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Selective oxidation and ammoxidation of propane on a Mo–V–Te–Nb–O mixed metal oxide catalyst: a comparative study

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Abstract

A comparative study on the selective oxidation and the ammoxidation of propane on a Mo–V–Te–Nb–O mixed oxide catalyst is presented. The catalyst has been prepared hydrothermally at 175 °C and heat-treated in N_2 at 600 °C for 2 h. Catalyst characterization results suggest the presence mainly of the orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) bronze in samples before and after use in oxidation and ammoxidation, although some little modifications have been observed after its use in ammoxidation reaction. Propane has been selectively oxidized to acrylic acid (AA) in the 340–380 °C temperature range while the ammoxidation of propane to acrylonitrile (ACN) has been carried out in the 360–420 °C temperature interval. The steam/propane and the ammonia/propane molar ratios have an important influence on the activity and the selectivity to acrylic acid and acrylonitrile, respectively. The reaction network in both oxidation and ammoxidation reactions as well as the nature of active and selective sites is also discussed. The catalytic results presented here show that the formation of both ACN and AA goes through the intermediate formation of propene.

Keywords: Propane oxidation and ammoxidation; The effect of water and ammonia; Molybdenum–vanadium–tellurium–niobium mixed metal oxide catalyst

1. Introduction

Acrylonitrile (ACN) and acrylic acid (AA) are important intermediates in petrochemistry. Actually, they are synthesized from propene using mixed metal oxides catalysts. However, important differences can be observed between both processes. While acrylonitrile is prepared in a single step, acrylic acid is obtained in a two-step process using two different catalytic systems and different reactions conditions [1].

Because of their widespread availability and low cost, considerable effort is being directed towards the development of new selective oxidation processes based on alkanes instead of the corresponding olefins. In the case of propane, both the ammoxidation and the selective oxidation are very interesting processes [2–5].

V–Sb–Al mixed oxides with a rutile structure have been reported as active and selective catalysts in the ammoxidation of propane to ACN [6–9] but they present low selectivity during the selective oxidation of propane [10]. The common feature of these catalysts is the presence of vanadium (as the key component in the oxidative dehydrogenation of propane to propene) and a mixed oxide matrix (known to be selective in the ammoxidation of propene) [6–9].

Mo–V–Te–Nb mixed oxides are interesting catalysts in the transformation of short-chain alkanes. Thus, it has been reported that ACN and AA can selectively be obtained in the ammoxidation [11–15] and the oxidation [16–20] of propane, whereas ethene can selectively be produced by the selective oxidative dehydrogenation of ethane [21,22]. The fact that Mo–V–Te–Nb mixed oxides could be used in both ammoxidation and/or oxidation while V–Sb–Al mixed oxides are only active in the ammoxidation process suggests important differences between both catalytic systems [23].

From the literature of patents it seems that the MoVTeNbO catalysts used in both reactions present similar compositions. On the other hand, the same type of active and selective sites in ammoxidation reaction could apparently be proposed to be selective in the oxidation of propane to acrylic acid, although a higher number of reaction steps

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could be considered for the oxidation of propane to acrylic acid [19,20]. Despite this interest, relatively few comparative studies have been published about these two reactions. However, a comparison of the catalytic performance of a MoVTeNbO catalyst in both ammoxidation and selective oxidation of propane can help to understand the nature of the active and selective sites in this catalyst.

In this paper, we show how acrylonitrile and/or acrylic acid can selectively be obtained on a MoVTeNbO mixed oxide catalyst prepared by hydrothermal synthesis. The catalytic results suggest that the reaction conditions must be optimized in each case in order to achieve, selectively, partial oxidation or ammoxidation products. The role of water and ammonia on activity and selectivity is also discussed.

2. Experimental

2.1. Catalyst preparation

A MoVTeNbO catalyst has been prepared by hydrothermal synthesis at 175 °C during 60 h, from an aqueous solution of ammonium heptamolybdate, vanadyl sulphate, telluric acid and niobium oxalate, with a Mo/V/Te/Nb atomic ratio of 1/0.36/0.17/0.12, according to a previous paper [19,20]. The solid was dried at 100 °C overnight and finally was calcined at 600 °C for 2 h in N_2 stream. The calcined sample presents a surface area, S_{BET}, of 10.6 $m^2 g^{-1}$ (Table 1).

2.2. Catalyst characterization

BET-specific surface areas were measured on a Micromeritics ASAP 2000 instrument (adsorption of krypton) and on a Micromeritics Flowsorb (adsorption of N_2).

X-ray diffraction patterns (XRD) were collected using a Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered CuK_α radiation (λ = 0.1542 nm).

Diffuse reflectance (DR)–UV–VIS spectra were collected on a Cary 5 equipped with a 'Prayting Mantis' attachment from Harric.

2.3. Catalytic tests

The catalytic tests were carried out in a fixed-bed quartz tubular reactor, working at atmospheric pressure, in the 350–440 °C temperature interval. The flow rate and the amount of catalyst were varied in order to achieve different propane conversion levels. The feed consisted of a mixture of propane/oxygen/helium/water or propene/oxygen/helium/ammonia with molar ratios of 4/8/88-x/x (x = 0–30) and 4/12/84-y/y (y = 0–8), respectively. Reactants and reaction products were analyzed by on-line gas chromatography, using three different 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 N_2, O_2, NO and CO; (iii) Porapak Q (3.0 m × 1/8 in.) to separate oxygenated products. Analysis of ammonia conversion and formation of HCN were performed using a titrametric method [9]. In all cases, yields of HCN lower than 2–3% were observed.

Blank runs showed that under the experimental conditions used in this work the homogeneous reaction could be neglected.

3. Results

3.1. Catalyst characterization

Reported in Fig. 1 are the XRD patterns of the heat-treated sample before and after the catalytic tests. The XRD patterns are characterized by the presence of peaks at 2θ = 7.7, 8.7, 14.0, 22.1, 23.5, 24.6, 26.2, 26.6, 27.3, 29.2, 30.4 and 35.4 that could be related to the presence of an orthorhombic crystalline phase, i.e. $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) [24] or $Mo_{7.5}V_{1.5}NbTeO_{29}$ [25], which has recently been confirmed from SAED and HREM results [26].

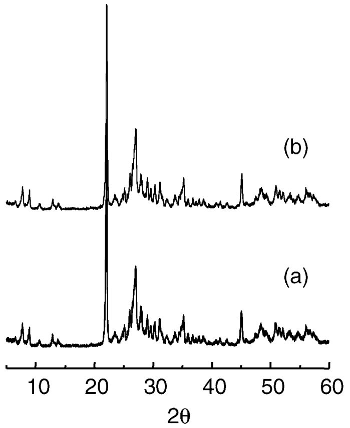


Fig. 1. XRD patterns of MoVTeNbO catalysts before (a) and after the catalytic test in propane ammoxidation (b).

Table 1
Characteristics of MoVTeNbO catalyst

Sample	S_{BET} ($m^2 g^{-1}$)	Mo–V–Te–Nb atomic ratio		
		AAS	XPS	EDX
Before calcination	ND	10.20-0.25-0.20	ND	ND
After calcination	10.6	1-0.20-0.20-0.20	1-0.11-0.19-0.20	1-0.23-0.11-0.22

ND = not determined.

On the other hand, the appearance of small peaks at 2θ = 22.1, 28.2, 36.2, 44.7, and 50.0 suggest the presence of a $Te_{0.33}MO_3$ (M= Mo, V and Nb) phase, an orthorhombically distorted unit cell derived from the hexagonal tungsten bronze [27,28], as minority. In addition to these, the presence of a rutile-type $(Mo_{0.93}V_{0.07})_5O_{14}$ [JCPDS, 31–1437] and/or $Nb_{0.09}Mo_{0.91}O_{2.80}$ [JCPDS, 23–1310], or a $Mo_{5-x}(V/Nb)_xO_{14}$ phase [19], cannot completely be ruled out. No differences have been found between the XRD pattern of calcined samples with those after their use in oxidation or ammoxidation, in agreement with that observed by Holmberg et al. [15]. These results, similar to those previously reported [19,20], are different from those published for MoVTeNbO catalysts prepared from slurries [11–19,24,25], in which the intensities of peaks related to $Te_{0.33}MO_3$ are generally higher to those related to $Te_2M_{20}O_{57}$. So, it can be concluded that the hydrothermal synthesis directs, selectively, the formation of the orthorhombic $Te_2M_{20}O_{57}$ phase [19,20].

Fig. 2 presents the DR spectra of the calcined sample, before (Fig. 2a) and after use in oxidation (Fig. 2b) and ammoxidation (Fig. 2c). The DRS spectrum of calcined MoVTeNbO sample is characterized by the presence of broad bands in the range of 250–400 nm and 500–700 nm. The appearance of a broad band in the range 250–400 nm can be related to the presence of Mo^{6+} and V^{5+} in addition to Te^{4+} and Nb^{5+} [27], while the bands in the 500–600 nm region may be assigned to Mo cations with an oxidation state lower than 6+ [27] (EPR results suggested an oxidation state of molybdenum of about 5.8 [20]). The presence of V^{4+} can be proposed (broad band in the 600–750 nm region) but difficult to quantify. So, Mo^{6+}/Mo^{5+}, V^{5+}/V^{4+}, Te^{4+} and Nb^{5+} are mainly present in our catalyst.

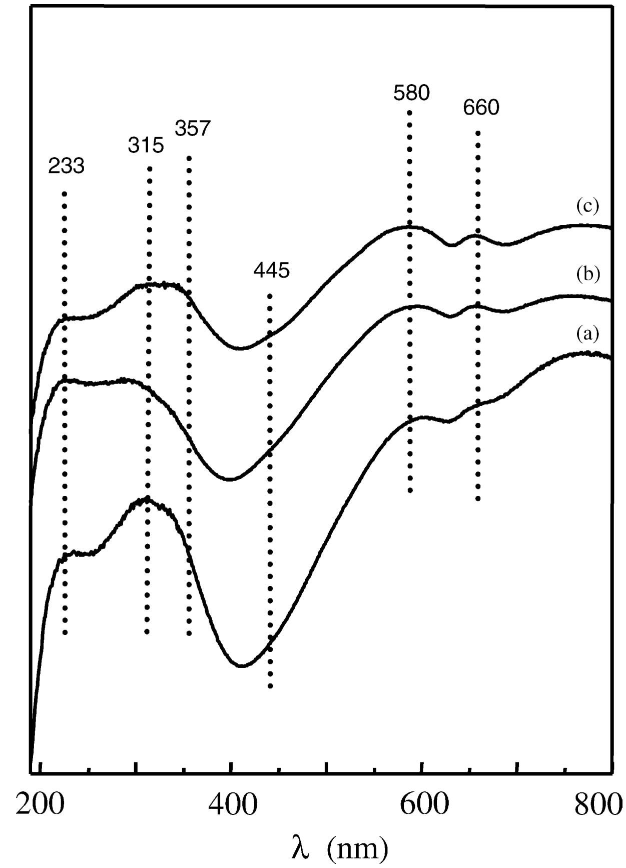


Fig. 2. Diffuse reflectance UV–VIS spectra of MoVTeNbO catalysts before (a) and after the catalytic tests in propane oxidation (b) or propane ammoxidation (c).

The DR–UV–VIS spectrum of the catalyst used in the propane oxidation reaction is similar to that obtained in the heat-treated sample. However, small differences can be seen in the sample used in the ammoxidation reaction. In this way, the intensity of the bands at about 250 and 580 nm increases for the catalyst used in the ammoxidation reaction. This can be related to an increase in the formation of Mo^{5+} species with respect to those observed in both the calcined sample or the catalyst used in propane oxidation.

3.2. Catalytic tests

Fig. 3 shows the variation of the propane conversion and the yield of AA or ACN with the reaction temperature obtained during the oxidation and the ammoxidation of propane on the MoVTeNbO catalyst. At the same reaction conditions, the conversion of propane during the propane oxidation was higher than that of the propane ammoxidation, while the O_2 consumption during the propane oxidation was lower than that in the propane ammoxidation. The high O_2 consumption observed during the ammoxidation reaction is a consequence of the partial combustion of NH_3, which is generally considered as a competitive reaction with the ammoxidation of propane [9]. So, ammonia seems to have

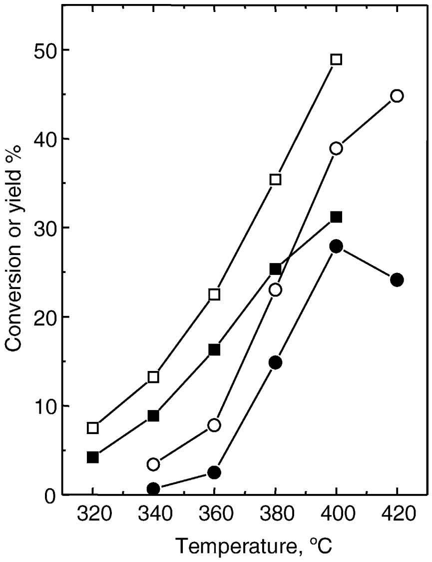


Fig. 3. Variation of the propane conversion (□, ○) and the yield of acrylic acid (■) or acrylonitrile (●) with the reaction temperature obtained during the oxidation (□, ■) and the ammoxidation (○, ●) of propane over a MoVTeNbO catalyst. Experimental conditions in text.

a partial inhibition in the selective propane activation during the ammoxidation reaction.

On the other hand, it can be said that N_2 was the only reaction product obtained during the NH_3 oxidation, as it has also been observed in the oxidation of NH_3 on V-based selective ammoxidation catalysts [7–9,23].

Fig. 4 shows the variation of the selectivities to the main reaction products with the reaction temperature during the oxidation (Fig. 4a) and the ammoxidation (Fig. 4b) of propane. Acrylic acid, CO and CO_2, in addition to acetic acid, were mainly obtained in the oxidation reaction, although small amounts of acetone and acrolein were also observed. On the other hand, acrylonitrile, CO and CO_2, in addition to acetonitrile, were mainly obtained in the ammoxidation reaction, although depending on the reaction conditions, AA can also be produced. In addition, traces of acrolein were also detected occasionally.

Besides of the reaction, the selectivity to propene decreases with the reaction temperature while the selectivity to AA (oxidation) or ACN (ammoxidation) presents a maximum of about 70% at 360 or 400 °C, respectively. On the other hand, carbon monoxide is mainly formed at high propane conversions and/or high reaction temperature, probably as a consequence of the consecutive oxidation of reaction products.

The selectivity to CO_2 increases with the reaction temperature in the propane oxidation (Fig. 4a), while a minimum at 400 °C in the selectivity to CO_2 is observed in the propane ammoxidation (Fig. 4b). So, a detailed study on the influence of the reaction conditions on the catalytic behavior in both reactions is needed in order to understand the reaction network and the nature of active and selective sites.

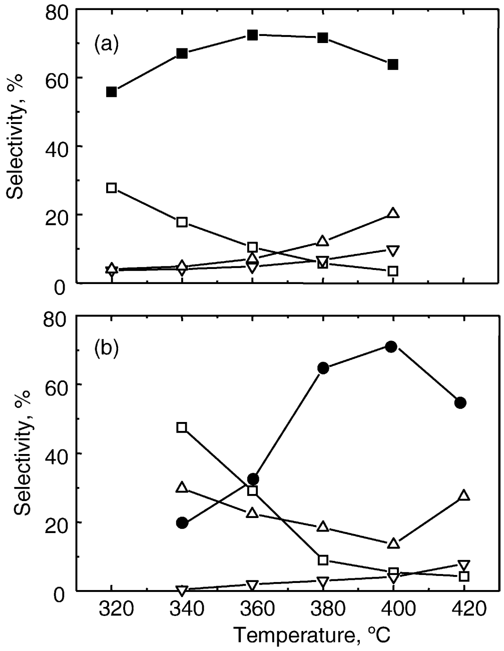


Fig. 4. Variation of the selectivity to the main reaction products with the reaction temperature obtained during the oxidation (a) and ammoxidation (b) of propane, respectively, on a MoVTeNbO catalyst. Experimental conditions as in Fig. 3.Symbols: selectivity to acrylic acid (■), acrylonitrile (●), propene (□), CO (▽) and CO_2 (Δ). Experimental conditions as in Fig. 3.

3.2.1. (a) Propane oxidation on MoVTeNbO catalyst

Reported in Fig. 5 is the selectivity to the reaction products as a function of the propane conversion obtained during the oxidation of propane at 380 °C. Acrylic acid, propene, and carbon oxides have mainly been observed. In addition to these, acetone and acetic acid were also observed with low selectivities. Propene is mainly observed at low propane conversion and can be considered as a primary reaction product. The selectivity to propene progressively decreases with a parallel increase in the selectivity to AA. So, AA is mainly formed from propene by consecutive reaction (the highest selectivity to AA observed at propane conversions between 25 and 50%). So, if we take into account the sum of both reaction products at propane conversion lower than 20%, it can be concluded that the reaction is carried out with a very selective activation of propane (selectivities to propene and AA higher than 80% are achieved).

Low selectivities to carbon oxides are observed at low propane conversions, but they slightly increase with the propane conversion. On the other hand, the sum of acetone and acetic acid slightly increase with the propane conversion, although the variation of their selectivities present an opposite trend (acetone is mainly formed at low conversion and acetic acid is mainly observed at high conversion). According to these results, a reaction network with parallel and consecutive reactions is proposed in Scheme 1. This is in agreement to previous results [19,20,29,30].

Fig. 6 presents the variation of the selectivity to AA (Fig. 6a) and propene (Fig. 6b), as well as the sum of selectivities of both reaction products (Fig. 6c) with the propane conversion obtained in the 320–400 °C temperature

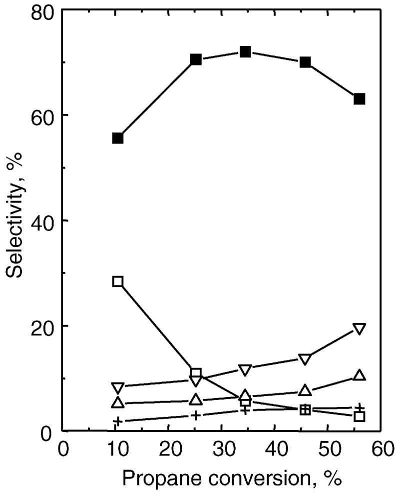
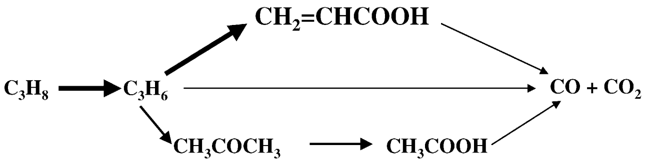


Fig. 5. Variation of the selectivity to the main reaction products with the propane conversion obtained during the oxidation of propane at 380 °C on a MoVTeNbO catalyst. Symbols: selectivity to acrylic acid (■), propene (□), acetic acid (+), CO (▽) and CO_2 (△).



Scheme 1. Reaction network for the oxidation of propane on a MoVTeNbO catalyst.

range. No variation in the selectivities to AA and propene with the reaction temperature has been observed in the 320–380 °C temperature interval. However, the selectivity to acrylic acid obtained at 400 °C presents a slight decrease with respect to those obtained at lower temperatures. These results suggest that the stability of AA decreases at reaction temperatures higher than 380 °C.

It has been suggested that AA needs the presence of steam in the feed. For this reason, the influence of the steam on the formation of AA has been investigated. Table 2 shows the catalytic results obtained at 360 and 400 °C with different steam/C_3H_8 ratios, while Fig. 7 presents the variation of the yield of acrylic acid with the reaction temperature obtained during the oxidation of propane with different propane/steam ratios. In the absence of stream, AA is formed, but low yields are achieved. However, both the propane conversion and the selectivity to AA increase with the steam/C_3H_8 ratios. So, the incorporation of steam increases the yield of acrylic acid, this increase being more important at high propane conversions.

Table 2
Influence of the steam/C_3H_8 ratio in the oxidation of propane over a MoVTeNbO catalyst[a]

H_2O/C_3H_6 ratio	T (°C)	Conversion (%)	Selectivity (%)[b]			
			AA	C_3H_6	CO	CO_2
0	360	3.6	15.2	64.7	6.3	13.3
3.75	360	5.7	41.1	48.0	3.7	5.4
7.50	360	7.5	50.0	35.3	6.1	5.5
0	400	13.6	30.8	39.8	9.4	19.7
3.75	400	17.3	57.0	19.1	7.5	15.0
7.50	400	21.5	58.5	14.3	9.3	16.3

[a] Reaction conditions: $C_3H_8/O_2/H_2O/He = 4/8/x/88-x$ (x = 0–30); W/F = 100 g_{cat} h $(mol_{C3})^{-1}$.

[b] Acrolein and acetic acid were also observed with selectivities lower than 3%.

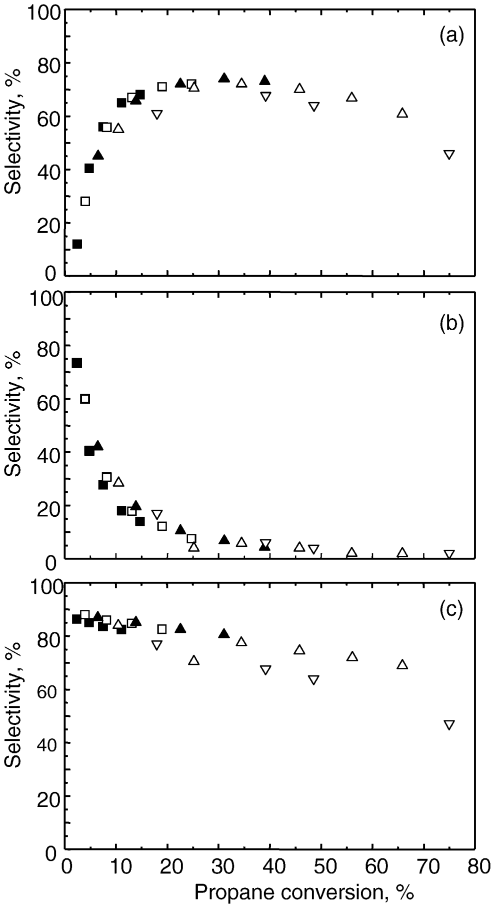


Fig. 6. Variation of the selectivity to acrylic acid (a) and to propene (b) and the sum partial oxidation products and (c), with the propane conversion obtained at various reaction temperatures: 320 (■), 340 (□), 360 (▲), 380 (Δ) and 400 °C (▽). Experimental conditions: propane/oxygen/steam/helium molar ratio of 4/8/30/58.

3.2.2. (b) Propane ammoxidation on MoVTeNbO catalyst

Fig. 8 shows the variation of the selectivity to the main reaction products obtained during the ammoxidation of propane at 380 °C. Acrylonitrile, propene and carbon oxides have mainly been observed. In addition to these, acetonitrile and acrylic acid were also observed, with relatively low selectivities, at high propane conversions. The selectivity to ACN increases and the selectivity to propene decreases with the propane conversion. In both cases the highest selectivities to ACN are observed at propane conversions of about 35–45% (Fig. 8). For this reason, acrylonitrile should mainly be formed from propene by consecutive reaction.

Low selectivities to carbon oxides are observed at low propane conversions, but they slightly increase with that. The formation of acetonitrile also increases slightly with the propane conversion. This could be formed in a similar way

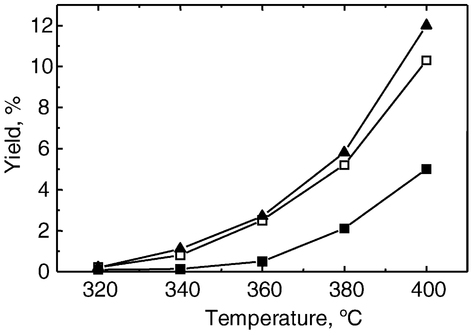


Fig. 7. Variation of the yield of acrylic acid with the reaction temperature obtained during the oxidation of propane with different steam/propane ratios. Symbols: H_2O/C_3H_8 molar ratios of 0 (■), 3.75 (□) and 7.50 (▲). Experimental conditions: propane/oxygen/steam/helium molar ratio of 4/8/x/88-x (x = 0–30); contact time, W/F, of 100 g_{cat} h $(mol_{C3})^{-1}$.

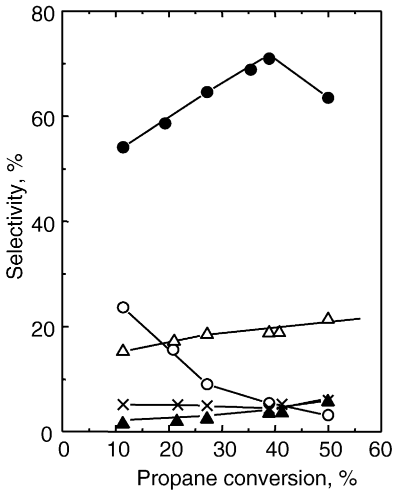
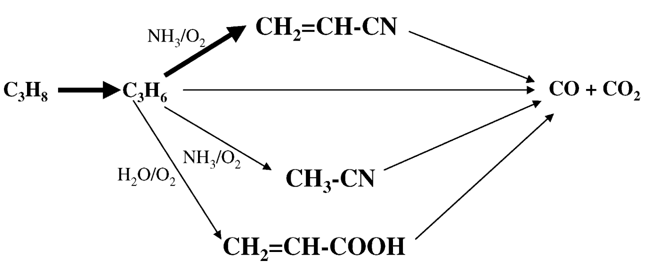


Fig. 8. Variation of the selectivity to the main reaction products with the propane conversion obtained during the ammoxidation of propane at 400 °C on a MoVTeNbO catalyst. Symbols: selectivity to acrylonitrile (●), propene (○), acetonitrile (■) CO (▲) and CO_2 (△).

than acetone and acetic acid in propane oxidation. On the other hand, acrylic acid can be observed at high reaction temperatures and/or high propane conversions in which ammonia is fully converted. This suggests that acrylic acid and acrylonitrile should be formed in the same active sites. However, the yield of ACN achieved during the ammoxidation was lower than the yield of acrylic acid achieved during the oxidation (Fig. 3). As it has been proposed for the VSb–O-based catalysts, a competition between oxygen and ammonia for the same site could explain this lower formation of ACN [10]. According to these results, a reaction network with parallel and consecutive reaction is proposed in Scheme 2.

Fig. 9 presents the variation of the selectivity to ACN (Fig. 9a) and propene (Fig. 9b), as well as the selectivity to partial reaction products (Fig. 9c) with the propane conversion obtained in the 340–420 °C temperature range. The selectivity to propene has been observed to decrease with the propane conversion, although it is not affected by the reaction temperature. However, the selectivity to ACN was lower at 420 °C. The results obtained here suggest that the formation and stability of ACN initially increases with the reaction temperature but it decreases at high reaction temperatures ($T > 420$ °C).



Scheme 2. Reaction network for the ammoxidation of propane on a MoVTeNbO catalyst.

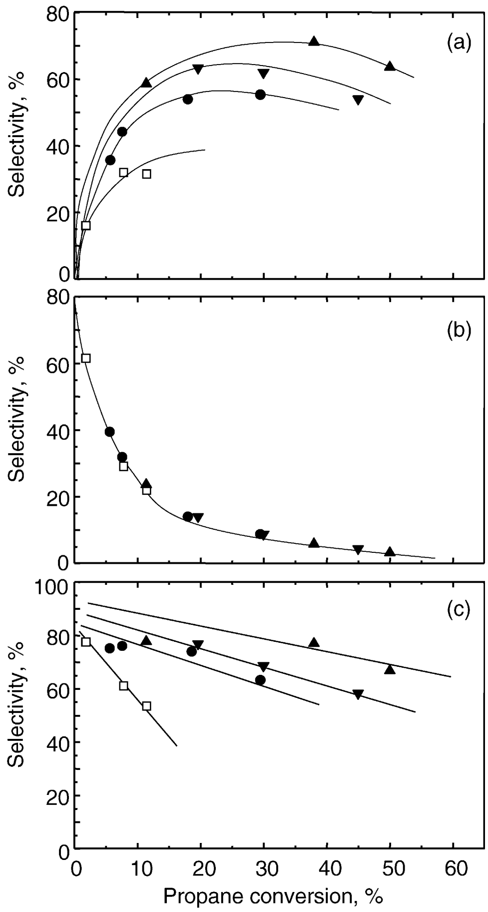


Fig. 9. Variation of the selectivity to acrylonitrile (a), propene (b) and the sum of partial oxidation products (c), with the propane conversion obtained at various reaction temperatures: 360 (●), 380 (▲), 400 (▼) and 420 °C (□). Experimental conditions: propane/oxygen/ammonia/helium molar ratio of 4/8/12/76.

On the other hand, the formation of ACN strongly depends on the presence of ammonia. For this reason, the influence of the ammonia on the formation of ACN has been investigated. Table 3 shows the catalytic results obtained at 400 and 440 °C with different NH_3/C_3H_8 ratios, while

Table 3
Influence of the NH_3/C_3H_6 ratio in the ammoxidation of propane over a MoVTeNbO catalyst[a]

NH_3/C_3H_8 ratio	T (°C)	Conversion (%)	Selectivity (%)[b]				
			ACN	AA	C_3H_6	CO	CO_2
0	400	12.1	–	27.1	37.0	14.2	20.1
1.5	400	14.5	62.8	–	20.2	2.0	10.4
3.0	400	11.2	54.1	–	23.6	2.1	15.2
0	440	28.0	–	12.0	10.0	33.0	41.5
1.5	440	30.7	50.6	9.6	9.3	7.8	19.3
3.0	400	29.8	59.9	–	8.7	7.4	20.4

[a] Reaction conditions: $C_3H_8/O_2/NH_3/He = 4/12/x/84\text{-}x$ (x = 0–12); W/F = 100 g_{cat} h $(mol_{C3})^{-1}$.

[b] Acrolein and acetonitrile were also observed with selectivities lower than 5%.

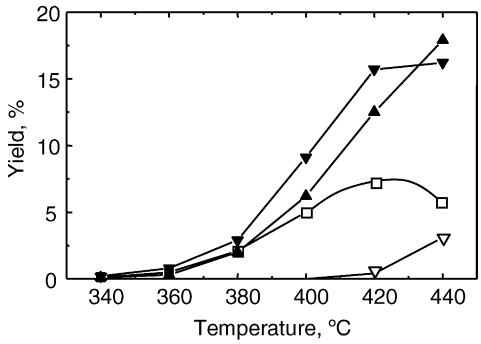


Fig. 10. Variation of the yield of acrylonitrile (▲, ▼) and acrylic acid (□, ▽) with the reaction temperature obtained during the ammoxidation of propane with different ammonia/propane ratios. Symbols: NH_3/C_3H_8 molar ratios of 0 (□), 1.5 (▼, ▽) and 3.0 (▲). Experimental conditions: propane/oxygen/ammonia/helium molar ratio of 4/12/*x*/88-*x* (*x* = 0–12); contact time, *W/F*, of 100 g_{cat} h $(mol_{C3})^{-1}$.

Fig. 10 shows the variation of the yield of ACN with the reaction temperature obtained at various NH_3/C_3H_8 ratios. In the absence of ammonia, only acrylic acid is obtained. The incorporation of ammonia increases both the propane conversion and the selectivity to ACN, although the catalytic results depend strongly on the NH_3/C_3H_8 ratio.

At low propane conversion, intermediate NH_3/C_3H_8 ratios are preferred. In fact, the use of high NH_3/C_3H_8 ratios favors an important decrease in the propane conversion, suggesting a competitive effect between oxygen and ammonia.

High NH_3/C_3H_8 ratios are needed, however, for high propane conversion. In this case, ammonia is totally transformed not only into ACN and acetonitrile but also in N_2 and/or NO_x. In this way, it can be reported that selectivities to N_2 higher than 95% have been observed during the oxidation of NH_3 on this catalyst. We must indicate that acrylic acid was also observed in experiments with a total ammonia conversion. So, it appears that, as observed in the case of steam during the selective propane oxidation, the optimal amount of ammonia to be feed in the ammoxidation reaction depends on the propane conversion level.

4. Discussion

It is generally accepted that both the ammoxidation [2–5,7–9,12–15] and the oxidation [2–5,19,20,29,30] of propane are initiated by the oxidative dehydrogenation of propane to propene (via H-abstraction of propane), as proposed in the oxidation of *n*-butane [31]. The Lewis acid site (V cation) and basic site (O^{2-}) interacts with α- and β-hydrogen of propane, respectively, to form propene [32]. Although the two reactions may share some fundamental reaction steps (specially those related with the alkane activation and the oxidative dehydrogenation of propane to propene), there are significant differences between both reactions, especially those involved in the ammonia activation and N-insertion [9,14,15,23].

Although similar catalytic systems were proposed for the selective oxidation/ammoxidation of propene [33], it may be quite unexpected that the same catalyst can present high selectivity in both oxidation and ammoxidation of propane without changes in the chemical composition. However, the different acidity required in both reactions could be partially equilibrated by the incorporation of water or ammonia in the feed, since they present a different basic character. In fact, the strength of the Lewis acid sites can be modified by the incorporation of water and/or ammonia changing not only the nature of partial oxidation products but also the selectivity to the main reaction products [2–5,34–37].

On the other hand, it has been reported that the formation rate of ACN in VSb–O-based catalysts can be described on the basis of two different sites for propane and for O_2 and NH_3 adsorption (competition between these two reagents for the same site) with a rate-determining step involving the reaction between adsorbed propane, O_2 and NH_3 [9]. So, a similar rate-determining step could be proposed in both the oxidation and the ammoxidation of propane on MoVTeNbO catalysts.

The presence of water in the selective oxidation of hydrocarbons favors higher selectivities to partial oxidation products [4,5,38,39]. This is also observed in the oxidation of propene to acrylic acid [40–42] or in the oxidation of propane to acrylic acid on undoped [43] and K-doped MoVSbO [44], Mo-Ni-O [45–46] or VPO [47] catalysts. Water is adsorbed preferentially on Lewis acid sites to give Bronsted acid sites. As a consequence, the strongest adsorbent sites, where carboxylic oxygen bonds to the cation leading to deep oxidation of the reaction intermediates, are removed from catalyst surface [39,47], thus, enhancing the selectivity of the process and allowing the re-oxidation of the catalyst surface [38–40]. Moreover, the steam can also estabilize the crystalline structure during the catalytic test [43]. According to our results, both the propane conversion and the selectivity to acrylic acid increase with the steam/propane ratio, suggesting that the presence of steam could also favor a fast desorption of the reaction intermediates and perhaps a higher catalyst reoxidation.

During the ammoxidation of hydrocarbons, the presence of ammonia should favor the transformation of M=O-sites to M=NH-sites, which should be responsible of the direct formation of acrylonitrile from propene [7,32,33]. Acrylic acid is also observed during the ammoxidation of propane under reaction conditions in which ammonia is fully converted. So, the same active sites seem to be involved in the two reactions, although the presence of ammonia should determine the M=O/M=NH ratio and the nature of the reaction product.

On the other hand, the production of ACN at low temperature is probably limited by the availability of the catalyst in the NH_3 activation [9,23]. In this way, MoVTeNbO catalysts seem to be more active and selective to ACN than V–Sb-based catalysts in the range of 380–440 °C.

It is evident that the acidity of the active sites will have a strong influence on the nature and the electronic state of the intermediates. Strongly adsorbed species could be formed on strong acid sites favoring the deep oxidation. However, slightly adsorbed species could be favored on centers with moderate acidity, favoring the partial oxidation reaction. So, the effect of steam or ammonia during the oxidation or ammoxidation reaction, respectively, could have a similar influence. However, the appearance of competitive reaction, i.e., NH_3 combustion [9,23], can modify the amount of NH_3 available by the selective ammoxidation.

On the other hand, acrylic acid can also be obtained during the ammoxidation of propane when all of ammonia is converted (Fig. 10). Although water was not incorporated in the feed, it could be formed from both the combustion of ammonia and the oxidative dehydrogenation of propane. So, water should also be present in the ammoxidation reaction.

4.1. The nature of active and selective crystalline phases

The nature of active and selective sites in the oxidation and ammoxidation on MoVTeNbO catalysts is still under discussion [12–20]. However, and according to our results, it can be concluded that the orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) bronze ($Mo_{7.5}V_{1.5}NbTeO_{29}$, according to [25]), could be the active and selective crystalline phase in both oxidation and ammoxidation of propane in our catalyst. In this way, it has recently been proposed that this phase is also active and selective in the oxidative dehydrogenation of ethane [21,22].

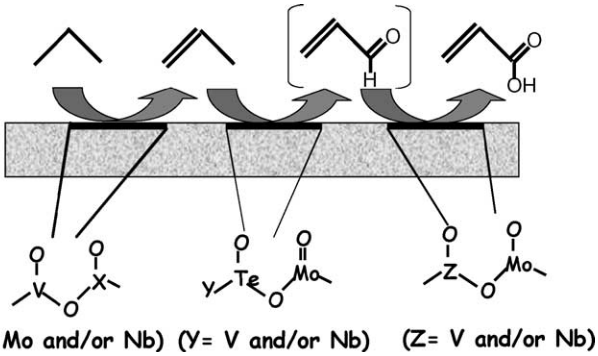
$Te_2M_{20}O_{57}$ (M = Mo, V and Nb) bronze is characterized by the presence of MO_7 pentagonal bipyramids, with all of their five equatorial edges in common with MO_6 octahedra, with hexagonal (occupied by tellurium cations in a $[TeO_3E]$ coordination) and heptagonal channels (empty) [24,25].

The MO_7 pentagonal bipyramids with their five equatorial edges in common with MO_6 octahedra observed in $Te_2M_{20}O_{57}$ phase are similar to those proposed in Mo_5O_{14} or $Mo_{5-x}(V/Nb)_xO_{14}$ [48]. Since $Mo_{5-x}(V/Nb)_xO_{14}$ seems to be active and selective in the oxidative dehydrogenation of ethane [49,50], this unit could be responsible for the propane activation in our catalyst. In addition, it has been reported that the catalytic activity of these catalysts is strongly related to its vanadium content. So, octahedral V^{5+} species (in V^5–O–Mo and or V^{5+}–O–Nb) can be proposed as the active sites in propane dehydrogenation, as it has been proposed during the oxydehydrogenation of ethane on these catalysts [20,21,51].

On the other hand, the hexagonal channels occupied by tellurium cations in a $[TeO_3E]$ coordination described for $Te_2M_{20}O_{57}$ phase are similar to that proposed for $Te_{0.33}MO_{3.33}$ (M = Mo, V and Nb) [27,28]. Since $Te_{0.33}MO_{3.33}$ phase is inactive in propane oxidation but active and selective in the oxidation of propene to acrolein ($Te_{0.33}Mo_{1-x}V_xO_{3.33}$) and acrylic acid ($Te_{0.33}Mo_{1-x}(V/Nb)_xO_{3.33}$) [52], Mo–O–Te pairs in the hexagonal channels occupied by tellurium cations should be responsible of the partial oxidation and ammoxidation of propene in our catalyst. The presence of V and/or Nb species in this hexagonal channels should determine the nature of partial reaction products [19].

According to these results, the following reaction steps can be proposed in the selective propane oxidation (Scheme 3) [19]: (i) the activation of propane in V-sites, Mo–O–V–O–X (X = Mo or Nb) like; (ii) the oxidation of propene in Mo-sites, Te–O–Mo–O–Y (Y = V or Nb) like and (iii) the oxidation of acrolein to acrylic acid in Mo-sites, Nb–O–Mo–O–Z (Z = Nb or V) like. This concept of multifunctionality of the active center containing all necessary key catalytic elements for propane (amm)oxidation agrees well with the structure recently proposed for the orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) bronze [24] (or $Mo_{7.5}V_{1.5}NbTeO_{29}$ according to refs. [15,25]). In a similar way, the following reaction steps can be proposed in the selective propane ammoxidation, with the ammonia activation occurring in Mo-sites [15,25]. Thus, the active and selective catalysts require several components. It is clear that a key factor to be considered in MoVTeNbO catalysts is the heterogeneity of the crystalline phases (three or four elements could be incorporated in a single crystalline phase without apparent modification), which could favor an optimal behavior in the different catalytic steps required, as it has been proposed in the selective oxidation and ammoxidation of olefins on multicomponent Mo-based catalysts [53]. However the influence of the minority presence of $Te_{0.33}MO_3$, $(Mo_{5-x}(VNb)_xO_{14})$ and MoO_3 is still unclear, although they could have a synergetic effect [54] similar to that proposed for MoO_3 in the selective oxidation of propene on multicomponent molybdate-based catalysts [55,56].

In conclusion, a MoVTeNbO catalyst, prepared hydrothermally from an aqueous solution of ammonium heptamolybdate, vanadyl sulphate, telluric acid and niobium oxalate, is active and selective in both the oxidation of propane to acrylic acid and in the ammoxidation of propane to acrylonitrile. The catalytic results presented here show that the formation of both ACN and AA goes through the intermediate formation of propene. Yields higher than 40%



Scheme 3. Reaction steps and nature of active and selective sites in the oxidation of propane to acrylic acid on MoVTeNbO catalysts.

have been achieved in both cases, although the amount of steam and ammonia, respectively, should be optimized.

The reaction temperature has little influence on the yield of oxidation and ammoxidation partial reaction products. Thus, the best results in the oxidation reaction were observed in the 320–380 °C temperature range while those in the ammoxidation reaction were observed in the 340–400 °C temperature interval. Other reaction conditions should also be studied, especially the C_3H_8/O_2 or C_3H_8/NH_3 ratio, in order to achieve higher propane conversions with high selectivites to partial (amm)oxidation products.

In addition, $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) phase, which is mainly observed in our catalyst, can be proposed as the active and selective phase in both the selective oxidation and the ammoxidation of propane. It presents an alkane activation site (V^{5+}-sites), an α-hydrogen-abstracting sites (Te^{4+}) and an O- and/or N-insertion site (Mo^{6+}) in a well-defined structure.

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