Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst

Baohua Zhang, Jiawen Ren*, Xiaohui Liu, Yun Guo, Yanglong Guo, Guanzhong Lu, Yanqin Wang*

Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, PR China

Abstract

A novel carbon-based solid-acid catalyst was simply prepared for the first time by the thermal treatment of p-toluenesulfonic acid (TsOH) with D-glucose at 180 °C in a sealed autoclave and it was proved to have high acidity and to be a highly efficient solid-acid catalyst in the reactions such as esterification of succinic acid with ethanol.

1. Introduction

The principles of green chemistry and increasing concerns about environmental issues have stimulated the research for recyclable strong solid acids to replace of conventional toxic and corrosive acid catalysts, such as sulfuric acid [1]. Integration of acidic functional groups (e.g., –SO3H) into solid surface, e.g. carbonaceous [2–5] or silica-based materials [6–9], has been explored to produce promising solid acids. Among them, the sulfonated carbon materials have received much attention due to their low costs, high stability, and high activities.

Sulfonated carbonaceous materials were usually synthesized through the oxidation of carbon materials by sulfur acid [10–12] or oleum [13,14] to generate sulfonic acid groups on the surface. For example, Hara et al. [10,11] obtained a series of carbon-based catalysts with acid densities ranging from 0.37 to 1.34 mmol H+/g by the sulfonation of incompletely carbonized sugars. Similarly, Budarin et al. [12] synthesized a mesoporous sulfonated Starbon-400 with 0.5 mmol/g SO3H loading. An ordered mesoporous phenol–formaldehyde resin was also functionalized with sulfonate groups by putting the material in the vapor of fuming sulfuric acid inside an autoclave [14]. Under optimal conditions, a surface acid concentration of 1.3 mmol H+/g was achieved on this material. All of these solid-acid catalysts were synthesized by two steps. The carbonaceous materials were prepared in first step and then were sulfonated at harsh oxidation conditions.

Herein we report an one-step facile and low-danger method to synthesize carbon-based solid-acid catalysts by commixing glucose and p-toluenesulfonic acid (TsOH) in a sealed vessel under thermal treatment of 180 °C. The reaction mechanism is most probably like this: firstly, the glucose was dehydrated into small organic molecules, mainly 5-(hydroxymethyl)-2-furaldehyde (HMF) [22], and the generated HMF could be hydrothermally carbonized into a carbon-rich resin as well as react with TsOH to ‘embed’ sulfonic acid groups. The result of the parallel reactions is that the obtained carbonaceous material was functionalized with sulfonic groups as shown in Scheme 1. Characterizations showed that this catalyst exhibited high ~SO3H loading of ~1.3 mmol/g and the catalytic performances were also investigated by using succinic acid esterification as a model reaction. The results showed that this carbon-based solid acid displayed much better activity and selectivity than those of sulfonated activated carbon and sulfonated D-glucose.

2. Experimental

2.1. Catalyst preparation

The carbohydrate-derived solid-acid catalyst was prepared via thermal treatment of the mixture of p-toluenesulfonic acid (TsOH)/glucose at 180 °C. In a typical synthesis, 2 g of D-glucose and 2 g of TsOH were comminxed in a 30 mL Teflon-sealed autoclave and maintained at 180 °C for 24 h. The obtained black products were filtered and washed with water and ethanol, and then oven-dried at 80 °C overnight. This sample was denoted as...
Glu-TsOH. As a comparison, 2 g of D-glucose without adding TsOH was also treated in the similar way and was denoted as Glu-180.

Two reference samples were also prepared by using concentrated H2SO4 as sulfonate agent. A 30 mL Teflon liner, containing 2 g of D-glucose or 1 g of activated carbon and 10 mL of concentrated H2SO4, was sealed into an autoclave and then put into an oven at 180 °C for 24 h. The obtained products were washed with hot distilled water (>80 °C) and filtered until no sulfate ions were detected in the filtration water, and dried at 80 °C overnight in air. The samples were denoted as Glu-SO3H and AC-SO3H, respectively.

2.2. Characterizations

The powder X-ray diffraction patterns were collected in the θ–2θ mode using a Bruker D8 Focus diffractometer (Cu Kα1 radiation, λ = 1.5406 Å), operating at 40 kV and 40 mA. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 M sorption analyzer. Before the measurements, the samples were degassed at 100 °C in vacuum for 12 h. FT-IR was carried out on a Nicolet Nexus 670 FT-IR spectrometer in the range of 400–4000 cm⁻¹. X-ray photoelectron spectra were measured using a Thermo ESCA LAB-250 spectrometer with monochromatic Al Kα radiation and the XPS results were calibrated using C1s peak at 284.8 eV. Thermal gravimetry analysis (TG) and differential thermal gravimetry (DTA) of the as-synthesized samples were performed at a heating rate of 10 K/min from 40 °C to 700 °C in flowing N2 by using a WCT-2 thermal analyzer.

2.3. Catalytic test

2.3.1. Succinic acid esterification reaction

In a typical catalytic experiment, 1 mmol succinic acid (SA, 0.118 g) and 80 mmol EtOH (4.6 mL) were added to a 25 mL round-bottom flask with 0.1 g of solid-acid catalyst, and then the temperature was increased to 80 °C. Few drops of reaction mixture were withdrawn periodically from the reaction mixture for GC analysis. Products were analyzed by GC–MS (PerkinElmer Clarus 500) and the products were proved to be monoethyl succinate (MES) and diethyl succinate (DIES) (Scheme 2).

2.3.2. Cycle usage test of Glu-TsOH catalyst

The stability of the catalyst was also tested by following procedure. After the reaction, the ‘used’ catalyst was separated from the solution by centrifugation and then washed with a large amount of ethanol for three times. After dried at 90 °C overnight, this catalyst was put into a fresh mixture of succinic acid/ethanol again with keeping same weight ratio of catalyst/succinic acid/ethanol. The product analysis was same as mentioned above.

3. Results and discussion

3.1. Carbonaceous materials properties

The XRD patterns of samples Glu-TsOH and Glu-180 are shown in Fig. 1. For sample Glu-180, which was prepared by the thermal treatment of glucose (C6H12O6 was used) at 180 °C in a sealed autoclave, the XRD pattern exhibits 1 weak broad diffraction peak at 2θ angle of 10–30 °C, which is attributed to (0 0 2) planes of amorphous carbon [11]. It is well known that the monodispersed carbon spheres could be synthesized by the hydrothermal carbonization of glucose [15] in water, but in our experiments, carbonaceous material with carbon element content larger than 74 wt% could be readily obtained without adding any water. The reason probably is that the carbonization could take place at the aid of water molecules which generated from the dehydration of glucose in our synthesis. The XRD pattern of Glu-TsOH displays similar pattern as Glu-180 but with higher intensity, indicating a relative better carbon framework than Glu-180. However, it should be noted that this carbon framework is still amorphous and far away from graphitization.

The FT-IR spectra of Glu-180 and Glu-TsOH are shown in Fig. 2. Compared to sample Glu-180, the distinguished features of Glu-TsOH in their FT-IR patterns are the typical stretching vibrations of C=O (1630 cm⁻¹) and C–O–C (1200 cm⁻¹) in the anhydride (Scheme 1), indicating the formation of TsOH as a sulfonate agent. The XPS results showed that the catalysts were successfully sulfonated and the sulfonic acid groups were present in the catalysts. The peaks at 284.8 eV and 288.4 eV were attributed to the C₁s and S2p peaks, respectively. The sulfur content in Glu-TsOH was calculated to be 7.8 wt%, which is higher than that in Glu-180 (5.2 wt%). The elemental analysis results showed that the carbon content in Glu-TsOH was 79.5 wt%, which is slightly lower than that in Glu-180 (81.6 wt%). The thermal gravimetry analysis (TG) and differential thermal gravimetry (DTA) of the as-synthesized samples were performed at a heating rate of 10 K/min from 40 °C to 700 °C in flowing N2 by using a WCT-2 thermal analyzer. The TG curves showed that the weight loss of Glu-TsOH was smaller than that of Glu-180, indicating that the catalyst was more stable. The DTA curves showed that the exothermal peak of Glu-TsOH was higher than that of Glu-180, indicating that the catalyst had higher thermal stability.

Fig. 1. XRD patterns of sample Glu-TsOH and Glu-180.

Fig. 2. Products obtained in the esterification reaction of succinic acid.
TsoH were the presence of new absorption bands at 1032 cm$^{-1}$, 1007 cm$^{-1}$ and 1118 cm$^{-1}$, which are attributed to SO$_3$H groups [16,17]. This indicates that the SO$_3$H groups were successfully incorporated into the carbon framework by adding TsoH in the synthesis system. On the other hand, the bands due to –OH stretching at 3420 cm$^{-1}$, C=O stretching at 1710 cm$^{-1}$, and C=C bonds stretching at 1620 cm$^{-1}$ were observed for both samples independently of the sulfonation.

The acid site densities of the catalysts were determined by acid–base back titration and the sulfur contents were measured by energy dispersive X-ray analysis (EDX). These results are listed in Table 1. It is obvious that samples Glu-TsoH and Glu-SO$_3$H exhibited higher sulfur content than AC-SO$_3$H. If all sulfur element in the catalysts was assumed as –SO$_3$H groups, the acid site densities of the catalysts were 0.5–1.3 mmol H$^+$ g$^{-1}$ depending on the synthesis conditions. But the acid titration experiments demonstrated much higher acid site densities than the estimations based on sulfur elemental analysis. The reason is that abundant phenolic –OH and –COOH groups were generated in the process of partial oxidation by concentrated sulfonic acid (for sample Glu-SO$_3$H and AC-SO$_3$H) or hydrothermal carbonization of glucose (for sample Glu-180) [11,18]. The strong sulfonation may also oxidize aliphatic CH$_3$/CH$_2$ groups to carboxylic acid groups [19], which may further explain the significant increase in total acid density after sulfonation, just like the Glu-SO$_3$H’s acid site is much higher than the Glu-TsoH’s in Table 1. The XPS analysis further proved most sulfur element in the catalysts is assigned to SO$_3$H groups with S$_{2p}$ binding energy of 168.0 eV [18].

### 3.2. Catalytic activity

Fig. 3 compares the conversions and selectivities to DIES for the esterification reaction of succinic acid with ethanol catalyzed by Glu-TsoH, Glu-180, Glu-SO$_3$H, and AC-SO$_3$H after 1 h, 2 h and 4 h. No pretreatment except drying the solid catalysts at 80 °C was carried out before the catalysts were added into the reaction mixtures. Since succinic acid esterification is a kind of autocatalytic reaction, the conversion and selectivity of blank solution (without adding any catalyst) under same condition are also shown in Fig. 3.

As shown in Fig. 3, except the non-sulfonated carbonaceous material Glu-180, AC-SO$_3$H shows the lowest conversion of succinic acid esterification and also the esterification rate, which will take more than 4 h to complete the reaction, whereas Glu-TsoH only need about 1 h. On the other hand, Glu-SO$_3$H displayed a similar conversion and esterification rate in the reaction compared to Glu-TsoH despite a big difference in total acid density from titration. These results can be well correlated to the loading of SO$_3$H (Table 1). AC-SO$_3$H has the lowest S content (except sample Glu-180) while Glu-TsoH and Glu-SO$_3$H exhibit similar S content. In other words, the loading of SO$_3$H groups is the key point for the activities of the catalysts.

Despite similar activities between Glu-TsoH and Glu-SO$_3$H, the selectivity to DIES for the Glu-TsoH catalyst was found to be about two times greater than that of Glu-SO$_3$H catalyst screened in the esterification within 1 h. This may be ascribed to the different surface properties with different synthesis conditions. According to some reports [12,20], a hydrophobic surface has been proved to be favorable in esterification reactions. This is because the water would contribute not only to a reverse hydrolysis [21] but also to a competitive protonation involving the water and the alcohol. Obviously, hydrophilic surface is not conducive to the esterification.

### Table 1

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$S_{\text{MB}}$ (m$^2$ g$^{-1}$)</th>
<th>S content (mmol g$^{-1}$)$^a$</th>
<th>Acid sites (mmol g$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glu-180</td>
<td>41</td>
<td>0</td>
<td>1.02</td>
</tr>
<tr>
<td>Glu-TsoH</td>
<td>&lt;1</td>
<td>1.27</td>
<td>1.99</td>
</tr>
<tr>
<td>Glu-SO$_3$H</td>
<td>&lt;1</td>
<td>1.35</td>
<td>3.20</td>
</tr>
<tr>
<td>AC-SO$_3$H</td>
<td>506</td>
<td>0.56</td>
<td>2.66</td>
</tr>
</tbody>
</table>

$^a$ Based on elemental sulfur analysis (EDX).

$^b$ Acid–base back titration, catalyst reacted with excess 0.05 M NaOH in aqueous solution at room temperature for 30 min before titration.

**Fig. 3.** The conversions and selectivities to DIES of the catalysts and blank solution (without catalyst) at different reaction time.
due to the absorption of water molecules generated in the reaction. To estimate the surface hydrophobicity of our catalysts, TG-DTA analysis was conducted and the mass loss below than 150 °C in TG curves, which is due to the loss of absorbed water, was considered to indicate the hydrophobic property. The TG curves of the catalysts (not shown) showed that Glu-SO₃H (containing 11 wt% water) was more hydrophilic than Glu-TsOH (8 wt%) while AC-SO₃H is the most hydrophilic sample (13.5 wt%). This result was well agreeable to their catalytic performances, is that Glu-TsOH displayed higher selectivity compared to Glu-SO₃H and AC-SO₃H.

The stability of the catalyst is of great importance for practical usage, so the cycle usage test of Glu-TsOH was conducted and the results are listed in Table 2. From Table 2 we can see that the conversions (4 h) of Glu-TsOH in six cycles were all above 95%, indicating a good stability. However, the selectivity to DIES decreased and kept at 33% in the last three cycles. The conversions and selectivities to DIES of Glu-TsOH after 10 h are also shown in Table 2 and the selectivities in the last three cycles kept at 73%. In fact, the activities and selectivities in last three cycles were still higher than some sulfonated activated carbons as well as sulfated zirconia from some reports [20,23], indicating that this method is effective for sulfonated carbon catalyst. The decrease in selectivity may be due to the changes in surface chemistry as indicated from less volatile content (weight loss in 150–800 °C) of 6-cycled catalyst in TGA analysis under N₂. We believe that this novel solid-acid catalyst provides an ideal combination of properties in terms of hydrophobicity, encouraging the inter-molecular dehydration and production of the more hydrophobic esters.

4. Conclusions

A novel and facile method for preparing highly active carbon-based solid-acid catalyst functionalized with sulfonic acid groups was reported. In this method, TsOH was used in the synthesis instead of concentrated/fuming sulfur acid and it makes the preparation safer by avoiding usage of dangerous chemicals. The so-prepared catalyst exhibits much higher catalytic activity than sulfonated active carbon in the reaction of esterification of succinic acid with ethanol. The cycle usage test indicated that the catalyst prepared by this method was relative stable. It would be noted that the method described here can be further extended to one-step synthesis of various functionalized carbon materials from saccharide and aromatic compounds with target functional groups, such as glucose/saliclyc acid system.

Acknowledgements

This project was supported financially by the 973 Program of China (2010CB732306), the National Natural Science Foundation of China (Nos. 20673037 and 20973058), the Commission of Science and Technology of Shanghai Municipality (08JC1407900) and East China University of Science and Technology, China.

References