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One-Pot Synthesis of a Novel Catalyst with Strong Acid Sites Based on Carbon/Silica Composite[1]

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Abstract—A novel catalyst with strong acid sites based on carbon/silica composite has been synthesized through one-pot hydrothermal carbonization of hydroxyethylsulfonic acid, glucose and tetraethyl orthosilicate (TEOS). The novel solid acid showed an acidity of 2.1 mmol/g, much higher than that of traditional solid acids such as Nafion and Amberlyst-15 (0.8 mmol/g). The catalytic activity of the solid acid was investigated in the acetalization and dimerization of α-methylstyrene. The results showed that the novel solid acid was very efficient for both hydrophilic and hydrophobic acid-catalyzed reactions. Because of the high acidity and catalytic activity the novel solid acid based on carbon/silica composite is a promising catalyst for the processes in green chemistry.

Keywords: carbon/silica composites based solid acid, hydrophilic and hydrophobic acid-catalyzed reactions, green chemistry

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1. INTRODUCTION

Large amounts of homogeneous acids such as sulfuric acid are annually consumed as unrecyclable catalysts. Separating homogeneous catalysts from reaction products involves difficulty and expense and huge volumes of waste that need to be treated [1–7]. Since heterogeneous catalysts are easier to separate than homogeneous systems and they can be reused considerable attention has been paid in recent years to possible means to substitute homogeneous acids by solid acid catalysts. Many solid acid catalysts have been applied to replace the unrecyclable liquid acids. Compared to the homogeneous acid catalyst, the solid acids are less active, unstable and expensive. Carbon based solid acid catalysts have received increasing attention in recent years because of high acidity and good activity they provide in catalytic reactions [8–10]. The solid acids were generally prepared through two steps. In the first step, the carbonization of biomass, such as sugar was carried out to form the polycyclic aromatic carbon sheets. Then the aromatic carbon sheets were sulfonated to bring the acid sites. The carbonization process was undertaken 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 severe method because the carbon surface is fairly inactive. In addition, the separation of sulfuric acid from the sulfonation mixture produced a lot of waste materials. In order to avoid the inefficient process, we suggested earlier using hydrothermal carbonization instead of the thermal treatment [11, 12]. The carbon based solid acid contains a large amount of hydrophilic functional groups, which provides good access for hydrophilic reactants to the SO_3H groups. However, the hydrophilic functional groups prevent incorporation of hydrophobic molecules into the acid sites, and for this reason the carbon based solid acid show little or no activity for hydrophobic acid-catalyzed reactions [13]. With an aim to develop effective catalysts for these reactions the carbon/silica based solid acid was synthesized. But the new method added the step of impregnating the sucrose to the mesopores of SBA–15 and the mesoporous molecular sieve must be used, which further increased the production cost. In this work a novel efficient procedure is described that serves to synthesize a novel solid acid based on carbon/silica composites. The procedure includes one-pot hydrothermal carbonization of hydroxyethylsulfonic acid, glucose and tetraethyl orthosilicate (TEOS) (Scheme 1). The catalytic activities of the novel solid acid based on carbon/silica composites was investigated in the 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

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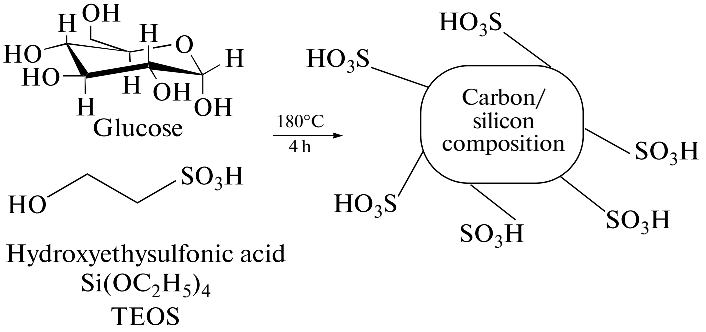
reaction without further purification. GC measurements were taken on a Shimadzu (GC-14B) gas chromatograph. GC–MS measurements were performed on an American Agilent 6890/5973N instrument.



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

2.1. Synthesis of the Novel Solid Acid Based on Carbon/Silica Composite

In a typical preparation, the mixture of the glucose (2 g), TEOS (2 g), hydroxyethylsulfonic acid (2 g) and 80 mL deionized water was placed in 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 180°C for 4 h. The resulting products were dried in a vacuum oven at 100°C overnight. The black solid was grinded into powder and washed with water until no acidity was detected in the filtrate. The novel solid acid based on carbon/silica composites was obtained after drying at 120°C overnight in an oven.

2.2. Acetalization of Benzaldehyde and 1,2-Ethanediol

In a typical preparation, benzaldehyde (0.1 mol), 10 mL cyclohexane, 1,2-ethanediol (0.15 mol) and the 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 reaction was monitored by GC analysis of the small aliquots for 1.5 h. On completion, the catalyst was recovered by filtering and washing with acetone, then dried in an oven at 80°C for about 1 h.

2.3. Dimerization of α-Methylstyrene

In a typical procedure, α-methylstyrene (25 mmol) and the catalyst (0.2 g) were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and a water-cooler condenser. The mixture was reacted over at 373 K for 4 h. Samples were withdrawn at intervals from the reaction mixtures and analyzed by gas chromatography using a capillary column. 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. RESULT AND DISCUSSION

3.1. Characterization of the Novel Catalyst

The acidity of the novel carbon/silica composites based solid acid was 2.1 mmol/g as measured by the neutralization titration. The titration was carried out as follows: carbonaceous material (40 mg) and 2 M 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 indicator [14]. The catalyst showed a much higher amount of 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_3–TPD) (Fig. 1). NH_3–TPD was carried out in a fixed-bed reactor equipped with a programmable temperature controller, at ambient pressure. About 1.0 g of sample was loaded into a quartz tube. The sample was preheated at 150°C for 3 h in flowing (dry) nitrogen. After cooling to 100°C, the sample was exposed to a stream of (dry) ammonia for 1 h at a flow rate of 20.0 mL/min. Then the sample was left in the flowing nitrogen at the same temperature for 10 h in order to purge any excess of ammonia and physically adsorbed ammonia. Finally, the TPD operation was performed by heating the sample from 25 to 750°C at a heating rate of 10°C/min. The result showed that the solid acid had strong acid sites from which ammonia was desorbed at temperatures of 400 to 600°C.

In our experiments TEOS was used to improve the BET surface area of the materials and the solid acid

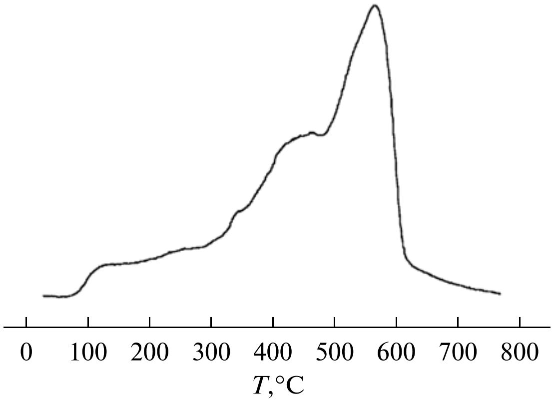


Fig. 1. The NH_3–TPD of the novel solid acid based on the carbon/silica composite.

with the BET surface of 532 m^2/g was obtained. The molar ratio of TEOS and hydroxyethylsulfonic acid affect both the acidity and the BET surface. As the amount of TEOS increases the catalyst shows an increase in the BET surface area and a reduction in acidity caused by the incorporation of additional amounts of silicon dioxide in the solid. On the other hand, with additional amounts of hydroxyethylsulfonic acid the catalyst shows a higher acidity and lower BET surface area because TEOS hydrolysis occurred quickly without interacting with glucose. The IR spectrum of the novel solid acid showed absorption bands at 1040 and 980 cm^{-1} from the sulfonic acid groups. FT–IR spectrum also showed that the solid acid contains other functional groups including C=C (1570 cm^{-1}), C–C (1140 cm^{-1}), C=O (1680 cm^{-1}) and OH (3400 cm^{-1}).

The elemental analysis of the novel solid acid based on carbon/silica composite showed following percentages: C 44.6%; H 5.5%; S 6.3%; Si 14.8%; O 28.8%. The spectrum of X-ray Photoelectron Spectroscopy (XPS) analysis also indicated that the sample containing 6.7% of S exhibited a single S 2*p* peak attributable to sulfonic acid groups at 168 eV. It can be thus inferred that the sulfur exists predominantly as sulfonic acid groups. On the other hand, an acidity of 2.1 mmol/g corresponds to the sulfur content of 6.7%, which is higher than the actually determined content. These results indicated that there are still a few other acidic groups such as carbonyl acid groups in the carbonaceous material and the oxygen content was as high as 28.8%, which also indicated that there were still many oxygen-containing groups in the material.

The SEM images of the novel solid acid based on carbon/silica composite show that the resulting particles are formed as spheres 2–5 μm in diameter (Fig. 2). It appears that carbon and silica components are completely mixed since different phases cannot be discriminated in the SEM images. Figure 2 also showed the spheres connected with each other in the carbon/silica composites structure. The element analysis also confirmed that the carbon and silica components were entirely mixed together and no core–shell structure could be recognized from the TEM.

3.2. Catalytic Activitiy for the Acetalization

The novel solid acid based on carbon/silica composite was applied to catalyze the acetalization of benzaldehyde and 1,2-ethanediol first (Fig. 3). For comparison, the results obtained with other catalytic systems are shown. These include concentrated sulfuric acid; zeolite (HY with an acidity of 0.8 mmol/g); Amberlyst-15 (strong acid cation exchange resin from Fluck with an acidity of 2.0 mmol/g), and the conventional carbon based solid acid produced through the sulfonation of the incomplete carbonized carbon sheet [8]. HY zeolite, an inorganic solid acid, exhibits relatively low activity, probably due to a moderate acidity, whereas Amberlyst-15 is quite active in the reaction. The novel solid acid based on carbon/silica composite exhibits a remarkably high activity for the acetalization. The activity level of this catalyst is higher than that of the conventional solid acids and is comparable to that of sulfuric acid.

A detailed account was given on reusability of the novel solid acid based on carbon/silica composite for the reaction. After reactions, the reaction mixture was cooled to room temperature; the catalyst was recovered by filtration. The recycled activity of the catalyst

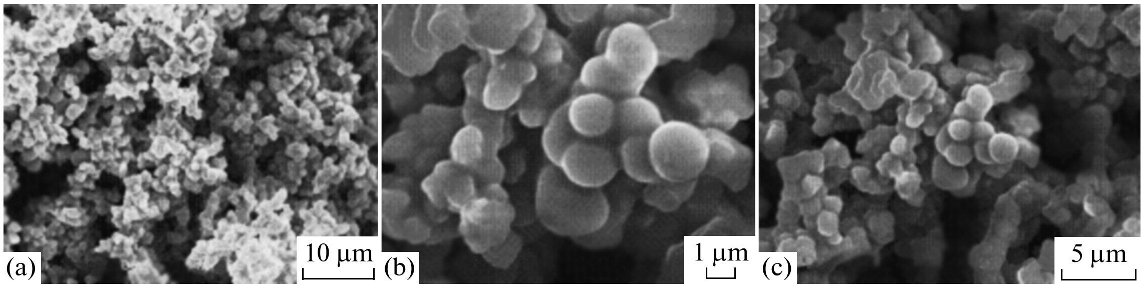


Fig. 2. The SEM images of the novel solid acid based on the carbon/silica composite.

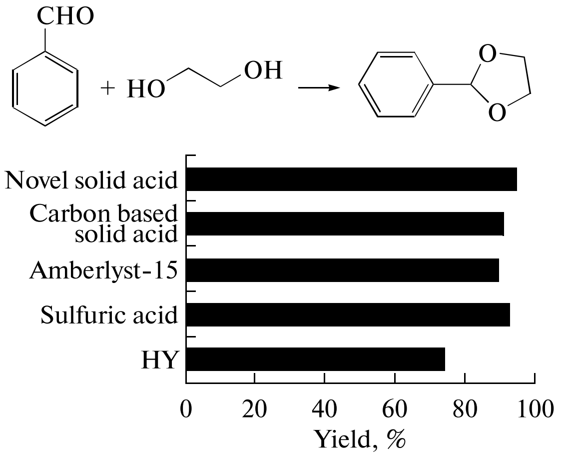


Fig. 3. Catalytic activity of the novel solid acid based on the carbon/silica composite for the acetalization.

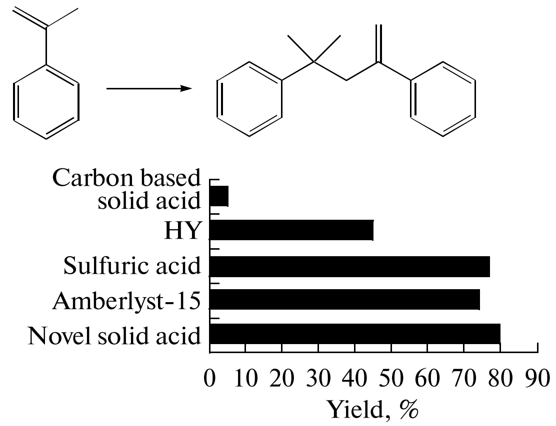


Fig. 4. Catalytic activity of the novel solid acid based on the carbon/silica composite for the dimerization of α-methylstyrene.

was investigated through the acetalization of benzaldehyde and 1,2-ethenediol. The results showed that the catalyst activity was stable. The yields remained unchanged even after the sample had been recycled five times. Furthermore, the catalytic activity of the recycled filtrate was investigated and the results showed no activity of the filtrate, which further confirmed that acid sites was not removed from the surface of the solid acid. These results support the suggestion of a high stability of the novel solid acid.

3.3. The Catalytic Activities for Dimerization of α-Methylstyrene

The novel solid acid based on carbon/silica composite was tested in the catalytic dimerization of α-methylstyrene (Fig. 4). HY zeolite with a high BET surface area exhibits relatively high activity for the reaction, whereas Amberlyst-15 is also quite active in the reaction. The hydrophobic molecule α-methylstyrene could reach the acid sites on the surface of the solid acid. However, the hydrophilic functional groups such as SO_3H, COOH, and phenolic hydroxyl (OH) groups prevent incorporation of hydrophobic molecules α-methylstyrene into the acid site on the traditional carbon based solid acid that shows a low BET surface area. The novel solid acid based on carbon/silica composite with a high BET surface area exhibits a remarkably high activity for the reaction. The activity is higher than that of the conventional solid acids and is comparable to that of sulfuric acid.

4. CONCLUSION

The novel solid acid based on carbon/silica composite was obtained through the hydrothermal carbonization. The novel process was more environment-friendly in the mild condition with little waste emission and high yield. The novel solid acid was very efficient for both hydrophilic and hydrophobic acid-catalyzed reactions with the activities comparable to those of sulfuric acid. The advantages of the catalyst include high acidity, large surface area, low cost and reasonable thermal and chemical stability, which made the novel heterogeneous catalyst an appropriate candidate for the replacement of the homogeneous catalysts in green processes.

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