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Mesostructured sulfated tin oxide and its high catalytic activity in esterification and Friedel–Crafts acylation

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A mesostructured sulfated tin oxide with large surface area (172 m^2/g) has been successfully prepared using a block copolymer as structure-directing agent, which is extensively characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption, and Thermogravimetric analysis (TG) techniques. The results indicate that the mesostructured sulfated tin oxide was tetragonal crystalline, and catalytic tests show that the mesostructured sulfated tin oxide is much more active than conventional one for esterification and Friedel–Crafts acylation.

KEY WORDS: mesostructured; sulfated tin oxide; tetragonal crystalline; esterification; Friedel–Crafts acylation.

1. Introduction

Since solid superacids of sulfated metal oxides are reported in the early of 80's, they have received much attention because of their potential application in industrial reactions [1–7]. Sulfated tin oxide (SO_4^{2-}/SnO_2) is one of the candidates with the strongest acidity on the surface, and its acidic strength is equal to that of sulfated zirconia at least [8–10]. Nevertheless, as a result of difficulty in preparation, compared with the relative ease of preparation of sulfated zirconia (SO_4^{2-}/ZrO_2), papers concerning SO_4^{2-}/SnO_2 have been quite few. However, the samples of SO_4^{2-}/SnO_2 exhibit good performances in a series of catalysis [11–14], particularly in esterification and Friedel–Crafts acylation [13, 14]. Notably, SO_4^{2-}/SnO_2 prepared by conventional method always has relative small surface area. Therefore, it is still a challenge to prepare SO_4^{2-}/SnO_2 by a facile route with large surface area.

Recently, it has been reported successful syntheses of ordered mesoporous oxides [15–17] and mesostructured sulfated zirconia [18, 19], which offers a possibility to synthesize mesostructured sulfated tin oxide with large surface area. More recently, two groups try to prepare mesostructured sulfated tin oxide in the presence of sulfur-containing surfactants, but it fails to remove surfactants due to its poor thermal stability [20, 21].

We demonstrate here that a mesostructured sulfated tin oxide (MST) with large surface area (up to 172 m^2/g) is successfully synthesized from a template of block copolymer (P123), followed by sulfation of the sample. Interestingly, thermal stability of MST is over 550 °C, and the surfactants in the sample are easily removed by calcinations. Furthermore, catalytic tests in esterification of cyclohexanol with acetic acid and Friedel–Crafts benzoylation of toluene with benzoyl chloride show that MST is more active than conventional sulfated tin oxide.

2. Experimental

Mesostructured sulfated tin oxide (MST) was synthesized in the following: (1) One gram of P123 ($EO_{20}PO_{70}EO_{20}$) was dissolved in 20 ml of deionic water, followed by addition of 3.51 g of $SnCl_4{\cdot}6H_2O$. After stirring for 60 min, pH value of the solution was adjusted to 8.0 by aqueous ammonia, forming a gel. (2) After stirring at 45 °C for 4 h, the gel was transferred into a stainless steel autoclave for crystallization at 100 °C for 48 h. (3) After the gel was mixed with 4 wt% CH_3COONH_4 for 4 h, the white precipitate was filtered and dried at 100 °C. (4) One gram of the precipitate was immersed into 15 ml of 3 M H_2SO_4 at room temperature for 30 min, followed by filtration at room temperature, drying at 100 °C overnight, and calcinations at 500 and 550 °C for 3 h, respectively. The final product is denoted as MST-X, where X stands for calcination temperature.

In comparison, conventional sulfated tin oxide (CST) was prepared based on previous reports [14]. The precipitate was treated in the same way with MST-X.

X-ray power diffraction patterns of samples were obtained using a Siemens D5005 instrument with CuKα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. Transmission electron microscopy experiments were performed on a JEM-200CX electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. The

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adsorption and desorption isotherms, BET surface and pore size distribution data of samples measured using a Micromeritics ASAP 2010M system at 77 K using nitrogen as an adsorbent. Thermogravimetric analysis (TG) was carried out using a NETZSCH STA 449C with a heating rate of 20 K/min from room temperature to 1100 °C. The samples were mounted horizontally and purged with a synthetic airflow of 100 ml/min.

Catalytic esterification and benzoylation were performed in a three-neck flask. The flask was kept in a oil bath with a temperature control all ±1 °C, and the reaction mixture was magnetically stirred. As a typical run of esterification of cyclohexanol with acetic acid, 200 mg of catalyst and 10.5 ml (0.1 mol) of cyclohexanol was added into a 100 ml flask. After increasing the temperature to 100 °C, 17.2 ml (0.3 mol) of acetic acid was introduced into the reactor. Samples were withdrawn from the reactor at regular intervals.

Benzoylation of toluene was carried out in a 50 ml flask. A mixture of 15 ml (141 mmol) of toluene, 0.492 g (3.5 mmol) of benzoyl chloride, and 500 mg of catalyst was stirred under nitrogen atmosphere at 100 °C. After reaction for 3 h, the products were analyzed by gas chromatography (Varian CP-3800) with a FID detector. During this reaction, 0.170 g (1 mmol) of dodecane as an internal standard also was introduced.

3. Results and discussion

Figure 1 shows small-angle and high-angle XRD patterns of MST-500 and MST-550 samples. Notably, both samples exhibit a broad peak at 0.7° in the low-angle XRD, which is assigned to the presence of mesostructure. Interestingly, the mesostructure of the two samples is stable for calcination at 500 and 550 °C, indicating their highly thermal stability. In contrast, mesostructured sulfated tin oxide templated from dodecylsulfonate surfactant completely loses its mesostucture for heating at 350 °C [20, 21].

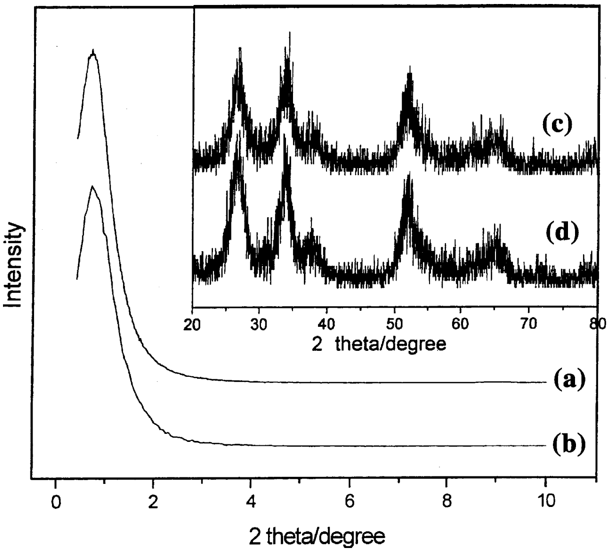

Figure 1. Small-angle XRD patterns of MST-500 (a) and MST-550 (b); and wide-angle XRD patterns of MST-500 (c) and MST-550 (d).

In the high-angle XRD, both samples show obvious peaks at ~27, 34, 38, 52, 65° (figure 1c and d), which are assigned to tetragonal phase of crystalline SnO_2 [22]. These results suggest that MST-X is composed of crystalline SnO_2 tetragonal phase, which is very important for the formation of strong acidic sites in sulfated tin oxide [13].

The TEM images of MST-500 and MST-550 (figure 2) show obvious mesostructures, in good agreement with those by small angle XRD patterns (figure 1a and b). Very importantly, the walls of MST-X samples are crystalline SnO_2, in good agreement with those by wide angle XRD patterns (figure 1c and d).

Figure 3 shows N_2 adsorption/desorption isotherms of MST-500 and MST-550 samples. Both samples have a hysteresis hoop at high relative pressure, which are reasonably related to the capillary condensation associated with mesoporosity. Correspondingly, the BJH pore size distribution of MST-500 and MST-550 shows a narrow pore size distribution at 3.1 and 3.9 nm, respectively. It is worthy to mention that BET surface areas of MST-X are much larger than those of CST-X (table 1).

Figure 4 shows the TG curves of MST-500 and MST-550 samples. Notably, there are two weight-loss steps: the first step below 200 °C is due to desorption of water; the second step between 500 and 900 °C is attributed to decomposition of sulfate species on the sample [22]. Based on the amount of weight loss, the amount of sulfate species is estimated on the surface of MST-500 (4.78 wt%) and MST-550 (3.48 wt%), which is higher than that of CST-500 (3.31 wt%) and CST-550 (2.96 wt%) (table 1).

Figure 5 shows the dependence of activity on reaction time in catalytic esterification of cyclohexanol with acetic acid as a typically industrial synthesis of flavors [23] over MST-X and CST-X samples. Notably, MST-X samples exhibit higher activities than CST-X samples. For example, when the reaction time reaches 6 h, MST-500 gives the conversion at 75%, while CST-500 exhibits the conversion at only 63%. The change in activity between MST-500 and CST-500 is reasonably attributed to the obvious difference in surface area and sulfate species (table 1)

Table 2 presents catalytic activities of MST-X and CST-X samples in Friedal-Crafts acylation of toluene with benzoyl chloride at the temperature of 100 °C. Similarly, MST-X samples also give higher activities than CST-X samples, which are also explained by the difference in sample surface area and sulfate species (table 1).

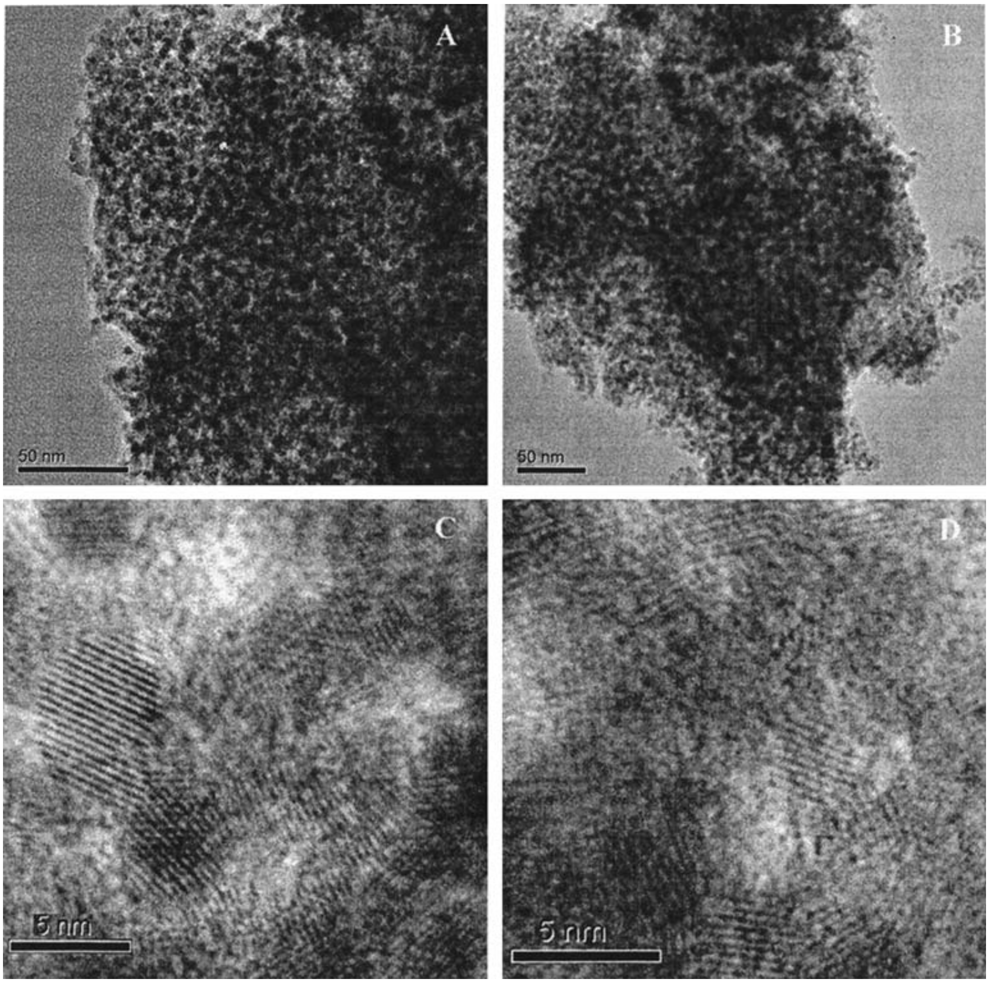

Figure 2. Low magnification TEM images of MST-500 (A) and MST-550 (B); and high magnification TEM images of MST-500 (C) and MST-550 (D).

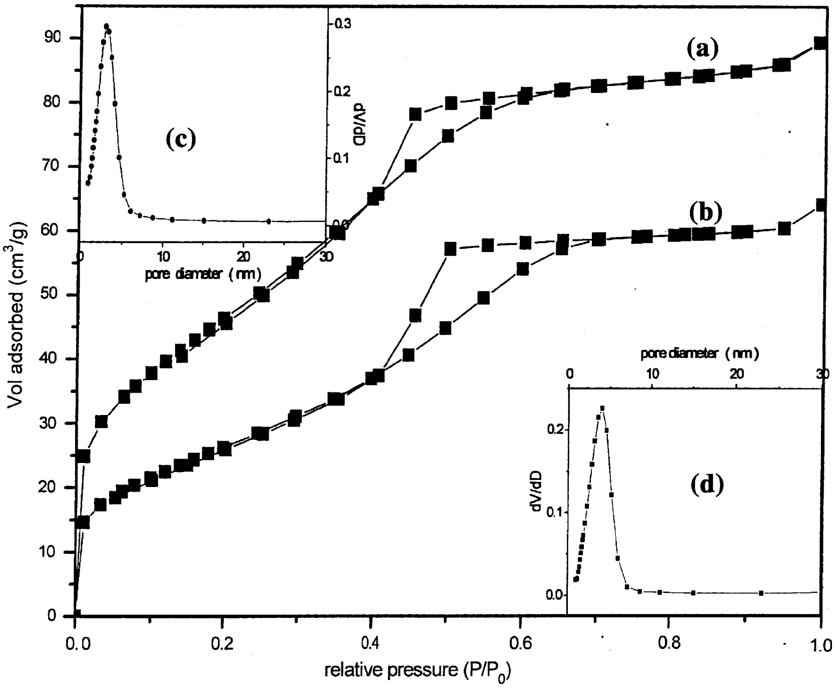

Figure 3. N2 adsorption/desorption isotherms of MST-500 (a) and MST-550 (b) and pore sizes distribution of MST-500 (c) and MST-550 (d).

Table 1
Textural properties of various samples

Sample	BET (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Sulfate content (%)
MST-500	172	0.17	3.1	4.78
MST-550	97	0.12	3.9	3.48
CST-500	93	0.13	–	3.31
CST-550	72	0.10	–	2.96

Table 2
Catalytic benzoylation of toluene with benzoyl chloride over various samples

Catalyst	Yield (%)	Selectivity (%)		
		o-	*m*-	*p*-
MST-500	89.2	20.0	3.7	77.3
CST-500	81.0	23.0	3.5	73.5
MST-550	79.8	19.6	3.5	76.9
CST-550	74.6	23.4	3.3	73.3

4. Conclusion

A mesostructured sulfated tin oxide with large surface area (MST-X) has been successfully synthesized from a template of block copolymer surfactants, followed by the sulfation of the sample. Catalytic tests show that MST-X samples are more active than conventional sulfated tin oxide (CST-X) for catalytic esterification of cyclohexanol with acetic acid and catalytic benzoylation of toluene with benzoyl chloride.

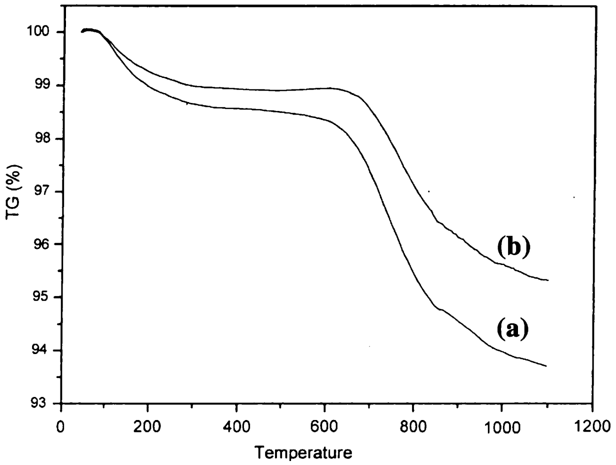

Figure 4. TG curves of MST-500 (a) and MST-550 (b).

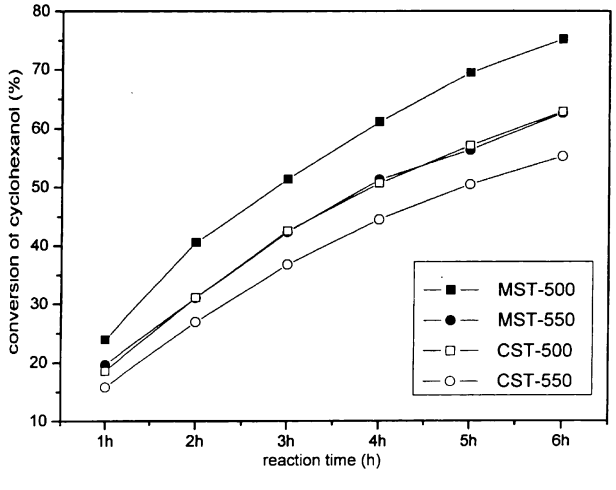

Figure 5. Dependence of cyclohexanol conversion on reaction time over MST-X and CST-X samples. The esterification of cyclohexanol with acetic acid was performed at temperature of 100 °C with a mole ratio of cyclohexanol to acetic acid at 1/3.

Acknowledgments

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