

Study of Loading SO_4^{2-} on Sb-SnO₂ Nanocrystal and its Calcination Temperature to Make Solid Superacid $\text{SO}_4^{\oplus}/\text{Sb-SnO}_2$

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Abstract

$\text{SO}_4^{2-}/\text{SnO}_2$ were reported to be a solid superacid with an acid strength equal to that of $\text{SO}_4^{2-}/\text{ZrO}_2$. But papers concerning the $\text{SO}_4^{2-}/\text{SnO}_2$ 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-SnO₂ 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 SnO₂ narrower. A saturated solution of ammonium sulfate was dropped into organic solutions containing a fixed amount of Sb-SnO₂ nano-powders in different ratio in order to load Sb-SnO₂ powder with ammonium sulfate. This method has an outstanding advantage that is the loading ratio of $(\text{NH}_4)_2\text{SO}_4$ to Sb-SnO₂ can come to very high and no free water causes the aggregation of Sb-SnO₂ nano powder. The methods of Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG) demonstrated that the working ratio of Sb-SnO₂ to $(\text{NH}_4)_2\text{SO}_4$ was 1:1.4 to 1:1.6 wt% and the most favorable calcination temperature for the generation of superficially sulfated groups of Sb-SnO₂ particles should fall between 380°C and 400°C. The adsorption reaction of indicator reveals that the solid acid, calcined Sb-SnO₂ with a bluish color had a $H_0 \leq -14.5$ 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 $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst is estimated to be H_0 (Hammett indicator) ≥ -14.52 , one of the strongest solid superacids. Sulfated zirconia (SO_4/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 ($\text{SO}_4^{2-}/\text{SnO}_2$) 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 $\text{SO}_4^{2-}/\text{ZrO}_2$ at least [7-9]. And SnO₂ is more readily available and cheaper than ZrO₂ [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_2SO_4 solution or by impregnation with $(\text{NH}_4)_2\text{SO}_4$; and (iii) calcination of the sulfated materials at a high temperature in air. For the synthesis of solid superacid $\text{SO}_4^{2-}/\text{SnO}_2$, however, it is difficult to prepare the tin oxide gel precursors from the SnCl_4 salts. [11] Hence, the synthesis and application of $\text{SO}_4^{2-}/\text{SnO}_2$ catalysts are seldom reported.

Herein we propose a novel three-step method for the preparation of solid superacid $\text{SO}_4^{2-}/\text{SnO}_2$. In contrast to the three-step process proposed by Matsushashi et al., the present method uses metal oxide crystals, instead of metal oxide gels, as precursors. Specifically, this method includes: (i) preparation of high purity nanometer metal oxide crystal with a lot of superficial hydroxyls; (ii) treatment of the gels with sulfate ions, where the as-prepared Sb-SnO₂ nanoparticles were dispersed in organic solvent and then impregnated with saturated ammonium sulfate solution to associate with $(\text{NH}_4)_2\text{SO}_4$ by water molecule adsorbed on $(\text{NH}_4)_2\text{SO}_4$; (iii) calcination [12] of the impregnated nano-powders. A coupling reaction of superficial

hydroxyls with $(\text{NH}_4)_2\text{SO}_4$ by losing NH_3 and H_2O undergoes at a proper temperature.

After calcination, the obtained solid powder has been firmly bonded with a group =SO₄ on its surface, which means that SO_4^{2-} is by no means a sulphate radical attached to nano particle any more. In virtue of Bronsted's and Lewis' acid-base theory, the attached SO_4^{2-} should be a base but an acid since its negative charge. Our experiments, however, demonstrated such calcined nano particles were a superacid. So we believed that the molecular structure of solid superacid should be noted as $\text{SO}_4^{\oplus}/\text{SnO}_2$ but $\text{SO}_4^{2-}/\text{SnO}_2$, the latter written form of solid superacid, including $\text{SO}_4^{2-}/\text{ZrO}_2$, is being widely and incorrectly adopted.

Matsushashi et al. [11] further indicated that papers concerning the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst have been quite few, because of difficulty in preparation, compared with the relative ease of preparation of the $\text{SO}_4^{2-}/\text{ZrO}_2$ material, in particular owing to the difficulty in preparation of the oxide gels from its salts SnCl_4 .

Experiments

The synthesis of the precursor, antimony doped stannic oxide

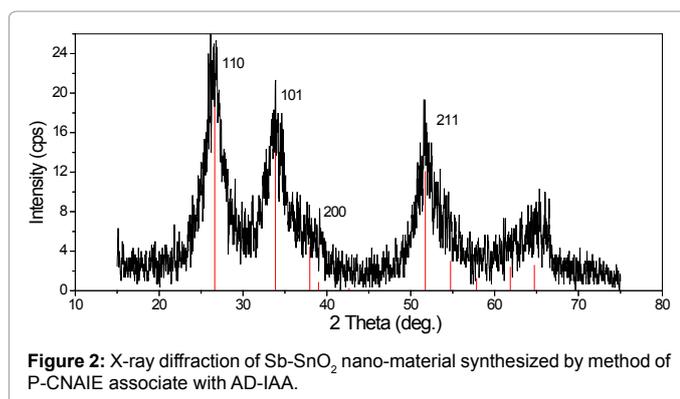
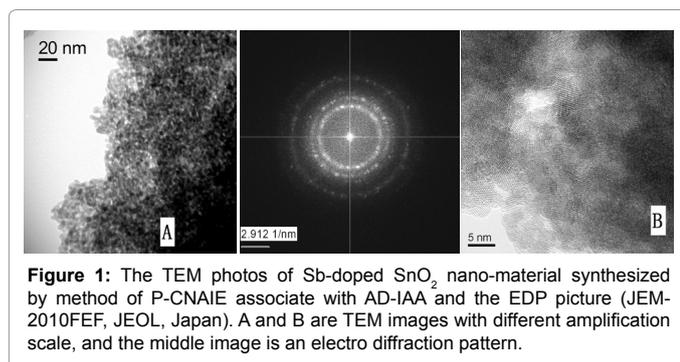
The Sb-SnO₂ nanocrystals were synthesized using the method "precipitation-condensation with non-aqueous ion exchange (P-CNAIE)" and dried with the assistance of the Iso-Amyl Acetate (AD-IAA). These two methods were developed in our lab and reported in the published literatures [13-15]. A typical procedure includes the following steps. In an airtight flask containing 200 mL anion-exchange

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Received July 26, 2014; Accepted September 18, 2014; Published September 23, 2014

Citation: Zhang X, Zhang XN, Ran QQ, Ouyang HM, Zhong H, et al. (2014) Study of Loading SO_4^{2-} on Sb-SnO₂ Nanocrystal and its Calcination Temperature to Make Solid Superacid $\text{SO}_4^{\oplus}/\text{Sb-SnO}_2$. Mod Chem appl 2: 135. doi:10.4172/2329-6798.1000135

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resin, 100 mL alcohol, and 10 mL of ammonia water, 200 mL ethanol solution containing SnCl₄·5H₂O (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 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.

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 were applied to a short column of ion exchange to remove any remaining chlorine, and were combined with the upper lightly turbid solution, in which the resulting dried powders were added and dispersed on a shaker. In succession, the combined solution was distilled and left behind a fine light-yellow powder of Sb-SnO₂. In this way, all of the metal hydrolysate can be recovered and an exact doping as experimenter desires was achieved.

The impregnation with (NH₄)₂SO₄

The sulfated Sb-doped SnO₂ crystals were prepared in our study as follows. 2 g of Sb-doped SnO₂ powder obtained in the synthesis of the precursor, antimony doped stannic oxide was placed in a 50 mL plastic centrifuge tube containing 45 mL of methanol. After the powders were dispersed on a shaker, 3.0 mL of saturated ammonium sulfate, equal to ~2 g of (NH₄)₂SO₄, was added in methanol solution, and then the tube continued to be shaken on a shaker violently as the saturated solution was dropped in methanol, when very tiny (NH₄)₂SO₄ precipitate

was separated in solution. The Sb-doped 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 Sb-SnO₂ nanocrystals was carried out at 380°C for 2~3 h.

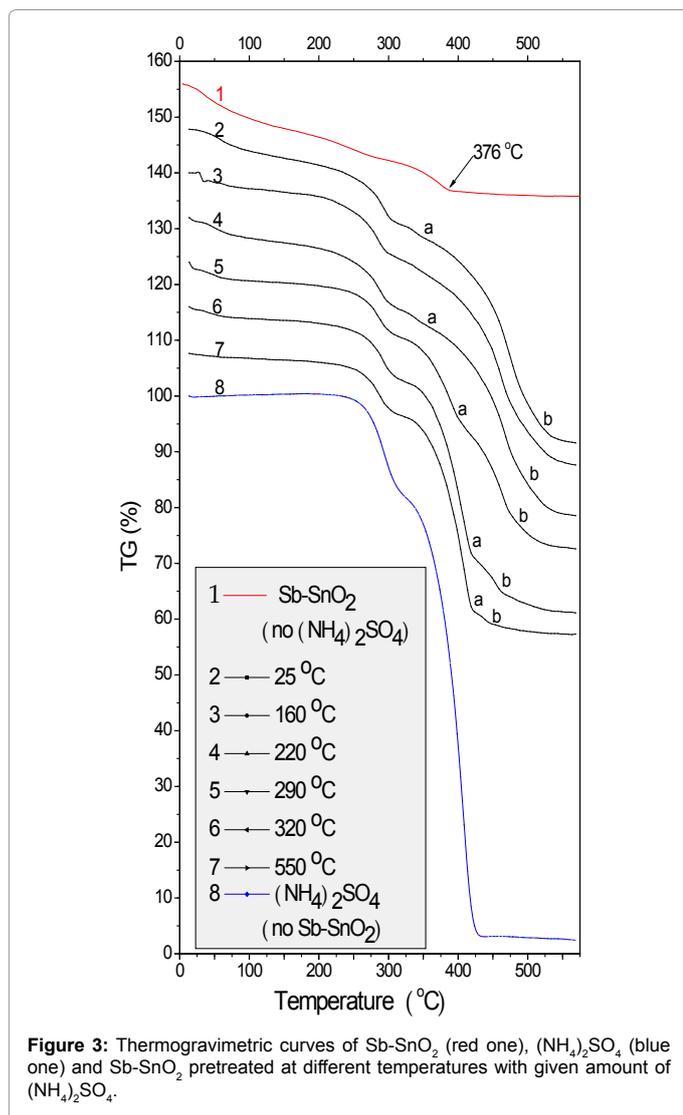
Results and Discussion

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 Sb 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 electro 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. 41-1445 from Jade 5.0, see the red bar in Figure 2.

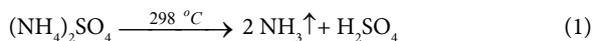
Crystal structure is of course important because the structure endows the material with some special properties, such as optical, semiconductor and electrical properties. On the other hand, superficial hydroxyl is, however, critical for the surface modification of nano-materials, and for hybrid nano-composites to mix with polymers.

In the calcination, it was found that superficial hydroxyl on Sb-SnO₂ nanoparticles had significant effect on the sulfating and roasting of Sb-SnO₂ nanocrystal, which had been demonstrated by Differential Scanning Calorimetry and Thermogravimetric analysis (DSC-TG). The fewer the number of superficial hydroxyl exist, the fewer the sulfated groups exist on the surface of Sb-SnO₂ nanocrystals. The thermogravimetric analysis (Figure 3) and differential scanning calorimetry (Figure 4) on the as-prepared powders support this view of point. Compared with curves 1 (Sb-SnO₂) and 8 ((NH₄)₂SO₄), curves 2 to 7 (Sb-SnO₂ + (NH₄)₂SO₄) have an additional segment from a to b in Figure 3. It is easy to understand that this segment probably implies the generation of superficially sulfated groups. Curves 2 to 7 are thermogravimetric curves of Sb-SnO₂ nanocrystals that were pretreated at different temperatures, from 25°C to 550°C, for 3 h and then impregnated with a given amount of (NH₄)₂SO₄ before thermogravimetric analysis. It can be seen that the higher the preprocessing temperatures is, the shorter the line segments from a to b, thus the fewer the amount of sulfated group is. As the preprocessing temperature increases, especially at/over 320°C (Figure 3), the weight losses of Sb-



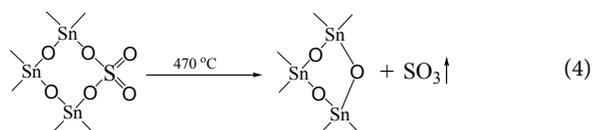
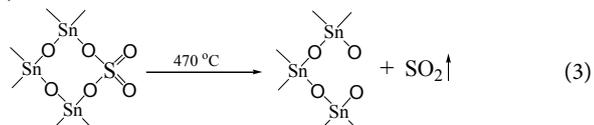
SnO₂ nanocrystals are heavier, resulting from the dehydration between hydroxyls and leading to the decrease of the quantity of the superficial hydroxyls. The decrease in amount of superficial hydroxyls brought about the decline of the quantity of superficially sulfated groups, and the decrease of acid 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:

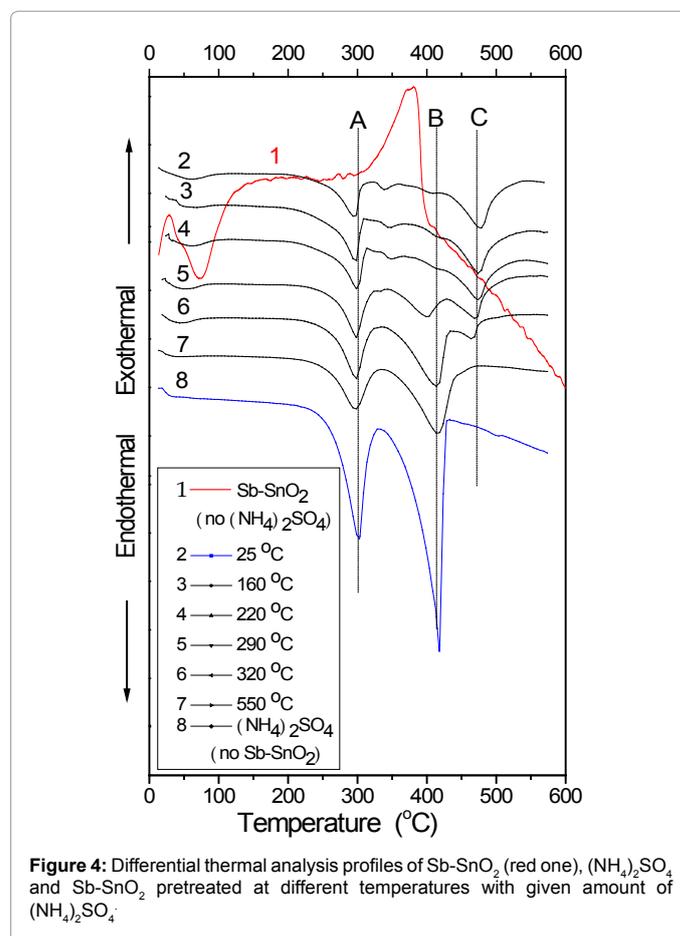


It should be pointed out that as the reaction of (NH₄)₂SO₄ with superficial hydroxyls of Sb-SnO₂ nanoparticles progressed, the amount of free (NH₄)₂SO₄ decreased and the decomposition temperature of H₂SO₄ decreased as well, see the peak B on curve 5 in Figure 4.

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.



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



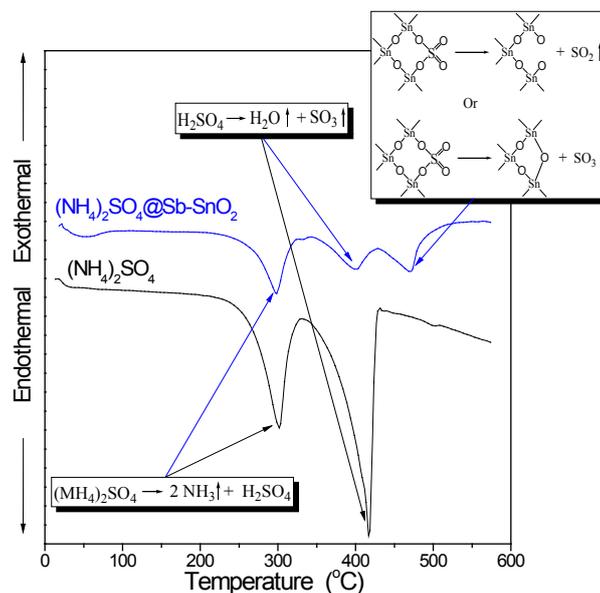


Figure 5: In the calcination, the decomposition of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 and the generation and the thermal cracking of superficially sulfated groups.

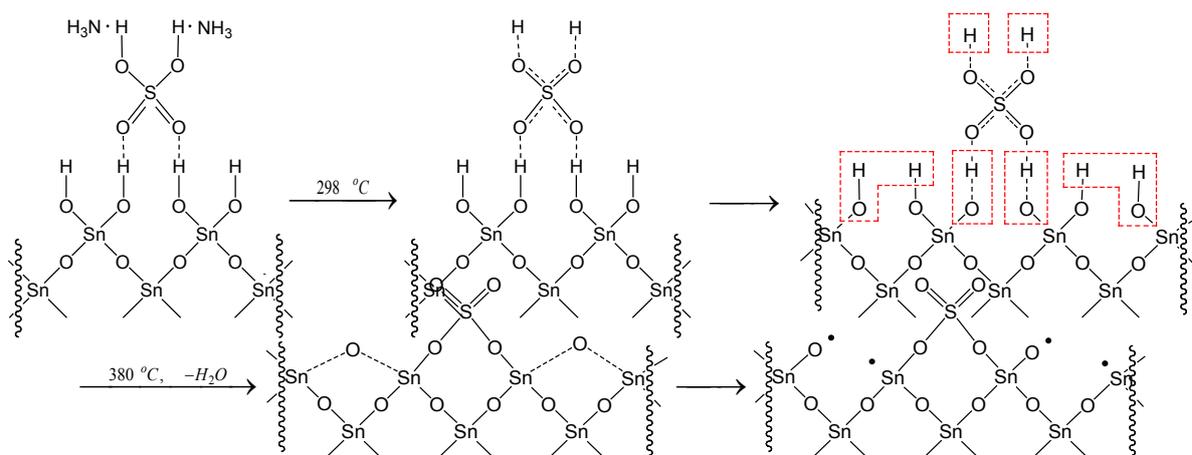


Figure 6: The generation process of solid super acid of Sb- SnO_2 in the calcination.

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 $(\text{NH}_4)_2\text{SO}_4$. 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_2SO_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 (pK_a or $\text{H}_0 = -11.4$), 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 $\text{H}_0 < -14.5$. All of the measurements convincingly demonstrated the calcined Sb- SnO_2 was a solid acid, more exactly solid superacid (Figure 7).

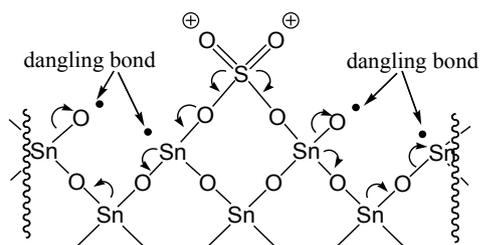


Figure 7: A proposed structure of Sb-SnO₂ solid super acid.

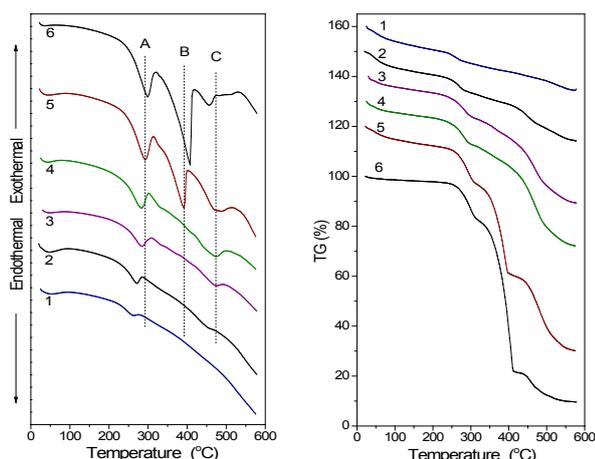


Figure 8: Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) profiles of 1.0 gram of Sb-SnO₂ exposed to 0.2 g (1), 0.4 g (2), 0.8 g (3), 1.2 g (4), 2.4 g (5), and 4.8 g (6). The optimum exposure ratio is 1:1.2 to 2.4 in weight.

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, $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{SnO}_2$ are absolutely impossible to show any acidity because group SO_4^{2-} is a conjugate base of H_2SO_4 . Based on the derivation of a series of chemical reaction in calcination 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 " SO_4 " bonded on Sb-SnO₂ nanoparticles and become a stable group " $=\text{SO}_4$ " of Sb-SnO₂ but an attached acid radical " SO_4^{2-} ", authors believed that the great enhancement of acidity of sulfated Sb-SnO₂ resulted from a number of dangling bonds around group= SO_4 . The both oxygen and tin with dangling bond are electron deficient groups and have electron-withdrawing effects, which leads to the transfer of negative charge from= SO_4 to dangling bonds and make = SO_4 a positive group with acidity. So, we proposed the solid superacid of Sb-SnO₂ should be noted as $\text{SO}_4^{\oplus}/\text{SnO}_2$ that, as a Lewis' acid, owns a great affinity for molecules bearing electron pair or negative ions.

Some further experiments concerning the impregnation of Sb-SnO₂ with ammonium sulfate were conducted using methods of Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) to study an optimal impregnation ratio of ammonium sulfate to Sb-SnO₂.

The nano-crystalline Sb-SnO₂ powders had to be dispersed in organic solvent since it could not be recovered if it scattered in water.

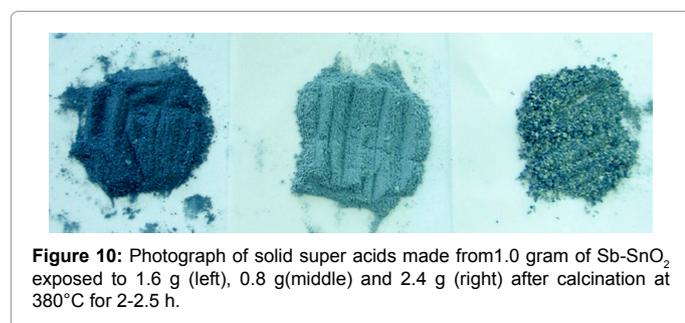
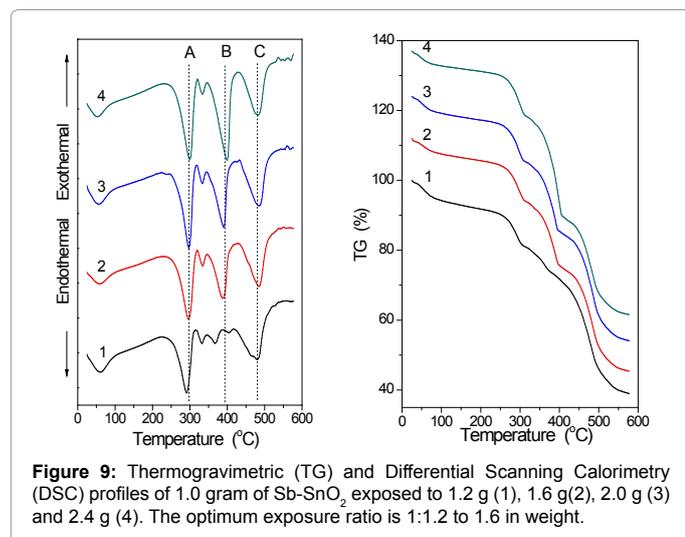
The ammonium sulfate, however, had to be dissolved in water for its solubility in organic solvent is very low. In the impregnation of Sb-SnO₂ powders with ammonium sulfate, a saturated solution of ammonium sulfate was dropped into organic solutions containing a fixed amount of Sb-SnO₂ nano-powder in 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 $(\text{NH}_4)_2\text{SO}_4$ fine particles. Without free water, for all water molecules were adsorbed on $(\text{NH}_4)_2\text{SO}_4$ fine particles. The dried powder was a uniform dispersion of powder of $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ in different ratio were studied on the Simultaneous TG-DSC Apparatus, STA 409PC, NETZSCH, Germany. The resulted analysis diagrams are showed in Figure 8. Here the Sb-SnO₂ nano-powder did not undergo any heat treatment and just impregnated with $(\text{NH}_4)_2\text{SO}_4$ directly in organic solvent. It can be simply and clearly identified the endothermic peaks and their height from the Thermo gravimetric (TG) and Differential Scanning Calorimetry (DSC) profiles of Sb-SnO₂ impregnated with different amount of $(\text{NH}_4)_2\text{SO}_4$. The height of peaks told us if there were excessive or deficient $(\text{NH}_4)_2\text{SO}_4$, 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 $(\text{NH}_4)_2\text{SO}_4$ being resolved into NH_3 and N_2SO_4 , the Peak B an endothermic one which resulted from the decomposition of H_2SO_4 , and the Peak C, without a doubt, was brought about by the absorption of heat contributed by the dissociation of a newly generated group= SO_4 . The Peak A was always presented in curves of all samples since the decompositions of $(\text{NH}_4)_2\text{SO}_4$ occurred for all samples but were different in their peak height due to different impregnation ratio, whereas, the Peak B only appeared as the amount of $(\text{NH}_4)_2\text{SO}_4$, or exactly H_2SO_4 , was excessive against superficial hydroxyl of Sb-SnO₂ because only the H_2SO_4 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 $(\text{NH}_4)_2\text{SO}_4$ from 1:1.2 to 1:2.4 wt%. The quantitative analyses of the ratio were conducted by the methods of differential 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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= SO_4 .

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 $(\text{NH}_4)_2\text{SO}_4$ would result in the blue solid superacid of Sb-SnO₂ with



little light yellow, while, a suitable or little excessive amount (1:1.4 and 1:1.6 wt%) of $(\text{NH}_4)_2\text{SO}_4$ could get a solid superacid of Sb-SnO_2 with an even blue after the calcination at 380°C . See the left one in Figure 10.

Conclusion

The nano-crystalline SnO_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_2 are crucial to prepare the solid superacid of Sb-SnO_2 , which is written as $\text{SO}_4^\ominus/\text{SnO}_2$.

This paper proposed the impregnated ratio of Sb-SnO_2 to $(\text{NH}_4)_2\text{SO}_4$ 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_2 solid superacid will be discussed in another paper.

Acknowledgement

The authors would like to extremely thank the "Chun Hui" Project from the Ministry of Education of China for funding the researches.

References

- Hino M, Kobayashi S, Arata K (1979) Solid catalyst treated with anion. 2. Reactions of butane and isobutane catalyzed by zirconium oxide treated with sulfate ion. Solid superacid catalyst. *J Am Chem Soc* 101: 6439-6440.
- Arata K (1990) Solid Superacids. *Advances in Catalysis* 37: 165-211.
- Arata K (1996) Preparation of superacids by metal oxides for reactions of butanes and pentanes. *Appl Catal A: General* 146: 3-32.
- Matsushashi H, Arata K (2006) Adsorption and desorption of small molecules for the characterization of solid acids. *Catalysis Surveys from Asia* 10: 1-7.
- Liu F, Martin-Mingot A, Jouannetaud MP, Bachmann C, Frapper G, et al. (2011) Selective synthesis of gem-chlorofluorinated nitrogen-containing derivatives after superelectrophilic activation in superacid HF/SbF_5 . *J Org Chem* 76: 1460-1463.
- Liu F, Martin-Mingot A, Jouannetaud MP, Zunino F, Thibaudeau S (2010) Superelectrophilic activation in superacid HF/SbF_5 and synthesis of benzofused sultams. *Org Lett* 12: 868-871.
- Matsushashi H, Hino M, Arata K, Tanabe K, Hattori H, et al. (1989) Acid-Base Catalysis. Kodansha Press, Tokyo, Japan, pages 357.
- Matsushashi H, Hino M, Arata K (1990) Solid catalyst treated with anion: XIX. Synthesis of the solid superacid catalyst of tin oxide treated with sulfate ion. *Appl Catal* 59: 205-212.
- Yamato T, Hideshima C, Surya Prakash GK, Olah GA (1991) Solid superacid-catalyzed organic synthesis. 4. Perfluorinated resins in sulfonic acid (Nafion-H) catalyzed Friedel-Crafts benzoylation of benzene and substituted benzenes. *J Org Chem* 56: 2089-2091.
- Au C, Wang Z, Ji W, Liu KC, Dai H (2006) Activation and conversion of propane over nano-sized MnOx-Moy (M=Cu, V) promoted sulfated yttria-stabilized zirconia-titania catalysts. *React Kinet Catal Lett* 87: 59-66.
- Matsushashi H, Miyazaki H, Kawamura Y, Nakamura H, Arata K (2001) Preparation of a Solid Superacid of Sulfated Tin Oxide with Acidity Higher Than That of Sulfated Zirconia and Its Applications to Aldol Condensation and Benzoylation. *Chem Mater* 13: 3038-3042.
- Xiang B, Xu H, Li W (2008) Effect of calcination temperature on the performance of nano-size iron oxide catalysts for ethylbenzene dehydrogenation. *React Kinet Catal Lett* 94: 175-182.
- Zhang X, Liang H, Gan F (2006) Novel Anion Exchange Method for Exact Antimony Doping Control of Stannic Oxide Nanocrystal Powder. *J Am Ceram Soc* 89: 792-798.
- Yang F, Zhang X, Mao X, Gan F (2007) Synthesis and Characterization of Highly Dispersed Antimony-Doped Stannic Hydroxide Nanoparticles: Effects of the Azeotropic Solvents to Remove Water on the Properties and Microstructures of the Nanoparticles. *J Am Ceram Soc* 90: 1019-1028.
- Sun Q, Gao ZX, Wen B, Sachtler WMH (2002) Spectroscopic Evidence for a Nitrite Intermediate in the Catalytic Reduction of NO_x with Ammonia on Fe/MFI . *Catal Lett* 78: 1-4.