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Cr/V/Sb mixed oxide catalysts for the ammoxidation of propane to acrylonitrile

Part I: Nature of the V species

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Abstract

Rutile-type Cr/V/Sb mixed oxides, catalysts for the ammoxidation of propane to acrylonitrile, were prepared and characterized. For atomic ratios between components equal to Cr/V/Sb 1/x/1 and 1/x/2 the systems were monophasic, but different types of compounds formed depending on the ratio between the three metals. The compositional parameter which most affected the nature of the compound formed was the (Cr + V)/Sb atomic ratio. When this ratio was between 2 and ≈1, a rutile $Cr^{3+}/V^{4+}/Sb^{5+}$ mixed oxide of composition $Cr_1V_xSb_1O_{4+2x}$ developed ($0 < x < 1$), which in practice corresponds to a solid solution between 1 $CrSbO_4$ and x VO_2. When the (Cr + V)/Sb ratio was between 0.5 and ≈1, a rutile $Cr^{3+}/V^{3+}/Sb^{3+}/Sb^{5+}$ mixed oxide of composition $CrV_xSb_{1+x+2z}O_{4+4x+4z}$ developed ($0 < x < 1$), which corresponds to a solid solution between 1 $Cr^{3+}Sb_z^{3+}Sb_{1+z}^{5+}O_{4+4z}$ and x $VSbO_4$. The distinction between the two classes of compounds was not clear-cut, and when the (Cr + V)/Sb atomic ratio was around 1, mixed oxides containing both V^{3+} and V^{4+} formed. Values of the (Cr + V)/Sb atomic ratio lower than ≈0.5 led to the additional formation of antimony oxide.

Keywords: Cr/V/Sb mixed oxides; Rutile; Propane ammoxidation; Acrylonitrile

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

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active species involved in the allylic ammoxidation of the unsaturated intermediate [15].

In previous works we have described the main chemical–physical features and reactivity of rutile-type Cr/Sb mixed oxides [10,16] and reported about a preliminary investigation on Cr/V/Sb mixed oxides [16]. The reasons for the choice of Cr as one component for the formulation of a catalyst for propane ammoxidation are the following: (i) $CrSbO_4$ is a rutile compound, isostructural with $VSbO_4$, and the contemporaneous presence of the two elements might lead to modification of the chemical–physical features and of the catalytic properties as compared to those of the single metal antimonates; (ii) chromia is a very efficient catalyst for the dehydrogenation [17] and oxidehydrogenation [18] of light paraffins, and thus might be a useful component in a rutile-based multifunctional system for propane ammoxidation. In the present work we compare the chemical–physical properties of Cr/V/Sb mixed oxides having atomic ratios equal to Cr/V/Sb 1/*x*/1, 1/*x*/2 and 1/*x*/3–5, with *x* comprised between 0 and 1, with the aim of studying the nature of the V species in systems having different amounts of Sb.

2. Experimental

Catalysts were prepared with the co-precipitation technique, developed for the preparation of rutile SnO_2-based systems claimed by Rhodia [19]. The preparation involves dissolving $Cr(NO_3)_3\cdot 6H_2O$, $VO(acac)_2$ and $SbCl_5$ in absolute ethanol, followed by dropping the solution into an aqueous solution maintained at $pH = 7$. A precipitate is obtained, which is separated from the supernatant liquid by centrifugation and filtration. The solid is then dried at 120 °C, and calcined in air at 700 °C for 3 h, with a heating rate of 5 °C/min.

The XRD patterns of the catalysts were collected with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. Data were collected in the range $16^\circ \leq 2\theta \leq 100^\circ$ with a 0.03° 2θ-step and 20 s per step. Full-profile fitting methods (Rietveld analysis [20]) were employed for the accurate determination of the lattice parameters and for the quantitative phase analysis of the crystalline components.

XPS experiments were carried out in an ultra-high-vacuum VG-Scientific ESCALAB 200-C spectrometer, equipped with a five channeltrons hemispherical analyzer. The data were acquired using Mg Kα radiation (1253.6 eV). The electrical charging of the surface due to the non-conductive nature of the catalysts was compensated for by referencing the energy scale to the C 1s peak of adventitious carbon, which was assumed to have an electron binding energy of 284.6 eV.

Raman spectra were obtained using a Renishaw 1000 instrument, with a Leika microscope, Ar laser at 514 nm, and power 25 mW (the power effectively used was either 25 or 50% depending on the V content in the samples).

The chemical analysis of the samples was obtained by energy dispersive spectroscopy (EDS) using a Jeol JSM-5400LV scanning electron microscope equipped with a EDAX microprobe PV-9900, after calibration using reference compounds.

3. Results

3.1. X-ray diffraction (XRD)

Catalysts containing Cr, V and Sb were prepared and characterized using as the reference compounds the Cr/Sb/O-based catalysts, which were studied in previous works [10,16]. Specifically, three series of catalysts were prepared, having atomic ratios Cr/V/Sb 1/*x*/δ (with Cr chosen as the reference element), where δ was equal to (i) 0.8–1.0 (this series of samples will be hereinafter referred to as Cr/V/Sb 1/*x*/1), (ii) 1.8–2.1 (series of composition Cr/V/Sb 1/*x*/2) and (iii) 3–5 (series of composition Cr/V/Sb 1/*x*/3–5). In the three series of catalysts the value of *x* was varied between 0 and 1.0. Some preliminary results concerning the series of composition Cr/V/Sb 1/*x*/2 were discussed in a previous work [16]. This series is now more thoroughly discussed on the basis of new experimental results and comparison with the other series of catalysts.

The main characteristics of the samples prepared are reported in Table 1. In particular, the atomic composition, as determined by SEM–EDX analysis, and the specific surface area are given for each sample. In the case of samples belonging to the series Cr/V/Sb

Table 1
Main characteristics of Cr/V/Sb/O catalysts with composition Cr/V/Sb 1/*x*/1, 1/*x*/2 and 1/*x*/3–5

Cr/V/Sb 1/x/δ, atomic ratio[a]	Surface area (m^2/g)	Cell parameters of the tetragonal cell, a (Å), c (Å), cell volume ($Å^3$)	c/a	Secondary crystalline phases[b,c]	Cr/V/Sb, atomic ratio in rutile[c]
1.0/0/0.8	37	4.601, 3.043, 64.43	0.661	–	1.12/0/0.88
1.0/0.3/1.1	59	4.598, 3.050, 64.48	0.663	–	0.91/0.18/0.91
1.0/0.5/0.9	50	4.588, 3.046, 64.13	0.664	–	0.87/0.26/0.88
1.0/0.8/1.1	32	4.585, 3.041, 63.91	0.663	–	0.75/0.50/0.75
1.0/0.9/0.9	36	4.576, 3.038, 63.61	0.664	3.0 wt.% V_2O_5	0.67/0.66/0.67
1/0/1.6	67	4.629, 3.046, 65.29	0.658	–	nd
1/0.2/1.7	67	4.621, 3.049, 65.13	0.660	–	nd
1/0.5/1.8	49	4.620, 3.048, 65.05	0.660	–	nd
1/0.8/2.0	40	4.610, 3.056, 64.96	0.663	–	nd
1/0.9/1.8	40	4.610, 3.049, 64.81	0.661	–	nd
0/1.0/2.1	20	nd	nd	26 wt.% α-Sb_2O_4	nd
1/0/2.8	54	4.641, 3.042, 65.65	0.655	14.6 wt.% Sb_6O_{13}	nd
1/0.2/5[d]	51	nd	nd	Sb_6O_{13}[e]	nd
1/1/5[d]	72	nd	nd	Sb_6O_{13}[e]	nd

[a] As determined by SEM–EDX.

[b] Principal crystalline phase: rutile.

[c] As determined by Rietveld analysis of the XRD pattern.

[d] The effective composition was not determined analytically; atomic ratios correspond to those employed for samples preparation.

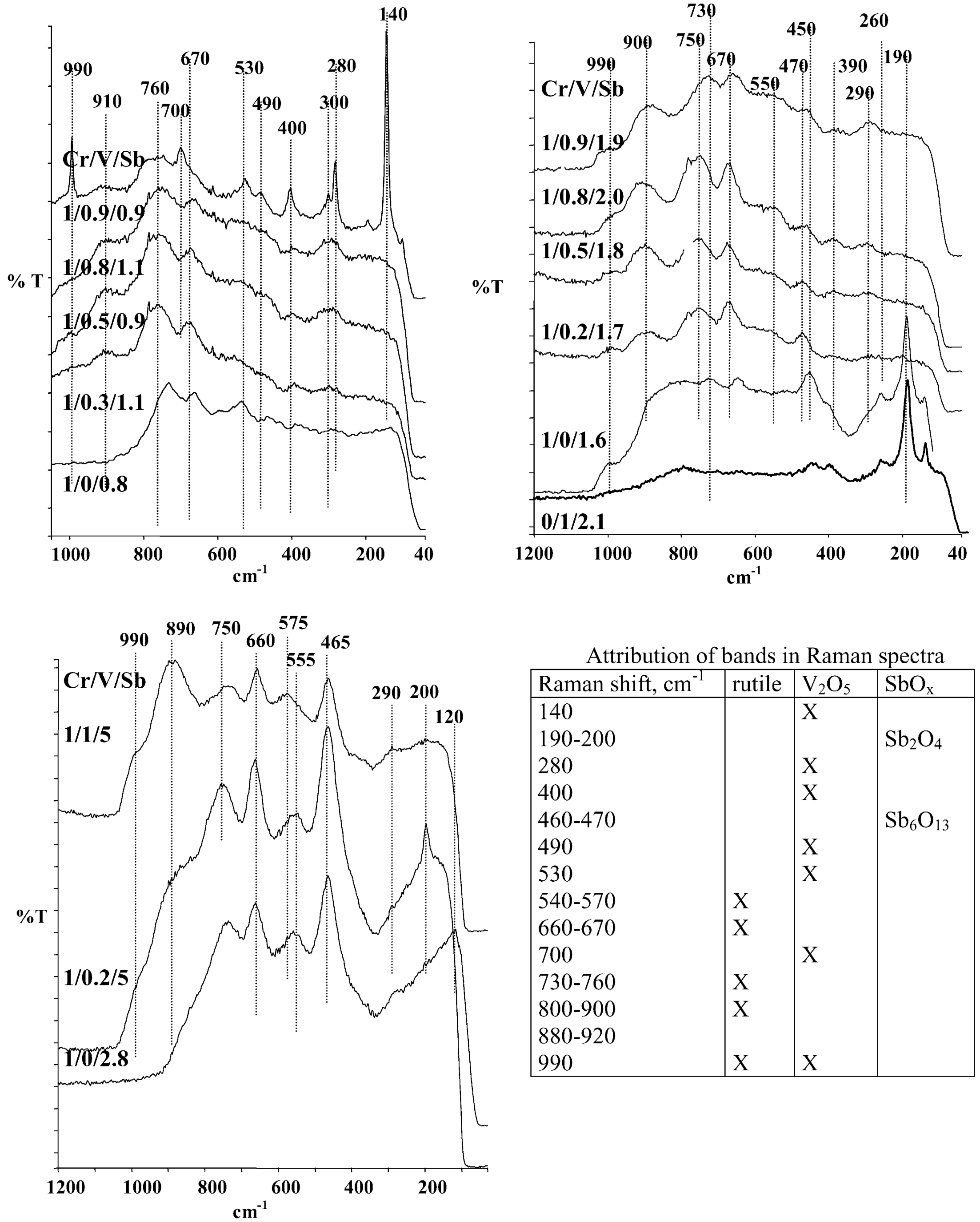
[e] As evaluated from a qualitative analysis of the XRD patterns.

1/*x*/1, the addition of V caused first an increase and then a progressive decrease in the value of the surface area. The crystallinity of the samples, as inferred from XRD patterns, however, was not substantially affected by the presence of V. Also in the case of samples belonging to the series Cr/V/Sb 1/*x*/2 did the surface area decrease for increasing V contents, while in the samples having a large excess of Sb (Cr/V/Sb 1/*x*/3–5 series), an opposite behavior was observed.

All the compounds belonging to the series Cr/V/Sb 1/*x*/1 and 1/*x*/2 were monophasic, and the patterns exhibited only the diffraction lines relative to the rutile structure. The only exception was the catalyst Cr/V/Sb 1/0.9/0.9 for which 3.0 wt.% of crystalline V_2O_5 was present. The volume of the tetragonal cell of the rutile structure, as determined by full profile fitting of the XRD pattern, is also reported in Table 1. The cell volume was similar for samples Cr/V/Sb 1/0/0.8 and 1/0.3/1.1, but then decreased almost linearly with further increases of the V content in the Cr/V/Sb 1/*x*/1 series. This is indicative of the possible formation of a solid solution of V in chromium antimonate, since the cation size of V^{4+} and V^{5+} ions is smaller than that of Cr^{3+} and Sb^{5+} (Cr^{3+} 0.69, Sb^{3+} 0.76, Sb^{5+} 0.60, V^{3+} 0.64, V^{4+} 0.58, V^{5+} 0.54 Å). The pattern fitting confirmed the presence of increasing amounts of V in the rutile structure for increasing *x* values, up to a maximum of an almost equiatomic amount of the elements for the sample Cr/V/Sb 1/0.9/0.9 (the determination of atomic ratios was done by fixing an equiatomic amount for Cr and Sb in ternary compounds). In this latter case, the cell parameters were close to those of stoichiometric rutile $Cr^{3+}V^{4+}Sb^{5+}O_6$ [21]. Similar behavior, with a decrease in the tetragonal cell volume for increasing values of *x*, was also observed in the case of samples belonging to the series Cr/V/Sb 1/*x*/2. Thus, the same considerations above reported also may apply to this series.

3.2. Raman spectroscopy

Raman spectra of samples are reported in Fig. 1. The most significant variations occurring with increasing V content were observed in samples belonging to the series Cr/V/Sb 1/*x*/3–5. In sample Cr/V/Sb 1/0/2.8 the band at Raman shift 465 cm^{-1} can be attributed to Sb_6O_{13} (in agreement with XRD patterns). Bands at 555, 660 and 750 cm^{-1} can be attributed to vibrations in rutile $CrSbO_4$; the same bands were observed in samples having increasing amounts of V (i.e., Cr/V/Sb



Attribution of bands in Raman spectra

Raman shift, cm^{-1}	rutile	V_2O_5	SbO_x
140		X	
190-200			Sb_2O_4
280		X	
400		X	
460-470			Sb_6O_{13}
490		X	
530		X	
540-570	X		
660-670	X		
700		X	
730-760	X		
800-900	X		
880-920			
990	X	X	

Fig. 1. Raman spectra of samples Cr/V/Sb 1/*x*/1 (top left), 1/*x*/2 (top right) and 1/*x*/3–5 (bottom left).

1/0.2/5 and 1/1/5), suggesting that the rutile structure was maintained in these samples. However, an additional band developed at 890 cm^{-1}, and its intensity was proportional to the V content; this band can be attributed neither to $CrSbO_4$, nor to any oxide of Cr, V or Sb, nor is present in the spectrum of sample V/Sb 1/2.1 (also reported in Fig. 1). The same band was observed in spectra of samples belonging to the Cr/V/Sb 1/*x*/2 series, while it was much weaker in spectra of samples Cr/V/Sb 1/*x*/1. A band falling in the region 800–900 cm^{-1} has been reported for $V_{0.92}Sb_{0.92}O_4$ [22]; it has been attributed to stretching vibrations involving two-coordinated O ions which develop as a consequence of the formation of cationic vacancies, and are thus typical of defective V antimonate.

In spectra of samples Cr/V/Sb 1/*x*/1 and 1/*x*/2 the bands relative to vibrations in the rutile compound were observed at Raman shift 730–750, 660–670, 540–560 cm^{-1} [10,16], while bands attributable to “free” antimony oxide were absent. In sample Cr/V/Sb 1/0.9/0.9 were the bands attributable to V_2O_5 evident, in agreement with indications from XRD. FT-IR spectra (not reported here) confirmed the absence of “free” antimony oxide in both Cr/V/Sb 1/*x*/2 and 1/*x*/1 series.

Therefore, bands typical of the rutile compounds were observed in all series of Cr/V/Sb samples examined, but in the presence of V an additional feature at 890–900 cm^{-1} developed only in samples belonging to the series Cr/V/Sb 1/*x*/2 and 1/*x*/3–5. This feature may be taken as an indication of the formation of either a rutile V antimonate, or of a rutile, mixed V/Cr antimonate.

3.3. X-ray photoelectron spectroscopy (XPS)

Results of XPS analysis for samples Cr/V/Sb 1/*x*/1 are summarized in Table 2. While for $x = 0.3$ and $x = 0.9$ a single signal relative to V $2p_{3/2}$ could be identified (the BE of which, however, differed by approximately 1 eV for the two samples), for intermediate *x* values an overlapping of two signals was present, with a contribution of the signal at higher BE which increased with increasing values of *x*. Thus, it is clear that for lower *x* values a V species with lower valence state was present, which was progressively replaced by a species having a higher valence state; the latter was the only species for high vanadia contents.

A definite attribution of the two signals either to the V^{3+}/V^{4+} couple or to the V^{4+}/V^{5+} couple is not possible. Several indications, however, make the former assignment more likely. First, it is known that in $CrVSbO_6$ (which almost corresponds to our sample having composition Cr/V/Sb 1/0.9/0.9, thus with the highest *x* value) vanadium is present as V^{4+} [21]. The presence of V^{5+} might only be justified by the formation of $CrVO_4$ or of V_2O_5; V_2O_5 indeed has been identified, but in a very small amount only in the sample having the highest value of *x*. Moreover, a signal at BE V $2p_{3/2}$ 516.1–516.2 eV in $VSbO_4$ has been attributed to a V^{3+} species [24–26], which is the same signal identified in our Cr/V/Sb 1/*x*/2 samples (Table 2).

The signal relative to Cr $3p_{3/2}$ was in the range typical for Cr^{3+}. The signal relative to Sb $3d_{3/2}$ is attributable to Sb^{5+}. The Sb/Cr atomic ratio was equal to 4.8 for $x = 0$, and became equal to 2.4–3.4 in

Table 2
Results of XPS characterization of samples with composition Cr/V/Sb 1/*x*/1 and 1/*x*/2

Cr/V/Sb 1/*x*/δ, atomic ratio[a]	Cr $3p_{3/2}$, BE (eV)	V $2p_{3/2}$, BE (eV)	Sb $3d_{3/2}$, BE (eV)	Sb/Cr (bulk, surface)	Cr/V (bulk, surface)
1.0/0/0.8	577.3	–	540.0	0.8, 4.8	–
1.0/0.3/1.1	577.3	516.5	540.6	1.1, 3.4	3.3, 1.5
1.0/0.5/0.9	577.1	516.5/517.6 (40/60)	540.5	0.9, 2.5	2.0, 2.6
1.0/0.8/1.1	577.4	516.3/517.3 (20/80)	540.4	1.1, 3.0	1.3, 1.6
1.0/0.9/0.9	577.5	517.5	540.5	0.9, 2.4	1.1, 0.9
1.0/0/1.6	577.6		540.6	1.6, 6.4	–
1.0/0.2/1.7	577.0	516.1	540.2	1.7, 5.6	5.0, 4.5
1.0/0.5/1.8	576.7	516.2	540.0	1.8, 6.0	2.0, 2.4
1.0/0.8/2.0	576.9	516.5	540.4	2.0, 6.0	1.2, 1.4
1.0/0.9/1.8	577.3	516.1	539.9	1.8, 5.8	1.1, 0.9

[a] As determined by SEM–EDX.

Cr/V/Sb 1/x/1 samples having $x > 0$; in all cases, therefore, the value was higher than the bulk one (bulk ratio around 1). The Cr/V ratio was significantly lower than the bulk one only in the sample having $x = 0.3$ (thus in the sample which also had the highest Sb/Cr surface ratio), while it was closer to the bulk one for samples having $x > 0.3$.

Different was the case for catalysts belonging to the series Cr/V/Sb 1/x/2. A single signal relative to V $2p_{3/2}$ was identified, falling at 516.1–516.5 eV. This indicates that a single V species develops in systems having an amount of Sb at least equal to the sum of Cr and V. The Sb/Cr surface ratio was considerably higher than the bulk one and similar in all samples, regardless of the value of x, while the Cr/V ratio was in all samples close to the bulk one.

One further difference between the two series of samples was the value of surface charging which developed during execution of XPS measurements. Specifically, in the Cr/V/Sb 1/x/1 series this value was close to 13 eV for samples having $x = 0$ and 0.3, but then progressively decreased for samples having values of x higher than 0.3. The sample having $x = 0.9$ behaved like a conductor. The same did not occur in samples Cr/V/Sb 1/x/2. The surface charge remained non-negligible (between 7 and 14 eV) for all samples, and thus all of them behaved like insulators.

4. Discussion

The progressive variation in the crystallographic parameters of the tetragonal cell of rutile in the series Cr/V/Sb 1/x/1 and 1/x/2 indicates a change in the composition of the mixed oxide, with the introduction of increasing amounts of V ions in the lattice. In the case of samples Cr/V/Sb 1/x/2, the development of a solid solution between $VSbO_4$ and $CrSbO_4$, thus of a mixed oxide of composition $Cr_1V_xSb_{1+x}O_{4+4x}$, was proposed [16]. This implies that as long as the value of x is lower than 1 (or, in general, until the atomic sum of Cr and V is lower than the atomic content of Sb), the excess Sb (i.e., Sb not included in the rutile) should be present as "free" antimony oxide. This hypothesis, however, is not confirmed by the Raman spectra. Already in the sample Cr/V/Sb 1/0.2/1.7, a relatively low amount of V was sufficient to have the complete disappearance of bands attributable to antimony oxide (which instead were well evident in the sample without V).

In a previous work it was proposed that in the Cr/Sb/O system a stoichiometric or almost stoichiometric $Cr^{3+}Sb^{5+}O_4$ develops for equiatomic Cr/Sb ratios used in preparation, while for Cr/Sb ratios lower than 1 a solid solution containing excess Sb forms [10]. Excess Sb may be in the form of Sb^{3+}, thus in practice replacing Cr^{3+} and yielding a mixed oxide of composition $Cr^{3+}_{1-y}Sb^{3+}_{y}Sb^{5+}O_4$ (which if expressed with reference to Cr^{3+} becomes $Cr^{3+}Sb^{3+}_{z}Sb^{5+}_{1+z}O_{4+4z}$; this in practice represents a solid solution between 1 $CrSbO_4$ and z $Sb^{3+}Sb^{5+}O_4$). In a sample having an atomic Cr/Sb ratio equal to 1/1.6, not all the Sb in excess was found to be accommodated in the solid solution, since evidence was obtained for the presence of extra-framework antimony oxide [10]. Simulation of the X-ray pattern led to the hypothesis that the effective atomic ratio between Cr and Sb in the rutile mixed compound was close to 1/1.2, thus implying an overall stoichiometry of the type: 1 $CrSb^{3+}_{0.1}Sb^{5+}_{1.1}O_{4.4} + 0.4SbO_n$ (Raman spectroscopy made it possible to identify the latter as a mixture of α-Sb_2O_4 and Sb_6O_{13}) [10].

Therefore, it can be hypothesized that in samples Cr/V/Sb 1/x/2 the tri-component solid solution indeed also contains Sb^{3+}, and has the following general composition: $Cr^{3+}V^{3+}_{x}Sb^{3+}_{z}Sb^{5+}_{1+x+z}O_{4+4x+4z}$. Thus the $Cr^{3+}Sb^{3+}_{z}Sb^{5+}_{1+z}O_{4+4z}$ solid solution (which develops in the absence of V) is also able to accommodate V^{3+} in the rutile lattice. In this case, the overall amount of Sb which is present in the framework of the mixed oxide is higher than in the case of a simple solid solution between $VSbO_4$ and $CrSbO_4$. This explains the substantial absence of "free" antimony oxide even in the sample having the lowest V content (Cr/V/Sb 1/0.2/1.7). Moreover, it is possible that for increasing V contents, V^{3+} rather than Sb^{3+} is preferably accommodated in the structure, up to the limit composition $Cr_{0.5}V_{0.5}Sb^{5+}O_4$ which develops for the sample having almost the equiatomic Cr/V ratio (Cr/V/Sb 1/0/0.9/1.8), and in which all Sb is engaged in the formation of the solid solution.

In the case of samples with composition Cr/V/Sb 1/x/1 the low amount of Sb as compared to the sum of Cr and V makes the hypothesis of development of a solid solution which includes V^{3+} (thus, of a mixed compound between the two antimonates) highly unlikely. An alternative hypothesis is the development of a solid solution between $CrSbO_4$ (since the Cr/Sb atomic ratio was close to 1) and VO_2 (which also is a rutile compound), in the same way as occurs between $VNbO_4$ (also a rutile compound) and VO_2 [23]. For equiatomic amounts of the components, the stoichiometric compound $Cr^{3+}V^{4+}Sb^{5+}O_6$ finally develops [21].

Raman spectra support the development of a mixed rutile antimonate in samples belonging to series Cr/V/Sb 1/x/2 and 1/x/3–5, with appearance of a new feature at 890–900 cm^{-1} the intensity of which was proportional to the V content in samples. The same did not occur in samples belonging to the series Cr/V/Sb 1/x/1; in this case therefore there is no indication in favor of the development of a mixed rutile Cr/V antimonate.

The above reported hypothesis are also supported by XPS spectra. If in samples Cr/V/Sb 1/x/2 and 1/x/1 the assignment of the signals to V^{3+} and V^{4+} species is correct, this indicates that the nature of the mixed compound that develops is a function of the amount of Sb in the system as compared to the amount of the transition metal ions. When the (Cr + V)/Sb atomic ratio is lower than or equal to 1 (such as in the Cr/V/Sb 1/x/2 samples) or even slightly higher than 1 (like in the Cr/V/Sb 1/0.3/1.1 sample), V is present as V^{3+}. When instead the (Cr + V)/Sb atomic ratio is higher than 1.2–1.3 (like in the Cr/V/Sb 1/x/1 samples with $x > 0.3$), the prevailing (but not exclusive) species is V^{4+}, which becomes the only species when the (Cr + V)/Sb ratio is close to 2. In this case the compound is a solid solution between VO_2 and $CrSbO_4$. This also agrees with the literature evidence about the presence of both V^{3+} and V^{4+} in non-stoichiometric vanadium antimonate [24,26–28].

In samples Cr/V/Sb 1/x/1, the Sb/Cr ratio as determined by XPS was higher than the bulk one, indicating a Sb enrichment for the outermost part of the rutile crystallites. However, the presence of increasing amounts of V led to a decrease of the surface Sb/Cr ratio. Surface enrichment in Sb was also found in the Cr/Sb/O system having an almost stoichiometric Cr/Sb ratio, despite the substantial absence of "free" antimony oxide (which, if present, might spread over the surface of the rutile thus yielding a high experimental value of the Sb/Cr ratio) [10]. This was explained by making the hypothesis that intracrystalline concentration gradients of the two metal ions had developed, with preferential segregation of Sb in the outermost part of the crystals and hence an enrichment of Cr in the core part [10]. This also explained why the Cr/Sb/O-based catalysts were poorly selective in propylene and gave good selectivity to acrylonitrile (20–25%) even in the absence of excess antimony oxide. The Sb surface enrichment in Cr/Sb/O catalysts provided the active sites able to transform the olefinic intermediate to acrylonitrile, thus making the system intrinsically multi-functional. This behavior is quite different from that of the V/Sb/O system, in which excess, dispersed antimony oxide is necessary to transform intermediate propylene to acrylonitrile [22,29,30]. Data relative to the Cr/V/Sb/O system of composition Cr/V/Sb 1/x/1 given in the present work also indicate that the presence of V in the rutile mixed compound caused a redistribution of Cr and Sb, with development of a Sb concentration in the outermost layers of the rutile crystallites lower than in samples having low values of x (however, the surface ratio remained nevertheless higher than the bulk one).

The redistribution of metal ions in the rutile for increasing values of x in the Cr/V/Sb 1/x/1 series may also be responsible for the different surface charging of the samples observed during XPS spectra recording. It is known that in rutile mixed oxides conductivity arises from the Me–Me interaction occurring in these solids, and transport properties arise from the delocalization of the d electrons of the metals which participate in this interaction [31]. In our samples, an increased Cr–V interaction occurring as a consequence of (i) the increase in V content and (ii) the redistribution of the three metal ions in the rutile crystallites from a surface-Sb-enriched situation to a more homogeneous distribution over the crystal, may lead to the experimentally observed increase in conductivity. The same did not occur in samples belonging to Cr/V/Sb 1/x/2 series, because in all catalysts a considerable Sb surface enrichment was found for all values of x; as a consequence of this, all the samples behaved like insulators.

In a recent paper by Millet and co-workers [7], the nature of the V species was found to be considerably affected by the amount of Fe in $V_{1-x}Fe_xSbO_4$ systems. For low values of x, both V^{4+} and V^{3+} species were found in the cationic-deficient structure (as in our

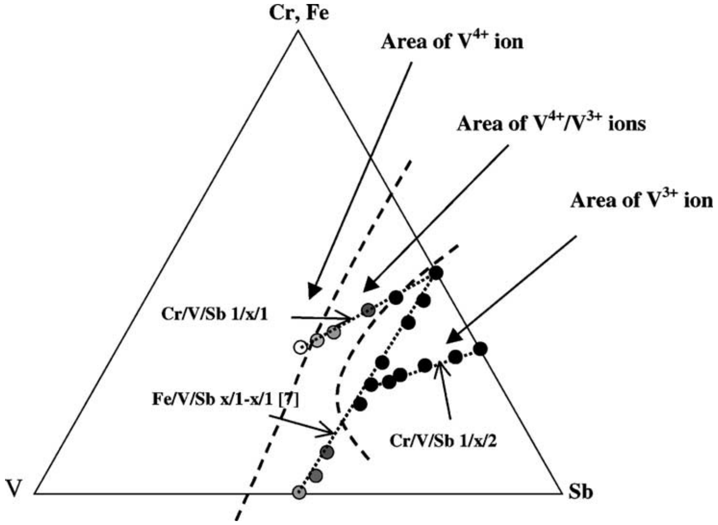


Fig. 2. Me/V/Sb/O samples (Me = Cr, present work, and Me = Fe in [7]) in a triangular composition diagram illustrating samples containing only V^{3+} (black circle), both V^{3+} and V^{4+} (gray-tone circles) and only V^{4+} (white circle).

Cr/V/Sb 1/*x*/1 samples when $x > 0.3$), while for large values of x in $V_{1-x}Fe_xSbO_4$ (i.e., for $x > 0.6$), only V^{3+} was found, as in our Cr/V/Sb 1/*x*/1 samples when the loading of V was low ($x = 0.3$) and in samples belonging to the Cr/V/Sb 1/*x*/2 series. If the compositions of catalysts described by Millet and co-workers [7] and those described in the present work are reported in a triangular composition diagram (Fig. 2) it becomes evident that analogies exist between the two types of compounds, and specifically compositional areas can be defined in which V^{3+} is the exclusive V species, as well as areas in which both V^{4+} and V^{3+} species are present. In just one composition amongst those studied, Cr/V/Sb 1/0.9/0.9, the one almost corresponding to the stoichiometry $CrVSbO_6$ (a compound the existence of which has been demonstrated [21]), is V exclusively present as V^{4+}. The data in Fig. 2 suggest that the main compositional parameter which determines the nature of the V species in rutile mixed oxides is the amount of Sb as compared to the sum of the transition metal ion(s). This might also explain the relative inconsistency of literature data concerning the V/Sb/O system. It is definitely accepted that for V/Sb atomic ratios close to 1, V exists in different valence states in non-stoichiometric rutile. Less clear is the nature of the V species when V/Sb ratios lower than 1 are used, but there are indications in literature that the binding energy of V $2p_{3/2}$ decreases with decreasing V/Sb ratio, pointing out a progressive increase in the relative amount of V ions having lower valence state [24].

5. Conclusions

Cr/V/Sb mixed oxides were prepared with the co-precipitation technique and calcined at 700 °C in air. The samples had the rutile structure, and were essentially monophasic when the composition was equal to Cr/V/Sb (atomic ratios) 1/*x*/1 and 1/*x*/2 ($0 < x < 1$). Only in samples with the composition Cr/V/Sb 1/*x*/3–5 was the presence of excess antimony oxide detected using Raman spectroscopy. The rutile mixed oxide was a solid solution in which the nature of the V ion was a function of the atomic ratio (Cr + V)/Sb. For samples having a ratio between 0.5 and ≈1, the V^{3+} ion was the prevailing species, while for samples having atomic ratios higher than ≈1 and lower than 2 both V^{3+} and V^{4+} species were identified. In the compound with the composition Cr/V/Sb 1/0.9/0.9 (atomic ratio (Cr + V)/Sb close to 2) the only species detected was V^{4+}. The relationship with analogous rutile systems, i.e., Fe/V/Sb/O and V/Sb/O, was studied and a general model was developed which takes into account the possible formation of different V valence states in function of the atomic ratio between components.

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