Synergistic Catalysis of Brønsted Acid and Lewis Acid Coexisted on Ordered Mesoporous Resin for One-Pot Conversion of Glucose to 5-Hydroxymethylfurfural

Kaixuan Wang, Chao Liang, Qingxiao Zhang, and Fang Zhang

The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, College of Chemistry and Materials Science, Shanghai Normal University, Shanghai 200234, China

ABSTRACT: A novel bifunctional ordered phenolic resin with Brønsted acid and Lewis acid sites (Yb(OTf)2/PhSO3H-MPR) was prepared for the first time by a two-step sulfonation and postgrafting protocol. The Brønsted acids (benzenesulfonic acids) were transformed from the phenyl groups that existed in the skeleton of ordered mesoporous phenolic resin. Meanwhile, the benzenesulfonic acids can coordinate with Yb(OTf)3 compound, resulting in the generation of Lewis acids in the pore channels of ordered phenolic resin. Yb(OTf)2/PhSO3H-MPR sample retained large specific surface and well-ordered hexagonal mesopores. As expected, it can promote one-pot cascade reaction by using glucose as the reactant to produce 5-hydroxymethylfurfural with good conversion and moderate selectivity. This synergistic catalytic performance could be attributed to its uniformly distributed Brønsted–Lewis acids. Meanwhile, the intrinsic hydrophobic pore surface can decrease the interference of water solvent, leading to enhanced catalytic efficiency. Besides, it was reused more than five times, showing good stability in water.

1. INTRODUCTION

The diminishing fossil resource is mingling with the growing environmental pollution, which brings serious challenges in our society. Accordingly, biomass is believed as the prospective feedstock to produce fuels and chemicals due to its sustainability, universality, and carbon neutrality.1–3 In this respect, biomass-derived carbohydrates are the most abundant and easily available platform chemicals. Therefore, substantial efforts were undertaken to design novel approaches to convert different carbohydrates to potential useful chemicals or intermediates.6–8 Among these compounds, 5-hydroxymethylfurfural (HMF) has received much attention since it can be used as an intermediate to the production of fuel components such as alkanes and furans. Moreover, the other valuable compounds such as 2,5-bis(hydroxymethyl)furans and 2,5-furandicarboxylic acid can be obtained by further oxidation of HMF. All of these oxidized products are important intermediates to synthesize the valuable polymers, including polyurethanes and polyamides.9–14 However, HMF is mainly used as an intermediate to the production of fuel components such as alkanes and furans.

In the initial investigation, many homogeneous catalysts have been used, such as metal salts, mineral acids, and enzymes.22–29 But they usually need the complicated catalyst separation treatment. To address this challenge, a number of heterogeneous catalysts have been tried in this one-pot transformation. However, the complex catalyst preparation, the harsh reaction conditions, and the expensive ionic liquid solvent are usually required in these heterogeneous catalytic systems.30,31 Most of the previously reported catalysts were metal oxide-based catalysts and their surfaces are hydrophilic. In this cascade reaction, the hydrophilic water solvent easily adsorbs on the solid catalysts, which unavoidably causes the competitive adsorption with the reactant and this phenomenon results in the reduced catalytic activity and/or selectivity.32–36 Moreover, it can destroy the framework of the solid catalysts, leading to the decreased catalyst stability. To this end, solid catalysts with suitable hydrophobicity can efficiently overcome these above-mentioned difficulties for chemical transformations in water. But the design of hydrophobic solid catalysts for one-pot cascade reaction of the conversion of glucose to HMF has rarely been reported until now.

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Recently, porous polymers have drawn widespread attention in different catalytic systems owing to their controllable hydrophobicity, good porosity, low density, and easy functionalization.37−39 To date, only a few acidic polymer catalysts have been demonstrated for the generation of HMF from glucose by using one-pot Brønsted acid and Lewis acid co-catalyzed reaction.40−45 But the pore size of the previously reported porous polymers is smaller than 2.0 nm, which resulted in the decreased active site accessibility and the following unsatisfactory catalytic performances. In this work, we reported for the first time on the synthesis of bifunctional ordered mesoporous phenolic resin with Brønsted−Lewis acid sites by a two-step sulfonation and postgrafting approach. The obtained Yb(OTf)2/PhSO3H-MPR catalyst displayed a large surface area and ordered hexagonal two-dimensional mesostructure. Meanwhile, the abundant Lewis acids (Yb(OTf)2) and Brønsted acids (PhSO3H) were uniformly dispersed in the framework of phenolic resin. As expected, it can deliver a good conversion and moderate selectivity in a one-pot cascade reaction for the synthesis of HMF from glucose. Moreover, it can be reused more than five times without a remarkable loss of catalyst activity.

2. RESULTS AND DISCUSSION

The fabrication procedure of Yb(OTf)2/PhSO3H-MPR material is depicted in Scheme 1. First, phenol and formaldehyde were chosen as the monomers to synthesize the soluble phenolic resin oligomers under alkaline conditions. Then, Pluronic F127 triblock copolymer was used as the template to assemble with resin oligomers by the ethanol solvent evaporation-induced self-assembly approach, giving phenolic resin oligomers/F127 composite. After removing the F127 template by simple calcination treatment, ordered mesoporous phenolic resin (MPR) was obtained. Next, MPR sample was sulfonated by reacting with chlorosulfonic acid and the partial benzene groups in the skeleton of MPR transferred to benzenesulfonic acid functional groups, leading to the formation of benzenesulfonic acid-functionalized phenolic resin with ordered mesostructure (PhSO3H-MPR). Finally, PhSO3H-MPR was employed as the support to coordinate with Yb(OTf)3 compound, resulting in bifunctional ordered mesoporous phenolic resin with Bronsted acid and Lewis acid (Yb(OTf)3/PhSO3H-MPR). We first optimized the amount of Bronsted acid in the PhSO3H-MPR sample by changing the dosage of chlorosulfonic acid, sulfonation time, and temperature (Table 1). The results showed that with the increasing amount of chlorosulfonic acid, the sulfur content was accordingly increased and the content reached to 1.76 mmol/g with 7.50 mL of chlorosulfonic acid. Then, we extended the sulfonation time (24 h) and raised sulfonation temperature (50 °C) to achieve the highest sulfur content (1.98 mmol/g). Subsequently, in the postgrafting of Yb(OTf)3, we adjusted the amount of PhSO3H-MPR support and grafting temperature and the results revealed that the amount of ytterbium was 0.249 mmol/g by using PhSO3H-MPR support and 100 mg of Yb(OTf)3 at 60 °C for 24 h (Table 2).

Small-angle XRD patterns of MPR and Yb(OTf)2/PhSO3H-MPR samples (Figure 1) showed that the as-prepared MPR sample displayed one obvious diffraction peak associated with the other two weak diffraction peaks. These peaks were attributed to (100), (110), and (200) planes, respectively.

Table 1. Optimization of Sulfur Content in the PhSO3H-MPR Sample

| entry | acid amount (mL) | time (h) | temperature (°C) | S (mmol/g) |
|-------|-----------------|----------|-----------------|------------|
| 1     | 0.5             | 12       | 0               | 0.0672     |
| 2     | 1.0             | 12       | 0               | 0.492      |
| 3     | 1.9             | 12       | 0               | 1.20       |
| 4     | 3.8             | 12       | 0               | 1.57       |
| 5     | 7.5             | 12       | 0               | 1.76       |
| 6     | 7.5             | 24       | 0               | 1.58       |
| 7     | 7.5             | 24       | 50              | 1.87       |
| 8     | 7.5             | 12       | 50              | 1.93       |
| 9     | 7.5             | 24       | 50              | 1.98       |

Table 2. Optimization of Ytterbium Amount in the Yb(OTf)3/PhSO3H-MPR Sample

| entry | Yb(OTf)3 (mg) | Yb/S | temperature (°C) | time (h) | Yb (mmol/g) |
|-------|---------------|------|-----------------|----------|-------------|
| 1     | 100           | 1:2  | 60              | 24       | 0.0832      |
| 2     | 100           | 1:1  | 60              | 24       | 0.132       |
| 3     | 100           | 2:1  | 60              | 24       | 0.187       |
| 4     | 100           | 4:1  | 80              | 24       | 0.249       |
which indicated that it had an ordered mesostructure with ideal two-dimensional hexagonal porous arrangement \((p6mm)\).\(^{46}\) Interestingly, \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) material exhibited similar peaks with only a little decreased peak intensity, revealing that it still has an ordered hexagonal mesostructure. Moreover, \(\text{N}_2\) adsorption–desorption isotherms of MPR and \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) samples were of typical type IV isotherm with \(H_1\) hysteresis loop, revealing the existence of mesopores (Figure 2).\(^{37}\) Meanwhile, the specific surface area, average pore size, and pore volume of MPR were 343 m\(^2\)/g, 3.8 nm, and 0.23 cm\(^3\)/g, respectively. Also, \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) had the surface area of 323 m\(^2\)/g, pore size of 3.6 nm, and pore volume of 0.20 cm\(^3\)/g. The slight decreases were due to the incorporation of Brønsted acids (\(\text{PhSO}_3\text{H}\)) and Lewis acids (\(\text{Yb} (\text{OTf})_3\)). Furthermore, TEM images of \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) (Figure 3) revealed that it had one-dimensional mesoporous channels with two-dimensional hexagonal arrangement. These results clearly demonstrated that our two-step sulfonation and postgrafting protocol can efficiently retain an ordered mesoporous structure of pristine phenolic resin.

Fourier transform infrared (FT-IR) spectra of the three samples of MPR, \(\text{PhSO}_3\text{H-MPR}\), and \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) (Figure 4) showed that the three samples displayed strong absorption peaks around 1620 cm\(^{-1}\). This peak was related to the stretching vibration of \(\text{C} = \text{C}\) bond of benzene ring skeleton, indicating that the three samples had a similar skeleton structure. But, it was worth noting that \(\text{PhSO}_3\text{H-MPR}\) and \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) samples exhibited new absorption peaks at 1030 cm\(^{-1}\), which was assigned to the \(\text{S} = \text{O}\) bond symmetric stretching vibration, indicating the existence of benzenesulfonic acid functional groups. For \(\text{Yb} (\text{OTf})_2/\text{PhSO}_3\text{H-MPR}\) sample, the additional peak at 1350 cm\(^{-1}\) was observed, which was the \(\text{C} = \text{F}\) bond vibration, which could be explained as the successful incorporation of \(\text{Yb} (\text{OTf})_3\) species. These results confirmed that both Brønsted acids and Lewis
acids existed on the Yb(OTf)2/PhSO3H-MPR sample. We further used X-ray photoelectron spectroscopy (XPS) spectra (Figure 5) to analyze the electronic states of these samples. XPS spectrum of Yb element of Yb(OTf)2/PhSO3H-MPR sample displayed that two peaks at 186.9 and 200.4 eV characteristic of Yb 4d5/2 and 4d3/2 binding energies were found. These results confirmed that all of the ytterbium species were trivalent compounds. For Yb(OTf)3 compound, Yb 4d5/2 and 4d 3/2 binding energies were 187.6 and 201.1 eV, respectively. Obviously, the binding energies of ytterbium species in Yb(OTf)2/PhSO3H-MPR shifted negatively by about 0.70 eV in comparison with Yb(OTf)3 (Figure 5a). This phenomenon was maybe due to the CF3SO3- ligands in Yb(OTf)3 being replaced by the SO3H groups in Yb(OTf)2/PhSO3H-MPR, which resulted in the generation of more electron-rich Yb(III) species. 47 The coordination reaction between Yb(OTf)3 and PhSO3H-MPR support was further confirmed by S 2p XPS spectra. As shown in Figure 5b, the binding energy of Yb(OTf)2/PhSO3H-MPR moved positively by 0.10 eV in comparison with PhSO3H-MPR. The slight change of S 2p binding energy was maybe due to the amount of PhSO3H groups being much more than that of Yb-(OTf)2SO3 groups. Therefore, we can safely confirm that Yb(OTf)2/PhSO3H-MPR sample had both Brønsted acids (PhSO3H) and Lewis acids (Yb(OTf)2SO3), as shown in Scheme 1.

To explore the utility of our Yb(OTf)2/PhSO3H-MPR catalyst, one-pot isomerization and dehydration cascade reaction by using glucose as the reactant to produce HMF was tested. The blank experiment without Yb(OTf)2/PhSO3H-MPR catalyst did not give HMF product (Table 3, entry 1). Then, we investigated the effect of the solvents, including water, toluene/water, valerolactone/water, tetrahydrofuran/water, and sec-butylphenol/water (Table 3, entries 2−6). We found that with only water as the solvent, both the conversion of glucose and the yield of HMF were quite low. But the addition of the polar organic solvents was a benefit for the catalytic activity and selectivity because the two-phase solvent can efficiently transfer HMF for water to the organic solvents, which reduces the amount of the byproducts. The results showed that SBP/water was the good solvent for this one-pot reaction, which delivered a conversion of 45% and yield of 21%. We extended the reaction time to 240 min and the optimal yield reached to 52%, which are the highest reported values using solid polymeric catalysts. Furthermore, we compared the results with those of the homogeneous catalysts, including H2SO4 as Brønsted acid and Yb(OTf)3 as Lewis acid. The result showed that the combination of homogeneous catalysts obtained inferior conversion (80%) and yield (49%). The good catalytic efficiency of Yb(OTf)2/PhSO3H-MPR catalyst could be related to its large surface area and ordered mesopores, which decreased diffusion limitation in this aqueous catalytic system. Moreover, the phenolic framework with hydrophobicity can reduce the competitive absorption of water solvent, leading to the enhanced catalytic activity.48 For intensive study of the hydrophobic effect, the vapor absorption experiments by using Yb(OTf)2/PhSO3H-MPR catalyst as the adsorbent and water and toluene as the adsorbates (Figure 6) were carried out. We found that these two isotherms were of typical type V curves, which indicated that there were weak absorbent-adsorbate interactions. But Yb(OTf)2/PhSO3H-MPR catalyst can absorb more toluene (39.6 wt %) than water (19.5 wt %), which revealed that the pore surface of Yb(OTf)2/PhSO3H-MPR catalyst was hydrophobic.

Table 3. Catalytic Performances of Different Catalysts in the Synthesis of 5-Hydroxymethylfurfural (HMF) from Glucose

| entry | catalyst | time (min) | conversion (%) | yield (%) | solvent         |
|-------|----------|------------|----------------|-----------|-----------------|
| 1     | blank    | 120        |                |           | SBP/H2O         |
| 2     | Yb(OTf)2/PhSO3H-MPR | 80        | 15             | 8.8       | toluene/H2O     |
| 3     | Yb(OTf)2/PhSO3H-MPR | 80        | 25             | 13        | GVL/H2O         |
| 4     | Yb(OTf)2/PhSO3H-MPR | 80        | 35             | 11        | THF/H2O         |
| 5     | Yb(OTf)2/PhSO3H-MPR | 80        | 20             | 6.4       | H2O             |
| 6     | Yb(OTf)2/PhSO3H-MPR | 80        | 45             | 21        | SBP/H2O         |
| 7     | Yb(OTf)2/PhSO3H-MPR | 120       | 56             | 34        | SBP/H2O         |
| 8     | Yb(OTf)2/PhSO3H-MPR | 240       | 75             | 52        | SBP/H2O         |
| 9     | Yb(OTf)2/PhSO3H-MPR | 240       | 80             | 49        | SBP/H2O         |

*Reaction conditions: 62.5 mg of glucose, T = 170 °C, 2.5 mL of organic solvent, 4.0 mL of water, and 0.25 g of catalyst. * pH = 3.5.
Furthermore, the hot-filtration experiment was used to make sure the immobilized Brønsted–Lewis acid species were the real active sites. After the reaction was conducted for 80 min, the conversion of glucose exceeded 50%. The reaction solution was directly centrifuged to remove Yb(OTf)$_2$/PhSO$_3$H-MPR catalyst and then the mother liquor allowed to react for another 120 min under the same reaction conditions. We found that no significant change in the glucose conversion or the HMF yield was observed, suggesting that the catalytic reactivity by the leaching sulfonic acid and Yb(OTf)$_3$ could be almost excluded in the present catalytic conditions. Also, the mother liquid in the reaction mixture was collected after each reaction for elemental analysis and inductively coupled plasma (ICP) test. These results revealed that very low amount of sulfur and ytterbium elements (less than 2.0 ppm) in the solution were detected. Moreover, we evaluated the reusability of the catalyst Yb(OTf)$_2$/PhSO$_3$H-MPR by subjecting to a one-pot cascade reaction of glucose to 5-hydroxymethylfurfural with five repetitions. As shown in Figure 7, it could be easily recovered from the reaction mixture by simple filtration and meanwhile the conversion of glucose and the yield of HMF did not exhibit a significant reduction. Small-angle XRD pattern (Figure 8a) and TEM image (Figure 8b) revealed that the reused Yb(OTf)$_2$/PhSO$_3$H-MPR catalyst still had the ordered mesoporous structure, which was similar to that of a fresh catalyst. Also, ICP analysis of the filtrate confirmed that the sulfur and ytterbium species were negligible. This good catalytic recyclability was maybe due to the PhSO$_3$H and Yb(OTf)$_2$ acid sites existing in the framework of ordered mesoporous phenolic resin, which inhibited the leaching of the catalytic species.

3. CONCLUSIONS

In summary, we successfully designed a novel protocol to synthesize bifunctional ordered mesoporous phenolic resin with Brønsted–Lewis acid by transforming phenyl groups in the resin skeleton and coordinating Yb(OTf)$_3$ with the generating benzenesulfonic acid groups. This bifunctional solid acid catalyst can efficiently catalyze one-pot isomerization and dehydration reaction by using glucose as the reactant to produce 5-hydroxymethylfurfural. Importantly, it was reused more than five times without a remarkable decrease of catalytic activity. These good catalytic performances were due to the acid species being uniformly distributed in the skeleton of mesoporous phenolic resin. Moreover, the hydrophobic pore surface can reduce the interference of the water solvent. This work provides the new protocol for the development of efficient bifunctional solid acid catalysts for more biomass utilization.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation. 4.1.1. Synthesis of Mesoporous Phenol-Formaldehyde Resin. In a typical preparation, 3.05 g of phenol was dissolved in 20 wt % sodium hydroxide aqueous solution (0.65 g) at 40 °C. After stirring for 10 min, 5.25 g of 37% formaldehyde solution was added dropwise to the mixture solution. Then, the temperature was raised to 70 °C and the solution was allowed to stir for 1.0 h under refluxing condition. After cooling to room temperature at 25 °C, the solution pH value was adjusted to about 7.0 by using 0.60 mol/L hydrochloric acid aqueous solution. The obtained solution was further treated by rotary evaporation and diluted with four times the volume of absolute ethanol to remove the solvents and sodium chloride, giving pale yellow phenolic resin oligomers. Next, 1.0 g of Pluronic F127 triblock copolymer (EO$_{106}$PO$_{70}$EO$_{106}$) was added to 20 mL of an absolute ethanol solution containing 5.0 g of phenolic resin oligomers. The mixture solution was stirred at 40 °C until a pale yellow transparent solution was formed. Subsequently, the mixture solution was transferred to a Petri dish and the ethanol solvent evaporated in the oven at 40 °C for 8.0 h. Then, it was further thermally polymerized at 100 °C for 24 h, giving phenolic resols/F127 surfactant composite. Finally, the composite was calcined at 380 °C for 6.0 h in N$_2$ atmosphere to remove F127 template, resulting in phenolic resin with ordered mesoporous structure, which was denoted as MPR.

4.1.2. Preparation of Ordered Mesoporous Phenolic Resin with Brønsted–Lewis Acid Sites. One gram of MPR was first dried at 110 °C for 6.0 h in vacum. The dried sample was added in 15 mL of CH$_2$Cl$_2$ and 10 mL of chlorosulfonic acid mixed solution. After degassing, the mixture was cooled to 0 °C and stirred for 12 h, followed by raising to 50 °C for another 12 h. Thereafter, the mixture was slowly added dropwise in 200 mL of ethanol. The product was washed by ethanol, filtered and dried, resulting in sulfonic acid-functionalized sample PhSO$_3$H-MPR. Finally, 1.0 g of PhSO$_3$H-MPR and 1.0 g of Yb(OTf)$_3$ were added into 15 mL of ethanol. The obtained mixture was stirred at 80 °C for 24 h. Then, the solid sample was filtered, washed twice by anhydrous methanol,
anhydrous tetrahydrofuran and anhydrous ethanol, and dried in vacuum at 100 °C for 8.0 h, generating \( \text{Yb(OTf)}_2/\text{PhSO}_3\text{-H-MPR} \) catalyst.

4.2. Characterization. Element Vario EL III analyzer was employed to measure the sulfur content. An inductively coupled plasma optical emission spectrometer (Varian VISTAMPX) was used to calculate the ytterbium loading. Rigaku D/max B diffractometer with Cu Kα radiation was chosen to collect X-ray powder diffraction (XRD) data. Micromeritics TriStar II 3020 analyzer was used to analyze \( \text{N}_2 \) adsorption−desorption isotherms at 77 K. Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda models were chosen to measure specific surface area \( (S_{\text{BET}}) \) and average pore diameter \( (D_p) \) of different samples, respectively. A JEOLEngineering Magna SS spectrometer was employed to collect Fourier transform infrared (FT-IR) spectra. The Perkin-Elmer PHI 5000C ESCA system was used to calculate the binding energy of different elements. All of the binding energy values in the obtained X-ray photoelectron spectra were calibrated by using C 1s = 284.6 eV as a reference. A Hiden Isochema IGA-002 intelligent gravimetric analyzer was chosen to analyze the surface hydrophobicity.

4.3. Activity Test. In a typical run, 1.0 mmol glucose, a certain amount of \( \text{Yb(OTf)}_2/\text{HSO}_3\text{-MPR} \) catalyst, 2.0 mL of tert-butylphenol, and 1.5 mL of water were mixed into a 25 mL schlenk tube. The mixture was stirred at 130 °C for 1.0 h. Then, the product in aqueous phase was analyzed by a high-performance liquid chromatography analyzer (Agilent 1200 Series) with a refractive index detector and Shodex SUGAR SC1011 column. The product in organic phase was analyzed by a high-performance liquid chromatography analyzer (Agilent 1200 Series) with a high-performance liquid chromatography analyzer (Agilent 1200 Series) with a UV detector and Agilent C18 column. The conversion of glucose and the yield of HMF were determined by glucose external standard method and tert-butylphenol internal standard method, respectively. In all of the tests, the reproducibility was checked by repeating each result at least three times and was found to be within ±5%.

Notes
The authors declare no competing financial interest.

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