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Investigations of Solid State Properties of Vanadium–Antimony Oxide Catalysts

Although a number of mixed oxides have been developed as catalysts for the oxidation of hydrocarbons, surprisingly few details of the fundamental chemical and structural properties of many of these materials have been established (*1*). Vanadium–antimony oxides appear to fall within such a category since, despite their catalytic properties (*2–5*), the vanadium–antimony–oxygen system has been subjected to only limited examination (*6–11*) with the nature of a compound corresponding to the name "vanadium antimonate" of formula "$VSbO_4$" having been the matter of some uncertainty (*6–9, 11*). However, during our recent investigations of the solid state reaction between vanadium(V) oxide and antimony(III) oxide we have shown (*12, 13*) that the course of the reaction and the nature of the rutile-type vanadium antimonate phase is critically dependent on the reaction conditions and the presence of oxygen. The results showed that a single-phase homogeneously oxidised material, $V_{1-y}Sb_{1-y}O_4$ ($0 < y < 0.1$), is formed in air whilst a biphasic product containing antimony-deficient vanadium antimonate, $VSb_{1-y}O_{4-2y}$ ($0 < y < 0.1$), and antimony tetroxide is produced in commercial nitrogen, and that a monophasic material, $VSb_{1-y}O_{4-\frac{3}{2}y}$ ($0 < y < 0.1$), is formed only under strictly oxygen-free conditions. We have also investigated (*14*) the structural properties of some of these phases, the changes induced by thermolysis, and the relationships between the various components in the system.

We report here on some subsequent investigations of vanadium–antimony oxides prepared according to methods described in the patent literature (*2*). A suspension of powdered antimony metal (24.6 g) was boiled in stirred concentrated (69–71%) nitric acid (118 cm^3), cooled, and added to ammonium metavanadate (9.2 g) in 1% hydrochloric acid. The mixture was evaporated, the residue dried (150°C, 16 h) in air, and finally calcined at 650 or 820°C (Table 1). Materials to be used as catalysts were wetted with ethanol and supported on glass beads. The catalysts were packed to a depth of 10 cm within a quartz-glass microreactor of 5 mm internal diameter, dried (70°C, 12 h) in air, supported in a Carbolite oven, and treated at 400 or 450°C with a flowing gaseous mixture (by volume) of 4% propene, 20% oxygen, and 76% nitrogen. The products were analysed with a Pye-Unicam 104 gas–liquid chromatograph fitted with a flame ionisation detector. Powder X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu*Kα* radiation. ESR spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz. Scanning electron microscopy was performed with a Cambridge S4 Stereoscan instrument and electron probe microanalysis recorded with an energy dispersive X-ray detector interfaced with the Stereoscan microscope.

Analysis of the X-ray diffraction patterns showed the unused catalysts to be biphasic materials containing vanadium antimonate and antimony tetroxide (Table 1). The formation of a discrete antimony oxide phase reflects the presence of excess antimony in the catalyst preparation. The sharper peaks in the X-ray diffraction patterns of the products formed at 820°C is indicative of the enhanced crystallinity of the catalysts prepared at higher temperature.

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TABLE 1

Phase Compositions of Vanadium–Antimony Oxide Catalysts

Catalyst	Thermal treatment	Phase composition
A	650°C/air/8 h	Vanadium antimonate and ca. 11% α-Sb_2O_4
B		
(i)	820°C/air/4 h	β-Sb_2O_4 and ca. 35–25% vanadium antimonate
(ii)	8 h	
(iii)	24 h	

The appearance of the β-modification of antimony tetroxide in the catalyst produced at 820°C is consistent with the formation (*12, 13*) of this polymorph at a similarly unusually low temperature during the preparation of vanadium antimonate from antimony(III) oxide and vanadium(V) oxide. The material was subsequently described (*14*) as a solid solution of ca. 5% vanadium in β-Sb_2O_4 and its low temperature stabilisation associated with the presence of incorporated vanadium. The larger concentration of the antimony tetroxide phase in the catalyst prepared at 820°C as compared with that formed at 650°C is consistent with the partial decomposition of vanadium antimonate into "β-Sb_2O_4" which occurs (*14*) at temperatures exceeding 800°C. It is clear therefore that vanadium antimonate catalysts prepared at the different temperatures reported in the patent literature (*2*) have distinctly different phase compositions which reflect the influence of thermal conditions on the formation and stability of phases in the vanadium–antimony–oxygen system.

The X-ray diffraction data for the vanadium antimonate phases were indexed according to a tetragonal unit cell and were characteristic of rutile-type solids with unit cell parameters (Table 2) similar to those reported (*11, 13*) for oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$. The ESR spectrum recorded from the catalyst prepared at 650°C was similar to that attributed to vanadium(IV) in oxidised vanadium antimonate (*15*) and other materials which contain vanadium(IV) (*16, 17*). The ESR spectra recorded from the catalysts prepared at 820°C showed broader signals which were more similar to those of vanadium(IV) in vanadium(IV) oxide and the compound $VOSb_2O_4$. Since X-ray diffraction failed to provide evidence for the existence of any reduced vanadium oxide phases in the vanadium–antimony oxide catalysts and ESR failed to detect vanadium(IV) in the vanadium-containing "β-Sb_2O_4", it seems that the X-ray diffraction data and ESR spectra recorded from the biphasic catalysts are consistent with the presence of oxidised vanadium antimonate. Given the presence of antimony(V) in the rutile-type phase (*11*), the oxidised vanadium antimonate which is formed in the catalysts may be described by the formulation (*11, 15*) $V(III)_{1-9y}V(IV)_{8y}Sb(V)_{1-y}O_4$. Hence the catalysts, although biphasic, are not analogous to other biphasic products which have been identified (*13*) in the vanadium–antimony–oxygen system during investigations of reactions between antimony(III) oxide and vanadium(V) oxide in commercial nitrogen and which contain the nonstoichiometric rutile-type phase of composition $VSb_{1-y}O_{4-2y}$ which does not contain vanadium(IV) (*15*). In this respect it is pertinent to record that a vanadium–antimony oxide prepared according to the patent literature but calcined in nitrogen gave a biphasic product containing vanadium antimonate and ca. 30% α-Sb_2O_4 which failed to give an ESR spectrum characteristic of vanadium(IV) in oxidised vanadium antimonate. The lattice parameters of the rutile-type phase in this catalyst

TABLE 2

Unit Cell Parameters (Å) of Vanadium Antimonate Phases in Vanadium–Antimony Oxide Catalysts

Catalyst	$a = b$	c
A	4.64 ± 0.01	3.03 ± 0.01
B		
(i)	4.60 ± 0.02	3.04 ± 0.01
(ii)	4.60 ± 0.01	3.05 ± 0.02
(iii)	4.61 ± 0.01	3.06 ± 0.02

prepared in nitrogen $a = b = 4.58 \pm 0.01$ Å, $c = 3.07 \pm 0.02$ Å were more similar to those of the vanadium antimonate of composition $VSb_{1-y}O_{4-2y}$. The results suggest that the nature of the vanadium antimonate in a material prepared according to the patent literature but heated in nitrogen is more similar to the product obtained by calcination of antimony(III) oxide and vanadium(V) oxide under similar anaerobic conditions than to the catalyst prepared by calcination in air. Hence the composition of the vanadium antimonate phase in the catalyst appears to be critically dependent on the gaseous environment in which the catalyst is calcined.

Examination of the vanadium–antimony oxide catalysts prepared at 820°C by scanning electron microscopy and electron probe microanalysis revealed the presence of large hexagonal "β-Sb_2O_4" plate-type crystals containing some vanadium (Fig. 1), similar to those described (*14*) as solid solutions of ca. 5% vanadium in β-Sb_2O_4, together with a considerable quantity of needle-shaped crystals similar to those previously identified as vanadium antimonate (*14*). Thus the morphology of the catalyst formed at high temperature also resembles that of materials prepared from solid state reactions between antimony(III) oxide and small quantities of vanadium(V) oxide at similar temperatures (*14*).

The X-ray diffraction patterns recorded from catalysts prepared at 650°C and subsequently treated at 400 and 450°C in the propene–oxygen–nitrogen gas stream were similar to those obtained from the unused materials except for the appearance of a small quantity of β-Sb_2O_4. Analogous changes were observed when the catalyst prepared in nitrogen was exposed to the oxygen–propene–nitrogen gas stream at 400°C. Similar changes have been reported (*18*) to occur in a catalyst composed of iron antimonate and β-Sb_2O_4 when used for the

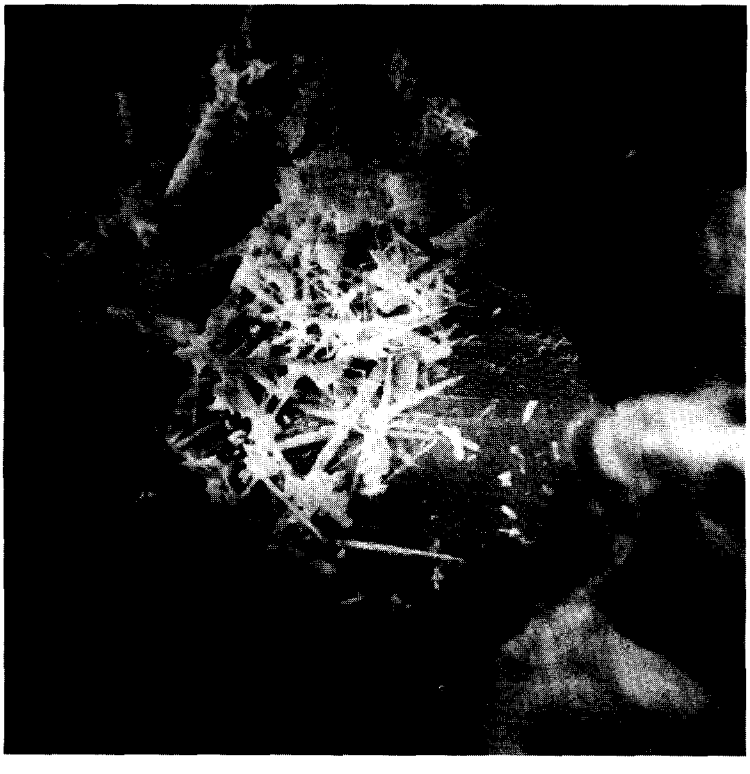

FIG. 1. Vanadium–antimony oxide catalyst, calcined at 820°C for 24 h in air. Magnification: 1900.

oxidation of propene in the absence of oxygen and have been associated (*18*) with the reduction of the rutile-type iron antimonate phase. In this respect it is relevant that, following its use in the catalytic reaction, the vanadium–antimony oxide catalyst containing oxidised vanadium antimonate gave an ESR spectrum showing a diminution of the vanadium(IV) signal and similar to that recorded when the catalyst was reduced in hydrogen at 300°C. The results are therefore consistent with the reduction of the catalyst during the catalytic reaction and, more specifically, with the reduction of vanadium(IV) in the oxidised vanadium antimonate phase.

The vanadium–antimony oxide catalyst calcined at 820°C for 24 h gave, after treatment in the propene–oxygen–nitrogen gas stream, X-ray diffraction patterns in which no discernable changes could be identified. Given the presence of β-Sb_2O_4 as the major component of this catalyst it is not unreasonable that any small scale transformation of the rutile-type phase to β-Sb_2O_4, as observed after exposure of the catalyst formed at low temperature to the catalytic reaction, would be undetected by this technique. Indeed, scanning electron microscopy and electron probe microanalysis also showed that the catalyst prepared at 820°C was unchanged during the catalytic process (Fig. 2). A similar resistance to change was observed when the catalyst was treated with hydrogen at 300°C. However, examination by ESR showed the signal characteristic of vanadium(IV) in the oxidised vanadium antimonate component of the biphasic catalyst formed at 820°C to be lost when the catalyst was treated in the propene–oxygen–nitrogen gas stream and in hydrogen. The results are similar to those recorded from the catalyst formed at low temperature and are consistent with the reduction of the rutile-type phase during the catalytic reaction.

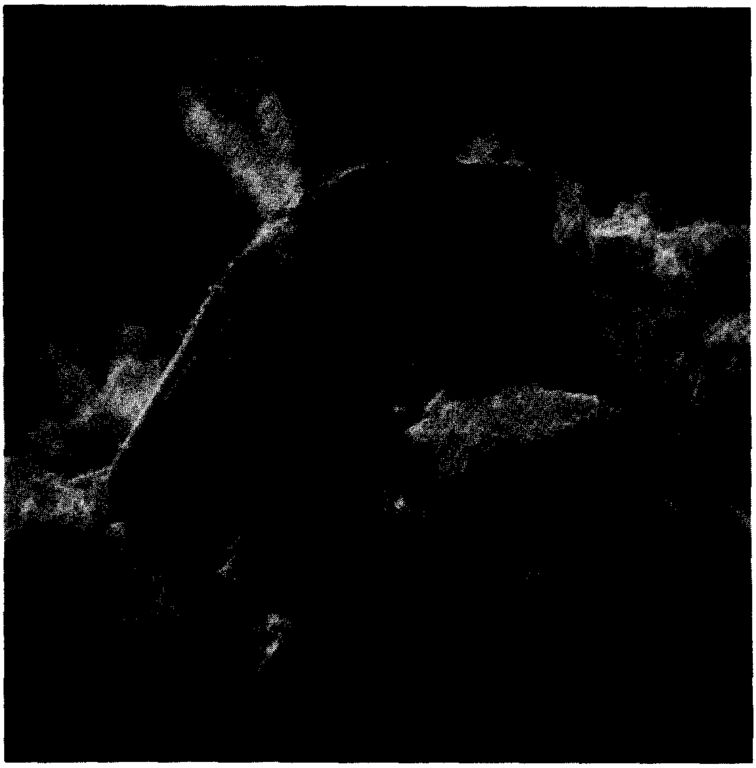

FIG. 2. Vanadium–antimony oxide catalyst, calcined at 820°C for 24 h in air, following treatment with propene–oxygen–nitrogen at 400°C. Magnification: 1900.

It seems therefore that the biphasic vanadium–antimony oxide catalysts formed at both low and high temperatures suffer reduction during the catalytic reaction which is mainly associated with the reduction of the oxidised vanadium antimonate phase. The results are quite consistent with the involvement of oxygen from the lattice of the vanadium antimonate phase during the oxidation reaction as envisaged (*1*) to occur when other mixed oxide catalysts have been used for the selective oxidation of hydrocarbons. In this respect it is also relevant to record that both oxidised vanadium antimonate, prepared by methods described previously (*13*), and the catalyst prepared at 650°C during the work reported here, lost weight (ca. 3.5%) when heated at 750°C for 24 h in nitrogen and gave ESR spectra showing the loss of vanadium(IV). These results are also consistent with reduction of the oxidised vanadium antimonate phase and are compatible with its potential properties as an oxidation catalyst.

Some preliminary qualitative studies by glc of the catalytic behavior of the vanadium–antimony oxides indicated that the catalyst prepared at 650°C containing oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$, with ca. 11% α-antimony tetroxide had the highest selectivity to acrolein from the oxidation of propene at 450°C. However, monophasic oxidised vanadium antimonate, prepared by the solid state reaction of antimony(III) oxide and vanadium(V) oxide in air (*13*), gave a mixture of organic compounds from the propene–oxygen–nitrogen gas stream whilst α-antimony tetroxide failed to give a significant amount of organic product. This qualitative indication that the selectivity of the catalyst is related to its biphasic nature is similar to observations reported (*18*) from investigations of an iron–antimony oxide catalyst containing iron antimonate and α-Sb_2O_4.

It is also interesting to note that the biphasic catalyst containing a reduced form of the antimony deficient vanadium antimonate, $VSb_{1-y}O_{4-2y}$, and ca. 10% α-Sb_2O_4 prepared in commercial nitrogen (*13*) also showed inferior selectivity at 450°C. Hence it would seem that the presence of the oxidised vanadium antimonate phase, $V_{1-y}Sb_{1-y}O_4$, containing vanadium(IV) which is formed in the biphasic catalysts prepared according to the patent literature is also significant in determining the nature of the products from the catalytic reaction.

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REFERENCES

1. Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York/London, 1974.
2. Brit. Pat. 1336136.
3. Brit. Pat. 1377211.
4. Brit. Pat. 1324693.
5. Brit. Pat. 1363455.
6. Vernon, L. W., and Milligan, W. O., *Tex. J. Sci.* 82 (1951).
7. Roth, R. S., and Waring, J. L., *Amer. Mineral.* **48**, 1348 (1963).
8. Renaud, R., *Rev. Chim. Miner.* **8**, 633 (1971).
9. Schuer, H., and Klemm, W., *Z. Anorg. Allg. Chem.* **395**, 287 (1973).
10. Darriet, D., Bovin, J.-O., and Galy, J., *J. Solid State Chem.* **19**, 205 (1976).
11. Birchall, T., and Sleight, A. W., *Inorg. Chem.* **15**, 868 (1976).
12. Berry, F. J., Brett, M. E., and Patterson, W. R., *J. Chem. Soc. Chem. Commun.* 695 (1982).
13. Berry, F. J., Brett, M. E., and Patterson, W. R., *J. Chem. Soc. Dalton Trans.* 9 (1983).
14. Berry, F. J., Brett, M. E., and Patterson, W. R., *J. Chem. Soc. Dalton Trans.* 13 (1983).
15. Berry, F. J., and Brett, M. E., *Inorg. Chim. Acta* **76**, L205 (1983).
16. Kasai, P. H., *Phys. Lett.* **7**, 5 (1963).
17. Faber, R. J., and Rogers, M. T., *J. Amer. Chem. Soc.* **81**, 1849 (1959).
18. Fattore, V., Fuhrman, Z. A., Manara, G., and Notari, B., *J. Catal.* **37**, 223 (1975).

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