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Acidic ion functionalized N-doped hollow carbon for esterification of levulinic acid

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Acidic ion functionalized N-doped hollow carbon (NHC-[C_4 N][SO₃CF₃]) has been successfully synthesized by quaternization of N-doped hollow carbon (NHC) with 1,4-butanesultone, followed by ion exchange with trifluoromethanesulonic acid. The catalyst was characterized by fourier transform infrared (FT-IR), scanning electron microscopy (SEM), acid-base titration techniques and other methods. And a hollow spherical catalyst with regular morphology, high acid density (2.72 mmol/g) and good stability was obtained. Various characterizations showed that NHC-[C_4 N][SO₃CF₃] possesses abundant nanopores (3.41 nm), large Brunauer–Emmett–Teller (BET) surface areas (154 m²·g⁻¹) and strong and controllable Brønsted acid sites. The as-prepared NHC-[C_4 N][SO₃CF₃] was then used for the acid-catalyzed esterification of levulinic acid with ethanol. At the optimum conditions, the highest conversion of levulinic acid reached 94.17% and high conversion was maintained after four recycles. Further investigation of the catalytic activity in the esterification of different aliphatic and aromatic alcohols with levulinate was carried out, showing good results.

KEYWORDS: Catalyst preparation; Esterification ; N-doped hollow carbon ; Acidic ion ; Levulinic acid

1. Introduction

Due to gradual depletion of fossil resources and the increasing demand for resources, the transformation and utilization of renewable resources have become the focus of global ^{1,2}. Biomass is regarded as one of the renewable resources to replace fossil fuels. Researchers pay more and more attention to the high value-added chemicals and platform compounds prepared by biomass ³. Among them, levulinate esters are very important and valuable platform compounds ⁴, which can undergo hydrolysis 5,6, reductive amination 7,8 and other reactions. Therefore, levulinate esters are widely used in perfumes, plasticizers, biofuels, etc ^{9,10}. Especially, as a shortchain fatty ester, ethyl levulinate (EL) has been used as a new hybrid biofuel of diesel and gasoline because of its similar properties to biodiesel, and it is considered to be one of the most stable second-generation biofuels ¹¹⁻¹³. EL can also be used as a chemical raw material in the perfume industry and a substrate for various organic condensation and addition reactions ^{14,15}. Since LA is readily hydrolyzed from biomass, more and more attention has been paid to the green process of esterification of LA with ethanol. Compared with cellulose hydrolysis, EL prepared by esterification can obtain higher conversion and yield at lower temperature and short time.

 ^a Key Laboratory of Synthetic and Biological Colloids, School of Chemistry and Materials Engineering, Jiangnan University, 1800 Lihu Street, Wuxi 214122, China.
 [†] Footnotes relating to the title and/or authors should appear here. Conventional esterification catalysts, such as concentrated sulfuric acid, phosphoric acid, p-toluenesulfonic acid and other homogeneous acid catalysts suffer from many problems including side reactions, corrosion of equipment, difficulty in separation and reuse ^{16,17}, which does not meet the principle of "green and sustainable chemistry". Therefore, it has become a top priority to seek and explore green and efficient catalysts to replace traditional catalysts. In recent years, due to the recyclability and environmental friendliness, heterogeneous solid acid catalysts such as sulfonated metal oxides ¹⁸⁻²⁰, functionalized organometallic skeleton ²¹, sulfonated SBA-15 ²², sulfonated carbon catalysts ²³⁻²⁵, sulphonated polystryne catalysts ²⁶ and functionalized ionic liquids 27 have received extensive attention. Among them, carbon materials are widely used in adsorption, catalysis and electrochemistry because of their many advantages, such as low density, high thermal stability, low cost and non-toxicity ^{28,29}. Owing to the high acid density, sulfonic acid functionalized carbon materials can be used in esterification, transesterification and hydration as effective solid acid catalysts. However, the bulk sulfonated carbon-based solid acid catalysts have very small BET surface area, resulting in low acidity and poor acid site accessibility, thereby limiting its catalytic activity ³⁰. These defects can be adjusted by designing the morphology and pore structure of the carbon-based solid acid, which can improve the mass transfer rate and increase the contact between the reactants and active sites. In addition, the sulfonation of active groups plays an important role in the performance of catalysts. Sulfonation reagents such as concentrated sulfuric acid can reduce the stability of catalysts, and lead to the random distribution and non-differential

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formation of acid active sites on the surface of catalysts. However, selective deposition of -SO₃H on the edge of carbon material with large specific surface area can improve the accessibility of large volume molecular reactants to acidic sites.

Herein, we propose a simple and efficient strategy to introduce strong Brønsted acid sites into N-doped hollow carbon materials. Carbon spheres with porous and regular shell-core structure were prepared by classical StÖber method, and then high acidity and controllable solid acid catalyst was obtained by quaternization and ion exchange treatment. The catalyst was used for esterification of levulinic acid with ethanol, showing excellent catalytic activity and reusability.

2. Experimental

2.1 Materials

Tetraethoxysilane (TEOS), formaldehyde, melamine, 1,4butane sultone, trifluoromethanesulonic acid (HSO₃CF₃) were purchased from Adamas, levulinic acid was purchased from Macklin, resorcinol, ammonia, anhydrous methanol, toluene, dichloromethane, anhydrous ethanol, N-pentanol, Octanol, Benzyl alcohol, 1,2-propanediol were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used without further purification.

2.2 Catalyst Preparation

Synthesis of core-shell SiO₂@resorcinol-formaldehyde nanospheres (SiO₂@RF). Core-shell SiO₂@RF nanospheres were prepared by two-step StÖber method ³¹. In a typical synthesis, 10% ammonia solution (20 mL) was slowly added to 150 mL of anhydrous ethanol, then tetraethoxysilane (TEOS, 3.4 mL) was added dropwise, stirring at room temperature for 1 h, 0.6 g of resorcinol and 0.6 mL of formaldehyde solution were added under stirring next. Afterwards, the brown solution was transferred to a 200 mL polytetrafluoroethylene high temperature reactor and reacted in an oven at 100 °C for 12 h. After cooling to room temperature, orange solid was separated by centrifugation and dried overnight at 80 °C.

Synthesis of N-doped hollow carbon spheres (NHC). 0.5 g of $SiO_2@RF$ and melamine (0.3 g) were dispersed in 3 mL of anhydrous methanol, stirred for several hours until methanol was completely evaporated at room temperature. The prepared power melamine/SiO2@RF was calcined at 600 °C for 1 h under nitrogen stream in the tube furnace, and the heating rate was 5 °C/min. Then the product was etched with 10 wt% HF to remove SiO2 totally, washed with deionized water to neutrality. The black power was dried at 70 °C and recorded as NHC.

Synthesis of acidic ion functionalized N-doped hollow carbon (NHC-[C₄N][SO₃CF₃]). The above 0.3 g of NHC was dispersed into 20 mL of toluene containing 0.1 g of 1,4-butane sultone, stirring at room temperature for 1 h. After stirring at 115 °C for 8 h under refluxing, the mixture was cooled to ambient temperature, the resultant product was collected by centrifugation and dried at 60 °C. Afterwards, the sample was treated with a mixture containing 25 mL of toluene and 1 mL of trifluoromethanesulonic acid at room temperature with vigorous stirring for 8 h. The final sample Was denthfuged and washed several times with dichloromethane, and dried overnight in an oven at 60 °C, named as NHC-[C₄N][SO₃CF₃].

2.3 Catalyst characterization

FT-IR spectra were recorded on a VECTOR22 type FT-IR spectroscopy analyzer in the $4000 \sim 500 \text{cm}^{-1}$ region. Raman Spectra were obtained on a inVia micro-confocal Raman spectrometer. XRD spectra were measured by Bruker D8-Advance X-ray diffractometer (CuK α , λ =0.15418 nm, tube voltage 40 kV. Tube current 40 mA, scan angle 10° \sim 90°, scan rate 4 (°)/min, scan step length 0.02°). Nitrogen (N_2) adsorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were measured by using a ASAP2020 MP automatic surface area and microporous physical adsorption instrument, and the samples were degassed at 150 °C for 6 h before analysis. The pore size distribution was calculated using BJH method. XPS was performed on American Thermo Fisher Scientific X-ray photoelectron spectroscopy analysis. TEM images were obtained by using a JEOL JEM-2010 plus transmission electron microscope. The microstructures and element distribution of the samples were collected on Japan Hitachi Co., Ltd. S-4800 Field Emission Scanning Electron Microscope (SEM) and Energy Spectrometer (EDS).

The acid-exchange capacity was determined by dispersing catalysts in aqueous solution of NaCl through a typical acidbase titration with NaOH solution ³². The measurement procedure was as follows: 0.15 g of catalyst was added to 20 mL NaCl solution (0.1 mol/L), stirred at room temperature for 24 h, and separated to obtain filtrate. Then the filtrate was titrated to neutral with 0.01 mol/L NaOH solution and the volume of NaOH solution consumed was recorded to calculate the total acid density.

2.4 Catalytic Reaction Procedure.

Esterification of levulinic acid with ethanol was carried out in a round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and an oil bath. Typically, 1 g of levulinic acid, 7.5 mL of ethanol and 0.05 g of catalyst were added into a 25 mL flask, and a small amount of the solution was taken to determine the initial acid value of the system, then heated to 70 °C and the reaction time was recorded. Then the acid value of the system was determined every hour until it remained unchanged. And the acid value of the solution was determined according to GB/T5530-2005.

3. Results and discussion

3.1 FT-IR

Fig. 1 shows the FT-IR spectra of the NHC and NHC- $[C_4N][SO_3CF_3]$. It can be seen from Fig.1 that the two samples exhibit at 3436 cm⁻¹, which assigns to –OH stretching vibration peaks. And the stretching vibration peaks of -CH₂, C=C and C-N appear at 2919, 1630 and 1401 cm^{-1 33}, respectively. While the peaks appearing at 1260 cm⁻¹ is associated with C-F stretching vibration peak. Moreover, around 1179 and 1034 cm⁻¹ are attributed to symmetric and asymmetric stretching vibration

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of S=O, which are from the -SO₃CF₃ group ^{34,35}. The peaks of the C-F bond and the S=O bond indicated that the strong acid ion is successfully introduced to the NHC carrier. Compared with the fresh catalyst, the catalyst after four recycles not only has the characteristic peaks of the carrier skeleton, but also the characteristic peaks of the active group, indicating that the active group of the catalyst is still stable after reusing for four cycles.



Fig. 1. FT-IR spectra of the NHC, NHC-[C_4N][SO_3CF_3] and used fourth times catalyst.

3.2 XPS

Fig. 2 exhibits the XPS spectra of NHC-[C₄N][SO₃CF₃]. As shown in Fig. 2a, there are six obvious signal peaks in the XPS spectra, corresponding to O 1s (532 eV), N 1s (399.7 eV), C 1s (283.7 eV) in the NHC skeleton ³⁶ and F 1s (687.3 eV), S 2s (232.8 eV), and S 2p (167.5 eV) from -[C₄N][SO₃CF₃]. Among them, C 1s can be deconvoluted and fitted into four peaks C-C (284.6 eV), C-N (286.1 eV), C-S (287.7 eV), C-F (291.9 eV), which is due to graft the -[C₄N][SO₃CF₃] group onto the NHC support (Fig. 2b) ³⁷. In addition, the three peaks obtained by the decomposition of N 1s appear at 398.7 eV, 400.5 eV, and 401.4 eV, and which can be attributed to C-N, N⁺-H, and N⁺-C (Fig. 2c) ³⁸. Wherein C- N and N⁺-H are derived from the NHC structure, and N⁺-Guids derived from the nitrogen atom in the NHC build at the set of the butane sultone. Similarly, the signals of S 2p associated with S $2p_{1/2}$ (168.1 eV) and S $2p_{3/2}$ (169.4 eV) can also be clearly observed (Fig. 2d)³⁹.

3.3 Raman

The Raman spectra of NHC and NHC-[C₄N][SO₃CF₃] are depicted in Fig. 3. The both samples show two broad signal peaks at around 1331 and 1574 cm⁻¹ corresponding to the D-band and the G-band, respectively ⁴⁰. The D-band is attributed to the SP³ hybridized graphite carbon atoms, which reflects the defects and disordered structures in the carbon material. The G-band belongs to the SP² carbon atoms ^{29,41}. The degree of graphitization of the sample is usually expressed by the intensity ratio of I_D/I_G ⁴². NHC-[C₄N][SO₃CF₃] exhibits higher intensity ratio (I_D/I_G=1.043) as compared with 0.982 of pure NHC. This result reflects the lower degree of graphitization or disordered carbonaceous structure of the catalyst, originating from the introduction of heteroatoms and indicating the active group is successfully grated onto the NHC.





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3.4 Morphology

Fig. 4 shows the SEM and TEM images of NHC and NHC- $[C_4N][SO_3CF_3]$. It can be seen from the Fig. 4a and d that the prepared samples possess monodispersed, regular, uniform and spherical nanostructure with no impurity on the surface. Moreover, the core-shell structure of the samples can be observed obviously from TEM images (Fig. 4b,c,e and f). And the carrier NHC presents hollow nanospheres with outer diameter about 250 nm and shell thickness around 20 nm. After grafting the $-[C_4N][SO_3CF_3]$ group, the catalyst maintains the same outer diameter as the carrier, but the shell thickness increases by 5 nm. This interesting phenomena implies that the -[C₄N][SO₃CF₃] group is successfully introduced to the surface of catalyst, resulting in thickening of the shell. In addition, Fig. S1 exhibits the SEM images of the fourth time used catalyst. As shown in Fig. S1, the used catalyst still maintains a regular spherical structure, but a small amount of introduction of active group $-[C_4N][SO_3CF_3]$, which the argely occupies and blocks the nanopores of catalyst? In addition, the total acidity of the samples measured by acid-base titration is also exhibited in Table 1. The catalyst has a high acidity of 2.72 mmol/g, which plays an important role in the high catalytic activity in the esterification.

Table 1. Physicochemical properties of NHC and NHC-[C ₄ N][SO ₃ CF ₃].				
sample	Total acidity ^a (mmol·g ⁻¹)	S _{BET} ^b (m²⋅g⁻¹)	D ^c (nm)	V ^d (cm³·g⁻ ¹)
NHC	-	608	4.91	2.12
$NHC-[C_4N][SO_3CF_3]$	2.72	154	3.41	0.75

^a Acid density measured by acid-base titration.



Fig. 4. SEM images of NHC (a) and NHC-[C₄N][SO₃CF₃] (d),TEM images of NHC (b,c), NHC-[C₄N][SO₃CF₃] (e,f).

catalyst is broken. Generally speaking, the original spherical morphology of the catalyst can be maintained after four recycles. Moreover, the EDS images of the catalyst NHC- $[C_4N][SO_3CF_3]$ are shown in Fig. S2. As can be seen that the contents of C, N, O, S and F element are more evenly and distributed on the catalyst.

3.6 Porosity Properties

The Fig. S3 shows the nitrogen adsorption/desorption isotherms and pore size distribution of the samples, and the corresponding data are shown in Table 1. The nitrogen adsorption/desorption isotherms of the carrier and the catalyst belong to the type IV isotherms, which is due to the condensation accumulation of nitrogen in the pores of the material and belongs to the mesoporous material ⁴³. And a H₄ type hysteresis loop appears in both samples at relative pressures in the range of 0.45-0.95. Fig. S3b further illustrates that the samples belong to mesoporous material with pore size of 4.91 and 3.41 nm, respectively. It can be seen from Table 1 that the BET surface area of the carrier NHC is 608 $m^2 \cdot g^{-1}$, while decreased to 154 $m^2 \cdot g^{-1}$ after grafting acidic group. Compared with the NHC, the decreased BET surface area, pore volume, and pore size can be originated from the ^b The data were obtained from N₂ desorption results.

^c Average pore size.

^d Total pore volume.

3.7 Catalytic Performance

Since the esterification of levulinic acid with ethanol is a reversible reaction, the reaction should be shifted to the right in order to improve the yield of ethyl levulinic acid. To this end, increasing the amount of raw material levulinic acid or ethanol is an effective means. However, considering that ethanol is cheaper, easier to obtain and recycle than levulinic acid, excessive ethanol is used to react. And the effects of reaction time, catalyst dosage, molar ratio of acid to alcohol and reaction temperature on the conversion of levulinic acid are demonstrated in the support information(Fig. S4-S7).



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Fig. 5. Effect of cycling times on the conversion of levulinic acid. Reaction conditions: 1 g levulinic acid, 7.5 mL ethanol, 0.05 g catalyst , 7 h and 70 °C.

The recyclability of the catalyst is an important factor in affecting the performance of the catalyst. The stability of the catalyst NHC-[C₄N][SO₃CF₃] was tested under the optimal experimental conditions. After the end of the reaction, the catalyst was separated by centrifugation and washed with ethanol several times, dried overnight in an oven at 80 °C, and used for the next reaction. The results are exhibited in Fig. 5. After cycling for four times, the conversion of levulinic acid can still reach more than 80%, indicating that the catalyst has good catalytic activity andreusability. The surface acid amount of the catalyst was determined to be 1.33 mmol/g after the fourth run, which may be due to the partial shedding of the active group during many experiments and washing processes, resulting in a decrease in catalytic activity.



Fig. 6. Catalytic esterification of levulinic acid with alcohols.(R: aliphatics or phenyl; n:1-8; x: 1,2)

After the characterization and activity test of the catalyst was completed, we next tested the esterification reaction of levulinic acid with different alcohols to investigate the effects of catalyst in the esterification of polyols, alcohols with different chain lengths and aromatic alcohols in the same conditions (Fig. 6). It can be seen from Table, 2, that the prepared catalyst has high activity for the following reactions. Also an interesting phenomenon is found: as the carbon chain grows, the conversion of levulinic acid gradually decreases. This may be attributed to the large molecule of long carbon chain alcohols, resulting in inadequate access to the pores of the catalyst and insufficiently contact with the catalyst. Moreover, the conversion of levulinic acid with dihydric alcohol is lower than that of monoalcohols, which is due to the larger steric hindrance of dihydric alcohol.

4. Conclusion

In this work, a strong acid ion functionalized N-doped carbonbased solid acid catalyst with perfect unique hollow spherical morphology was successfully prepared and studied the activity in the probe reaction of levulinic acid with ethanol, as well as the esterification reaction of levulinic acid and polyols, alcohols with different chain lengths and aromatic alcohols, which exhibited good catalytic activity. The unique hollow and porous spherical structure contributes greatly to the excellent performance of the catalyst, which provides the catalyst with larger BET surface area (154 m²·g⁻¹) and more acidic sites (2.72 mmol/g).

The prepared solid acid catalyst was used for the esterification reaction of levulinic acid with ethanol. The optimum conditions for the reaction are as follow: molar ratio of levulinic acid to ethanol was 1:15, reaction temperature was 70 °C, the catalyst dosage was 5 wt.% of levulinic acid, the



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conversion of levulinic acid reached 94.17%. And the conversion of levulinic acid reached 83.57% after reusing for four cycles.

Conflicts of interest

There are no conflicts to declare.

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