Nano-magnesium oxide as hard template synthesis of lignin carbon-based solid acids and its application for cellulose hydrolysis

ZIHAO MA, RUNMING GONG, YING HAN, XING WANG, GUANGWEI SUN, YAO LI, AND JINGHUI ZHOU

ABSTRACT: In comparison with templates of zeolites and silica, a template of nano-magnesium oxide (nano-MgO) has some unique advantages. Namely, it is easily removed by dilute noncorrosive acid solution, is recyclable for nano-MgO precursors, and has tunable pore size by selecting various nano-MgO precursors. In this study, the nano-MgO as a hard template synthesis of lignin carbon-based solid acids catalyst was characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD). After using nano-MgO as a hard template, the resulting nano-MgO mesoporous carbon-based solid acids (MLCSAs) presented a uniform porous morphology and the smooth surface became rough. When the carbonization temperature was 400°C, the catalytic activity of MLCSAs for the hydrolytic reaction of cellulose was greater than lignin carbon-based solid acids (LCSAs) without nano-MgO as a hard template.

Application: Mills can prepare lignin carbon-based solid acid using the method described in this paper.

With the ever-increasing price of petroleum and environmental pollution caused by the combustion of fossil fuels, the search for new renewable and ecologically friendly alternatives to traditional fuels is increasingly urgent [1-4]. Lignin, nature's dominant aromatic polymer, is found in most terrestrial plants in the approximate range of 15%–40% dry weight and provides structural integrity. Traditionally, most large-scale industrial processes that use plant polysaccharides have burned lignin to generate the power needed to productively transform biomass into useful products. Therefore, development of renewable lignin-based polymers requires improved processing technologies coupled to tailored bioenergy crops incorporating lignin with the desired chemical and physical properties. Lignin is a carbon-rich (approximately 55%–66%) renewable resource and is the second most abundant biopolymer in nature after cellulose. If used properly, lignin could further improve the economic viability of bioderived alternative carbon materials.

Compared with traditional liquid acids, solid acids have the advantages of less corrosivity, easy separation, and regeneration. Solid acid catalysts have attracted much attention in recent years because they are environmentally friendly, highly stable, and easily recycled. Among various types of solid acids for the hydrolysis of cellulose, carbon-based solid acids have superior catalytic activities [5].

Carbon-based solid acids were prepared by sulfonation of incompletely carbonized natural polymers, such as sugars, cellulose, and starch, or by incomplete carbonization of sulfo-polycyclic aromatic compounds [6-7]. A problem with this method is the low porosity and low surface area of carbon-based solid acids, which can hinder the diffusion of reactant to active sites. The template synthesis route should increase the porosity and surface area and be a useful method for synthesis of mesoporous carbon. This synthesis procedure includes several steps, such as the pore filling of a porous template with a carbon precursor, its carbonization in oxygen-free atmosphere, and subsequent liberation of the carbon replica by dissolving the template in acids or bases [7-11]. Ryoo et al. reported that ordered carbon molecular sieves exhibiting Bragg diffraction of X-ray lines have been synthesized for the first time, using mesoporous silica molecular sieves as the template [12]. Subsequently, several methods have been reported to synthesize sulfonated mesoporous carbon using silica templates, such as SBA-15 (Sigma-Aldrich; St. Louis, MO, USA), ZSM-5 (ExxonMobil Oil; Irving, TX, USA), and MCM-48 (ExxonMobil). When those sulfonated mesoporous carbons were used as the catalyst, the cellulose was selectively hydrolyzed into glucose with the glucose yield as high as 74.5% [13-20]. Salinas-Torres et al. reported the synthesis of mesoporous carbons with lignin as the carbon precursor and Zeolite Y (CBV300) and Zeolite B (CP814E) (Zeolyst International; Malvern, PA, USA) as the templates [21]. In comparison with templates of zeolites and silicas, a nano-magnesium oxide (nano-

MgO) template has some unique advantages. Namely, nano-MgO can easily be removed by a dilute noncorrosive acid solution, it can be recycled for nano-MgO precursors, and it has tunable pore size by selecting various nano-MgO precursors. Therefore, the nano-MgO template strategy for preparation of advanced nanoporous carbons has a good possibility of large-scale application.

In the present work, the use of oxidized lignin as a carbon source and nano-MgO as the template to prepare carbon-based solid acids under different carbonization temperatures was studied. The nano-MgO mesoporous carbon-based solid acids (MLCSAs) were analyzed by a series of characterization techniques. The hydrolysis performance of the MLCSAs was also investigated.

MATERIALS AND METHODS

All commercial reagents in this study were analytical grade and used without further purification. Sulfuric acid (H_2SO_4) (98%), sodium hydroxide (NaOH), and nano-MgO were purchased from Aladdin Reagent Inc., Shanghai, China. Lignin was supplied by a bioethanol plant.

Lignin carbon-based catalyst preparation

Oxidized lignin was prepared according to the reported procedure [22]. Nano-MgO was impregnated with oxidized lignin in 1% (w/v) NaOH at a mass ratio of 1:1 (oxidized lignin/nano-MgO), and the mixture was kept in a microwave hydrothermal synthesizer at 90°C for 4 h. Then, the resultant lignin/nano-MgO composite was kept in a tubular furnace at 350°C–500°C in N_2 atmosphere and maintained for 2 h. The resultant lignin/nano-MgO composite was washed with 2% (v/v) hydrogen chloride solution to remove the nano-MgO framework. Mesoporous carbon was obtained after filtration, washing, and drying. Subsequently, the mesoporous carbon was sulfonated using H_2SO_4 at 150°C for 10 h. The mixture was filtered, washed with deionized water until the wash water was approximately pH 7–8, and dried. The sulfonated sample was denoted as carbon-based solid acid.

Characterization methods

The crystalline of the lignin carbon-based solid acids (LCSAs) were investigated by X-ray diffraction (XRD) with an XRD-7000S (Shimadzu Corp.; Kyoto, Japan) using a copper (Cu) Kα radiation source in the 50°C–60C° 2θ range with a scanning step length of 5°/min. The catalyst morphologies were determined by a JSM-7800F scanning electron microscope (SEM) (JEOL Ltd.; Tokyo, Japan). The functional groups of the catalysts were characterized by Fourier transform infrared (FTIR) spectroscopy. The samples were dried at 105°C, and then 1 mg samples were mixed with 200 mg potassium bromide in a full pellet after grinding.

Determination of the density of -SO_3H

Catalyst (0.05 g) was weighed in a 100-mL beaker and 20 mL 1M sodium chloride solution was added. The solution was treated for 30 min with ultrasonic oscillation, ensuring that all H^+ of sulfonate groups on the catalyst were exchanged by Na^+, and then removed and filtered into a 250-mL conical bottle. Then, 10 mL of the filtrate was taken from the 250-mL conical flask, 3–4 drops of phenolphthalein indicator were added, and the volume of the consumed NaOH standard solution was titrated to the end point with 0.01 mol/L of NaOH standard solution. At the same time, a blank experiment was performed using Eq. 1 to calculate sulfonate group density:

$$D_{SO_3H}\ (\text{mmol/g}) = \frac{10\text{mmol/L} \times (V_{NaOH} - V_{BLANK}) \times 2}{0.05} \quad (1)$$

Evaluation of hydrolysis performance

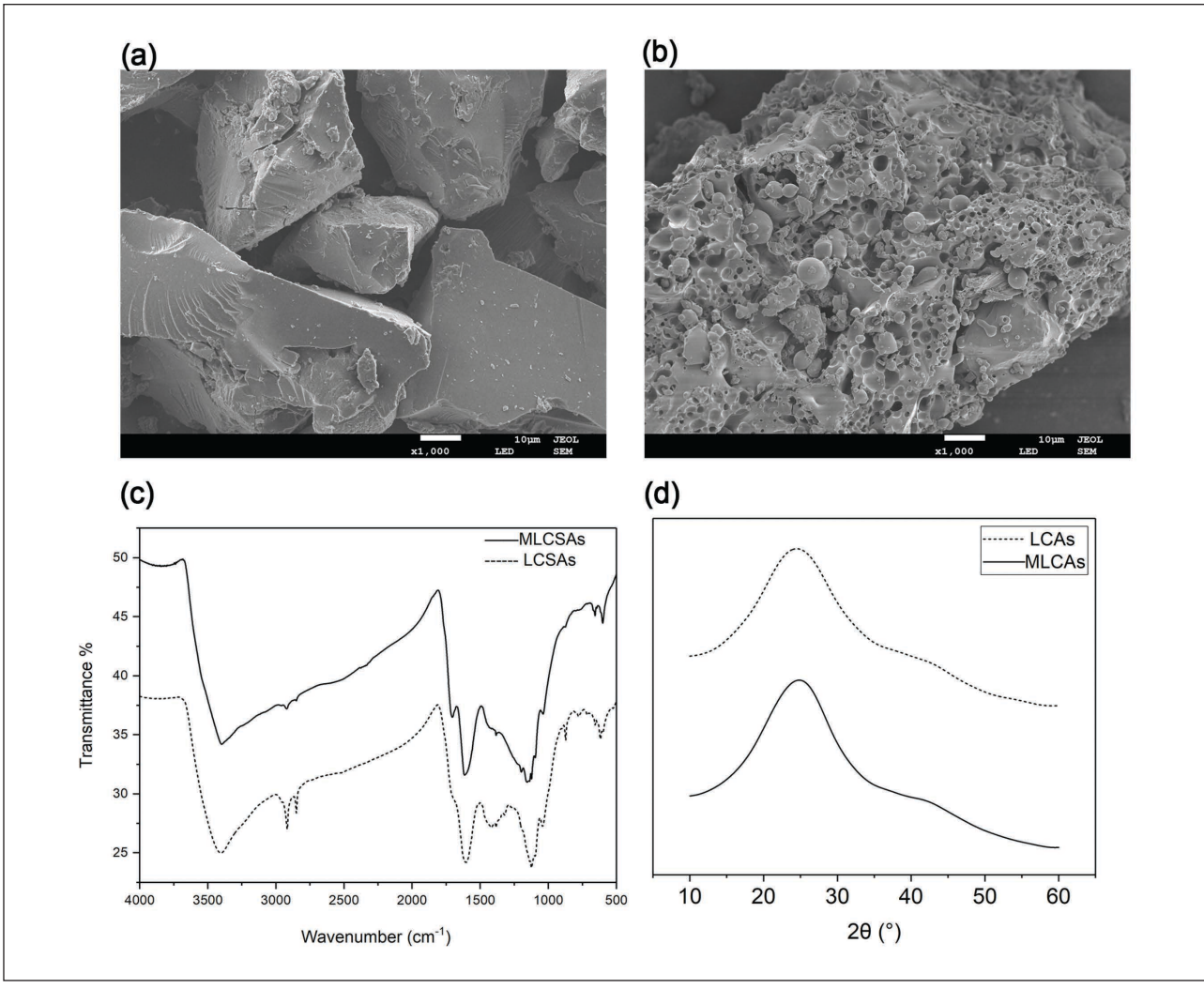
For hydrolysis of cellulose, 0.1 g pretreated cellulose, deionized water (10 mL), and 0.2 g carbon-based solid acids were added into a Teflon-lined stainless steel autoclave and reacted at 150°C for 6 h. After reaction, the yield of reducing sugar was estimated by the means of 3,5-dinitrosalicylic acid (i.e., the DNS method) [23].

RESULTS AND DISCUSSION

Effect of nano-MgO template on the synthesis of lignin carbon-based solid acids

The physicochemical properties of the as-prepared lignin carbon-based solid acids (LCSAs) and nano-MgO as hard template synthesis of MLCSAs were investigated by means of SEM, FTIR, and XRD. The carbonization temperature of LCSAs and MLCSAs is 400°C. **Figure 1** shows the SEM images of the LCSAs and MLCSAs. The MLCSAs present a uniform porous morphology, and the LCSAs present a smooth morphology (Fig. 1a). After using nano-MgO as hard template, the smooth surface becomes rough (Fig. 1b), indicating the morphology evolution during the nano-MgO as hard template synthesis of the lignin carbon-based solid acids process.

The identification of the surface functional groups was achieved by means of FTIR analysis, as shown in Fig. 1c. The FTIR spectra of MLCSAs and LCSAs were compared. The broad and intense band centered at 3434 cm^{-1} was -OH stretching vibration. The absorption at 1628 cm^{-1} was the peak of aromatic rings. The peaks at 2910 and 1365 cm^{-1} correspond to the stretching vibration and in-plane flexural vibration of C–H, respectively. The bands at 1177 cm^{-1} (symmetric stretching) and 1043 cm^{-1} (symmetric stretching) were ascribed to the O=S=O vibration modes of -SO_3H [24,25], which was indicative of the -SO_3H groups loaded on the surface of the catalysts. The FTIR analysis indicated that, when magnesium acetate is the template, the C–S and C=O peak strength are higher, which means that the preparation of solid acids with magnesium acetate as template has more carboxyl and sulfonate groups than without template. When no template is used, the C–H bond strength is greater than that of magnesium acetate as template agent, which means



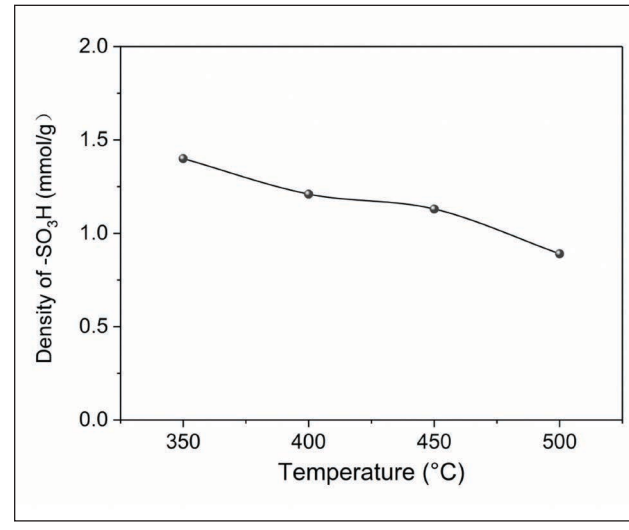
1. The physicochemical properties of the as-prepared lignin carbon-based solid acids (LCSAs): (a) scanning electron microscope (SEM) image of LCSAs, (b) SEM image of nano-MgO mesoporous carbon-based solid acids (MLCSAs), (c) Fourier transform infrared (FTIR) spectra of MLCSAs and LCSAs, and (d) and X-ray diffraction (XRD) patterns (d) of MLCSAs and LCSAs.

that solid acids prepared by no template agent have a higher degree of aromatic condensation.

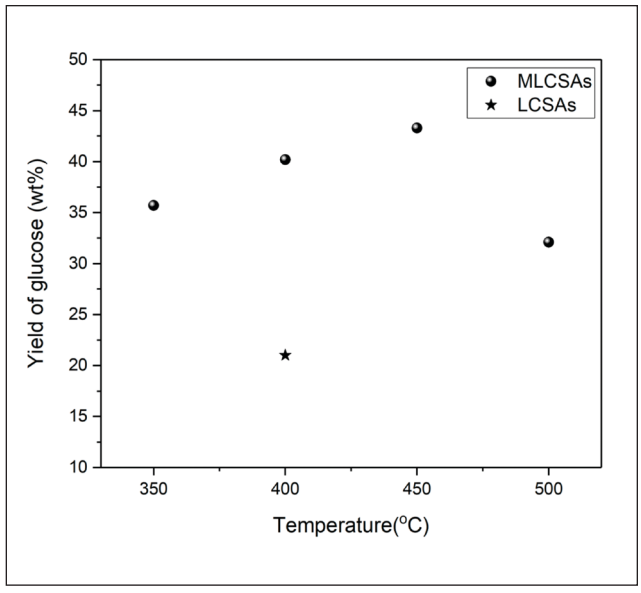
The XRD patterns of samples (Fig. 1d) exhibited one strong diffraction peak at 15°C–30C° 2θ along with a weak peak at 40C°–50C° 2θ. This result indicated that the MLCSAs and LCSAs were typical of amorphous carbonaceous materials that consist of aromatic carbon sheets oriented in a random fashion [26]. As shown in Fig. 1d, after adding nano-MgO as template, diffraction peaks became sharp and strong, which proved the aromatic carbon sheets were arranged in a more orderly space and the structure tended to be graphite.

Effect of carbonization temperature on the catalytic activity of mesoporous carbon-based acids

The effect of carbonization temperature on the density of sulfonic acid groups (SO_3H) of MLCSAs is shown in **Fig. 2**. The density of SO_3H groups is decreased with increased car-



2. Effect of the carbonization temperature on the density of sulfonic acid (-SO_3H) (mmol/g).



3. Catalytic activity of MLCSAs and LCSAs for the hydrolytic reaction of cellulose.

bonization temperature in the range of 350°C–500°C. This result indicated that the samples carbonized at higher temperature are resistant to sulfonation due to the increased hardness of the carbon material accompanying plane growth and stacking of the carbon sheets [27]. Meanwhile, the samples carbonized at lower temperatures contain high densities of SO_3H groups, similar to the results for the cellulose-derived carbon catalyst [19]. Therefore, it is considered that the samples carbonized at lower temperatures can also incorporate large amounts of hydrophilic molecules such as H_2SO_4 into the carbon bulk, due to the high density of hydrophilic functional groups bound to the flexible carbon sheets. This incorporation provides good access to the SO_3H groups in the carbon material, resulting in high catalytic performance.

The catalytic activity of MLCSAs for the hydrolytic reaction of cellulose is shown in **Fig. 3**. When the carbonization temperature is 400°C, the yields of reducing sugars (glucose) were 21.1% and 40.2% with MLCSAs and LCSAs, respectively. This result indicated that the nano-MgO as hard template synthesis of lignin carbon-based solid acids is beneficial for hydrolytic reaction of cellulose. When the carbonization temperature of MLCSAs is between 350°C and 450°C, the yield of reducing sugars (glucose) is gradually increased. Higher carbonization temperatures improve the adsorption of solid acids onto cellulose and increase the reaction between -SO_3H sites and cellulose. Thus, for the hydrolysis of cellulose, it is essential that the solid acid adsorbs or attaches to cellulose. In addition, when the carbonization temperature of MLCSAs is further increased to 500°C, the yield of reducing sugars is decreased to 32.1%. This might be because the density of -SO_3H and adsorption capacity between solid acids and cellulose were both decreased.

CONCLUSIONS

The use of oxidized lignin as a carbon source and nano-MgO as the template to prepare carbon-based solid acids under different carbonization temperatures were studied. With the increase of carbonization temperature, the catalytic performance of MLCSAs exhibited significant changes. Optimum carbonization temperatures of MLCSAs were found to be 450°C. The hydrolysis activities of MLCSAs were always higher than that of LCSAs, which was related to their aromatic structures, such as the densities of sulfonic acid groups. The results indicated that MLCSAs are an effective and green alternative to liquid acids and expensive enzymes for economic and feasible production of chemical products. It is possible that MLCSAs might have wide applications in other catalyzed reactions. **TJ**

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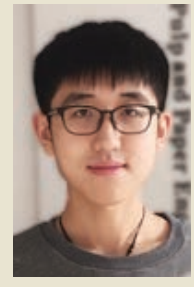
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The ever-increasing price of petroleum and environmental pollution caused by the combustion of fossil fuels have made the search for new renewable and ecologically friendly resources as alternatives to traditional fuels an increasingly urgent matter. Whereas our previous research was focused on depolymerization of lignin, we undertook this research with the hope of further using lignin and converting it into more useful products.

A problem with the traditional method is the low porosity and low surface area of carbon-based solid acids, which might hinder the diffusion of reactant to active sites. In comparison with templates of zeolites and silicas, a template of nano-magnesium oxide (nano-MgO) has some unique advantages. It is easily removed by a dilute noncorrosive acid solution, it can be recycled for nano-MgO precursors, and it has tunable pore size by selecting various nano-MgO precursors.

A surprising discovery was that nanomaterials as templates can prepare mesoporous carbon materials very well. Therefore, more research will be done in this area.

Mills can benefit from the preparation process we outlined. Our next step will be to further optimize the types of templates.

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