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Catalysis and structure of the $SbVO_4/Sb_2O_4$ system for propane ammoxidation

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Abstract

Pure $Sb_{0.9}V_{0.9}O_4$ and various preparations with excess of either vanadia or antimony oxide, including mechanical mixtures, have been investigated for propane ammoxidation to acrylonitrile. The catalysts were characterized before and after use in catalysis by various methods, including electron microscopy, infrared spectroscopy and XPS. The catalytic data show that preparations with $\approx SbVO_4$ and α-Sb_2O_4, compared with the single phases, are more selective to acrylonitrile formation on the condition that the excess antimony oxide is present while synthesising the $\approx SbVO_4$ phase. Considering the catalytic data together with the results from the characterisations, various possibilities are discussed to explain the role of excess α-Sb_2O_4 in propane ammoxidation. Possibilities that can be excluded on rational grounds are catalysis on two phases, or, at grain boundaries, an influence on the morphology of $\approx SbVO_4$ from α-Sb_2O_4, the formation of α-Sb_2O_4 containing vanadium, defect formation, creation of active sites by the spillover of oxygen, and formation of VSb_2O_5. Instead, the observed synergy effect is due to the formation of $\approx SbVO_4$ enriched with antimony at the surface, creating isolation to a suitable level of the V-centres. The explanation is consistent with several observations including catalytic data for a series of vanadium compounds with different vanadium content, showing that structural isolation of the vanadium is necessary for obtaining high selectivity to acrylonitrile.

Keywords: Structure; $SbVO_4/Sb_2O_4$ system; Propane ammoxidation

1. Introduction

The $SbVO_4/Sb_2O_4$ system is an important subsystem in the multicomponent catalyst formulations that presently are under development for propane ammoxidation [1]. About twenty years ago Birchall and Sleight [2] reported that stoichiometric $SbVO_4$ was not obtained when heating mixtures of V_2O_5 and Sb_2O_3 in air or in a sealed tube. Instead phases of the type $Sb_{1-x}V_{1-x}O_4$ (oxidized phase) and $Sb_{1-y}V_{1+y}O_4$ (reduced phase) were formed. Later on, Berry et al. [3] reported two different reduced phases. The series $Sb_{1-y}VO_{4-2y}$ was obtained when heating V_2O_5 and Sb_2O_3 in either a closed tube or in commercial nitrogen. In oxygen-free nitrogen the series $Sb_{1-y}VO_{4-1.5y}$ was claimed to form, while the formula for the material formed in air was given as $Sb_{1-y}V_{1-y}O_4$. Also, there has been some uncertainty about the oxidation states of the metal constituents [4], though the early Mössbauer data by Birchall and Sleight [2] showed that the antimony was in the pentavalent state. In contrast to the three series previously reported [3], we have recently established that by heating equimolar mixtures of V_2O_5 and

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Sb_2O_3 in flowing gas at 800°C with various O_2/N_2 ratios, the products formed all belong to the same continuous and cation deficient series $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, with $0 < x < 0.2$ [5]. At reducing conditions a solid solution between $Sb_{0.9}V_{1.1}O_4$ and VO_2, i.e. $Sb_{0.9-y}V_{1.1+y}O_4$ is formed where $0 < y < 0.7$. The electron diffraction patterns of the end members of the two series revealed the formation of different superstructures that all are due to ordering of either cations or cation vacancies. A bond valence analysis has confirmed that in these materials with rutile-type of structure the cation positions are occupied with Sb(V), V(III) and V(IV), while Sb(III) and V(V) are not readily accommodated in the structure [6].

For propane ammoxidation it is now well established that preparations with both $\approx SbVO_4$ and α-Sb_2O_4 compared with the single phases are more selective for acrylonitrile formation [1,7,8]. For low temperature preparations, one of the roles of excess antimony oxide is to assure the complete reaction of V_2O_5 to form $\approx SbVO_4$, because free vanadia promotes the conversion of ammonia to nitrogen [9]. Moreover, it has been reported that antimony species during the ammoxidation migrates from α-Sb_2O_4 to the surface of $\approx SbVO_4$, forming supra-surface antimony sites [10]. As a result, a catalyst is obtained that is less reduced and more selective for acrylonitrile formation. However, the phase cooperation between $\approx SbVO_4$ and α-Sb_2O_4 is yet not fully worked out. In the present work this question is addressed and comparisons of samples prepared by various methods are reported concerning the variation of catalytic data with time on stream and characterization with infrared spectroscopy, XPS and electron microscopy.

2. Experimental

2.1. Catalyst preparation

$Sb_{0.9}V_{0.9}O_4$ (2.0 m^2/g) was prepared by heating an equimolar mixture of V_2O_5 (Riedel-de-Haën, p.a.) and Sb_2O_3 (Merck, p.a.) in air at 800°C for 18 h. A V_2O_5 catalyst (5.1 m^2/g) was prepared by calcining NH_4VO_3 (Merck, p.a.) in air at 450°C for 2 h. α-Sb_2O_4 (0.6 m^2/g) was obtained from Sb_2O_3 after calcining in air for 30 h at 800°C. Two mechanical mixtures $Sb_{0.9}V_{0.9}O_4/V_2O_5$ and $Sb_{0.9}V_{0.9}O_4/\alpha$-$Sb_2O_4$ were prepared with the ratios Sb:V = 1:2 and Sb:V = 2:1, respectively, by mixing particles with diameters in the range 150–425 μm without further treatment. Preparations with the same two Sb:V ratios were as well prepared from slurries of Sb_2O_3 in water solution with NH_4VO_3, which then were heated under reflux before drying followed by calcination at 610°C [8,10]. The surface areas obtained for Sb:V = 1:2 and Sb:V = 2:1 were 9.9 and 3.6 m^2/g, respectively. Another sample with excess antimony oxide (Sb:V = 2:1) was prepared by heating V_2O_5 and Sb_2O_3 in air at 800°C for 18 h, giving a specific surface area of 1.4 m^2/g.

Moreover, $AlVO_4$ (0.2 m^2/g) was prepared from stoichiometric amounts of $Al(OH)_3$ (Riedel-de-Häen, p.a.) and V_2O_5, which were heated at 670°C for 4 days. β-$Sb_{1.9}V_{0.1}O_4$ [11] (1.2 m^2/g) was made by heating a mixture of Sb_2O_3 and V_2O_5 at 900°C for 6 days. The rutile-related phase $Al_{1-x}SbV_xO_4$ [12,13] (1.3 m^2/g) was made starting from a mixture with $Al(OH)_3$, Sb_2O_3 and V_2O_5 (Al:Sb:V = 9:9:2), which was heated at 900°C for 6 days. All samples were sieved and the fractions with diameters in the interval 150–425 μm were used as catalysts.

2.2. Experiments with vapour phase deposition of antimony oxide

To check for the possibility of vapour phase deposition of antimony oxide on $Sb_{0.9}V_{0.9}O_4$, experiments were performed at 550–800°C in a dual bed. Air was passed first through a bed with antimony oxide, charged as either Sb_2O_3 or α-Sb_2O_4, and then through a second bed with pure $Sb_{0.9}V_{0.9}O_4$. The two beds were sepa-

rated with a plug of quartz wool and were kept at the same temperature. The heating rate from ambient up to the end temperature was 10°C/min. The Sb:V surface ratio of the $Sb_{0.9}V_{0.9}O_4$ phase was determined by XPS before and after the experiment.

2.3. Activity measurements

Activity measurements were performed at 480°C in a plug-flow reactor made of glass. The composition of the reactant flow was propane 14.3 vol%, ammonia 14.3 vol%, oxygen 28.6 vol%, water vapour 7.1 vol%, and nitrogen 35.7 vol%. Thus, the ratio propane:ammonia:oxygen was stoichiometric for acrylonitrile formation. Analysis was performed on-line using a gas chromatograph [8]. Analysis with time-on-stream was performed after heating the catalyst in air to the reaction temperature and subsequently switching to the reactant composition.

2.4. Characterizations

FTIR spectra were recorded on a Bruker IFS 66 spectrometer. Disks containing 3 mg sample and 200 mg KBr were pressed. Spectra were recorded in an atmosphere with dry air. The resolution was 2 cm^{-1} and 1000 scans were averaged.

XPS measurements were performed with a Kratos XSAM 800 instrument using Mg K_α X-ray radiation (1253.6 eV). Charging effects were overcome by mixing the sample with acetylene black (Carbon Philblack 1-ISAF from Nordisk Philblack AB). The C1s signal was set to a position of 284.3 eV.

For X-ray powder diffraction, the samples were crushed and mounted on adhesive tape. Films were recorded using a Guinier-Hägg focusing camera with Cu $K_{\alpha 1}$ radiation and with Si as internal standard.

Scanning electron micrographs were recorded at 20 kV using a JSM-840A microscope. The specimens were covered with a layer of gold by sputtering.

Energy dispersive X-ray microanalysis was carried out in a transmission electron microscope JEM-2000FX fitted with a Link AN10000 analysis system. The phases were first identified by electron diffraction and thin edges were then analysed using a beam approximately 500 Å in diameter and an acceleration voltage of 200 kV.

High resolution transmission electron microscopy was performed in a JEM-4000EX instrument operated at 400 kV and possessing a structural resolution of 1.6 Å. Samples were lightly ground in methanol and the dispersion was then transferred to copper grids covered with a holey carbon film. In the microscope, thin crystals positioned over the holes in the carbon film were examined by diffraction and imaging techniques.

3. Results and discussion

3.1. Propane ammoxidation on different Sb-V-O preparations

Fig. 1 shows the variation with time-on-stream of the conversion and the selectivities to propylene, acrylonitrile and degradation products ($C_2 + C_1$). The data are for low conversion to emphasise the ability of the samples to convert propane to intermediate propylene [7,10] and the further conversion of propylene to acrylonitrile. The conversion and the selectivities over the sample prepared as $Sb_{0.9}V_{0.9}O_4$ show no change with time-on-stream (Fig. 1a). $Sb_{0.9}V_{0.9}O_4$ is selective to propylene formation and the selectivity to acrylonitrile is not more than 9% under the present conditions. Previously we have reported for this type of preparation that with increase in conversion, the selectivity to acrylonitrile levels off at 15% [12]. The mechanical mixture with excess antimony oxide $Sb_{0.9}V_{0.9}O_4/\alpha$-$Sb_2O_4$ shows similar selectivity levels and behaviour with time (Fig. 1b), though the somewhat higher selectivity to propylene and the lower selectivity to acrylonitrile formation are due to contribution from α-Sb_2O_4. The

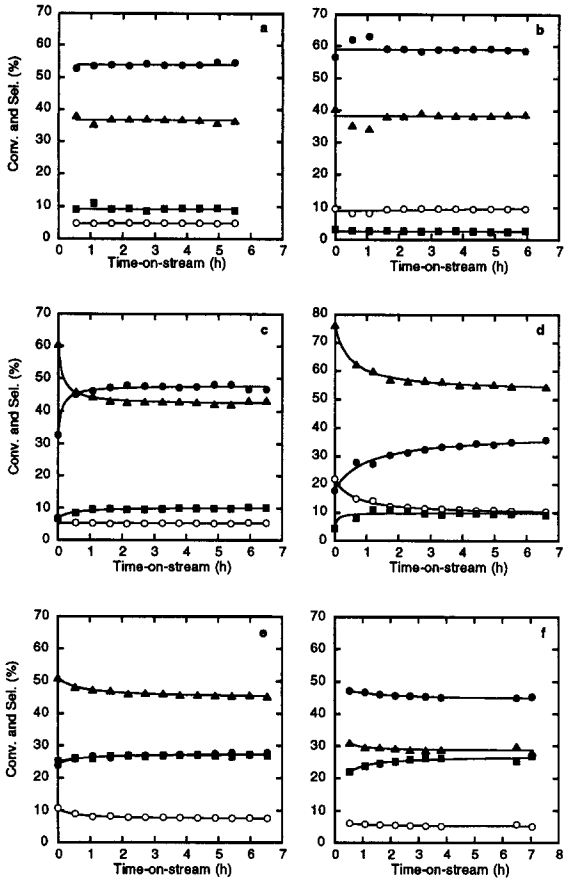

Fig. 1. Variation with time-on-stream of the conversion (○) and the selectivity to propylene (●), acrylonitrile (■) and degradation products (▲) over (a) $Sb_{0.9}V_{0.9}O_4$; (b) mechanical mixture $Sb_{0.9}V_{0.9}O_4$ / α-Sb_2O_4 (Sb:V = 2:1); (c) mechanical mixture $Sb_{0.9}V_{0.9}O_4$ / V_2O_5 (Sb:V = 1:2); (d) slurry preparation $Sb_{0.9}V_{0.9}O_4$ / V_2O_5; (Sb:V = 1:2); (e) slurry preparation $Sb_{0.9}V_{0.9}O_4$ / α-Sb_2O_4 (Sb:V = 2:1); and (f) $Sb_{0.9}V_{0.9}O_4$ / α-Sb_2O_4 (Sb:V = 2:1) prepared by heating V_2O_5 and Sb_2O_3 at 800°C. Reaction temperature, 480°C; and feed, C_3H_6:NH_3:O_2:H_2O:N_2 = 2:2:4:1:5. The amount of catalyst was chosen to give propane conversions of about 5–10%.

latter phase at low propane conversion has been found selective to propylene formation [8,10], but unselective to acrylonitrile formation both in propane [8,10] and in propylene ammoxidation [14]. Thus, the results show that no improvement in the selectivity to acrylonitrile is achieved by mixing α-Sb_2O_4 with $Sb_{0.9}V_{0.9}O_4$ to form a mechanical mixture.

Fig. 1c and Fig. 1d show data for the two vanadia-rich samples (Sb:V = 1:2), which according to XRD in fresh form consist of $Sb_{0.9}V_{0.9}O_4$ and V_2O_5. Both samples show decrease in the selectivity to C_1–C_2 degradation products with time and a corresponding increase of the selectivities to propylene and acrylonitrile. It is obvious that both samples are selective to propylene formation at low conversions, but unselective to acrylonitrile formation. The selectivity to the latter product is not more than 10%. According to XRD data, the changes in the selectivities with time-on-stream are a consequence of reduction of the vanadia and consequent formation of a solid solution of the type $Sb_{0.9-y}V_{1.1+y}O_4$ [5]. The slurry preparation shows lower selectivity to propylene formation (≈ 35%) than does the mechanical mixture (≈ 50%). This difference is due to the higher conversion level over the slurry preparation, showing that with increase in conversion the intermediate propylene is degraded over V-rich samples. Moreover, compared with $Sb_{0.9}V_{0.9}O_4$, the sum of the selectivities to propylene and acrylonitrile is less over the two V-rich samples, showing that excess vanadia is detrimental to the catalyst properties [9].

Fig. 1e and Fig. 1f show data for the two Sb-rich samples (Sb:V = 2:1) that were prepared by the slurry method and by heating of V_2O_5 and Sb_2O_3, respectively. XRD shows that the preparations consist of $Sb_{0.9}V_{0.9}O_4$ together with α-Sb_2O_4. For both samples, the conversion and the selectivity to degradation products decrease slightly with time-on-stream, while the selectivity to acrylonitrile simultaneously increases from about 22 to 26%. Moreover, the sample that was calcined at 800°C is more selective to propylene and less selective to degradation products than is the slurry preparation that was calcined at lower temperature (610°C). Compared with the other preparations (Fig. 1a to Fig. 1d), including the mechanical mixture of $Sb_{0.9}V_{0.9}O_4$ with α-Sb_2O_4, the selectivity to acrylonitrile has been improved more than a factor two at the same conversion level, showing the importance of having excess antimony oxide present while synthesising the catalyst.

The data in Fig. 1e and Fig. 1f clearly shows a synergy effect, since the samples prepared under excess with antimony oxide are more selective to acrylonitrile than are each of the pure constituents $Sb_{0.9}V_{0.9}O_4$ (Fig. 1a) and α-Sb_2O_4 [8,10]. Considering that the mechanical mixture (Fig. 1b) is not selective to acrylonitrile, we can as explanation for the synergy effect exclude dual phase catalysis, i.e. that propylene is formed on one of the phases followed by readsorption and transformation to acrylonitrile on the second phase.

3.2. Importance of grain boundaries

Table 1 includes some of our previous data [10], which here will be discussed in a new perspective. The data concern catalysts with various Sb:V atomic ratios prepared by the slurry method, except for the preparation with Sb:V = 1 that was pure $Sb_{0.9}V_{0.9}O_4$ prepared by heating an oxide mixture as is described under experimental. It is clear that the specific activity decreases with increase in antimony content, indicating that vanadium centres are required to have an active catalyst. The data, moreover, show that Sb:V ratios greater than unity give more efficient conversion to acrylonitrile of the intermediate propylene, which is evident considering that the increase in nitrile selectivity goes with a decrease in the selectivity to propylene at constant propane conversion. Thus, the selectivity to acrylonitrile seems to be related to the content of antimony in the catalyst formulation. However, it is worthy to note that the most important factor for a selective catalyst is to be prepared with excess α-Sb_2O_4 and that for Sb:V > 1 the selectivity to acrylonitrile is generally independent of the antimony content in a wide range of Sb:V ratios. From this result it follows that catalysis at the grain boundaries between $\approx SbVO_4$ and α-Sb_2O_4 is not the origin for the synergy effect. If it were, and depending on the particle sizes of the two phases, the selectivity to acrylonitrile should either pass through a maximum or constantly increase when the Sb:V ratio is varied from 1:1 to 7:1.

The XPS data in Table 1 show for samples with excess α-Sb_2O_4 (Sb:V > 1) that the Sb:V ratio increases upon use of the sample in the ammoxidation. The increase is not due to selective deposition of coke on active V-sites. This conclusion is obvious considering the modest variation in Fig. 1a, 1b, 1e and 1f of the conversion with time-on-stream. Instead, we have concluded [10] that under reaction conditions there is migration of antimony from α-Sb_2O_4 to the surface of $\approx SbVO_4$. In support of this conclusion was the observation that there was a concurrent shift of the XPS Sb $3d_{3/2}$ binding energy, which increased by about 0.2 eV [8,10]. In this regard, it is not clear whether the migration

Table 1
Sb:V ratios determined by XPS for Sb-V-O catalysts together with activity data for propane ammoxidation [a]

Sb:V atomic ratio			Selectivity [c] (%)		Total rate (μmol/m^2/min)
Nominal	XPS, fresh	XPS, used [b]	C_2H_3CN	C_3H_6	
0.5	0.6	0.4	7	64	72
1	1.1	1.1	7	69	53
2	2.0	2.7	25	35	25
3	2.6	2.7	28	37	17
4	3.8	4.8	16	43	26
5	12.6	16.5	25	44	16
6	5.3	8.7	18	33	12
7	9.7	18.5	24	56	8

[a] Feed, propane:ammonia:oxygen:water:nitrogen = 2:2:4:1:5; temperature, 480°C.
[b] After use of the sample for 7 h in propane ammoxidation.
[c] Selectivities given after 7 h on stream at 4% propane conversion.

occurs through the gas phase or involves contact between particles. To solve this question, we report here experiments with vapour treatment of the pure $Sb_{0.9}V_{0.9}O_4$. The results are given in Table 2, and they show no increase in the Sb:V ratio of $Sb_{0.9}V_{0.9}O_4$ when treated at 800°C. When the deposition was tried at 550 and 610°C, a small increase in the Sb:V ratio was measured by XPS. Considering the limited number of experiments that were performed and the divorced result, an unambiguous increase of the Sb:V ratio cannot be asserted. Therefore, complementary activity measurements were performed on these materials and the data obtained are reported in Table 2. Comparison of these data with those in Table 1 for $Sb_{0.9}V_{0.9}O_4$ shows similar values. The lower selectivity to propylene for the vapour treated samples is due to primarily the slightly higher conversion level. From these results the conclusion can be drawn that the observed migration of antimony species occurs through surface diffusion and not through the gas phase. Fig. 1e and Fig. 1f show some improvement in the selectivity to acrylonitrile with time-on-stream that can be associated with the observed migration of antimony species. In the case of the mechanical mixture $Sb_{0.9}V_{0.9}O_4/\alpha$-$Sb_2O_4$, no such increase in selectivity was observed (Fig. 1b), which can be explained by the relatively large particle sizes (150–425 μm) and the consequent few contact zones between the phases. In the slurry and the solid state preparations, on the other hand, the phases are more dispersed resulting in a considerably higher frequency of particle contact.

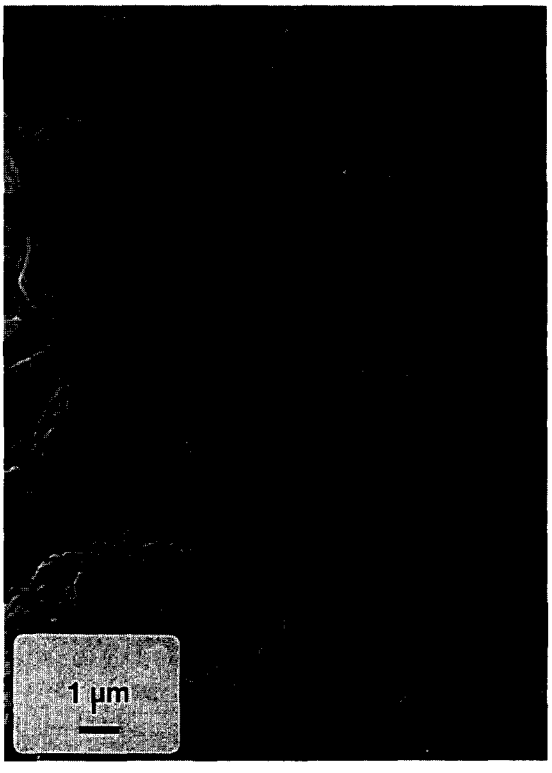

Fig. 2. Scanning electron micrograph of an $Sb_{0.9}V_{0.9}O_4$ / α-Sb_2O_4 catalyst.

3.3. Electron microscopy of ≈ $SbVO_4$ / α-Sb_2O_4

Fig. 2 is a scanning electron micrograph of a typical slurry preparation with both $Sb_{0.9}V_{0.9}O_4$ and α-Sb_2O_4. Two types of crystals can be

Table 2
Sb:V ratios determined by XPS for vapour treated $Sb_{0.9}V_{0.9}O_4$ together with activity data for propane ammoxidation [a]

Treatment [b]	Sb:V atomic ratio		Selectivity [c] (%)		Total rate (μmol/m²/min)
	XPS, fresh	XPS, treated	C_2H_3CN	C_3H_6	
α-Sb_2O_4, 800°C, 4 h	1.2	1.2			
Sb_2O_3, 800°C, 4 h	1.2	1.1			
Sb_2O_3, 610°C, 4 h	1.2	1.5	9	50	49
Sb_2O_3, 550°C, 8 h	1.1	1.4	6	53	49

[a] Feed, propane:ammonia:oxygen:water:nitrogen = 2:2:4:1:5; temperature: 480°C.
[b] A bed with $Sb_{0.9}V_{0.9}O_4$ was treated with an air stream passing from a separate first bed with antimony oxide. The column gives the antimony oxide phase that was charged, the final temperature that was the same for both beds and the time of treatment at the final temperature, which was approached at 10°C/min.
[c] Selectivities measured at 8% propane conversion after vapour treatment.

distinguished, large irregular plates and small crystals that are well faceted. By X-ray microanalysis and electron diffraction, the large crystals were identified as α-Sb_2O_4, while the small crystals are $Sb_{0.9}V_{0.9}O_4$. We have previously demonstrated that gentle grinding of the material produced separate α-Sb_2O_4 and $Sb_{0.9}V_{0.9}O_4$ crystals [10]. Fig. 3 shows a low resolution transmission electron micrograph of a group of $Sb_{0.9}V_{0.9}O_4$ crystals with typical rutile morphology. The crystals are prismatic along the *c* axis and are terminated by pyramidal faces. It can be noted that the crystal surfaces are clean. Transmission electron micrographs of typical α-Sb_2O_4 surfaces are in Fig. 4. The surfaces are clean and quite flat in the [001] direction, but rough in [100].

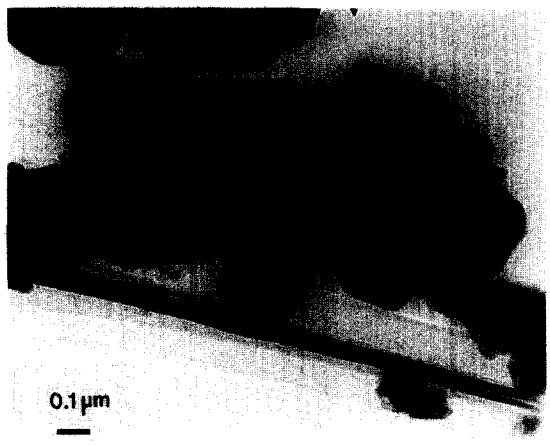

Fig. 3. Low resolution transmission electron micrograph of typical $Sb_{0.9}V_{0.9}O_4$ crystals.

The investigation with scanning and transmission electron microscopy gave no evidence for extended intergrowth between phases, or, epitactic growth of $\approx SbVO_4$ on α-Sb_2O_4. Therefore, there is no evidence for a morphological effect causing the synergy effect, as has been proposed to be the case for the V_2O_5/TiO_2 system [15]. Neither was the formation of an oriented film of antimony oxide on $\approx SbVO_4$ observed. In the case of the related system α-Sb_2O_4/SnO_2, an oriented Sb_2O_4 layer has been proposed to be the active constituent for propylene oxidation [16].

Vanadium doped β-Sb_2O_4, $Sb_{1.9}V_{0.1}O_4$, can be prepared by heating Sb_2O_3 and V_2O_5 at high temperature [11]. Looking for the possibility of formation of V-doped α-Sb_2O_4 as an explanation to the synergy effect, X-ray microanalysis of the α-Sb_2O_4 crystals in preparations with $Sb_{0.9}V_{0.9}O_4$ gave no evidence for vanadium en-

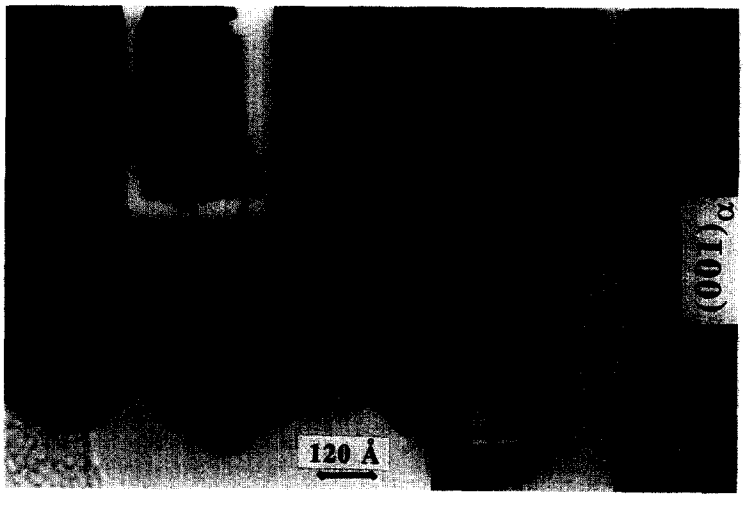

Fig. 4. Transmission electron micrographs of an α-Sb_2O_4 crystal, showing flat (001) faces and rough faces in the [001] direction.

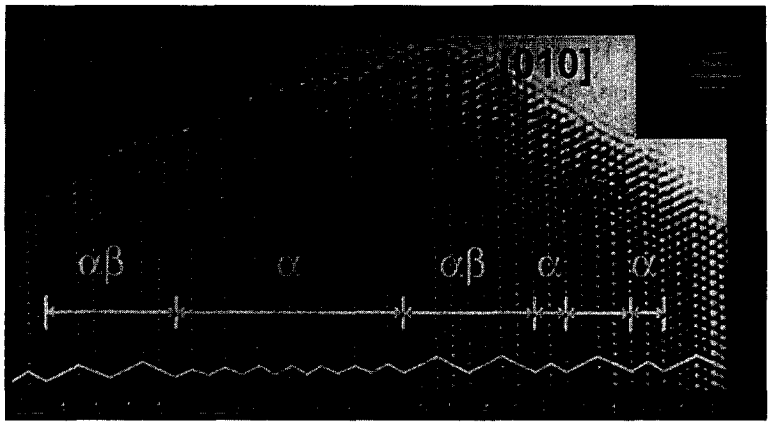

Fig. 5. High resolution transmission electron micrograph of α-Sb_2O_4 having areas with improper slab width between glide reflection planes (indicated as αβ).

tering the α-structure. However, defects of the type shown in Fig. 5 were observed. The defects appear as slabs with improper width between glide reflection planes. The normal slab width in perfect α-Sb_2O_4 comprises two polyhedra with Sb^{3+} and Sb^{5+}, respectively, while in β-Sb_2O_4 the slab is in principle infinitely thick [17]. Consequently, the appearance of four polyhedra wide slabs can be regarded as a step in the transformation of α-Sb_2O_4 to the β-form. The defects were observed in slurry preparations both freshly prepared and after use in ammoxidation. From a catalytic point of view it is important to mention that the same types of defects also were observed in the pure α-Sb_2O_4 that was obtained by calcination of Sb_2O_3, and which never had been in contact with vanadia. This observation definitely shows that incorporation of vanadium is not a prerequisite for formation of the defects and that these are not responsible for the synergy effect, since the mechanical mixture (Fig. 1b) is not a good catalyst.

3.4. Reduction and reoxidation of ≈ $SbVO_4$

Infrared spectra before and after use in ammoxidation of pure $Sb_{0.9}V_{0.9}O_4$, the $Sb_{0.9}V_{0.9}O_4$/α-Sb_2O_4 catalyst that was prepared by solid state reaction at 800°C and the $Sb_{0.9}V_{0.9}O_4$/α-Sb_2O_4 mechanical mixture are given in Fig. 6. The bands in the region below 800 cm^{-1} at 540, 665 and 720 (shoulder) cm^{-1} are typical of rutiles [18,19], while it has been demonstrated that the bands at 1015 and 880 cm^{-1} are due to the existence of cation vacancies in the $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$ structure [5]. It was found that the intensities of the latter two bands relative to that at 540 cm^{-1} are propor-

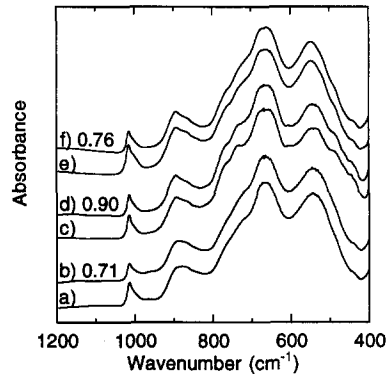

Fig. 6. Infrared spectra of Sb-V-O catalysts before and after use in ammoxidation for 7 h: (a) $Sb_{0.9}V_{0.9}O_4$, fresh; (b) $Sb_{0.9}V_{0.9}O_4$, used; (c) $Sb_{0.9}V_{0.9}O_4$/α-Sb_2O_4 (Sb:V = 2:1) prepared by heating of V_2O_5 and Sb_2O_3 at 800°C, fresh; (d) the previous sample after use; (e) mechanical mixture $Sb_{0.9}V_{0.9}O_4$/α-Sb_2O_4 (Sb:V = 2:1), fresh; and (f) mechanical mixture $Sb_{0.9}V_{0.9}O_4$/α-Sb_2O_4 (Sb:V = 2:1), used. The value that is given in the figure for each of the used samples is the absorbance of the peak at 1015 cm^{-1} relative to the same absorbance for the fresh sample after normalising the spectra to the typical rutile band at 540 cm^{-1}. The spectra for the mechanical mixture have been recorded for the ≈ $SbVO_4$ phase after separation from the α-Sb_2O_4 particles.

tional to the number of vacancies per unit cell and are absent for the reduced end member $Sb_{0.9}V_{1.1}O_4$. Thus, the difference between the fresh and the used sample in absorbance at 1015 cm^{-1}, when normalised with respect to the absorbance at 540 cm^{-1}, gives information about the degree of reduction. The changes in intensity of the 1015 cm^{-1} band are included in Fig. 6. For the calcined $Sb_{0.9}V_{0.9}O_4/\alpha$-$Sb_2O_4$, 90% of the absorbance of the band at 1015 cm^{-1} remains after use, while the corresponding value for the pure $Sb_{0.9}V_{0.9}O_4$ and the mechanical mixture $Sb_{0.9}V_{0.9}O_4/\alpha$-$Sb_2O_4$ is 71 and 76%, respectively. These results show that the sample that is the most selective to acrylonitrile formation, also is the less reduced one after use in ammoxidation. This finding agrees with previous Raman results for slurry preparations with various Sb:V ratios [10]. The question that arises is whether a nitrile selective catalyst is less reduced because of the reoxidation process being more facile, or, the reduction process being slowed down.

The oxidation state of the catalyst, i.e. the x-value in $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, depends on the rates of reduction and reoxidation, which are functions of the partial pressures of reactants and the temperature. The reduction/reoxidation of $Sb_{0.9}V_{0.9}O_4$ can be written as:

$$Sb_{0.9}V_{0.9}O_4 \leftrightarrow 9/11Sb_{0.9}V_{1.1}O_4 + 0.9/11Sb_2O_3 + 5.3/22O_2 \quad (1)$$

For simplicity the reduction process is written as complete reduction to the reduced end member of the series, though only partial reduction is achieved under normal operating conditions. This is manifested by the fact that the bands at 1015 and 880 cm^{-1} are visible in the infrared spectra of the used catalysts (see Fig. 6). Considering Eq. (1), it is possible that the excess antimony oxide speeds up the reoxidation process either by forming gaseous species, e.g. Sb_4O_6, or by contact between phases. An influence from gaseous antimony oxide can be ruled out as an explanation for catalysts being prepared with excess antimony oxide being less reduced after use in ammoxidation, because the α-Sb_2O_4 in the mechanical mixture could not limit the reduction of the $Sb_{0.9}V_{0.9}O_4$ phase (spectrum f in Fig. 6). Also, an effect on the reoxidation rate by the contacts between the reduced $\approx SbVO_4$ and α-Sb_2O_4 in the well-dispersed preparations is not certain, considering that the alternative reaction below can occur, leading to segregation of vanadia.

$$y/10O_2 + Sb_{0.9}V_{1.1}O_4 \leftrightarrow Sb_{0.9}V_{0.9}O_4 + 1/5VO_y \quad (2)$$

Considering the equations, it is obvious that an essential role of the excess antimony oxide is to prevent the segregation of free vanadia and it entering a solid solution. Free vanadia is known to catalyse the degradation of ammonia under the present conditions with high temperature [9], and the solid solution was found to be a poor catalyst (see paragraph 3.1).

Another possibility why a catalyst that is selective to acrylonitrile becomes less reduced can be an influence from the reaction rate. This is in line with the data in Fig. 7, where total reaction rates for slurry preparations with excess α-Sb_2O_4 have been plotted against the antimony content together with theoretical curves. The latter were calculated as linear combina-

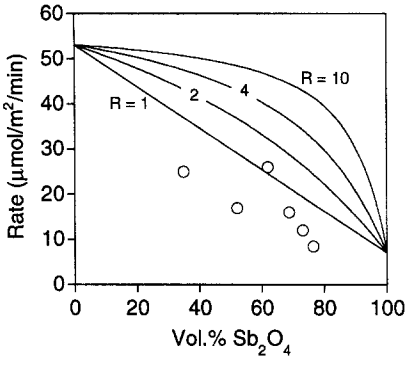

Fig. 7. Total reaction rates (○) for Sb-V-O catalysts in propane ammoxidation as a function of the content of Sb_2O_4 (data from Table 1). Theoretical curves are shown as linear combinations of the measured activities for $Sb_{0.9}V_{0.9}O_4$ and α-Sb_2O_4, assuming various ratios of crystallite diameters defined as $R = d(Sb_2O_4)/d(\approx SbVO_4)$.

tions of the activities for $Sb_{0.9}V_{0.9}O_4$ and α-Sb_2O_4, assuming various ratios between the crystallite sizes of the two phases. The ratios were selected considering that the investigation with electron microscopy, see Figs. 2–4, shows that compared with α-Sb_2O_4, the crystallites of ≈ $SbVO_4$ are considerably smaller. Strikingly, for the Sb-V-O catalysts the measured activities are below the theoretical curves, showing that the ≈ $SbVO_4$ phase in itself becomes less active per unit surface area when prepared in the presence of excess α-Sb_2O_4.

3.5. Surface modification

The results show a synergy effect that is not due to dual phase catalysis, catalysis at grain boundaries, or, epitactic growth of ≈ $SbVO_4$ on α-Sb_2O_4. Furthermore, the present investigation gave no evidence for VSb_2O_5 [20] with V^{4+} and Sb^{3+} being formed in the catalysts either before or after use in the ammoxidation. The formation of VSb_2O_5 requires strongly reducing conditions [4].

In several cases, synergy effects have been explained by spillover of oxygen from a donor phase to an acceptor phase, thereby creating highly active centres [21]. For the present results, such an explanation would be opposed to the following facts (i) the mechanical mixture, compared with the slurry and solid state preparations, has low activity for the transformation of the intermediate propylene to acrylonitrile (Fig. 1b), (ii) the selectivity to acrylonitrile is largely independent on the Sb:V atomic ratio in the range 2–7 (Table 1), and (iii) we have observed the formation of supra-surface antimony sites on ≈ $SbVO_4$ [8,10], created by surface migration of antimony species from α-Sb_2O_4 (paragraph 3.2). Therefore, as explanation we propose surface modification of the ≈ $SbVO_4$ phase as the origin to the synergy effect.

We have observed detectable migration of antimony species during catalysis from α-Sb_2O_4 to ≈ $SbVO_4$ when the phases are well dispersed, but this migration gives only minor improvement in the selectivity to acrylonitrile (Fig. 1e and Fig. 1f). Moreover, we have found that to obtain a catalyst that is selective to acrylonitrile, the excess antimony oxide has to be present in the synthesis and cannot be added afterwards. These observations can be explained by an Sb-rich ≈ $SbVO_4$ surface being created already during the synthesis and calcination of the catalyst at high temperature (> 600°C). Therefore, the antimony content of the $SbVO_4$ surface and the selectivity to acrylonitrile become rather insensitive to the Sb:V ratio in the synthesis as long as Sb:V > 1 (Table 1), and the effect of secondary migration during ammoxidation becomes of minor importance. Thus, it can be proposed that the surface enrichment with antimony creates isolation of V-sites to a suitable level, giving a selective catalyst. Isolation of V-centres being a crucial factor is consistent with the plots in Fig. 8, where catalytic data for various oxides have been plotted against the vanadium content as obtained from unit cell data. It can be seen that the activity for the conversion of propane increases almost linearly with the vanadium content, while the selectivity to acrylonitrile at fixed propane conversion (15%) increases considerably with decreasing vanadium content. The plots in Fig. 8 infer that isolation of V-sites to a suitable level creates a surface that is less active, but more selective for

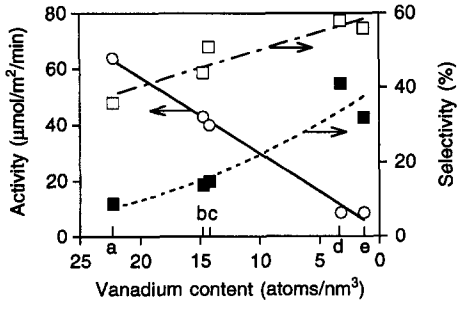

Fig. 8. Total reaction rate and selectivities as a function of the vanadium content in the catalyst. Activity (○), selectivity to acrylonitrile (■); and selectivity to C_3 products (□) (propylene + acrylonitrile). Data for 15% propane conversion are plotted for the pure phases as indicated on the abscissa V_2O_5 (a), ≈ $SbVO_4$ (b), $AlVO_4$ (c), $Al_{1-x}SbV_xO_4$, $x = 0.2$ (d), and β-$Sb_{1.9}V_{0.1}O_4$ (e).

Fig. 9. High-resolution transmission electron micrograph from an antimony rich Sb-V-O preparation showing surface modulation in $\approx SbVO_4$ (arrows).

acrylonitrile formation, observations that are consistent with the present data for the $\approx SbVO_4/\alpha\text{-}Sb_2O_4$ system.

Verification of the formation of an antimony enriched $\approx SbVO_4$ surface is not an easy task. XPS is not a suitable technique in this regard due to the excess antimony oxide has to be present in the synthesis itself. High-resolution transmission electron microscopy, however, can give some information. Fig. 9 is a micrograph of an $\approx SbVO_4$ crystal prepared under excess of antimony oxide. The edge shows modulation of the surface in form of areas with differing contrast, which are indicated by arrows. No information about the composition variations at the surface was obtainable from X-ray micro-analysis considering the width (50 nm) of the beam. The darker areas, which are a few nm wide, could possibly be Sb-rich patches, while the lighter areas correspondingly could be less rich in antimony. Though not unambiguously conclusive, this result at least shows that the surface can accommodate some variation in antimony content, which is in support of our conclusion that an Sb-rich $\approx SbVO_4$ surface being selective to acrylonitrile formation can form when the synthesis is carried out with an excess of antimony oxide.

4. Conclusions

Concerning the preparation of and the catalysis on Sb-V-O catalysts for propane ammoxidation, the following conclusions can be drawn.

In the presence of excess antimony oxide, a $\approx SbVO_4$ phase with an antimony enriched surface is formed during the catalyst synthesis at high temperature.

Surplus antimony sites create isolation of the V-centres at the $\approx SbVO_4$ surface. The structurally isolated V-centres are active and selective to acrylonitrile formation.

Propane ammoxidation on the (Al)-Sb-V-O system is a new example of the validity of the site isolation principle as it was formulated by Callahan and Grasselli more than thirty years ago [22].

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