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Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst

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HIGHLIGHTS

- Catalytic hydrolysis of cellulose was studied in ionic liquid.
- $Fe_3O_4@SiO_2–SO_3H$ showed high catalytic activity for the hydrolysis of cellulose.
- RS was obtained in a high yield of 73.2% under the optimal hydrolysis conditions.
- This catalytic system could be reused for several times without losing activity.

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ABSTRACT

Catalytic hydrolysis of cellulose into reducing sugar (RS) over solid acid catalysts is one of efficient pathways for the conversion of biomass into fuels and chemicals. In this study, we developed a new method for the hydrolysis of cellulose into RS in ionic liquids catalyzed by a core–shell $Fe_3O_4@SiO_2–SO_3H$ acid catalyst, which was prepared by the immobilization of sulfonic acid groups on the surface of silica-encapsulated Fe_3O_4 nanoparticles. The effect of various reaction parameters, such as reaction temperature, catalyst loading and the amount of water used, were studied. The $Fe_3O_4@SiO_2–SO_3H$ showed a good activity with RS yield of 73.2% under the moderate conditions of 130 °C after 8 h reaction. Importantly, the catalyst $Fe_3O_4@SiO_2–SO_3H$ could be easily separated from reaction mixtures by a permanent magnet. In addition, the catalyst showed a high stability during the hydrolysis of cellulose and it could be reused for several times without the significant loss of its activity.

1. Introduction

Efficient and economical hydrolysis of lignocellulosic biomass to reducing sugar (RS) is one of the key pathways for the efficient generation of fuels and feed stock chemicals from abundant biomass. The abundant cellulose is considered a non-digestible fiber, which represents a promising feedstock for the production of chemicals and fuels [1–5]. However, the β-glycosidic linkages of sugar molecules contained in the cellulose chain are strongly protected by the extensive intra- and inter-molecular hydrogen bonds and van der Waals interactions, making hydrolysis of cellulose challenging [6].

Various methods, including mineral acid-catalyzed hydrolysis [7,8], enzymatic hydrolysis [9], and hydrolysis in supercritical water [10], have been reported to promote the hydrolysis of cellulose. However, some distinct drawbacks are present in these traditional methods such as the corrosion of reactors, high cost of enzymes, and harsh reaction conditions, which limits the practical utility. The use of heterogeneous catalysts may overcome the above mentioned drawbacks. Recently, hydrolysis of cellulose over heterogeneous catalysts has been widely investigated [11–14]. Although heterogeneous catalysts are often recycled more easily than their homogeneous counterparts, the tedious recovery procedure *via* filtration or centrifugation and the inevitable loss of solid catalysts in the separation process still limited their application particularly for the small nano-sized particles.

Recently, magnetic nanoparticles (MNPs) based catalysts have recently been receiving growing attention, as they can be readily separated from the reaction mixture by a permanent magnet [15–17]. The surface of the MNPs can be modified with various functional groups to construct various catalysts [18–20]. Some common methods, including oxidation of immobilized thiols to sulfonic acids [21], sulfonation of supported phenyl groups [22], ring opening of perfluorosulfonic acid sultones [23], and

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immobilization of perfluorosulfonic acid triethoxysilanes [24], have been used to construct acidic catalysts. However, those methods usually require tedious procedures. Herein, we developed a simple method for the synthesis of a magnetic nanoparticle with core–shell structure ($Fe_3O_4@SiO_2$) functionalized sulfonic acid group as environmental-friendly and recyclable catalyst for the hydrolysis of cellulose (Scheme 1). Firstly, the core–shell structure of $Fe_3O_4@SiO_2$ was prepared. Then sulfonic acid groups were immobilized on the surface of $Fe_3O_4@SiO_2$ by the reaction of sulfonic acid chlorides with the surface hydroxyl groups of $Fe_3O_4@SiO_2$. In addition, the hydrolysis of cellulose was carried out in the common ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), since [Bmim]Cl was a powerful ability to dissolve cellulose. In the previous report, it showed that up to 25 wt.% of cellulose could be dissolved in [Bmim]Cl [23–24]. Unlike the hydrolysis of cellulose in heterogeneous environments such as hydrolysis of cellulose in water, the solubility of cellulose in [Bmim]Cl makes the catalytic sites easily access the β-glycosidic bonds, which facilitates the hydrolysis of cellulose [25,26].

2. Experimental section

2.1. Materials

[Bmim]Cl was synthesized and characterized according to the known procedures described in our previous work [27]. Avicel PH-101 (DP 220) cellulose was purchased from Sigma (St Louis, USA), and was dried under vacuum at 100 °C for 24 h before use. $FeSO_4{\cdot}7H_2O$ (99.5%), $FeCl_3{\cdot}6H_2O$ (99.5%), aqueous NH_3 (28 wt.%), chlorosulfonic acid ethanol (99.5%), and tetraethoxysilane (TEOS, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glucose was purchased from ABCR GmbH & Co. (Karlsruhe, Germany). All other reagents were purchased from the local supplier and used directly without further purification.

2.2. Preparation of the catalyst

The core–shell structure support of $Fe_3O_4@SiO_2$ was prepared and characterized as described in our previous work [28]. The magnetic acid catalyst ($Fe_3O_4@SiO_2–SO_3H$) was prepared in a similar way that was used for the preparation of silica supported sulfonic acids [29]. Typically, 2 g of $Fe_3O_4@SiO_2$ was charged into a suction flask, which was equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting of HCl gas over an adsorbing solution of NaOH was used. Then chlorosulfonic acid (0.7757 g mol) was added dropwise at room temperature. After the complete addition of chlorosulfonic acid, the resulting mixture was shaken for 30 min. Then the catalyst $Fe_3O_4@SiO_2–SO_3H$ was washed successively with ethanol, and dried under vacuum over night. Finally, 2.5 g of $Fe_3O_4@SiO_2–SO_3H$ was obtained with a brown color.

2.3. Catalyst characterization

FT-IR measurements were recorded on a Nicolet NEXUS-6700 FTIR spectrometer with a spectral resolution of 4 cm^{-1} in the wave number range of 500–4000 cm^{-1}. The sulfur content was conducted on a 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer). The amount of H^+ in the $Fe_3O_4@SiO_2–SO_3H$ was determined by acid–base titration according to the following reaction (Eq. (1)). The librated H_3O^+ was titrated by standard NaOH solution.

$$Fe_3O_4@SiO_2 - SO_3H + H_2O \rightarrow Fe_3O_4@SiO_2 - SO_3^{-1} + H_3O^+ \quad (1)$$

2.4. Typical procedures for the hydrolysis of cellulose

Cellulose (0.16 g) in [Bmim]Cl (2.0 g) was heated with stirring at 100 °C to form a transparent solution. Followed by the addition of H_2O (0.027 g, 1.52 mole equiv. to glucose units) and the catalyst $Fe_3O_4@SiO_2–SO_3H$ (100 mg), the mixture was stirred at a given temperature. Time zero was taken after the addition of the catalyst. At different time intervals, samples were withdrawn, weighed (recorded as M_1), immediately diluted with cold water, centrifuged at 10,000 rpm for 5 min, measured the volume (recorded as V_1 mL) and analyzed the content of reducing sugar (RS) by Imoto method [30].

2.5. Preparation of Imoto reagent

The Imoto reagent was prepared as follows: 182 g of potassium sodium tartrate, 6.3 g of 3, 5-dinitrosalicylic acid (DNS) and 262 mL of 2 M NaOH were added into 500 mL of hot deionized water (50 °C) in sequence. After the mixture turned clear, 5 g of phenol and 5 g of sodium sulfite were added into the solution, stirring until homogeneous solution was formed, then cooled to room temperature. Finally, deionized water was added to make the total volume up to 1000 mL to give the Imoto reagent.

2.6. TRS analysis

A mixture containing 0.5 mL of Imoto regent and 0.5 mL of the sample was heated at 100 °C for 5 min. After the reaction mixture was cooled down to room temperature with cold water, 4 mL of distilled water was added. Then the absorbance was measured at 540 nm using UV–Vis spectrophotometer. The concentration of the TRS was calculated by employing a standard curve prepared using glucose. The mass of RS M_T and the yield of RS were calculated as follows,

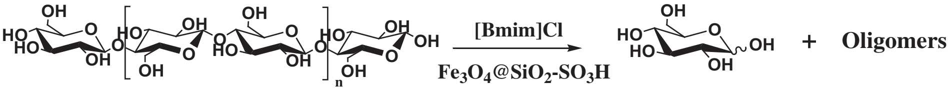
$$M_T\ (\mathrm{mg}) = \mathrm{RS\ concentration}\ (\mathrm{mg/mL}) \times V_1\ (\mathrm{mL}) \times M_o/M_1$$

$$\mathrm{RS\ yield} = M_T/160 \times 100\% \times 0.9$$

In which, M_T is the mass of RS, V_1 is the volume of the sample, M_0 is the total mass of the reaction solution and M_1 is the mass of sample withdrawn from the reaction mixture.

2.7. Analysis of hydrolysis products

After reaction, the catalyst was separated from the reaction mixture by a permanent magnet, and the reaction mixture was centrifuged to remove insoluble byproducts. Then the clear liquid was filtered with a 0.45 μm syringe filter prior to analysis by high-performance liquid chromatography (HPLC). The chromatographic separations were carried out using a Sugar-Pak-1 column and RI detector. Sulfuric acid aqueous solution (0.01 mmol L^{-1}) was used as the mobile phase at a flow rate of 0.6 mL min^{-1}.



Scheme 1. Schematic illustration of the hydrolysis of cellulose in [Bmim]Cl.