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ScienceDirect
Catalysis Today 118 (2006) 366–372
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Tunning the Nb addition to Sb-V-O catalysts for an efficient promotion of the ammoxidation of propane to acrylonitrile

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Abstract

The effect of niobium dopant on Sb-V oxide catalysts supported on alumina is reported with the purpose of understanding the promoting effect of Nb and preventing the non-desired inert $SbNbO_4$ phase. Two different catalyst syntheses have been tested: the most common in which Sb is added as Sb_2O_3 suspension and a novel one in which it is molecularly dissolved as a tartrate complex. The effect of adding Nb to alumina-supported Sb-V oxide catalysts depends on the preparation method. The preparation via Sb_2O_3 suspension affords segregated Sb oxide, which results in lower Sb-V interaction. The preparation via Sb tartrate complex affords molecularly dissolved Sb species that combine more easily with V or Nb species. The higher dispersion of Sb in the tartrate method also promotes its interaction with Nb dopant. The Sb tartrate preparation method is preferred for binary Sb-V supported oxide catalyst, while the Sb_2O_3 suspension method is preferred for Nb-promoted Sb-V supported oxide catalyst, which results in a very efficient catalyst for propane ammoxidation.

Keywords: V-Sb-Nb-Al-O; Oxidation; Ammoxidation; Propane; Acrylonitrile; Structure–activity relationship; In situ Raman; XRD

1. Introduction

Acrylonitrile is a product worldwide used to make acrylic fibres, acrylonitrile–butadiene–styrene (ABS) and styrene–acrylonitrile (SAN) resins, acryl and poliacrylamides, elastomers and other interesting products. Nowadays, acrylonitrile is produced by ammoxidation of propylene on catalyst made of promoted Fe-Bi-Nb-O (bp America) or promoted Fe-Sb-O (Nitto) [1,2]. The direct conversion of propane into acrylonitrile by reaction with ammonia and oxygen is an alternative route to the conventional propylene ammoxidation since propylene is more expensive than propane; however, the reaction conditions to activate the C–H bond in propane are more energy demanding, which has a negative effect on selectivity [3,4].

Several catalytic systems have been studied for this reaction. The most promising results are achieved with the Mo-V-Nb-Te system [2,5–7] and with Sb-V based catalysts [1,8,9], specially alumina-supported Sb-V catalysts [10–13].

There are several studies in literature about the use of dopants on the Sb-V-O system. The Sb-V-W-Al-O system [11] leads to a solid solution $Sb_{0.9}V_{0.9-x}W_xO_4$ and it is observed that activity increases with vanadium content while tungsten content makes the system more selective towards acrylonitrile. There are some studies about the effect of Ti [14,15], which improves the catalytic performance of the Sb-V-O system. Albonetti et al. [16] studied the effect of tin on the Sb-V-O system and again they concluded that vanadium enhances the activity. The molecular understanding of such promotion is elaborated elsewhere [15]. More recently, Roussel et al. [17] have studied the effect of Fe to this system, they found a solid solution between $VSbO_4$ and $FeSbO_4$; in this case this structure led to catalytic sites able to activate propane but less selective to acrylonitrile with low loading iron-substituted vanadium.

Niobium compounds and materials such as niobium pentoxide, niobic acid, niobium phosphate and mixed oxides containing niobia prove to be useful in catalysis as supports and as promoters for different reactions [18,19], especially for oxidation reactions [20–23]. Niobium oxide is similar to vanadium oxide [24], but it presents lower reducibility, so it may be easier to control non-desired reactions, such as ammonia elimination. In addition, niobium oxide presents more acidity that vanadium oxide.

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0920-5861/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cattod.2006.07.011

A previous work [25] on supported-niobia Sb-V-O catalysts demonstrates that Nb centres are selective for acrylonitrile formation. Nevertheless, alumina seems to be a better support for this system because it acts like an inert support that improves the dispersion of the Sb and V metal oxides making favorable the formation of $VSbO_4$ active phase during propane ammoxidation [26]. The aim of present work is to study the effect of adding niobium to the Sb-V system using alumina as support. This may provide the advantages of Nb promotion and limit the non-desired $SbNbO_4$ phase. So, Nb was added to 1Sb1V/Al and 1Sb3V/Al catalysts, those that have been found as the most active to AC formation [13].

Two different catalysts synthesis have been tested, the most common in which Sb is added as Sb_2O_3 suspension and one in which it is totally dissolved using a new method in which Sb is added as an organic complex with tartaric acid [27,28].

2. Experimental

2.1. Preparation of samples

The Nb-Sb-V/Al-(Sb_2O_3) catalysts were prepared by the slurry method. Sb_2O_3 (Aldrich, p.a.) was added to an aqueous solution of NH_4VO_3 (Sigma, p.a.) and an ammonium niobium soluble complex (Niobium Products), heating and stirring at 80 °C for 50 min, then γ-Al_2O_3 (Girdler Südchemie, 160 m^2/g) was added. The resulting dissolution was dried in a rotavapor at 80 °C. The resulting solid was dryed at 115 °C for 24 h and then was calcined at 400 °C for 4 h. The Nb-Sb-V/Al-(SbT) catalysts were prepared according to a method described elsewhere [27,28]; dissolving the necessary quantity of antimony acetate (Aldrich) on tartaric acid (Sigma) 0.3 M. This solution was kept under stirring until all antimony was dissolved. Then, NH_4VO_3 (Sigma), ammonium niobium soluble complex (Niobium Products) and γ-Al_2O_3 were added. The resulting disolution was dried in a rotavapor at 80 °C. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h. Some samples without Nb, V or Sb were prepared for comparative proporses following the same procedure.

Catalysts were prepared so that a total coverage of V + Sb or V + Sb + Nb would correspond to the dispersion limit on alumina. The dispersion limit was determined by Raman spectroscopy in a VO_x/Al_2O_3 series, as the maximum surface loading of VO_x units that remain dispersed, with no crystalline V_2O_5 (at V/nm^2) [29]. Sb/V atomic ratio changed in the 1–3 interval and Nb/Sb ratio in the 1–2 range.

2.2. Characterization

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 ($0.05 < P/P_o < 0.27$), 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 Kα radiation ($\alpha = 0.15418$ 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 Al from the sample holder are present.

Raman spectra were run with a single monochromator Renishaw System 1000 equipped with a cooled CCD detector (200 K) and holographic super-Notch filter. The holographic Notch filter filters the elastic scattering, and the Raman signal remains higher than when triple monochromator spectrometers are used. The samples were excited with the 514 nm Ar line; spectral resolution was ca. 3 cm^{-1} and spectrum acquisition consisted of 10 accumulations of 30 s. The spectra were obtained under dehydrated conditions (ca. 390 K) in a hot stage (Linkam TS-1500). 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 thermoconductivity 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. Test were made using the following feedstock: 25% O_2, 9.8% propane, 8.6% ammonia and the rest helium. The total flow rate was 20 ml/min corresponding to a gas-space velocity (GHSV) of about 3000 h^{-1}. The quantity of catalyst and total flow were determined in our previous work in order to avoid internal and external diffusion contributions. 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. Surface areas

The BET surface areas of the catalysts are listed in Table 1. The BET surface area values are quite similar but it should be noted that the catalysts prepared with tartrate complex present the highest area values. The atomic molar ratio Sb/V and Sb/Nb does not appear to have a clear effect on BET area values.

3.2. XRD

Reference samples showed the following diffraction peaks [13]: Sb_2O_3 shows diffraction peaks at 19.4, 25.47, 28.09, 28.38, 28.61, 33.79, 47.07, 50.53 and 60.80°. Sb_2O_4 shows diffraction peaks at 19.91, 25.839, 29.032, 30.35, 33.78, 37.37, 40.32, 48.87, 51.25, 53.11, 53.99, 56.17, 62.39 and 63.25°. $VSbO_4$ shows diffraction peaks at 27.44, 35.12, 39.219, 40.392,

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

Catalyst	%Sb	%V	%Nb	Sb + V + Nb Surface coverage	Nominal atomic ratio Sb/V	Nominal atomic ratio Sb/Nb	BET area (m^2/g)
Al_2O_5	0	0	0	–	–	–	160
1Sb1V/Al-(Sb_2O_3)	10.13	4.20	0	1	1	–	117
1Sb1V1Nb1/Al-(Sb_2O_3)	5.81	2.28	4.20	1	1	1	126
1Sb1V1Nb2/Al-(Sb_2O_3)	6.30	2.63	9.60	1	1	0.5	126
1Sb1V/Al-(SbT)	9.38	3.77	0	1	1	–	139
1Sb1V1Nb1/Al-(SbT)	5.12	2.17	3.92	1	1	1	150
1Sb1V1Nb2/Al-(SbT)	6.01	2.46	8.92	1	1	0.5	138
1Sb3V/Al-(Sb_2O_3)	15.00	2.11	0	1	3	–	121
1Sb3V1Nb1/Al-(Sb_2O_3)	10.68	1.49	2.72	1	3	1	118
1Sb3V/Al-(SbT)	12.89	1.82	0	1	3	–	123
1Sb3V1Nb1/Al-(SbT)	10.85	1.52	2.77	1	3	1	125

53.592, 56.61, 64.04, 67.31 and 68.37° and V_2O_5 shows diffraction peaks at 15.36, 20.28, 21.73, 26.15, 31.03, 32.39, 34.31, 41.29, 45.489, 47.36 and 51.25°.

The XRD patterns of the Sb-V-Nb-O/Al catalysts are shown in Figs. 1 and 2. Fig. 1 shows the effect of the niobium addition to the 1Sb1V/Al catalyst for the catalysts prepared via Sb_2O_3 (Fig. 1A) and via tartrate complex (Fig. 1B). These samples present patterns dominated by the peaks of the alumina support near 46 and 67°. The XRD pattern of $VSbO_4$ phase is only observed in the used 1Sb1V/Al-(SbT) catalyst (Fig. 1B), prepared with the tartrate method. Sb_2O_4 pattern is only appreciated in the 1Sb1V/Al-(Sb_2O_3) sample; so, antimony oxides are only detected in the sample prepared with the Sb_2O_3 method and without niobium.

Fig. 2 shows the effect of niobium doping to the 1Sb3V/Al catalyst prepared via Sb_2O_3 (Fig. 2A) and via tartrate complex (Fig. 2B). The pattern of fresh catalyst 1Sb3V/Al-(Sb_2O_3) presents the patterns of Sb_2O_3 and Sb_2O_4 oxides. But only the diffraction pattern of the Sb_2O_4 oxide is present in the used sample. The pattern of Sb_2O_4 oxide can be appreciated in the

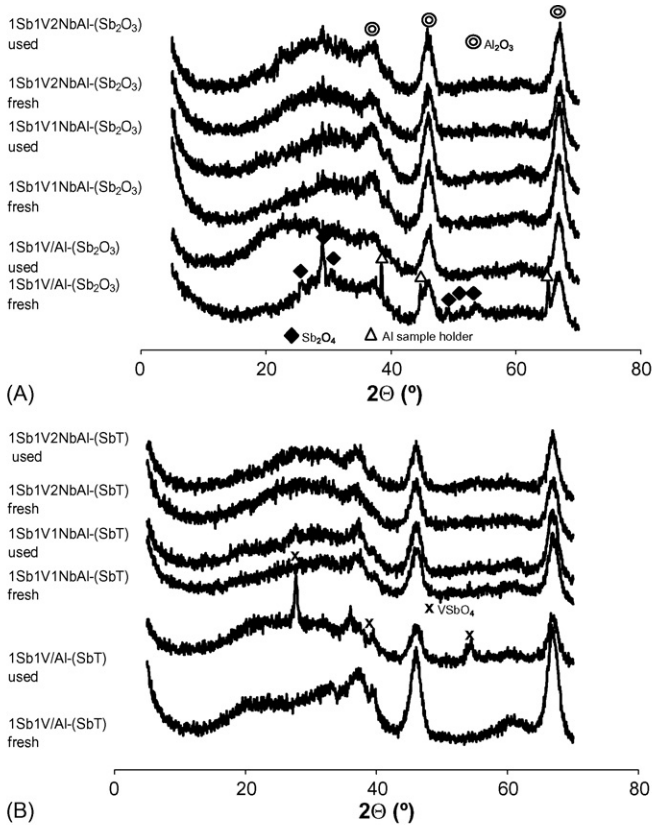

Fig. 1. XRD patterns of the alumina-supported catalysts with Sb/V = 1 and prepared with (A) Sb_2O_3 and (B) with tartrate.

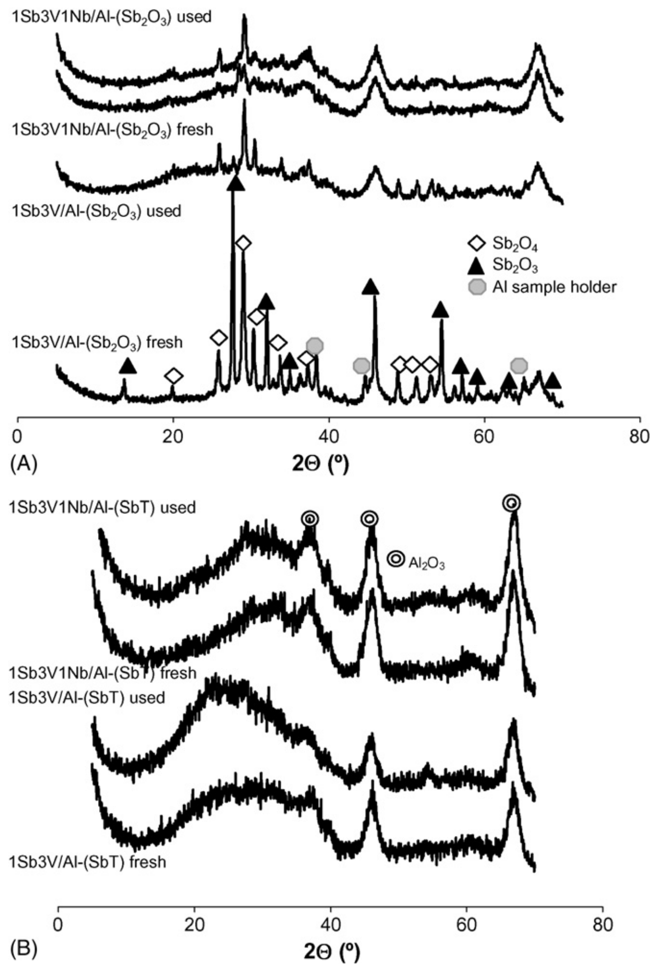

Fig. 2. XRD patterns of the alumina-supported catalysts with Sb/V = 3 and prepared with (A) Sb_2O_3 and (B) with tartrate.

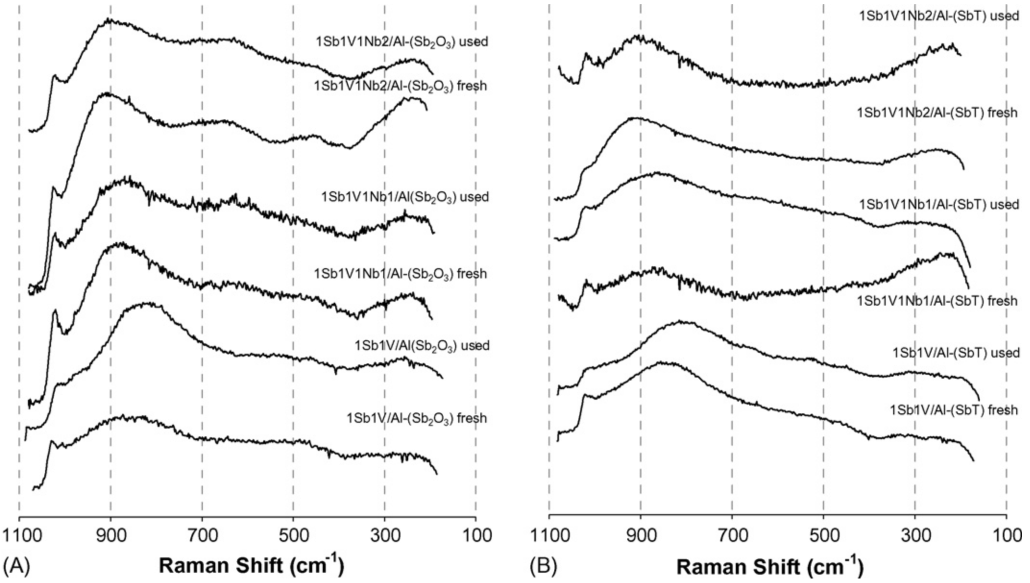

Fig. 3. Raman spectra of the alumina-supported catalysts with Sb/V = 1 and prepared with (A) Sb_2O_3 and (B) with tartrate.

diffractogram of fresh and used 1Sb3V/Al-(Sb_2O_3) catalyst. The XRD patterns of catalysts prepared with tartrate method (Fig. 2B) only show diffraction pattern that corresponds to the alumina support. So, with the tartrate method, no crystalline antimony oxide is detected by XRD, even in samples at Sb/V = 3.

3.3. Raman spectroscopy

Reference sample Sb_2O_3 shows Raman bands at 190, 255, 372, 451 and 716 cm^{-1}, Sb_2O_4 shows Raman bands at 190, 261, 399 and 459 cm^{-1} and V_2O_5 shows Raman bands at 143, 283, 302, 405, 480, 526, 698 and 994 cm^{-1}. $SbVO_4$ shows a broad band between 700 and 900 cm^{-1} [13,15].

Fig. 3 shows the effect in the Raman spectra of the addition of Nb to the 1Sb1V/Al catalyst for the catalysts prepared with Sb_2O_3 (Fig. 3A) and for the catalysts prepared with tartaric acid (Fig. 3B). The Raman peaks of antimony oxides are not observed on the spectra of catalysts with Sb/V = 1 atomic ratio. All the spectra present a band near 1027 cm^{-1}, sensitive to hydration; typical of dispersed surface VO_x species. The Raman spectra of catalysts 1Sb1V/Al-(Sb_2O_3) and 1Sb1V/Al-(SbT) present a broad band centered at 880 cm^{-1} and after reaction they present the band centered at 800 cm^{-1}, this is due to the formation of dispersed $VSbO_4$ phase [13,15,30,31]. XRD pattern of 1Sb1V/Al-(Sb_2O_3) sample did not shown signals of $VSbO_4$, visible by Raman spectroscopy, this is indicative that $VSbO_4$ is present as small aggregates unable to give a XRD pattern. The nature of the two Raman bands that coalesce near 800 cm^{-1} is discussed elsewhere [15]. Catalysts with niobium present a band near 900 cm^{-1}, more evident in samples prepared with Sb_2O_3; this band has been identified in V-Nb/Al_2O_3 samples [32] and belongs to V-Nb-O mixed phases.

Fig. 4 shows the effect of the addition of Nb to the 1Sb3V/Al catalyst in the Raman spectra of catalysts prepared via

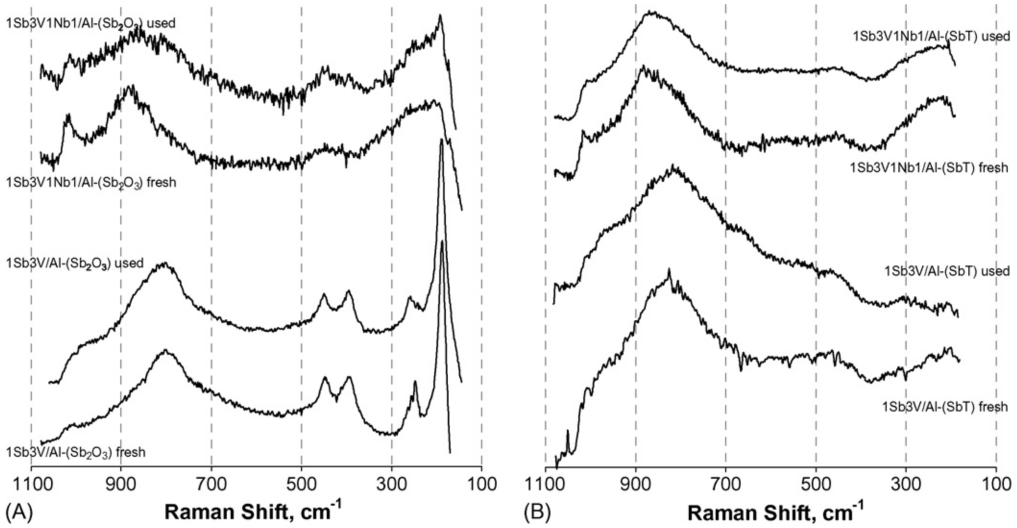

Fig. 4. Raman spectra of the alumina-supported catalysts with Sb/V = 3 and prepared with (A) Sb_2O_3 and (B) with tartrate.

Sb_2O_3 (Fig. 4A) and via the tartaric acid method (Fig. 4B). The Raman spectra of fresh and used 1Sb3V/Al-(Sb_2O_3) (Fig. 4A) present bands near 190, 255, 372 and 451 cm^{-1} which are typical of Sb_2O_4. The strongest band of Sb_2O_4 oxide (190 cm^{-1}) can be observed in the used 1Sb3V1Nb1/Al-(Sb_2O_3) catalyst. So, Sb_2O_4 phase is detected in samples prepared with Sb_2O_3 being more evident in the samples that do not contain niobium. In accordance with the XRD patterns, Sb oxides are not detected in the Raman spectra of catalysts prepared via the tartrate method (Fig. 4B). This is due to the weak Raman bands of amorphous Sb oxide [28]. The broad Raman band near 800 cm^{-1}, typical of $VSbO_4$ phase dispersed on alumina [13], is observed in the spectra of fresh and used 1Sb3V/Al-(Sb_2O_3) and 1Sb3V/Al-(SbT). So, $VSbO_4$ formation is favored at Sb/V above 1. Nb-doped catalysts shift the broad Raman at 800 cm^{-1} ($VSbO_4$) due to the contribution of the V-Nb-O band at 900 cm^{-1}. Nb-doped catalysts, 1Sb3V1Nb1/Al-(Sb_2O_3) and 1Sb3V1Nb1/Al-(SbT) (Fig. 4A and B), present a band near 1027 cm^{-1} sensitive to hydration, typical of dispersed surface VO_x species, such band is more intense in the fresh samples.

3.4. Activity measurements

The catalysts were tested during time on stream (TOS) up to 6 h, until they reach constant activity. Catalysts with Sb excess, 1Sb3V1Nb1/Al-(Sb_2O_3) and 1Sb3V1Nb1/Al-(SbT) remained relatively stable during TOS operation (Fig. 5A and D). The activity found for these samples with Sb/V = 3 was low compared with that obtained with the Sb/V = 1 catalysts. On the contrary, catalysts with Sb/V molar ratio of 1 showed a different performance: catalysts prepared with Sb_2O_3 increase acrylonitrile and acetonitrile yields during the first 2–3 h, acrylonitrile is the main product for these catalysts (Fig. 5B and C). Catalysts prepared via the tartrate method deactivate with time (Fig. 5E and F).

Fig. 6 shows the yields to principal products obtained at 440 °C during propane ammoxidation. Fig. 6A and B show the activity behavior of the binary catalysts: 1V/Al, 1Nb/Al, 1Sb/Al-(SbT) and 1SbAl-(Sb_2O_3), none of these elements is separately selective for acrylonitrile formation. The catalyst 1V/Al is the most active, but it is selective to CO_x and propylene.

1Sb1V/Al-(SbT) catalyst is more active and selective for propane ammoxidation than 1Sb1V/Al-(Sb_2O_3). Fig. 6 illustrates the effect of Nb addition to catalysts prepared using Sb_2O_3 suspension or the tartrate method (SbT). The effect of adding Nb is strongly dependent on the preparation method, SbT versus Sb_2O_3-series. Prior to Nb addition, unpromoted 1Sb1V/Al-(Sb_2O_3) catalyst reaches 10% acrylonitrile yield, being propylene and CO_2 the main products. For the (Sb_2O_3)-series; acrylonitrile becomes the main product if niobium is added to it (catalyst 1Sb1V1Nb1/Al-(Sb_2O_3) and 1Sb1V1Nb2/Al-(Sb_2O_3)). The Nb-promoted catalysts reach an acrylonitrile yield above 20% for catalyst 1Sb1V1Nb2/Al-(Sb_2O_3) at 440 °C (Fig. 6A). These catalysts increase acrylonitrile yield

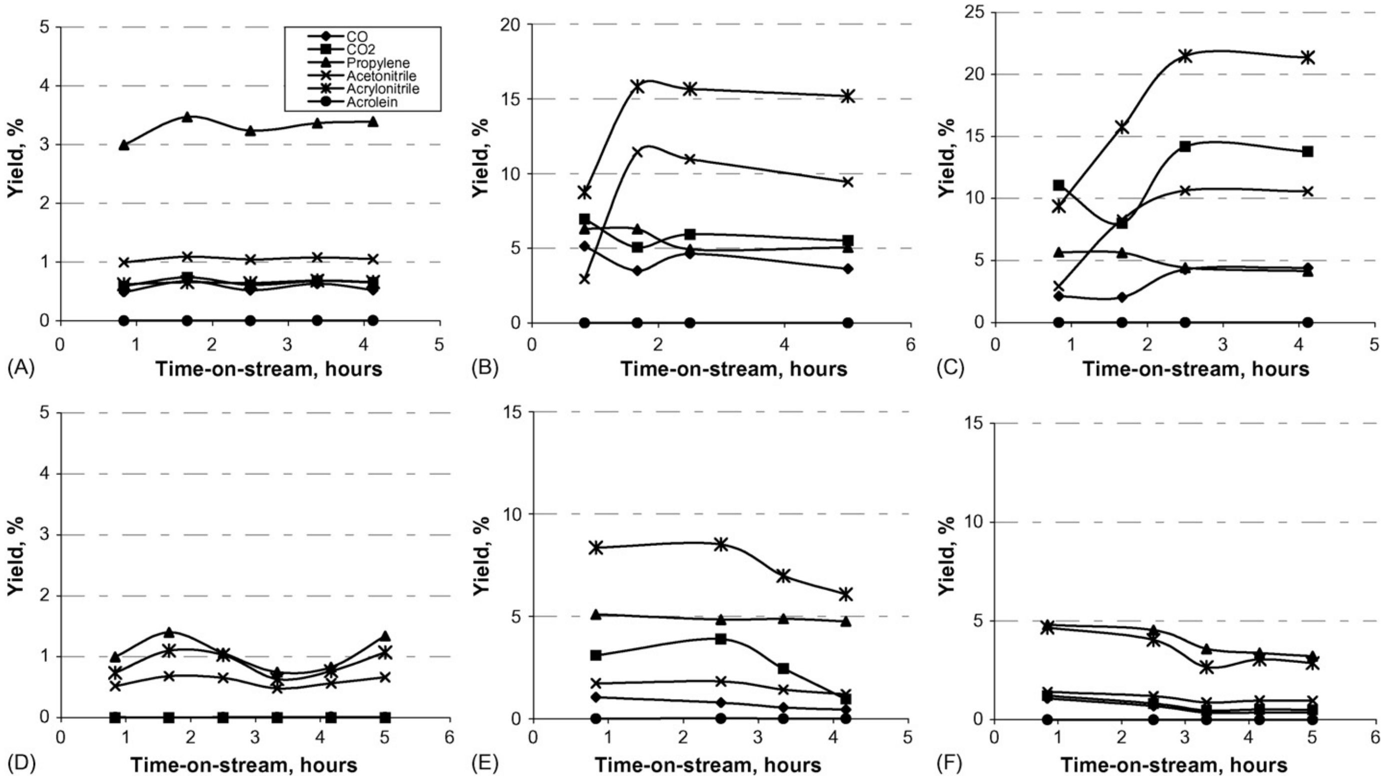

Fig. 5. Yields vs. time on stream for (A) 1Sb3V1Nb1/Al-(Sb_2O_3), (B) 1Sb1V1Nb1/Al-(Sb_2O_3), (C) 1Sb1V1Nb2/Al-(Sb_2O_3), (D) 1Sb3V1Nb1/Al-(SbT), (E) 1Sb1V1Nb1/Al-(SbT) and (F)1Sb1V1Nb2/Al-(SbT). Reaction conditions: total flow 20 ml/min; feed composition (vol.%): $C_3H_8/O_2/NH_3$/He (9.8/25/8.6/56.6), 200 mg of catalysts, temperature 440 °C.

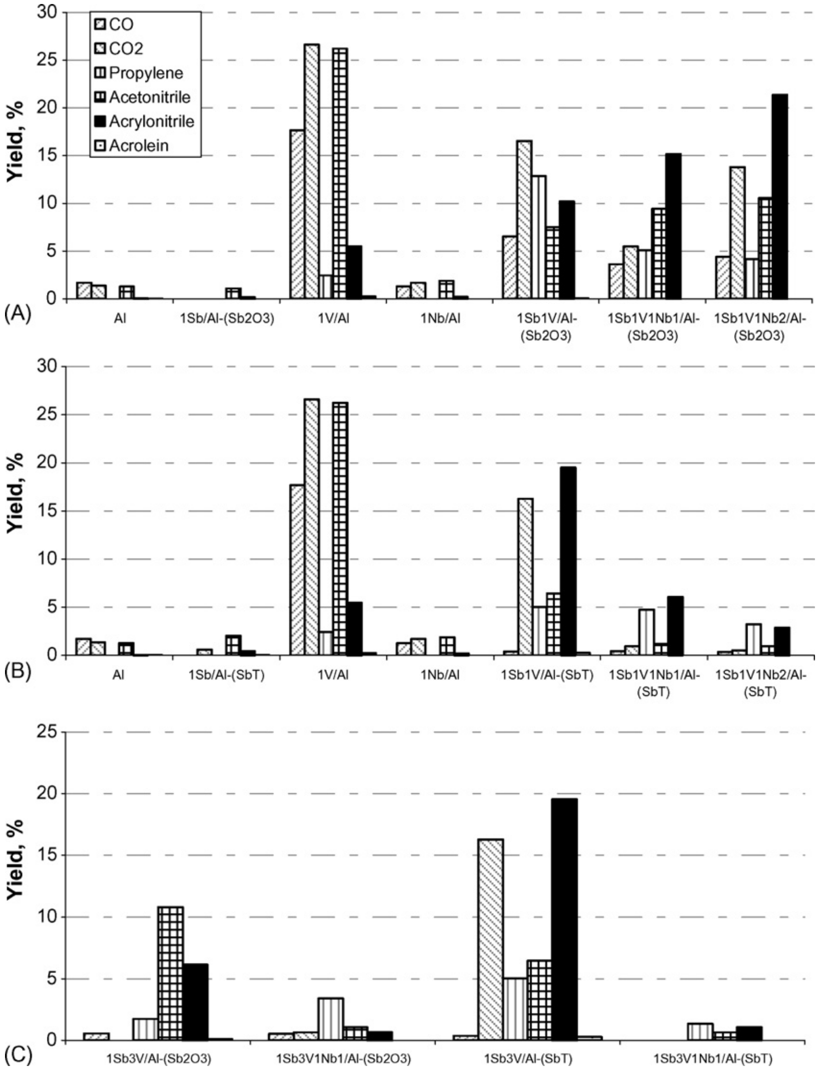

Fig. 6. Yields to principal reaction products for alumina-supported catalysts (A) with Sb/V = 1 and prepared with Sb_2O_3, (B) with Sb/V = 1 and prepared with tartrate and (C) with Sb/V = 3. Reaction conditions: total flow 20 ml/min; feed composition (vol.%): $C_3H_8/O_2/NH_3/He$ (9.8/25/8.6/56.6), 200 mg of catalysts, temperature reaction 440 °C.

with time on stream. The effect of Nb addition is very different on the (SbT)-series. On the contrary, this enhancement of the acrylonitrile yields is not observed when niobium is added to catalyst 1Sb1V/Al-(SbT) (Fig. 6B). The alumina-supported Sb-V system prepared by the tartrate method at Sb/V = 1 is more selective than that prepared via Sb_2O_3 suspension; however, the addition of Nb reverses the effect of preparation method on the selectivity trend. The acrylonitrile yields decrease from ca. 20 to ca. 5% when Nb is added to 1Sb1V/Al-(SbT).

Fig. 6C shows the effect of adding Nb to the catalysts with Sb/V molar ratio of 3. As it happened with the catalysts 1Sb1V/Al-(SbT) and 1Sb1V/Al-(Sb_2O_3), the catalyst prepared with tartrate, 1Sb3V/Al-(SbT) is much more active and selective to the acrylonitrile formation than that prepared with the antimony oxide suspension, 1Sb1V/Al-(Sb_2O_3). But the acrylonitrile yields decreased drastically for both catalysts, when Nb dopant is added (1Sb3V1Nb1/Al-(Sb_2O_3) and 1Sb3V1Nb1/Al-(SbT)).

4. Discussion

The tartrate method molecularly disperses antimony and it generates an amorphous layer of Sb oxide [28], which makes the reaction of Sb with other components more favorable. This trend is further confirmed in this paper. The XRD patterns of binary alumina-supported catalysts (Fig. 1B) exhibit the diffraction pattern of $VSbO_4$ phase, but it is not observed in the corresponding ternary catalysts (Figs. 1 and 2). The higher structural reactivity of the amorphous Sb oxide phase promotes the reactivity with both, vanadium and niobium species. The antimony tends to react with Nb into $SbNbO_4$, that has been described as inactive for acrylonitrile formation during propane ammoxidation [25,26], and the Sb-Nb interaction appears stronger than the V-Sb interaction [33]. Raman bands of $SbNbO_4$ phase appears at 845, 686 and 621 cm^{-1}, being the most intense the one at 845 cm^{-1}. These bands are quite difficult to appreciate in these samples due to the presence of the broad Raman bands of Nb_2O_5 support in that region. This accounts for the activity and selectivity decrease upon addition of Nb to the catalyst prepared with the tartrate method (Fig. 6B).

When the catalysts have excess Sb, the formation of $SbVO_4$ phase is more favorable [13]. Fig. 4 confirms the formation of this phase in the Raman spectra of catalyst with Sb/V atomic ratio of 3. But the addition of niobium to catalysts with Sb/V = 3 makes the system unselective to acrylonitrile formation (Fig. 6C) and form the inert $SbNbO_4$ phase forms.

Good results for propane ammoxidation are achieved when niobium is added to alumina-supported catalysts prepared with Sb_2O_3 at Sb/V = 1 (Fig. 6A). Niobium sites make the system more selective to acrylonitrile formation. This is not the case for the catalysts prepared via the tartrate method. The dispersion state of Sb sites is the major difference between both preparation methods. The effect of niobium dopant for propane ammoxidation on Sb-V oxide based system has been studied before. Relevant conclusions are: (a) when Nb_2O_5 is used as support for the Sb-V-O system, good performance is recorded below monolayer, when niobium centers are accessible [26]; (b) niobium and vanadium can interact forming phases selective for acrylonitrile [25,26]; (c) the tartrate method promotes the formation of the inert $SbNbO_4$ phase by reaction with niobia support [33]. The information of niobia-supported systems is relevant to niobia-doped Sb-V-O catalysts on alumina. The best results are achieved for the Nb-doped catalysts prepared via Sb_2O_3 suspension, while Nb-free catalysts are most efficient if prepared by the tartrate method at Sb/V = 1.

5. Conclusions

The effect of adding Nb to alumina-supported Sb-V oxide catalysts depends on the preparation method of these catalysts. The *preparation via Sb_2O_3 suspension* affords segregated Sb oxide, which results in lower Sb-V interaction in the supported binary Sb-V oxide catalysts. This makes the binary catalysts less efficient for propane ammoxidation. In this system, the addition of Nb significantly promotes ammoxidation performance to the best acrylonitrile yield values.

The *preparation via Sb tartrate complex* affords molecularly dissolved Sb species that readily combine with vanadium into $VSbO_4$ in the supported binary Sb-V oxide catalysts. The higher dispersion of Sb in the tartrate method also promotes its interaction with Nb dopant. The Nb-Sb interaction prevails over the Sb-V interaction, leading to inefficient $SbNbO_4$ at the expense of the efficient $VSbO_4$ phase.

Thus, the Sb tartrate preparation method is preferred for binary Sb-V supported oxide catalyst, while the Sb_2O_3 suspension method is preferred for Nb-promoted Sb-V supported oxide catalyst.

Acknowledgments

This research was funded by CICYT, Spain, under PROJECT QUI98-0784, and REPSOL-YPF, Spain. Project CTQ2005-02802/PPQ from Spanish Ministry of Education and Science funded this research. M.O.G.-P. thanks the Ministry of Science and Technology of Spain, for a doctorate studies fellowship. The authors thank Dr. M.A. Vicente from Salamanca University for his help with the XRD analysis and his helpful discussions.

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