

# Synthesis of novel carbon/silica composites based strong acid catalyst and its catalytic activities for acetalization

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**Abstract.** Novel solid acid based on carbon/silica composites are synthesized through one-pot hydrothermal carbonization of hydroxyethylsulfonic acid, sucrose and tetraethyl orthosilicate (TEOS). The novel solid acid owned the acidity of 2.0 mmol/g, much higher than that of the traditional solid acids such as Nafion and Amberlyst-15 (0.8 mmol/g). The catalytic activities of the solid acid are investigated through acetalization. The results showed that the novel solid acid was very efficient for the reactions. The high acidity and catalytic activities made the novel carbon/silica composites based solid acid hold great potential for the green chemical processes.

**Keywords.** Carbon/silica composites based solid acid; acetalization; green chemistry.

## 1. Introduction

Large amount of homogeneous acids such as, sulfuric acid was annually consumed as the acid catalyst for the production of various important chemicals, which needed the tedious separation of the catalysts from the homogeneous reaction mixture and produced large amount of wastes (Harton 1999; Misono and Acad 2000; Anastas and Kirchoff 2002; Clark 2002; DeSimone 2002; Okuhara 2002; Anastas and Zimmermann 2003). Solid acid catalysts received much attention for the potential substitution of the homogeneous acids with the advantages of easy separation and reusability. Many solid acid catalysts have been applied to replace the unrecyclable liquid acids. Compared to the homogeneous acid catalysts, the solid acids were less active, less stable and expensive. Carbon based solid acid catalysts attracted more and more attention for the high acidity and catalytic activities (Hara *et al* 2004; Toda *et al* 2005; Okamura *et al* 2006). The solid acids were generally prepared through two steps. In the first step, the carbonization of biomasses, such as sugar was carried out to form the polycyclic aromatic carbon sheets. Then the aromatic carbon sheets were sulfonated to introduce the acid sites. The carbonization process occurred at high temperature for a long time and various wastes were produced during the process, which caused heavy pollution. Although the surface sulfonation of carbon materials is now a well-established process, it is a rather harsh method because of the inactive carbon surface. Furthermore, the separation of sulfuric acid from the sulfonation mixture produced many wastes. In order to overcome inefficient process, hydrothermal carbonization was used instead of the thermal treatment in our previous work (Liang *et al* 2010a, b). The carbon based solid acid owned large

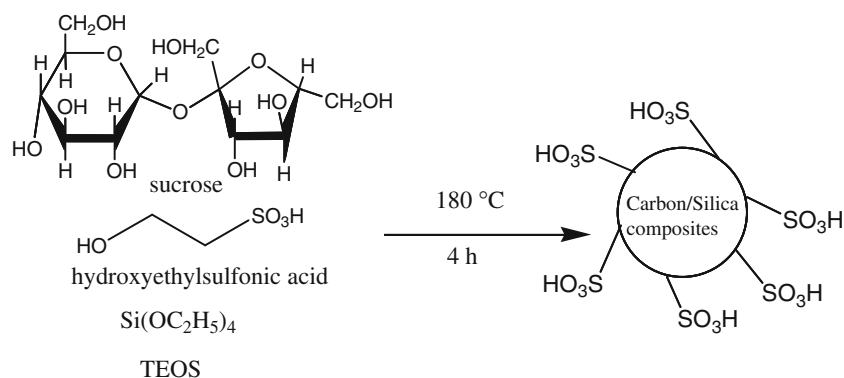
amount of hydrophilic functional groups, which provided good access for hydrophilic reactants to the SO<sub>3</sub>H groups. However, the hydrophilic functional groups prevent incorporation of hydrophobic molecules to the acid sites, and thereby hydrophobic acid-catalyzed reactions proceed in poor or with no catalytic activity (Nakajima *et al* 2009). The novel carbon/silica composites based solid acid was synthesized for the purpose. However, the new method added the step of impregnating sucrose to the channels of SBA-15, which further added to the cost for the use of the mesoporous molecular sieve. Here the novel efficient procedure has been developed for the synthesis of novel carbon/silica composites based solid acid through one-pot hydrothermal carbonization of hydroxyethylsulfonic acid, sucrose and tetraethyl orthosilicate (TEOS) (scheme 1). The catalytic activities of the novel carbon/silica composites based solid acid were investigated through acetalization. The results showed that the novel solid acid was very efficient for the reactions.

## 2. Experimental

All organic reagents were commercial products of the highest purity available (>98%) and used for the reaction without further purification. GC measurements were taken on a Shimadzu (GC-14B) gas chromatograph. GC-MS measurements were performed on an American Agilent 6890/5973N instrument.

In a typical procedure for the synthesis of carbon/silica composites based solid acid, a mixture of 2 g sucrose, 2 g TEOS, 2 g hydroxyethylsulfonic acid and 80 ml deionized water was stirred at room temperature and transformed to 100 ml Teflon-lined stainless steel autoclaves. The mixture was heated in an oven at 180°C for 4 h. The resulting products were dried in a vacuum oven at 100°C overnight. The

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**Scheme 1.** The synthesis route of novel carbon/silica composites based solid acid.

black solid was grinded into powder and washed with water until no acidity was detected in the filtrate. The novel carbon/silica composites based solid acid was obtained after drying at 120°C overnight in an oven.

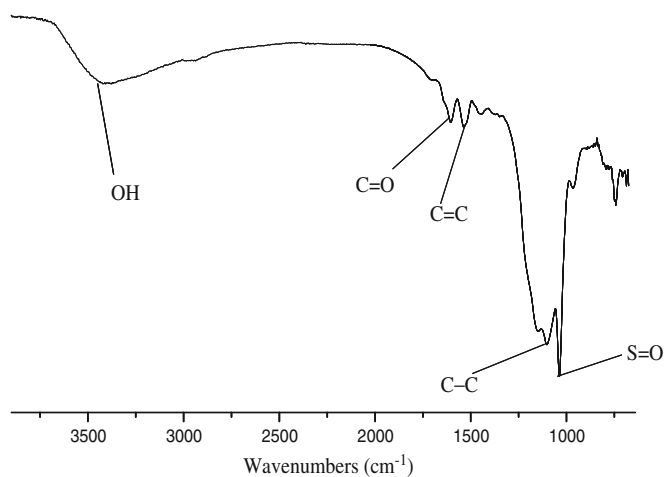
Typical procedure for the synthesis of acetals like aldehyde or ketone (0.1 mol), 10 ml cyclohexane, diol (0.15 mol) and catalyst (0.05 g) were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and a thermometer, and a Dean–Stark apparatus was used to remove the water continuously from the reaction mixture. The process of the reaction was monitored by GC analysis of the small aliquots withdrawn at half an hour intervals. On completion, the catalyst was recovered by filtering and washing with acetone, then dried in an oven at 80°C for about 1 h.

### 3. Results and discussion

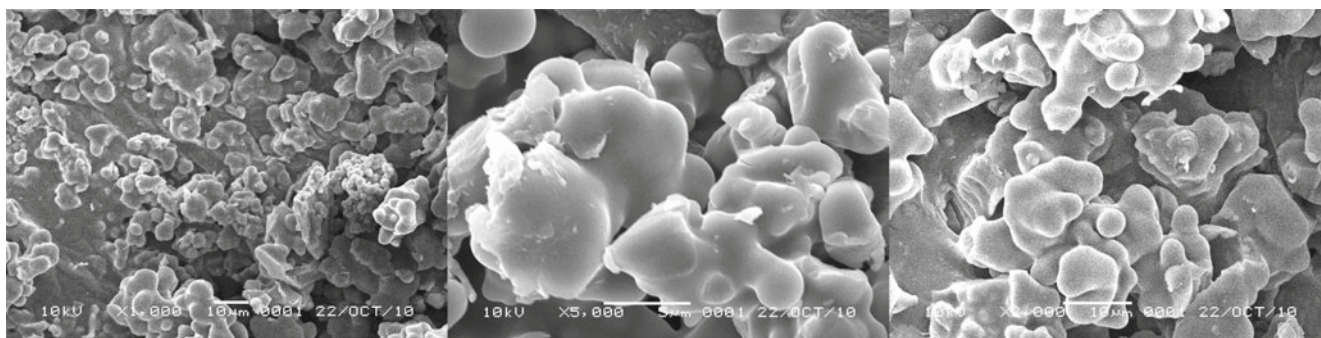
The acidity of the novel carbon/silica composites based solid acid was 2 mmol/g, which was determined through the neutralization titration. The titration was carried out as follows: carbonaceous material (40 mg) and 2 N aqueous NaCl (4 ml) were stirred at room temperature for 24 h. The solids were filtered off and washed with water (4 × 2 ml). The combined filtrate was titrated with 0.01 N NaOH using phenol red as an indicator (Margelefsky *et al* 2008). The catalyst owned much higher acidity than that of the common heterogeneous acid catalysts such as Nafion and Amberlyst-15 (0.8 mmol/g). The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH<sub>3</sub>–TPD). The result showed that the solid acid had strong acidity in which ammonia desorbed at 400–600°C. The BET surface of the novel solid acid reached a value of 532 m<sup>2</sup>/g. The element analysis of the novel carbon/silica composites based solid acid showed the composition as follows: C 45.3%; H 5.6%; S 6.0%; Si 15.8%; O 27.3%. The spectrum of X-ray photoelectron spectroscopy (XPS) analysis also showed S content of 6% with a single S2p peak attributable to sulfonic acid groups at 168 eV, which indicated that almost all the

S existed in the forms of sulfonic acid groups. On the other hand, the acidity of 2 mmol/g required an S content of 6.4%, which was higher than the actual content. These results indicated that there were still a few other acidic groups such as carbonyl acid groups in the carbonaceous material and the O content was as high as 27.3%, which also indicated that there were still many oxygen-containing groups in the material. The acidity of the novel solid acid increased when more hydroxyethylsulfonic acid was used. Here TEOS was used to improve BET surface of the materials for high BET surface and solid acid with BET surface of 126 m<sup>2</sup>/g was obtained. The molar ratio of TEOS and hydroxyethylsulfonic acid simultaneously change the acidity and BET surface. More TEOS caused high BET surface and reduce the acidity for the high concentration of the silicon dioxide in the solid, while more hydroxyethylsulfonic acid caused high acidity and lower BET surface for TEOS hydrolysis which occurred quickly without interacting with sucrose.

The IR spectrum of the novel solid acid (figure 1) showed the sulfonic acid group absorbability at 1040 cm<sup>-1</sup>,



**Figure 1.** IR spectrum of novel carbon/silica composites based solid acid.



**Figure 2.** SEM images of novel carbon/silica composites based solid acid.

which confirmed the existence of the sulfonic acid groups. FT-IR spectrum also showed that the solid acid contain resident functionalities including C=C ( $1570\text{ cm}^{-1}$ ), C-C ( $1140\text{ cm}^{-1}$ ), C=O ( $1680\text{ cm}^{-1}$ ) and OH ( $3400\text{ cm}^{-1}$ ).

The SEM images of the novel carbon/silica composites based solid acid showed that the resulting particles owned the shapes of spheres with a diameter of 2–5  $\mu\text{m}$  as depicted in figure 2, which also indicated that carbon and silica mixed well with each other and no different phases were observed in SEM images. Figure 2 also showed the spheres connected with each other in the carbon/silica composites structure. Here the reaction condition attached much importance to the materials. Almost no solid products were obtained in the initial 2 h period and the black solid formed after that. The

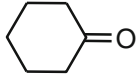
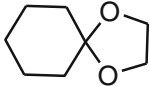
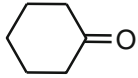
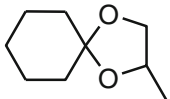
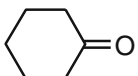
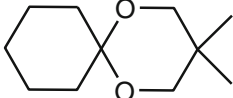
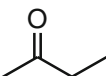
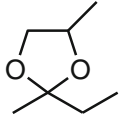
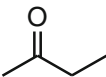
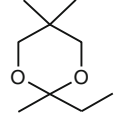
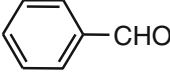
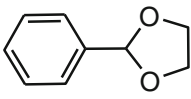
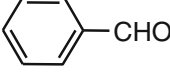
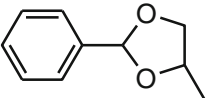
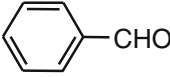
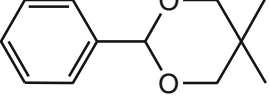

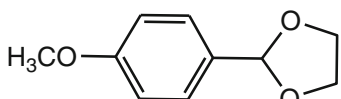
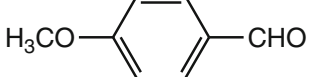
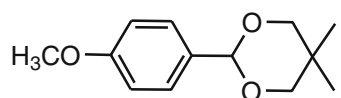

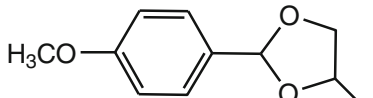

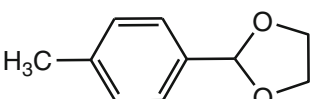
yield reached a peak value after 4 h and remained almost the same. The particle size increased quickly from 20 nm in 2.5 h with little solid formed to 2–5  $\mu\text{m}$  in 4 h. On the other hand, the particle size was affected greatly by the reaction temperature. High temperature accelerated the reaction process and the solid acid with a particle size of 50  $\mu\text{m}$  formed when the reaction was carried out at  $220^\circ\text{C}$ .

The catalytic activities of the novel carbon/silica composites based solid acid were investigated through the acetalization of various carbonyl compounds and diols (table 1). As was anticipated, all carbonyl compounds were successfully transformed to the corresponding products. The results in table 1 clearly demonstrated that the novel carbon/silica composites based solid acid was very efficient with high

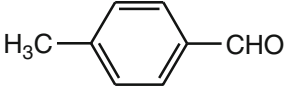
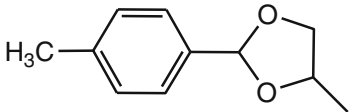
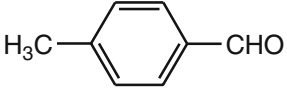
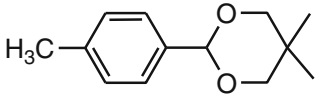
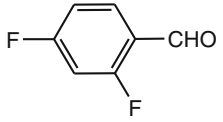
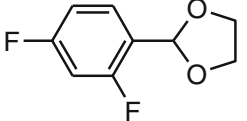
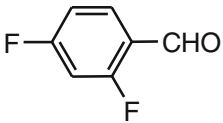
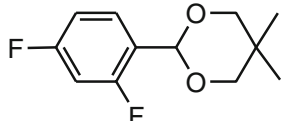

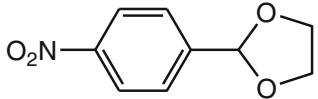
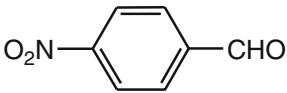
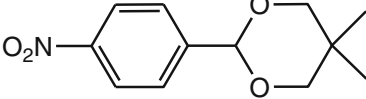
**Table 1.** Acetalization of various carbonyl compounds and diols <sup>a,b</sup>.

Entry	Substrate	Product	Reaction time (h)	Yield <sup>a,b</sup> (%)
1	<chem>ClCC=O</chem>	<chem>ClCC1OCOC1</chem>	0.5	99
2	<chem>ClCC=O</chem>	<chem>ClCC1OC(C)OC1</chem>	1.0	99
3	<chem>ClCC=O</chem>	<chem>ClCC1OC(C)(C)OC1</chem>	1.0	98
4	<chem>CCC=O</chem>	<chem>CCC1OC(C)OC1</chem>	1.0	99
5	<chem>CCC=O</chem>	<chem>CCC1OC(C)(C)OC1</chem>	1.5	98

**Table 1.** (continued).

Entry	Substrate	Product	Reaction time (h)	Yield <sup>a,b</sup> (%)
6			1.5	99
7			1.5	99
8			1.5	98
9			2.0	92
10			3.0	90
11			2.0	95
12			2.0	94
13			3.5	91
14			3.5	90
15			4.5	87
16			4.0	90
17			2.5	92

**Table 1.** (continued).

Entry	Substrate	Product	Reaction time (h)	Yield <sup>a,b</sup> (%)
18			3.0	91
19			4.0	89
20			1.5	97
21			2.5	93
22			1.5	95
23			2.0	92

<sup>a</sup>All reactions were carried out under Dean–Stark conditions; <sup>b</sup>conversion and selectivity were determined by GC using an internal standard method based on carbonyl compounds. In all cases, corresponding products were exclusively obtained.

**Table 2.** Activity comparison of different catalysts <sup>a,b</sup>.

Entry	Catalyst	Catalyst amount (mg)	Time (h)	Yield (%)
1	Novel catalyst	50	2.0	95
2	H <sub>2</sub> SO <sub>4</sub>	50	3.0	93
3	PTSA	60	3.5	90
4	Carbon based acid	100	3.0	90
5	Amberlyst-15	120	3.5	88

<sup>a</sup>All reactions were carried out under Dean–Stark conditions; <sup>b</sup>conversion and selectivity were determined by GC using an internal standard method.

yields for most reactions. Aliphatic aldehydes transformed to the corresponding acetals smoothly under the reaction conditions (entries 1–5). The ketalization reactions were also examined over the system. Cyclohexanone worked very well with almost complete conversion for the low steric hindrance of the carbonyl group (entries 6–8). The linear chain ketones such as butanone owned relatively low activity

for the reactions with moderate yields (entries 9–10). Aromatic aldehyde, such as benzaldehyde, could also be acetalized to afford the corresponding 1,3-acetal with high yields (entries 11–13). The groups attached to the aromatic ring also attached much importance to the reactivities. The aromatic aldehydes with electron-donating groups such as methyl or methoxyl groups showed relatively low activity, which reduced

the reactivities of the carbonyl groups (entries 14–19). On the other hand, electron-withdrawing groups enhanced the reactivities and the aromatic aldehydes with *F* and nitro groups showed higher activities (entries 20–23). Different diols such as 1,2-ethanediol, 1,2-propylene glycol and neopentyl glycol were all transformed to the acetals smoothly. The conversions reduced as follows: 1,2-ethanediol > 1,2-propylene glycol > neopentyl glycol for the steric hindrance of the diols.

A comparative study on the catalytic activities of the novel catalyst with the reported catalysts were taken through the reaction between benzaldehyde and 1,2-ethanediol (table 2). Amberlyst-15 was obtained from Fluck with an acidity of 0.8 mmol/g. The results showed that the novel carbon/silica composites based solid acid owned higher activity than the traditional carbon based solid acid produced through the sulfonation of the incomplete carbonized carbon sheet (Hara *et al* 2004). The mild carbonized condition made the novel catalyst a better choice for industrial applications. The novel catalyst showed much better activity than that of the homogeneous catalyst PTSA and the widely used Amberlyst-15. Therefore, novel catalyst owned great potential in the green processes for the substitution of homogeneous catalysts.

One property of the catalyst is heterogeneous catalytic process. Thus, the recovery of catalysts is very convenient. After reactions, by cooling the reaction mixture to room temperature, the catalyst was recovered by filtration. The recycled activity of the catalyst was investigated through acetalization of benzaldehyde and 1,2-ethenediol carefully. The results showed the high stability of the catalyst. The yields remained unchanged even after the catalyst had been recycled for the fifth time. The catalytic activity of filtrate showed almost no activity, which further confirmed the stability of the novel catalyst and no acid sites dropped during the catalytic process.

#### 4. Conclusions

The novel carbon/silica composites based solid acid synthesized through the one-pot hydrothermal carbonization. The

novel process was more environment-friendly in mild conditions with little waste emission and high yield. The novel solid acid showed high activities for the acetalization with an average yield of over 93%. The catalyst owned the advantages of high acidity, low cost, high BET surface for the hydrophobic acid-catalyzed reactions and high thermal and chemical stability, which made the novel heterogeneous catalyst hold great potential for the replacement of the homogeneous catalysts in the green chemical processes.

#### Acknowledgements

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