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The formation of metal antimonates by mechanical milling and the conversion of α-Sb_2O_4 to β-Sb_2O_4

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The mechanical milling of α-Fe_2O_3 or V_2O_5 with Sb_2O_3 results in the formation of small particle $FeSbO_4$ or $VSbO_4$. Milling also induces the conversion of cubic Sb_2O_3 to the orthorhombic modification and the transformation of α-Sb_2O_4 to β-Sb_2O_4. The milling-induced α- to β-Sb_2O_4 phase transition is even more facile in the presence of vanadium or iron.

1. Introduction

Metal antimonates have been known for many years, for example, iron antimonate of composition $FeSbO_4$ was first reported [1] in 1943 during an investigation of rutile-related solids of composition ABO_4, and $VSbO_4$ was characterised [2] in 1951. The materials have normally been prepared by high temperature calcination of Sb_2O_3 with either α-Fe_2O_3 or V_2O_5, or by the calcination of precipitates containing the elements at elevated temperatures. The fundamental properties of the materials have attracted a steady degree of attention over the past fifty years with, for example, the structural properties normally being associated with a random distribution of the cations over the cationic sites in oxygen octahedra. However, subsequent studies have shown that the materials are more complex in nature than previously thought. For example, convergent beam electron diffraction [3] has shown that iron and antimony in iron antimonate are ordered in a triple rutile-related structure and that the degree of order, as well as the nature of cationic oxidation states, depends on the method of preparation [4]. The materials have also attracted interest because of their activity as catalysts for hydrocarbon oxidation [5–8] but new applications now seem possible given recent reports [9] which have described their potential for gas sensing applications. One of the disadvantages of the high calcination temperatures involved in the conventional synthetic routes is that they produce large particles with low surface areas. The need to prepare high surface area materials is reflected in the development of sol-gel [10], slurry [11, 12], and precipitation [13] methods for the synthesis of those materials. Mechanical methods to spread antimony oxide on titania surfaces have been reported [14] and catalysts have been prepared from ball milled mixtures of titanium dioxide, vanadium pentoxide and antinomy trioxide [15]. We report here on the formation of small particle metal antimonates by mechanical milling of iron- or vanadium-oxides with antimony oxides.

2. Experimental

Mixtures of α-Fe_2O_3 or V_2O_5 and Sb_2O_3 with a transition metal to antimony ratio of 1:1 were dry milled in a Retsch PM400 planetary ball mill using stainless steel vials (250 ml) and balls at 200 rpm. The powder to ball weight ratio was 1:20.

X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using Cu K_α radiation.

3. Results and discussion

3.1. Iron antimonate

The X-ray powder diffraction patterns recorded from the mixture of α-Fe_2O_3 and Sb_2O_3 following mechanical milling in air for various periods of time are collected in Fig. 1.

The X-ray powder diffraction pattern recorded from the unmilled mixture showed it to contain corundum-related α-Fe_2O_3 and the senarmontite phase of Sb_2O_3. Milling for 3 h showed the onset of conversion of senarmontite to the valentinite modification of Sb_2O_3. The observation is interesting because senarmontite has long been known [16] to be the stable form of Sb_2O_3 at temperatures below 570°C. In separate experiments (Fig. 2) we found that the cubic senarmontite form of Sb_2O_3 was completely converted to the orthorhombic valentinite form of Sb_2O_3 by mechanical milling in air for only 6 h. No evidence was found for oxidation to Sb_2O_4 even after 250 h of milling.

Both results demonstrate that milling is a facile means of inducing phase transitions in Sb_2O_3. X-ray powder diffraction showed that continued milling of

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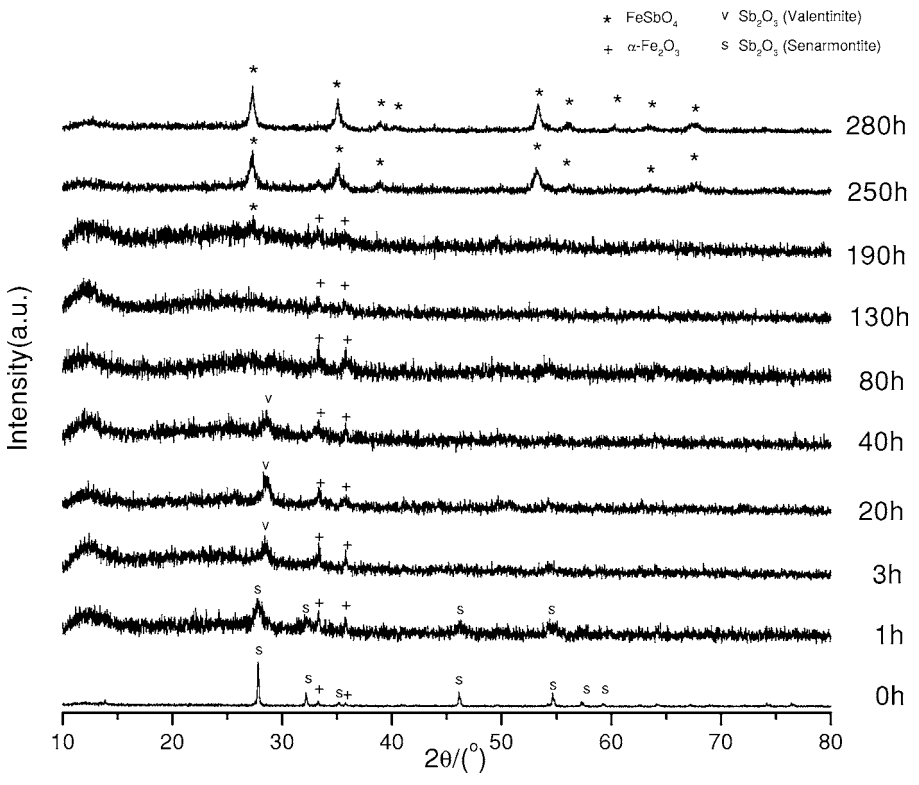

Figure 1 X-ray powder diffraction patterns recorded from a mixture of α-Fe_2O_3 and Sb_2O_3 following mechanical milling for various periods of time.

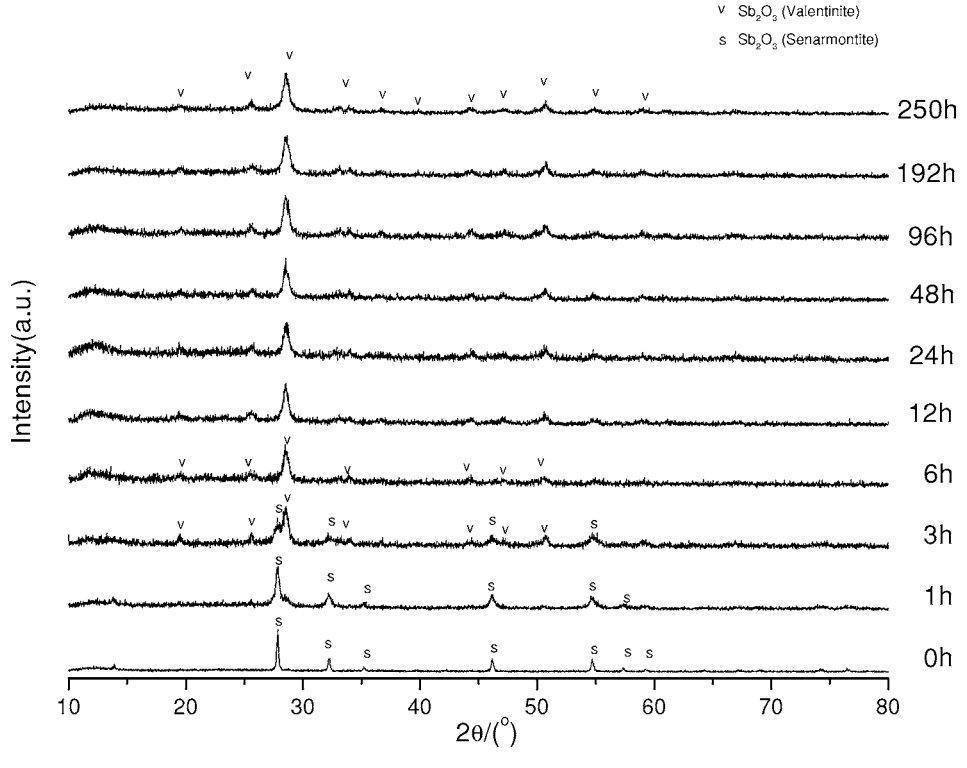

Figure 2 X-ray powder diffraction patterns showing the conversion of the senarmontite form of Sb_2O_3 to the valentinite form of Sb_2O_3 by mechanical milling.

the mixture of α-Fe_2O_3 and Sb_2O_3 (Fig. 1) resulted in a broadening of the diffraction peaks and, after 80 h of milling, the formation of a nearly amorphous material. After 190 h of milling the mixture gave an X-ray powder diffraction pattern which showed the development of a peak at 27.27° 2θ characteristic of $FeSbO_4$. Further milling gave rise to more peaks with intensities which increased with further milling consistent with particle growth and crystallisation and, after 280 h, $FeSbO_4$ with a particle size estimated by the Scherrer method from the diffraction peak width of ca. 20 nm was observed. This contrasts with a particle size of ca. 40 nm when $FeSbO_4$ was formed by heating a mixture of α-Fe_2O_3 and Sb_2O_3 in air at 900°C (56 h), cooling to room temperature and grinding in a pestle and mortar before heating in air at 1000°C (48 h).

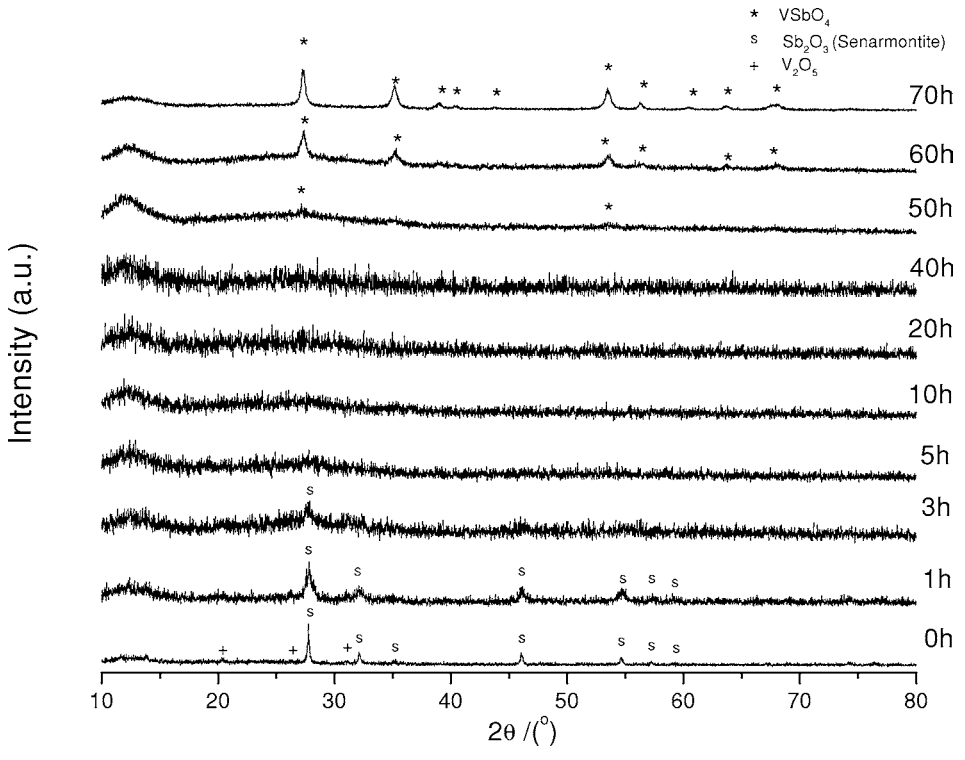

Figure 3 X-ray powder diffraction patterns recorded from a mixture of V_2O_5 and Sb_2O_3 following mechanical milling for various periods of time.

3.2. Vanadium antimonate

The X-ray powder diffraction patterns recorded from the mixture of V_2O_5 and Sb_2O_3 following mechanical milling in air for various periods of time are collected in Fig. 3.

The results showed the diffraction peaks to broaden as the duration of milling was increased to 3 h. In contrast to the results recorded from the pure senarmontite form of Sb_2O_3 and the mixture of α-Fe_2O_3 with senarmontite Sb_2O_3, no evidence was found for the conversion of senarmontite to the valentinite form of Sb_2O_3. Instead, the peak broadening was consistent with the rapid formation of a poorly crystalline mixture which remained amorphous to X-rays until milled for 50 h when peaks characteristic of $VSbO_4$ were observed. The appearance of $VSbO_4$ after 60 h demonstrates that the reaction between V_2O_5 and Sb_2O_3 in the ball mill is more rapid than that between α-Fe_2O_3 and Sb_2O_3 under similar conditions. The crystallite size, determined from the X-ray powder diffraction data of $VSbO_4$ formed after 70 h of milling, of ca. 23 nm was similar to that of $FeSbO_4$ formed after 280 h of milling, but smaller than that of $VSbO_4$, ca. 50 nm, made by heating a mixture of V_2O_5 and Sb_2O_3 in air at 750°C. The formation of small particle $VSbO_4$ from V_2O_5 may have analogies with the redox chemistry involved in forming similar materials by sol-gel methods [10]. Taken together with the data recorded from the mechanical milling of α-Fe_2O_3 and Sb_2O_3 the results show that milling techniques are suitable methods for the preparation of small particle metal antimonates with high surface areas appropriate for use as heterogenous catalysts.

3.3. The conversion of α-Sb_2O_4 to β-Sb_2O_4

A mixture of V_2O_5 and α-Sb_2O_4 was also mechanically milled under identical conditions. The results (Fig. 4) also showed the onset of formation of $VSbO_4$ after 110 h of milling. However, of greater interest was the appearance of a peak at 27.6° 2θ in the X-ray powder diffraction pattern recorded from the mixture after milling for 5 h which is characteristic of β-Sb_2O_4. The result is unexpected since α-Sb_2O_4 is only converted to the β-polymorph at 1130°C [17] by a mechanism described [17] in terms of the dissociation of α-Sb_2O_4 into Sb_2O_3 which recombines with oxygen and condenses as β-Sb_2O_4. The conversion of α- to β-Sb_2O_4 by mechanical milling was therefore subjected to further examination.

The X-ray powder diffraction patterns recorded after milling α-Sb_2O_4 for different periods of time are collected in Fig. 5. After 3 h of milling a peak at 27.6° 2θ characteristic of β-Sb_2O_4 appeared. The X-ray powder diffraction pattern characteristic of β-Sb_2O_4 developed with further milling and was accompanied by a decrease in the intensity of the pattern characteristic of α-Sb_2O_4. After 20 h of milling the X-ray powder diffraction pattern showed nearly complete conversion to β-Sb_2O_4 with a crystallite size, estimated by the Scherrer method from the X-ray powder diffraction data, of ca. 15 nm. A similar result was obtained when α-Sb_2O_4 was milled in an atmosphere of argon for 20 h. Hence the results suggest that mechanical milling facilitates the α- to β-Sb_2O_4 phase transformation in the solid state.

However, it has also been shown that the calcination of α-Sb_2O_4 containing a small amount of V_2O_5 lowers the temperature of the α- to β-Sb_2O_4 phase transformation to ca. 810°C [18]. We therefore milled a mixture of α-Sb_2O_4 with 4% V_2O_5 and recorded the X-ray powder diffraction patterns after different periods of milling. The results are collected in Fig. 6. The results show the onset of formation of β-Sb_2O_4 after only 1 h and, with

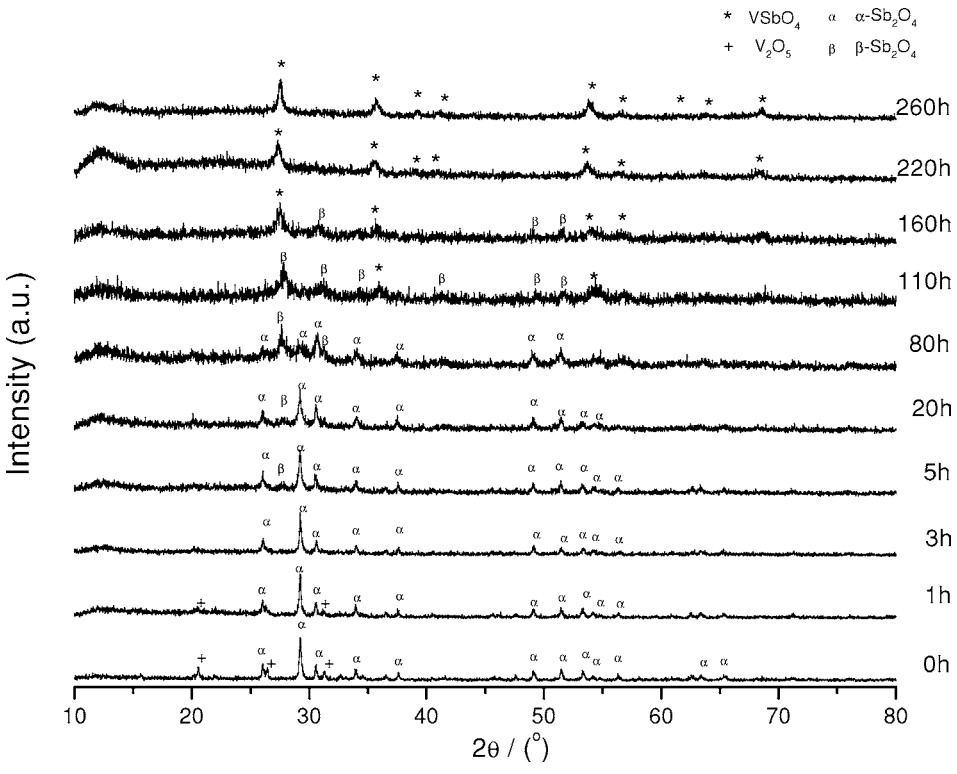

Figure 4 X-ray powder diffraction patterns recorded from a mixture of V_2O_5 and α-Sb_2O_4 following mechanical milling for various periods of time.

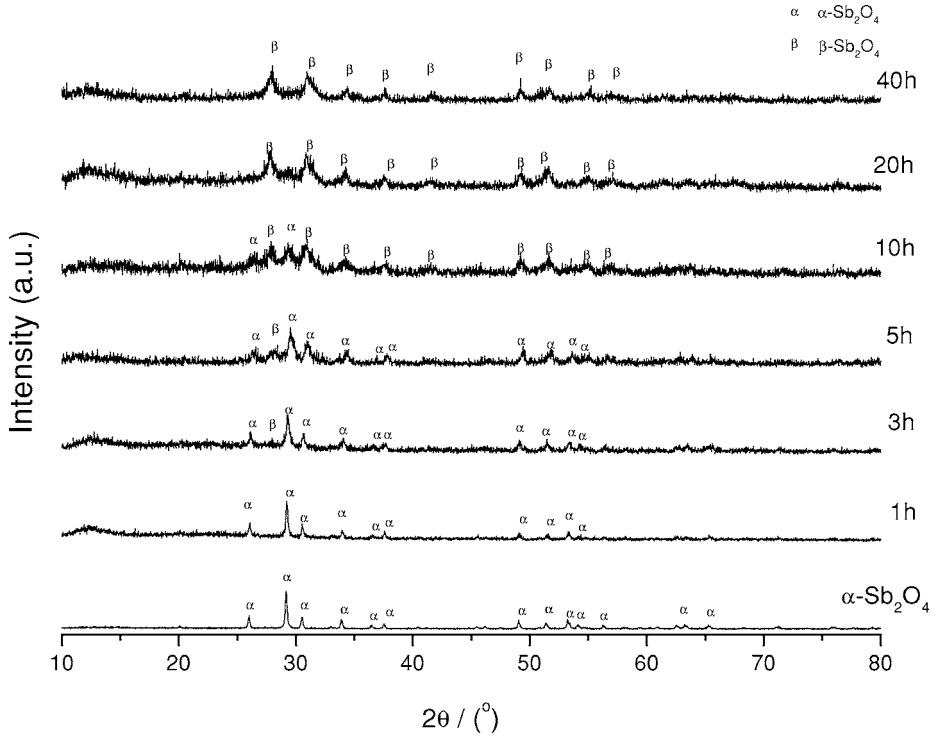

Figure 5 X-ray powder diffraction patterns recorded from α-Sb_2O_4 following mechanical milling for various periods of time.

further milling, the decrease in intensity of peaks corresponding to α-Sb_2O_4 and V_2O_5 and the development of the pattern characteristic of β-Sb_2O_4. After 20 h of milling the pattern showed nearly complete conversion of α-Sb_2O_4 to β-Sb_2O_4 with a crystallite size determined from the X-ray powder diffraction data of ca. 15 nm. We subsequently found that milling of a mixture of α-Sb_2O_4 with 4% α-Fe_2O_3 for 20 h induced the conversion of α- to β-Sb_2O_4.We presume that vanadium or iron may be incorporated within the structure as found previously [18] and note that the presence of vanadium induces the onset of conversion of α-Sb_2O_4 to β-Sb_2O_4 after only one hour of milling. Hence the results demonstrate that mechanical milling is able to induce the conversion of α- to β-Sb_2O_4 by a solid state mechanism and that the phase transition is rendered even more facile by the incorporation of vanadium or iron.

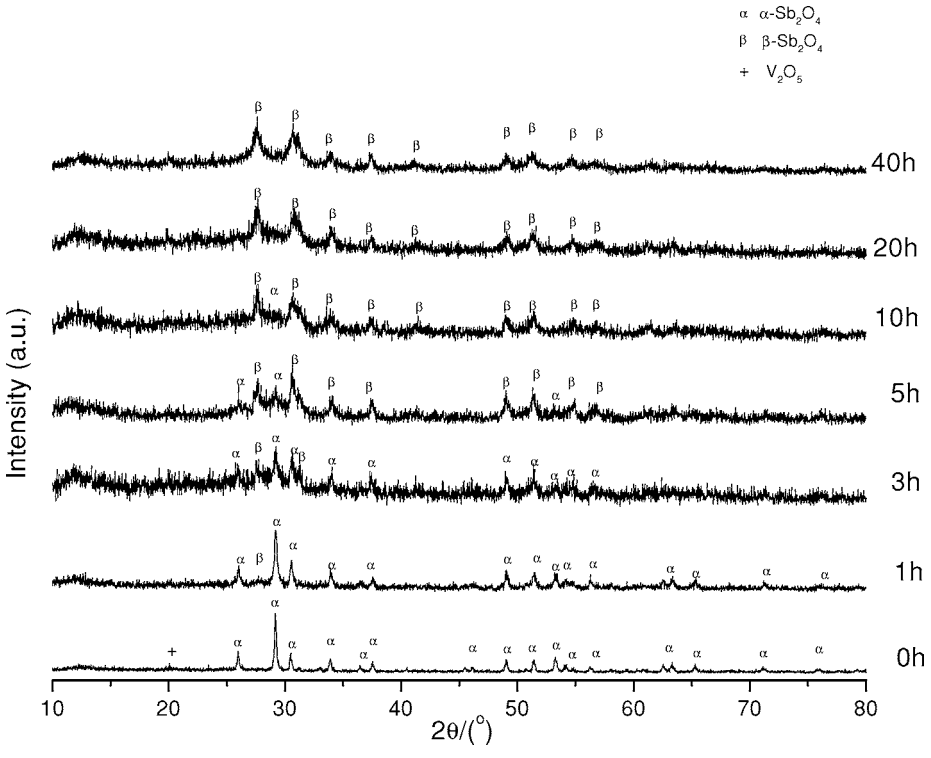

Figure 6 X-ray powder diffraction patterns recorded from a mixture of α-Sb_2O_4 and 4% V_2O_5 following mechanical milling for various periods of time.

4. Conclusion

Mechanical milling has been found to induce the solid state reaction between iron- or vanadium-oxides with Sb_2O_3 to form small particle metal antimonates. Milling also induces the conversion of cubic Sb_2O_3 to orthorhombic Sb_2O_3 and the transformation of α-Sb_2O_4 to β-Sb_2O_4 by a solid state process which is even more facile in the presence of vanadium or iron.

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