Ammoxidation of propane over V-Sb and V-Sb-Nb mixed oxides

M.O. Guerrero-Pérez 1, M.V. Martínez-Huerta 2, J.L.G. Fierro, M.A. Bañares *

Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049-Madrid, Spain

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Abstract

Pure VSbO₄ phase is not active for propane ammoxidation, unless some segregated α-Sb₂O₄ is present on its surface. Surface vanadium may be necessary to activate propane. For the ternary Sb-V-Nb oxide catalysts; Sb-V-O, Nb-V-O and Sb-Nb-O phases may form. SbNbO₄ is inert and forms at the expense of efficient Sb-V-O and V-Nb-O phases. The extent of formation of these phases strongly depends on the preparation method. The Sb precursor determines if V-Sb or Nb-Sb is the preferred interaction. Tuning the interaction of Sb with the other elements affects the catalyst structure and performance.

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1. Introduction

Acrylonitrile has been industrially produced from propylene as an important intermediate for the preparation of fibers, important polymers as styrene–acrylonitrile, acrylonitrile–butadiene–styrene, and other valuables chemicals [1]. The direct conversion of propane into acrylonitrile by reaction with oxygen and ammonia is an alternative route to the conventional propylene ammoxidation since propylene is typically more expensive than propane. The economic implications of this new route are very important, but the activation of propane is the limiting step [2]. Since the adsorption rate of propane is near ten times smaller than that of propylene [3] the conversion of propane is at least ten times smaller than propylene [4]. In addition, the reaction conditions to activate the C–H bond in propane are more energy demanding, which has a negative effect on selectivity.

There are several studies about the catalysts used for propane ammoxidation, but most of the works concentrate on two types of catalysts [1,5]: the antimonates with rutile structure [6,7] and the molybdates [1–18]. Both catalyst systems usually incorporate vanadium as an essential ingredient. Mo-V catalysts modified with Nb and Te may afford near 50% yield to acrylonitrile [2] and acrylonitrile yields of 60% have been reported for the antimonates system [9]. Despite the large relevance of these catalysts, the nature of the active site is still not fully understood. Sb-V-O catalysts with an excess of V are highly active and selective for propane oxidative dehydrogenation (ODH) while an excess of Sb affords Sb-V-O catalysts that are more efficient for propane ammoxidation [19].

Several preparation methods have been reported for the Sb-V-O-based catalysts and it is concluded that the preparation method has an important effect on the structure and on the performance [12,20,21]. The methods most usually studied correspond to patents filed in 1988 by Standard Oil Co. [9–11] and it consists on keeping in reflux during several hours an aqueous suspension of NH₄VO₃ or V₂O₅ and Sb₂O₃. Others studies use solutions of V⁴⁺ in oxalic acid to which antimonic acid is added [22] or even prepare catalysts with a solution of VCl₃ and SbCl₅ on HCl [8,23]. Brazdil et al. have also developed a sol–gel method for this kind of catalysts [21]. The aim of all these preparation methods is to provide an intimate contact between Sb⁵⁺ and V⁴⁺ in order to improve their redox reaction to form VSbO₄ phase [24], which is directly related to acrylonitrile formation [2,13,19–24], and provides the catalyst with a high specific area. More recently, mechanical activation has also proved to be an interesting method to prepare VSbO₄ phases [25].
Grasselli [1,5] reports on ternary mixed metal oxide catalysts with the formula V\textsubscript{Sb}\textsubscript{M}\textsubscript{O}\textsubscript{4}, where M stands for W [13,26], Te [9,13], Ni [13,27], Mg [13], Nb [13], Sn [28,29], Bi [30], Al [26,32,33], Fe [34], and Ti [35], among others. Usually the metal M forms a solid solution with the rutile structure of V\textsubscript{Sb}O\textsubscript{4} forming mixed phases with Sb and V, like Al\textsubscript{1−x}V\textsubscript{x}Sb\textsubscript{O}\textsubscript{4} [32] or Sb\textsubscript{0.9}V\textsubscript{0.0}−1\textsubscript{x}O\textsubscript{4} [26] or V-Sb-Ti-O [58]. Niobium compounds and materials such as niobium pentoxide, niobic acid, niobium phosphate, and mixed oxides containing niobia are shown to be useful on catalysis as supports and as promoters for different reactions [37–41]. Specially, catalysts containing niobium have been found active in dehydrogenation reactions [42–44] and the dehydrogenation of propane is commonly proposed as the first step in propane ammoxidation [23,45–47], so Nb seems to be a key element on propane ammoxidation to acrylonitrile, specially mixed oxides containing Nb (Mo-V-Nb-Te catalysts) have been found active and selective propane ammoxidation [13,48–50].

A third element may also be present as the cation of an oxide support. The use of an oxide to support/promote V\textsubscript{Sb}O\textsubscript{4} is particularly interesting, for instance, alumina-supported V\textsubscript{Sb}O\textsubscript{4} [31]; it performs like bulk V\textsubscript{Sb}O\textsubscript{4} with a more economic resolution was ca. 3 cm\textsuperscript{−1} and the spectrum acquisition time was 300 s. The spectra were obtained under dehydrated conditions (ca. 390 K) in a hot stage (Linkam TS-1500). Raman spectroscopy provides information about the bulk of the material.

X-ray diffraction patterns were recorded on a Siemens Krystalloflex D-500 diffractometer using Cu Kα radiation (λ = 0.15418 nm) and a graphite monochromator. Working conditions were 40 kV, 30 mA, and scanning rate of 2° min\textsuperscript{−1} for Bragg’s angles (2θ) from 5 to 70°. Nitrogen adsorption isotherms (−196°C) were recorded on an automatic Micromeritics ASAP-2000 apparatus. Prior to the adsorption experiments, samples were outgassed at 413 K for 2 h. BET areas were computed from the adsorption isotherms (0.05 < P/ P\textsubscript{0} < 0.27), taking a value of 0.164 nm\textsuperscript{2} for the cross-section of the adsorbed N\textsubscript{2} molecule at −196°C. ICP analyses were performed in a 3300 Perkin-Elmer apparatus. Around 100 mg of sample were dissolved with nitric, chloride, and fluoride acids in a microwave oven.

Table 1
Precursors used during synthesis, composition and BET area of catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Composition*</th>
<th>BET surface area (m\textsuperscript{2} g\textsuperscript{−1})</th>
<th>Method</th>
<th>Precursors</th>
</tr>
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<tr>
<td>Sb-V-O catalysts</td>
<td></td>
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<tr>
<td>SV1</td>
<td>V\textsubscript{Sb}</td>
<td>0.6</td>
<td>–</td>
<td>NH\textsubscript{4}VO\textsubscript{3}, Sb soluble complex</td>
</tr>
<tr>
<td>SV3</td>
<td>V\textsubscript{Sb\textsubscript{3}}</td>
<td>0.5</td>
<td>–</td>
<td>NH\textsubscript{4}VO\textsubscript{3}, Sb soluble complex</td>
</tr>
<tr>
<td>SV5</td>
<td>V\textsubscript{Sb\textsubscript{5}}</td>
<td>0.8</td>
<td>–</td>
<td>NH\textsubscript{4}VO\textsubscript{3}, Sb soluble complex</td>
</tr>
<tr>
<td>SV7</td>
<td>V\textsubscript{Sb\textsubscript{7}}</td>
<td>0.6</td>
<td>–</td>
<td>NH\textsubscript{4}VO\textsubscript{3}, Sb soluble complex</td>
</tr>
<tr>
<td>Sb-V-Nb-O catalysts</td>
<td></td>
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</tr>
<tr>
<td>SVN1A</td>
<td>V\textsubscript{0.8}S\textsubscript{0.1}B\textsubscript{0.3}</td>
<td>72</td>
<td>1</td>
<td>SbCl\textsubscript{3}, NH\textsubscript{4}VO\textsubscript{3}, Nb\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{5}</td>
</tr>
<tr>
<td>SVN1B</td>
<td>V\textsubscript{0.8}S\textsubscript{0.1}B\textsubscript{0.3}</td>
<td>19</td>
<td>1</td>
<td>SbCl\textsubscript{3}, NH\textsubscript{4}VO\textsubscript{3}, Nb\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{5}</td>
</tr>
<tr>
<td>SVN2</td>
<td>V\textsubscript{0.8}S\textsubscript{0.1}B\textsubscript{0.3}</td>
<td>8</td>
<td>2</td>
<td>SbCl\textsubscript{3}, (C\textsubscript{2}O\textsubscript{4})\textsubscript{2}VO, Nb\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{5}</td>
</tr>
<tr>
<td>SVN3</td>
<td>V\textsubscript{0.8}S\textsubscript{0.1}B\textsubscript{0.3}</td>
<td>12</td>
<td>3</td>
<td>SbCl\textsubscript{3}, (C\textsubscript{2}O\textsubscript{4})\textsubscript{2}VO, Nb\textsubscript{2}O\textsubscript{5}</td>
</tr>
</tbody>
</table>

* Based on the ICP element analyses.
Activity measurements were performed using a conventional microreactor with on-line gas chromatograph equipped with a flame ionization and thermal conductivity detector. The correctness of the analytical determinations was checked for each test by verification that the carbon balance (based on the propane converted) was within the cumulative mean error of the determinations (±10%). Tests were made using 0.2 g of sample with particle dimensions in the 0.25–0.125 mm range. The axial temperature profile was monitored by a thermocouple sliding inside a tube inserted into the catalytic bed. Tests were made using the following feedstock: 25% O2, 9.8% propane, 8.6% ammonia, and helium balance. The total flow rate was 20 ml min\(^{-1}\) corresponding to a gas-space velocity (GHSV) near 3000 h\(^{-1}\). The quantity of catalyst and total flow were determined in order to avoid internal and external diffusion contributions. Yield and selectivity values were determined on the basis of the moles of propane feed and products, considering the number of carbon atoms in each molecule.

3. Results

3.1. Sb-V-O system

Table 1 represents the composition and BET area values for the Sb-V-O catalysts. The BET area values are quite low for these catalysts, probably due to the high calcination temperature. The XRD patterns of the fresh catalyst are displayed in Fig. 1. SV1 pattern (Sb/V = 1) corresponds to the V\(_{0.92}\)Sb\(_{0.92}\)O\(_4\) phase (JCPDS file 16-0600), the patterns of SV3, SV5, and SV7 catalysts (Sb/V = 3, 5, and 7, respectively) correspond to V\(_{0.86}\)Sb\(_{0.86}\)O\(_4\) and \(\alpha\)-Sb\(_2\)O\(_4\) phases (JCPDS file 11-0694 and 32-0042).

The Raman spectra of the fresh and used catalyst are represented in Fig. 2. The spectrum of the fresh SV1 catalyst presents a band centered at 880 cm\(^{-1}\), which has been assigned to the \(\text{Sb}_{0.92}\text{V}_{0.92}\text{O}_{4}\) phase[19]. The weak Raman band near 1020 cm\(^{-1}\) is not sensitive to humidity, so this band must correspond to the V\(_{0.86}\)Sb\(_{0.86}\)O\(_4\) phase and not to surface vanadium oxide species. However, this band is quite broad, and it is not possible to provide a conclusive absence of surface vanadium oxide species.

The Raman spectra of catalysts with antimony excess (SV3, SV5, and SV7) present modes at 190, 255, 372, 451, and 716 cm\(^{-1}\) that correspond to the \(\alpha\)-Sb\(_2\)O\(_4\) phase [51]; these bands are very strong while V\(_{0.86}\)Sb\(_{0.86}\)O\(_4\) possesses a low Raman section; therefore, Fig. 2B blows-up the 530–1030 cm\(^{-1}\) window. The weak bands at 610, 650, 710, 749, and 820 cm\(^{-1}\) that correspond to the \(\alpha\)-Sb\(_2\)O\(_4\) phase are evident. Raman spectra of all catalysts with antimony excess show the bands that correspond to the \(\alpha\)-Sb\(_2\)O\(_4\) phase. The SV1, SV3, and SV5 catalysts exhibit the bands of V\(_{0.86}\)Sb\(_{0.86}\)O\(_4\) phase; these bands are particularly weak for catalyst SV7. The Raman spectra show no appreciable changes for the used catalysts. These catalysts exhibit a steady-state operation for at least 20 h. Fig. 3 represents the yields to different products for

![Fig. 1. XRD patterns of fresh Sb-V-O catalysts.](image1)

![Fig. 2. (A) Raman spectra of fresh and used Sb-V-O catalysts. (B) Spectra between 530 and 1030 cm\(^{-1}\) with \(\alpha\)-Sb\(_2\)O\(_4\) reference phase.](image2)
catalysts SV1, SV3, SV5, and SV7 at 500 °C. The catalyst with the highest vanadium content (SV1, with Sb/V = 1) is the most active and presents the highest yield to acrylonitrile; however, selectivity to acrylonitrile is rather low. Sb excess leads to less active, but more acrylonitrile selective, catalysts. The catalysts SV5 is most selective towards acrylonitrile.

3.2. Sb-V-Nb-O system

XRD patterns of fresh and used Sb-V-Nb-O catalysts are represented in Fig. 4. The catalyst SVN2 presents a diffraction pattern that corresponds to the phases Nb₂O₅ (JCPDS 30-0873), α-Sb₂O₄ (JCPDS 11-0694), and VSbO₄ (JCPDS file 16-0600). After reaction, the diffraction peaks of VSbO₄ become more intense. Catalyst SVN3 exhibits a pattern quite similar to that of SVN2, it presents the pattern of Nb₂O₅ and Sb₂O₄ phases after reaction (Fig. 4) (JCPDS 16-0907). Fresh and used SVN1A catalyst present the pattern of SbNbO₄ phase after reaction (Fig. 4) (JCPDS 7-0061), while after reaction it presents those of Nb₂O₅ and α-Sb₂O₄. SVN1A is amorphous but it exhibits the pattern of SbNbO₄ phase after reaction (Fig. 4) (JCPDS 7-0061). Fresh and used SVN1B catalyst present the pattern of SbNbO₄ and α-Sb₂O₄ phases, and the diffraction peaks of SbNbO₄ become more intense for the used sample.

Fig. 4 shows the Raman spectra of fresh and used Sb-V-Nb-O catalysts. The Raman spectra of fresh and used SVN2 and SVN3 are very similar with broad bands near 900, 700, and 200 cm⁻¹, typical of Nb₂O₅ TT crystalline phase [52,53]. The Raman spectrum of the fresh SVN1A catalyst (Fig. 5) shows broad Raman bands that correspond to Nb₂O₅ phase but after reaction it exhibits Raman bands at 190, 255, 372, and 451 cm⁻¹, typical of α-Sb₂O₄ phase [51] and features near 845, 686, and 621 cm⁻¹ that correspond to SbNbO₄ phase [52,53]. Spectra of fresh and used SVN1B catalyst show Raman bands that correspond to α-Sb₂O₄ and SbNbO₄ phases. Mixed V-Nb-O phases, if present, could not be observed. These possess weak Raman bands [54].

Fig. 5. Raman spectra of fresh and used Sb-V-Nb-O catalysts.
4. Discussion

Sb-V-based oxide structures are directly related to propane ammoxidation reaction. In particular, VSbO₄ appears closely related to efficient catalysts [55]. In excess of Sb, the V₅₋Sb₂O₄/O₅ system is more selective to acrylonitrile formation. SV₁ is active (Fig. 3), to the production of carbon oxides, propylene and acrylonitrile; the higher activity at lower Sb/V atomic ratios is probably related to the higher vanadium content [55–57]. Bulk Sb-V-O samples with Sb/V > 1 are more selective to the formation of acrylonitrile [1,2,19,55]. Our results are consistent with those works: samples possessing VSbO₄ and α-Sb₂O₄ phases, like SV₃, SV₅, and SV₇, are more selective to acrylonitrile formation than the pure VSbO₄ phase, as can be observed in Fig. 3. The excess of Sb renders the Sb-V-O system more selective; however, total conversion is much lower. Surface vanadium oxide species, on the other hand, appear critical to activate propane [49,58]. Surface vanadium oxide species also activate conversion of propane towards oxidative dehydrogenation reaction, even in the presence of Sb [58,59]. The effect of Sb/V atomic ratio is not clearly understood yet. Nilsson et al. [19] have found that the best rate for formation of acrylonitrile is achieved with catalysts with Sb/V = 2. Centi and Mazzoli [8] reported catalysts with Sb/V > 1 as the most active on acrylonitrile formation and Chiang and Lee [60] concluded that the best activity results are achieved with catalysts with Sb/V = 1. In general, mixed α-Sb₂O₅/V₅₋O₄ phases are selective to acrylonitrile formation; the results presented are in accordance with this point. However, the origin of these differences on the Sb/V values may be due to the fact that surface composition does not usually correspond to the bulk composition. Obviously, catalytic performance is directly affected by the surface composition of the catalysts, where the molecules react. There appears to be a delicate interaction between segregated Sb oxide, surface vanadium oxide species, and V₅₋O₄ that renders the system efficient for propane ammoxidation [49]. It may be due to a cooperative effect between these phases, as it has been pointed out previously [19,26]. Operando Raman-GC studies during propane ammoxidation on supported Sb-V systems suggest that such cooperation may be due to a migration cycle of Sb⁵⁺ species that facilitate the redox cycle of vanadium species [49,58], which involves surface V⁴⁺⁺ species and lattice V³⁺ sites in V₅₋O₄ [49,55].

The interplay between Sb and V for propane ammoxidation is strongly affected by the presence of a third element [1,5,9,13,26–36]. Niobia is particularly interesting since many possible interactions may take place, leading to V-Nb-O, V-Sb-O, and Sb-Nb-O phases [52,53], some of which are present in catalysts developed by Mitsubishi [17,18] and by bp [21]. The V-Nb-O phases are efficient for propane ammoxidation in niobia-supported vanadia catalysts [52] and SbNbO₄ does not appear active for propane ammoxidation [53].

The bulk V-Sb-Nb-O catalysts have been prepared following different preparation methods to differently affect their structures.

SVN2 and SVN3 are prepared by interaction between vanadium acetyl acetonate and SbCl₅ with different niobium precursors. They possess similar structures; according to combined XRD and Raman spectroscopy: V₅₋SbO₄ and Nb₂O₅ phases are present, but not SbNbO₄. The absence of the V₅₋SbO₄ diffraction pattern for SVN3, visible to Raman spectroscopy, must be due to the small size of its domains. Some antimony remains segregated as α-Sb₂O₄; which becomes more evident in used samples. Thus, the trend of antimony to migrate to the catalysts surface observed with supported Sb-V-O catalysts [45,51], is also observed in the present work for bulk Sb-V-Nb-O catalysts. These catalysts perform propane ammoxidation better that the SV series and the other SVN catalysts. This is consistent with the beneficial effect of niobia on the performance reported for V₅₋SbO₄ [52]. Thus, the presence of both V₅₋SbO₄ and Nb₂O₅ account for the better performance, compared to SV series.

SVN1A and SVN1B are prepared by interaction between NH₄VO₃ and SbCl₃ and niobium oxalate. They possess similar structures, both possess SbNbO₄ but not V₅₋SbO₄ or Nb₂O₅, according to Raman spectroscopy (Fig. 5) and XRD patterns (Fig. 4). The formation of V₅₋SbO₄ is not observed for SVN1A or SVN1B (from SbCl₅); in these catalysts; antimony reacts preferentially with niobia. SbNbO₄ phase is inert for propane ammoxidation [52,53]. The presence of SbNbO₄ and absence of V₅₋SbO₄ accounts for their poor ammoxidation performance.

Apparently, niobia precursor is not critical for Sb-V-Nb interactions since niobia oxalate may result in either Nb₂O₅ or SbNbO₄. However, the oxidation state of the antimony chloride follows a trend: SbCl₃ interacts preferentially with vanadia; SbCl₅, with niobia. Using SbCl₅, Sb, and V interact forming mixed phases like V₅₋SbO₄ and Nb₂O₅ crystalline phase, regardless of niobia precursor (SVN2, SVN3). Such interaction is consistent with the redox reaction between Sb⁵⁺ and V⁴⁺⁺ to form V₅₋SbO₄ [21,24]. In these catalysts, the V₅₋SbO₄ phase becomes more evident after propane ammoxidation, so this phase is further formed during reaction. The in situ formation of this phase during propane ammoxidation has been reported for alumina-supported Sb-V-O catalysts using operando Raman-GC methodology [24].

The interaction between Sb, V, and Nb can be tuned by the oxidation state of antimony chloride. SbCl₃ promotes the Sb-Nb interaction, which leads to SbNbO₄. This phase is not active for propane ammoxidation; but, in addition, the interaction between Sb and Nb prevents Sb-V or Nb-V interactions. V₅₋SbO₄ and V-Nb-O phases are efficient for propane ammoxidation. Therefore, this system would not be efficient. On the other hand, SbCl₅ promotes the Sb-V interaction, forming V₅₋SbO₄ and segregating niobia as Nb₂O₅ on calcination. Niobia-promoted V₅₋SbO₄ performs better than V₅₋SbO₄ [52]. The exact nature of these catalysts if not fully understood, the promotion could be due to the acidic sites of niobia and to the combination of V and
Nb into V-Nb-O phases, which are efficient for propane ammoxidation [52], along with VSB04. Therefore, it is possible to prepare Nb-promoted Sb-V-O catalysts in a single step by appropriate control of the precursors.

SVN1A, SVN1B, and SVN2 use niobium oxalates, SVN3 uses Nb2O5 suspension. All the catalysts prepared with SbCl3 possess SbNbO4. For a given niobium precursor (oxalate), Nb3 into V-Nb-O phases, which are efficient for propane ammoxidation to acrylonitrile, especially when Sb/V is near 5. The presence of Nb-V-O phases could not be detected but its behavior with respect to the Sb-V-O mixed oxide catalysts. The interaction between Sb and V is stronger with SbCl3, while the interaction between Nb and Sb appears stronger with SbCl5.

5. Conclusions

Pure VSB04 phase does not appear to be efficient for propane ammoxidation to acrylonitrile. It appears that some segregated Sb oxide is necessary for the catalytic cycle. The combination of VSB04 with α-Sb2O3 enhances the selectivity to acrylonitrile, especially when V/Sb is near 5. The presence of surface vanadium species cannot be determined in detail, but it may be important, since it would be at the surface, which is directly exposed to the reactants.

For V-Sb-Nb oxide catalysts, the niobium precursor does not appear to have a critical effect; however, the antimony precursor shows a trend:

(a) SbCl3 precursor results in preferential antimony–niobium interaction; the formation of the SbNbO4 phase is observed and the catalyst is neither active nor selective to acrylonitrile formation. Antimony interacts with niobium at the expense of the VSB04 and α-Sb2O3active phases.

(b) SbCl5 precursor favors the redox reaction with vanadium to form the VSbO4 active phase. Nb improves the catalytic behavior with respect to the Sb-V-O mixed oxide catalysts. The presence of Nb-V-O phases could not be detected but its presence may not be ruled out either.

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References
