Effect of synthesis method on stabilized nano-scaled Sb–V–O catalysts for the ammoxidation of propane to acrylonitrile

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A new synthesis method to prepare V–Sb–O phases on Al₂O₃ and Nb₂O₅ substrates has been investigated and compared with previous works in which a conventional synthesis method was used. The new preparation method leads to an amorphous layer of Sb oxide, which had not been described previously; its Raman bands are reported for the first time. This new method provides an intimate contact between Sb and V during synthesis. It has a clear influence on the structure and catalytic properties of the final catalysts. The total amount (Sb + V), the Sb/V atomic ratio, and the specific support determine acrylonitrile production. Depending on catalyst stoichiometry, different preparation methods are preferred. Standard Sb₂O₃ suspension method is preferred at Sb/V atomic ratios above 1. The new tartrate method is preferred at Sb/V = 1 atomic ratio, resulting in the best catalytic performance.

KEY WORDS: V–Sb–Al; V–Sb–Nb; V–Sb–O; oxidation; ammoxidation; propane; acrylonitrile; structure–activity relationship; Raman; XRD; tartrate; nano-scaled oxide; AlSbO₄.

1. Introduction

Acrylonitrile is widely used as intermediate for the preparation of synthetic rubbers, synthetic resins and fibers [1–3]. It is currently produced by ammoxidation of propylene in fluid bed reactors with catalysts based on promoted Fe–Bi–Mo–O (bp America) or promoted Fe–Sb–O (Nitto). The direct conversion of propane into acrylonitrile by ammoxidation of propane is an alternative route to the conventional propylene ammoxidation since propane is substantially cheaper than propylene. In this reaction, the activation of propane is the limiting step [4]. Since the adsorption rate of propane is near 10 times smaller than that of propylene [5], the conversion of propane is at least 10 times smaller than that of propylene [6]. The reaction conditions to activate the C–H bond in propane are more energy demanding, which has a negative effect in selectivity. The use of homogeneous–heterogeneous processes to promote propane to propylene conversion upstream the catalyst bed is an option [7]. However, other side reactions, like ammonia oxidation to nitrogen in the presence of molecular oxygen [8] or propylene formation may take place simultaneously. The low activity of propane has also led to use gas phase additives (e.g., H₂S or CH₃Br) as radical generators. However, environmental concerns do not make this option attractive. Therefore, the efforts focus on a catalyst for the direct ammoxidation of propane into acrylonitrile with no additives in the gas phase.

There are several studies about catalysts used for propane ammoxidation. They include the antimonates with rutile structure [9–15] and the molybdates [16–20], both systems usually incorporate vanadium as the key element. Mo–V catalysts modified with Nb and Te may afford near 60% yield to acrylonitrile [3,19] and acrylonitrile yields of 40% have been reported for the antimonates system [13]. Despite the large relevance of these catalysts, the nature of the active site at the outermost layer is not fully understood yet. Sb–V–O catalysts with an excess of V are essentially efficient for propane oxidative dehydrogenation (ODH) while an excess of Sb affords Sb–V–O catalysts more efficient for propane ammoxidation [21]. The use of nano-scaled oxide phases maximizes the surface-to-volume ratio allowing better insight on the nature of the active sites. The nano-scaled phases are stabilized versus sinterization by the use of a support [22,23].

Several synthesis methods have been proposed for the Sb–V–O based catalysts. These affect dramatically the catalytic performance behavior of the catalysts [24]. The most common method corresponds to patents filed in 1988 by Standard Oil Co. [13–15] and consist on refluxing for several hours an aqueous dispersion of NH₄VO₃ or V₂O₅ with Sb₂O₃. Others studies try to keep vanadium as V⁴⁺ in oxalic acid and then add antimonic acid to this solution [25] or prepare catalysts with a solution of VCl₃ and SbCl₅ on HCl [12, 26]. A sol-gel method has also been reported for this kind of catalysts [27].

A common feature to several synthesis methods is that the antimony does not dissolve, but forms a suspension. Sb₂O₃ is very insoluble, even at pH = 0, which

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prevents an efficient Sb–V interaction. It would be desirable to promote a redox reaction between V$^{5+}$ and Sb$^{3+}$ solution towards V$^{3+}$/V$^{5+}$ and Sb$^{3+}$ as vanadium antimonate, which is the active phase for propane amoxidation [10,22]. This work studies a new synthesis method in which Sb$^{3+}$ is totally dissolved in tartaric acid solution as a soluble complex [28] in order to address this issue. The normal potentials of the redox system for Sb and V depend on pH and at acid pH the V$^{5+}$ has a higher potential than the Sb$^{3+}$, so the redox reaction between them is favored. Tartaric acid has two functions: (1) it acts as a complex agent with antimony keeping it dissolved; and (2) it gives an acid pH that favors V$^{5+}$ and Sb$^{3+}$ redox reaction to form V$^{3+}$, V$^{4+}$ and Sb$^{5+}$. Different Sb/V molar ratios and total Sb + V coverages on niobia and alumina samples are prepared by the proposed tartrate method and are compared to those prepared by the conventional synthesis methods, with NH$_4$VO$_3$ and Sb$_2$O$_3$, previously reported [29,30].

2. Experimental and Methods
2.1. Preparation of samples

The Sb–V catalysts were prepared dissolving the required amount of antimony acetate (Aldrich) in tartaric acid (Sigma) 0.3 M. This solution was kept under stirring until all antimony dissolves. Then, NH$_4$VO$_3$ (Sigma) and the corresponding support were added. Two different supports were used: γ-Al$_2$O$_3$ (Girdler Südchemie) and Nb$_2$O$_5$ (Niobium Products). The solution was dried in a rotatory evaporator at 80 °C at 0.3 atm. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h in air. The catalysts were prepared so that a total coverage of V + Sb would correspond to 25%, 50%, 100%, and twice their dispersion limit (“monolayer”) on the corresponding support. The dispersion limit, understood as the maximum surface loading of VO$_x$ units that remain dispersed, with no crystalline V$_2$O$_5$, was determined by Raman spectroscopy to be near 9 VO$_x$ units per nm$^2$ for alumina and niobia supports, in accordance to previous reports on several supports [31]. The Sb/V atomic ratio ranged in the 1–5 interval. Reference catalysts with no Sb or no V were also prepared.

For the sake of simplicity, all the supported catalysts are labeled as “xV$_3$Sb/Al” or “xV$_3$Sb/Nb” where “x” represent the fraction of dispersion limit (“monolayer” coverage) of V + Sb atoms on corresponding support and “y” represents the Sb/V ratio. When alumina is used as support, the name of catalyst is followed by “/Al”; when it is niobia, it is followed by “/Nb”.

2.2. Characterization

Nitrogen adsorption isotherms (−196 °C) were recorded with an automatic Micromeritics ASAP-2000 apparatus. Prior to the adsorption experiments, samples were outgassed at 140 °C for 2 h. BET areas were computed from the adsorption isotherms (0.05 < P/ P$_0$ < 0.27), taking a value of 0.164 nm$^2$ for the cross-section of the adsorbed N$_2$ molecule at (196 °C). X-ray diffraction patterns were recorded on a Siemens Krystalloflex D-500 diffractometer using Cu K$_\alpha$ radiation (α = 0.15418 nm) and a graphite monochromator. Working conditions were 40 kV, 30 mA, and scanning rate of 2°/min for Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°. In some cases, the peaks of Bragg’s angles (2θ) from 5 to 70°.

The Raman spectra were run with a single monochromator Renishaw System 1000 equipped with a cooled CCD detector (−73 °C) and holographic super-Notch filtering. The holographic Notch filter removes the elastic scattering while the Raman signal remains high. The samples were excited with the 514 nm Ar line; spectral resolution was ca. 3 cm$^{-1}$ and spectrum acquisition consisted of 20 accumulations of 30 s. The spectra were obtained under dehydrated conditions (ca. 120 °C) in a hot stage (Linkam TS-1500) under dry air stream. Hydrated samples were obtained at room temperature after and under exposure to a stream of humid synthetic air.

2.3. Activity measurements

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%). To prevent participation of homogeneous reactivity, the reactor was designed to minimize gas-phase activation of propane. 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. Test were made using the following feedstock: 25% O$_2$, 9.8% propane, 8.6% ammonia in helium. The total flow rate was 20 ml/min corresponding to a gas-space velocity (GHSV) of about 3000 h$^{-1}$. Yields and selectivities in products 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. Antimony supported on alumina

Reference samples generate the following diffraction peaks [29]: Sb$_2$O$_3$, at 19.4, 25.47, 28.09, 28.38, 28.61, 33.79, 47.07, 50.53 and 60.80°. Sb$_3$O$_4$ shows diffraction
peaks at 19.91, 25.83, 29.03, 30.35, 33.78, 37.37, 40.32, 48.87, 51.25, 53.11, 56.17, 62.39 and 63.25. V3O4 shows diffraction peaks at 27.44, 35.12, 39.21, 40.39, 53.60, 56.61, 64.04, 67.31 and 68.37° and V2O5 shows diffraction peaks at 15.36, 20.28, 21.73, 26.15, 31.03, 32.39, 34.31, 41.29, 45.48, 47.36 and 51.25°.

Figure 1 shows the XRD patterns (1A) and Raman spectra (1B) of the catalysts prepared without vanadium using the standard suspension method [29] and the new tartrate method. The XRD patterns of the samples prepared with antimony tartrate complex present no diffraction peaks. The XRD patterns of the Sb/Al catalysts are shown in figure 1(a). 1SbAl and 2SbAl prepared with the new tartrate method show no diffraction pattern of any Sb-containing phase. 1SbAl prepared by the suspension method shows no diffraction pattern of Sb-containing phases, either. 2SbAl does show the diffraction pattern of α-Sb2O3 (JCPDS file 11-694). The broad feature between 20–35°2θ in the SbAl samples prepared by the tartrate method is in the same region than the most intense diffraction peaks of α-Sb2O3 (JCPDS file 11-694).

Reference sample Sb2O3 shows Raman bands at 190, 255, 415 and 451 cm−1. Sb2O4 shows Raman bands at 190, 261, 399 and 459 cm−1 and V2O5 shows Raman bands at 143, 283, 302, 405, 480, 526, 698 and 994 cm−1. V3O4 shows a broad band between 700 and 900 cm−1 [29]. The Raman spectra of the samples prepared with tartaric acid present weak broad Raman bands at 780, 600, 468 and 210 cm−1 that must correspond to an amorphous antimony oxide closely interacting with the support. The Raman spectrum (figure 1(b)) of the sample 2SbAl prepared with Sb2O3 shows Raman bands at 190, 255, 372 and 451 cm−1 that correspond to the Sb2O4 phase [29], in agreement with the XRD pattern. The Raman spectra of the sample 1Sb/Al prepared with Sb2O3 present very weak Raman bands that resemble those of α-Sb2O4 phase and to the amorphous antimony oxide.

Sb2O3 and Sb2O4 structures are not detected when the soluble complex is used as antimony precursor even when the total coverage is higher than the dispersion limit. Instead these structures, the tartrate method promotes the formation of an amorphous antimony oxide. Catalysts 2Sb/Al prepared with both methods were treated in air at 900 °C for 12 h in order to know more details about the nature and reactivity of the antimony oxides with alumina. The structure of the catalyst prepared with Sb2O3 does not change and the results are not shown; after the treatment, the catalyst possesses Sb2O4 on alumina. On the contrary, XRD and Raman spectroscopy evidence the formation of a new Sb–Al–O phase for the sample prepared with the tartrate method. The Raman bands at 819, 720 and 336 cm−1 must correspond to the AlSbO4 phase (JCPDS 4-0564) detected by XRD (figure 1(c)).

Figure 2 shows the activity results for propane ammoxidation at 500 °C. Acetonitrile is the principal reaction product for all the catalysts. The samples prepared with Sb2O3 suspension are more selective to acetonitrile; whereas these prepared with tartaric acid are more selective to acrylonitrile. In any case, good results for propane ammoxidation to acrylonitrile are not achieved when the catalyst is only composed by antimony.

3.2. Al2O3 supported Sb–V–O catalysts

BET specific areas of the catalyst are listed in the Table 1. The BET area values decrease with surface coverage of Sb + V on Al2O3 from ca. 160 to 110 m²/g. The atomic Sb/V ratio does not have a clear effect on BET area values.

Figure 3(a) shows the X-ray diffraction patterns of the fresh and used catalysts at monolayer coverage on alumina and different Sb/V molar ratios. Most of them only exhibit some broad peaks that correspond to Al2O3. The used catalysts 1Sb1V/Al and 1Sb2V/Al exhibit the diffraction peaks of VSbO4 phase (JCPDS...
Acrolein/C176 or [22]. UV-Raman spectra show well resolved Raman band provides structural understanding of the redox phenomena in the V–Sb–O system under redox cycles [36].

The Raman spectra of catalysts with coverages of 25 and 50% the dispersion limit, do not present any Raman band. Weak Raman bands near 1024 cm\(^{-1}\) are present in almost all catalysts, these bands are typical of the \(V = O\) mode of tetrahedral surface VO\(_x\) species [32,33].

This band is affected by hydration, which confirms that it belongs to surface dispersed VO\(_x\) species. The corresponding series prepared by the Sb\(_2\)O\(_3\) suspension method [29], present intense Raman bands and diffraction patterns characteristic of Sb\(_2\)O\(_3\) and \(\alpha\)-Sb\(_2\)O\(_4\). Nilsson et al. have observed amorphous species in antimony vanadium oxides [21]; they assigned a broad weak Raman band at 600–800 cm\(^{-1}\) to these species. Three weak features in figure 4(b), between 400 and 800 cm\(^{-1}\) suggest the presence of some surface Sb oxide species, observed in Sb/Al catalysts prepared by the tartrate method (Cf. figure 1(b)).

All the catalysts at dispersion limit and above present a broad Raman band centered at 800 cm\(^{-1}\) (between 700 and 900 cm\(^{-1}\)) typical of VSbO\(_4\) [29]. Such phase forms during propane ammoxidation. This trend of Sb–V–O/Al\(_2\)O\(_3\) catalysts to form VSbO\(_4\) during reaction has been followed in detail with catalysts prepared with Sb\(_2\)O\(_3\) by operando Raman-GC spectroscopic study [22,34,35]. Deconvolution of the Raman band near 800 cm\(^{-1}\) has shown that it consists of two Raman bands at 835 and 795 cm\(^{-1}\) [22]. UV-Raman spectra show well resolved peaks at 734 and 810 cm\(^{-1}\) [36]. Fresh catalysts with lower Sb/V ratios, 1Sb\(_2\)V/Al and 1Sb\(_2\)V/Al, present this band at 850 cm\(^{-1}\), and shift to 800 cm\(^{-1}\) upon use in reaction. The broad Raman band near 850 cm\(^{-1}\) in the fresh samples is due to the contribution of band near 880 cm\(^{-1}\), which reduces in ammonia [36]. During ammoxidation, non-net oxidizing conditions dominate; operando Raman-GC studies uncover the interplay between segregated surface vanadia and antimony oxides with VSbO\(_4\) during the catalytic cycle [35]. The detailed analysis on the nature and reactivity of the 880 cm\(^{-1}\) Raman band provides structural understanding of the redox phenomena in the V–Sb–O system under redox cycles [36].

Figure 5(a) shows the effect of total Sb + V coverage on alumina on the yields to different products and on the specific rate of formation of acrylonitrile per vanadium site at 480 °C. The main products for the catalysts with 25 and 50% dispersion limit loading and Sb/V = 5 atomic ratio are CO\(_x\), and propylene, the CO\(_x\) become

![Figure 2](Image 2)

Figure 2. Yields to principal products obtained for catalysts containing only antimony. Reaction conditions: total flow 20 ml/min; feed composition (% volume): C\(_3\)H\(_6\)/O\(_3\)/NH\(_3\)/He (9.8/25/8.6/56.6), 200 mg of catalysts, temperature reaction 500 °C.

### Table 1
Composition and BET area of alumina-supported Sb–V–O catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sb + V “monolayer”</th>
<th>Sb/V atomic ratio</th>
<th>%Sb</th>
<th>%V</th>
<th>BET Area m(^2)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25Sb(_2)V/Al</td>
<td>0.25</td>
<td>5</td>
<td>4.72</td>
<td>0.40</td>
<td>153</td>
</tr>
<tr>
<td>0.5Sb(_2)V/Al</td>
<td>0.5</td>
<td>5</td>
<td>8.38</td>
<td>0.70</td>
<td>156</td>
</tr>
<tr>
<td>1Sb(_2)V/Al</td>
<td>1</td>
<td>1</td>
<td>9.38</td>
<td>3.77</td>
<td>139</td>
</tr>
<tr>
<td>1Sb(_2)V/Al</td>
<td>1</td>
<td>2</td>
<td>11.49</td>
<td>2.39</td>
<td>111</td>
</tr>
<tr>
<td>1Sb(_2)V/Al</td>
<td>1</td>
<td>3</td>
<td>12.89</td>
<td>1.82</td>
<td>123</td>
</tr>
<tr>
<td>1Sb(_2)V/Al</td>
<td>1</td>
<td>4</td>
<td>13.23</td>
<td>1.38</td>
<td>114</td>
</tr>
<tr>
<td>1Sb(_2)V/Al</td>
<td>1</td>
<td>5</td>
<td>13.64</td>
<td>1.19</td>
<td>123</td>
</tr>
<tr>
<td>2Sb(_2)V/Al</td>
<td>2</td>
<td>5</td>
<td>20.13</td>
<td>1.69</td>
<td>110</td>
</tr>
</tbody>
</table>
The main products are propylene and acrylonitrile at dispersion limit loading. For Sb/V = 5 atomic ratio, acrylonitrile becomes the main product at higher coverages. The number of mmol of acrylonitrile produced per mmol of vanadium in the bulk, i.e., the rate of the reaction per vanadium site is the highest for the catalyst with twice the dispersion limit loading on alumina at Sb/V molar ratio of 5, which produces 10 mmol of acrylonitrile per mmol of vanadium and second.

Figure 5(b) shows the effect of Sb/V molar ratio in the yields to different products and in the specific rate of formation of acrylonitrile per vanadium site at 480 °C for catalysts at the dispersion limit loading of Sb + V on alumina. Catalysts with large excess of antimony (Sb/V molar ratios of 4 to 5) present acrylonitrile and

![Figure 3. XRD patterns of fresh and used alumina-supported catalysts with one monolayer and different Sb/V molar ratios (a) and with Sb/V molar ratio of 5 and different coverages (b).](image)

![Figure 4. Raman spectra of alumina-supported catalysts. (a) Catalysts with one monolayer and different Sb/V molar ratios. (b) Catalysts with Sb/V = 5 and different coverages.](image)
propylene as the main products; at lower Sb/V atomic ratios, acrylonitrile becomes the main product. The specific rate of formation of acrylonitrile per vanadium site increases as Sb/V ratio decreases. So, the highest yields to acrylonitrile are obtained for Sb/V molar ratios between 1 and 3. The trends described in figures 5(a) and (b) are very similar to those obtained with other catalysts with the same Sb/V molar ratios and Sb + V total coverage on alumina prepared via SbO3 suspension; in line with the trends observed for alumina supported catalysts prepared via the SbO3 suspension after stabilization on stream for several hours [29].

All the catalysts prepared by the tartrate method were tested during time on stream (TOS) for at least 20 h at 480 °C and the activity and product distribution remain stable for all catalysts studied, including 1Sb/V/Al and 1Sb2/V/Al. The catalysts prepared with Sb2O3 showed a different behavior with TOS [29]; they show an increase in conversion values during the first 15 h, mainly due to a decrease in the yield to CO and a concomitant increase in the yields of propylene and acrylonitrile; for the rest of Sb/V and Sb + V values, the activity and product distribution versus TOS remained constant.

Table 2 compares selectivities and propane conversion values for the alumina-supported catalysts prepared with the tartrate method and via Sb2O3 suspension [29]. There are some differences between both series. The acrylonitrile selectivity is higher for catalysts prepared by the tartrate method, especially for catalysts with Sb/V = 1, but the propane conversion values are higher for catalysts prepared with Sb2O3. The higher acrylonitrile yields observed for Sb/V = 1 catalyst prepared with the tartrate method can be related to the presence of V5O4 phase on this catalyst, that is absent in the corresponding catalyst prepared with Sb2O3.

3.3. Nb2O5 supported catalysts

Table 3 lists the BET specific areas of the niobia-supported catalyst. The BET area values decrease with surface coverage of Sb + V on Nb2O5 from 107 m²/g to 17 m²/g. The atomic Sb/V ratio does not appear to have a clear effect on BET area values. This decrease in BET area values with coverage is more intense on niobia-supported catalysts than on alumina-supported, which could be indicative of a stronger interaction with niobia support. This trend has also been observed with catalysts prepared via Sb2O3 [30].

The XRD patterns of fresh and used niobia-supported catalysts are displayed in figure 6. Figure 6(a) shows the effect of Sb/V molar ratio on the diffraction

![Figure 5](image-url)

**Figure 5.** Effect of total Sb + V coverage on alumina (a) and of Sb/V molar ratios (b) on the yields to different products and on the specific rate of formation of acrylonitrile per V site at 480 °C. Catalysts prepared by the tartrate method. Reaction conditions: total flow 20 ml/min; feed composition (% volume): C3H8/O2/NH3/He (9.8/25/8.6/56.6), 200 mg of catalysts, temperature reaction 480 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Antimony precursor</th>
<th>Propane conversion (%)</th>
<th>Propylene selectivity (%)</th>
<th>Acrylonitrile selectivity (%)</th>
<th>CO2 selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Sb/V/Al</td>
<td>Sb2O3</td>
<td>84.9</td>
<td>24.2</td>
<td>33.3</td>
<td>36.4</td>
</tr>
<tr>
<td>1Sb2/V/Al</td>
<td>Tartrate complex</td>
<td>59.5</td>
<td>17.8</td>
<td>52.1</td>
<td>28.2</td>
</tr>
<tr>
<td>1Sb/V/Al</td>
<td>Sb2O3</td>
<td>57.1</td>
<td>6.2</td>
<td>42.1</td>
<td>47.9</td>
</tr>
<tr>
<td>1Sb2/V/Al</td>
<td>Tartrate complex</td>
<td>31.5</td>
<td>15.0</td>
<td>45.9</td>
<td>34.0</td>
</tr>
<tr>
<td>1Sb/V/Al</td>
<td>Sb2O3</td>
<td>42.0</td>
<td>32.0</td>
<td>38.7</td>
<td>25.0</td>
</tr>
<tr>
<td>1Sb2/V/Al</td>
<td>Tartrate complex</td>
<td>10.1</td>
<td>24.0</td>
<td>44.4</td>
<td>19.6</td>
</tr>
<tr>
<td>1Sb/V/Al</td>
<td>Sb2O3</td>
<td>15.6</td>
<td>34.3</td>
<td>29.0</td>
<td>28.8</td>
</tr>
<tr>
<td>1Sb2/V/Al</td>
<td>Tartrate complex</td>
<td>6.7</td>
<td>33.5</td>
<td>35.8</td>
<td>15.7</td>
</tr>
<tr>
<td>1Sb/V/Al</td>
<td>Sb2O3</td>
<td>10.1</td>
<td>40.4</td>
<td>24.7</td>
<td>24.0</td>
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<tr>
<td>1Sb2/V/Al</td>
<td>Tartrate complex</td>
<td>5.9</td>
<td>33.7</td>
<td>38.6</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Reaction conditions: total flow 20 ml/min; feed composition (% volume): C3H8/O2/NH3/He (9.8/25/8.6/56.6), 200 mg of catalysts, 480 °C.
patterns of catalysts with a coverage of one monolayer and figure 6(b) shows the effect of Sb + V total coverage at Sb/V = 5. All of them show the diffraction peaks of Nb$_2$O$_5$ phase being the used samples more crystalline than the fresh ones, this was also observed with niobia-supported catalysts prepared with Sb$_2$O$_3$ [30].

Neither fresh nor used catalysts generate the α-Sb$_2$O$_4$ diffraction peaks. The SbNbO$_4$ diffraction pattern is visible in fresh and used 2Sb 5V/Nb and 1Sb 7V/Nb, which are the catalysts with higher antimony contents. On the contrary, when Sb$_2$O$_3$ was used as precursor, SbNbO$_4$ phase was detected only in the used samples and α-Sb$_2$O$_4$ diffraction peaks was found in fresh 2Sb 5V/Nb [30].

Figure 7 shows the Raman spectra of fresh and used catalysts with one monolayer and different Sb/V molar ratios (figure 7(a)) and with Sb/V = 5 and different Sb + V coverages (figure 7(b)). Unlike the catalysts prepared with Sb$_2$O$_3$ suspension [30], the V = O Raman mode at 1024 cm$^{-1}$, typical of dispersed VO$_x$ species is not present. Fresh 1Sb/V/Nb shows Raman bands at 145, 195, 283, 302, 405, 480, 526, 697 and 995 cm$^{-1}$, typical of bulk V$_2$O$_5$. Weak Raman bands at 190 and 261 cm$^{-1}$ in the fresh and used 2Sb$_2$V/Nb evidence the presence of α-Sb$_2$O$_4$ phase. The absence of its diffraction pattern underlines that the size of these domains must be below 4 nm.

The broad Raman band near 900 cm$^{-1}$ that corresponds to Nb$_2$O$_5$, disappears after use in propane ammoxidation and a band near 660 cm$^{-1}$ shifts to 700 cm$^{-1}$ during reaction. This is due to a change in the crystalline phase of the Nb$_2$O$_5$ support, which is evident for all catalysts, but to a lower extent for 1Sb 7V/Nb, 1Sb 5V/Nb and 1Sb 3V/Nb.

The Raman bands at 845, 621 and 378 cm$^{-1}$ are observed on fresh and used 2Sb$_2$V/Nb catalysts, these bands correspond to the SbNbO$_4$ phase [30]. This phase presents also a band at 686 cm$^{-1}$ that cannot be observed here due to the intense Raman band at 660 cm$^{-1}$ of the Nb$_2$O$_5$ support.

Figure 8 shows the yields to the principal reaction products and the specific rate of formation of acrylonitrile per vanadium site for niobia-supported catalysts at 500°C. Figure 8(a) shows the effect of Sb + V coverage for catalysts with Sb/V molar ratio of 5 and figure 8(b) shows the effect of Sb/V molar ratio for catalysts at the dispersion limit loading. The profiles in figure 8(a) are similar to those obtained when Sb$_2$O$_3$ was used as antimony precursor [30]. Below and above the monolayer, the system is selective to acrylonitrile formation. The activity is lowest at monolayer coverage. Such minimum is also observed with different preparation methods [30]. The highest acrylonitrile yields are obtained for Sb/V molar ratios between 1 and 3.

All catalysts were tested under TOS operation. Only 1Sb 7V/Nb exhibit an increase to acrylonitrile yields with time (from 20 to 30%), this catalyst exhibits an important rearrangement of vanadia species, since crystalline V$_2$O$_5$ is no longer present after reaction.
Table 4 compares catalytic data obtained for samples prepared in this paper (tartrate method) and samples prepared via Sb$_2$O$_3$ suspension [30]. Catalysts with coverages below monolayer or with a large excess of antimony are not much active with either preparation method. However, the preparation method has an effect at Sb/V = 1 or with a moderate excess of antimony. The Sb$_2$O$_3$ suspension on niobia affords more efficient catalysts with a moderate Sb excess, e.g., catalysts 1Sb$_3$V/Nb and 2Sb$_5$V/Nb. However, the tartrate method affords the best system at stoichiometric (Sb/V = 1) ratios.

4. Discussion

4.1. Alumina-supported catalysts

The general trends observed with Sb/V molar ratio and with Sb + V coverage are similar to those observed when the catalysts are prepared via Sb$_2$O$_3$ suspension on alumina [29]. The higher acrylonitrile yields are obtained at Sb + V coverages above the dispersion limit, due to the formation of V$_2$Sb$_4$O$_8$ phase. V$_2$Sb$_4$O$_8$ phases do not form below the monolayer coverage.

Similarly to catalysts prepared via the Sb$_2$O$_3$ suspension [35], the best results are obtained for the catalysts with Sb/V molar ratios between 1 and 3. However, the use of different antimony precursors has an effect on the structure and performance of the supported Sb–V oxide system. In the absence of vanadium, crystalline Sb$_2$O$_3$ and α-Sb$_2$O$_4$ oxides do not form with the tartrate method, which leads to a new amorphous antimony oxide phase. To the best of our knowledge, this amorphous antimony oxide has not been observed before and its Raman bands (780, 600, 468 and 210 cm$^{-1}$) are reported for the first time here. This amorphous antimony phase is structurally more reactive than the Sb$_2$O$_3$.
and α-Sb₂O₄ phases and reacts with alumina forming AlSbO₄ (Raman bands at 819, 720 and 336 cm⁻¹). These bands are also reported for the first time. In the presence of V, the new method strongly favors the entanglement between V and Sb; leading to VSbO₄.

Alumina-supported V–Sb–O catalysts prepared with the conventional Sb₂O₃ suspension exhibit an intense activation during time-on-stream; both, conversion and selectivity increase [29]. This increment in acrylonitrile yield for catalyst 1Sb₁V/Al prepared with Sb₂O₃ suspension is due to the progressive formation of VSbO₄ during reaction; which has been determined by the simultaneous determination of structure and activity in an operando Raman-GC study [22,35]. Unlike the catalyst prepared with Sb₂O₃ suspension, the fresh catalyst 1Sb₁V/Al prepared with the tartrate method does possess the VSbO₄ phase (figure 4). This catalyst does not show any significant improvement in the acrylonitrile yield values during the first hours of reaction. Such trend is consistent with the relevance of VSbO₄ phase for ammoxidation reaction. Thus, the active phase is already present in the fresh catalyst. In addition, the catalyst prepared with the tartrate method exhibits higher selectivity to acrylonitrile. The VSbO₄ phase must be nano-scaled with less than 5 nm range, since it hardly generates a X-ray diffraction pattern.

The better performance of the sample prepared by the tartrate method must be due to the high dispersion of Sb species and small particle size of the oxides, that maximizes the interaction between VSbO₄, surface vanadia and segregated antimony oxide species. Such interaction is critical for the performance of these catalysts, since the interaction between segregated Sb oxide and VSbO₄ facilitates the redox cycle between surface V⁵⁺ oxide species and bulk V³⁺ sites in VSbO₄ [35,37].

### 4.2. Niobia-supported catalysts

Catalysts with Sb + V coverage below monolayer supported on alumina do not form VSbO₄ and are not efficient for propane ammoxidation to acrylonitrile [30]. On niobia, acrylonitrile does form below Sb + V monolayer coverage, when no VSbO₄ forms. Thus, acrylonitrile formation must be due to the interaction between surface vanadia species with niobium centers. Sb on niobia is not active due to the formation of SbNbO₄. The selectivity profiles are different to those of VSbO₄ [30]. At coverages above the Sb + V dispersion limit, VSbO₄ forms and the activity/selectivity profiles are like those of alumina-supported VSbO₄ [30]. So, activity must be due to VSbO₄ above Sb + V monolayer on niobia.

Nb₂O₅ support may interact with Sb and V. The interactions between niobia support and surface V and Sb species are strongly affected by the specific antimony precursor. The tartrate precursor provides molecularly dissolved antimony, which is more reactive than antimony present in Sb₂O₃ suspension. Niobia-supported catalysts prepared by the tartrate method possess SbNbO₄ upon calcination; i.e., in the fresh catalyst. However, such phase is not present in fresh catalysts prepared via Sb₂O₃ suspension [30]. In those catalysts, SbNbO₄ phase forms during reaction [30]. The tartrate method strongly promotes the reactivity of antimony species. On alumina, niobium interaction with vanadia dominates over that with alumina. However, on niobia, all possible interactions appear promoted: V–Nb, Sb–V and Sb–Nb. Nb–V and Sb–V interactions lead to efficient catalysts for propane ammoxidation. However, the Nb–Sb interaction leads to SbNbO₄, which is not active for propane ammoxidation; and, in addition, it removes Sb and Nb sites that would have coordinated with V to form efficient V–Sb or V–Nb

### Table 4

Comparative of propane conversion and yield values obtained for catalysts via Sb₂O₃ suspension [30] and the new tartrate method for niobia supported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Antimony precursor</th>
<th>Propane conversion (%)</th>
<th>CO yield (%)</th>
<th>CO₂ yield (%)</th>
<th>Propylene yield (%)</th>
<th>Acetonitrile yield (%)</th>
<th>Acrylonitrile yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>56.0</td>
<td>11.0</td>
<td>15.2</td>
<td>5.1</td>
<td>1.3</td>
<td>23.2</td>
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<tr>
<td>1Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>55.8</td>
<td>6.1</td>
<td>14.5</td>
<td>2.8</td>
<td>1.5</td>
<td>29.4</td>
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<tr>
<td>1Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>47.9</td>
<td>2.0</td>
<td>19.6</td>
<td>0.0</td>
<td>1.9</td>
<td>24.0</td>
</tr>
<tr>
<td>1Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>12.3</td>
<td>0.4</td>
<td>1.7</td>
<td>2.1</td>
<td>0.4</td>
<td>7.6</td>
</tr>
<tr>
<td>1Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>1Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>1.2</td>
<td>0.0</td>
<td>0.3</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>1Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>7.2</td>
<td>0.0</td>
<td>1.1</td>
<td>2.0</td>
<td>0.4</td>
<td>3.6</td>
</tr>
<tr>
<td>1Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>5.0</td>
<td>0.0</td>
<td>0.4</td>
<td>1.6</td>
<td>0.3</td>
<td>2.5</td>
</tr>
<tr>
<td>2Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>30.6</td>
<td>1.9</td>
<td>10.3</td>
<td>1.6</td>
<td>0.8</td>
<td>15.9</td>
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<tr>
<td>2Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>20.7</td>
<td>0.5</td>
<td>10.4</td>
<td>1.9</td>
<td>0.7</td>
<td>7.0</td>
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<tr>
<td>0.25Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>6.7</td>
<td>0.0</td>
<td>0.9</td>
<td>2.7</td>
<td>0.5</td>
<td>2.6</td>
</tr>
<tr>
<td>0.25Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>10.0</td>
<td>0.0</td>
<td>0.8</td>
<td>2.1</td>
<td>1.5</td>
<td>5.6</td>
</tr>
<tr>
<td>0.5Sb₁V/Nb</td>
<td>Sb₂O₃</td>
<td>13.2</td>
<td>0.6</td>
<td>1.6</td>
<td>3.1</td>
<td>0.6</td>
<td>8.1</td>
</tr>
<tr>
<td>0.5Sb₁V/Nb</td>
<td>Tartrate complex</td>
<td>13.9</td>
<td>0.6</td>
<td>2.8</td>
<td>2.2</td>
<td>0.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Reaction conditions: total flow 20 ml/min; feed composition (% volume): C₃H₈/O₂/NH₃/He (9.8/25/8.6/56.6), 200 mg of catalysts, 500 °C.
phases. Above, Sb + V monolayer coverage on niobia, Sb–V interaction dominates, and the trends are similar to those reported for alumina above monolayer coverage. Thus, catalysis is dominated by the V–Sb–O system on both supports, while a different catalytic system operates below monolayer coverage on niobia. Comparing both preparation methods, the tartrate method affords best results at Sb/V = 1; and the worst, above 1, due to Sb–Nb interactions.

At monolayer coverage on niobia, the activity is very low, probably because Nb centers are not accessible due to coverage and VSbO4 is not stable. As the Sb/V atomic ratio increases, the formation SbNbO4 makes the system inactive.

5. Conclusions

The use of tartrate precursor for antimony renders it more structurally reactive. Its reactivity must be due to the formation of an amorphous Sb oxide phase. Its Raman bands are described for the first time in literature. This phase may combine with alumina support and with niobia support, in competition with V–Sb interaction. The relative trends for interaction with Sb are qualitatively illustrated in Scheme 1, and it follows the trend Nb > V > Al. Sb–V, V–Nb and Sb–Nb interaction are more likely than Sb–Al or V–Al solid-state reactions. V–Al interaction is not observed in these catalysts, and the AlSbO4 phase is only formed at high temperature in the absence of vanadia. However, on niobia, all interactions appear possible, the relative concentrations of V, Sb and Nb appear to determine the interplay between V, Sb and Nb. On niobia, VSbO4 active phase forms above the Sb + V dispersion limit. Both, atomic Sb/V ratio and total Sb + V coverage determine the best preparation method for a specific support. On both series, the tartrate method produces best catalysts at stoichiometric Sb/V atomic ratio. Alumina affords better systems than niobia, since the former tends to combine with highly reactive Sb species into SbNbO4, which is not active and removes Nb and Sb sites that would coordinate with V into active V–Sb and V–Nb oxide phases.

![Scheme 1. Possible interactions of supported Sb and V oxides on alumina and niobia.](image)

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**References**