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Effect of the oxide support on the propane ammoxidation with Sb–V–O-based catalysts

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Abstract

The role of Nb_2O_5 and γ-Al_2O_3 oxide supports on the ammoxidation of propane on supported mixed Sb–V oxide at different Sb + V surface coverages is studied. Sb and V oxide species on alumina and on niobia support show different structural features that reflect in different performance during the ammoxidation of propane to acrylonitrile. Niobia-supported catalysts are much more selective to acrylonitrile than alumina-supported ones. Alumina interacts weakly with the supported oxides while niobia forms new phases through solid state reactions with the supported oxides during catalytic operation that must account for its higher selectivity values towards acrylonitrile and higher specific rate of acrylonitrile formation per vanadium site.

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

1. Introduction

Nitriles such as acrylonitrile have been industrially produced as important intermediates for the preparation of fibers, synthetic resins, synthetic rubbers and other valuable chemicals. 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 several times more expensive than propane. The economic implications of this new route are very important. Thus, in 1997 British Petroleum started a demonstration plant to make acrylonitrile, using propane, and estimated to decrease production costs ca. 20% compared with conventional propylene-based technology [1]. In this reaction, the activation of propane is the limiting step. Since the adsorption rate of propane is nearly 10 times smaller than that of propylene [2] the conversion of propane is at least 10 times smaller than that of propylene [3]. The reaction conditions to activate the C–H bond in propane are more energy demanding, which has a negative effect on selectivity.

Most of the reported works are concentrated on antimony-based catalysts, like vanadium antimonates with rutile structure [4–7] or on molybdates [8–12]. The molybdates can be promoted with Bi [8]. Some molybdates may possess scheelite structure [9–11]. Mo–V catalysts modified with Nb and Te may afford near 50% yield to acrylonitrile [12]. On Sb–V–O-based catalysts, the presence of alumina endows the system with better performance [11,13]. 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 more efficient for propane ammoxidation [13]. Total coverage of Sb + V on alumina determines the extent of formation

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of $SbVO_4$ phases [14] and an efficient propane ammoxidation requires V and Sb species combined into $SbVO_4$ phases.

The catalysts show adsorption of both ammonia and propane [3,15–17]. However, different catalyst formulations may lead to different limiting steps in the reaction route. Propane is likely to react via a hydrogen abstraction from a single methylene group followed by removal of a hydrogen atom from a primary carbon in a subsequent step [18]. Transient experiments show that short-lived NH_x fragments are active species in the formation of acrylonitrile from propane [17]. IR studies suggest a competitive adsorption of ammonia during ammoxidation reaction [5]. Oxygen is provided through the lattice of the oxide and molecular oxygen from gas-phase regenerates the catalyst [3]. Recent transient studies confirm this trend for Sb–V–O catalysts [19]. Antimonate catalysts appear to be limited by ammonia activation [20]. In this sense, the study of the relevance of niobia as a support is interesting since its acidic character may promote the interaction of ammonia with the catalyst. Niobium oxide is similar to vanadium oxide [22], but it presents lower reducibility, so it maybe easier to control other non-desired reactions, such as ammonia elimination.

Alumina has been described as a good support of this system and there are several patents with synthesis procedures for the Al–Sb–V–O system [21] and in a previous work [14] it has been shown than antimony vanadium oxides supported on alumina are active and selective for propane ammoxidation. But the details on the structure and nature of surface species on Sb–V–Al mixed metal oxide catalysts are not fully understood. Under the conditions used here, alumina does not react with the supported oxides. Thus, structural transformation may only occur among species dispersed on the surface of alumina support, which could be named as “horizontal” interactions. However, niobia support does react with Sb and V into new oxides. Thus, niobia-supported mixed Sb–V oxides may undergo structural transformations among surface species (“horizontal” interactions) but it may also undergo interaction between the support and the supported oxides, which could be named as “vertical” interactions. Therefore, understanding the nature of the active sites in niobia-supported oxide catalysts maybe difficult since “horizontal” interactions among surface Sb and V oxide species (Sb–V–O phases) coexist with “vertical” interactions between the supported oxides and the oxide support (V–Nb–O, Sb–Nb–O and Sb–Nb–V–O phases). This work studies the effect of niobium oxide as support for this system. This work compares structural characteristics and performance of alumina- and niobia-supported Sb–V–O catalysts. The effect of total Sb + V coverage and the effect of the oxide support are evaluated on the activity/selectivity for propane ammoxidation to acrylonitrile.

2. Experimental

Catalysts have been prepared by following the slurry method. Sb_2O_3 (Aldrich) was added to an aqueous solution of NH_4VO_3 (Sigma), this solution was kept under stirring at 80 °C for 50 min, then, support was added. The resulting solution was dried in a rotatory evaporator at 80 °C. The resulting solid was dried at 115 °C for 24 h and then calcined at 400 °C for 4 h. Catalysts were prepared so that a total coverage of Sb + V would correspond to 1/4, 1/2, 1 and twice their dispersion limit. The dispersion limit is understood as the maximum surface loading of VO_x units that remain dispersed with no crystalline V_2O_5, determined by Raman spectroscopy, to be near 9 atoms/nm^2 of support [23]. The Sb/V atomic ratio was fixed at 5 but two catalysts were prepared as references with Sb/V molar ratio of 1. Reference catalysts containing only one of metals, Sb or V, were prepared at dispersion limit following the same slurry method.

Raman spectra were run with a single monochromator Renishaw System 1000 equipped with a thermoelectrically cooled CCD detector (−73 °C) 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 the spectrum acquisition time was 300 s. The spectra were obtained under dehydrated conditions (ca. 390 K) in a hot stage (Linkam TS-1500).

X-ray diffraction patterns were recorded on a Siemens Krystalloflex D-500 diffractometer using Cu Kα radiation ($\lambda = 0.15418$ 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°. 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 ($0.05 < P/Po < 0.27$), taking a value of 0.164 nm^2 for the cross-section of the adsorbed N_2 molecule at −196 °C.

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. Test were made using the following feedstock: 25% O_2; 9.8% propane; 8.6% ammonia; the rest helium. Note that the proportion of O_2/He is similar to O_2/N_2 in the air. The total flow rate was 20 ml/min 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

The BET surface area values are listed in Table 1. The BET area values decrease with surface coverage. The decrease of BET area values is most intense on niobia-supported catalysts than on alumina-supported oxides, which could be indicative of a stronger interaction with niobia support.

XRD patterns of fresh and used catalyst are represented in Fig. 1. The alumina-supported fresh catalysts present XRD patterns that correspond to antimony oxides (Sb_2O_3, JCPDS file 11-689 and α-Sb_2O_4, JCPDS file 11-694) (Fig. 1A). These patterns disappear after propane ammoxidation when Sb + V coverage is more than one monolayer while Sb_2O_3 remains unaffected if Sb + V coverage is below monolayer. Fresh niobia-supported catalysts do not show any clear diffraction pattern (Fig. 1B) since the niobium pentoxide support is amorphous. However, after reaction, niobia-supported catalysts are more crystalline and exhibit the diffraction patterns of crystalline Nb_2O_5 TT phase (JCPDS file 7-0061). This phase change is reported to occur at temperatures higher than 500 °C [24], which is reached during propane ammoxidation. The used $2Sb_5V$/Nb catalyst presents diffraction peaks at 30.5° and 25.8° that correspond to the $SbNbO_4$ phase (JCPDS file 16-907).

The Raman spectra of fresh and used catalyst are represented in Fig. 2. Reference Sb_2O_3 exhibits

Table 1
Composition and BET area values of Sb–V–O catalysts

Catalyst	BET surface area (m^2/g)	Sb (%)	V (%)	Sb + V monolayer	Sb/V atomic ratio
Al_2O_3	160.0	0	0	–	–
1V/Al	129.8	0	8.70	1	–
1Sb/Al	105.9	19.9	0	1	–
$0.25Sb_5V$/Al	146.9	5.06	0.42	0.25	5
$0.5Sb_5V$/Al	138.7	9.40	0.76	0.5	5
$1Sb_5V$/Al	128.0	17.60	1.45	1	5
$2Sb_5V$/Al	78.0	26.79	2.37	2	5
$1Sb_1V$/Al	118.0	10.13	4.20	1	1
Nb_2O_5	107.3	0	0	–	–
1V/Nb	38.2	0	6.21	1	–
1Sb/Nb	44.1	14.54	0	1	–
$0.25Sb_5V$/Nb	71.1	3.59	0.30	0.25	5
$0.5Sb_5V$/Nb	59.5	6.86	0.76	0.5	5
$1Sb_5V$/Nb	40.8	12.41	1.07	1	5
$2Sb_5V$/Nb	24.0	20.95	1.85	2	5
$1Sb_1V$/Nb	41.4	7.31	3.06	1	1

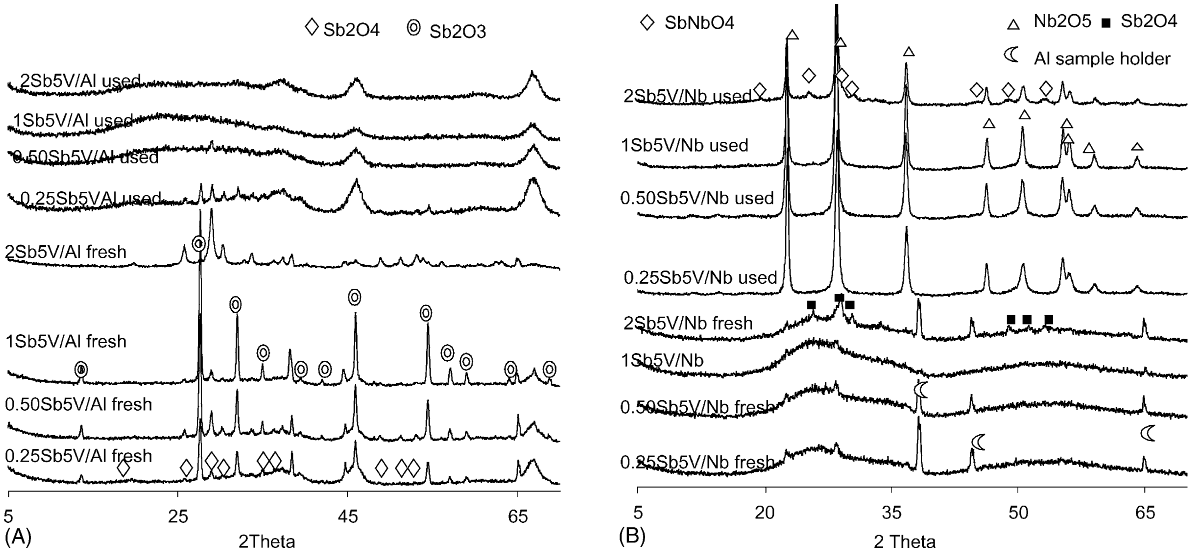

Fig. 1. XRD patterns of fresh and used catalysts: (A) alumina-supported Sb–V oxide catalysts; (B) niobia-supported Sb–V oxide catalysts.

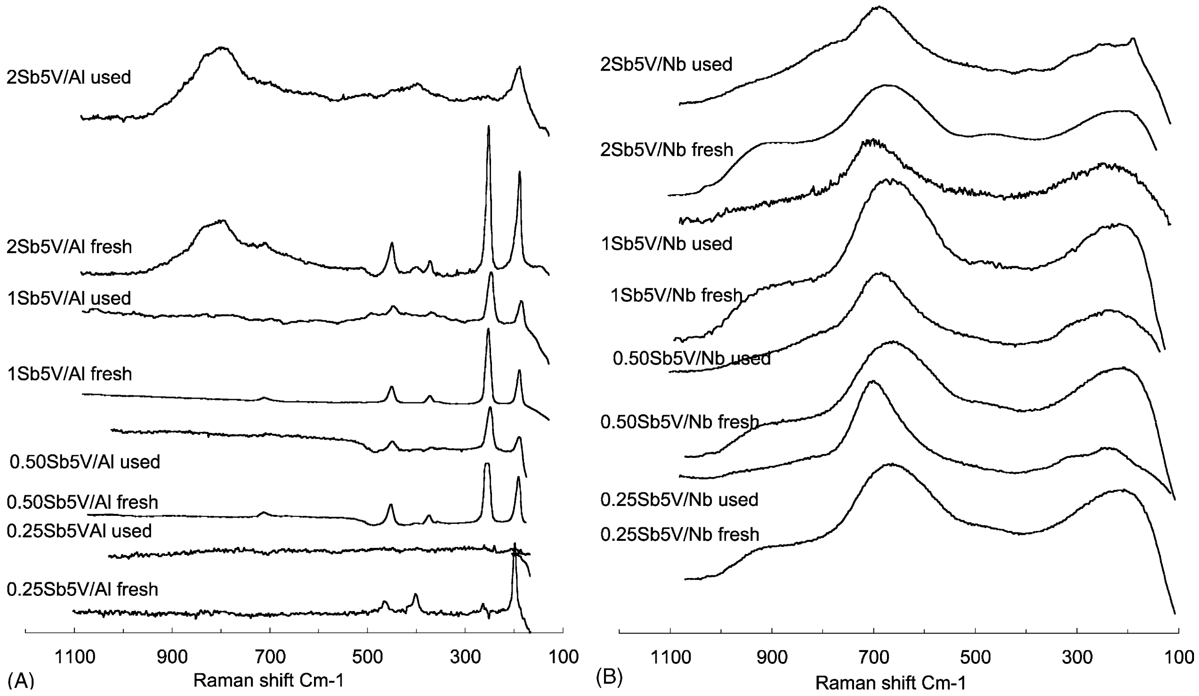

Fig. 2. Raman spectra of fresh and used catalysts: (A) alumina-supported Sb–V oxide catalysts; (B) niobia-supported Sb–V oxide catalyst.

Table 2
Propane ammoxidation on alumina and on niobia-supported catalysts[a]

Product yield (%)	Al_2O_3	1V/Al	1Sb/Al	$1Sb_1V/Al$	Nb_2O_5	1V/Nb	1Sb/Nb	$1Sb_1V/Nb$
CO	6.0	31.6	0.0	11.8	0.0	15.9	0.0	11.0
CO_2	18.5	19.2	0.9	21.9	2.4	31.4	0.0	15.2
Propylene	0.6	3.3	0.8	16.2	3.6	3.5	0.0	5.1
Acetonitrile	3.1	14.8	2.0	5.2	0.6	9.3	0.2	1.3
Acrylonitrile	0.1	3.3	0.9	29.2	0.3	15.8	0.2	23.2
Acrolein	0.1	0.3	0.03	0.2	0.0	0.1	0.01	0.1

[a] Reaction conditions: 500 °C, $W = 200$ mg, $F = 20$ ml/min ($C_3H_8/O_2/NH_3/H_2O/He = 9.8/25/8.6/0/56.6$ vol.%).

Raman bands at 190, 255, 372, 451 and 716 cm^{-1} and reference α-Sb_2O_4 at 190, 261, 399 and 459 cm^{-1} [14]. The spectra of fresh and used alumina-supported catalyst present bands that correspond to these Sb oxides. The spectrum of fresh $2Sb_5V/Al$ presents bands that correspond to Sb_2O_3 and a broad band centered at 800 cm^{-1} typical of $SbVO_4$ phase [14], the spectrum of used catalysts presents the band of $SbVO_4$ phase and bands of Sb_2O_4. The Raman spectra of niobia-supported catalysts show how fresh catalysts are amorphous and the spectra of used catalysts correspond to the crystalline Nb_2O_5 TT phase [25]. Due to the very intense Raman bands of niobia support, it is difficult to assess the presence of other phases. Raman spectra of catalyst $2Sb_5V/Nb$ present a shoulder centered at 1024 cm^{-1}, sensitive to hydration, typical of surface dispersed vanadium oxide species, this band is not present in the corresponding $2Sb_5V/Al$ catalyst.

Table 2 shows the yield to the different products at 500 °C that show reference values for the oxide supports, binary and ternary catalysts. The catalytic behavior of supports is quite different. Conversion on alumina is significantly higher than on niobia. In addition, niobia affords a significant selectivity towards propylene, while CO_2 is the main reaction product on alumina. Sb oxide on alumina or niobia modulates the total oxidation profiles. The addition of vanadium enhances the activity, mainly towards CO_2, on both supports. In addition, 1V/Al shows activity towards acetonitrile while 1V/Nb affords a significant amount of acrylonitrile. This must be due to the V–Nb interaction. When Sb and V are present, the main oxidation product is acrylonitrile, on both supports. Therefore, V, Sb and Nb are important components for an ammoxidation catalyst.

The yield values to the different reaction products are represented in Fig. 3. Global activity increases with Sb + V coverage on the alumina-supported series. Below monolayer coverage, the system is not selective since the main oxidation products are CO and propylene. At monolayer coverage and above, selectivity profile changes towards acrylonitrile formation, which reaches yield values near 26%. Niobia-supported series show a different dependence on Sb + V coverage. Below monolayer coverage the niobia-supported series is more selective than alumina-supported series, being acrylonitrile and propylene the main reaction products. Above Sb + V monolayer coverage on niobia, the yield to acrylonitrile becomes dominant at the expense of propylene. Thus, selectivity profiles are different below and above monolayer coverage and in addition, depend on the oxide support. The acrylonitrile yields on the niobia-supported catalyst, with coverage lower than monolayer, is higher than for the alumina supported ones, which are more selective towards CO_x. Above monolayer, alumina-supported series show high selectivity values to acrylonitrile and a significant production of propylene. On the other hand, niobia-supported catalysts show high selectivity to acrylonitrile and CO_2 as the second reaction product, being propylene production tenfold lower than that of acrylonitrile. Therefore, the presence of Nb must afford new catalytic sites. In this line, Fig. 4 presents the milimoles of acrylonitrile produced per second and per milimole of vanadium. The specific rate of acrylonitrile formation is higher on niobia-supported catalysts at Sb + V coverage below one monolayer. Thus, vanadium sites on niobia posses a more efficient environment. Sb + V coverage has different effects on the specific rate of acrylonitrile formation, depending on the oxide support. The presence of exposed niobia sites must be important for the reaction since specific acrylonitrile formation rate goes through a minimum at monolayer coverage. The profile of Sb + V coverage

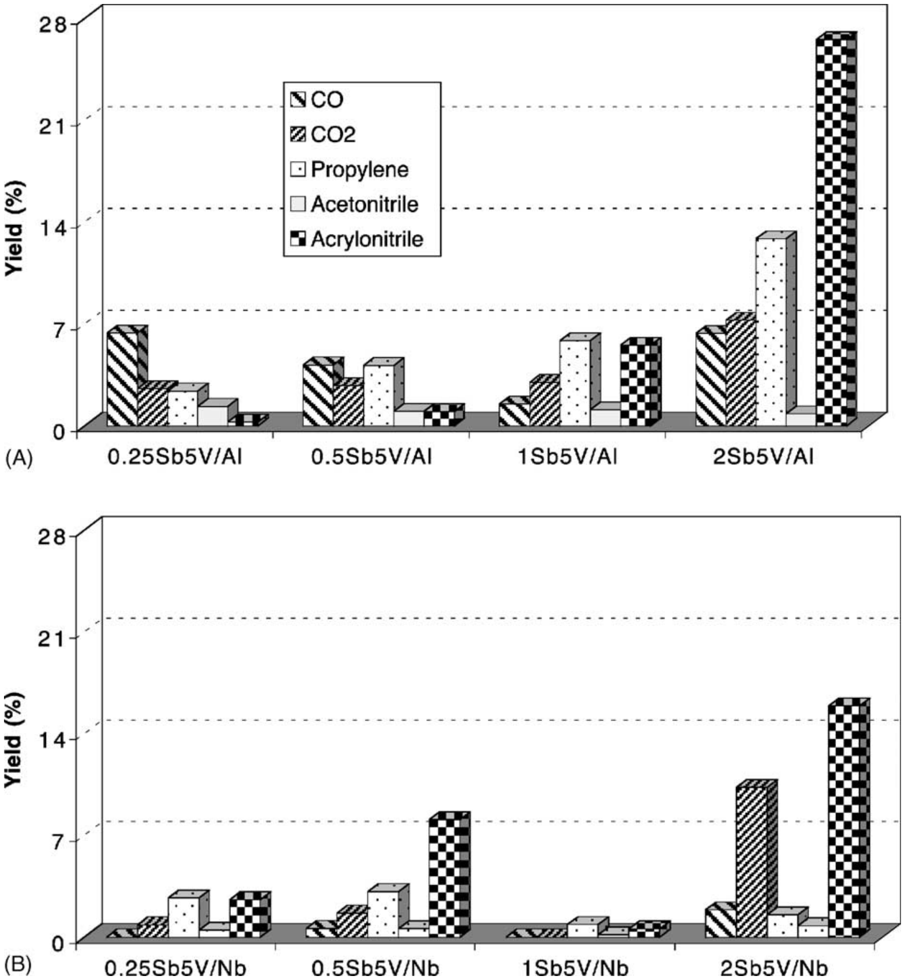

Fig. 3. Yields to different products. Reaction conditions: 500 °C; total flow 20 ml/min; feed composition (vol.%): $C_3H_8/O_2/NH_3$ (9.8/25/8.6); 200 mg of catalysts.

on niobia has been confirmed in several replica experiments with these samples. Above monolayer coverage, it is likely that aggregation of supported oxides in three-dimensional aggregates leave some niobia support exposed. Alumina-supported series shows quite a different trend. Below Sb + V monolayer coverage on alumina, the specific rate of acrylonitrile formation is very low and it increases by an order of magnitude at monolayer coverage and above (Fig. 4). It is interesting to underline that the highest specific rates for acrylonitrile formation are reached below Sb + V monolayer coverage on niobia and above the Sb + V monolayer coverage on alumina. This must be indicative of a change in the nature of the active site present on each series.

Fig. 5 presents the ammoxidation of propane versus reaction temperature for the catalysts with half a monolayer coverage, $0.5Sb_5V/Al$ and $0.5Sb_5V/Nb$. The catalyst supported on alumina shows a very different behavior once it produces acetonitrile as the main reaction product at temperatures below 440 °C while propylene and CO_x dominating at higher temperatures (Fig. 5A). Acrylonitrile is the major product at all temperatures for the catalyst supported on niobia (Fig. 5B). $0.5Sb_5V/Nb$ shows a remarkable increase in acrylonitrile yield at 460 °C. This transient period

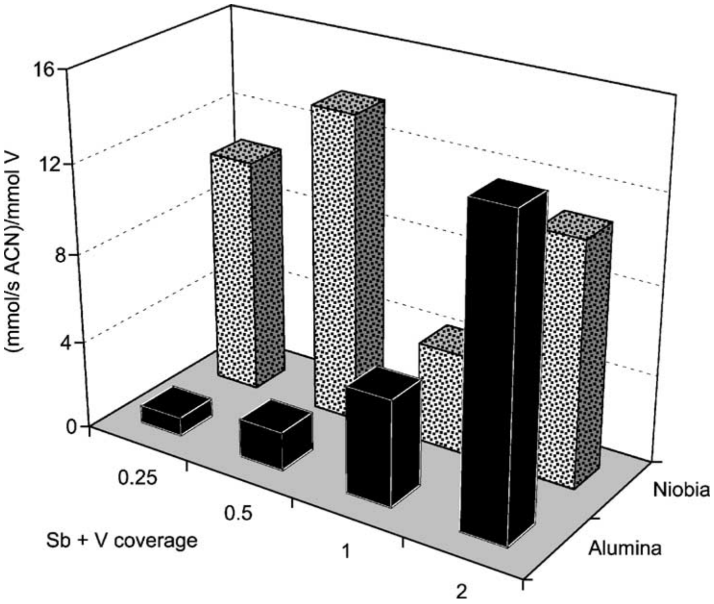

Fig. 4. Specific rate of formation of acrylonitrile per V site at 500 °C. Reaction conditions: total flow 20 ml/min; feed composition (vol.%): $C_3H_8/O_2/NH_3$ (9.8/25/8.6); 200 mg of catalysts.

where both conversion and selectivity increase is a common feature in niobia-supported Sb–V–Oxide catalysts. Fig. 6 provides a detailed view of conversion and yield versus time on stream (TOS). When the reaction temperature is increased to 500 °C, the propane conversion increases from 5 to 14%. This trend below monolayer coverage on niobia differs from that observed on alumina-supported Sb–V oxides [14], where catalytic activity remains constant. Alumina-supported Sb–V oxides need Sb + V coverage of one monolayer and above to show transient activity profiles versus TOS [14]. The nature of the active site on niobia series must be different than on alumina series.

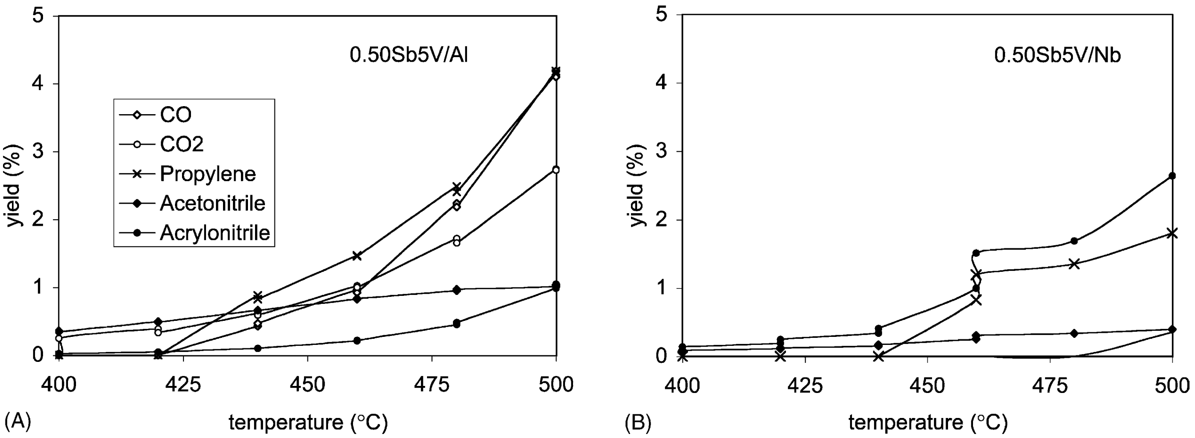

Fig. 5. Yields to different reaction products versus temperature for 0.5Sb5V/Al (A) and 0.5Sb5V/Nb (B). Total flow 20 ml/min, feed composition (vol.%): $C_3H_8/O_2/NH_3/H_2O$ (9.8/25/8.6/0); 200 mg of catalyst.

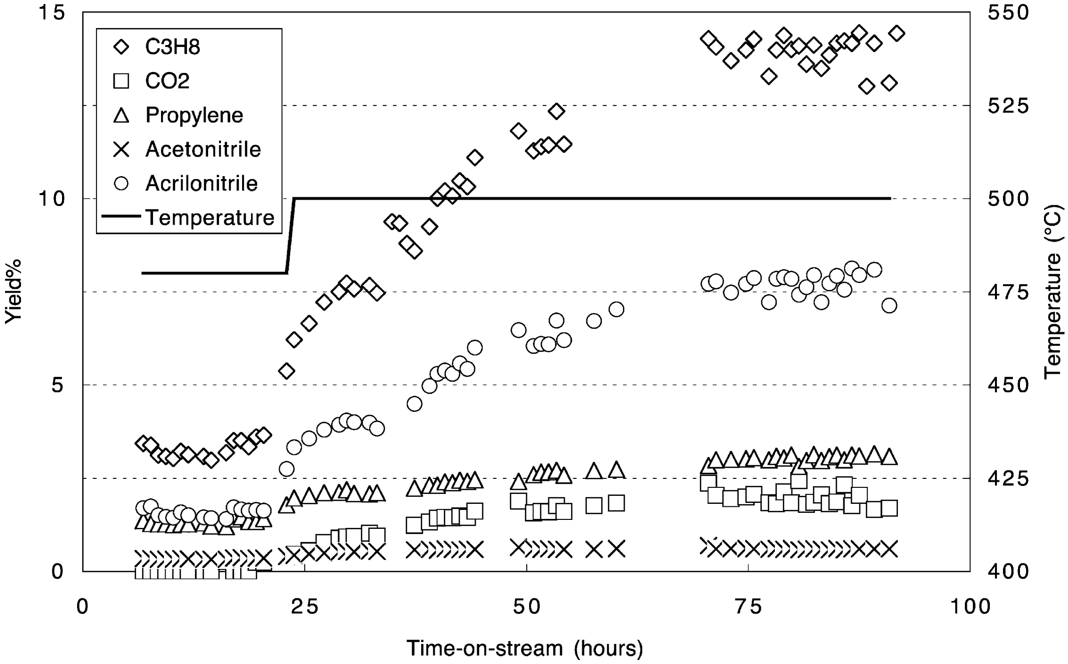

Fig. 6. Yields and propane conversion versus reaction time an temperature for catalyst 0.5Sb5V/Nb. Total flow 20 ml/min, feed composition (vol.%): $C_3H_8/O_2/NH_3/H_2O$ (9.8/25/8.6/0); 200 mg of catalyst.

4. Discussion

The BET area values suggest a stronger interaction between niobia support and the supported oxides than on alumina. Both, XRD and Raman spectra evidence the formation of compounds involving Nb. XRD patterns and Raman spectra indicate the presence of Sb oxides in fresh and used catalysts and support phases for alumina supported catalysts. Mixed phases between Sb and V like $SbVO_4$ that have been identified in other works [14,26–29], are only present in catalyst 2Sb5V/Al. This is due to the low surface coverage of V and Sb on the support, which minimizes the chances to Sb + V interaction. In addition, $SbVO_4$ phases on alumina are not stable below monolayer coverage [14]. On the other hand, an interaction between Al with the metals V and Sb [30,31] has not been identified, probably due to the low calcination temperature used here. However, niobia support interacts with the supported oxides forming $SbNbO_4$ identified in used $2Sb_5V/Nb$.

The distribution of products obtained after propane ammoxidation is strongly affected by the support. Below monolayer, niobia-supported catalysts are not as active as the alumina-supported catalysts but they are selective towards acrylonitrile, while CO_x is the main product on alumina-supported catalysts. Above the Sb+V monolayer coverage, the alumina-supported catalysts perform better than the corresponding niobia-supported ones. It has been shown that efficient ammoxidation of propane on V–Sb oxides supported on alumina require not only the presence of Sb and V but also the formation of $SbVO_4$ phases [14]. $SbVO_4$ phases are not stable below monolayer coverage. Thus, if niobia-supported Sb–V–O catalysts are efficient for this reaction it must not be due to the presence of $SbVO_4$ phases. It must be related to the interaction of V oxide with niobia support, which is in line with the reference activity data shown in Table 2, where 1V/Nb affords 15.8% yield towards acrylonitrile. In addition, the presence of Sb, appears critical in both catalytic systems to moderate non-selective oxidation processes.

The niobia-supported catalysts are more selective to acrylonitrile than the alumina ones below monolayer coverage. The activity of pure supports is low, but clearly unselective for alumina, while niobia produces propylene. Below monolayer coverage, part of the oxide support remains exposed, which is detrimental in the case of alumina. However, exposure of niobia may not account for higher selectivity and specific rates toward acrylonitrile. It is possible that Nb and V combine in a new phase efficient for propane ammoxidation. The active site for alumina-supported catalysts is $SbVO_4$ [14,29]. Alumina-supported catalyst with dispersions limit higher than monolayer are able to form this phase and afford good selectivity values towards acrylonitrile [14]. Niobia-supported catalysts below dispersion limit improve acrylonitrile yields with TOS and this is not due to the formation of $SbVO_4$ active phase. In this case, acrylonitrile formation must be due to a different center of $SbVO_4$. This improvement can be attributed to the phase transition of niobium pentoxide and the formation of $SbNbO_4$ during reaction. A more complete study evidences a closer link between these parameters [25].

5. Conclusions

The specific oxide support has a strong effect on the molecular structure and catalytic performance of supported mixed Sb–V oxides during propane ammoxidation. Alumina support favors the dispersion of the Sb and V metal oxides below monolayer coverage and forms the active $SbVO_4$ phases above the $Sb + V$ dispersion limit. Niobia-supported catalysts below monolayer coverage affords acrylonitrile selectivity values higher than on alumina series. This is due to the role played by Nb centers for propane ammoxidation. The presence of Nb affords new more selective catalytic sites to the Sb–V mixed oxide system.

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