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Synthesis, characterization and evaluation as catalysts for propane ammoxidation of VMoSbO systems with rutile-type structure

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Abstract

Monophasic, rutile-type Mo/V/Sb mixed oxides were synthesized with the co-precipitation procedure; Mo^{6+} replaced for V^{4+} in the lattice of V antimonate, and the (Mo + V)/Sb ratio remained approximately constant. The addition of Mo increased the catalytic activity in propane ammoxidation, but the catalysts became less selective to acrylonitrile, due to the increased contribution of combustion, and more active in ammonia oxidation to molecular nitrogen. This was attributed to an enhanced Lewis acidity, which increased the interaction of the catalyst with ammonia and favored its unselective transformation.

Keywords: Propane ammoxidation; Acylonitrile; Mo/V/Sb mixed oxides; Rutile-type mixed oxides

1. Introduction

Rutile-based systems, including V/Sb/(W, Al)/O [1–6], Fe/V/Sb/O [7,8], Sn/V/Sb/O [9], Cr/Sb/O [10], Ga/Sb/O [11] and V/Nb/Sb/O [12], are known to be efficient catalysts for the ammoxidation of propane to acrylonitrile. The particular properties of these systems arise from the following chemical–physical features: (i) formation of mixed oxides in which the components essential for the activation of paraffins (i.e., V, but also Fe, Ga or Cr) and those which are active in the O/N insertion on the allylic-type intermediate, belong to the same structure and can effectively co-operate in the transformation of the alkane, and (ii) ability to disperse antimony oxide on its surface, in the form of a supra-surface layer above *quasi*-$VSbO_4$ [13], which also plays an important role in the reaction mechanism. The rutile structure in some cases is surface-enriched in Sb [10,14], and this also may provide the development of specific sites (Sb^{5+}=O, Sb^{3+}–O–Sb^{5+}) which have been proposed to be the active species involved in the allylic ammoxidation of the unsaturated intermediate [15].

A second class of catalysts active and selective in the ammoxidation of propane are those based on V/Mo/Nb/Sb(Te) mixed oxides [16,17], which first were developed by Mitsubishi and later were claimed as catalysts for several different reactions of alkanes oxidation, including oxidation of ethane to acetic acid, oxidation of propane to acrylic acid, and oxidehydrogenation of ethane to ethylene. The catalytic properties of these materials derive from the development of specific structures, in which cooperation between V, Mo and co-elements is particularly effective [18,19]. In these classes of catalytic materials, Mo is supposed to play the role of NH^{2-}-insertion onto the allylic intermediate, in the same way as it happens in Bi molybdates for propylene ammoxidation.

Starting from the classification of catalysts for propane ammoxidation, and with reference to the specific role which has been assigned in literature to each element in these multifunctional systems, we have decided to study the possibility of formation of V/Mo/Sb/O systems, by investigation of the nature of crystalline compounds formed. The investigation was focussed on compositions in which the ratio between elements are far from compositions claimed for the Mitsubishi systems. In the present work we report about the catalytic performance, in propane ammoxidation and oxidation, of monophasic V/Mo/Sb mixed oxides characterized by the rutile-type structure, never described before in liter-

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ature, while in another related paper we describe in details the chemical–physical characterization of the different crystalline compounds which form when the atomic ratios between the three metals are varied [20].

2. Experimental

Catalysts were prepared with the co-precipitation technique, developed for the preparation of rutile SnO_2-based systems claimed by Rhodia [21]. The preparation involves dissolution of $MoO_2(acac)_2$, $VO(acac)_2$ and $SbCl_5$ in absolute ethanol, followed by dropping the solution into an aqueous solution maintained at pH 6–7 through ammonia addition. A precipitate is obtained, which is separated from the supernatant liquid by centrifugation and filtration. The solid is then dried at 120 °C, calcined first at 340 °C for 1 h and then at 700 °C for 3 h, with a heating rate of 5°/min.

The chemical analysis of the catalysts was obtained by atomic absorption, treating the samples at 1100 °C in a Pt/Au crucible in the presence of Li tetraborate, followed by acid leaching. Powder X-ray diffraction (XRD) patterns were obtained using a BRUKER D5005 diffractometer and Cu Kα radiation. Patterns were recorded with 0.02° (2θ) steps over 10–80° angular range with 10 s counting time per step. Ammonia adsorption and TPD were carried out with a Thermoquest TPDRO 1100 instrument, by first evacuating the sample, then feeding pulses of ammonia at 120 °C, and then heating the sample in He flow up to 600 °C. The nature and amount of compounds desorbed were evaluated by using a TCD and a VGQ quadrupole connected with the TPD instrument.

Table 1
Samples prepared, composition (as determined by AA-ICP), and specific surface area (the composition has been referred to $O_{4.00}$)

Catalyst, no.	Atomic Mo/V/Sb ratios in solution	Effective catalyst composition[a]	Surface area (m^2/g)
Mo0	0/2/1	$V_{0.92}Sb_{0.92}O_{4.00}$	7
Mo1	0.4/2/1	$Mo_{0.10}V_{0.79}Sb_{0.92}O_{4.00}$	9
Mo2	0.6/2/1	$Mo_{0.17}V_{0.73}Sb_{0.96}O_{4.00}$	11
Mo3	1/2/1	$Mo_{0.21}V_{0.62}Sb_{0.79}O_{4.00}$	12

[a] The amount of O has been determined by difference from the sample weight.

Catalytic tests were carried out in a laboratory stainless steel fixed-bed reactor operating at atmospheric pressure. 2 cm^3 of catalyst were loaded, shaped in particles having size ranging between 0.42 and 0.55 mm. The catalyst particles were mixed with an equal amount of inert particles (α-alumina). The following reaction conditions were used: (i) propane ammoxidation: feed composition 25 mol.% propane, 10% ammonia, 20% oxygen, remainder helium; residence time 2.0 s; (ii) propane oxidation: feed composition 6% propane, 10% oxygen, 33% steam, remainder helium; residence time 2.0 s. Products were analyzed by means of gas chromatography. A Hay-sep T column (TCD) was

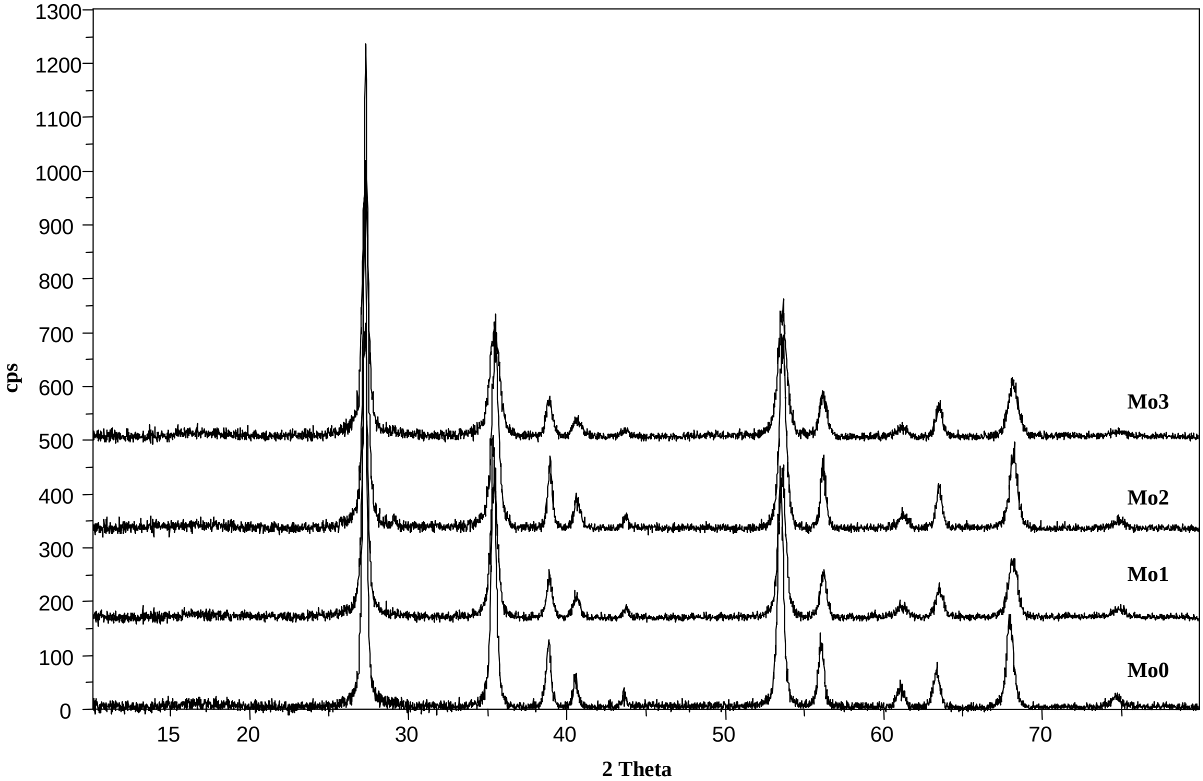

Fig. 1. X-ray diffraction patterns of V/Mo/Sb/O samples.

used for the separation of CO_2, NH_3, C_3H_8, H_2O, HCN, acrolein, acetonitrile and acrylonitrile, a MS-5A column (TCD) for the separation of O_2, N_2 and CO, and a Porapak QS column (FID) for the separation of propane and propylene. A fused-silica Poraplot Q column (FID) was used for the separation of acetic acid, acrolein, acrylic acid and propionic acid.

3. Results and discussion

The relative amounts of the elements in the starting solution, the effective composition of solids as determined by chemical analysis of calcined samples, and the value of specific surface area for samples prepared are reported in Table 1. The composition of the solid was quite different from that of the starting solution; in general, the precipitation of V and Mo was not quantitative. However, it is worth noting that even though starting solutions had similar V/Sb atomic ratio, in the final solid the V/Sb ratio decreased for increasing amounts of Mo in the solution, and thus the (V+Mo)/Sb ratio in the solid was almost constant. This suggests the possibility that the precipitate which develops by dropping the alcoholic solutions into the aqueous solution is indeed a true precursor, thus a mixed oxohydrate in which increasing amounts of Mo replace for V when the Mo/V in the alcoholic solution is increased. Also, a pH around 7 falls inside to the insolubility domain for V^{4+} oxohydrate, but not for Sb^{5+} and Mo^{6+} oxohydrates; this in favor of the formation of a mixed precursor, of variable composition, unsoluble in this pH range.

Fig. 1 plots the X-ray diffraction patterns of samples. All samples were very crystalline and monophasic; other evidences were obtained about the absence of additional amorphous compounds (e.g., MoO_3 or SbO_x), and about the formation of a true solid solution, in which, starting from $V_{0.92}Sb_{0.92}\phi_{0.16}O_4$, Mo^{6+} replaces for V^{4+} according to the following approximate stoichiometry: ${Sb_{0.92}}^{5+}{V_{0.68-3x}}^{4+}{V_{0.24}}^{3+}{Mo_{2x}}^{6+}\phi_{0.16+x}O_4$. In the formula, ϕ stands for the cationic vacancies which are present already in non-stoichiometric vanadium antimonate, and the number of which increases as a consequence of replacement of three atoms of V^{4+} with two of Mo^{6+} [20]. This represents the first example of rutile-type solid solution including Mo in the structure.

The catalytic performance of samples Mo0 as a function of the reaction temperature is summarized in Fig. 2. Fig. 2a plots the conversion of propane, ammonia and oxygen as function of the reaction temperature, under propane-rich conditions. Fig. 2b plots the selectivity to propylene, cyanhydric acid, acetonitrile and acrylonitrile, while Fig. 2c shows the selectivity to carbon dioxide, carbon monoxide and nitrogen (the latter, with respect to converted ammonia). The conversion of propane and ammonia was limited by oxygen. The distribution of products was considerably affected by the reaction temperature; in the temperature range between 320 and 420–440 °C, an increase of temperature caused a progressive decrease of the selectivity to propylene (the main product at low propane conversion), in favor of the formation of acrylonitrile. The selectivity to cyanhydric acid, carbon

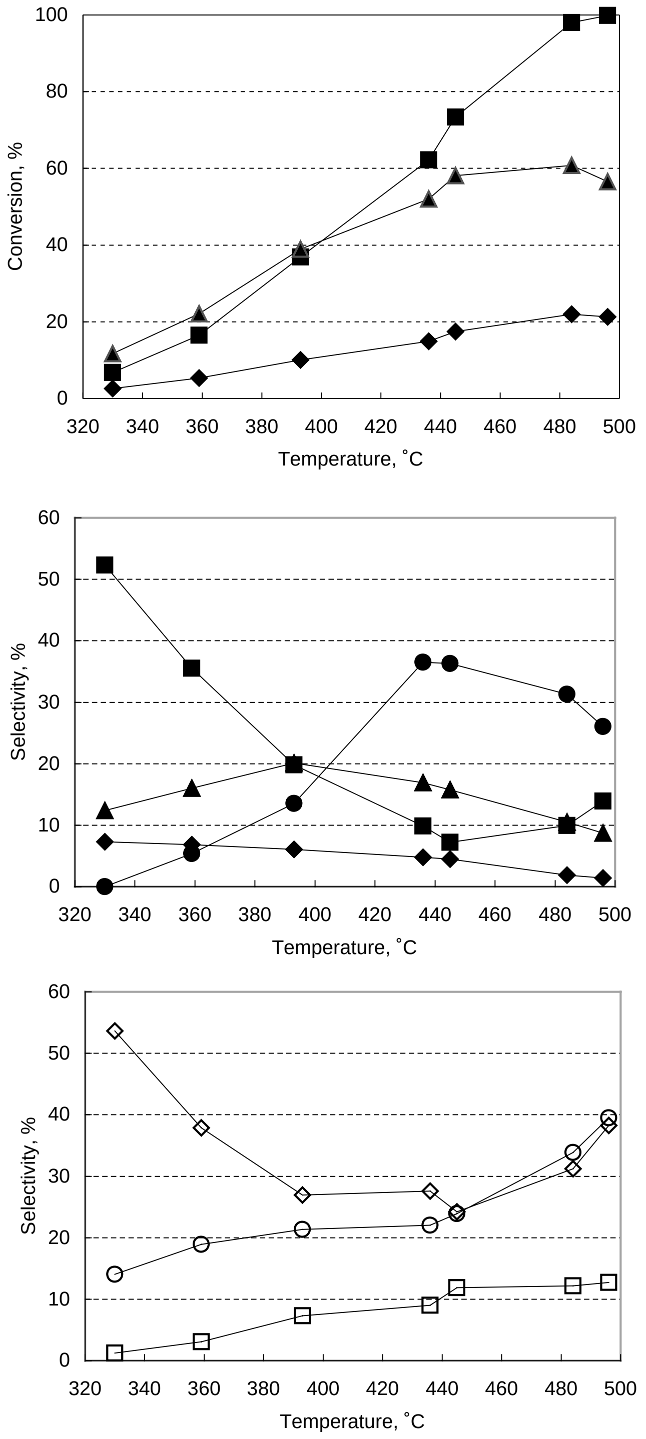

Fig. 2. Catalytic performance of sample Mo0 in propane ammoxidation as a function of reaction temperature. Top: conversion of propane propane (◆), of ammonia (▲), and of oxygen (■). Middle: selectivity to acrylonitrile (●), to propylene (■), to acetonitrile (◆), and to cyanhydric acid (▲). Bottom: selectivity to carbon monoxide (□), to carbon dioxide (○) and to nitrogen (with reference to ammonia converted) (◇).

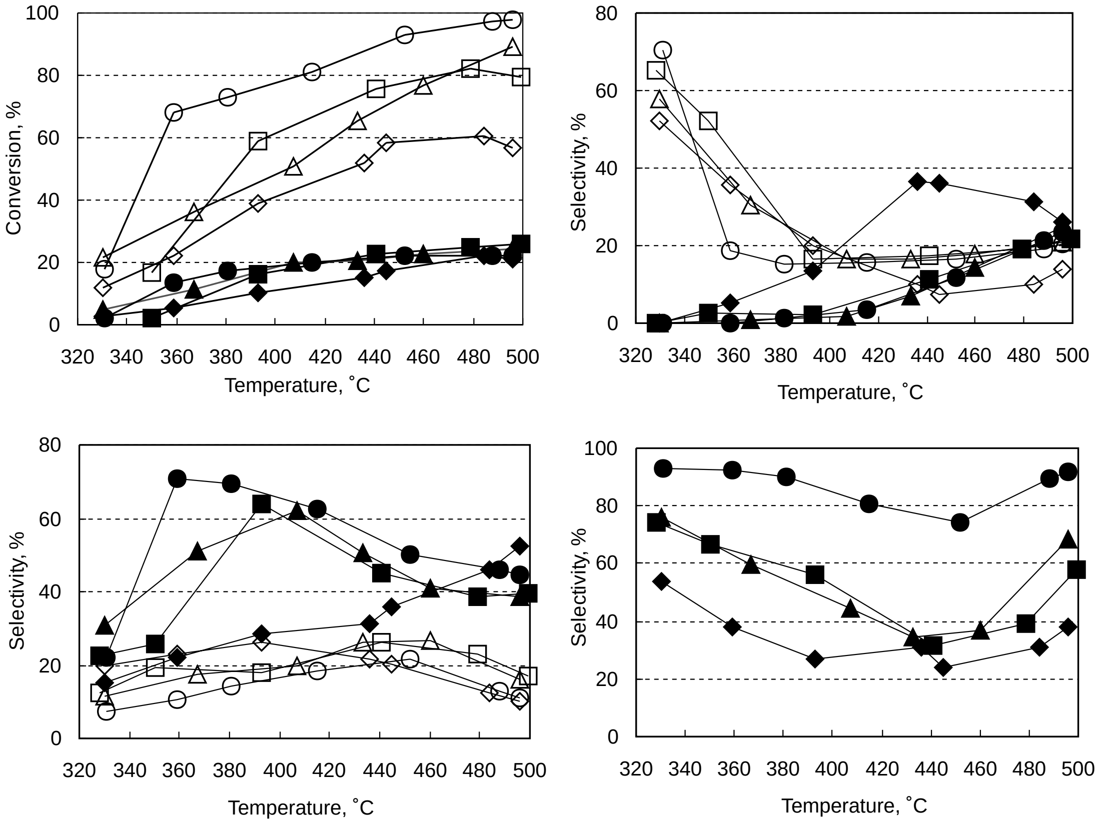

Fig. 3. Catalytic performance in propane ammoxidation as a function of temperature. Top left: conversion of propane (full symbols) and of ammonia (open symbols). Top right: selectivity to acrylonitrile (full symbols) and to propylene (open symbols). Bottom left: selectivity to acetonitrile + cyanhydric acid (open symbols) and to carbon monoxide + carbon dioxide (full symbols). Bottom right: selectivity to N_2 referred to converted ammonia. Catalysts: Mo0 (◆), Mo1 (■), Mo2 (▲), Mo3 (●).

monoxide and carbon dioxide also increased, while that to acetonitrile decreased. One relevant point is the high initial selectivity to propylene. This is due to the low concentration of sites able to make the allylic ammoxidation on the olefin, and is typical of V/Sb/O catalysts having high V/Sb atomic ratios [22]. Above 440 °C, instead, the selectivity to acrylonitrile and cyanhydric acid declined, with a corresponding increase in selectivity to propylene and to carbon dioxide. Therefore, the lower formation of acrylonitrile is to be attributed not only to the higher extent of consecutive transformations, but also to a decreased availability of selective allylic ammoxidation sites, as a consequence of oxygen depletion.

The trend relative to ammonia combustion to molecular nitrogen, with a minimum at around 450 °C, indicates that a change in the reaction mechanism occurs above this Temperature. The initial decrease of selectivity to nitrogen (in the 320–440 °C temperature range) corresponds to an opposite trend for the selectivity to acrylonitrile and, at a minor extent, to cyanhydric acid. This suggests that increasing temperatures favor the generation of the selective sites, specific for allylic ammoxidation on the intermediate product, propylene. Above 400 °C, instead, ammonia is preferably converted to nitrogen.

Fig. 3 compares the propane and ammonia conversions and the distribution of products, as functions of temperature, with the four samples prepared. The introduction of Mo led to the following effects:

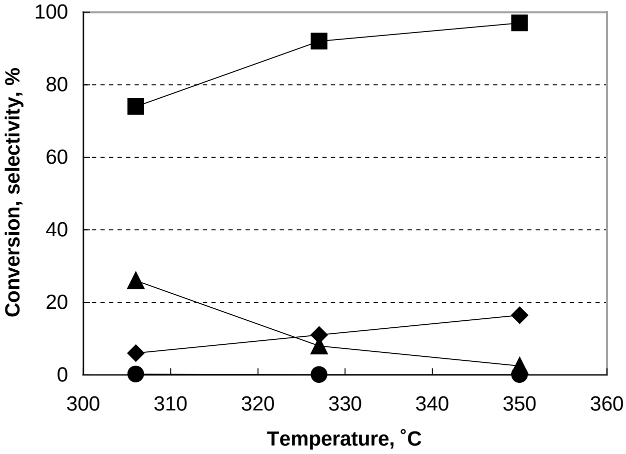

Fig. 4. Catalytic performance in propane oxidation as a function of temperature for sample Mo1. Propane conversion (◆), selectivity to carbon monoxide + carbon dioxide (■), to acetic acid (▲) and to acrylic acid (●).

(a) the activity in propane and in ammonia conversion was enhanced; the effect on the latter was greater, and this indicates an increased interaction with ammonia;

(b) the selectivity to acrylonitrile noticeably decreased, and in correspondence that to carbon oxides increased; the same still holds if the comparison is made at the same level of conversion. Moreover, in Mo-containing samples a maximum in selectivity to CO_2 was observed, which shifted towards lower temperatures for increasing amounts of Mo in samples. Sample Mo0, instead, did evidence a continuous increase of the selectivity to CO_2 with temperature. In correspondence, no maximum in the selectivity to acrylonitrile was shown with Mo-containing samples. Selectivity to cyanhydric acid and to acetonitrile was substantially unaffected by Mo content in catalysts. The formation to propylene also was unaffected by the presence of Mo for low levels of propane conversions, while it was at high temperatures, under conditions of high oxygen conversion. In fact, in Mo-containing catalysts the selectivity to propylene was never lower than 17%. One further difference between samples concerned the selectivity to molecular nitrogen, which remarkably increased on increasing the Mo content.

Therefore, the effect of Mo on catalytic performance was the opposite than the expected one; no new sites of allylic ammoxidation were generated by insertion of Mo^{6+} in the framework, while the non-selective activation of propane (yielding carbon oxides) and ammonia (yielding molecular nitrogen) were enhanced.

Sample Mo1 was also tested as catalyst for propane oxidation; results are summarized in Fig. 4. The catalyst was active, reaching a propane conversion of 16% at 350 °C; however, the prevailing products were carbon oxides, with a selectivity to acetic acid close to 25% for low conversion levels, and less than 1% to acrylic acid. Surprisingly, no propylene was detected. The data obtained suggest that in the presence of ammonia active sites are generated in the reaction environment which are specifically active in the transformation of propane to propylene. The latter desorbs into the gas phase, while is transformed into acrylonitrile at high temperature, i.e., under conditions at which insertion of the NH^{2-} species is feasible. In the absence of ammonia, in-

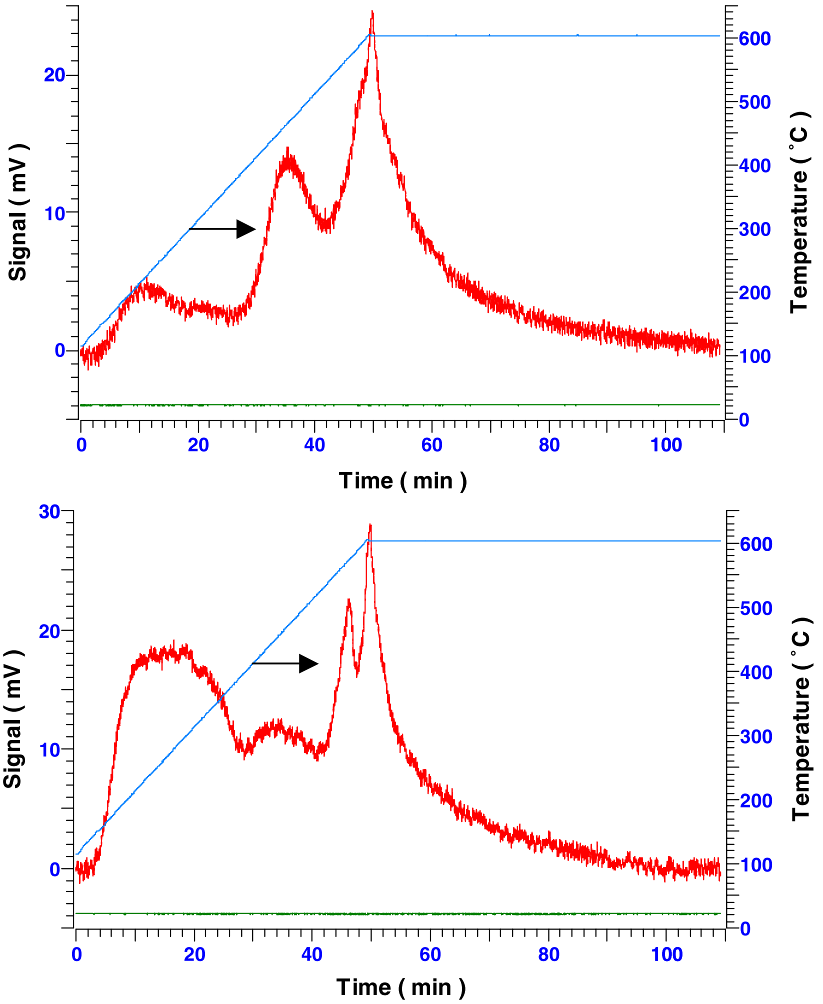

Fig. 5. NH_3-TPD profiles of samples Mo0 (top) and Mo1(bottom).

stead, the catalyst is unable to (oxi)dehydrogenate propane to propylene, and burns the alkane or transforms it directly into acetic acid.

The effect of Mo introduction in the rutile framework, and specifically the enhanced, unselective interaction with ammonia, has also been studied by performing ammonia adsorption and TPD tests. NH_3-TPD profiles for samples Mo0 and Mo1 are reported in Fig. 5. The desorption profile is very complex, and shows three main peaks:

(a) The first peak, beginning at around 150 °C and ending at 350–400 °C, corresponds to ammonia desorption; also molecular nitrogen was detected in the case of sample Mo1. The greater intensity of this peak in Mo-containing sample indicates the affinity of this element for ammonia, and the development of active sites characterized by a stronger acidity.

(b) The second peak, ending at around 500–550 °C, is relative to water desorption, and does not seem to be much affected by the introduction of Mo. Dehydration of the surface as a consequence of hydroxy groups condensation may be responsible for this peak.

(c) The third peak occurs at high temperature, and corresponds to molecular oxygen release; thus, it is due to the self-reduction of V under helium. An additional peak starting before 550 °C is present in the Mo-containing sample, which also is due to molecular oxygen release, and which can be associated to the self-reduction of Mo^{6+} species.

Samples Mo1 and Mo3 were characterized after reaction. X-ray diffraction patterns did not evidence the segregation of crystalline compounds due to permanence in the reaction environment, but a lowering of the crystallinity degree was observed for all samples. Raman spectra evidenced a non-homogeneity of some spent catalysts; in the case of sample Mo3, the spectrum recorded when the beam was focussed on some particles was substantially the same as that of the corresponding calcined catalyst, while in some other particles the segregation of MoO_3 was evident. This means that the multi-component solid solutions may be non-stable under defined reaction conditions (e.g., in hot-spot areas of the reactor), and that segregation into V antimonate and molybdenum oxide may occur.

4. Conclusions

Monophasic V/Mo/Sb mixed oxides, having the rutile structure, were prepared with the co-precipitation procedure. Samples contained increasing amounts of Mo in the rutile lattice, but the (V + Mo)/Sb atomic ratio remained approximately constant. Materials were tested as catalysts for the ammoxidation of propane under hydrocarbon-rich conditions. The addition of Mo in the structure increased the activity towards propane and ammonia with respect to the V/Sb/O catalyst, but worsened the catalytic performance, since the selectivity to acrylonitrile decreased. This was due to an increased combustion of propane and oxidation of ammonia to molecular nitrogen. The introduction of Mo in the rutile lattice did not provide the development of allylic (amm)oxidation sites, but rather generated species characterized by an increased affinity for ammonia, and by a preferential transformation of the latter into nitrogen.

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