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ScienceDirect

Catalysis Today 128 (2007) 161–167

CATALYSIS TODAY

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The synthesis of rutile-type V/Sb mixed oxides, catalysts for the ammoxidation of propane to acrylonitrile
A comparison of high-energy milling and co-precipitation methods

N. Ballarini [a,b], F.J. Berry [c], F. Cavani [a,b,*], M. Cimini [a,b],
X. Ren [c], D. Tamoni [a], F. Trifirò [a]

[a] *Dipartimento di Chimica industriale e dei Materiali, Alma Mater Studiorum Università di Bologna,*
Viale Risorgimento 4, 40136 Bologna, Italy
[b] *INSTM, Research Unit of Bologna, Italy*
[c] *Chemistry Department, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK*

Abstract

This paper describes the preparation of rutile-type V/Sb mixed oxide (vanadium antimonate) with the ball-milling (mechano-chemical) method starting from single metal oxides, as well as the comparison with a similar system prepared by the co-precipitation method. Samples were tested as catalysts for the gas-phase ammoxidation of propane to acrylonitrile. The mechano-chemical method allowed the preparation of the rutile-type mixed oxide characterized by smaller crystallite size than the catalyst prepared by co-precipitation and calcined at 450 °C. The calcination at 700 °C of the sample prepared by the mechano-chemical method led to a crystalline vanadium antimonate characterized by a higher concentration of cationic defects than the corresponding calcined sample prepared by co-precipitation. This led to a considerably higher activity in propane ammoxidation, but to a lower selectivity to acrylonitrile.

Keywords: Propane ammxodation; Acrylonitrile; Mechano-chemical synthesis; Solid-state synthesis; Rutile; Vanadium antimonate

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1. Introduction

The preparation of mixed oxide catalysts for hydrocarbon oxidation is usually carried out using co-precipitation methods characterized by disadvantages such as: (i) the use of aqueous or organic solutions containing the various metal cations and the corresponding anions, the latter being found at the end in the process waste effluents as co-products that have to be separated and disposed of, and (ii) thermal treatments during which noxious components are released into the gas-phase. Furthermore, the control of the reciprocal dispersion of components in multi-metal catalysts, as well as of the degree of crystallinity and catalyst morphology – two important factors affecting the catalytic performance – is often difficult due to problems encountered both in obtaining homogeneous precursors and in the control of conditions during thermal treatment.

One method for the preparation of multi-component mixed oxides that potentially offers advantages as compared to conventional methods is the solid-state synthesis achieved by high-energy milling, starting from mixtures of single metal oxides [1]. Mechano-chemical treatment of solids may alter their morphology and texture, but is also known to induce the formation of solid solutions. This technique is particularly suitable for the production of nanocrystalline materials, and has been applied for the synthesis or activation of several catalysts, either bulk or supported, including V/Ti/O [2–4], V/Sb/Ti/O [5,6] and V/P/O [7,8].

Recently, some of us published a study on the synthesis of rutile-type V and Fe antimonates by mechanical milling [9].

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[*] Corresponding author at: Dipartimento di Chimica industriale e dei Materiali, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy. Tel.: +39 0512093680; fax: +39 0512093680.
E-mail address: fabrizio.cavani@unibo.it (F. Cavani).

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doi:10.1016/j.cattod.2007.06.080

Rutile is the structure adopted by many trivalent metal antimonates, e.g., $CrSbO_4$, $VSbO_4$, $FeSbO_4$, $GaSbO_4$, and by metal niobates as well. Metal antimonates are catalysts which are active and selective for the ammoxidation of propane to acrylonitrile [10–14]. This reaction represents an effective alternative to the current industrial production of acrylonitrile from propylene, due to the lower cost of propane as compared to the olefin [15–17].

Rutile-type metal antimonates are polyfunctional systems, whose components play different roles in the multi-electron complex transformation of the alkane, including the propane activation and oxidehydrogenation and the allylic ammoxidation of the unsaturated intermediate to acrylonitrile. With regard to this, the rutile-type structure possesses the flexibility required to accommodate various elements in its framework, with the formation of a great variety of solid solutions, and, therefore, it offers the optimum system for the development of multi-component catalysts.

In this paper, we describe the preparation of V/Sb/O catalysts by the high-energy, ball-milling technique and compare the main bulk characteristics and catalytic performance of these materials with the corresponding system prepared by co-precipitation, for the reaction of propane ammoxidation to acrylonitrile.

2. Experimental

Two methods were used for the preparation of catalysts: (i) co-precipitation, formerly used for the synthesis of Cr/V/Sb/O [18,19] and Sn/V/Sb/O [11], and (ii) high-energy ball-milling, also called mechano-chemical synthesis. The co-precipitation procedure involved the dissolution of $VO(acac)_2$ and $SbCl_5$ (V/Sb atomic ratio 1.0) in absolute ethanol, followed by dropping the solution into a buffered aqueous solution maintained at pH 7. A precipitate was obtained, which was separated from the supernatant liquid by centrifugation and filtration. As for the mechano-chemical procedure, V_2O_5 and Sb_2O_3 were mixed in the desired proportions (V/Sb atomic ratio 1.0) and put into a vessel, together with stainless-steel spheres and spheres/metal oxides weight ratio equal to 20/1 (Retsch mill instrument). Then the solids were kept under milling conditions for 70 h [9].

Co-precipitated samples were dried at 140 °C overnight, and then treated in flowing air from 140 °C to the final temperature: 300, 450, 550 or 700 °C. Samples prepared with the mechano-chemical method were either used as such for catalytic tests, or thermally treated at 700 °C. Catalysts were preliminarily kept under reaction conditions for the time necessary to reach a stable catalytic performance. Samples were identified according to the method of preparation used (either C, for co-precipitation, or M, for mechano-chemical synthesis) and temperature of thermal treatment. Samples downloaded after reaction were identified with the suffix spent.

The XRD patterns of the catalysts were obtained with Ni-filtered Cu Kα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. Laser–Raman spectra were obtained using a Renishaw 1000 instrument; the samples were excited with the 514 nm Ar line. FT-IR spectra were recorded by using a Perkin-Elmer 1700 Instrument (KBr disk technique). Specific surface areas were measured by the BET, single-point method with nitrogen adsorption (Thermo Instrument).

Catalytic tests were carried out in a laboratory stainless steel fixed-bed reactor operating at atmospheric pressure. 1.8 g of catalyst was loaded, shaped into particles with size ranging from 0.42 to 0.55 mm. The following reaction conditions were used: feed composition 25 mol% propane, 10% ammonia, 20% oxygen, remainder helium; residence time 2.0 s. The reactor outlet was kept at 170 °C. On-line sampling of a volume of either the feedstock or effluents was obtained by means of three heated valves. Three different columns were used for the product identification. Two of these were: a Hay-sep T column (TCD detector) for the separation of CO_2, NH_3, $C_3H_8 + C_3H_6$, H_2O, HCN, acrolein, acetonitrile and acrylonitrile, and a MS-5A column (TCD detector) for separation of O_2, N_2 and CO. Hay-sep T was also used as a filter to avoid the contamination of MS-5A by CO_2. The third column was a packed column filled with Poropak QS (FID detector), which is used for the separation of propane from propylene.

3. Results and discussion

3.1. The synthesis of rutile-type V/Sb/O: a comparison of preparation procedures

Table 1 lists the samples prepared, and the corresponding specific surface area values, after calcination (fresh catalysts) and after reaction (spent catalysts). The surface area of sample C depended on the calcination temperature. The maximum surface area of 34 m^2/g was obtained after a thermal treatment at 550 °C (sample C550); a subsequent calcination at 700 °C

Table 1
Catalysts prepared and their main characteristics

Sample, code	Preparation method	Temperature of calcination (°C)	Surface area after calcination (m^2/g)	Surface area after reaction (spent samples) (m^2/g)
C300	Co-precipitation	300	Nd	Nd
C450	Co-precipitation	450	23	18
C550	Co-precipitation	550	34	16
C700	Co-precipitation	700	26	7
M	Ball-milling	Not applied	18	6
M700	Ball-milling	700	14	7

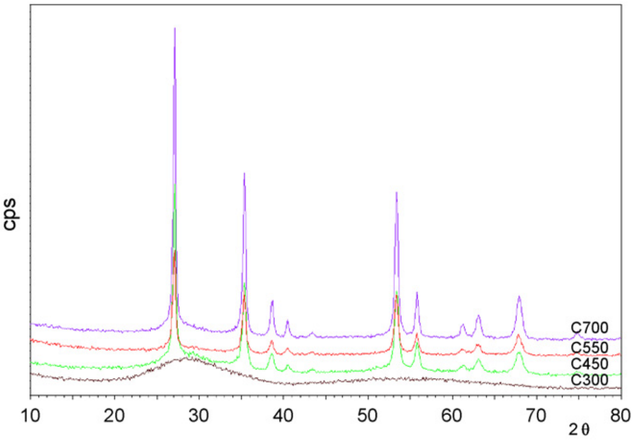

Fig. 1. X-ray diffraction patterns of the catalyst prepared by co-precipitation, calcined at 300 °C (C300), 450 °C (C450), 550 °C (C550) and 700 °C (C700).

(sample C700) led to a decrease of surface area, which corresponded to an increase in the sample crystallinity (see XRD patterns in Fig. 1). A peculiarity of the co-precipitation procedure is the production of rutile-type mixed oxides having a higher surface area than those prepared by more conventional techniques, such as the slurry method [11,18,19].

In the case of the catalyst prepared by the mechano-chemical synthesis, the surface area of the uncalcined sample M (18 m^2/g) was higher than that of the two compounds used as starting materials (V_2O_5 8 m^2/g, Sb_2O_3 < 5 m^2/g). This suggests that a change in the particles morphology in the two compounds had occurred as a consequence of the high-energy treatment. Also in this sample, the surface area decreased when a high-temperature thermal treatment (i.e., sample M700) was applied.

Figs. 1 and 2 plot the X-ray diffraction patterns of samples C and M, respectively, calcined at increasing temperatures. In the first case, after thermal treatment at 300 °C the sample was amorphous, but already after calcinations at 450 °C the typical reflections of the rutile vanadium antimonate were apparent. Higher temperatures led to an increase of the sample cystallinity. The average crystal size (as evaluated from the XRD pattern) increased from 23 ± 3 nm for C450 to 31 ± 4 nm for C700. Sample M already had a certain amount of rutile compound, but there was also a large fraction of amorphous or microcrystalline compound. A further calcination treatment led to significantly increased crystallinity; the average crystalite size of sample M was 18 ± 3 nm versus 29 ± 4 nm for sample M700.

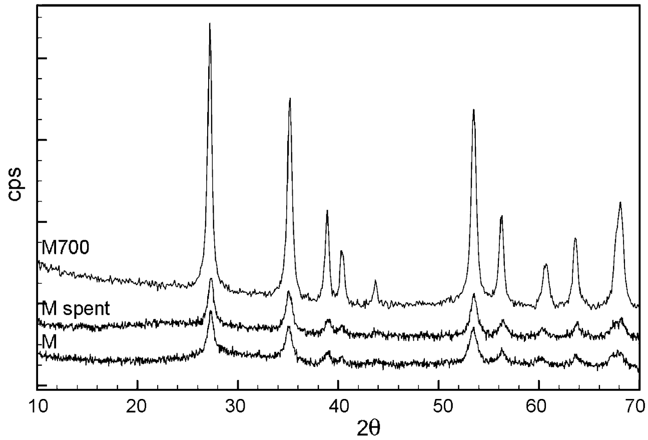

Fig. 2. X-ray diffraction patterns of the catalyst prepared by the mechano-chemical synthesis, without any post-synthesis thermal treatment (M) and calcined at 700 °C (M700), and of sample M after reactivity tests (Mspent).

XRD patterns demonstrate that the direct synthesis of vanadium antimonate is possible by the mechano-chemical method [9]. The mechanism of formation of the mixed oxide necessarily implies the reciprocal diffusion of metal ions in the two oxides and the solid-state redox reaction between V^{5+} and Sb^{3+} ions, in order to generate the reduced V species and Sb^{5+}. These two phenomena are likely to be aided by: (i) the mechanical fracture of the V and Sb oxide particles with the destruction of the long-range crystalline order, and (ii) high local temperatures developed thanks to the considerable kinetic energy applied to the solids, due to the fact that most of the energy is lost in the form of heat [1]. Also, the exothermal redox reaction between V and Sb may contribute to temperature rises.

With this method, chemical phenomena are aided by the heavy deformation introduced into the particles, which generates an array of crystal defects, such as dislocations, stacking faults, and increased numbers of grain boundaries. This defective structure enhances the diffusivity of elements. In literature, the measured temperature rise in high-energy ball-milling is not higher than 200 °C, but – in some cases – several-hundred-degree temperature rises have been estimated in theory [1,and references therein]. The Tamman temperature (half of the melting temperature, T_m; T_m 953K for V_2O_5, and 903 K for Sb_2O_3) is considered to be the reference temperature that makes the ionic diffusion kinetically significant. Therefore, in our case, it can be suggested that the temperature that develops on the catalyst surface during the ball-milling operation is not lower than 200–250 °C. However, there is additional information suggesting that the true local temperature may be much higher than 250 °C, possibly close to 400–450 °C. In fact, sample M was used as the catalyst in the reaction of propane ammoxidation in the temperature range between 400 and 520 °C, with no preliminary thermal treatment: on that occasion, it immediately exhibited a stable catalytic performance without any need for an equilibration period. That indicates that the catalyst did not undergo considerable chemical or morphological changes due to the reaction temperature. The XRD pattern of the downloaded sample (also reported in Fig. 2) provides an additional support to this theory by showing no change as compared to the fresh M catalyst.

It is worth noting that the XRD pattern of a reference sample prepared by the thermal treatment of V_2O_5 and Sb_2O_3, ground together in a mortar, still showed the pattern of the single metal oxides. This means that in this case neither the redox reaction nor the formation of any mixed compound had occurred.

Fig. 3 compares the FT-IR spectra of samples M, M700, C450 and C700. While differences between M and C450 spectra were not significant (both samples were not fully crystallized, as it appears from the corresponding XRD patterns, but exhibited the reflections typical of rutile), those between corresponding

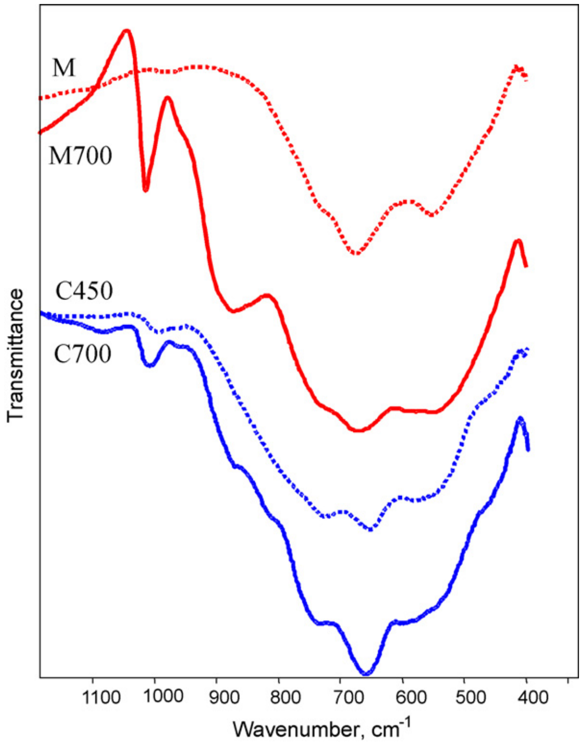

Fig. 3. FT-IR spectra of the catalyst prepared by co-precipitation, calcined at 450 °C (C450) and 700 °C (C700), and of the catalyst prepared by the mechano-chemical synthesis, without any post-synthesis thermal treatment (M) and calcined at 700 °C (M700).

samples calcined at 700 °C were remarkable. Specifically, bands at 880 and 1015 cm^{-1}, attributed to the Sb–O–Sb and Sb–O–V^{4+} stretching vibrations involving coordinatively unsaturated O^{2-} ions [20], were more intense in M700. This means that the latter contained a higher concentration of defective cationic sites than C700.

Several different compositions have been reported in literature for the V/Sb/O system, none of which is a stoichiometric $VSbO_4$ [21–25] For instance, $V_{0.92}Sb_{0.92}O_{0.16}O_4$ [21] is a cation-deficient structure, with 0.04 cationic positions unoccupied for each O^{2-} anion. It contains Sb^{5+}, while vanadium is present both as V^{4+} and as V^{3+}. The electroneutrality is guaranteed for the composition ${V_{0.28}}^{3+}{V_{0.64}}^{4+}{Sb_{0.92}}^{5+}O_4$ [25]. The ratio between V^{3+} and V^{4+} can vary depending on the method of preparation (the atmosphere and temperature of the thermal treatment are especially significant). This compound belongs to the $V_{1-x}Sb_{1-x}O_{2x}O_4$ series, which is preferentially formed by the treatment in air, and in which the concentration of cationic vacancies is proportional to the amount of V^{4+} sites. Other authors have also pointed out the presence of defects in rutile V/Sb/(Me) mixed oxides [26–31].

Cationic vacancies play an important role in the catalytic performance of rutile-type mixed oxides [18,26–31]. For instance, it was found that an increased concentration of cationic vacancies and isolated V^{4+} species in V/Sb/(Fe)/O systems, due to the introduction of increasing amounts of Fe in the lattice, led to a proportionally higher activity [30]. The formation of V^{4+} in Cr/V/Sb mixed oxides had the similar effect of increasing propane conversion considerably [19].

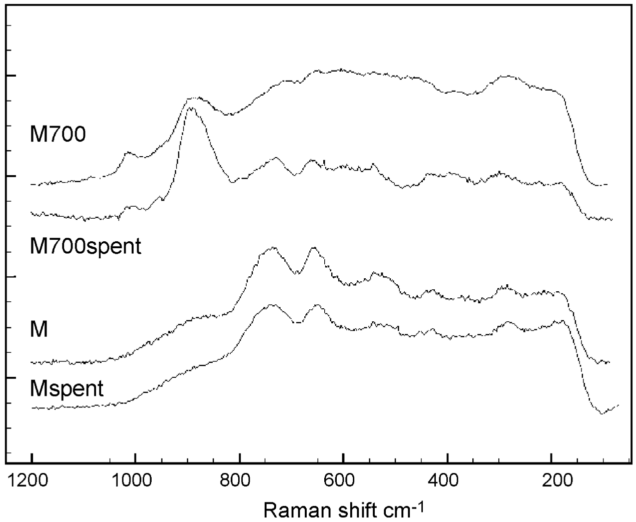

Fig. 4. Raman spectra of the catalyst prepared by the mechano-chemical synthesis, without any post-synthesis thermal treatment (M) and calcined at 700 °C (M700), and of the corresponding catalysts downloaded after reaction in propane ammoxidation (Mspent and M700spent).

Therefore, the greater concentration of cationic vacancies of sample M700 may be connected with a higher amount of oxidized V ions developed by the calcination treatment, as compared to the corresponding sample prepared with the co-precipitation procedure. This difference is likely related to the defective morphology of the solid prepared with the mechano-chemical method. The development of defects is also apparent from the Raman spectra reported in Fig. 4. The spectrum of sample M did not show any band attributable either to V oxide or to any Sb oxide. Bands at ≈800–900 (very broad), 750, 660 and 500–550 cm^{-1} are attributable to the rutile-type mixed oxide [20,32,33]. Upon calcination at 700 °C (M700) additional bands developed at 880–900 and 1010–1020 cm^{-1}, related to vibrations of bonds involving O^{2-} ions associated with cationic vacancies. The same bands were also seen in M700 downloaded after reaction (M700spent); furthermore, the intensity of the band at 880–900 cm^{-1} was remarkably higher than in the corresponding sample before reaction (M700). This suggests that the concentration of oxidized V sites increased under reaction conditions. Very weak bands developed at ≈180 and 400 cm^{-1}, an occurrence that may be attributed to the segregation of some α-Sb_2O_4. Conversely, no evidence was obtained for the segregation of V_2O_5.

It is worth noting that the Raman spectrum of catalyst Mspent (also reported in Fig. 4) was the same as that one of the corresponding catalyst before reaction (sample M). Therefore, a modification of structural features during reaction only occurred for the sample that had been pre-calcined in air at 700 °C (M700spent versus M700). This indicates that the development of the defective lattice in sample M700 also facilitated further changes occurring during reaction.

In conclusion, data indicate that the high-energy ball-milling method leads to the development of rutile-type V/Sb mixed oxides which have crystallite size in the nano-range, i.e., lower than in samples prepared by co-precipitation and thermal treatment at 450 °C. The features of the sample are those of an almost-stoichiometric rutile mixed oxide, with the absence of any V or Sb oxide and low concentration of cationic vacancies. However, the thermal treatment in air at 700 °C not only leads to an increased crystal size and, hence, to the annihilation of the morphological defects introduced by the high-energy milling method, but also to the extensive oxidation of V, and thus to the generation of a great concentration of cationic vacancies. These features are maintained, and even increased, during the reaction of propane ammoxidation.

3.2. Catalytic tests of propane ammoxidation

Fig. 5 plots the effect of temperature on both the reactants conversion and the distribution of products, for sample M. The limiting reactant was oxygen, which was totally converted at 510 °C, while at this temperature the propane conversion obtained was lower than 20%. Ammonia also reached high conversion, but most of it was converted to N_2 (Fig. 5, bottom). As for the products distribution, the selectivity to acrylonitrile was low below 400 °C, the prevailing products under these conditions being acetonitrile, cyanhydric acid, propylene and carbon dioxide. An increase in temperature led to an increased selectivity to acrylonitrile, CO and CO_2 while the formation of all the other by-products declined. However, after 470 °C the formation of acrylonitrile also decreased, with a corresponding increase in the formation of carbon oxides. The selectivity to N_2 did not change remarkably with a variation in temperature; in fact, the overall selectivity to the N-containing products of propane transformation (acrylonitrile, acetonitrile and cyanhydric acid) was rather constant throughout the entire range of temperatures studied. The performance of sample M was similar to that of other rutile-type catalysts described in literature [18,28].

Figs. 6 and 7 compare the conversion of propane and the selectivity to acrylonitrile for samples C and M, respectively, calcined at increasing temperatures. The thermal treatment led to a considerable enhancement of activity for both series of samples; this is not attributable to an increase in the specific surface area, as is apparent from the comparison of the corresponding values reported in Table 1. Therefore, it is possible to attribute this effect to a higher concentration of oxidized V sites, as inferred from the higher concentration of cationic vacancies (Figs. 3 and 4).

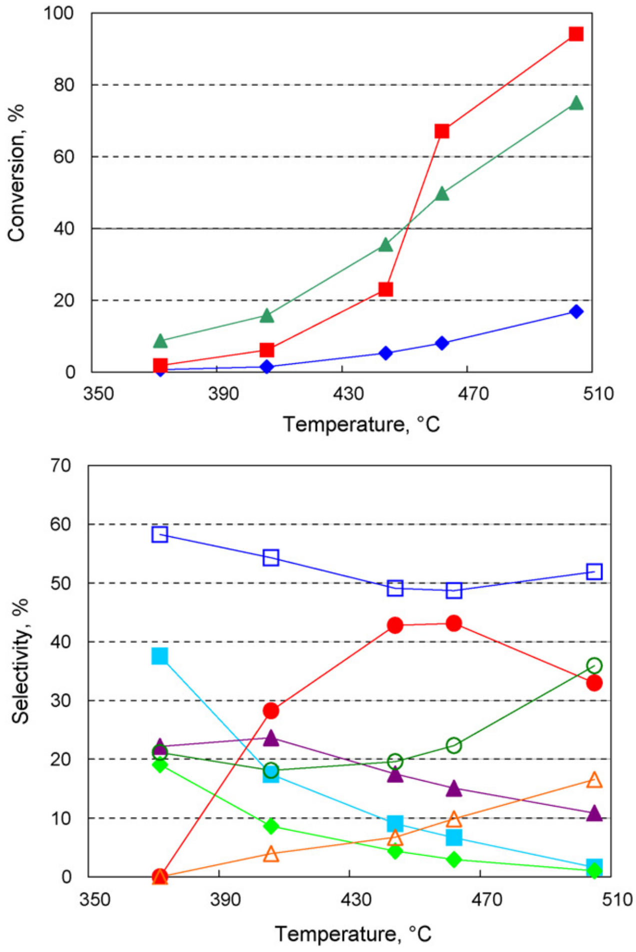

Fig. 5. (Top) Effect of temperature on conversion of propane (◆), oxygen (■) and ammonia (▲). (Bottom) Effect of temperature on selectivity to acrylonitrile (●), acetonitrile (◆), cyanhydric acid (▲), propylene (■), carbon monoxide (△), carbon dioxide (○), and N_2 (with respect to converted ammonia) (□). Catalyst M.

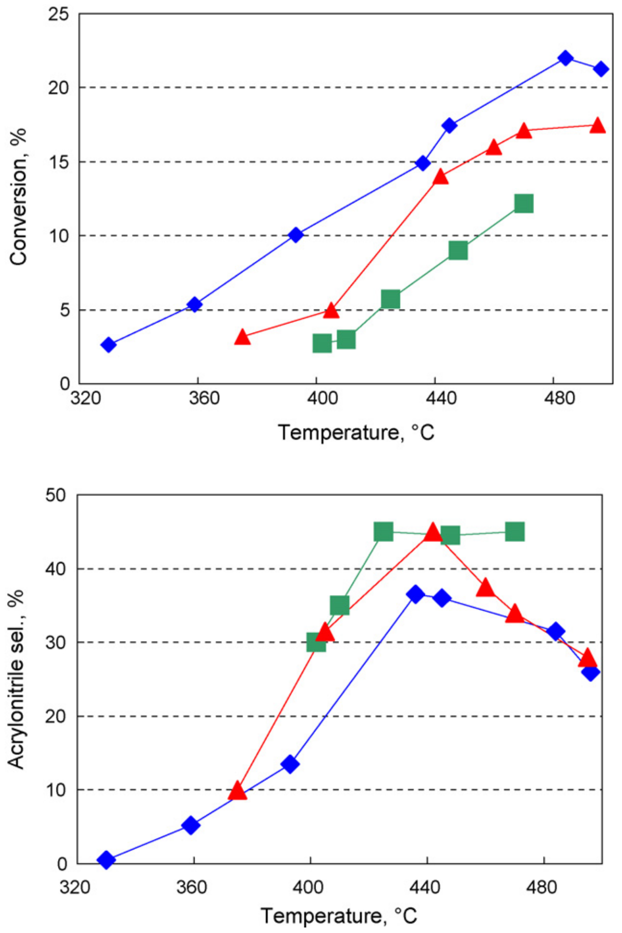

Fig. 6. (Top) Effect of temperature on propane conversion. (Bottom) Effect of temperature on selectivity to acrylonitrile. Catalysts: C450 (■), C 550 (▲) and C 700 (◆).

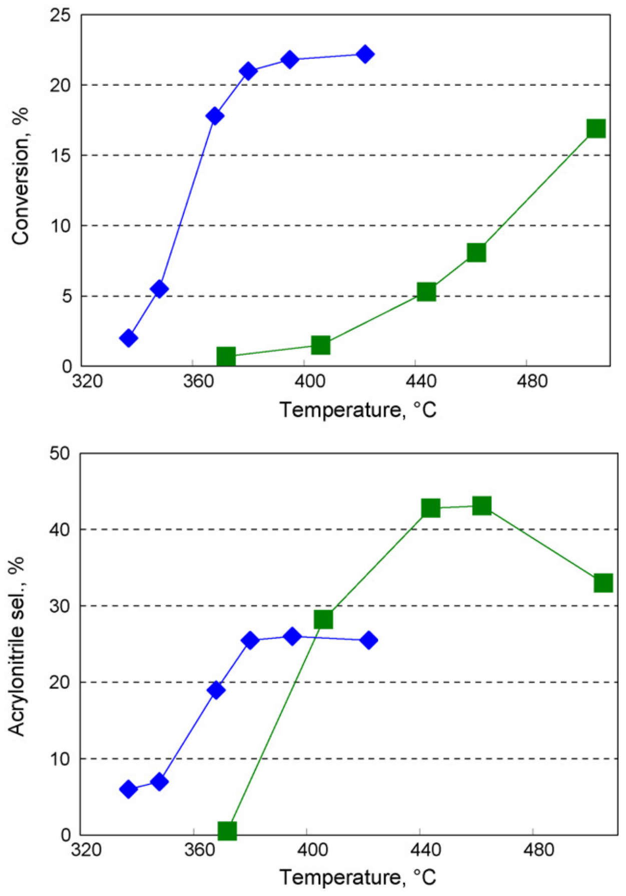

Fig. 7. (Top) Effect of temperature on propane conversion. (Bottom) Effect of temperature on selectivity to acrylonitrile. Catalysts: M (■) and M700 (◆).

Sample M700 was by far the most active catalyst amongst all samples studied; total oxygen conversion was reached at 400 °C. Once again, this is likely to be related to the high concentration of oxidized V sites, as inferred from the very intense bands in IR and Raman spectra attributed to Sb–O–V and Sb–O–Sb bonds vibrations associated to coordinatively unsaturated O ions.

On the other hand, the effect on selectivity to acrylonitrile was just the opposite; Figs. 6 and 7 (bottom) show that for sample C the increase in calcination temperature had a slight negative effect on the selectivity to acrylonitrile, while the same effect was quite notable in the case of sample M. The low selectivity to acrylonitrile obtained with M700 was due to the greater formation of carbon oxides and molecular nitrogen. It can be suggested that an excessive concentration of oxidized V sites increases the contribution of propane and ammonia combustion and hence leads to a lower selectivity to acrylonitrile. It is worth noting that the Raman spectrum of M700spent (Fig. 4) did not evidence any band attributable to V_2O_5; the latter is known to be responsible for propane and ammonia combustion in rutile-type V/Sb mixed oxides [18].

4. Conclusions

The high-energy ball-milling method has been adopted for the mechano-chemical synthesis of rutile-type V/Sb mixed oxides. Prepared samples and samples obtained by the conventional co-precipitation technique were compared and tested as catalysts for the gas-phase ammoxidation of propane to acrylonitrile. The mechano-chemical method led to the rutile-type V/Sb mixed oxide characterized by smaller crystallite size and higher morphological defects than the corresponding sample prepared by co-precipitation and calcined at mild temperature (450 °C). The calcination at 700 °C of the sample prepared with the mechano-chemical method led to a vanadium antimonate characterized by a higher concentration of cationic vacancies than the corresponding sample prepared by co-precipitation. This led to a considerably higher activity in propane ammoxidation; however, the selectivity to acrylonitrile was lower.

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