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Novel magnetic carbon based solid acid for alkylation of benzene and dodecene

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HIGHLIGHTS

- The novel magnetic carbon based solid acid has been synthesized.
- The solid acid owned the core shell structure and easy accessible acidic sites.
- The solid acid showed high activities for the hydrophobic alkylation.
- The simple magnetic separation and high stability were the key properties of the process.
- The high activities for alkylation greatly enlarged the application field of carbon based acid to hydrophobic reactions.

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ABSTRACT

Novel magnetic carbon based solid acid has been synthesized through the hydrothermal carbonization of glucose with magnetic cores and sulfonation of carbonaceous intermediate with hydroxyethylsulfonic acid. The carbon based solid acid owned the core–shell structure and high BET surface, which provided the easily accessible acid sites on the shell. The magnetic solid acid exhibited high activities for the hydrophobic alkylation of benzene and dodecene with complete conversion of dodecene, which was difficult for the traditional carbon based acids for low hydrophilic surface. The simple magnetic recovery process and high stability added the advantages of the solid acid. The high activities, reusability and simple recovery process were the key properties of the solid acid, which hold great potential for green chemical processes.

1. Introduction

Acid catalysts were very important in chemical industries for producing various important chemical products [1]. The homogeneous catalysts such as sulfuric acid, p-toluenesulfonic acid and $AlCl_3$ were widely used in chemical processes. However, these catalysts suffered from the tedious post treatment for the removal of catalysts. Furthermore, large amounts of wastes were produced during the process, which caused serious pollution. Solid acid catalysts owned the advantages of easy separation after reactions and could be recovered by filtration, which greatly reduced the wastes emission [2]. Therefore, solid acids became the good choice and various solid acids were developed in recent years [3]. However, the solid acids owned lower acidity and stability than sulfuric acid, which resulted in lower activities [4]. Solid acids also suffered from diffusion difficulty for the heterogeneous catalytic process. Recently, the carbon based solid acid catalysts with high acidity and thermal stability have received wide attention [5,6]. The solid acids were generally synthesized via two steps. First, saccharides were carbonized to form the carbon intermediates. The carbonization process was carried out at high temperature (~400 °C) under nitrogen atmosphere to form the polycyclic aromatic carbon sheets. The carbon intermediates should be controlled properly to offer enough active sites for the following sulfonation. Then, the carbon intermediates were sulfonated in large amounts of sulfuric acid or fuming sulfuric acid. The harsh sulfonation conditions were taken owing to the low activities of the carbon intermediates. Moreover, the carbon based solid acids owned low BET surface (~2 m^2/g). It was generally known that the heterogeneous catalytic process included three steps. The reactants adsorbed in the solid catalyst. Then the adsorbed reactants interacted with catalytic sites to form the product and the product desorbed to release the active sites. For the solids with low BET surface, the essential adsorption process was limited, which was harmful to the catalytic activities. For the high acid density on surface, the carbon based solid acids

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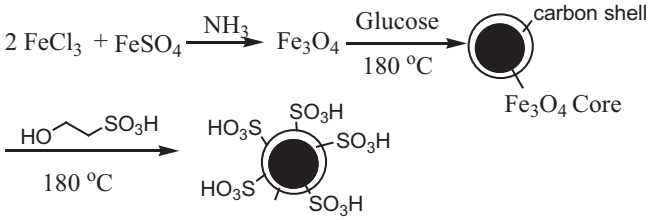

Scheme 1. The synthetic route of the magnetic carbon based solid acid.

showed high activities for hydrophilic reactions such as biodiesel synthesis and esterification [7,8]. As to the hydrophobic reactions, the reactants were difficult to reach the acid sites for the repulsion from the polar functionalities on the low surface, which resulted in low activities [9]. Some methods were adopted to increase the BET surface. The mesoporous SBA-15 was used as the hard template to produce porous carbon/silica composite solid acids [10]. However, the mesoporous template added the catalyst cost. The carbon based acids from porous carbon intermediates were produced to enlarge the BET surface [11,12]. Moreover, the application fields of the solid acids were still limited in the hydrophilic reactions such as esterification and the formation of Bisphenol A. The thermal carbonization step required high temperatures (>400 °C) and various wastes were released, which caused the heavy air pollution. In order to simplify the process, the green one-pot hydrothermal carbonization method was used to synthesize the carbon based solid acid in our previous work [13,14]. The carbonization was carried out in closed system, which prohibited the waste emission. The carbon based solid acids displayed high activities for various reactions such as acetalization, esterization and Michael addition. However, the hydrophobic reactions such as alkylation of aromatic compounds were still hard to be catalyzed by those carbon based solid acids. The magnetic materials have attracted wide attention with the magnetic properties and chemical modifiable surface [15–19]. Solid catalysts often suffered from the reduced activities for the diffusion hindrance compared to homogeneous catalysts [20]. Here the novel magnetic carbon based solid acid was synthesized through the hydrothermal carbonization of glucose with magnetic cores and sulfonation of carbonaceous intermediate with hydroxyethylsulfonic acid (Scheme 1). The novel solid acid owned the magnetic properties, which could be recovered by simple and easy magnetic attraction after reactions. The acid sites were dispersed on the carbonaceous shell over the external surface of magnetic core, which greatly reduced the diffusion limitations and provided the easy accessible acidic sites for reactants. The catalytic activities of the solid acid were investigated through the alkylation of benzene and dodecene. The results showed that the solid acid showed high activities for the hydrophobic alkylation, which greatly enlarged the application fields of carbon based solid acid.

2. Experimental

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

2.1. Synthesis of the magnetic carbon based solid acid

The magnetic core was synthesized by coprecipitation method [21]. The $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ with molar ratio of 2:1 were dissolved. Then, NH_3 solution was added to keep the pH between 11 and 12. The magnetic core was obtained by the magnetic attraction and washed with water.

Glucose (2 g) was dissolved in 80 mL water. Then, 0.2 g magnetic core was dispersed in the solution using ultrasonic vibration. The mixture was transferred to the 100 mL Teflon-lined stainless steel autoclaves and heated in an oven at 180 °C for 4 h. The carbon intermediate was magnetic attracted, washed with water and ethanol, and dried in an oven.

The 2-hydroxyethylsulfonic acid (0.6 g) was mixed with 1 g ethanol. Then, the carbon intermediate (1 g) was added to the mixture with grinding. The mixture was transferred to quartz furnace. The temperature was raised to 180 °C with the rate of 1 °C/min and kept for 4 h in nitrogen atmosphere. The black solid product was washed with water until no acidity detected in residual. The novel magnetic carbon based acid was obtained after drying at 120 °C.

2.2. The alkylation of benzene and 1-dodecene

The benzene, 1-dodecene and catalyst were mixed and mechanically stirred at the desired temperature. The alkylation process was monitored by the GC analysis. On completion, catalyst was recovered by magnetic attraction using an external magnet. The chromatographic analysis of the reaction mixture was carried out using Shimadzu (GC-14 C) gas chromatograph equipped with a FID detector using HP-5 capillary column. The products were confirmed by GC–MS.

3. Results and discussion

3.1. Characterization of the novel magnetic carbon based solid acid

The acidity of the magnetic carbon based solid acid could be adjusted through the raw materials ratio. The acidic sites were derived from 2-hydroxyethylsulfonic acid and the higher acidity was obtained with more hydroxyethylsulfonic acid amount. For the magnetic carbon based solid acid, the sulfonation could not be carried out by sulfuric acid to avoid the corrosion of the magnetic cores. The hydroxyethylsulfonic acid was used as the mild sulfonation reagent by the interaction of hydroxyl groups with carbon intermediate. The effect of the raw material composition on the acidity of the solid acid was shown in Table 1. Although more acid amount offered higher acidity, the magnetic core would be destroyed by hydroxyethylsulfonic acid with too high amount. The solid acid with acidity of 1.8 mmol/g was obtained with 0.6 g hydroxyethylsulfonic acid and 1 g carbon intermediate (entry 1). The higher acidity of 2.6 mmol/g was obtained with 1 g acid amount (entry 2). However, the magnetic property of the solid acid was weakened for the corrosion of the magnetic core. Only 0.8 g solid acid was obtained, which confirmed that the magnetic core was corroded by the acid. The carbon shell effectively protected the magnetic core from the acidity. The thickness of carbon shell also affected the acidity. The thicker carbon shell would provide more active sites for sulfonation. But the magnetism decreased with carbon shell for low magnetic core content (entry 3).

Table 1
The effect of the raw material composition on the acidity of solid acid.

Entry	Glucose (g)[a]	Hydroxyethylsulfonic acid (g)[b]	Acidity (mmol/g)
1	2	0.6	1.8
2	2	1.0	2.6
3	3	0.6	1.7
4	1	0.6	0.8
5	2	0.4	1.0

[a] For each hydrothermal carbonization process, 0.2 g magnetic core was used.
[b] Carbon intermediate (1 g) was applied for sulfonation.