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Phase Cooperation in Oxidation Catalysis

Structural Studies of the Iron Antimonate-Antimony Oxide System

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The compositions $FeSb_2O_6$ and $FeSb_5O_{12}$ of the two-phase $FeSbO_4-\alpha$ -Sb₂O₄ system, an active and selective catalyst for the oxidation and ammoxidation of propylene, have been structurally characterized by Rietveld analysis of powder neutron-diffraction data. Results of the analysis indicate that the presence of Sb_2O_4 has no effect on the bulk structural parameters of $FeSbO_4$. Specifically (a) the unit cell of $FeSbO_4$ does not depend upon the presence of Sb_2O_4 or calcination temperature, (b) antimony atoms are not found in the intersticies of the coexisting iron antimonate and (c) the apparent Sb/Fe ratio is 1 in iron antimonate. Additionally, the Sb/Fe occupancy in the rutile $FeSbO_4$ structure is random as no supercell reflections were observed. Results of scanning electron microscope and X-ray photoelectron spectroscopy experiments have been interpreted to show that Sb enrichment occurs on coprepared samples of the two-phase mixture. Based on this evidence and the lack of alteration of the bulk structures of both phases it is suggested that surface alteration in this two-phase system is the key to enhanced selective catalytic oxidation activity.

Among the ternary oxide systems that catalyse olefin oxidation reactions, $Bi_2O_3 \cdot nMoO_3$, $SnO_2 \cdot Sb_2O_4$, USb_xO_y and $FeSbO_4 - Sb_2O_4$, the latter is perhaps the least well understood. For the first three systems listed, descrete phases have been identified as being the active catalytic agent.¹ The iron antimonate-antimony oxide system is unusual in that a coexistence of both phases is needed to realize maximum selectivity.²⁻⁴ The individual phases of the system, $FeSbO_4$ and α -Sb₂O₄, have been structurally characterized, but the synergistic effect of the two-phase system in olefin oxidation is not well understood. Sb_2O_4 is, by itself, a selective but not active catalyst, while FeSbO₄ is active but not as selective.⁴ Most workers attribute activity to the FeSbO₄ phase, while numerous experiments have documented that good catalytic oxidative activity and selectivity is only realized when an excess of Sb_2O_4 is present.²⁻⁵ In order to correlate these findings, numerous proposals that deal with the coexistence of these phase have been forwarded. Some of these are listed here: (1) an excess of Sb_2O_4 is needed to promote formation of $FeSb_2O_x$, either as a discrete phase³ or on the surface of $FeSbO_4$,^{2,3} (2) dissolution of Sb into $FeSbO_4$ confers improved catalytic properties on the phase, 6, 7 (3) 'phase cooperation' between Sb₂O₄ and FeSbO₄ effects catalytic behaviour in olefin oxidation² and (4) an excess of Sb_2O_4 is needed to insure complete reaction of all Fe₂O₃,⁵ a well known deep-oxidation (waste-forming) catalyst.

As two of these postulates [(1) and (2)] require bulk structural alteration of $FeSbO_4$, it was concluded that a careful investigation of an $FeSbO_4$ -Sb₂O₄ mixture was in order.

Although the two phases have been separately characterized, a simultaneous structure refinement of both phases on a coprepared mixture has never been reported. The application of Rietveld analysis (least-squares fits of models to powder diffraction profiles) to neutron-diffraction data results in a powerful tool for metal oxide structure determination. The ability to model accurately the line shape of a neutron-diffraction Bragg reflection and near equal scattering lengths of most of the elements makes powder neutron diffraction an extremely powerful and precise structural probe. Additionally, the inherent ability of Rietveld analysis to refine simultaneously multiple phases in a given sample allows precise structure investigations of multiphase powder samples, providing overlap is not severe. Consequently we have collected neutrondiffraction data on two powdered samples: $FeSb_2O_6$ ($FeSbO_4 \cdot \frac{1}{2}Sb_2O_4$) and $FeSb_5O_{12}$ $(FeSbO_4 \cdot 2Sb_2O_4)$. Hypotheses based on models from data of the former sample are applicable to issues in oxidation catalysis, as it is the Sb/Fe ratio (Sb/Fe = 2) that exhibits excellent catalytic activity and is often the composition of choice^{2-3, 4-7} for testing. From a structure-determining point of view this material is not ideally suited for a neutron-diffraction experiment because Bragg peaks due to Sb_2O_4 are an order of magnitude smaller than those due to $FeSbO_4$, and this makes the resulting model of Sb₂O₄ imprecise. Neutron-diffraction data for the FeSb₅O₁₂ system, however, yield models of comparable precision for both phases. The results of the multiphase refinement for Sb_2O_4 from this system (Sb/Fe = 5) can therefore be used as a fixed contribution to the refinements of the $FeSb_2O_6$ system. Hence, by judicious combination of the results from both compositions one can make significant arguments regarding both the structural and catalytic features of $FeSb_y O_z$ materals.

EXPERIMENTAL

SAMPLE PREPARATION

Samples of $FeSb_u O_z$ were prepared as follows. An aqueous solution of $Fe(NO_3)_3$ (Baker reagent grade) was added to an Sb sol (12% Sb₂O₅ by weight, Nalco Co.) and the mixture was heated and stirred until dry. After drying overnight at 120 °C the mixture was fired at 425 °C for 3 h. Heat treatment of $FeSb_5O_{12}$ consisted of firing the mixture at 800 °C for 6 h twice with grinding in between. X-ray diffractograms taken after each heat treatment indicated that no increase in crystallite size had occurred during the second calcination. Finally, the mixture was fired at 900 °C for 16 h. For FeSb₂O₆ calcination was carried out at 800 °C for 3 h.

A portion of the $FeSb_5O_{12}$ mixture was examined on a Cambridge Instruments scanning electron microscope equipped with a Kevex EDX analyser. The mixture was dusted on a silver-painted aluminium pin and then was sputtered with carbon. Examination in the miscroscope revealed a broad particle-size distribution, ranging from 10 to 200 μ m. Elemental analysis of numerous particles also gave varied results; the Sb/Fe ratio ranged from 4.4. to 10.3. Significantly, no particle was observed with a Sb/Fe ratio of 1 or 2, which would correspond to an FeSbQ₄ or FeSb₂O₆ phase, respectively. Almost all particles observed appeared not to be isolated single crystals, rather each appeared to be coated with small crystallites. In view of the diffraction-experiment results (vide infra) it would appear that larger crystals of FeSbO₄ are coated with smaller crystals of Sb₂O₄. A micrograph of the FeSb₅O₁₂ material is presented in plate 1(a) and an elemental scan (for Fe) in plate 1(b). Comparison of the micrographs indicates that the large particles contain iron.

In order to confirm the hypothesis that the surface is Sb-enriched, X-ray photoelectron spectra were taken of the FeSb₅O₁₂ sample on a Kratos XSAM800 X-ray photoelectron spectrometer instrument at 15 keV, 20 mA power using Mg Ka X-rays. The relative atomic abundances were calculated with the following formula:

$$N_{\rm Fe}/N_{\rm Sb} = C_{\rm Fe}\sigma_{\rm Fe}/C_{\rm Sb}\sigma_{\rm Sb} \tag{1}$$

where σ is the cross-section⁸ and C is the area counts per sweep. The result of this calculation was 1/17.8, indicating a surface enrichment of Sb above that of the known 1/5 stoichiometry.

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Plate 1



Plate 1. (a) Scanning electron micrograph of $\text{FeSbO}_4 \cdot 2\text{Sb}_2\text{O}_4$. (b) An Fe map of the same area as (a).

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NEUTRON-DIFFRACTION DATA FOR FeSb₅O₁₂

Room-temperature powder neutron-diffraction data were collected at atmospheric pressure at the University of Missouri Research Reactor with the new position-sensitive detector diffractometer. Data were collected in (4) 25° spans of the detector from 12.5 to 112.5° (2 θ) with neutrons of 1.287 Å wavelength. The sample was contained in a $\frac{1}{4}$ in. diameter thin-wall vanadium can to eliminate parasitic Bragg scattering from the container. An oscillating radial collimator in front of the detector eliminated neutrons scattered from the beam by air and minimized the experimental background. Data were collected for 12 h.

The data were corrected for the efficiency variation of the detector (due to the parallax effect of the linear detector) and rebinned into 0.1° intervals. No correction was made for the variation in peak width with detector setting (another parallax effect), but previous experience has shown this to have only a small effect on R_{wp} and almost no effect on R_{Bragg} or on the refined crystal parameters.

Rietveld profile analysis was carried out with a locally modified version of DBW 3.2, obtained from Dr R. Young, ⁹ University of Georgia. Data from 15 to $110^{\circ}(2\theta)$ were used in the analysis. A contribution of 0.001 or greater of the maximum of any Bragg peak was included in the calculation of the profile. Starting parameters for FeSbO₄ were taken from an X-ray powder determination¹⁰ and for Sb₂O₄ from a powder neutron-profile analysis.¹¹ Initially a four-term background function and a three-term Gaussian profile function were varied in the least-squaring process. As the refinement continued more variables were included; in the final cycles of least squares a total of 42 parameters were varied. Global parameters varied were four background and a 2θ zero. Various parameters were varied for the individual phases. For FeSbO₄ [space group $P4_2/mnm$, Fe/Sb located on special position (0, 0, 0), one O atom at special position (x, x, 0)], these were a three-term Gaussian profile (half-width) function, scale factor, two cell parameters, one temperature factor for Fe/Sb, Sb and Fe occupancies, one position term and a temperature factor for O. For α -Sb₂O₄ (space group $Pna2_1$) a three-term Gaussian profile function, scale factor, three cell parameters, a temperature factor for each unique Sb atom, one temperature factor for all O atoms and 17 position parameters [the z position parameter for Sb(1) was fixed] were varied. Results of the refinement are reported in table 1. Comparison of the Gaussian profile functions from the two phases indicates that the average iron antimonate crystal size is larger than that of the α -Sb₂O₄.

Additional refinements were carried out making use of an extrapolated background. With the exception of the temperature factors, the results of the two kinds of refinements were virtually identical. Because the profile agreement factors for the refined background refinements are lower, only results from that least squaring are reported herein.

Calculated, observed and difference diffractograms are presented in fig. 1. All observed Bragg reflections are accounted for by the presence of the two phases $FeSbO_4$ and α -Sb₂O₄. Specifically, there are no extra Bragg peaks due to a trirutile phase (FeSb₂O₆) or β -Sb₂O₄.

The occupancies of the Fe and Sb atoms in the FeSbO₄ phase were independently refined to establish the oxide stoichiometry (this is equivalent to refining the scattering length of the site). The final values for Fe and Sb are 0.12(1) and 0.10(1), respectively [results for the extrapolated background least squares being 0.12(1) and 0.12(1)]. Additionally, refinements were attempted where Sb was placed in an octahedral hole $(0, \frac{1}{2}, \frac{1}{2})$ and a tetrahedral hole $(0, \frac{1}{2}, \frac{1}{4})$. In each case the temperature factor of this interstitial was constrained to be equal to that of the Fe/Sb at (0, 0, 0). In both cases the occupancies could be refined to values not significantly different from zero [-0.02(1) and 0.00(1), respectively]. These results indicate that there is little bulk solubility of Sb in FeSbO₄ and that the Fe/Sb ratio is 1.

NEUTRON-DIFFRACTION DATA FOR FeSb₂O₆

Room-temperature time-of-flight (TOF) data were collected using the special-environment powder diffractometer (SEPD) at the intense pulsed-neutron source (IPNS) at Argonne National Laboratory at atmospheric pressure. A detailed description of the SEPD and IPNS has been published.¹² The sample was contained in a thin-walled seamless vanadium tube *ca*. ¹/₂ in. in diameter and 4 in. long capped with Al plugs. Data from *ca*. 2×10^6 pulses, collected over *ca*. 18 h, were used to analyse FeSb₂O₆. Data from the backscattering banks ($2\theta = 150^\circ$)

parameter	α -Sb ₂ O ₄	FeSbO ₄		
(A) constant-wavelength data				
space group	<i>Pna</i> $2_1, Z = 4$	$P4_2/mnm, Z = 2$		
cell parameters (Å)				
a	5.441 (2)	4.6365 (6)		
b	4.800(1)	4.6365 (6)		
С	11.766 (3)	3.0742 (6)		
V	307.72	66.09		
half-width parameters ^a				
U	2.22	0.95		
V	-1.13	-0.34		
W	0.61	0.49		
final agreement factors				
R _{wp}	5.42%	_		
R	7.05%			
$R_{\rm exp}^{\nu}$	1.77%	_		
R _{Bragg}	2.33% (349 reflections)	2.49% (49 reflections)		
	(B) time-of-flight data ^{b}			
cell parameters (Å)				
a	5.440 (2)	4.640 (1)		
b	4.809 (1)	4.640 (1)		
С	11.755 (3)	3.077 (2)		
V	307.53 (8)	66.24 (4)		
final agreement factors				
R _{wp}	8.41%			
$R_{\rm p}^{"P}$	5.80%			
$R_{\rm exp}^{\prime}$	2.99%			

Table 1. Final parameters for the multiphase refinements of $FeSbO_4$ and α -Sb₂O₄

^a FWHM**2 = $U \tan^2 \theta + V \tan \theta + W$. ^b Time of flight (in μ s) = 7569.58 $d - 2.99 d^2 - 9.92$; maximum 19 ms, minimum 6150 μ s.

with a minimum time of flight of 6150 μ s ($d_{\min} \approx 0.81$ Å) and a maximum time of flight of 19 ms were used in the least-squares refinement. A Rietveld-type analysis adopted for time-of-flight data with multiphase capabilities was used.¹³ A contribution of 0.001 or greater of the maximum of any Bragg peak was included in the calculation of the profile. Starting parameters for both compounds were taken from the data-analysis procedure described above for $FeSb_5O_{12}$. During all the least-squares refinements described below, positional parameters for the α -Sb₂O₄ were held fixed. This was dictated by the small size of the Bragg peaks of Sb₂O₄ as compared with those of $FeSbO_4$ (see fig. 2). Parameters refined were as follows: three background parameters (YBK = BK1 + BK2 * EXP[-BK3 * d]), one adsorbtion parameter (A = 1/[1 + ABS * d]), two peak-shape parameters for each phase, a scale factor for each phase, cell constants (three for orthorhombic antimony oxide, two for tetragonal iron antimonate), two isotropic temperature factors for each of the two phases (one for each of the two kinds of atoms and/or positions) and the x parameter for the oxygen at (x, x, 0) in FeSbO₄. Additionally, in two separate refinements an Sb atom was placed in a tetrahedral and octahedral hole in FeSbO₄, the isotropic temperature factor was fixed to be identical to that of the Fe/Sb at (0, 0, 0) and the occupancy was allowed to vary. The final values for the occupancies were 0.00(1) and -0.01(1), respectively. This establishes that there is little solubility of Sb in the



Fig. 1. Experimental constant-wavelength neutron data (points) and calculated profile (line) for $FeSb_5O_{12}$ from the Missouri research reactor. A difference plot is given below. Tick marks indicate the position of Bragg peaks for both phases (FeSbO₄ and α -Sb₂O₄).

intersticies in iron antimonate for this composition. The experimental data, calculated diffractogram and difference plot are presented in fig. 2. As for the data for $FeSb_5O_{12}$, all observed Bragg peaks can be accounted for by the presence of two phases, $FeSbO_4$ and α -Sb₂O₄.

COMPARISONS OF THE NEUTRON REFINEMENTS

Fig. 1 and 2 display the raw data and calculated profiles for the two systems refined. Comparisons of the model parameters from the two refinements for FeSbO₄ are excellent. The thermal parameters [0.65(10) and 0.69(10) for Fe/Sb and O, respectively, for FeSb₅O₁₂, as against 0.4(5) and 0.4(6) for FeSb₂O₆] compare favourably, and values of the only structural parameter, x (x, x, 0), for the O atom are also identical [0.3055(6) and 0.3053(16) for FeSb₅O_x and FeSb₂O_x, respectively].

Final fractional coordinates for α -Sb₂O₄ (from refinements of the constant-wavelength data for FeSbO₄/2Sb₂O₄) are presented in table 2 and a list of distances and angles in table 3. Scattering lengths for Fe, Sb and O were 0.95, 0.56 and 0.575 Å, respectively.⁹ Refined cell constants for FeSbO₄ are a = 4.6365(6), c = 3.0742(6) Å and V = 66.09(1) Å³ (constantwavelength data) and a = 4.640(1) Å, c = 3.077(2) Å and V = 66.24(4) Å³ (time-of-flight data). Because all Bragg peaks are included in the unit-cell determinations (349 reflections for α -Sb₂O₄ and 49 for FeSbO₄) the resultant lattice parameters are very precisely determined. Consequently the excellent agreement between these results and those of Amador and Rasines¹⁰ [4.6388(2) Å, 3.0773(2) Å and 66.22 Å³, respectively, based on X-ray data] are not surprising. The slight differences are probably attributable to a small error in neutron wavelength for the reactor (constantwavelength) data. For α -Sb₂O₄ results here are a = 5.441(2) Å, b = 4.800(2) Å and c = 11.766(3) Å (reactor data on FeSb₅O₁₂), a = 5.441(1) Å, b = 4.808(1) Å and c = 11.755(3) Å (time-of-flight data on FeSb₂O₆). Cell constants from an earlier reported neutron powder-profile analysis are markedly different, a = 5.456(1) Å, b = 4.814(1) Å and c = 11.787(2) Å,¹¹ but are closer to results on ASTM card no. 11-694, a = 5.436 Å,



Fig. 2. Experimental time-of-flight neutron data (points) and calculated profile (line) from Argonne National Laboratory for $FeSb_2O_6$. A difference plot is given below. Tick marks indicate the position for Bragg peaks of $FeSbO_4$ only. Smaller peaks without tick marks are due entirely to the α -Sb₂O₄ phase.

Table 2. Final atom	ic parameters (fractional	$ $ coordinates) for α -Sb ₂ O	4
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atom	10 ³ x	10 ³ y	10 ³ z	B _{iso}
Sb(1)	-31(3)	31 (2)	-2^{a}	0.12 (10) ^b
Sb(2)	377 (3)	17 (4)	247 (3)	
O(1)	322 (2)	159 (4)	93 (2)	0.47 (12)
O(2)	152 (2)	717 (2)	192 (3)	_
O(3)	82 (3)	192 (2)	307 (2)	
O(4)	361 (2)	824 (3)	405 (2)	

^a The z coordinate of Sb(1) was fixed. ^b Temperature factors of like atoms were constrained to be identical.

b = 4.810 Å and c = 11.76 Å. The good match between our results for the two data sets discussed here and those of others indicates that the calibration of the instruments and the refinements are accurate. We consider the results here to be of the highest precision.

The raw time-of-flight neutron-diffraction data for $FeSbO_4/0.5 Sb_2O_4$ and the constantwavelength raw neutron-diffraction data for $FeSbO_4/2Sb_2O_4$ are available as Supplementary publication no. SUP 56190. See Notice to Authors, J. Chem. Soc., Faraday Trans. 1, 1985, 81(1).

1	6	9	9
	-	-	

$\mathrm{Sb}_{2}\mathrm{O}_{4}$	this work	ref. (11)
$Sb(1)-O(1)^{a}$	2.30 (2)	2.37
$Sb(1)-O(1)^{b}$	2.03 (2)	1.86
Sb(1)-O(3)	2.51 (3)	2.62
$Sb(1)-O(4)^a$	2.01 (2)	2.09
$Sb(1) - O(4)^{b}$	2.22 (2)	2.17
Sb(2)-O(1)	1.94 (2)	2.01
$Sb(2)-O(2)^a$	1.98 (2)	1.98
$Sb(2)-O(2)^{b}$	2.00 (2)	2.05
$Sb(2)-O(3)^{a}$	1.92 (3)	1.92
$Sb(2)-O(3)^{b}$	1.94 (2)	1.92
Sb(2)-O(4)	2.08 (4)	2.04
$\angle O(1)$ -Sb(1)-O(1)	82 (1)	82.5
$\angle O(1)^a$ -Sb(1)-O(4) ^a	146 (1)	145.6
$\angle O(1)^b$ -Sb(1)-O(4) ^b	74 (1)	89.2
$\angle O(1)^a$ -Sb(1)-O(4) ^a	72 (1)	66.8
$\angle O(1)^b$ -Sb(1)-O(4) ^a	88 (1)	78.6
∠O(4)Sb(2)O(1)	167 (1)	170.3
$\angle O(2)^{a}$ -Sb(2)-O(3) ^b	177 (1)	175.6
$\angle O(2)^b$ –Sb(2)–O(3) ^a	171 (1)	176.6
FeSbO₄ ^c	this work	ref. (10)
M–O ^b	1.996 (2)	1.960
$M-O^{b}$	2.005 (3)	2.066
weighted average	1.999 `´	1.995

Table 3. Selected distances (in Å) and angles (in °) in FeSbO₄ and Sb₂O₄, and comparisons with earlier work

^{*a*, *b*} Alternate crystallographic positions of chemically identified oxygen atoms. ^{*c*} M = Fe or Sb.

RESULTS

Structures of the individual phases have already been investigated, FeSbO₄ with powder X-ray diffraction⁹ and α -Sb₂O₄ with powder neutron diffraction,¹¹ so only a brief discussion will be given here.

 α -Sb₂O₄ is a layered compound in which corrigated sheets of edge-sharing Sb⁵⁺ octahedra are separated by Sb³⁺ layers with asymmetric oxygen coordination. The structure is represented in fig. 3. The octahedral Sb⁵⁺ coordination is quite symmetric and the Sb–O distances range from 1.92(2) to 2.08(2) Å, averaging 1.98(2) Å. The oxygen coordination about the Sb³⁺ atoms is very asymmetric, presumably owing to the lone-pair effect. These lone pairs line up in channels perpendicular to the [100] face. Sb–O distances for these Sb³⁺ ions range from 2.00(2) to 2.51(3) Å. As noted above in lattice-parameter comparisons, there are marked discrepancies between our model and that proposed earlier. Not surprisingly, comparison between the Sb–O distances listed here and those of others¹¹ are also at odds. These discrepancies are recorded in table 2. The excellent match between lattice parameters from two kinds of neutron sources (spallation source, time-of-flight data and nuclear reactor constant-wavelength data) and from two different samples reported here offers strong support for the precision of the model presented here.



Fig. 3. Stereographic ORTEP diagram displaying the [100] face of α -Sb₂O₄. Open spheres represent O atoms and filled spheres Sb atoms.

For FeSbO₄ the Fe and Sb atoms both occupy the special position (0, 0, 0); the lack of supercell reflections attests to the random nature of the Fe/Sb occupancy. The only structural parameter to be varied is the x position parameter of the lone unique oxygen atom [located at (x, x, 0)]. The results of our refinement yield a value of x different from that of the X-ray refinement [0.3055(6) and 0.3053(16) as against 0.318, respectively]. In the resultant model the MO₆ octahedran is more symmetric as compared with the X-ray model. Because of the near equality of neutron-scattering lengths of O, Fe, and Sb as compared with X-ray scattering form factors, the ability to model accurately a neutron-diffraction peak profile and the good agreement between our results on two systems from two neutron sources we believe the precisions of the neutron refinements are significantly higher.

Analysis of the diffraction data indicates that the only phases present are FeSbO₄ and α -Sb₂O₄. All diffraction peaks are accounted for by these phases. Specifically, there are no extra lines suggestive of a trirutile phase (with c' = 3c). Therefore, reports of the formation of a trirutile phase under these synthesis conditions are to be regarded with suspicion. Additionally, for each refinement that included nuclear density in the octahedral or tetrahedral holes in the FeSbO₄ structure, the occupancy of this intersticial was refined to a value not significantly different from zero. Based on this there is no evidence for the incorporation of an excess of Sb (or Fe) into the FeSbO₄ phase. The neutron-diffraction results also demonstrate that the Fe/Sb ratio is essentially 1 in FeSbO₄, even in the presence of an excess of Sb₂O₄. Therefore, the refinements have demonstrated that the presence of Sb₂O₄ has no effect on the bulk structure of iron antimonate.

Furthermore, the cell volumes of FeSbO₄ in FeSbO₄-2Sb₂O₄ calcined at 900 °C and FeSbO₄ in FeSbO₄-0.5Sb₂O₄ calcined at 800 °C are also virtually identical to each other and to that of pure FeSbO₄. This is further evidence that the presence of α -Sb₂O₄ (and variation in calcination temperature) have no effect on the bulk structure of iron antimonate. Further support for this argument is found in the excellent structural match between the FeSb₅O₁₂ and FeSb₂O₆ systems.

Despite the structural evidence presented above, we are faced with a preponderance of data that establish the need to have a coexistence of both phases (prepared simultaneously, not mixed after preparation) to achieve maximum catalytic performance.¹⁻⁷ Because there is no bulk structural modification, one is left with the possibility of surface modification of FeSbO₄ to correlate these data. These possible modifications fall into two general categories. Surface structure modification can occur, where an excess of Sb is incorporated into the FeSbO₄ crystal, perhaps forming islands with FeSb₂O₆ stoichiometry,² and/or Fe incorporation into the surface of α -Sb₂O₄. The second possibility leaves both structures unchanged but orients the Sb₂O₄ crystals on iron antimonate, allowing the phases to produce synergistically the desired oxidation product. As direct observation of either of these possibilities may not be possible we are left to draw inferences from existing data.

One such inference, the large difference in crystallite size as measured by the diffraction experiment and observed in the electron microscope, and the apparent coating of FeSbO₄ crystals with small Sb_2O_4 crystallites, has lead us to investigate the latter hypothesis. To this end we have employed two programs, MATCH1 and MATCH2,¹⁴ to investigate possible epitaxy between FeSbO₄ and Sb_2O_4 . MATCH1 generates two-dimensional crystallographic networks of the two compounds and searches for matches based on cell-dimension fits. MATCH2 takes the cell-matching information generated by MATCH1 and compares atomic positions in planes (motifs) for the two phases. Use of this software allows one to find planes of atoms in the two crystals that are suitably matched for epitaxial growth, looking for phase boundaries that minimize dislocation density and atom movement.

Applying this procedure to FeSbO₄ and α -Sb₂O₄, MATCH1 found many excellent lattice fits of crystallographic faces with low indices and low dislocation densities (< 10¹⁰ interfacial dislocations per cm²). Analysis of these networks with MATCH2





indicated that atoms on the [110] face of $FeSbO_4$ matched those of the [001] face of Sb_2O_4 . The [001] direction is perpendicular to the layers of Sb atoms described above. An outline of the Sb^v octahedral coordination layer is given in scheme 1 (metal atoms only). All distances are in angstroms and a unit-cell outline is shown. A similar outline of the [110] face of FeSbO₄ is given in scheme 2. The mismatch in distances is small (in the range 2.2–3.6%) and it is easy to envisage a coherent phase boundary between these faces. Based on this a schematic diagram of a possible active catalyst is given in scheme 3. For a three-step mechanism of propylene oxidation there are two possibilities for active sites:

$$CH_3 - CH = CH_2 \xrightarrow{Sb^{3*}} CH_2 - CH - CH_2 \text{ (allyl formation)}$$
(2)

$$CH_2 - CH - CH_2 \xrightarrow{Sb^{5^*}} CH_2 = CH - CHO (two step, 4e^- oxidation)$$
 (3)

$$Sb^{3+} + 2Fe^{3+} \longrightarrow 2Fe^{2+} + Sb^{5+}$$

$$\left. \begin{array}{c} (4) \\ (catalyst reoxidation) \end{array} \right\}$$

$$\left. \begin{array}{c} (5) \\ (5) \end{array} \right\}$$

There is a great deal of evidence that elements with lone pairs of electrons are needed to activate propylene and form the allylic intermediate. Bi_2O_3 is known to dimerize propylene selectively.¹⁵ Sb₂O₃ also displays a high selectivity to hexadiene formation from propylene.¹⁶ These facts implicate metalloids with free pairs of electrons not involved in M—O bonding as being crucial to allyl formation, an intermediate widely held to be important in propylene oxidation.¹⁷ Metals in their highest oxidation states are well suited for O insertion. The resulting reduction of the metal (Mo⁶⁺ to Mo⁴⁺ in molybdates and Sb⁵⁺ to Sb³⁺ in atimonates) is chemically reasonable. Evidence in support of this is more plentiful for molybdenum oxides [*e.g.* MoO₃ oxidizes methanol to formaldehyde (with Fe)¹⁸ and allyl radicals to acrolien¹⁹] than antimonates as there are, strictly speaking, no 'pure' Sb⁵⁺ oxides. However, we ascribe the role of oxidation (or O insertion) to Sb⁵⁺. One function of the FeSbO₄ crystal may be in

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active-site reconstruction (catalyst reoxidation). The facile redox couple $(Fe^{3+}+e^- \rightarrow Fe^{2+})$ would facilitate O_2 chemisorption with the FeSbO₄ acting as the oxidant for the reduced Sb₂O₄. This would require some reduction of Fe³⁺ to Fe²⁺ on a working catalyst (as has been observed²⁰). Note also that for the scheme above, the [001] face of the Sb₂O₄ crystal would not be suitable for an active site, as only Sb⁵⁺ or Sb³⁺ (but not both) are exposed on this face. Faces that present both Sb oxidation states of Sb are the [100] and [010] faces (indicated by A and B in scheme 3). These crystal faces would then most likely contain the sites of catalytic activity. Oriented crystals of Sb₂O₄ have been implicated in propylene oxidation catalysis in other systems.¹

The second possibility for an active-site model is at the interface between the two phases. At a coherent interface between [110] of $FeSbO_4$ and [001] of Sb_2O_4 , the local stoichiometry is Sb/Fe = 3, with Sb⁵⁺, Sb³⁺, Fe³⁺ and Fe²⁺ present. In short, these coherent phase boundaries would contain all the necessary elements for olefin oxidation.

Alternate possibilities for active sites include shear planes and intergrowth regions in either of the individual phases. The latter possibility appears to be ruled out based on the well defined crystallography of the system. The existence of shear planes (or zones) cannot be excluded on the basis of the crystal data if they are non-periodic and/or have a very large (ca. 40 Å) periodicity. If the periodicity is very large, however, the impact of such line defects upon catalytic activity (the number of active sites) would be small. Numerous non-periodic shear planes would give rise to diffuse scattering which may not be obvious in powder studies, hence the possibility of their existence cannot be excluded. High-resolution electron-microscopy studies are needed to clarify this hypothesis.

CONCLUSIONS

We have performed structure refinements of the two-phase (FeSbO₄-Sb₂O₄) system with powder neutron-diffraction data. Based on the results of these structure refinements we conclude the following. Under the synthesis conditions employed no trirutile phase (FeSb₂O_x or Fe₂Sb₂O_x) is observed and the Fe/Sb occupancy in FeSbO₄ is entirely random and uniform. The effect of an excess of Sb₂O₄ and calcination temperature on bulk FeSbO₄ is negligible. Specifically, there is no lattice expansion, contraction or incorporation of an excess of Sb into iron antimonate. Assuming oxidation states of Fe³⁺ and Sb⁵⁺ there is no oxygen or metal deficiency in bulk FeSbO₄.

Based on the conclusions arrived at above, the enhancement of selective oxidative catalytic activity of the two phases over that of the individual components is necessarily due to surface modification (possibly mutual) of the two phases and/or a phase cooperation effect. We (and others) have proposed a model whereby α -Sb₂O₄ crystallites are oriented on the surface of FeSbO₄ and thereby create catalytically active sites not found in either of the isolated phases. Whether the active sites are at the phase interface or nearby on chemically modified single phases is impossible to determine given the experimental data presently available. That Sb can be found in excess in a surface layer of FeSbO₄ has already been suggested.^{2, 3} Recent observations that small amounts of vanadium²¹ or molybdenum²² can exist in solid solution with Sb₂O₄ (triggering the α to β transition) raises the intriguing possibility that surface modification of Sb₂O₄ (Fe dissolution) can confer increased oxidation catalytic activity on this phase. At any rate it may be a moot point to ascribe oxidation activity to a single phase in this system, as it is clear that a coexistence of both α -Sb₂O₄ and FeSbO₄ is necessary for optimum catalytic activity.

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