Study of Loading SO$_4^{2-}$ on Sb-SnO$_2$ Nanocrystal and its Calcination Temperature to Make Solid Superacid SO$_4^{2-/Sb-SnO_2}$

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**Abstract**

SO$_4^{2-/SnO_2}$ were reported to be a solid superacid with an acid strength equal to that of SO$_4^{2-/ZrO_2}$. But papers concerning the SO$_4^{2-/SnO_2}$ catalyst have been quite few, because of difficulty in preparation of the oxide gels from its salts SnCl$_4$. A highly dispersed light yellow powder, Sb-SnO$_2$ nanocrystal, was obtained by the synthesis method of "P-CNAIE" and the drying method of "AD-IAA". The Sb doping made the energy gap of nano-crystalline SnO$_2$ narrower. A saturated solution of ammonium sulfate was dropped into organic solutions containing a fixed amount of Sb-SnO$_2$ nano-powders in different ratio in order to load Sb-SnO$_2$ powder with ammonium sulfate. This method has an outstanding advantage that the loading ratio of (NH$_4$)$_2$SO$_4$ to Sn-SnO$_2$ can come to very high and no free water causes the aggregation of Sn-SnO$_2$ nano powder. The methods of Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG) demonstrated that the working ratio of Sb-SnO$_2$ to (NH$_4$)$_2$SO$_4$ was 1:1.4 to 1:1.6 wt% and the most favorable calcination temperature for the generation of superficially sulfated groups of Sb-SnO$_2$ particles should fall between 380°C and 400°C. The adsorption reaction of indicator reveals that the solid acid, calcined Sb-SnO$_2$ with a bluish color had a H$_0$ ≤ -14.5 at least.

**Keywords:** Solid superacid; Stannic oxide; Nanocrystal; Impregnation; Ammonium sulfate; Calcination temperature

**Introduction**

Acid catalysts, especially superacid catalysts, play a vital role in the chemical industry of our time. Many organic reactions such as esterification, condensation, cracking, alkylation, saturated hydrocarbon isomerization, can be economically and effectively accomplished with the presence of acid catalysts.

In 1979, Hino et al. [1] indicated, for the first time, that the acid strength of the SO$_4^{2-/ZrO_2}$ catalyst estimated to be H$_0$ (Hammett indicator) ≥ -14.52, one of the strongest solid superacids. Sulfated zirconia (SO$_4^{2-/ZrO_2}$) is a typical solid superacid and exhibits a high catalytic activity for the skeletal isomerization of saturated hydrocarbons and other reactions [2-6]. Sulfated tin oxide (SO$_4^{2-/SnO_2}$) was later reported by Matsushashi et al. [4] to be one of the candidates with the strongest acidity, acid strength of which is almost equal to that of SO$_4^{2-/ZrO_2}$ at least [7-9]. And SnO$_2$ is more readily available and cheaper than ZrO$_2$ [10].

Matsushashi et al. [11] concluded in 2001 that the preparation of many solid superacids of sulfated metal oxides commonly underwent three steps: (i) preparation of amorphous metal oxide gels as precursors; (ii) treatment of the gels with sulfate ion by exposure to a H$_2$SO$_4$ solution or by impregnation with (NH$_4$)$_2$SO$_4$; and (iii) calcination of the sulfated materials at a high temperature in air. For the synthesis of solid superacid SO$_4^{2-/SnO_2}$, the latter written form of solid superacid, including SO$_4^{2-/ZrO_2}$, is being widely and incorrectly adopted.

**Experiments**

**The synthesis of the precursor, antimony doped stannic oxide**

The Sn-SnO$_2$ nanocrystals were synthesized using the method "precipitation–condensation with non-aqueous ion exchange (P-CNAIE)" and dried with the assistance of the Iso-Amyl Acetate (AD-IAA). These two methods were developed in our lab and reported in the published literatures [13-15]. A typical procedure includes the following steps. In an airtight flask containing 200 mL anion-exchange...
resin, 100 mL alcohol, and 10 mL of ammonia water, 200 mL ethanol solution containing SnCl₂·5H₂O (18.0%, w/v) and SbCl₃ (0.665%, w/v) were added dropwise with fast stirring. At the same time, NH₃ gas was aerated in the reaction solution. The reaction solution was held close to neutral pH by adjusting the speed of addition. After the addition was complete, the reaction solution was separated from the ion-exchange resin particle through a glass-sand funnel and reacted repeatedly with fresh anion-exchange resin on a shaker. The final chlorine-free colloid solution was held idle on a bench to allow the stratification of the turbid solution. The upper lightly turbid solution was removed and kept aside for final recovery of all solid content, and the lower dense precipitated liquid was distilled off water absorbed on the colloid and solvents.

All the exchanged ion-exchange resins were collected and repeatedly washed with fresh solvent to collect any residual precipitate on the surface of the resins. The washed solvent was applied to a short column of ion exchange resin particle through a glass-sand funnel and reacted repeatedly with fresh anion-exchange resin on a shaker. The final chlorine-free colloid solution was held idle on a bench to allow the stratification of the turbid liquid. The upper lightly turbid solution was removed and kept aside for final recovery of all solid content, and the lower dense precipitated slurry was added ~80 mL of iso-amyl acetate to make a co-boiling system. The pale-yellow dispersive fine powders were obtained by co-distilling off water absorbed on the colloid and solvents.

The impregnation with (NH₄)₂SO₄

The sulfated SnO₂ powders loaded with (NH₄)₂SO₄ were separated by centrifugation and further washed in anhydrous alcohol. The process was repeated for three times and finally centrifuged at 4000 r/min. The final sediment was dried under an infrared ray lamp and a dispersed powder was obtained.

The coupling reaction of superficial hydroxyls with (NH₄)₂SO₄

The mixed powders obtained in the impregnation with (NH₄)₂SO₄ were transferred on a corundum plate, and then calcinated in a muffle furnace. The calcination to couple “SO₄” on superficial hydroxyls of Sn-SnO₂ nanocrystals was carried out at 380°C for 2~3 h.

Results and Discussion

Through the synthesis method of “P-CNAIE” and the drying method of “AD-IAA”, highly dispersed pale yellow powders were obtained. Based on our observation, without doping of the antimony, the colloidal solution of stannic chloride and finally dried powders always presented white colour, which implicates that the yellow color of as-prepared powders is caused by doping antimony or, more exactly, by Sn doping into crystal lattice of stannic oxides, because yellow is caused by the formation of crystal with variation of band gap, instead by cluster or hydrolysate that has a forbidden band.

Figure 1 shows TEM images and electron diffraction pattern of nano-meter sized material synthesized in the experiment section. The diffraction pattern, the middle image, indicates that the obtained nano material has a determinate crystal structure, which is also confirmed by the TEM image B, from which a layer lattice structure can be distinctly identified. The TEM image A shows the size of as-prepared powders is significantly less than 20 nm. In addition, XRD pattern in Figure 2 illustrates the degree of crystallization and the size of nano particle. Diffraction peaks and their position in the pattern indicate the nano material is stannic oxide crystal, and broad and weak peaks suggest that crystals are nano-meter sized. The positions of peaks are consistent with the standard one that showed in the X-Ray Powder Diffraction Standards of SnO₂, PDF No. 41-11445 from Jade 5.0, see the red bar in Figure 2.

Figure 2: X-ray diffraction of Sn-SnO₂ nano-material synthesized by method of P-CNAIE associate with AD-IAA.
SnO₂ nanocrystals are heavier, resulting from the dehydration between hydroxyls and leading to the decrease of the quantity of the superficial hydroxyls. The decrease in amount of superficial hydroxyls brought about the decline of the quantity of superficially sulfated groups, and the decrease of acid strength or catalytic activities of nanoparticles.

Figure 4 is Differential Scanning Calorimetry (DSC) curves, which more clearly showed the variation of and the difference between samples 1 to 8 due to the distinct images of endothermic peaks and exothermic peaks. The red line has a clear exothermic peak that was caused by the crystallization of superficial hydroxyls of Sb-SnO₂ nanoparticles at ~ 376°C. And the blue one is the differential thermal curve of (NH₄)₂SO₄ with two glaring endothermic peaks. The two endothermic peaks are associated with the decomposition of (NH₄)₂SO₄ into NH₃, H₂O and SO₃, corresponding to the chemical reaction on following equations:

\[
(NH_4)_2SO_4 \xrightarrow{298 \degree C} 2NH_3 \uparrow + H_2SO_4
\] (1)

\[
H_2SO_4 \xrightarrow{410 \degree C} H_2O \uparrow + SO_3 \uparrow
\] (2)

Based on the above discussed, a summary is drawn in Figure 5, which simply and clearly illustrates the three endothermic peaks. It can be easily understood that the third endothermic peak on the blue curve in Figure 5 should belong to the splitting action of a new group. This

Nevertheless, it is noted that a third endothermic peak appeared in differential thermal curves of samples 7 to 2. The third endothermic peak only appeared in the curves of Sb-SnO₂ plus (NH₄)₂SO₄ and become more obvious as the pretreatment temperatures of Sb-SnO₂ decreased. The appearance of the third peak suggests the cleavage of a chemical bond. As compared with differential thermal curves of Sb-SnO₂ and (NH₄)₂SO₄, the third peaks on curves 6 to 2 suggests a bonding reaction took place between superficial hydroxyl and (NH₄)₂SO₄ or more exactly, between superficial hydroxyl and H₂SO₄. Therefore, the breaking of bonds represented by the third peak should belong to superficially sulfated groups, which were newly generated groups in the calcination process. We speculate the breaking of bonds contributing to the absorption of heat might follow the cracking reaction as equations (3) and (4) show.

\[
(NH_4)_2SO_4 \xrightarrow{470 \degree C} 2NH_3 \uparrow + SO_2 \uparrow
\] (3)

\[
H_2SO_4 \xrightarrow{470 \degree C} H_2O \uparrow + SO_3 \uparrow
\] (4)
new group generated in the calcination process by "\( =\text{SO}_4 \)" bonding to Sb-SnO\(_2\) nano-particle against the endothermic peaks on black curve of (NH\(_4\))\(_2\)SO\(_4\). In other words, the calcination did make "\( =\text{SO}_4 \)" group loaded on the Sb-SnO\(_2\) nanoparticles forming a solid superacid with a stable "\( =\text{SO}_4 \)" group.

According to the data shown in Figures 3-5, we proposed that the most favorable temperature for the generation of superficially sulfated groups of Sb-SnO\(_2\) particles should fall between 380°C and 400°C, before the decomposition temperature of H\(_2\)SO\(_4\) and after the crystallization temperature of Sb-SnO\(_2\). To illustrate the generation of solid superacid of Sb-SnO\(_2\), the authors here proposed that a series of chemical reaction such as Figure 6 shows might occur on the surface of Sb-SnO\(_2\) as the preparation of solid superacid of Sb-SnO\(_2\) underwent.

According to the proposed, group "\( =\text{SO}_4 \)" is absolutely impossible to attach to Sb-SnO\(_2\) nano-particle in the form of SO\(_4^{2-}\). It should be a group bonded on Sb-SnO\(_2\) particle since the dissociation temperature of bonded "\( =\text{SO}_4 \)" is up to 470°C.

The relative acid strength of the calcined Sb-SnO\(_2\) powders was measured by the adsorption reaction of indicator. The powders (ca. 0.5 g) were calcined at 380°C ~ 390°C in air for 3 h and then placed in a glass vacuum desiccator as the powder was hot. After the sample was pretreated in a vacuum for 2 h and cooled down to room temperature, some cyclohexane solution containing 5% of Hammett indicator was sucked into the vacuum desiccator. The desiccator was heated to 60°C by placing it in a constant water bath, which resulted in the exposure of powder to the indicator vapor. The present powder sample was gradually colored by indicator and changed distinctly the colorless basic form of p-nitrotoluene (pKa or H\(_0\)= -11.4), m-nitrotoluene (-12.0), m-nitrochlorobenzene (-13.2), 2,4-dinitrotoluene (-13.8) and 2,4-dinitrofluorobenzene (-14.5) to the yellow conjugate acid form, that is to say, the acid strength of the solid acid is estimated at least to be H\(_0\) < -14.5. All of the measurements convincingly demonstrated the calcined Sb-SnO\(_2\) was a solid acid, more exactly solid superacid (Figure 7).
As an acid, the sulfated Sb-SnO₂ should be able to release hydrogen proton or have electron pair acceptors to accept molecules bearing electron pair or negative ions in term of Bronsted's proton theory or in the light of Lewis theory of acids and bases. According to the molecular structural forms put forward by Hino et al. [1], however, SO₄²⁻/ZrO₂ and SO₄²⁻/SnO₂ are absolutely impossible to show any acidity because group SO₄²⁻ is a conjugate base of H₄SO₄. Based on the derivation of a series of chemical reaction in calculation and through analysis of the possible structures of Sb-SnO₂ solid acid, a more reasonable structure is proposed in Figure 7.

Because the calcination had the group "SO₄²⁻" bonded on Sb-SnO₂ nanoparticles and become a stable group "=SO₄" of Sb-SnO₂ but an attached acid radical "SO₄²⁻", authors believed that the great enhancement of acidity of sulfated Sb-SnO₂ resulted from a number of dangling bonds around group=SO₄. The both oxygen and tin as SO₄ from=SO₄ to dangling bonds and make =SO₄ a positive group with dangling bond are electron deficient groups and have electron-deficiency, so we proposed the solid superacid of Sb-SnO₂ should be noted bearing electron pair or negative ions.

The ammonium sulfate, however, had to be dissolved in water for its solubility in organic solvent is very low. In the impregnation of Sb-SnO₂ powders with ammonium sulfate, a saturated solution of ammonium sulfate was dropped into organic solutions containing a fixed amount of Sb-SnO₂ nano-powder in different ratio. The ammonium sulfate precipitated as it dropped into organic solvent and Sb-SnO₂ nanoparticles coupled the precipitate via water molecules that adsorbed on (NH₄)₂SO₄ fine particles. Without free water, for all water molecules were adsorbed on (NH₄)₂SO₄ fine particles. The dried powder was a uniform dispersion of powder of (NH₄)₂SO₄ fine particles and Sb-SnO₂ nano-particles. The outstanding advantage of the method presented here, that is the impregnation of Sb-SnO₂ powder with saturated ammonium sulfate, is that the impregnation ratio of (NH₄)₂SO₄ to Sb-SnO₂ can come to very high and no free water that will cause the aggregation of Sb-SnO₂ nano powder.

To obtain an optimal impregnation ratio of ammonium sulfate to Sb-SnO₂, a series of Sb-SnO₂ nano-powder impregnated with (NH₄)₂SO₄ in different ratio were studied on the Simultaneous TG-DSC Apparatus, STA 409PC, NETZSCH, Germany. The resulted analysis diagrams are shown in Figure 8. Here the Sb-SnO₂ nano-powder did not undergo any heat treatment and just impregnated with (NH₄)₂SO₄ directly in organic solvent. It can be simply and clearly identified the endothermic peaks and their height from the Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) profiles of Sb-SnO₂ impregnated with different amount of (NH₄)₂SO₄. The height of peaks told us if there were excessive or deficient (NH₄)₂SO₄ by which an optimal impregnation ratio of ammonium sulfate to Sb-SnO₂ was easily discovered. We have got the knowledge of what the peaks implied based on foregoing discussion, that is, the Peak A was an endothermic peak that caused by (NH₄)₂SO₄ being resolved into NH₃ and N₂SO₄, the Peak B an endothermic one which resulted from the decomposition of H₂SO₄, and the Peak C, without a doubt, was brought about by the absorption of heat contributed by the dissociation of a newly generated group=SO₄. The Peak A was always presented in curves of all samples since the decompositions of (NH₄)₂SO₄ occurred for all samples but were different in their peak height due to different impregnation ratio, whereas, the Peak B only appeared when the amount of (NH₄)₂SO₄, or exactly H₂SO₄, was excessive against superficial hydroxyl of Sb-SnO₂ because only the H₂SO₄ that did not associate with superficial hydroxyl would decomposed.

Obviously, the optimal impregnation ratio should be located between curves 4 and 5 in Figure 8 because curve 5 has a large endothermic peak but curve 4 does not. To diagnose a more accurate optimum ratio of ammonium sulfate to Sb-SnO₂, the authors carried out a series precise experiments in the small range of ratio of Sb-SnO₂ to (NH₄)₂SO₄ from 1:1.2 to 1:2.4 wt%. The quantitative analyses of the ratio were conducted by the methods of differentia scanning calorimetry and thermogravimetry. The thermal analysis curves, especially DSC curves, in Figure 9, showed the ratio at 1:1.2 wt% did not have endothermic peak B, suggesting impregnated (NH₄)₂SO₄ was not enough against the superficial hydroxyl, and the ratios at 1:1.6, 1:2.0 and 1:2.4 wt% all had projecting endothermic peaks at peak B, meaning impregnated (NH₄)₂SO₄ were excessive.

In the preparation of solid superacid of Sb-SnO₂ nanocrystal, the working ratio was selected at 1:1.4 to 1:1.6 wt%, a little excessive, in order to make full use of the superficial hydroxyl of Sb-SnO₂ and get more superacid group=SO₄.

Figure 10 is a picture of solid superacid of Sb-SnO₂. The picture shows the deficiency (1:0.8 wt%) or excess (1:2.4 wt%) of impregnated (NH₄)₂SO₄ would result in the blue solid superacid of Sb-SnO₂ with
Figure 9: Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) profiles of 1.0 gram of Sb-SnO\textsubscript{2} exposed to 1.2 g (1), 1.6 g(2), 2.0 g (3) and 2.4 g (4). The optimum exposure ratio is 1:1.2 to 1.6 in weight.

Figure 10: Photograph of solid super acids made from 1.0 gram of Sb-SnO\textsubscript{2} exposed to 1.6 g (left), 0.8 g(middle) and 2.4 g (right) after calcination at 380°C for 2-2.5 h.

little light yellow, while, a suitable or little excessive amount (1:1.4 and 1:1.6 wt%) of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} could get a solid superacid of Sb-SnO\textsubscript{2} with an even blue after the calcination at 380°C. See the left one in Figure 10.

Conclusion

The nano-crystalline SnO\textsubscript{2} doped with Sb (III) that was synthesized by method of “P-CNAIE” and the drying method of “AD-IAA” could be calcined to give a solid superacid after sulfated. It must be noted that a suitable amount of impregnated ammonium sulfate and a calcination temperature adapting to SnO\textsubscript{2} are crucial to prepare the solid superacid of Sb-SnO\textsubscript{2}, which is written as SO\textsubscript{4}\textsuperscript{2-}/SnO\textsubscript{2}.

This paper proposed the impregnated ratio of Sb-SnO\textsubscript{2} to (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} should be between 1 g to 1.4 g and 1.6 g and the calcination temperature be 380°C to 400°C, and hence an even blue solid superacid powder was obtained. About the catalytic properties of Sb-SnO\textsubscript{2} solid superacid will be discussed in another paper.

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