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One-Pot Synthesis of a Novel Magnetic Carbon Based Solid Acid for Alkylation[1]

Siyi Zhang, Junqiao Li, Genzhong Ji, and Xuezheng Liang*
School of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing, 312000, China
**e-mail: liangxuezheng@126.com*

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Abstract—Magnetic carbon based solid acid has been synthesized via the one-pot hydrothermal carbonization of chitosan, magnetic core and hydroxyethylsulfonic acid at 160°C for 4 h. Chitosan was used as the carbon resource to protect the magnetic core from hydroxyethylsulfonic acid. The magnetic carbon based solid acid owned high BET surface and core shell structure, which provided the easily accessible acid sites on the carbon shell. The novel carbon based solid acid exhibited high activities for the hydrophobic alkylation of 1-dodecene and benzene, which was difficult to activate by traditional carbon based solid acids. The simple magnetic recovery added the advantages of the solid acid. The high activities for hydrophobic reactions, high stability and magnetic recovery were the key properties of the solid acid, which greatly enlarged the application area of the solid acid.

Keywords: magnetic carbon based solid acid, catalysts, composite materials, alkylation

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1. INTRODUCTION

Acid catalysts were very important in chemical industries for producing various useful chemicals [1, 2]. Sulfuric acid was the widely-used acid catalyst and large amounts of sulfuric acid were consumed annually worldwide. However, the liquid acid was difficult in separation and enormous wastes were formed during the energy-consuming post-treatment process [3]. Therefore, the solid acids with easy recovery received wide attention [4]. The carbon based solid acids were the promising catalysts with high acidity and stability, which held great potential in substituting the liquid acids in green chemistry [5–7]. These solid acids were generally prepared through the carbonization and sulfonation. First, the carbohydrate compounds were incompletely decomposed to form the polycyclic aromatic carbon sheets at relatively high temperature (400–550°C). The carbonization should be well controlled to confirm sufficient sites for sulfonation. Then, sulfonation by concentrated sulfuric acid or fuming sulfuric acid was taken to introduce the sulfonic acid groups. Besides sugars, various materials such as vegetable oil asphalt [8], petroleum asphalt [9] and glycerol [10] were used as carbon resources. The carbon based solid acids owned high acidity, which showed excellent performances for various reactions. However, these solid acids owned very low BET surface (~2 m^2/g) with abundant polar functionalities. For hydrophilic reactants such as organic acids and alcohols, the polar functionalities increased the affinity, which resulted in high activities. However, the solid acids showed very low activities for hydrophobic reactions with the repulsion effect of the hydrophilic groups [11]. Therefore, the carbon based solid acids with easily accessible acidic sites for hydrophobic reactants were highly demanded. The hard template method was applied to synthesize of the mesoporous carbon/silica composite based solid acids [12]. But the use of mesoporous molecule sieves added the production cost. The more economical activating methods were used to increase the surface. The pretreated raw materials such as impregnating the cellulosic precursor [13] and mesoporous starch [14–16] were applied for the synthesis of the carbon based solid acids. However, their applications were still limited in the hydrophilic reactions. The mild hydrothermal carbonization was also used to produce the carbon intermediate in our previous work [17]. The other materials such as corncob were also used in hydrothermal carbonization and good results were received [18]. In order to simplify the synthetic process, the one-pot hydrothermal carbonization of sugar and hydroxyethylsulfonic acid was developed for the synthesis of carbon based solid acids [19, 20]. However, these carbon based solid acids still restricted in hydrophilic reactions. For the hydrophobic reactions, these solid acids showed low activities. Magnetic materials gained wide applications in various fields such as data storage, magnetic resonance imaging and bio-

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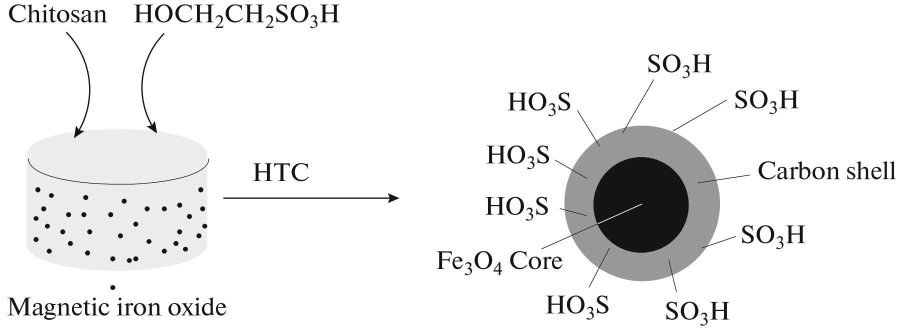
medicine, which could be easily functionalized with certain groups to create active surface [21].

Here the novel magnetic carbon based solid acid with core shell structure was presented through the one-pot hydrothermal carbonization of chitosan, magnetic core and hydroxyethylsulfonic acid at 160°C for 4 h (Scheme 1). The acid sites were dispersed around the external carbon shell, which greatly reduced the diffusion difficulty and provided the easily accessible active sites for reactants. In order to avoid the corrosion of the magnetic core by hydroxyethylsulfonic acid, chitosan was selected as the carbon resource. The amino-groups in chitosan could act as the acid binding agents. The magnetic carbon based solid acid showed high activities for the hydrophobic alkylation of benzene with 1-dodecene, which was hard for traditional carbon based solid acids. The results greatly enlarged the application area of the magnetic carbon based solid acid.

The synthesis route of magnetic carbon based solid acid



Scheme 1.

2. EXPERIMENTAL

All organic reagents were commercial products of high purity available and used for the reactions without further purification.

2.1. Synthesis of the Magnetic Carbon Based Solid Acid

The magnetic core was obtained by coprecipitation [22]. The solution of $FeCl_3$ and $FeCl_2$ with the molar ratio of 2 : 1 was stirred at room temperature (25°C). Then, NH_3 solution was dropped to adjust the pH value between 11 and 12. The magnetic core was collected by magnet and washed with water.

Chitosan (0.5 g) was added to 80 mL water with stirring for 10 min. Then, 0.3 g 2-hydroxyethylsulfonic acid was added to the mixture to form the chitosan solution. Finally, 0.5 g magnetic core was dispersed in the solution using ultrasonic vibration. The obtained mixture was hydrothermal carbonized at 160°C for 4 h in 100 mL Teflon-lined stainless steel autoclaves. The resulted solid was magnetic attracted and washed with water. The magnetic carbon based solid acid was obtained after drying at 100°C overnight.

2.2. Alkylation of Benzene with 1-Dodecene

The benzene, 1-dodecene and catalyst were placed in the flask with mechanically stirring. The alkylation was carried out at certain temperature. The reaction process was monitored by GC analysis. After reactions, the catalyst was recycled by the simple magnetic attraction. The quantitative analysis of the reaction system was carried out on chromatographic analysis using Shimadzu gas chromatograph (GC-14C). The qualitative analysis of products was taken by GC–MS on Agilent 7890A.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Novel Magnetic Carbon Based Solid Acid

Chitosan was dehydrated to form the aromatic rings and double bonds during the hydrothermal carbonization, which contained various reactions such as polymerization, aldolization and Diels–Alder [23]. Hydroxyethylsulfonic acid owned hydroxyl groups, which involved in those reactions to introduce sulfonic acid groups. Here the carbonization should be carried out around the magnetic core to form the core–shell structure and the hydroxyethylsulfonic acid also acted as the catalyst. However, hydroxyethylsulfonic acid would cause the corrosion of magnetic core. Therefore, chitosan with $-NH_2$ groups was used as the carbon resource, which also acted as the acid binding agent. In order to form the magnetic carbon based solid acid with core shell structures, the feed composition of raw materials should be carefully controlled. The magnetic core would be destroyed when hydroxyethylsulfonic acid amount was too high. On the other hand, the solid acid with low acidity was obtained with low usage. Also, chitosan would involve in self-carbonization when the amount of chitosan

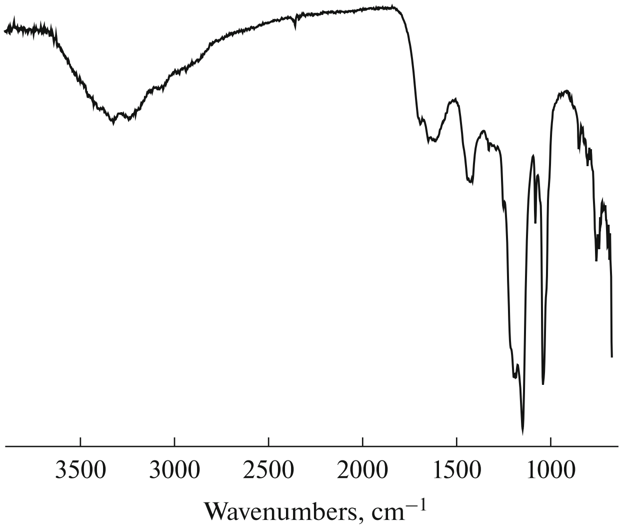


Fig. 1. IR spectrum of the carbonaceous material.

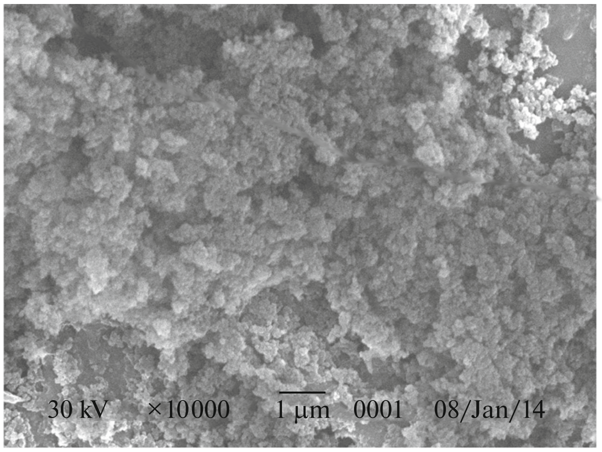


Fig. 2. SEM image of the magnetic carbon based solid acid.

was too high. Also, the chitosan could not be well dissolved with little acid amount. The magnetic carbon based solid acid with the acidity of 1.1 mmol/g was obtained when 0.5 g chitosan and 0.3 g 2-hydroxyethylsulfonic acid were used. The acidity increased with hydroxyethylsulfonic acid amount. However, the magnetic core was serious corroded when the hydroxyethylsulfonic acid amount increased over 1.0 g. The magnetic carbon with low acidity was obtained when the hydroxyethylsulfonic acid amount was quite low.

The Fourier transform infrared spectroscopy (FT-IR) spectrum of the magnetic carbon based solid acid was displayed in Fig. 1. The strong absorbability at 1041 cm^{-1} was assigned to the S=O stretching vibration, which confirmed the existence of the sulfonic acid groups. Also, FT-IR showed the strong C–O stretching vibration peaks in 1100–1250 cm^{-1}, which suggested the rich oxygen-containing groups in the solid acid. The absorbed peak at 1425 cm^{-1} was attributed to the C–N stretching vibration, which was derived from the chitosan. FT-IR spectrum also showed that the solid contained the C=O (1674 cm^{-1}) groups, which existed in the forms of esters or carbonyl acids. For the high absorption of the hydroxyl groups, the multiple broad peaks from 2700–3500 cm^{-1} were found, which also contained other functionalities such as Ar–H (3020 cm^{-1}), C–H groups (2950 cm^{-1}).

The scanning electron microscopy (SEM) image of the solid acid showed the packed structures with the particle sizes of 10–20 nm as depicted in Fig. 2. The particles gathered together for the magnetic attraction. The bulky molecules of chitosan were easy to coat around the magnetic core. The dehydration reactions occurred between the hydroxyl groups and the functionalities from different particles could also involved in the reactions, which enhanced the gathering trend. To improve the solid yields, the hydrothermal carbonization was carried out in relatively high concentration, which caused the reactions between different particles occurred more frequently and formed some bulky particles [24]. The magnetic attractions enhanced the gathered process especially at the first stage of the reactions. The distances between particles increased with the reaction for the carbonaceous shell became thicker, which weakened the magnetic attraction. Also, the ethyl sulfonic acid groups bonded to the carbon shell owned certain steric hindrance, which prevented the gathering. As a result, the solid acid owned the gathered structures with small particle size.

The TEM image of the solid acid displayed the sphere structures with the diameter about 10–20 nm (Fig. 3). The magnetic core was coated by carbon to form the protective shell from the acidity. The carbon shell also supplied enough active sites to introduce the sulfonic acid groups, which made the acidic sites around the external surface easily accessible to reactants. The high concentration of reactants in hydrothermal carbonization caused the uneven dispersion of the magnetic cores. The high partial concentration of the chitosan formed the thick carbon shell of 8–10 nm in some particles. On the other hand, the gathered magnetic cores caused the thin shell of 3–5 nm. Except for the unevenly dispersed particles, all the magnetic cores were coated by carbon shell, which formed the good guard against the acid. However, the carbon shell was not the dense enough to stop the H$^+$ ions permeating into the magnetic core [25]. Hydroxyethylsulfonic acid amount should be carefully controlled. The acid sites covered on the carbon shell would greatly decrease the diffusion difficulty, which benefited the catalytic activities especially for hydrophobic reactants.

The element analysis of the solid acid showed the results: C 12.8; H 0.9%; S 3.5%; Fe 54.3%. The S content agreed well with the acidity, which indicated that

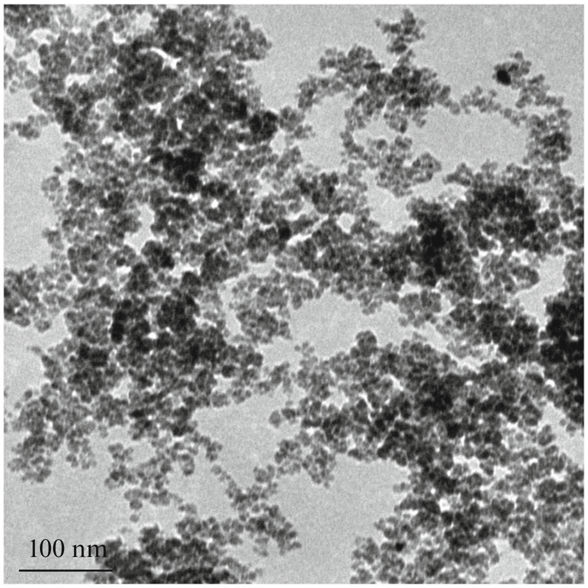


Fig. 3. TEM image of the magnetic carbon based solid acid.

the sulfur element existed main in the forms of sulfonic acid groups. It could be concluded that the magnetic attached much importance to the solid acid, which offered the magnetic properties and the accessible acidic sites in the carbon shell. The high magnetic core content effectively decreased the solid acid cost.

The thermogravimetry (TG) analysis was carried in the air atmosphere (Fig. 4). The result showed that the carbon based solid acid owned high thermal stability with the weight loss from 200°C, which was very high for the sulfonic acid groups functionalized solid acid. The carbon shell was destroyed when the temperature reached 400°C and the sharp weight lost occurred. The carbon shell totally decomposed with the process and the pure magnetic core iron oxide was obtained with 25% weight loss, which agreed well with the element results. The high inexpensive iron oxide content also reduced the catalyst cost.

The magnetic carbon based solid acid owned the BET area of 116 m^2/g, which offered high surface for the reactions. The aggregation of the particles formed some packed pores, which enlarged the BET surface. The high BET surface and the acid sites around the external carbon shell would greatly reduce the diffusion difficulty and confirm the high activities.

Figure 5 showed the XRD pattern of the magnetic carbon based solid acid. The diffraction peaks at 30.2°, 35.4°, 43.4°, 51.5°, 57.4° and 62.5° were assigned to the (220), (311), (400), (422), (511), and (440) planes of the magnetic Fe_3O_4 respectively [25]. The solid acid owned the similar peaks to the magnetic core, which indicated that the iron oxide structure was well kept during the carbonization process. The chitosan was the proper acid binding agent for the reactions. The proper composition of raw materials and mild carbonization condition were the key factor to keep the magnetic properties of the novel carbon based solid acid.

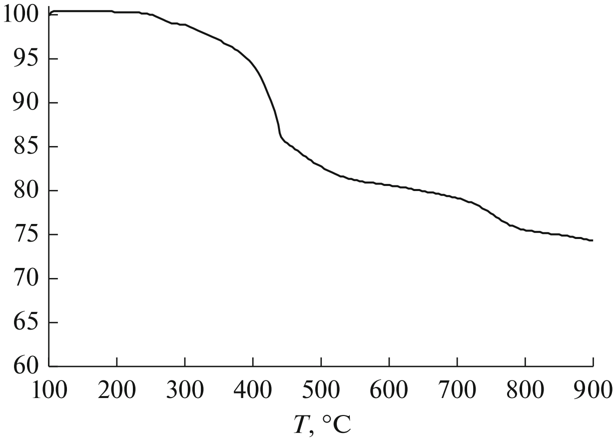


Fig. 4. TG analysis of the magnetic carbon based solid acid.

3.2. *Catalytic Activities for Alkylation of Benzene and 1-Dodecene*

The effect of the reaction time on the alkylation was investigated (Fig. 6). The solid acid showed very high activities for the reaction with 100% conversion. About 85% dodecene was transformed to the alky products within 10 min, which indicated that the solid acid was very efficient for the reaction. Although the acidity was not very high for the solid acid, the acidic sites around the external surface were quite accessible for reactants, which benefited the mass transfer efficiency and confirmed all the acidic sites fully func-

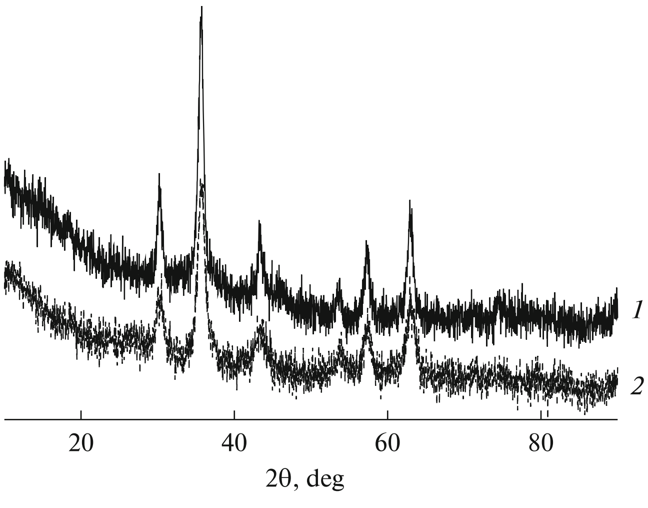


Fig. 5. XRD patterns of the magnetic carbon based solid acid: *1*—magnetic core, *2*—carbon based solid acid.

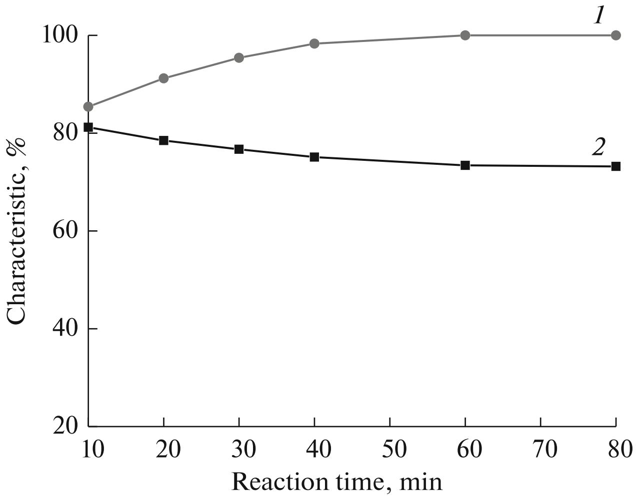


Fig. 6. Effect of the reaction time on the reaction. Reaction conditions: dodecene 4.2 g, benzene 18.5 g, catalyst 0.23 g, 80°C. The conversion (*1*) was calculated on dodecene and selectivity (*2*) was based on the 2- or 3-dodecylbenzene.

tioned during the catalytic activities. Dodecene was completely conversed after 1 h. On the acidic condition, dodecene could undertake various transformations including polymerization and alkylation via carbenium ions mechanism [27]. 1-Dodecene was transformed to 2-carbenium ions, which were easy to rearrange into 2-, 3-, 4-, 5-, 6-dodecyl carbenium ions and formed different linear dodecylbenzene products (LAB). Besides the LABs, the branched products were also formed via the carbenium cations rearrangement, which were the undesired products due to the weak biodegradability. The 2- or 3-LABs were the isomers desired products, which could be well biodegraded. The solid acid also achieved the high selectivity of 81% for the 2- or 3-LABs in first 10 min. The reaction gradually reached the equilibrium with the time and the thermodynamic stable products 4-, 5-, 6-LABs were formed. Therefore, the selectivity was decreased and the selectivity of 74.4% was achieved when dodecene was completely conversed. The hydrophobic dodecene accessed into the sulfonic acid sites on the solid surface and formed the carbenium cations. Then the cations were attacked by benzene to form the LABs. The acid strength of the solid acid was middle and the carbenium cations formed slowly. The benzene molecules attacked the carbenium cations before the carbenium was totally formed, which effectively prevented the cations rearranging. Also, the polar functionalities on the carbon shell caused high steric hindrance for hydrophobic dodecene. The conformation of the bulky carbenium cations from dodecene could not transform smoothly for the steric hindrance, which effectively improved the selectivity of 2- or 3-LABs. Therefore, the high selectivity was obtained for the solid acid. Furthermore, no branched products were formed using the solid acid. The reaction was completed after 60 min with high selectivity of 73.4%. So 60 min was the optimal reaction time.

Table 1. Effect of the molar ratio on the reaction[a, b]

Benzene, g	1.85	9.3	18.5	20.3
Conversion, %	85.4	97.5	100	100
Selectivity, %	25.3	65.6	73.4	73.2

[a] Reaction conditions: dodecene 4.2 g, catalyst 0.23 g, 80°C, 60 min.
[b] The conversion was calculated on dodecene, and selectivity was based on the 2- or 3-dodecylbenzene.

The effect of molar ratio of benzene and dodecene on the reaction was also investigated (Table 1). The benzene amount was very important for the reaction. The conversion of dodecene increased with adding benzene amount, which accounted for increasing collision probability of reactants. The total conversion was reached with the benzene amount of 18.5 g.

The selectivity seemed more sensitive to the benzene amount. The multi alkylated products were often formed during the alkylation for the alkyl groups with electron donating ability activated aromatic rings. Besides the relatively low conversion of 85.4%, the selectivity was quite low with only 15.4% to 2-, 3-LABs, when 1.85 g benzene was used with the molar ratio of 1 : 1. Benzene amount was not enough attack the carbenium cations during the formation process. Therefore, the rearrangement of the cation was heavily occurred, which formed the 4-, 5- and 6- isomers [28]. The undesired branched products were also formed via the carbenium cations alkyl migration rearrangement. Furthermore, the multi alkylated products were formed with little benzene amount, which also resulted in the low conversion. On the other hand, the multi alkylated products could be effectively avoided with more benzene amount. When the benzene amount was increased to 18.5 g, the multi alkylated and branched products were disappeared. Further increasing the benzene amount seemed useless for the reaction. Therefore, 18.5 g benzene was used for the reaction with the molar ratio of 10 : 1.

The reaction temperature was also investigated (Table 2). Limited by the boiling point of benzene (80°C), the alkylation temperature was investigated below 100°C. The reaction temperature was also greatly affected reaction. The conversion was low at low temperature (40°C) and the reaction could not be effectively activated. On the other hand, the selectivity was quite high at low temperature. It was generally known that the reaction occurred at low temperature was the typical dynamic control process [29]. The carbenium cations were produce at very low speed and the benzene attacked cations during the formation process, which effectively avoided the cation rearrangement and resulted in the high 2- or 3-LABs selectivity. With increasing temperature, some carbenium cations could be produced quickly and the rearrangement also carried out, which reduced the selectivity for 2- and 3-LABs. For the 100% conversion was obtained at 80°C and the selectivity was decreased when further increasing the reaction temperature. The reaction temperature was chosen as 80°C.

The catalyst amount was also investigated (Table 3). The catalyst was very efficient for the reaction with the conversion of 91.4% with only 0.1 g solid acid (0.44 wt %). The core shell structure and high BET surface provide the easily accessible active sites for reactants. The acidic sites could fully involve in the catalytic process, which resulted in the high activity of the novel solid acid. Both the conversion and selectivity increased when adding the catalyst amount. More catalyst amount provided more active sites, which promoted the reaction.

Also, the probability of the isomerization of the dodecylbenzenes by the solid acid was also observed. The mixture of LABs and the solid acid was treated and stirred at 120°C for 3 h. The composition of the LABs was analyzed after the treatment and no changes occurred. This result confirmed that LABs isomers were produced from the carbenium cations rearrangement instead of dodecylbenzenes. Further increasing the catalyst amount, the many carbenium cations were produced at the same time, which caused the rearrangement probability and decreased selectivity.

3.3. Recycled Activity of the Magnetic Carbon Based Solid Acid

Besides the high activities, the magnetic property of the solid acid also added the recovery efficiency. After reactions, the solid acid could be easily recovered via magnetic attraction. The recycled catalytic activities of the solid acid were investigated (Fig. 7). The results showed that the solid acid owned very high stability. The reaction yield remained almost the same after being recycled for six times with the yield of 73.4% for 2- or 3-LABs. The recycled solid acid still owned the total conversion and selectivity for the LABs. The recycled magnetic carbon based solid acid owned the acidity of 1.07 mmol/g after being recycled for six times, which was almost the same as fresh catalyst. The element analysis of the recycled solid acid showed little changes, which further confirmed the high stability of the solid acid. Furthermore, the XRD pattern showed the magnetic properties were well kept for the solid acid.

3.4. Comparative Study on Different Acid Catalysts

To compare the catalytic activities, the traditional acid catalysts were also investigated (Table 4). For the traditional alkylation catalyst $AlCl_3$, dodecene was completely transformed with 100% conversion. However, the large catalyst amount caused the serious pollution and difficulty in product purification. Furthermore, the undesired branched products were also formed with 15% selectivity, which accounted for the high activities of the Lewis acid for the rearrangement reactions. For sulfuric acid, the strong acid sites chelated quickly with 1-dodecene to form carbenium cations, which were easy to rearrange and formed the isomers.

For the strong acidity, the carbenium cations could be totally formed, which would cause the rearrangement to form the thermodynamic stable products. As a result, 4-, 5- or 6-LABs were formed, which reduced the selectivity to the more biodegradable products 2- and 3-LABs.

The traditional carbon based solid acid [5] with low BET surface (~2 m^2/g) and the polar functionalities was also investigated here. The catalyst showed poor

Table 2. Effect of the reaction temperature on the reaction[a, b]

T, °C	40	60	80	100
Conversion, %	66.8	86.8	100	100
Selectivity, %	82.1	75.6	73.4	69.3

[a] Reaction conditions: dodecene 4.2 g, benzene 18.5 g, catalyst 0.23 g, 60 min.
[b] The conversion was calculated on dodecene and selectivity was based on the 2- or 3-dodecylbenzene.

Table 3. Effect of the catalyst amount on the reaction[a, b]

Catalyst amount, g	0.10	0.16	0.23	0.29
Conversion, %	91.4	97.1	100	100
Selectivitiy, %	71.3	72.5	73.4	72.5

[a] Reaction conditions: dodecene 4.2 g, benzene 18.5 g, 80°C, 60 min.
[b] The conversion was calculated on dodecene and selectivity was based on the 2- or 3-dodecylbenzene.

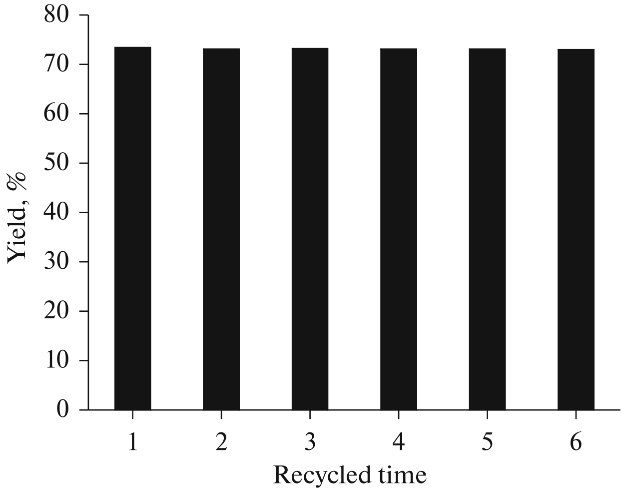


Fig. 7. Recycled activity of the solid acid.

Table 4. Alkylation of benzene and dodecene[a, b]

Catalyst	Catalyst amount, g	Reaction time, min	Conversion, %	Selectivity, %
Novel magnetic solid acid	0.20	60	100	73.4
Sulfonated carbon [5]	1	400	4.5	65.5
Carbon base acid	2	360	35.2	67.2
$AlCl_3$	2.8	180	100	50.9
H_2SO_4	1.8	300	98.7	55.8

[a] The reaction conditions: dodecene 4.2 g, benzene 18.5 g, 80°C.

[b] The conversion was calculated on dodecene and selectivity was based on the 2- or 3-dodecylbenzene.

activities with the conversion below 5%, which accounted for the inaccessible active sites to hydrophobic reactants. The novel magnetic carbon based solid acid owned high BET surface and the core shell structures, which made the hydrophobic reactants quite accessible to acidic sites. Dodecene could reach the acidic sites easily and interact with the active sites to form the carbenium ion intermediates, which resulted in high activity.

Also, the carbon based solid acid was also synthesized under the same reaction condition without using of the magnetic core. The solid acid owned the acidity of 1.0 mmol/g and relatively high BET surface of 45 m^2/g, which provided some accessible acidic sites for the reactants. The catalyst showed the conversion of 35.2% for the reaction, which was quite lower than the magnetic solid acid. These results indicated that the core–shell structure attached great importance for the high activities, which provided the easily accessible active sites for reactants. Therefore, the novel magnetic carbon based acid owned some activity for the hydrophobic alkylation. The high activities, low catalyst amount, short reaction and the high selectivity were the main advantages of the novel carbon based solid acid. These results indicated that the novel solid acid hold great potential in the hydrophobic reactions, which greatly enlarge the application field of the carbon based solid acids.

4. CONCLUSIONS

The novel magnetic carbon based solid acid was synthesized via the one-pot hydrothermal carbonization of chitosan, magnetic core and hydroxyethylsulfonic acid at 160°C for 4 h. The carbon based solid owned high BET surface and the core-shell structures, which made the acid sites on the carbon shell easily accessible by reactants. The novel solid acid owned high activities for the hydrophobic benzene and dodecene involved alkylations with complete conversion and high selectivity to the easy biodegradable 2- or 3- dodecylbenzene, which greatly enlarge the application fields of the carbon based solid acids. The core–shell structure attached great importance for the high activities and the solid acid synthesized without magnetic core showed poor activity for the reaction. The magnetic property also provided the more simple and efficient recovery process of the solid acid. The high activities, easy accessible acidic sites, high thermal and chemical stability and the magnetism were the key characteristics of the novel solid acid, which also hold great potential in green chemistry.

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