

CHAPTER 4

Discussion on tin dioxide and tin monoxide

4.1 Tin Dioxide

In this work $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as the starting material to produce SnO_2 . Senguttuvan and Malhotra, (1997) also used the same starting materials. However the experimental procedure in this work is much simpler. The product obtained in their work is in the form of thin films whereas in our work the product was obtained as a semi-amorphous gel, which when heated to 500°C and above gives a crystalline SnO_2 powder TGA results also show that the formation of crystalline SnO_2 is complete after 500°C .

Wu *et al*, (1996) used $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as the starting agent and so did Svetlana *et al*, (1997). The method by Wu *et al*, (1996) mixed together diluted solution of aqueous SnCl_4 and alcoholic SnCl_4 which was aged and dried to form SnO_2 xerogel. In the method used by Svetlana *et al*, (1997), SnO_2 was prepared by conventional hydrolysis of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. A measured amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in de-ionised water in an ice bath and liquid ammonia was slowly added to the stirred solution to achieve complete precipitation of α -Stannic acid. The precipitate was centrifuged and washed with deionised water until the absence of chloride ion.

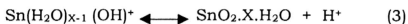
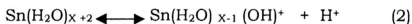
The SnO₂ powder was also prepared by means of the creosol technique. Previously this method has been applied for the synthesis of Al₂O₃, Cr₂O₃ and Fe₂O₃. The technique is based on the pH controlled treatment of an aqueous solution containing a multivalent metal nitrate by anion-exchange with a resin in OH⁻ form. Freeze drying of the colloid solutions results in the formation of an amorphous metal hydroxide that can be transformed to corresponding oxide by thermal dehydration. However, an attempt to treat the solution of SnCl₄ (0.01M) by anion-exchange was unsuccessful: addition of the first portions of the ion-exchanger resulted in the formation of a precipitate.

The simplicity of our method is very clear and we believe that the process of SnO₂ formation occurs follows:

It is well recognised that when dissolved in water metal cations such as Sn⁺² are solved by water molecules



The solvated complex is hydrolyzed to different extents



From TGA studies x value is caculated to be $X = 1.6$. The proton H^+ will combine with chloride Cl^- ions to form HCl making the yellow solution obtained during stirring acidic as mentioned in chapter 3.

The cloudiness of the white mixture is due to light scattering by increasing the amount of sols, this cloudiness was also reported by Wu et al, (1996). However, their mixture did not turn yellow as was obtained in this work.

Solutions containing high tin dichloride require a longer time to produce the gel as shown in Fig. (3.2). This indicates that the condensation reaction slows down, as the $SnCl_2 \cdot 2H_2O$ content increases. From this study also it seems that a pH value of about 1.4 is necessary for the formation of the gel. The solution becomes very acidic quickly Fig. (3.4), because of the formation of HCl as a result of the dissolution and hydrolysis of the $SnCl_2 \cdot 2H_2O$. X-Ray diffractogram Fig. (3.5) and Fig. (3.6) proves that the gel is tin dioxide, even in the semi-amorphous phase peaks due to dioxide are quite distinct.

Ocana et al, (1993) prepared spherical SnO_2 particles of narrow size distribution by hydrolysis of $SnCl_2$ aerosol in the presence of ammonium. Under such preparation condition the materials obtained was also semi-amorphous with an XRD pattern showing only three broad peaks although the XRD pattern obtained in the present work

is also characteristic of a semi-amorphous phase it is more crystalline than that obtained by Ocana *et al* (1993).

From SEM micrograph the semi-amorphous phase is almost spherical in shape with grain size about 1 μm , the grain seems to sticking to each other but upon heating the grains have joined with one another and at 800°C seems to acquire unique polyhedral shapes Fig. (3.9). The crystalline nature of this phase is well exhibited from the X-Ray Diffractogram Fig. (3.6).

The deduction on the mechanism of gel formation described in the early part of the discussion insists that the tin dioxide product is hydrated and the room temperature FTIR spectrum shows the presence of the band at 3400 cm^{-1} that is characteristic of water. Thus room temperature FTIR supports the idea of the mechanism of gel formation that was introduced. Upon heating at 500°C and 800°C the intensity of the water band decreases. This means that the sample still contains water, this water band could be due to the interaction of water molecules in the air with infrared spectrometer. If this is so then the intensity of the water band for the sample heated at 800°C must be about the same as the intensity of the water band for the sample heated at 500°C. However this is not so because the water band still exist with a lower intensity. These results imply that the initial amount of water molecule in the sample must be less than what has been calculated; possibly the sample after heating at 500°C

and 800°C is a hemihydrate containing (0.5H₂O) which is difficult to remove.

4.2 Discussions on tin monoxide

Films of SnO have been studied by Geurts *et al.* (1984), Uen *et al.* (1988) and Choi *et al.* (1997). In this work SnO was prepared by the precipitation method again with SnCl₂.2H₂O as the starting materials. The preparation of SnO is temperature dependent requiring a temperature of 100°C to insure good yield of tin monoxide. The XRD pattern shows peaks at $2\theta = 30^\circ, 33^\circ, 37^\circ, 47^\circ, 57^\circ, 63^\circ, 64^\circ$ this is in agreement with the JCPDS data. The peak at 30° correspond to (101) plane, the peak at 33° is the (110) plane, the peak at 37° is attributed to (002) plane, the peak at 47° is attributed to (200) plane, the peak at 52° is attributed to (112) plane and the peak at 57° is attributed to (211) plane (Choi *et al.*, 1997). There is also a peak at 18° in the XRD pattern of the present work, this peak (18°) and that at 37° correspond to (001) and (002) planes of the α -SnO phase (Uen *et al.*, 1988). Hence it is possible that the tin monoxide produced in this work is that of the α -SnO with a tetragonal structure. The (002) peak has also been observed by Geurts *et al.* (1984). Further confirmation that this sample is α -SnO is due to the peaks at about 62° corresponding (202) plane of α -SnO, and the peak at $\sim 65^\circ$. Thermal analysis shows that our sample contains water and this also

supported by FTIR, thermal studies also show that the tin monoxide has 9 water of crystallisation and oxidized to tin dioxide above 170° C. SEM micrograph for room temperature tin monoxide for two magnifications (2000x and 10000x) are shown in Fig. (3.13, a,b). The tin monoxide seems to be arranged in a floret structure but when emmersed in water for three weeks the tin monoxide seems to form agglomerates Fig. (3.13, c).

4.3 Discussions on the transformation of tin monoxide to tin dioxide

Geurts et al, (1984) have studied the oxidation of SnO to SnO₂ by XRD. They have shown that the (002) plane of SnO at 37° diminishes as the temperature increases and a peak at 33° to 34° which corresponds to (011) plane of SnO₂. Such phenomenon has also been observed in the present work.

FTIR of tin monoxide shows significant band at 1630, 1245, 1024 cm⁻¹ and 611 cm⁻¹. When heated to 500 °C and 800 °C the bands at 1245 cm⁻¹ and 1024 cm⁻¹ disappear. The band at 1630 cm⁻¹ is shifted to 1637 cm⁻¹ and the band at 611 cm⁻¹ is also shifted to higher wave numbers. The disappearance and shifting of the bands are indication of tin monoxide oxidation.