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Preparation of Ga_2O_3 Doped Sulfonated Tin Oxides as a Highly Active and Recyclable Heterogeneous Solid Acid Catalyst for Aldol Reactions

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Ga_2O_3 doped sulfonated tin oxide catalysts were prepared via co-condensation method in ethanol solvent, followed by sulfonation and calcination. The samples were characterized by isothermal nitrogen adsorption/desorption, powder X-ray diffraction (XRD), thermal gravimetric analysis (TG), Raman spectra and DRIFT spectra. The number of acid sites on the catalysts was measured with the potentiometric titration of butyl amine. The results showed that the addition of small amounts of Ga_2O_3 to sulfonated tin oxide resulted in an enhanced acid site density, which makes Ga_2O_3 doped sulfonated tin oxide catalysts highly active for aldol reactions. The catalyst containing 1.5% Ga_2O_3 exhibited much higher activity than those of SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2 and H_3PO_4 in aldol condensation of prenal and prenol for citral precursor, which is a important in fragrance industry. Besides the high activity, the catalyst also exhibited good recyclability, making 1.5% GST an efficient and promising solid catalyst for aldol reactions.

Keywords: Sulfated Tin Oxides, Ga_2O_3, Doped, Aldol Reaction, Citral Precursor.

1. INTRODUCTION

Acid catalyzing reactions have widely used in producing various important chemicals in industry. The most traditional used acid catalysts are H_2SO_4, H_3PO_4, HF and $AlCl_3$.[1] However, the equipment corrosion and the need for post neutralization are undesired with these catalysts, as it will increase the operation units, additional waste and cost. To avoid these problems, using solid heterogeneous acid catalysts to replace these liquid acid catalysts have been favored. Many different kinds of solid acid catalysts, such as sulfonated carbonized sugar,[2] Nafion acid resins,[3,4] sulfated metal oxides,[5,6] tungstated zirconia,[7] have been reported with high catalytic activities in quite a lot of acid catalyzing reactions. Particularly, sulfonated metal oxides have received wide attention due to their high surface acidity and catalytic activity in many acid reactions such as isomerization, esterification and alkylation.[8–10] Among these sulfonated metal oxides, sulfonated zirconia (SO_4^{2-}/ZrO_2) is one of the most studied acid catalysts. Compared to SO_4^{2-}/ZrO_2, sulfated tin oxides (SO_4^{2-}/SnO_2) usually have stronger acidity and exhibit higher catalytic activity in some acid catalyzed reactions.[11,12] However, studies related to SO_4^{2-}/SnO_2 are very rare because of the difficulty in preparation of this type of catalysts.[10] During the preparation of SO_4^{2-}/SnO_2, stannic hydroxide gel precursor was usually obtained as fine particles, resulting in difficulty in the filtration of precipitates. In addition, the acidity was relative low due to the low surface area of SO_4^{2-}/SnO_2. Therefore, it is highly desirable to develop an efficient route to synthesis of SO_4^{2-}/SnO_2 with high surface area and abundant acid sites as well as facile filtration.

In this study, we solve the above problems with small amounts of Ga_2O_3 modified SO_4^{2-}/SnO_2, which was prepared through a two-step chemical co-precipitation method. The addition of a certain amount of Ga_2O_3 increased the specific surface of SO_4^{2-}/SnO_2 catalyst and SO_4^{2-} loading, thereby improved the catalytic activity.

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When used as the solid acid catalyst for aldol condensation of prenal and prenol, 1.5% Ga_2O_3-doping SO_4^{2-}/SnO_2 showed the highest catalytic performance, and much higher than those of SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2 and H_3PO_4. After the reaction, the filtered catalyst can be used repeatedly over 5 times without obvious deactivation. Furthermore, the reaction solution without further processing can be directly used on the next reaction run. It not only greatly improved the production efficiency, but also reduced environmental pollution.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Catalysts

The SO_4^{2-}/SnO_2 catalyst was prepared by a two-step chemical co-precipitation method. In the first step, 35.06 g $SnCl_4 \cdot 5H_2O$ was dissolved in 200 mL water at room temperature; Then the solution was dispersed in 200 mL ethanol. Then 25–28% aqueous ammonia was added dropwise slowly with stirring and the final pH of the solution was adjusted to 8. The precipitate was filtered and subsequently washed with 50 wt% aqueous ethanol until all chloride was eliminated. The precipitate was collected by filtration and dried at 393 K for 12 h. In the second step, the obtained tin oxide powder (2.0 g) was placed in a glass flask with 25 mL of 3 $mol \cdot L^{-1}$ H_2SO_4; After stirred for 0.5 h, the precipitate was filtered by suction, dried at 393 K for 12 h, and finally calcined at 775 K in air for 3 h for obtaining SO_4^{2-}/SnO_2 (denoted as ST).

Ga_2O_3 (GST) doped SO_4^{2-}/SnO_2 were also prepared by chemical co-precipitation method. In the first step, $Ga(OH)_3$–$Sn(OH)_4$ was obtained by adding 25–28% aqueous ammonia slowly into an aqueous solution of $SnCl_4 \cdot 5H_2O$ and $Ga(NO_3)_3 \cdot 6H_2O$. The second step was the same as the SO_4^{2-}/SnO_2 (ST) catalyst. The obtained catalysts marked *X*% GST, *X*% represented the mol content of Ga_2O_3 in Ga_2O_3–SO_4^{2-}/SnO_2 (GST).

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-II A (30 kV, 40 mA), using nickel filtered Cu Kα radiation with wavelength of $\lambda = 1.5406$ Å. The scan speed was 6°/min in the range from 10–80°. Thermal gravimetrical analysis (TG) was performed using a Rigaku Thermoflex System with a heating rate 10 K/min from room temperature to 1050 °C in the air atmosphere. Specific surface areas were determined through the Brunauer-Emmet-Teller (BET) method. The samples were submitted to physical N_2 adsorption/desorption assays at −196 °C in the ASAP 2000 equipment. The catalysts were previously activated at 350 °C under 1.3×10^{-2} Pa. Potentiometric titration was adopted to measure the total acidity of the catalysts.[13] The sample (0.05 g) was suspended in 10 mL acetonitrile and agitated for 3 h. The suspension was titrated at 0.05 mL/min with 0.1 N *n*-butyl amine in acetonitrile. The Raman spectra were carried out in a LabRam micro-spectrometer equipped with a 8 mW Ar ion laser as excitation source ($\lambda = 514.5$ nm). The spectral range 0–1200 cm^{-1} was studied. GRAMS/32 software (Galactic Inc. Salem NH) was used to analyze all spectra. Diffuse reflectance FTIR spectra characterization is recorded on Bruker Vector 22 infrared spectrometer.

2.3. Reaction Studies

Aldol condensation for preparing citral precursor was carried out at 75 °C in a three necked round bottom flask fitted with a magnetic stirrer, a thermometer, a reflux condenser and a distillation column (with the number of theoretical plates of 8–12). A mixture of 100 g of prenal, 250 g of prenol, 40 g toluene and 1.5 g of catalyst was added to the flask. The concentrations of the reaction species were periodically determined by a gas chromatography equipped with a 30 m HP-5 capillary column and a FID on Agilent Technologies 7890A.

3. RESULTS AND DISCUSSION

The SO_4^{2-}/SnO_2 (denoted as ST) and Ga_2O_3-doped SO_4^{2-}/SnO_2 (denoted as GST) catalysts were prepared through a two-step chemical co-precipitation method. The main difference of our method with traditional synthesis route is that 50 wt% aqueous ethanol was used instead of pure water in the preparation of precursors. It could effectively avoid the formation of stannic hydroxide gel precursor, which is usually obtained as fine particles, resulting in hard filtration of precipitates. The possible reason is that the presence of ethanol can prevent stannic hydroxide gel dissociation and become fine particles.

The prepared catalysts were first characterized by XRD to determine the crystal structures. Figure 1 shows the XRD patterns of SO_4^{2-}/SnO_2 (ST) and *x*-GST ($x = 1.0$, 1.5, 2.0 and 3.0%) samples. The diffraction peaks of all samples can be ascribed to tetragonal phase of crystalline SnO_2.[14] There was no characteristic peak of Ga_2O_3, implying that Ga_2O_3 were highly dispersed in sulfonated tin

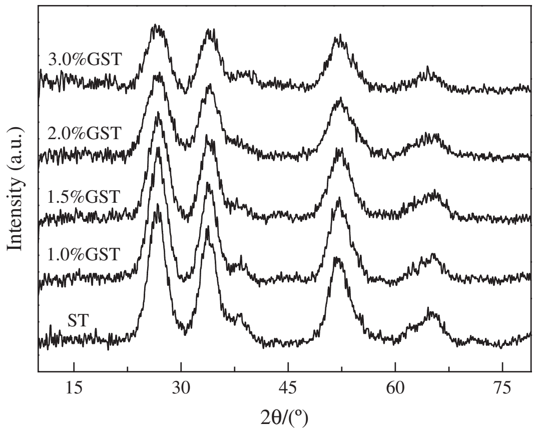

Figure 1. XRD patterns of the samples.

oxides. Furthermore, it was found that the width of ST peaks became broader after doping Ga_2O_3, suggesting the sizes of ST diminished.

The diffuse reflectance FTIR spectra characterization was then carried out to confirm the existence of sulfonated species on the catalysts. Taken ST and 1.5% GST catalysts for comparison, their DRFTIR spectra were shown in Figure 2. It can be clearly seen that four peaks at 1040 cm^{-1}, 1160 cm^{-1}, 1310 cm^{-1} and 1350 cm^{-1} at the range of 1000–1400 cm^{-1}, which can be ascribed to the absorption peaks of the vibration bidentate ligands of Sn^{4+} ions with SO_4^{2-}. Furthermore, the peaks intensity became stronger after doping Ga_2O_3 into ST, indicating that a small amount of Ga_2O_3 doping could help the sulfonated tin oxides to increase the sulfur sites on the surface.[15] Raman spectrum also supported this conclusion. As shown in Figure 3, peaks near 998 and 1034 cm^{-1} were the characteristics of S–O and S=O stretching modes of hydrated sulfate groups.[16] The intensity of the S–O and S=O bands vibration increased after doping Ga_2O_3 in sulfated tin oxide, suggesting higher sulfate content in the GST compared with that in ST. All these results suggest that sulfate was successfully immobilized on the surface of ST and GST, and the amounts of sulfate increased after Ga_2O_3 doping. In Raman spectra, other three peaks at 474, 684 and 776 cm^{-1} were corresponding to the E_g, A_{1g} and B_{2g} vibration modes of tetragonal rutile SnO_2 structure. This result is agreement with XRD. In other words, Ga_2O_3 doping did not change the structure of the bulk SnO_2.

Thermogravimetric analysis (TG) was further used to determine the contents of sulfate in the catalysts. As shown in Figure 4, two weight-loss stages were observed in the TG curves: the first step below 200 °C was due to the desorption of water, the second step between 500 and 900 °C was attributed to the decomposition of sulfate. According to the weight-loss curves at the second step, the content of sulfate species in all samples was calculated and list in Table I. It can be seen that 1.5% GST had the highest amounts of sulfate of about 10.7 wt%, which was higher than that in ST (8.1 wt%). It may be speculated that the small amount of Ga_2O_3 could enhance the interaction between sulfate species and SnO_2 and further raise the amount of sulfate species. Moreover, the more sulfate species may be associated with the higher catalytic activity for sulfonated metal oxides.[17]

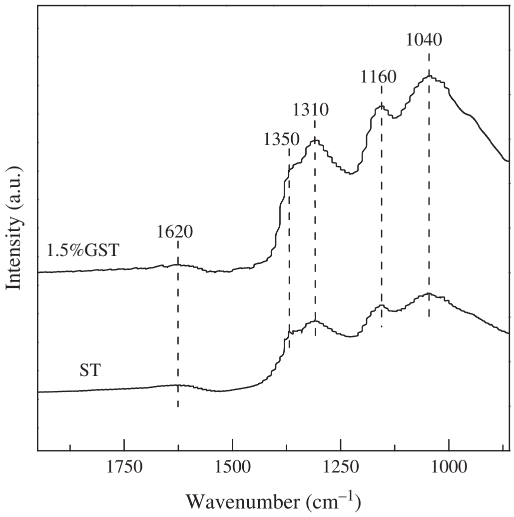

Figure 2. DRIFT spectra of ST and 1.5% GST catalysts.

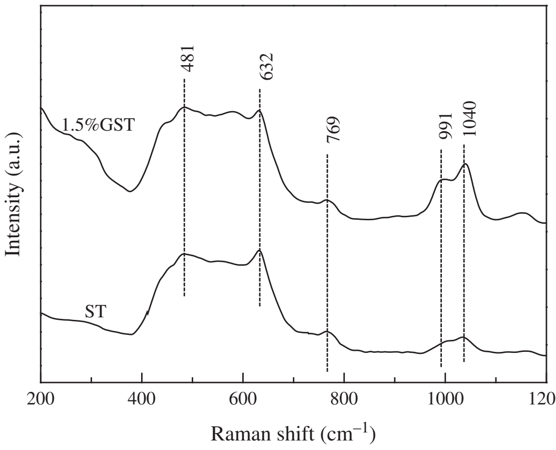

Figure 3. Raman patterns of the samples.

The surface acidity and acidic number of the catalysts was further investigated in detail through Potentiometric titration method with *n*-butyl amine.[18, 19] In general, $E >$ 100 mV corresponding super acid sites, $0 < E < 100$ mV correspond to strong acid sites, while the weak acid sites expressed with $-100 < E < 0$ mV and $E < -100$ mV correspond to very weak sites. The potentiometric titration curves of the catalysts were depicted in Figure 5. And the number of acid sites were determined according to the curves, and were listed in Table I. The number of super acid sites, strong acid sites and total acid sites of GST series samples are 0.154–0.279, 0.027–0.051 and 0.203–0.415 mmol/g, respectively, which are obviously higher than those of ST (0.094, 0.015 and 0.143 mmol/g, respectively). As the doping content of Ga_2O_3 increased,

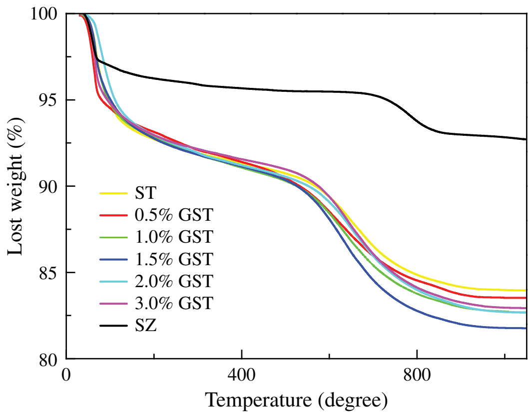

Figure 4. TG curves of the catalysts calcined at 500 °C.

Table I. Structural parameters of various sulfated tin oxides.

Samples	S_{BET} (m^2/g)	$W(SO_4^{2-})$ (%)[b]	Number of acid sites (mmol/g)			
			$E > 100$ mV	0 mV$< E <$ 100 mV	-100 mV$< E <$ 0 mV	Total
SZ[a]	102	3.7	0.021	0.007	0.019	0.047
ST	145	8.1	0.094	0.015	0.034	0.143
1.0% GST	173	9.8	0.178	0.027	0.022	0.223
1.5% GST	184	10.7	0.279	0.051	0.085	0.415
2.0% GST	179	10.3	0.252	0.039	0.044	0.335
3.0% GST	174	9.5	0.154	0.031	0.078	0.263

Notes: [a]SZ was calcined at 650 °C for 3 h and all sulfated tin oxides samples were calcined at 500 °C for 3 h. [b]Sulfate content were calcined from TG curves.

the number of strong acid sites and total acid sites first increased and then decreased. 1.5% GST possessed the highest amount of acid sites, which was in line with the fact this sample has the biggest surface area and sulfate content (Table I). The surface areas of catalysts were analyzed by N_2 adsorption–desorption method. As shown in Table I, the BET surface areas of GST series catalysts are 162–184 m^2/g, which were evidently higher than that of ST (145 m^2/g).

Citral is one of the key intermediate chemical stock material for a variety of high valued chemicals in pharmaceutical and fragrance industries, including vitamin A, ionone, methyl ionone, citronellol, nerol and geraniol etc.[20–23] The global annual output is around 40 thousand tons. Synthesis of citral is mainly from the aldol condensation reaction between prenal and prenol, followed by decomposition and rearrangement.[24–27] In the condensation reaction of prenal and prenol, the traditional method is to use liquid acid catalysts with medium acidity, such as phosphoric acid.[27] Therefore, it is also highly desirable to improve this process with solid acid catalyst. With the above GST heterogeneous solid acid catalysts, we first test their activity for aldol condensation in preparing citral precursor. Figure 6 shows the curves of conversion versus time at 75 °C on various catalysts. Only 1.8% conversion after 10 h was observed from aldol condensation of prenal with prenol in blank test without catalyst. Traditional SZ and homogeneous H_3PO_4 gave conversions of 51.3% and 48.4%, respectively. ST gave the conversion of 68.7% under the same conditions, which was higher than those of SZ and H_3PO_4. Notably, GST exhibited higher activity than ST, indicating that doping small amounts of Ga_2O_3 into sulfated tin oxide could markedly improve the catalytic activity for the aldol condensation. It was also observed that the GST catalysts showed a volcano pattern regarding the doping content of Ga_2O_3, i.e., the conversion increased to a maximum then declined with increasing doping content of Ga_2O_3. This transformation trend agrees well with the trend of number of very strong and strong acid sites with increasing doping content of Ga_2O_3. Notably, 1.5% GST sample has the highest activity with conversion of 86.7% after reaction for 10 h. The highest activity of 1.5% GST can be ascribed to the high surface area, sulfate species content, very strong and strong acid sites (Table I).

The recycling property is important for GST heterogeneous catalyst. After each cycle of reaction, 1.5% GST catalyst was separated by centrifugation to decant reaction mixtures, washed several times with methanol to remove the adsorbed reactants and products. The catalyst was then dried at about 50 °C and reused in a new reaction cycle

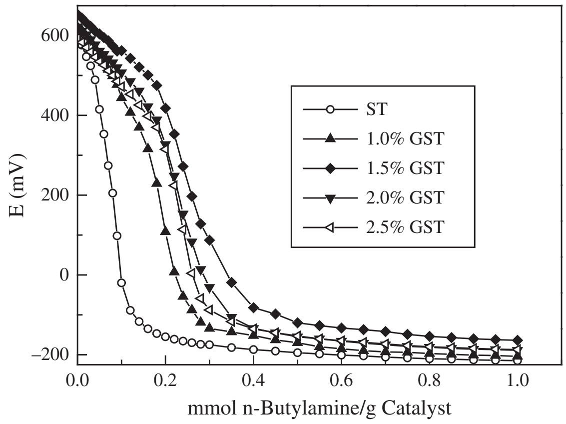

Figure 5. Potentiometric titration curves of the samples.

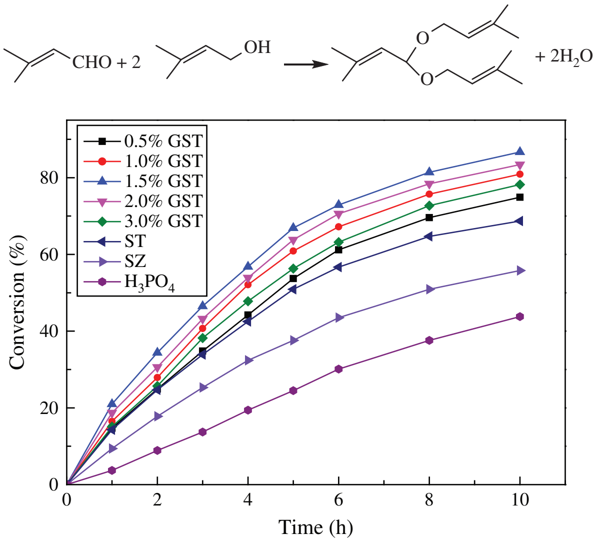

Figure 6. Prenal conversion depends on reaction time over various catalysts.

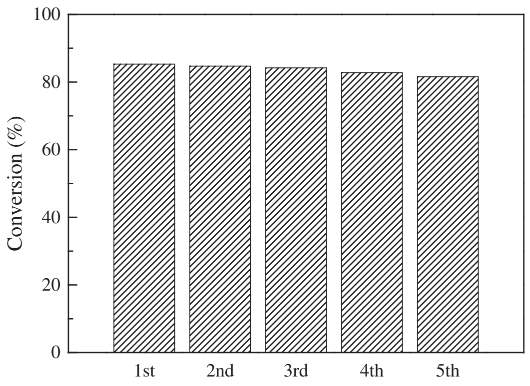

Figure 7. Catalyst reusability for the aldol condensation of prenal with prenol at 60 °C (reaction time = 10 h).

without any further treatment. As shown in Figure 7, only a slight drop of activity was observed after 5 cycles. The total acid sites of catalyst after fifth used (0.411 mmol/g) were nearly the same as the fresh catalyst (0.415 mmol/g). This result suggested that the GST catalyst was very stable. Together with the superior activity, 1.5% GST is a promising solid catalyst for aldol reaction.

4. CONCLUSIONS

We prepared a series of Ga_2O_3 doped sulfonated tin oxides by co-precipitation method in ethanol solution, followed by sulfonation and calcination. Compared with sulfonated tin oxide, a small addition of Ga_2O_3 to sulfonated tin oxide resulted in a decreased tin oxide crystallite size and increased surface area. In addition, Ga_2O_3 could help to stabilize the surface sulfate complexes and increase the effective acid sites on the catalysts. The Ga_2O_3 doped sulfonated tin oxide catalysts exhibited much higher catalytic activities than SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2 and H_3PO_4 in aldol condensation of prenal and prenol for citral precursor synthesis. The Ga_2O_3-doped catalyst with 1.5% Ga_2O_3 showed the highest catalytic performance. Furthermore, no obvious catalyst activity loss was observed after 5 cycles, indicating the good recyclability.

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