A new ternary mixed oxide catalyst for ammoxidation of propane: Sn / V / Sb

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The catalytic properties of a Sn / V / Sb mixed oxide for propane ammoxidation to acrylonitrile are studied in this paper. In particular the antimony and vanadium amounts were changed in order to optimize the relative atomic ratio. The ternary sample with the best catalytic performance was compared with the analogous binary samples (Sn / Sb and Sb / V). The results obtained indicate that vanadium is responsible for the paraffin activation, nevertheless much vanadium produces a lot of carbon oxides. Antimony is responsible for the insertion of nitrogen in the molecule (it can be considered as an acrylonitrile selectivity modulator); nevertheless, too much antimony deactivates the catalyst. Tin does not act only as a dispersive matrix for the active sites, but leads to the formation of a polyfunctional catalyst, increasing the rate of acrylonitrile formation from the intermediate propene. From a structural point of view, this catalytic system can be described as a homogeneous system, containing microfields of rutile type oxide (SnO_2), promoted with antimony and vanadium in substitutional solid solution, dispersed in an excess of amorphous antimony oxide.

Keywords: acrylonitrile, ternary mixed oxide, tin, vanadium, antimony

1. Introduction

Acrylonitrile (ACN) is at present being produced by the ammoxidation of propene on catalysts made of promoted Fe–Bi–Mo–O (SOHIO) or promoted Fe–Sb–O (Nitto). Nevertheless, in recent years some companies have decided to invest in research on the ammoxidation of propane [1].

One of the more interesting catalytic systems for the direct ammoxidation of the paraffin is Sb / V / O [2–7]. The synthesis of these catalysts is usually made by solid state reaction between V_2O_5 and Sb_2O_4 at 700°C or by reaction between NH_4VO_3 and Sb_2O_3. Mössbauer analysis shows that antimony is mainly in its pentavalent state, so a large amount of vanadium is reduced, with the formation of $V^{III}Sb^{V}O_4$ and the possible presence of V^{IV} in substitutional or interstitial solid solution coordinations. Centi et al. [3] and Nilsson et al. [4] have shown that an excess of antimony brings about a decrease in activity, but also a large increase in the selectivities and in the yields in acrylonitrile and propene. The best catalyst for the synthesis of acrylonitrile from propane has a large excess of antimony ($Sb/V = 5.0$). This excess seems to quicken the transformation of the intermediate propene to acrylonitrile. In contrast, an excess of vanadium brings about an increase in activity, but also a low selectivity in acrylonitrile due to the increased production of propene and carbon oxides.

The Sn / Sb / O system [7] has been widely studied in recent years as a catalyst active in allylic oxidation and ammoxidation. The best preparation method for these compounds involves coprecipitation from a solution of Sn(IV) and Sb(V) chlorides [8,9]. Calcination at temperatures higher than 700–900°C (depending on the bulk antimony / tin ratio) provokes segregation on the surface of α-Sb_2O_4 particles [10]. An antimony surface enrichment, especially for a concentration of antimony lower than 20–30% [11] and the formation of Sb(III) [9] are evidenced during the thermal treatment. The catalytic activity depends considerably on the Sn / Sb ratio and on the calcination temperature [10,12,13]. In the literature there is also disagreement about the nature of the active sites for allylic oxidation on this system: isolated Sb^{3+} species surrounded entirely by Sn^{4+} ions in a specific environment [9,10]; an oriented film of Sb_2O_4 supported on a solid solution of Sb^{5+} in Sn(IV) oxide [8,13]; a solid solution of Sb^{5+} ions in a rutile type matrix [14]; and two “gem” $Sb^{5+}{=}O$ groups [15].

In order to create a new ternary mixed oxide catalyst for propane ammoxidation we decided to mix these two systems: Sb / V, in order to activate the paraffin, and Sn / Sb, which has been already utilized to ammoxidate the relative olefin. The samples characterized in this paper have been synthesized by an original method of preparation [16,17] consisting in a pH-controlled coprecipitation from an ethanolic solution of the starting materials. In particular we have studied the effects of the antimony and vanadium amounts in the Sn / V / Sb ternary system; moreover, we have compared the ternary catalyst with the best catalytic performance with the analogous binary systems in order to better understand the role of the three ions in the ternary sample.

2. Experimental

2.1. Catalyst preparation

The coprecipitation of vanadium, antimony and tin oxohydrates was achieved as follows [16]: initially a solution of anhydrous $SnCl_4$ in anhydrous ethanol was prepared; then $VO(acac)_2$ and $SbCl_5$ were dissolved, in this order, in the solution, in order to obtain the desired Sn/V/Sb ratio (table 1). The sequence of the dissolution of the salts is very important in order to obtain an homogenous solution. The $VO(acac)_2$ complex hydrolyzes in a stepwise fashion: hydrolysis of the intermediate $VO(acac)^+$ is much slower than the bis-chelate complex at room temperature. When anhydrous $SnCl_4$ is dissolved in the organic medium, strongly acid conditions are developed, that are required for the rapid cleavage of both the vanadyl diketonate ligands. This allows a complete hydrolysis of the stable $VO(acac)_2$. In addition, the solvolysis effect produced during the dilution of $SnCl_4$ in the organic medium further enhances the hydrolysis. This solution was added dropwise to an aqueous solution of CH_3COONH_4, having an initial pH of around 7.0 (typically 2 M solutions were utilized). During the precipitation of the oxohydrates the pH, which decreases due to the release of HCl, was maintained constant by the addition of an ammonia solution. In fact, the pH must not be higher than 7.5 (in order to avoid V^{4+} oxidation and to allow precipitation of antimony oxohydrate) and not lower than 5 in order to avoid redissolution of the vanadium and tin oxohydrates. When the precipitation is carried out at a pH outside the mentioned range, there is no simultaneous precipitation of the catalyst components. The resulting precipitate was filtered, washed and dried overnight at 120°C; then calcined at 350°C for 1 h and at 700°C for 3 h.

2.2. Characterization

The catalysts were tested in a conventional laboratory apparatus with a tubular fixed-bed, working at atmospheric pressure. The analyses of propane, propene, acrylonitrile, acetonitrile and uncondensable gases were made by gas-chromatographic techniques; ammonia and hydrogen cyanide were detected by absorptions and titrations. The catalyst (2 ml) was loaded as grains (30–40 mesh) and the contact time of 2 s was used. A thermocouple, placed in the middle of the catalyst bed, was used to verify that the axial temperature profile was within 3°C.

Surface areas were determined by the BET method with nitrogen absorption at $-196°C$ using a Carlo Erba instrument. Fourier transformed infrared (FT-IR) spectra in transmission were recorded using a Perkin-Elmer 7200 Fourier transform spectrometer and KBr disk technique. X-ray diffraction patterns (powder technique) were obtained using Ni-filtered Cu Kα radiation ($\lambda = 1.542$ Å) with a Philips computer controlled instrument (PW1.050/81).

Table 1
Atomic ratios and surface areas of the samples analyzed

Sample	Atomic ratio	Surface area (m^2/g)
1	Sn : V = 1.0 : 0.05	31
2	Sn : V : Sb = 1.0 : 0.05 : 0.5	62
3	Sn : V : Sb = 1.0 : 0.05 : 1.0	39
4	Sn : V : Sb = 1.0 : 0.05 : 2.0	56
5	Sn : Sb = 1.0 : 1.0	60
6	Sn : V : Sb = 1.0 : 0.1 : 1.0	54
7	Sn : V : Sb = 1.0 : 0.2 : 1.0	46
8	Sn : V : Sb = 1.0 : 0.3 : 1.0	64
9	Sb : V = 1.0 : 0.2	6

3. Results and discussion

3.1. Surface area

The surface areas (table 1) of the samples containing tin are quite high with respect to the value reported in the literature for the Sn/Sb system. The antimony and vanadium amount in the system does not seem to influence in a unique way the surface area of the catalysts.

In contrast, sample 9 (Sb/V) shows a low surface area: it is the only one which is not characterized by a principal rutile type phase, but by an antimony oxide with traces of the rutile type structure. This is due to the high content of antimony with respect to vanadium: in fact, if we prepare a sample with the same content of the two ions, the principal phase is the $SbVO_4$ rutile type and the surface area is higher [19]. Hence, the rutile type phase is important to obtain a sample with a quite high surface area.

3.2. X-ray diffraction

Reported in figure 1 are the X-ray patterns of samples 1, 2, 3 and 4 with different contents of antimony (respectively 0, 32, 49 and 66% molar ratio). Sample 1, without antimony, shows clearly the diffraction lines of the rutile SnO_2 phase. No other diffraction lines are observed. In the presence of increasing amounts of antimony, up to a content of 49%, the pattern was not modified. Low intense diffraction lines typical of crystalline Sb_6O_{13} appear only for sample 4 (antimony content of 66%). Thus, a large amount of antimony is present in all the samples, as amorphous oxide.

Samples 5, 3, 6 and 7, containing Sn : Sb = 1 : 1 and different amounts of V, (respectively 0, 2.4, 4.8 and 9.1% molar ratio) exhibit the same pattern relative to the rutile phase (figure 1). In the presence of increasing amounts of vanadium, the pattern is not modified, even when vanadium is over 5% (limit of sensitivity to concentration of crystalline phase).

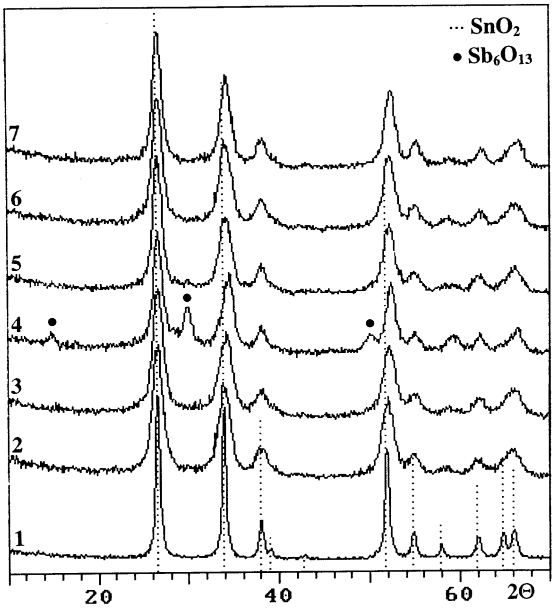

Figure 1. XRD patterns of the samples. (A) With increasing antimony amount: sample 1 (Sn : V = 1.0 : 0.05), sample 2 (Sn : V : Sb = 1.0 : 0.05 : 0.5), sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0) and sample 4 (Sn : V : Sb = 1.0 : 0.05 : 2.0). (B) With increasing vanadium amount: sample 5 (Sn : Sb = 1.0 : 1.0), sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0), sample 6 (Sn : V : Sb = 1.0 : 0.1 : 1.0) and sample 7 (Sn : V : Sb = 1.0 : 0.2 : 1.0).

In figure 1, in the samples 1, 2, 3 and 4, it is possible to see a shift of the reflection to higher 2θ values with increasing antimony content. In order to evidence the interactions between the SnO_2 matrix with the antimony and the vanadium, the parameters a and c of the SnO_2 tetragonal cell (table 2) were measured. These parameters decrease as the content of antimony in the samples increases, showing a cell contraction due to the substitution of Sn^{4+} with smaller ions. In particular, owing to the dimension of the ions in solution ($Sn^{4+} = 0.71$ Å, $Sb^{3+} = 0.76$ Å, $Sb^{5+} = 0.62$ Å), it is possible to hypothesize the introduction of a small amount of Sb^{5+} inside the rutile structure, in substitutional solid solution. The excess of antimony is present as amorphous oxide. After calcination these samples at higher temperatures, it is possible to see the appearance of crystalline antimony oxide [17], due to its crystallites size increasing. Moreover, the utilization of a pH-controlled coprecipitation method of preparation permits to obtain a solid solution even with thermal treatment at 700°C. Sb^{3+}, introduced as a dopant in SnO_2, produces a donor level which is ionized already at room temperature [17, and references therein]. According to Vincent [18], Sb-doped SnO_2 is a controlled valence semiconductor [19] which means that introducing Sb^{3+} ions produces no other defects, in contrast to non-stoichiometric semiconductors. The conductivity is due to the electrons formed by oxidations in air at high temperatures, according to the following reaction (1) [18]:

$$Sn^{4+}_{(1-\delta)}Sb^{3+}_{\delta}O^{2-}_{(2-\delta/2)} \xrightarrow{(\delta/4)O_2} Sn^{4+}_{(1-\delta)}Sb^{5+}_{\delta}e_{\delta}O^{2-}_{2}$$

where δ is the amount of antimony in solid solution. The absence of free electrons in anionic vacancies in Sb-doped SnO_2 explains the formation of a solid solution accompanied by the stabilization of Sb^{5+} ions in octahedral coordination.

The trend of the cell parameters with the vanadium content is more complex (table 2). Although the introduction of vanadium in the SnO_2 rutile type structure [20] has evidenced a solubility limit and in this case the presence of antimony modifies the system considerably, the increase in vanadium content modifies the volume of the rutile type cell, indicating the substitution of tin with smaller ions, as i.e. V^{4+}.

As we said before, sample 9 (Sb/V) is characterized by a principal α-Sb_2O_4 phase with lower amount of the $SbVO_4$ rutile type phase [21].

3.3. *FT-IR spectroscopy*

Infrared analysis of these samples in the region of skeletal vibrations (400–1100 cm^{-1}) provided some evidence about differences between samples with the same XRD diffractogram.

The spectrum of sample 1 (Sn : V = 1.0 : 0.05), characterized by main bands at 640–680 cm^{-1} and 540 cm^{-1}, connected to the SnO_2 rutile phase, is reported in figure 2. The SnO_2 pure oxide is characterized by three bands at 680, 620 and 520 cm^{-1} [20]. With the introduc-

Table 2
Cell parameters and volume of the samples with increasing antimony and vanadium amount. The error of parameters, reported in brackets, are referred to the last number

Sample	Composition		a (Å)	c (Å)	V (Å^3)
1	Sn : V : Sb = 1.0 : 0.05 : 0	Sb = 0%	4.727 (2)	3.177 (2)	70.99
2	Sn : V : Sb = 1.0 : 0.05 : 0.5	Sb = 32%	4.724 (3)	3.151 (3)	70.31
3	Sn : V : Sb = 1.0 : 0.05 : 1.0	Sb = 49%	4.712 (3)	3.147 (3)	69.87
4	Sn : V : Sb = 1.0 : 0.05 : 2.0	Sb = 66%	4.715 (3)	3.114 (3)	69.22
5	Sn : V : Sb = 1.0 : 0 : 1.0	V = 0%	4.720 (3)	3.134 (3)	69.82
3	Sn : V : Sb = 1.0 : 0.05 : 1.0	V = 2.4%	4.712 (3)	3.147 (3)	69.89
6	Sn : V : Sb = 1.0 : 0.1 : 1.0	V = 4.8%	4.705 (3)	3.145 (3)	69.62
7	Sn : V : Sb = 1.0 : 0.2 : 1.0	V = 9.1%	4.702 (4)	3.136 (3)	69.33

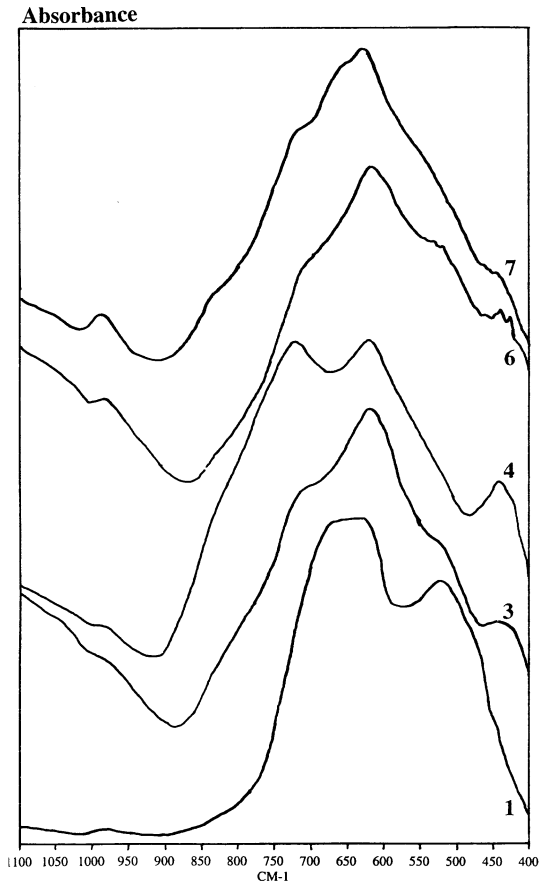

Figure 2. FT-IR spectra of the samples. (A) With increasing antimony amount: sample 1 (Sn : V = 1.0 : 0.05), sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0) and sample 4 (Sn : V : Sb = 1.0 : 0.05 : 2.0). (B) With increasing vanadium amount: sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0), sample 6 (Sn : V : Sb = 1.0 : 0.1 : 1.0) and sample 7 (Sn : V : Sb = 1.0 : 0.2 : 1.0).

tion of vanadium, the relative intensities of the three bands change and their wave numbers shift slightly, giving the two bands described before. Moreover, a low intense band at 988 cm^{-1} due to the stretching of the V=O double bond is visible. This shifting to lower frequencies with respect to the absorbance of the crystalline V_2O_5 (1022 cm^{-1}) may be attributed to two effects, firstly to the interactions between the vanadyl species and the rutile type SnO_2 matrix and secondly to the electronic effect due to the presence of neighboring reduced vanadium sites.

The presence of antimony in the system again changes the spectra. Only the bands at about 615 cm^{-1} for the stretching of the Sn–O bond and at 988 cm^{-1} for the V=O bond are visible (samples 2 and 3). With an excess of antimony (sample 4), in addition of the bands just described, a quite intense band at around 760 cm^{-1} is also present, typical of the Sb_6O_{13} phase, just seen in the XRD characterization.

The evolution of the infrared spectra with increasing vanadium content (samples 3, 6 and 7) is also shown in figure 2. In this case, modification occurred only for the band at 988 cm^{-1}. The intensity of this band increases with increasing vanadium content.

3.4. Catalytic tests

The catalytic performance in propane ammoxidation of the sample containing increasing amounts of antimony and vanadium is reported in figures 3–6. Catalytic tests were performed using a feed of $C_3H_8 : NH_3 : O_2 : He = 8 : 8 : 20 : 64$ and a contact time about 3.0 s.

Reported in figure 3 are conversion vs. reaction temperature and in figure 4 acrylonitrile selectivity and yield vs. antimony amount at 475°C. It is possible to see that, as the amount of antimony increases (samples 2–3–4), the activity decreases considerably (figure 3), meanwhile the acrylonitrile selectivity increases (figure 4). The maximum acrylonitrile yields are reached with sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0): sample 2 with less antimony is characterized by a very low acrylonitrile selectivity; sample 4 with more antimony is characterized by a very low activity.

Nevertheless, even if the acrylonitrile selectivities reached with sample 3 are interesting (i.e. $S_{\mathrm{ACN}} = 40\%$ at $C = 20\%$), working at temperatures around 500°C has an opposite effect, i.e. enhancing the production of carbon oxides, also by the consecutive reaction of combusting the desired product. In order to minimize this effect and to enhance the activity without decreasing too much the acrylonitrile selectivity, we decided to increase the amount of vanadium (keeping the amount of antimony constant) in sample 3. Samples 6, 7 and 8 were prepared, which contain respectively twice, four and six times the amount of vanadium in sample 3.

Reported in figure 5 are conversion vs. reaction temperature and in figure 6 acrylonitrile selectivity and yield vs. vanadium amount at 450°C. It is possible to see that

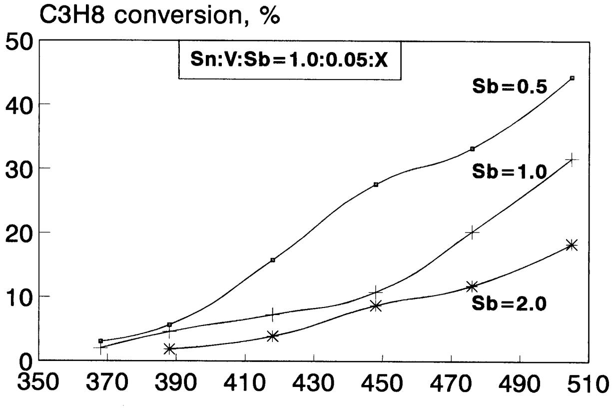

Figure 3. Conversion vs. temperature of the samples with increasing antimony amount: sample 2 (Sn : V : Sb = 1.0 : 0.05 : 0.5), sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0) and sample 4 (Sn : V : Sb = 1.0 : 0.05 : 2.0); reaction conditions – $C_3H_8 : O_2 : NH_3 : He = 8 : 20 : 8 : 64$ and contact time of 3.0 s.

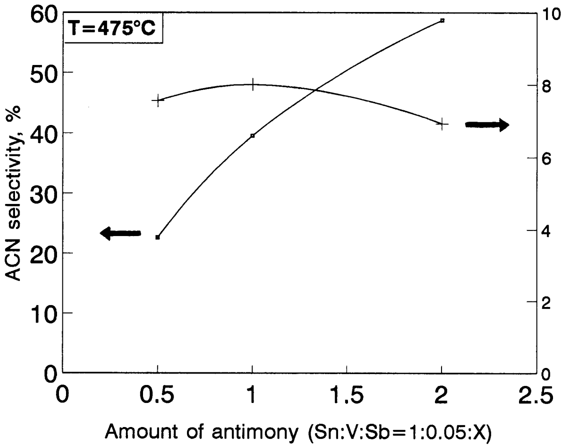

Figure 4. Selectivity at iso-conversion (20%) of the samples with increasing antimony amount: sample 2 (Sn : V : Sb = 1.0 : 0.05 : 0.5), sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0) and sample 4 (Sn : V : Sb = 1.0 : 0.05 : 2.0); same reaction conditions as figure 3.

the vanadium creates sites which increase the activity of the sample (figure 5). The acrylonitrile selectivity at 450°C remains quite constant for the sample 3, 6 and 7, whereas the yield increases. On the contrary, sample 8 with the highest vanadium content (V/Sn = 0.3) shows a decrease in acrylonitrile selectivity and yield with respect to sample 2 (V/Sn = 0.2). The ratio V/Sn = 0.2 seems to be the stabilization limit of vanadium in the system. Higher amounts of vanadium are not sufficiently dispersed in the catalyst matrix, leading to combustion.

In other words, the influence of the vanadium on the catalytic performance of this system is to enhance the activity, shifting the conversion line to lower temperatures. In this way it is possible to obtain high conversion at a lower temperature, minimizing the undesired consecutive reaction of combustion. Hence the quantity of the desired product is enhanced.

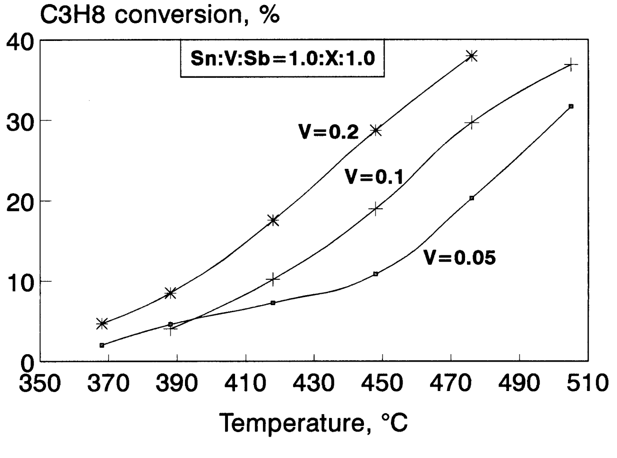

Figure 5. Conversion vs. temperature of the samples with increasing vanadium amount: sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0), sample 6 (Sn : V : Sb = 1.0 : 0.1 : 1.0) and sample 7 (Sn : V : Sb = 1.0 : 0.2 : 1.0); same reaction conditions as figure 3.

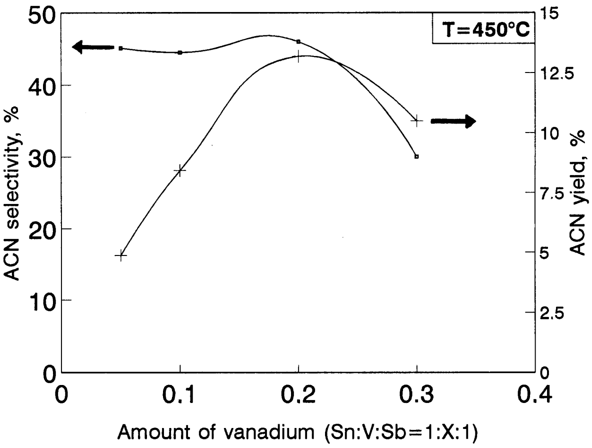

Figure 6. Selectivity at iso-conversion (30%) of the samples with increasing vanadium amount: sample 3 (Sn : V : Sb = 1.0 : 0.05 : 1.0), sample 6 (Sn : V : Sb = 1.0 : 0.1 : 1.0) and sample 7 (Sn : V : Sb = 1.0 : 0.2 : 1.0); same reaction conditions as figure 3.

The present data indicate some interesting aspects of the catalytic chemistry of Sn/V/Sb mixed oxides. In fact, the results show that the Sn/V matrix is responsible for the activation of propane, while antimony is necessary to introduce some selective sites of acrylonitrile synthesis. The sample with the best performance is sample 7 with the ratio Sn : V : Sb = 1 : 0.2 : 1, which reaches conversion of 40% and acrylonitrile selectivity higher than 40% in the experimental conditions employed.

Hence by this characterization and catalytic data, it is possible to describe the structure of sample 7 (Sn/V/Sb = 1 : 0.2 : 1), which is the sample with the best catalytic performances in the ammoxidation of propane to acrylonitrile. From a structural point of view, this catalytic system can be seen as a homogeneous system, containing microfields of rutile type oxide (SnO_2) promoted with antimony and vanadium in substitutional solid solution: in other words a ternary mixed oxide. These microfields are dispersed in an excess of amorphous antimony oxide, which crystallites have dimensions lower than 10 nm.

The catalytic performances strongly depend on the quantities of vanadium and antimony in the system. The vanadium seems to increase the activation of the propane, meanwhile the antimony has mainly a moderate function on the oxidative property of the system, permitting the nitrogen insertion in the molecule (in other words it can be considered as a selectivity modulator).

In order to better understand the structure of this ternary catalyst (sample 3: Sn/V/Sb = 1 : 0.2 : 1), we compare this sample with the two analogous binary systems (sample 5 Sn/Sb = 1 : 1 and sample 9 Sb/V = 1 : 0.2), prepared in the same way, by testing them in the reaction of propane ammoxidation, under the same conditions (contact time of 2 s and feed $C_3H_8 : O_2 : NH_3 : He = 25 : 20 : 10 : 45$). The two binary systems have different properties: Sn/Sb is utilized mainly to ammoxidize the olefin and Sb/V, which is very active from propane, is not highly selective to acrylonitrile, due to a high production of propene.

Reported in figure 7 are the selectivities at the conversion of 20% for sample 9 (Sb/V) and sample 7 (Sn/V/Sb). Wheras these two systems have a similar activity (sample 7 a little higher), the selectivities in the products are different: the binary sample has a lower acrylonitrile selectivity and a higher propene selectivity with respect to the ternary system. By assuming that propene is the first intermediate in the propane ammoxidation [21], we could make the hypothesis that in the Sb/V system the rate of propene transformation to acrylonitrile is relatively lower than the rate of propane desorption. Adding tin, we increase the rate of propene conversion.

Reported in figure 8 are the productivity in acrylonitrile (ACN produced per time on stream per catalyst volume) of these three systems. It is possible to see that the Sb/V sample produces more acrylonitrile with respect to the Sn/Sb sample: the difference is due to the higher activity of the former. The ternary system is the catalyst with the highest acrylonitrile productivity: as said before, the activity is little higher but the acrylonitrile selectivity is much higher, due to the quick transformation of the intermediate olefin, with respect to the Sb/V system.

Hence, the obtained results show that in the ternary system the tin does not only act as a dispersive matrix for the active sites, but brings about the formation of a polyfunctional catalyst, containing two promoted systems: Sn/Sb promoted with V and Sb/V promoted with Sn.

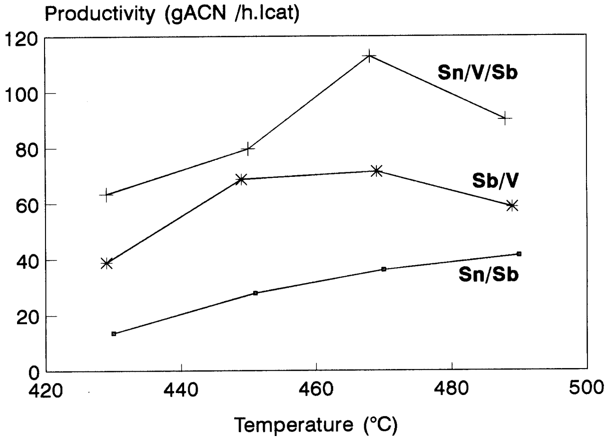

Figure 8. Productivity in acrylonitrile (ACN produced per time on stream per catalyst volume) of the binary (Sn/Sb and Sb/V) and the ternary (Sn/V/Sb) systems from propane; same reaction conditions as figure 7.

4. Conclusion

The Sn/V/Sb catalyst prepared from the organic phase is not a simple mixture of different oxides, but a polyfunctional catalytic system, where the active sites for propane dehydrogenation and propene ammoxidation are in close contact. The reaction network on this ternary system can be explained through the hypothesis that the activation of propane occurs on the active sites containing vanadium and the created intermediate is transformed quickly to acrylonitrile on the active sites consisting in tin and antimony.

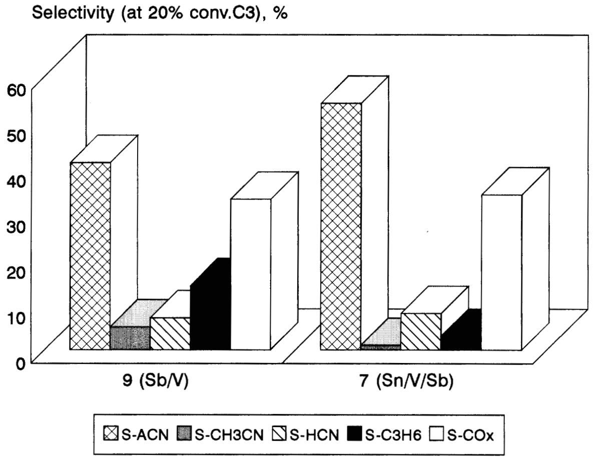

Figure 7. Selectivity at iso-conversion (20%) of sample 7 (Sn : V : Sb = 1.0 : 0.2 : 1.0) and sample 9 (Sb : V = 1.0 : 0.2); reaction conditions – $C_3H_8 : O_2 : NH_3 : He = 25 : 20 : 10 : 45$ and contact time of 2.0 s.

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