytic activity of catalysts obtained during the oxidation of propene at 380 °C and a contact time, W/F of 400 g_{cat} h mol^{-1}. In all cases, the catalytic activity increases with both the Mo/Te ratio and the V-content, with the Nb-free catalysts presenting catalytic activities lower than the corresponding Nb-containing catalysts. On the other hand, acrolein, acrylic acid and carbon oxides were mainly observed during the propene oxidation. Fig. 2 presents the selectivity to the main partial oxidation products, i.e. acrolein and acrylic acid, obtained at 380 °C and a propene conversion of 30%. Acrolein was mainly obtained on Nb-free Mo-Te-V catalysts, while acrylic acid was mainly obtained on Nb-containing catalysts. Since the V-free sample (sample Cat-12) was also active and selective in the oxidation of propene to acrylic acid, it can be concluded that the presence of Nb ions seems to be related to the oxidation of propene to acrylic acid, while Te-O-Mo-O-Te and/or V-O-Mo-O-Te sites are responsible of the high selective activation of propene.

No propane oxidation was observed neither in the V-free MoTeNb sample nor in the Nb-free Mo-Te-V catalysts, although, in these cases, the catalytic tests were carried out at relatively high contact times ($W/F = 2000\, g_{cat}\, h\, mol^{-1}\, C_3$) and high reaction temperatures (420 °C). Propane was easily transformed into partial oxidation products on Mo-Te-V-Nb catalysts (Table 1), although the highest catalytic activity was achieved on the catalyst with Mo/Te and Mo/V molar ratios of 4 and 3.2, respectively. The low catalytic activity of Mo-V-Te-Nb samples with high V-content (samples Cat-8 and Cat-11, with a Mo/Te ratio of 6) with respect to those with a lower V-content (samples Cat-7 and Cat-10, with a Mo/Te ratio of 4) could be related to the presence of $VOMO_4$ in catalysts with high V-contents. So, the presence of this phase seems to have a negative effect on catalytic activity in propane oxidation.

On the other hand, propene, acrylic acid and carbon oxides were the main reaction products during the oxidation of propane on Mo-Te-V-Nb catalysts, although acetic acid and acrolein were also detected as minority products. Fig. 3 shows the selectivities to the main partial oxidation products, i.e. propene and acrylic acid, obtained at 380 °C and a propane conversion of 20%. The highest selectivities to acrylic acid were achieved on samples with Mo/Te ratio higher than 2, especially on catalysts with high $Mo + Te/V$ ratios of 4 (Cat-7) can be observed (Table 1). In this way, it can be noticed that a yield of acrylic acid of 30% has been obtained at 380 °C and a propane conversion of 65% on this catalyst.

The catalytic activity in propene oxidation seems to be related to the Mo-content of the catalysts while highest catalytic activities in propane oxidation were achieved on catalysts with a Mo/Te ratio of 4 (samples Cat-7 and Cat-10) (Table 1). So, it can be concluded that different active sites are involved in the activation of propane and propene, in agreement to previous reported results [5–8]. When considering the XRD results of Cat-7, two crystalline phases were

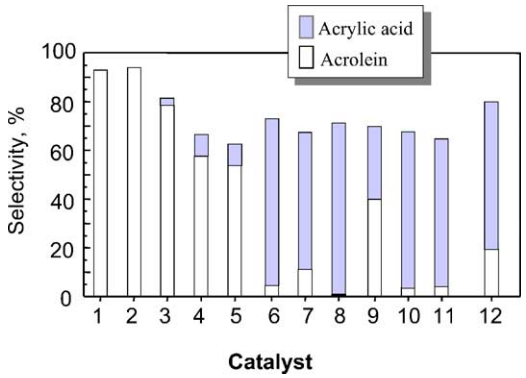

Fig. 2. Selectivity to the main reaction products (at a propene conversion of 30%) of Nb-free and Nb-containing Mo-V-Te mixed oxide catalysts obtained during the oxidation of propene at 380 °C. Catalysts as in Table 1. Experimental conditions in text.

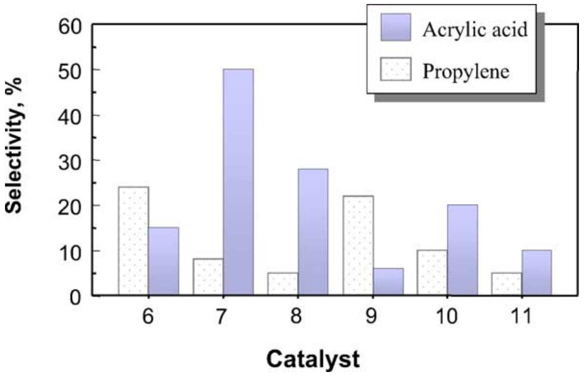

Fig. 3. Selectivity to the main reaction products (at a propane conversion of 20%) of Nb-containing Mo-Te-V mixed oxide catalysts obtained during the oxidation of propane at 380 °C. Catalysts as in Table 1.

observed: $Te_{0.33}MO_{3.33}$ and $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb). The presence of at least two phases have also been proposed previously [5–10], although the role of each phases is still under discussion.

$Te_{0.33}MO_{3.33}$ bronzes type phase was mainly observed in Mo-Te-V catalysts but also in Mo-V-Te-Nb catalysts with low Mo/Te ratios. In all of these cases, they were inactive in propane oxidation and active and selective in the oxidation of propene to acrolein (Mo-Te-V catalysts) or acrylic acid (Mo-V-Te-Nb catalysts). So, they should only be involved in the propene oxidation [11] and could be considered as the phase M2 proposed by Ushikubo et al. [7].

Orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb) phase has been mainly observed in the most active and selective catalysts for the oxidation of propane to acrylic acid (Table 1). This crystalline phase is characterised by the presence of MO_7 pentagonal bipyramids, with all of their five equatorial edges in common with MO_6 octahedra as in θ-Mo_5O_{14}, with hexagonal (occupied by tellurium cations in a (TeO_3E coordination)) and heptagonal channels (empty) [8,10,13]. Since MO_7 pentagonal bipyramids could be the active sites in ethane activation [12], $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb) bronze could be by themselves responsible of the high effective activation of propane in these catalysts. In addition, its hexagonal channels with tellurium occupying the centre of the channel (similar to those observed in $Te_{0.33}MO_{3.33}$ bronzes) could also be involved in the selective oxidation of propene to acrylic acid. In this way, it has been observed that $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb) crystalline phase $Te_{0.33}MO_{3.33}$-free can selectively be obtained by hydrothermal synthesis [5,6]. Since these catalysts (prepared hydrothermally) are active and selective in the oxidation [5,6] and the ammoxidation [8,13] of propane, $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb) could be considered by itself the active and selective crystalline phase for the one-step selective oxidation and ammoxidation of propane. However, a synergism due to a cooperation between phases should also be considered in catalysts prepared from slurries [14].

The Nb^{5+} ions in these cases seem to be directly involved in the formation of acrylic acid from propene. However, it could also be responsible of the formation of $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb) bronzes, since no $Te_2M_{20}O_{57}$ bronzes have been reported in Nb-free MoVTeO catalysts.

In conclusion Mo-V-Te mixed oxide catalysts resulted active and selective in the oxidation of propene to acrolein, while Nb-containing catalysts (Mo-Te-Nb-O and Mo-V-Te-Nb-O catalysts) were active and selective in the oxidation of propane to acrylic acid.

The different catalytic behaviour of these catalysts could be related to the presence of different crystalline phases: (a) $Te_{0.33}(Mo/V/Nb)O_{3.33}$, which is active and selective in the oxidation of propene to acrolein (Nb-free MoVTe mixed oxides) and acrylic acid (Nb-containing MoVTe mixed oxides); (b) $Te_2M_{20}O_{57}$ (M = Mo, V, and Nb), which is active and selective in the oxidative activation of propane to propene and/or acrylic acid. Other crystalline phases were also observed depending on the catalyst composition, being some of them responsible of the different catalytic performance observed in our catalysts.

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