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An Electron Spin Resonance Investigation of the Vanadium–Antimony–Oxygen System

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The various phases which may be formed in the vanadium-antimony-oxygen system by different reparative methods have been examined by e.s.r. to elucidate the nature of the cationic oxidation states. Oxidised vanadium antimonates of formula $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$ and the compound of composition $VOSb_2O_4$ give e.s.r. spectra indicative of the presence of vanadium(IV) whilst vanadium antimonates prepared in nitrogen of formula $VSb_{1-y}O_{4-3/2y}$ and $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$ appear to contain vanadium(III).

Introduction

Although materials described as '$VSbO_4$' have been reported [1–4] to result from the solid state reaction between equimolar quantities of vanadium(V) oxide and antimony(III) oxide, subsequent investigations [5] have cast doubt on the stoichiometry of the compounds. We have recently shown [6, 7] that the nature of these products is critically dependent upon the reaction conditions such that a single phase homogeneously oxidised material, $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$, is formed from the reaction in air whilst a biphasic product containing antimony deficient vanadium antimonate, $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$, and diantimony tetraoxide is produced in commercial nitrogen, and a monophasic material, $VSb_{1-y}O_{4-3/2y}$ $(0 < y < 0.1)$, is formed under strictly oxygen free conditions.

The nature of the cationic oxidation states is also a matter of uncertainty and, despite magnetic susceptibility studies [4] showing the absence of vanadium(V) and antimony-121 Mossbauer spectroscopy [5] revealing the presence of antimony(V) in an antimony deficient vanadium antimonate, the characterisation of the cationic species has been given sparse attention. Furthermore, although the synthesis of vanadium antimonate catalysts from aqueous media has been reported in the patent literature [8], their phase compositions and the nature of the cationic oxidation states, which are both matters of potential relevance to their catalytic properties for hydrocarbon oxidation, do not appear to have been investigated. It is also relevant to note the report [9] of a different vanadium-antimony oxide of formula $VOSb_2O_4$ which has been formed from solid state reactions between a variety of vanadium- and antimony-oxides.

Electron spin resonance is a powerful technique by which paramagnetic cationic species in these materials may be examined and we report here on the investigation of the cationic oxidation states by this method.

Experimental

Vanadium antimonates of composition $V_{1-y}Sb_{1-y}O_4$, $VSb_{1-y}O_{4-3/2y}$ and $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$ were prepared from vanadium(V) oxide and antimony(III) oxide [6, 7]. The vanadium antimonate catalysts were synthesised according to the patent preparation [8] and calcined in air at either 650 °C or 820 °C for 8 hours. The compound of formula $VOSb_2O_4$ was synthesised from the reaction between vanadium(IV) oxide and antimony(III) oxide according to the method described in the literature [9].

X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation. E.s.r. spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz and g-values were measured relative to DPPH (diphenylpicrylhydrazyl, $g = 2.0036$).

Results and Discussion

The oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$, gave an e.s.r. spectrum (Fig. 1) centred on $g \approx 2$ which does not correspond to the signal attributed to animony(IV) [10] but which resembles that

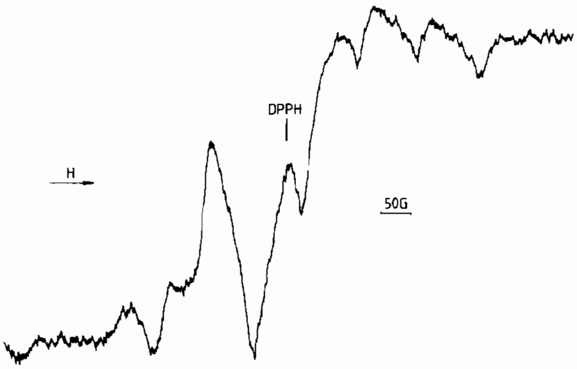

Fig. 1. E.s.r. spectrum recorded from oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$.

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reported for low concentrations of vanadium(IV) in tin(IV) oxide [11] and oxovanadium(IV) adsorbed onto ion exchange materials [12]. The detection of vanadium(IV) in the oxidised vanadium antimonate is, at least partially, consistent with its formulation [5] as $V(III)_{1-9x}V(IV)_{8x}Sb(V)_{1-x}O_4$. In contrast, the vanadium antimonates formed from the reaction between vanadium(V) oxide and antimony(III) oxide in nitrogen with compositions $VSb_{1-y}O_{4-3/2y}$ and $VSb_{1-y}O_{4-2y}$ failed to produce e.s.r. spectra. Given the sensitivity of e.s.r. to low concentrations of vanadium(IV) [11], the magnetic susceptibility evidence for the absence of vanadium(V) [4], and the detection by Mossbauer spectroscopy of antimony(V) in these materials [5], it seems reasonable to suggest that vanadium is present as vanadium(III) which, although paramagnetic, is only observed by e.s.r. at low temperatures [13, 14]. The result is therefore not consistent with the formulation $V(III)_{1-y}$-$V(IV)_{2y}Sb(V)_{1-y}O_4$ which has been proposed [5] for similar antimony deficient rutile-type vanadium antimonates which are formed with diantimony tetraoxide in evacuated sealed tubes and which have been described as solid solutions of vanadium(IV) oxide in vanadium antimonate. It seems therefore that the non-stoichiometric vanadium antimonates prepared in nitrogen contain vanadium(III) and antimony(V) whilst homogeneous oxidation which occurs during the reaction between vanadium(V) oxide and antimony(III) oxide in air gives rise to the formation of vanadium(IV).

The vanadium antimonates prepared according to the method described in the patent lieterature [8] were shown by X-ray diffraction to contain vanadium antimonate and diantimony tetraoxide. The presence of Sb_2O_4 is presumably a reflection of the excess antimony used in the preparation. The material calcined at 650 °C gave an e.s.r. spectrum characteristic of vanadium(IV) [11, 12] and similar to that recorded from oxidised vanadium antimonate, $V_{1-y}Sb_{1-y}O_4$. The observation is therefore consistent with the formation of oxidised vanadium antimonate by calcination in air (*vide supra*). However, the material calcined at 820 °C gave a broad line e.s.r. signal, $g = 1.95 \pm 0.01$, which, although different from the signal observed for vanadium(IV) in oxidised vanadium antimonate, resembles that recorded from vanadium(IV) oxide. Hence, rutile-type vanadium antimonates formed according to the patent literature [8] appear to be oxidised and contain vanadium(IV).

The e.s.r. spectrum recorded from the compound $VOSb_2O_4$ consisted of a single broad resonance, $g = 1.97 \pm 0.01$, similar to that recorded from vanadium(IV) oxide and the vanadium antimonate catalyst formed at 820 °C in air. Hence, the e.s.r. spectrum confirms the description [9], based on magnetic data, of the material in terms of $(SbO_2)_n^{n-}$ chains linked by oxovanadium(IV) ions.

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