Article (Special Issue on the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013))

# Nanocoating of magnetic cores with sulfonic acid functionalized shells for the catalytic dehydration of fructose to 5-hydroxymethylfurfural

Xiaochen Zhang [a], Min Wang [a], Yehong Wang [a], Chaofeng Zhang [a,b], Zhe Zhang [a,b], Feng Wang [a,*], Jie Xu [a,#]

[a] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

A magnetically recyclable acid catalyst composed of an $Fe_3O_4$ core and sulfonic acid functionalized silica shell has been prepared using the reverse microemulsion method. The $Fe_3O_4$ core was coated with a phenyl modified silica shell nanolayer, and the phenyl groups were subsequently sulfonated to generate a solid sulfonic acid catalyst. The resulting acid catalyst showed higher activity than the conventional A-15 catalyst and comparable activity to several homogeneous sulfonic acid catalysts for the dehydration of fructose to 5-hydroxymethylfurfural (HMF). This process gave a fructose conversion of 99% with an HMF yield of 82% following 3 h in dimethylsulfoxide at 110 °C. Furthermore, the catalyst could be magnetically separated and recycled several times without losing its activity.

## 1. Introduction

In recent years, the conversion of biomass into chemicals of commercial value has attracted considerable levels of attention [1–4]. 5-Hydroxymethylfurfural (HMF) can be derived from sugars and is considered to be an important platform molecule in terms of its ability to be transformed into a variety of fine chemicals or biofuels [5–9].

Significant research efforts have been directed towards the development of methods for the preparation of HMF via the acid catalyzed dehydration of fructose. Homogeneous catalysts generally show high levels of efficiency towards the catalytic dehydration of fructose to HMF, and a number of different catalysts have been investigated for this purpose, including mineral acids [10,11], organic acids [12], Lewis acids [13–15], and ionic liquids [3,16]. Although excellent yields have been achieved for the dehydration of fructose to HMF using homogeneous catalysts, the development of heterogeneous catalytic systems for this transformation is highly desired because of the ease with which these systems can be separated from the reaction mixture and recycled. Solid acid catalysts, such as niobium oxide [6], phosphate [17], H-form zeolites [18], sulfated zirconia [19], and acidic ion-exchange resins [5,20] have been used for the dehydration of fructose. Among the acid catalysts tested,

those bearing sulfonic acid groups have been shown to be particularly efficient. Conventional solid sulfonic acids, however, such as A-15 and Nafion NR50 [20] are not readily accessible to the substrates because of their bulky character and generally show lower activity than homogenous catalysts. One general way to overcome this problem is to disperse the solid acid sites or to graft the acid groups onto porous materials to maximize the exposure of the substrate to the acidic sites [21–23]. The development of new strategies capable of providing substrates with greater exposure to the active sites of the catalyst, as well as allowing for the facile separation of the catalyst at the end of the reaction, still represents a significant challenge to the design of heterogeneous acid catalysts.

In this study, we developed a nanocoating method capable of effectively exposing the active sites on the outer surface of magnetic nanoparticles (MNPs) as well as allowing for the catalyst to be separated and recycled using magnetic force. In contrast to previously reported magnetically recyclable catalysts with bulk character, the current study involves extremely thin (4 nm) sulfonic acid functionalized silica shells that were coated onto $Fe_3O_4$ nanocores of 10 nm in diameter. These characteristics were favorable for the diffusion of molecules, and the catalysts themselves showed higher activity than the conventional solid sulfonic acid catalyst A-15 and comparable levels of activity to the homogeneous sulfonic acid catalysts for the dehydration of fructose to HMF. This process gave 99% fructose conversion with an HMF yield of 82%. Furthermore, the catalyst could be magnetically separated and recycled several times.

## 2. Experimental

### 2.1. Preparation of $Fe_3O_4@Si/Ph-SO_3H$

The MNPs were prepared according to a previously reported procedure [24–26]. Briefly, 25 mL $NH_4OH$ solution (28 wt%) was rapidly added to a solution of $FeSO_4·7H_2O$ (2.35 g) and $FeCl_3·H_2O$ (4.1 g) in 100 mL deionized water at room temperature, and the resulting solution was mechanically stirred in an oil bath at 80 °C under an Ar atmosphere. During the course of the reaction, oleic acid (1 mL) was slowly added to the reaction mixture in a drop-wise manner over a period of 1 h. The resulting MNPs were washed with ethanol before being transferred with a magnet and dispersed in cyclohexane (50 mL).

The $Fe_3O_4@Si/Ph$ was prepared using a water-in-oil reverse microemulsion according to our previously reported method [27]. Poly(oxyethylene)nonylphenol ether (NP-7, 8 g), $n$-butanol (15 g), cyclohexane (25 mL), water (5.5 g), and aqueous ammonia (2 g) were mixed with the cyclohexane solution of MNPs (5 mL) prepared above to give a microemulsion. Tetraethoxysilane (TEOS, 1.0 g) and phenyltriethoxysilane (PTES, 0.4 g) were then slowly added to the microemulsion in a drop-wise manner. The mixture was stirred for 12 h and then treated with ethanol to destroy the microemulsion. The resulting solid material was collected and washed twice with ethanol to remove the surfactants before being dried at 100 °C. The dried powder (0.3 g) was re-dispersed in 15 mL of fuming sul-

furic acid (15 wt% $SO_3$) under ultrasonic irradiation at room temperature for 30 min, and then washed repeatedly with hot distilled water until the pH of the supernatant liquid was neutral. The $Fe_3O_4@Si/Ph-SO_3H$ material was obtained after drying at 100 °C.

### 2.2. Characterization

The microstructures of the materials were examined by transmission electron microscopy (TEM) on a JEOL JEM-2000 EX electron microscope (Japan) at an accelerating voltage of 120 kV. The morphologies of the materials were determined by scanning electron microscopy on a JSM-7800F system (Japan). The infrared (FT-IR) spectra were measured as KBr disks on a Bruker Tensor 27 FT-IR spectrometer (Germany) with 16 scan at a resolution of 4 cm$^{-1}$. The thermal stability data were collected on a Netzsch STA 409 PC (Germany) and ThermoStar™ (Germany) using $O_2$ as a carrier gas with a gas flow of 40 mL/min. The acidities of the materials were determined using a Mettler Toledo G20 Compact Titrator (Switzerland). The X-ray diffraction (XRD) patterns were measured on a Rigaku D/max 2500 PC X-ray diffractometer (Japan) with Cu $K_\alpha$ radiation (tube voltage 40 kV, tube current 30 mA, scan rate 10 °C/min). Nitrogen adsorption-desorption isotherms were measured on a QuadraSorb SI4 system (USA).

### 2.3. Acidity titration

$n$-Butylamine was dissolved in acetonitrile in a 500 mL volumetric flask to give a 12.34 mol/L solution of $n$-butylamine. A quantity of $Fe_3O_4@Si/Ph-SO_3H$ materials was dissolved in 50 mL acetonitrile, and the solution was stirred 30 min in the titrator to equilibrate electric potential. The system was then flushed with the above $n$-butylamine solution, and the electrode was inserted. The above $n$-butylamine-acetonitrile solution was then titrated according to the incremental titration method. The VEQ value (i.e., the consumption volume of $n$-butylamine-acetonitrile at the equivalence point) was then obtained, and the average acid density of the solution was calculated to be 12.43 μmoL/g (sample). The acidity of A-15 was also measured under the same conditions for comparison (Table 1).

### 2.4. Catalytic reaction

For a typical catalytic reaction, fructose (0.02 g) and the catalyst (0.01 g) were mixed in dimethylsulfoxide (DMSO, 1.0 mL). The catalytic reaction was conducted at a variety of different temperatures over specific times under Ar with stirring. At the end of the reaction, the catalyst was separated from the mixture by magnetic force, and the reaction solution was analyzed by liquid chromatography on an Agilent 1260 Infinity system (USA). The conversion was measured on a PrevaiL Carbohydrate ES column (5 μm, 4.6 mm × 250 mm) using a mobile phase composed of acetonitrile and water (75:25, v/v) with a flow rate of 1 mL/min. The column and detector were operated at 35 °C, and an injection volume of 20 μL was used for the