Fabrication of a Novel and High-Performance Mesoporous Ethylene Tar-Based Solid Acid Catalyst for the Dehydration of Fructose into 5-Hydroxymethylfurfural

Shuang Zhang,† Zaihang Zheng,† Caiyi Zhao,‡ and Long Zhang*,†

†School of Chemical Engineering, Changchun University of Technology, No. 2055 Yanan Street, Changchun 130012, P. R. China
‡Institute of Petrochemical Technology, Jilin Institute of Chemical Technology, No. 45 Chengde Street, Jilin 132022, P. R. China

ABSTRACT: In this article, a novel and high-performance mesoporous carbon-based solid acid catalyst was prepared using ethylene tar (ET) as a precursor, which is a byproduct of ethylene production. First, ET was carbonized at 550 °C by using magnesium acetate as the template. After that, the mesoporous ET-based solid acid catalyst was obtained by a one-step sulfonation process that removes the templates simultaneously. On the basis of these facts, the maximum yield of 5-hydroxymethylfurfural (5-HMF) in the presence of an ET catalyst during the dehydration of fructose can reach 87.8%. This effective catalytic activity is mainly attributed to the large specific surface area and high density of sulfonic acid groups existing in the ET catalyst. Moreover, no distinct activity drop was observed during five recycling runs that confirmed good recyclability and thermal stability of the ET catalyst. This research provides a novel and promising method for the utilization of ET as a low-cost, recyclable, and high-performance catalyst.

1. INTRODUCTION

With the huge consumption of fossil fuels, the research on biomass-based chemicals has become an attractive issue to solve the problem of energy scarcity.1–5 Among the numerous biomass-derived chemicals, 5-hydroxymethylfurfural (5-HMF) as an acid-catalyzed dehydration product of fructose is one of the versatile platform chemicals, which plays an important role in the synthesis of biofuels and other valuable chemical intermediates such as 2,5-furandicarboxylic acid, 2,5-furandicarbaldehyde, levulinic acid (LA), and so on.5–7 In recent years, great efforts have been taken for exploiting the effective way in promoting the formation of 5-HMF by the dehydration of cellulose, glucose, and fructose.3–7 A range of catalysts have been employed, including liquid acids,6–10 H-mordenites/zeolites,11–14 phosphates of transition metals,15–18 ion-exchange resins,19–20 and carbon-based solid acids.21–27 However, these catalysts usually have some disadvantages, such as separation difficulty, high price, low specific surface area, low activity, and poor thermal stability.

Recently, carbon-based solid acid from polynuclear aromatic hydrocarbons as the raw material has aroused researchers’ interest owing to its advantages in mechanical stability and chemical inertness.28 A lot of experiments have been conducted in investigating the preparation of a carbon-based solid acid catalyst with polynuclear aromatic hydrocarbons as the raw material. Hara et al. have reported a solid acid catalyst containing SO3H groups by the incomplete carbonization of naphthalene in concentrated sulfuric acid.29 The acid density of products can reach 4.9 mmol/g that is much higher than other traditional solid sulfonic acid catalysts. Daengprasert et al. have found that when sulfonated naphthalene-based catalyst is employed for the conversion of fructose into 5-HMF, the yield of 5-HMF can reach 29.8%.30 Tanemura et al. have reported the synthesis of strong acidic sulfonated naphthalene, pyrene, phenantherene resins with p-xylene glycol, or terephthalaldehyde as the cross-linking agent.31–33 In addition, they have also carried out the experiments in the synthesis of the strongly acidic sulfonated polynaphthalene, polypyrene, and polyanthracene via an oxidative coupling reaction using FeCl3 in nitrobenzene under nitrogen.34 These sulfonated condensed polynuclear aromatic (S-COPNA) resins are insoluble in boiling water and many hot organic solvents and can be recycled without an obvious loss of activity. Moreover, the activity of S-COPNA resins is much higher than that of conventional solid acids.

However, most of the reported catalysts from polynuclear aromatic hydrocarbons have low specific surface area and incomplete pore system, which reduces the probability of contact of reactants and the internal surface acidic sites of a catalyst.35–37 Furthermore, the expensive raw materials limit its wide-ranging applications. As a sort of byproduct in the production of ethylene, the output of ethylene tar (ET) is...
The mixture was carbonized at a certain temperature. In this work, a facile and effective method was carried out in preparing mesoporous ET-based solid acid. ET was used as the raw material to prepare a mesoporous carbon-based solid acid catalyst via one-step sulfonation process by using concentrated sulfuric acid as the sulfonating agent. Compared with the traditional two-step method of removing templates originated from ET, this method can further increase surface area and simplify the preparation process. The crystal water of magnesium acetate was removed by heating it at 140 °C in an oven until it reaches a constant weight before use. ET was provided by PetroChina Jilin Petrochemical Company. The volatile molecules (<250 °C) of ET were removed by vacuum distillation before use.

2. EXPERIMENTAL SECTION

2.1. Materials. Fructose (>99%), 5-HMF (>99%), LA (>99%), and polyvinyl pyrrolidone K30 (PVP-K30, >98%) were obtained from Sigma Reagent Company. Isopropyl alcohol, magnesium acetate, concentrated sulfuric acid, and acetonitrile were purchased from Beijing Chemicals Co. Ltd. The crystal water of magnesium acetate was removed by heating it at 140 °C in an oven until it reaches a constant weight before use. ET was provided by PetroChina Jilin Petrochemical Company. The volatile molecules (<250 °C) of ET were removed by vacuum distillation before use.

2.2. Preparation of a Mesoporous ET-Based Solid Acid Catalyst. First, ET and magnesium acetate in a mass ratio of 2:8 were mixed by mechanical grinding. The mixture was heated to a certain temperature at a heating rate of 5 °C/min in a nitrogen atmosphere and maintained for 1 h. After cooling down to room temperature, the obtained carbonized product was taken out from the tube furnace. Then, a one-step method was employed to accomplish the dissolution of MgO and the sulfonation of a carbonized product by concentrated sulfuric acid at the same time. Along with concentrated sulfuric acid, the carbonized product was added into a three-necked flask and stirred at 150 °C for 15 h under the nitrogen atmosphere. After that, the system was cooled down to ambient temperature and washed with hot water until the filtrate became neutral. Finally, the product was dried in a vacuum oven at 80 °C for 12 h to obtain the mesoporous ET-based solid acid catalyst, which is denoted as the ET catalyst. The preparation process of the catalyst is shown in Scheme 1.

2.3. Dehydration of Fructose. The reaction procedure was as follows: D-fructose, isopropyl alcohol, catalysts, and PVP-K30 were added into a stainless steel reactor with a Teflon liner equipped with a magnetic stirrer. Dehydration was initiated by heating the reaction system to a certain temperature. After the reaction was completed, the reactor was cooled to ambient temperature, and the catalyst was obtained by filtering under vacuum. Finally, the catalyst was washed three times with ethanol and dried at 80 °C for 12 h for the next use. The filtrate was diluted with deionized water for the analysis of the conversion, yield, and selectivity.

The conversion of fructose was analyzed by an Agilent 1100 high-performance liquid chromatography (HPLC) system equipped with a refractometer detector using a COSMOSIL Sugar-D Packed column (250 mm × 4.6 mm and 5 μm) at 30 °C. The mobile phase was 75% acetonitrile and 25% water (v/v) to analyze the conversion of fructose at a flow rate of 1.0 mL/min.

The yield of 5-HMF was analyzed using an Agilent 1260 HPLC system equipped with a UV detector (284 nm) and an Extend-C18 column (250 mm × 4.6 mm and 5 μm) at 35 °C.
Table 1. Specific Surface Area Analysis, Acid Density Analysis, and the Yield of 5-HMF Obtained in Different Carbonization Temperatures \( ^a, ^b, ^c, ^d, ^e \)

| BET surface area (m²/g) | before sulfonation | after sulfonation | acid density (mmol/g) | the yield of 5-HMF (%) |
|------------------------|-------------------|------------------|-----------------------|-----------------------|
|                        |                   |                  |                       |                       |
| carbonization temperature (°C) | before | after | one-step | two-step | one-step | two-step | one-step | two-step | one-step | two-step |
| 400                    | 66.41             | 6.06             | 2.00                  | 4.21                  | 4.21        | 42.1      | 42.0     |
| 450                    | 159.01            | 27.62            | 9.12                  | 4.21                  | 4.21        | 43.5      | 42.5     |
| 500                    | 644.70            | 333.89           | 52.48                 | 4.35                  | 4.20        | 69.9      | 50.3     |
| 550                    | 939.34            | 552.40           | 280.19                | 4.99                  | 4.28        | 87.8      | 66.8     |
| 600                    | 1040.25           | 816.71           | 732.36                | 3.83                  | 3.52        | 53.1      | 49.6     |

“Irrating mass ratio of ET/Mg(CH₃COO)₂ is 2/8. 

“Before sulfonation: removal of templates with 2 M dilute sulfuric acid. 

“One-step method: removal of templates and sulfonation were performed simultaneously, sulfonation temperature 150 °C, sulfonation time 15 h, and incomplete carbonized products/concentrated sulfuric acid (g/mL) = 1/10. 

“Two-step method: first, the removal of templates with 2 M dilute sulfuric acid and then sulfonated at 150 °C for 15 h, and incomplete carbonized products/concentrated sulfuric acid (g/mL) = 1/10. 

“Yield of 5-HMF: reaction temperature 130 °C, reaction time 140 min, fructose 0.5 g, catalyst 0.25 g, isopropyl alcohol 7 mL, and PVP-K30 0.2 g.

The thermal stability of the catalyst was measured using a Q5000 thermogravimetric analysis (TGA) instrument under flowing nitrogen with a heating rate of 10 °C/min from 25 to 800 °C.

3. RESULTS AND DISCUSSION

3.1. Effect of Carbonization Temperature on the BET Surface Area and Acid Density of the Catalyst. The detailed data for the specific surface area and acid density of the ET catalyst are presented in Table 1. Obviously, it can be observed that with the increase of carbonization temperature, the specific surface area of the ET catalyst gradually increases, be it for before sulfonation or for after sulfonation. In contrast to the specific surface area of the ET catalyst before sulfonation, the specific surface area of the ET catalyst after sulfonation decreases, be it for a one-step method or for a two-step method. This phenomenon is mainly caused by the collapse of a partial pore of the ET catalyst during the sulfonation reaction. Moreover, the specific surface area of the ET catalyst after sulfonation for the one-step method is higher than that of the two-step method in different temperatures. Therefore, it can be concluded that the simple one-step method can effectively prevent the collapse of the pores of the ET catalyst and obtain high specific surface area to some extent.

As shown in Table 1, with the increase of carbonization temperature, the acid density of the ET catalyst obtained by the one-step method or the two-step method first increases and then decreases. The increase of the specific surface area leads to the increase in the binding sites of the SO₃H groups and an incomplete carbonized product. As a result, the acid density of the ET catalyst gradually increases. However, when the carbonization temperature further increases, more carbons are formed, resulting in a rigid structure and rendering sulfonation difficult. Therefore, the acid density of the ET catalyst decreases.

The yields of 5-HMF obtained by the one-step method and the two-step method are also presented in Table 1. The yield of 5-HMF obtained by the one-step method is higher than that of the two-step method in different carbonization temperatures. Obviously, this is because the specific surface area and acid density of the one-step method are higher than those of the two-step method. When the carbonization temperature is 550 °C, the catalyst obtained by the one-step method not only has the highest acid density (4.99 mmol/g) and a relatively high specific surface area (552.4 m²/g) but also can obtain the...
highest yield of 5-HMF (87.8%). On the basis of these data, the ET catalyst is chosen in the following experiments.

3.2. Mesoporous Structure of the Catalyst. The mesoporous structure of the ET catalyst was verified by N₂ adsorption isotherm and pore size distribution. As shown in Figure 1a, it can be seen that the characteristic type IV isotherm and a typical H₂ hysteresis loop appear in the relative pressure (P/P₀) range of 0.4–0.7, and the specific surface area calculated by the BET method is about 552.4 m²/g. The BJH pore size distribution indicated that the average pore size is about 37 nm, as shown in Figure 1b. On the basis of the analysis, this mesoporous structure is beneficial for the utilization of the inner surface active sites of the ET catalyst.

3.3. FT-IR Spectra. The FT-IR spectra of ET are presented in Figure 2a. The strong peak at 3440 cm⁻¹ is assigned to the characteristic stretching vibration of the phenolic O–H groups. The peak at 2924 cm⁻¹ is ascribed to the stretching vibration of C–H groups for saturated hydrocarbon. The absorption peak at 1631 cm⁻¹ is assigned to the stretching vibration of C=O groups in the aromatic nucleus. The weak peak at 746 cm⁻¹ is originated from the out-of-plane bending vibration of C–H groups in the aromatic ring. In addition, the FT-IR spectra of the carbonized product and the ET catalyst are presented in Figure 2b,c. The adsorption of the carbonized product at 503 cm⁻¹ is due to the incorporation of magnesium oxide. The increase in the intensity of C=C groups of the ET catalyst illustrates that sulfonation promotes the further polycondensation of carbonized products. The FT-IR spectra of ET (a), carbonized product (b), and ET catalyst (c).

3.4. X-Ray Diffraction. The ET, carbonized product, and ET catalyst are analyzed by XRD. The XRD pattern of ET is presented in Figure 3a. The XRD pattern displayed a C(002) diffraction peak at 2θ = 22.76°, which is attributed to the amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion. The definitive C(101) graphite peak at 2θ = 42.84° indicated the presence of more graphite-like structures. The XRD pattern of the carbonized product is presented in Figure 3b, displaying diffraction peaks at 36.80°, 42.83°, 62.01°, 74.52°, and 78.38°, which are consistent with the XRD spectrum of magnesium oxide. Magnesium oxide is the decomposition product of magnesium acetate after releasing CO and CO₂ gas under high temperature. No other peaks are found because the XRD patterns of ET and the ET catalyst are analyzed by XRD. The XRD pattern of the carbonized product is presented in Figure 3c, which indicated that the templates have been completely removed.

3.5. Morphology of the Catalyst. The TEM image of the mesoporous ET catalyst is shown in Figure 4. It can be seen that these mesopores are distributed randomly and that the morphology of the catalyst is also irregular. In addition, the formation of these disordered mesopores is due to the dissolution of the nanosized MgO. Furthermore, the average pore diameter of the catalyst on the TEM image is roughly consistent with the BJH pore size distribution plot.

3.6. Thermal Stability of the Catalyst. The TGA curves of the ET catalyst are shown in Figure 5. The TGA curves illustrated that a slight weight loss appears at 70–110 °C, which is attributable to the loss of free moisture adsorbed on the surface of the ET catalyst. The TGA curve tends to be flat at 110–320 °C, which indicated that there is almost no weight loss in this temperature range. After 320 °C, the apparent weight loss of the catalyst is observed because of decom-

Figure 1. N₂ adsorption isotherm (a) and BJH pore size distribution plot (b) of the ET catalyst.

Figure 2. FT-IR spectra of ET (a), carbonized product (b), and ET catalyst (c).

Figure 3. XRD patterns of ET (a), carbonized product (b), and ET catalyst (c).
Region 1: dehydration reactions of fructose were carried out at different temperatures. The results in Figure 6a show that high temperature is beneficial to the conversion of fructose. When the reaction temperature increases from 110 to 130 °C, the selectivity of 5-HMF increases from 64.8 to 71.4% and the yield of 5-HMF increases from S2 to 64.2%. The low selectivity and yield below 130 °C are ascribed to the existence of partial dehydrated intermediates. When the temperature is higher than 130 °C, the yield and selectivity decrease. This is because 5-HMF is decomposed into LA, 5-HMF self-polymerization, or cross-polymerization at high temperature. Therefore, the temperature of 130 °C is selected as the optimum temperature for the fructose dehydration into 5-HMF over the ET catalyst.

From the results presented in Figure 6b, a series of dehydration reactions of fructose were carried out at different time ranges from 110 to 150 min. With the increase of reaction time from 110 to 140 min, the yield of 5-HMF increases from 63.8 to 66.2% and the conversion of fructose increases from 86.5 to 95.4%. Nevertheless, prolonging the reaction time from 140 to 150 min results in a slight decrease in the yield of 5-HMF and a continuous increase in the conversion of fructose. This phenomenon may be due to the formation of polysaccharides in humans. Consequently, 140 min is selected as the ideal time for the dehydration of fructose into 5-HMF with the ET catalyst.

As shown in Figure 6c, the dosage of the catalyst has a significant effect on the dehydration reaction of fructose. The yield, selectivity, and conversion rapidly increase within the dosage of the catalyst in the range of 0.1−0.25 g; the results can be ascribed to an increase in the amount of available sulfonic acid sites. Further increase in the dosage of the catalyst results in a slight decrease in yield and selectivity. The main reason is that an excessive catalyst can lead to a consequent formation of various intermediate, parallel, and consecutive products. Thus, the optimum catalyst dosage is 0.25 g and the yield of 5-HMF can reach 81.8%.

Most of the dehydration reactions of fructose are chosen using dimethyl sulfoxide (DMSO) as the solvent; however, the high boiling point of DMSO (189 °C) is not conducive to the separation of 5-HMF. Therefore, we choose isopropyl alcohol with the low boiling point (82 °C) as the solvent. The effect of the dosage of isopropyl alcohol on the dehydration reaction of fructose is given in Figure 6d. It can be seen that the solvent has little effect on the conversion of fructose. However, when using 6 mL of isopropyl alcohol, the selectivity and the yield of 5-HMF are lower, and the color of the reaction mixture is dark brown. It indicates the formation of condensation products such as coke. The yield of 5-HMF remains nearly unchanged when the dosage of isopropyl alcohol is in the range of 7−10 mL. Hence, 7 mL of isopropyl alcohol is chosen as the appropriate dosage of the solvent in subsequent experiments.

The effect of the dosage of additive PVP-K30 on the reaction was also investigated. PVP-K30 is a kind of green hydrophilic polymer, which contains the monomer structure of N-methyl pyrrolidinone (NMP) and the chain structure of polyethylene. It has been confirmed that NMP can absorb water produced in the reaction and inhibit a series of side reactions during the dehydration of fructose, such as polymerization, condensation, and hydration of 5-HMF and degradation of 5-HMF producing LA, formic acid, and so on. The effect of the dosage of additive PVP-K30 on the reaction is shown in Figure 6e. With the increase of the dosage of PVP-K30, the conversion of fructose between 94 and 97.9% is not significantly changed. However, the yield and selectivity of 5-HMF first increase and then decrease. When the dosage of PVP-K30 is 0.2 g, the yield and selectivity reach a maximum value of 87.8 and 89.7%, respectively. It can be seen that the addition of PVP-K30 can inhibit the occurrence of the side reaction, but excess addition will lead to a viscous system, which are not conducive to the formation of 5-HMF. Thus, the proper dosage of PVP-K30 is 0.2 g.

As shown in Table S1, when no catalyst was used, 9.2% conversion of fructose and 2.1% yield of 5-HMF were obtained. In addition, it is found that 5-HMF (87.8%), LA (5.5%), and other unknown byproducts can be obtained by using the ET catalyst (550 °C) of the highest acid density. In addition, the catalytic performances of the ET catalyst were compared with that of Amberlyst-15 and SBA-15-SO₃H. We can see that Amberlyst-15 has a high acid density and a low specific surface area. SBA-15-SO₃H has a high specific surface area and a low acid density. The maximum yield of 5-HMF was obtained by using the ET catalyst, which is higher than that of Amberlyst-15 and SBA-15-SO₃H. Hence, it can be concluded that the catalyst...
with high surface area and high acid density is beneficial to the formation of 5-HMF. Moreover, the apparent activation energy of the reaction can be decreased by using the ET catalyst (Table S2).

3.7.2. Recyclability of the Catalyst. The recyclability of the catalyst is of vital importance for industrial production. Thus, the recyclability of the ET catalyst was examined five times in repeated reactions under the optimum reaction conditions. After each recycling experiment, the recovered catalyst was washed three times with ethanol and dried at 80 °C for 12 h before the next test. As shown in Figure 7, it can be seen that the yield, conversion, and selectivity decrease only 10.0, 7 and 5% after five cycles, respectively. Thus, the results demonstrated that the ET catalyst can be reused in the dehydration of fructose.

4. CONCLUSIONS

ET, as a byproduct in the ethylene industry, is readily available at low cost; yet, it has barely been developed toward any economically and technically rewarding applications. In this work, ET has been successfully used to prepare a novel and high-performance mesoporous ET-based solid acid catalyst by a one-step sulfonation process that removes the templates simultaneously. It demonstrates that the ET catalyst has
excellent catalytic performance in the conversion of fructose into 5-HMF because of its large specific surface area and high density of sulfonic acid groups. Under the optimum reaction conditions, the maximum yield of 5-HMF can reach 87.8%, and no distinct activity drop was observed during recycling runs that confirmed good recyclability and thermal stability of the ET catalyst. The apparent activation energy of the reaction can be decreased by using the ET catalyst. Moreover, on the basis of these facts, the synthetic route of this novel catalyst provides a promising method for the utilization of ET.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00771.

Surface properties and catalytic performances of different catalysts; effect of different temperatures on the conversion of fructose without catalyst; effect of different temperatures on the conversion of fructose with ET catalyst; and apparent rate constants of the conversion of fructose at different temperatures (PDF)

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: zhanglongzhl@163.com (L.Z.).

ORCID®

Long Zhang: 0000-0002-5719-135X

Notes

The authors declare no competing financial interest.

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