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# Influence of gel composition in the synthesis of MoVTeNb catalysts over their catalytic performance in partial propane and propylene oxidation

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ABSTRACT

MoVTeNb mixed oxides catalysts have been prepared by a slurry method with different molar compositions (Mo/Te ratio from 2 to 6 and Nb/(V + Nb) ratio from 0 to 0.7) in the synthesis gel leading to different crystalline phases distribution and catalytic behaviour in the partial oxidation of both propane and propylene to acrylic acid. Chemical analysis indicates that the composition of samples before and after the heat-treatment changes, especially the Te-content, since a significant amount of Te is lost during the heat-treatment step when the amount of oxalate (from niobium oxalate) increases in the synthesis gel. Thus, the nature of the crystalline phases and the catalytic performance of heat-treated materials will be related to the final chemical composition. On the other hand, only the catalysts presenting $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) crystalline structure, the so-called M1 phase, were active and selective in the partial oxidation of propane to acrylic acid. Moreover, all catalysts were active and relatively selective to the formation of O-containing products, i.e. acrolein and/or acrylic acid, during the partial propylene oxidation although the more active ones were those presenting M1 phase.

## 1. Introduction

The functionalization of light alkanes is a challenging matter for many research groups, due especially to their comparatively low price compared to the corresponding olefins. At present only the selective oxidation of n-butane to maleic anhydride is industrially developed [1]. Therefore the exploration of new catalytic systems for the oxidation of short chain alkanes in gas phase has generated special interest from both fundamental aspects and industrial applications.

In the last decade, MoVTeNb mixed oxides were proposed as active and selective catalysts in the ammoxidation of propane to acrylonitrile [2] and in the partial oxidation of propane to acrylic acid [3]. More recently, they have also shown to be very active and selective in the oxidative dehydrogenation of ethane to ethylene [4,5].

Typically MoVTeNb catalysts present as main crystalline phases [6–31]: (i) orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V, Nb), named as M1 phases [7–10] and (ii) orthorhombic distorted HTB-type phase $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb), called as M2 phase [7–11]. In addition to these, minority phases like $TeMo_5O_{16}$ or (V, Nb)-containing $Mo_5O_{14}$ or $MoO_3$ can also be observed as a result of the different preparation and/or activation procedure. The orthorhombic M1 phase is active and selective by itself in the direct oxidation of propane to acrylic acid, while pseudo-orthorhombic phase is not able to activate propane. However, some synergetic effect could exist between both phases (especially at high propane conversions) increasing the acrylic acid yield [13–16].

Active and selective MoVTeNbO catalysts are obtained by heat-treatment of precursors at 600 °C flowing $N_2$. These precursors are generally prepared by hydrothermal synthesis or by precipitation/evaporation of aqueous solutions of the components. It must be commented that the starting reagents added in the synthesis gel affect the final material in a different way depending on the preparation method, although the influence of the nature of these reagents on both crystalline phases and catalytic performance is not fully clear.

Regarding the incorporation of vanadium, MoVTeNb catalysts have been typically prepared with ammonium metavanadate when employing slurry method [2,3,6–12,17] or with vanadyl sulphate when using the hydrothermal method [12,13,18–21]. In the case of tellurium it is known that the employment of different tellurium sources and methods of synthesis leads to the formation of catalysts with different crystalline structures and different catalytic behaviours [22–24]. In addition, the pH of the synthesis gel [25,26] and the presence of reducer in the synthesis gel [10,27–31] have a strong influence on both the nature of crystalline phases and the catalytic performance in partial oxidation of propane. In this way, we must indicate that the presence of oxalate [27–30] or other reducers such as hydrazine sulphate, hydrazine hydrate,

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hydroxyacetone [10,27] or ammonium chloride [31], has only a positive influence on catalytic performance when an optimum amount of reducer is present in the synthesis gel.

The present investigation has focused on the synthesis, the characterization and the catalytic behaviour of MoVTeNbO catalysts synthesized by a slurry method. The aim of this study is to shed a little light on the influence of the synthesis gel chemical composition on: (i) the nature the crystalline phases obtained, (ii) the chemical composition of resulting catalysts (e.g. the heat-treated samples), and (iii) the catalytic performance of MoVTeNbO catalysts.

## 2. Experimental

Three sets of MoVTeNbO catalysts with Mo/Te atomic ratios of 2, 4 and 6 have been prepared, in which the Nb/(V + Nb) atomic ratio has been varied between 0 and 0.7 so that the (Mo + Te)/(V + Nb) atomic ratio was kept constant at 2.8.

The catalysts were prepared as follows. Aqueous solutions of ammonium heptamolybdate tetrahydrate (Aldrich), telluric acid (Aldrich) and ammonium niobium oxalate (CBMM) were mixed. Next, the proper vanadyl sulphate (Aldrich) amount was added to the former solution. This mixture was then heated at 80 °C and stirred until complete water evaporation took place. The solid obtained (around 10 g) was dried overnight at 100 °C. Finally the catalysts were heat-treated in flowing $N_2$ (100 ml/min) at 600 °C during 2 h, using a quartz tube with an internal diameter of 5 cm.

Chemical analyses of the catalysts were carried out by Atomic Absorption Spectroscopy (in the case of Mo, V and Te elements) or Inductively Coupled Plasma Atomic Emission Spectroscopy ICP (for Nb element). X-ray diffraction (XRD) patterns were collected using a Phillips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA, and employing nickel-filtered Cu K$\alpha$ radiation ($\lambda = 0.1542$ nm).

The catalytic experiments were carried out at atmospheric pressure in a fixed-bed quartz tubular reactor (i.d. 12 mm; length 400 mm). The catalyst samples (0.3–0.5 mm particle size) were diluted with silicon carbide (1–6 g) and introduced into the reactor to keep a constant volume in the catalytic bed. In the propane oxidation tests the flow rate was varied from 20 to 100 ml/min and the amount of catalysts from 0.1 to 5 g in order to achieve different hydrocarbon conversions. The reaction temperature studied was in the 340–420 °C range although it was mainly focused at 380 °C. The feed consisted in a mixture of $C_3H_8/O_2/H_2O/He$ or $C_3H_6/O_2/H_2O/He$ with a molar ratio of 4/8/30/58 or 1.5/6/15/77.5, respectively.

Reactants and reaction products were analysed by on-line gas chromatography using two different columns: (i) molecular sieve 5 Å (3 m), and (ii) Porapack Q (3 m) [12]. Several blank runs were carried out at reaction temperatures and no hydrocarbon conversion was observed.

## 3. Results and discussion

### 3.1. On the nature of the crystalline phases obtained

In Table 1 the main features of the catalysts prepared in this work are summarized (i.e. the chemical composition of solids before and after heat-treatment, and the crystalline phases detected by XRD of the heat-treated materials). In addition, it must be indicated that these heat-treated catalysts presented in general low BET surface areas (not shown). Thus, catalysts with molar ratio $Nb/(V + Nb) < 2$ presented surface areas lower than 10 $m^2\,g^{-1}$, whereas surface areas from 10 to 15 $m^2\,g^{-1}$ were observed in samples with Nb/(V + Nb) molar ratio higher than 2. The presence of oxalate anion in the synthesis gel could favour the achievement of catalysts with higher surface areas [29].

Fig. 1 shows the XRD patterns of samples before the heat-treatment. Nb-free materials show a crystalline pattern with main diffraction peaks at $2\theta = 8.2°$, 16.4°, 18.3°, 21.8°, 22.6°, 24.4°, 28.0°, 28.6°, 29.8°, 31.5° and 37.6°, while the presence of Nb leads to amorphous patterns with broad bands centred at $2\theta = 12°$, 22.5° and 27.5°. This indicates that the partial substitution of vanadyl sulphate by niobium oxalate in the synthesis gel prevents the formation of some crystalline phases in the catalyst precursors.

The XRD patterns of catalysts (heat-treated samples) are shown in Fig. 2. For the set with a nominal Mo/Te atomic ratio of 2 (A-series catalysts), the Nb-free catalyst mainly presents the

**Table 1**

Characteristics of MoVTeNbO catalysts before (as-synthesized) and after heat-treatment at 600 °C flowing $N_2$.

| Catalyst | As-synthesized samples[a] | | | Heat-treated samples[b] | | | |
|---|---|---|---|---|---|---|---|
| | Mo/Te | Nb/(V + Nb) | Mo/V/Nb/Te | Mo/Te | Te/(M)[c] | Mo/V/Nb/Te | Crystalline phases[d] |
| A0 | 2 | 0.00 | 1/0.53/0.00/0.50 | 2.0 | 0.33 | 1/0.55/0.00/0.51 | M2 |
| A1 | 2 | 0.15 | 1/0.47/0.08/0.50 | 2.1 | 0.30 | 1/0.47/0.08/0.51 | M2 |
| A2 | 2 | 0.29 | 1/0.39/0.16/0.50 | 2.2 | 0.28 | 1/0.41/0.18/0.45 | M2 |
| A3 | 2 | 0.36 | 1/0.33/0.20/0.50 | 2.7 | 0.24 | 1/0.32/0.20/0.39 | M2, M1 |
| A4 | 2 | 0.50 | 1/0.26/0.26/0.50 | 3.3 | 0.18 | 1/0.28/0.20/0.31 | M1 |
| A5 | 2 | 0.71 | 1/0.16/0.39/0.50 | 4.9 | 0.13 | 1/0.18/0.41/0.20 | $Mo_{5-x}(V/Nb)_xO_{14}$, $V_{0.95}Mo_{0.97}O_x$ |
| B0 | 4 | 0.00 | 1/0.44/0.00/0.25 | 4.0 | 0.18 | 1/0.42/0.00/0.27 | M2 |
| B1 | 4 | 0.15 | 1/0.39/0.07/0.25 | 3.7 | 0.19 | 1/0.37/0.07/0.22 | M2 > M1 |
| B2 | 4 | 0.30 | 1/0.32/0.14/0.25 | 5.4 | 0.13 | 1/0.29/0.14/0.18 | M2, M1 |
| B3 | 4 | 0.39 | 1/0.27/0.17/0.25 | 9.8 | 0.07 | 1/0.24/0.19/0.10 | M1 |
| B4 | 4 | 0.50 | 1/0.22/0.22/0.25 | 20 | 0.04 | 1/0.24/0.22/0.05 | Amorphous |
| B5 | 4 | 0.70 | 1/0.14/0.32/0.25 | nd | nd | nd | $MoO_2$ > amorphous |
| C0 | 6 | 0.00 | 1/0.41/0.00/0.17 | 6.0 | 0.12 | 1/0.38/0.00/0.19 | M2, $TeMo_5O_{16}/TeMo_4O_{13}$ |
| C1 | 6 | 0.15 | 1/0.36/0.06/0.17 | – | – | nd | M2, M1, $Mo_{5-x}(V/Nb)_xO_{14}$ |
| C2 | 6 | 0.30 | 1/0.30/0.13/0.17 | 11 | 0.07 | 1/0.30/0.14/0.09 | M2, M1, $Mo_{5-x}(V/Nb)_xO_{14}$ |
| C3 | 6 | 0.39 | 1/0.25/0.16/0.17 | 32 | 0.02 | 1/0.24/0.17/0.03 | $Mo_{5-x}(V/Nb)_xO_{14}$, $V_{0.33}Mo_{0.67}O_2$ |
| C4 | 6 | 0.50 | 1/0.22/0.22/0.17 | 63 | 0.01 | 1/0.22/0.22/0.02 | Amorphous, $MoO_2$ |
| C5 | 6 | 0.70 | 1/0.13/0.30/0.17 | – | – | nd | $MoO_2$ > amorphous |
| B0-oxal | 4 | 0.00 | 1/0.44/0.00/0.25 | 20 | 0.04 | 1/0.44/0.00/0.05 | M2, $Mo_{5-x}(V/Nb)_xO_{14}$, $V_{0.95}Mo_{0.97}O_x$ |

[a] Atomic ratio in samples before the heat-treatment; nd: not determined.

[b] Atomic ratio in samples after the heat-treatment.

[c] Te/M (M = Mo + V + Nb).

[d] Crystalline phases, detected in heat-treated samples, by indexing XRD patterns; $M1 = Te_2M_{20}O_{57}$; $M2 = Te_{0.33}MO_{3.3}$.

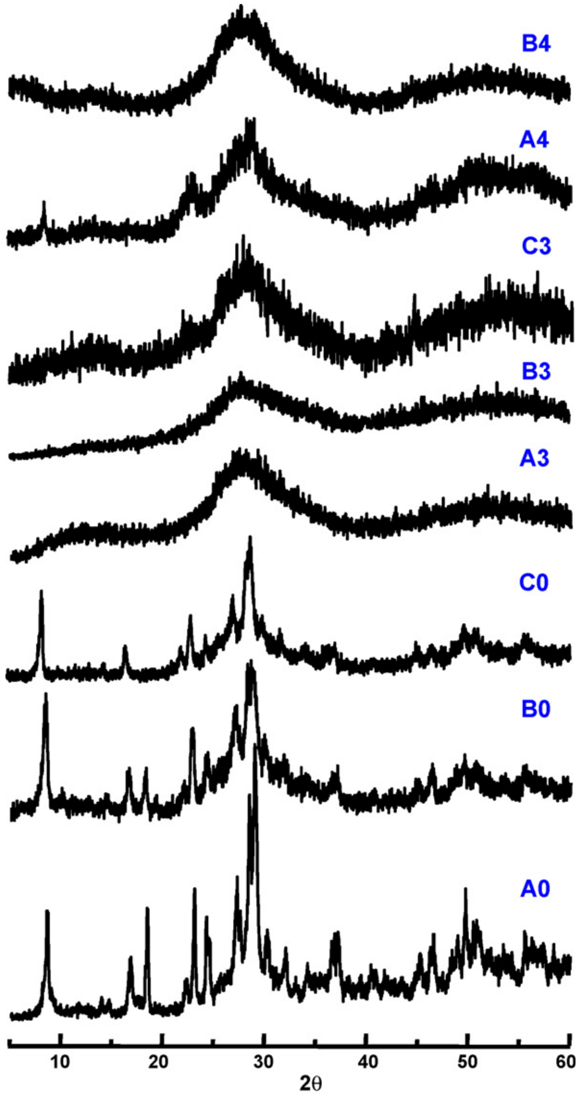

**Fig. 1.** XRD patterns of some selected Nb-free (A0, B0, C0) and Nb-containing MoVTe (A3, B3, C3, A4, B4) precursors (before the heat-treatment).

characteristic diffraction peaks of $Te_{0.33}MO_{3.3}$ crystalline structure (named M2 phase). If vanadium is partially replaced by niobium (up to a Nb/(V + Nb) atomic ratio of 0.3), no apparent change in XRD patterns is observed. Similarly, it has been previously reported that Nb can be incorporated into M2 phase structure in vanadium positions at low Nb/V ratios [7–9,32]. However, a further increase in Nb-loading leads to the appearance of diffraction peaks corresponding to $Te_2M_{20}O_{57}$ structure (M1 phase) and a decrease in the relative amount of $Te_{0.33}MO_{3.3}$ (M2 phase). Thus, it seems that $Te_2M_{20}O_{57}$ is the only crystalline phase present for a Nb/(V + Nb) atomic ratio of 0.5 (sample A4).

Finally, in samples with an excess of Nb (i.e. Nb/(V + Nb) molar ratio higher than 0.7), the structure of $Te_2M_{20}O_{57}$ is lost and peaks corresponding to $Mo_{5-x}(V/Nb)_xO_{14}$ and $V_{0.95}Mo_{0.97}O_x$ [JCPDS: 18-852] can be appreciated in XRD patterns (Fig. 2).

For a nominal Mo/Te atomic ratio of 4 (B-series catalysts), the Nb-free catalyst also presents the $Te_{0.33}MO_{3.3}$ structure but it is not as clear as for a Mo/Te of 2, showing small peaks associated to the presence of $Mo_5TeO_{16}$ and $Mo_4TeO_{13}$. When Nb is added peaks corresponding to $Te_2M_{20}O_{57}$ structure can be observed, being almost the only crystalline phase detected for a Nb/(V + Nb) ratio of 0.4 (sample B3). Again, a further increase in the Nb-content (Nb/(V + Nb) = 0.5) leads to the disappearance of M1 phase structure, resulting in an amorphous diffraction pattern with only two remarkable peaks (one sharp and one broad peak centred at $2\theta = 22^\circ$ and 28°, respectively). Finally, diffraction patterns with the characteristic peaks of $MoO_2$ an $Nb_2O_5$ phases has been observed in samples with the highest Nb-loading.

For the catalyst set with Mo/Te atomic ratio of 6 (C-series catalysts), the low Te-content favours the formation of other crystalline phases, which in turn increase the amount of diffraction peaks in XRD patterns. The Nb-free sample shows diffraction peaks of $Te_{0.33}MO_{3.3}$ phase and other mixed oxides as $TeMo_5O_{16}$/$TeMo_4O_{13}$. As in the other cases, the incorporation of Nb tends to favour the loss of the $Te_{0.33}MO_{3.3}$ structure and also favours the appearance of $Te_2M_{20}O_{57}$ peaks up to a certain Nb-loading in which the later structure is also lost. Mixed oxides phases like $Mo_{5-x}(V/Nb)_xO_{14}$ [JCPDS: 31-1437, 27-1310] and $V_{0.33}Mo_{0.67}O_x$ [JCPDS: 30-849] are also detected in the catalysts with medium Nb-content (C1 and C2), being the main phases present for Nb/(V + Nb) molar ratio of 0.4. At the highest Nb-loadings (C4 and C5 samples) no characteristics peaks of M1 or M2 phases are observed whereas diffractions corresponding to monoclinic $MoO_2$ structure [JCPDS: 32-0671] are predominant.

It is also important to indicate that, in addition to the XRD observations of the crystalline phases, micro-structural characterization by means of selected area electron diffraction (SAED) and high resolution electron microscopy (HREM) has confirmed the presence to a minor extent of other bronzes composed by MoVTeNbO, with particle sizes too small to be detected by XRD [12]. Hence, in those catalysts in which the presence of M1 phase is observed by XRD, it is also observed by HREM/SAED the presence of $M_{17}O_{47}$ crystalline phase (with M = Mo, V, Te, Nb; and calculated cell parameters: $a = 2.16$ nm, $b = 1.96$ nm, and $c = 0.39$ nm) and of a crystalline phase derived from a tetragonal tungsten bronze type structure (TTB structure, with cell parameters: $a = \sqrt{2}a_{TTB}$ and $c = c_{TTB}$), which show atomic ratios of $Te_{1.6}(Mo_{0.63}Nb_{0.28}V_{0.09})O_{47}$ and $Te_{0.6}(Mo_{0.68}Nb_{0.23}V_{0.09})_{11}O_{47}$, respectively [12]. This suggests that Te could also incorporate into the pentagonal channels present in these structures. On the other hand, TTB type structures have never been observed previously in MoVTeNbO materials prepared by hydrothermal synthesis (employing vanadyl sulphate as vanadium source) or by slurry method (from ammonium metavanadate). This fact suggests that the source of vanadium could play an important role in the synthesis of this kind of material strongly depending on the employed catalyst preparation method.

### 3.2. On the loss of Te during activation step

The chemical analyses of MoVTeNbO samples before and after the heat-treatment at 600 °C flowing $N_2$ are shown in Table 1. If the Mo/V/Nb atomic ratio remains nearly constant between the samples before and after the heat-treatment, a remarkable loss of tellurium is observed in heat-treated samples. In this way, the Mo/Te ratio in heat-treated samples increases when increasing the Nb/(Nb + V) ratio, this effect being more important in C-series catalysts.

A possible explanation for the loss of tellurium could be related to the presence of oxalate anions (reducing agent) from the niobium oxalate, which could facilitate the reduction of tellurium cations to metallic Te. Fig. 3 plots the loss of Te during the heat-treatment step with the oxalate-content (from the Nb-source) in the synthesis gel. It can be seen that a remarkable loss takes place when the oxalate-content increases. It is very likely that the loss of tellurium is related to the presence of oxalate ions of the niobium source, by means of the reduction to metallic tellurium, which is straightaway detached from the solid by melting ($Te^0$ m.p. of 450 °C) during heat-treatment at 600 °C in $N_2$ stream.

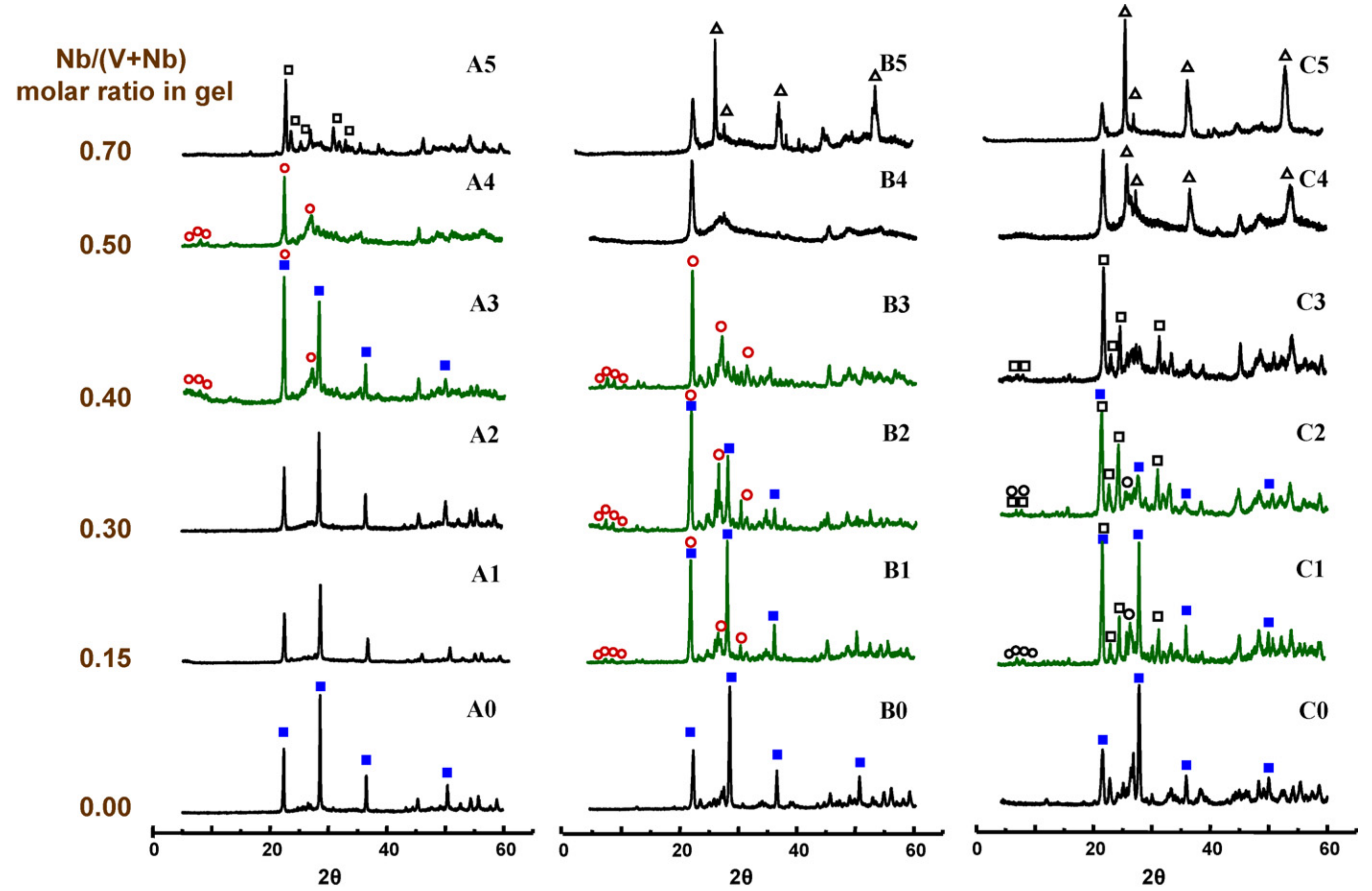

**Fig. 2.** XRD patterns of heat-treated MoVTeNbO catalysts prepared with Mo/Te atomic ratio of 2 (A0–A5), 4 (B0–B5) or 6 (C0–C5) and Nb/(V + Nb) atomic ratios between 0 and 0.7. Symbols: (■) $Te_{0.33}MO_{3.3}$ (M2 phase), (○) $Te_2M_{20}O_{57}$ (M1 phase), (M = Mo, V or Nb), (△) monoclinic $MoO_2$, and (□) other mixed oxides $Mo_x(V/Nb)_yO_z$. Characteristics of catalysts in Table 1.

It must be noticed that, due to the flow of nitrogen, metallic tellurium is pushed across sintered quartz bed throughout the container tube and is removed from the final heat-treated catalyst. It was then possible to pick up the lost tellurium as sharp needles at the bottom of the container tube. In this way, the XRD and the chemical analysis of this residue confirmed that these sharp needles only contained tellurium metal.

These results also show that the Te-loss does not significantly change with Mo/Te ratio (Fig. 3). The loss of tellurium is not completely linear, since Te-loss is negligible at low oxalate contents, while it clearly increases when increasing the oxalate-content in the synthesis gel. In fact, it has been empirically determined that per each three molecules of oxalic acid present in the as-synthesized samples around one atom of tellurium is detached during the heat-treatment.

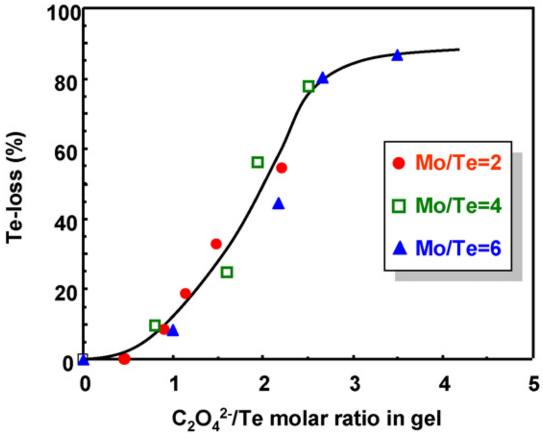

**Fig. 3.** Variation of the loss of tellurium (achieved during the heat-treatment step) with the oxalate/Te ratio in the synthesis gel. Mo/Te ratio in gel of 2 (●), 4 (□) or 6 (▲). Characteristics of catalysts in Table 1.

To confirm the role of oxalate anions, a new MoVTeO catalyst (not shown in Fig. 3) was prepared with the same composition as B0 catalysts but with the addition of oxalic acid ($C_2O_4^{2-}$/(Mo + V + Te) molar ratio of 0.5) in the synthesis gel (and named as B0-oxal). If in the B0 catalyst the loss of tellurium was undetectable, the corresponding catalyst prepared in the presence of oxalic acid presented a loss of tellurium of 83% from its initial Te-loading after the heat-treatment at 600 °C in flowing $N_2$.

The change of the chemical composition of MoVTeNbO catalysts during the heat-treatment step has not been widely studied. If a small decrease of tellurium loading is observed when the sample was heat-treated in flowing nitrogen [28,30,33] this fact was not observed when the sample was initially pre-calcined in static air (at 250–300 °C) before the final heat-treatment in $N_2$ at 600 °C [30].

On the other hand Oliver et al. [25] studied the influence of the pH in the preparation method of MoVTeNbO catalysts. Apart from a different catalyst structure and catalytic behaviour during the oxidation of propane to acrylic acid, a loss of tellurium was observed, especially in those samples prepared at high pH. Nonetheless, it was probably the different oxidation/reduction degree of the precursors of these catalysts, which determined the extent of the Te-loss.

**Table 2**
Catalytic results during propane oxidation on MoVTeNb catalysts.

| Catalyst | Propane conversion (%)[a] | Selectivity (%) | | | | |
|---|---|---|---|---|---|---|
| | | Acrylic acid | Propene | Acrolein | CO | $CO_2$ |
| A0 | <0.2 | – | – | – | – | – |
| A1 | <0.2 | – | – | – | – | – |
| A2 | <0.4 | – | – | – | – | – |
| A3 | 5.7 | 29.7 | 49.0 | 0.2 | 6.8 | 13.1 |
| A4 | 9.9 | 40.4 | 33.9 | 0.1 | 8.6 | 16.8 |
| A5 | 1.0 | 0 | 90.7 | 0 | 3.7 | 5.6 |
| B0 | <0.2 | – | – | – | – | – |
| B1 | 10.3 | 47.6 | 27.9 | 0.1 | 7.6 | 13.1 |
| B2 | 5.6 | 31.2 | 48.6 | 1.1 | 6.7 | 11.8 |
| B3 | 12.8 | 46.4 | 27.2 | 0 | 8.8 | 15.8 |
| B4 | 21.0 | 0 | 11.0 | 0.1 | 33.3 | 52.3 |
| C0 | <0.2 | – | – | – | – | – |
| C1 | 4.8 | 4.7 | 64.2 | 0.1 | 10.9 | 18.3 |
| C2 | 16.0 | 10.1 | 25.3 | 0.1 | 22.5 | 42.7 |
| C3 | 23.2 | 0 | 13.7 | 0.1 | 33.0 | 47.3 |
| C4 | 29.3 | 0 | 7.5 | 0.1 | 38.6 | 48.9 |

[a] Propane conversion and selectivity to main products for at 380 °C and a contact time, W/F, of 1 $kg_{cat}$ h $(mol_{C_3H_8})^{-1}$.

### 3.3. On the catalytic behaviour during propane oxidation

Table 2 presents the catalytic behaviour during the propane oxidation of MoVTeNbO mixed oxides catalysts. Propylene, acrylic acid and carbon oxides were the main products obtained, although traces of acrolein, acetone and acetic acid were also detected.

Fig. 4a shows the evolution of the selectivity to the main reaction products with the propane conversion at 380 °C for A4 catalyst. It can be observed that propene is an unstable primary product, while the acrylic acid is an unstable secondary product. We must indicate that this catalyst, but also B3 catalyst, presented the best catalytic performances, reaching yields to acrylic acid close to 25%, with selectivity to acrylic acid around 60%. It must be informed that the catalysts presenting lower selectivity to acrylic acid displayed a higher decomposition of acrylic acid when increasing the propane conversion level.

Fig. 5 shows the variation of the catalytic activity (Fig. 5a) and the selectivity to acrylic acid (Fig. 5b) with the Nb/(Nb + V) molar ratio in gel of MoVTeNbO catalysts prepared with several Mo/Te molar ratios in gel. As a general trend, the catalytic activity increases when increasing both Nb- and Mo-loading, being the most active catalysts those prepared with the highest Mo/Te ratio in gel. Nevertheless, the catalysts with the highest Nb-loading did start to lose their activity.

On the other hand, the selectivity to acrylic acid initially increases with the Nb-content (Fig. 5b). Moreover, high Nb-loadings lead to a decrease in the selectivity to acrylic acid, while no acrylic acid was observed for catalysts with the highest Nb-content.

The influence of the chemical composition on the capability of forming acrylic acid from propane is shown in Fig. 6. Nominal Mo/Te atomic ratios between 2 and 4 seem to be optimal. In addition, there is also an optimal V/Nb ratio but in a way that the higher the Te-content the higher the Nb-loading must be to obtain high acrylic acid yields.

Even though there is a slight perceivable influence of the chemical composition, the catalytic performance of these catalysts seems to be more related to the nature of crystalline phases present in the catalyst. Thus, comparing catalytic results with the crystalline phases present in each catalyst (Table 1) a relationship between selective catalysts and the presence of diffraction peaks

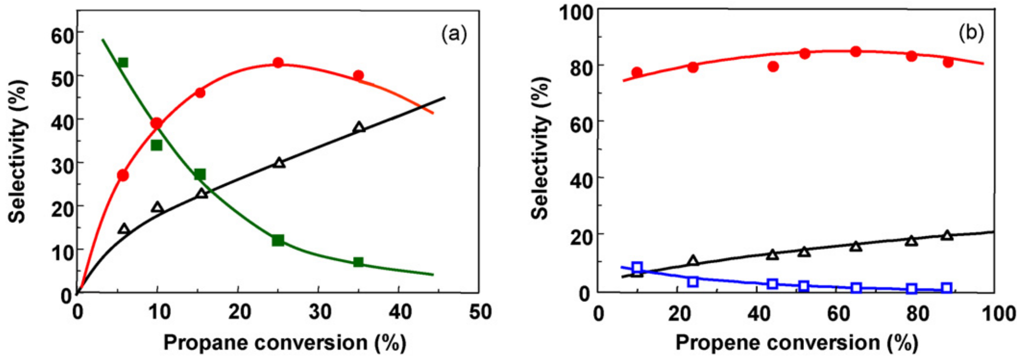

**Fig. 4.** Variation of the selectivity to the main reaction products with the hydrocarbon conversion obtained during the partial oxidation of propane (a) or propylene (b) over A4 catalyst at a reaction temperature of 380 °C. Symbols: propylene (■), acrolein (□), acrylic acid (●), and $CO_x$ (△). Reaction conditions in text.

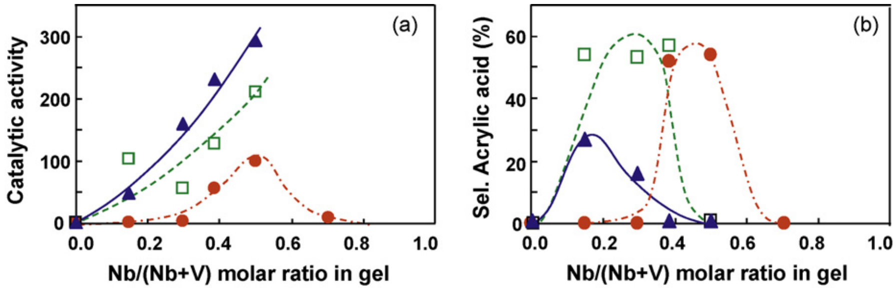

**Fig. 5.** Variation of catalytic activity (in $10^2$ $mol_{C_3H_8}$ $h^{-1}$ $kg_{cat}^{-1}$) (a) and the selectivity to acrylic acid (b) with the Nb/(V + Nb) atomic ratio in gel for catalysts prepared with Mo/Te atomic ratio of 2 (●), 4 (□) or 6 (▲). *Note*: the catalytic activity for propane oxidation has been obtained at a contact time, W/F, of 1 $kg_{cat}$ h $mol_{C_3H_8}^{-1}$ and a reaction temperature of 380 °C; the selectivity to acrylic acid has been obtained at propane iso-conversion of 25% and reaction temperature of 380 °C.

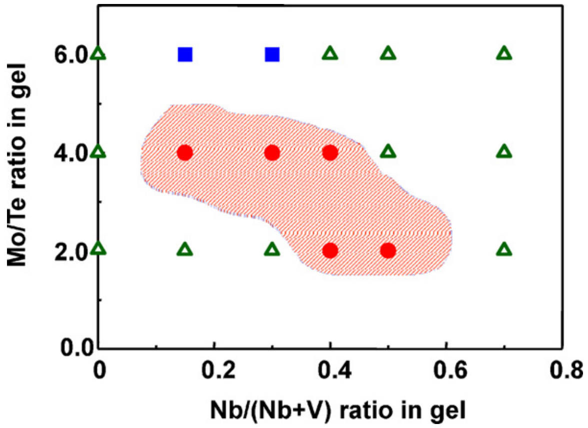

**Fig. 6.** Influence of the Mo/Te and Nb/(Nb + V) ratios in the synthesis gel on the yield of acrylic acid achieved during the partial oxidation of propane over MoVTeNbO catalysts. Symbols: (●) high acrylic acid yields, (■) medium acrylic acid yields and (△) very low acrylic acid yields.

corresponding to orthorhombic $Te_2M_{20}O_{57}$ phase is noticed, with the most selective catalysts being those which present almost exclusively M1 phase, i.e. A4 and B3 (Fig. 2).

It must be remarked that Nb-free catalysts have been shown inactive during the propane oxidation to acrylic acid. In this way, the main crystalline phase detected in ternary MoVTe samples of the present work is the $Te_{0.33}MO_{3.33}$ phase (with peaks at $2\theta = 22.1°, 28.2°, 36.2°, 44.7°$ and $50.0°$) which has been reported to be incapable to activate propane [14,32]. Besides, the other crystalline phases observed in these catalysts ($TeMo_5O_{16}$, $TeMo_4O_{13}$ and $MoO_3$) were individually prepared, then tested in the same reaction conditions employed with the rest of catalysts, and were found inactive in propane oxidation.

Accordingly, it could be thought that Nb is necessary to form the active phases in catalysts prepared by slurry method using $V^{4+}$ as vanadium reagent (vanadyl sulphate) or commonly slurry method with $V^{5+}$ source (ammonium metavanadate) [2,3,6–12,17], since M1 phase was only observed for those catalysts with certain Nb/V ratio. However, the presence of oxalate must be also considered in the preparation of active and selective catalysts [29,30].

On the other hand, although the synthesis of these materials leads to the formation of M1 and M2 phases, in addition to other mixed oxides structures as $TeMo_5O_{16}$, $TeMo_4O_{13}$ and $MoO_3$ [25,28], only the formation of bronzes with TTB type structure (inactive in propane oxidation) seems to be specific from materials prepared by slurry method employing vanadyl sulphate as vanadium source. For this reason, and in agreement with the current results, the catalysts obtained by this way are less active than those prepared by slurry method employing $V^{5+}$ reagent, but also than those obtained hydrothermally in which it is possible to obtain $Te_2Mo_{20}O_{57}$ structure in a more selective way.

### 3.4. On the catalytic behaviour during propene oxidation

Table 3 shows the catalytic behaviour of MoVTeNbO catalysts in the propene oxidation. Acrylic acid, acrolein, CO and $CO_2$ were the main reaction products obtained. Other products such as acetaldehyde, acetone and acetic acid were also observed in minor amounts.

All the catalysts tested were shown capable to activate the olefin. Thus, whereas the catalysts presenting only $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb) phase were inactive for the propane oxidation, they showed catalytic activity if propene was the substrate. In any case, the general order of activity is the same to that found in the alkane oxidation. Catalysts without Nb showed the less activity with high selectivity to acrolein and low to acrylic acid. Increasing the Nb-content and the Mo/Te ratio resulted in a higher catalytic activity. Again, the samples with $Te_2M_{20}O_{57}$ present in their structure were the most selective to acrylic acid.

Fig. 4b shows the evolution of the propene conversion, and the selectivity to acrylic acid, acrolein and $CO_x$ with the propene conversion at a reaction temperature of 380 °C over one of the most effective catalysts, i.e. A4 sample. These results suggest that acrylic acid can be directly obtained from propene oxidation, but also by acrolein as primary intermediate, during propene selective oxidation over MoVTeNbO catalysts, as previously proposed [19,33]. Selectivity to acrylic acid close to 90% at propene conversions of 65% was achieved at 380 °C on the A4 catalyst.

Nb-free MoVTeO catalyst prepared from gel containing oxalic acid (B0-oxal catalyst) was also tested in the propene oxidation. The conversion reached 45% in the reaction conditions of Table 3, ten times higher than that obtained over the corresponding oxalic-free MoVTe catalyst, B0 (propene conversion of 5%). In addition, sample B0-oxal presented selectivities of 30 and 40% to acrolein and acrylic acid, respectively; while only acrolein was observed over B0 catalyst. Accordingly, the presence of Nb ions in the structure, but also the presence of oxalate anions in the catalyst

**Table 3**
Catalytic results during propene oxidation on MoVTeNb catalysts.

| Catalyst | Propene conversion (%)[a] | Selectivity (%) | | | | | | Yield to acrylic acid (%) |
|---|---|---|---|---|---|---|---|---|
| | | Acrylic acid | Acrolein | Acetic acid | Acetone | CO | $CO_2$ | |
| A0 | 5.1 | 0.0 | 95.3 | 0.0 | 1.8 | 1.0 | 1.9 | 0.0 |
| A1 | 5.8 | 28.3 | 53.7 | 2.5 | 6.2 | 3.6 | 3.8 | 0.5 |
| A2 | 9.7 | 69.5 | 8.6 | 1.9 | 6.5 | 6.5 | 6.0 | 6.7 |
| A3 | 39.6 | 89.6 | 0.9 | 1.2 | 1.5 | 3.9 | 2.6 | 35.5 |
| A4 | 64.9 | 86.4 | 0.4 | 0.1 | 2.2 | 7.4 | 3.4 | 56.1 |
| A5 | 4.5 | 31.3 | 34.0 | 4.2 | 9.2 | 6.2 | 14.2 | 1.4 |
| B0 | 5.8 | 13.2 | 71.2 | 4.8 | 4.5 | 1.8 | 2.7 | 0.8 |
| B1 | 58.3 | 88.5 | 0.3 | 1.2 | 2.3 | 5.1 | 2.4 | 51.6 |
| B2 | 54.5 | 87.6 | 0.5 | 1.3 | 2.2 | 5.6 | 2.5 | 47.8 |
| B3 | 63.0 | 83.7 | 1.3 | 2.9 | 1.3 | 7.1 | 3.5 | 52.7 |
| B4 | 79.9 | 46.4 | 0.4 | 13.1 | 1.2 | 26.0 | 12.8 | 37.1 |
| C0 | 4.9 | 14.7 | 50.5 | 3.4 | 13.4 | 12.6 | 7.2 | 0.7 |
| C1 | 38.1 | 76.1 | 0.4 | 4.0 | 5.6 | 9.1 | 4.5 | 29.0 |
| C3 | 84.1 | 15.4 | 0.2 | 17.8 | 0.6 | 45.7 | 20.1 | 13.0 |
| C4 | 86.9 | 2.0 | 0.2 | 12.3 | 0.5 | 62.6 | 23.1 | 1.7 |
| B0-oxal | 45.0 | 40.4 | 30.3 | 4.2 | 3.2 | 12.2 | 9.7 | 18.2 |

[a] Propene conversion and selectivity to main products at 380 °C and a contact time, W/F, of 543 $g_{cat}\,h\,(mol_{C_3H_6})^{-1}$.

precursors has a strong influence on the catalytic performance of these catalysts.

## 4. Conclusions

From the study of MoVTeNb mixed oxides catalysts, prepared by a slurry method and using different molar compositions (Mo/Te ratio from 2 to 6 and Nb/(V + Nb) ratio from 0 to 0.7) in the synthesis gel, it can be concluded that both the nature of crystalline phases and the catalytic performance strongly depend on the composition of the synthesis gel.

On the other hand, the chemical analysis of the as-synthesized and heat-treated catalysts indicates that the Te/M ratio (M = Mo, V, Nb) in heat-treated samples decreases when increasing the Nb/Te or oxalate/Te ratio in the synthesis gel. This Te-loss is explained by the presence of reducing species such as oxalate anions during the heat-treatment in $N_2$ which favours a partial reduction of $Te^{6+}$ to $Te^0$. Since $Te^0$ has a melting point of *ca.* 450 °C, whereas the heat-treatment is carried out at 600 °C, it can melt detaching from solid and decreasing the Te/(Mo + V + Nb) ratio in heat-treated samples. Accordingly, the nature of the crystalline phases and the catalytic performance of heat-treated materials strongly depend on the final chemical composition of catalysts. The partial substitution of vanadium by niobium in these catalysts is a crucial factor as the M1 phase formation is favoured over the M2 phase. In this way, only the catalysts presenting $Te_2M_{20}O_{57}$ (M = Mo, V, Nb) were active and selective in selective propane oxidation to acrylic acid. In the case of propene oxidation all catalysts were active and relatively selective to the formation of partial oxidation products, i.e. acrolein and/or acrylic acid, although the most active ones were those presenting M1 phase.

The optimal catalysts present a relatively wide range of chemical compositions, although it seems apparent that with a higher Te-content in the synthesis gel a greater amount of niobium is required to achieve an optimal catalytic performance.

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## References

[1] S. Alboneti, F. Cavani, F. Trifirò, Catal. Rev. Sci. Eng. 38 (1996) 413.

[2] T. Ushikubo, I. Sawaki, K. Oshima, K. Inumaru, S. Kovayakawa, K. Kiyono, EP Patent 0,603,836 (1993).;
T. Ushikubo, I. Sawaki, K. Oshima, K. Inumaru, S. Kovayakawa, K. Kiyono, US Patent 5,442,328 (1993).

[3] T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, US Patent 5,380,933 (1995).;
T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, EP Patent 0,608,838 B1 (1997).

[4] J.M. Lopez Nieto, P. Botella, M.I. Vázquez, A. Dejoz, Chem. Commun. 17 (2002) 1906.

[5] J.M. López Nieto, P. Botella, M.I. Vázquez, A. Dejoz, Patent WO 03,064,035 (2003).

[6] T. Ushikubo, K. Oshima, A. Kayou, M. Hatano, Stud. Surf. Sci. Catal. 112 (1997) 473.

[7] J.M.M. Millet, H. Roussel, A. Pigamo, J.L. Dubois, J.C. Jumas, Appl. Catal. A 232 (2002) 77.

[8] P. DeSanto, D.J. Buttrey, R.K. Grasselli, C.G. Lugmair, A.F. Volpe, B.H. Toby, T. Vogt, Zeits. F. Krist. 219 (2004) 152.

[9] P. DeSanto, D.J. Buttrey, R.K. Grasselli, C.G. Lugmair, A.F. Volpe, B.H. Toby, Top. Catal. 23 (2003) 23.

[10] H. Tsuji, Y. Koyasu, J. Am. Chem. Soc. 124 (2002) 5608.

[11] E. García-González, J.M. López Nieto, P. Botella, J.M. González-Calbet, Chem. Mater. 14 (2002) 4416.

[12] P. Botella, E. García-González, J.M. López Nieto, J.M. González-Calbet, Solid State Sci. 7 (2005) 507.

[13] M. Baca, A. Pigamo, J.L. Dubois, J.M.M. Millet, Top. Catal. 23 (2003) 39.

[14] M. Baca, M. Aouine, J.L. Dubois, J.M.M. Millet, J. Catal. 233 (2005) 234.

[15] J. Holmberg, R.K. Grasselli, A. Andersson, Appl. Catal. A: Gen. 270 (2004) 121.

[16] P. Korovchenko, N.R. Shiju, A.K. Dossier, U.M. Gram, M.O. Guerrero-Pérez, V.V. Guliants, Top. Catal. 50 (2008) 43.

[17] P. Beato, A. Blume, F. Girsdies, R.E. Jentof, R. Schlögl, O. Timpe, A. Trunschke, G. Weimberg, Q. Basher, F.A. Hamid, S.B.A. Hamid, E. Omar, L. Mohd Salim, Appl. Catal. A 307 (2006) 137.

[18] K. Oshihara, T. Hisano, W. Ueda, Top. Catal. 15 (2001) 153.

[19] P. Botella, J.M. López Nieto, B. Solsona, A. Mifsud, F. Márquez, J. Catal. 209 (2002) 445.

[20] P. Botella, J.M. López Nieto, A. Martínez-Arias, B. Solsona, Catal. Lett. 74 (2001) 149.

[21] A. Celaya Sanfiz, T.W. Hansen, F. Girgsdies, O. Timpe, E. Rödel, T. Ressler, A. Trunschke, R. Schlögl, Top. Catal. 59 (2008) 19.

[22] P. Botella, P. Concepción, J.M. López Nieto, Y. Moreno, Catal. Today 99 (2005) 51.

[23] X. Tu, N. Furuta, Y. Sumida, M. Takahashi, N. Niiduma, Catal. Today 117 (2006) 259.

[24] R. Feng, X.-J. Yang, W.-J. Ji, H.-Y. Zhu, X.-D. Gu, Y. Chen, S. Han, H. Hibst, J. Mol. Catal. A 267 (2007) 245.

[25] J.M. Oliver, J.M. López Nieto, P. Botella, A. Mifsud, Appl. Catal. A 257 (2004) 67.

[26] Y. Zhu, W. Lu, H. Wan, J. Catal. 246 (2007) 382.

[27] H. Tsuji, K. Oshima, Y. Koyasu, Chem. Mater. 15 (2003) 2112.

[28] R.K. Grasselli, J.D. Burrington, D.J. Buttrey, P. DeSanto, C.G. Lugmair, A.F. Volpe, T. Weingand, Top. Catal. 23 (2003) 5.

[29] F. Ivars, P. Botella, A. Dejoz, J.M. López Nieto, P. Concepción, M.I. Vázquez, Top. Catal. 38 (2006) 59.

[30] G.Y. Popova, T.V. Andrushkevich, L.S. Dovlitova, G.A. Aleshina, Yu.A. Chesalov, A.V. Ishenko, E.V. Ishenko, L.M. Plyasova, V.V. Malakhov, M.I. Khramov, Appl. Catal. A 353 (2009) 249.

[31] Z. Deng, H. Wang, W. Chu, W. Yang, Chin. J. Catal. 29 (2008) 1032.

[32] P. Botella, J.M. López Nieto, B. Solsona, Catal. Lett. 78 (2002) 383.

[33] E. Balcells, F. Borgmeier, I. Grißtede, H.-G. Lintz, Catal. Lett. 87 (2003) 195.