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

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ABSTRACT

A magnetically recyclable acid catalyst composed of an Fe₃O₄ core and sulfonic acid functionalized silica shell has been prepared using the reverse microemulsion method. The Fe₃O₄ 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.

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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,

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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 $\text{Fe}_3\text{O}_4@\text{Si}/\text{Ph-SO}_3\text{H}$

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 $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (2.35 g) and $\text{FeCl}_3\cdot \text{H}_2\text{O}$ (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 $\text{Fe}_3\text{O}_4@\text{Si}/\text{Ph}$ 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 $\text{Fe}_3\text{O}_4@\text{Si}/\text{Ph-SO}_3\text{H}$ 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 $\text{Cu } K_\alpha$ 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 $\text{Fe}_3\text{O}_4@\text{Si}/\text{Ph-SO}_3\text{H}$ 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 $\mu\text{mol/g}$ (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 $\times$ 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

Table 1
Physical properties of the nanomaterials and A-15.

Sample	Acid density ^a (mmol/g)	<i>A</i> _{BET} (m ² /g)	<i>V</i> _{pore} ^b (cm ³ /g)	<i>V</i> _{pore} ^c (cm ³ /g)
Fe ₃ O ₄ @Si/Ph	—	69.8	0.1785	0.0049
Fe ₃ O ₄ @Si/Ph-SO ₃ H	0.01243	138.1	0.2544	0.0185
A-15	2.27	42 ^d	0.36 ^d	—

^a Calculated by titration.

^b Total pore volume with $p/p_0 = 1$.

^c Micropore volume calculated using the *t*-method.

^d As reported by Singh [28].

analyses. The yield was measured with a ZORBAX SB-C18 column (5 μ m, 4.6 mm $\times$ 150 mm) using a mobile phase composed of methanol and water (20:80, v/v) with a flow rate of 0.7 mL/min. The column and detector were operated at a temperature of 35 $^{\circ}$ C and an injection volume of 2.5 μ L was used for the analyses. The conversion of fructose and yield of HMF were quantified using external standards.

3. Results and discussion

As shown in Scheme 1, the magnetic Fe₃O₄ particles were prepared via the co-precipitation of FeSO₄ and FeCl₃. TEM images of the particles (Fig. 1) revealed that the mean diameter of

Scheme 1. Preparation of the magnetic solid nanoparticles with core/shell structure. MNP: magnetic nanoparticle; TEOS: tetraethoxysilane; PTES: phenyltriethoxysilane.

Fig. 1. TEM image (a) and the corresponding particle size distribution plot (b) for the Fe₃O₄ particles; SEM image (c) of the Fe₃O₄@Si/Ph-SO₃H particles (the insert is a TEM image of a single particle) and the corresponding particle size distribution plot (d).

Fig. 2. XRD patterns of Fe₃O₄ (1), Fe₃O₄@Si/Ph (2), and Fe₃O₄@Si/Ph-SO₃H (3).

the resulting Fe₃O₄ nanoparticles was around 10 nm. These Fe₃O₄ particles were then coated with a phenyl functionalized silica nanoshell of about 4 nm in thickness (Fe₃O₄@Si/Ph) using the reverse microemulsion method. The resulting Fe₃O₄@Si/Ph particles were then treated with oleum to allow for the introduction of the sulfonic acid groups. Following the silica coating process, an amorphous silica peak around 23 $^{\circ}$ appeared in the XRD pattern of the material (Fig. 2). The XRD patterns of Fe₃O₄@Si/Ph and Fe₃O₄@Si/Ph-SO₃H were almost identical, which indicated that the Fe₃O₄ core had not been destroyed during the sulfonation process because of the protection afforded by the silica shells. Furthermore, the magnetism of the core was preserved, with the particles responding quickly to the presence of a magnet (Fig. 3). The TEM and SEM images of the material clearly showed that the Fe₃O₄@Si/Ph-SO₃H particles synthesized in the current study were nanoparticles with a typical core-shell structure. The surface area and pore volume for the Fe₃O₄@Si/Ph and Fe₃O₄@Si/Ph-SO₃H particles were 69.8 and 138.1 m²/g and 0.18 and 0.25 cm³/g, respectively (Table 1). The observed increases in these values were attributed to the formation of pores in the particles during the sulfonation process.

The compositions of the materials were characterized by

Fig. 3. Magnetic performance of the nanomaterial before (a) and after (b) sulfonation.

Fig. 4. FT-IR spectra of $\text{Fe}_3\text{O}_4\text{@Si/Ph}$ (1), $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ (2), the used $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ (3), and Fe_3O_4 (4).

FT-IR (Fig. 4). Typical bands associated with the formation of a condensed siloxane network were present in the spectra of the $\text{Fe}_3\text{O}_4\text{@Si/Ph}$ and $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ particles (Si–O–Si bands around 1095, 802, and 465 cm^{-1}). The peak at 951 cm^{-1} was attributed to the different modes of the Si–OH bond. Weak peaks characteristic of phenyl ring vibrations were detected at 733 and 699 cm^{-1} in the enlarged spectra, which indicated that the phenyl groups had been successfully attached to the material [27,29,30]. Following the sulfonation process, the resonance peaks assigned to the $-\text{SO}_3\text{H}$ groups around 1035 and 1215 cm^{-1} [31], overlapped with the Si–O–Si bond vibration peaks. However, the sulfur element was detected by energy-dispersive X-ray spectroscopy (EDX, 0.07 wt%). The bands at 631 and 585 cm^{-1} belonging to Fe_3O_4 had shifted slightly because of the effect of the siloxane network [26].

The thermal stability of $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ was examined by thermal gravimetric analysis (TGA) and temperature-programmed oxidation-mass spectrometry (TPO-MS). The weight loss of 6% at around 150 $^{\circ}\text{C}$ was attributed to the loss of physically adsorbed water, with the weight remaining constant beyond this point up to 200 $^{\circ}\text{C}$ (Fig. 5(a)). Further weight loss events also occurred at 200, 350, and 600 $^{\circ}\text{C}$, with similar trends also observed in the ion current (Fig. 5(b)). The latter two losses were attributed to the decomposition of the residual oleic acid and phenyl groups (Fig. 5). These results indicated

Fig. 5. Thermal analysis of $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$. (a) TGA; (b) TPO-MS.

that the material had relatively high thermal stability and was stable under the reaction conditions ($< 200\text{ }^{\circ}\text{C}$).

With the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ material in hand, we proceeded to investigate its catalytic performance towards the dehydration of fructose (Table 2). Without the sulfonation step, the resulting $\text{Fe}_3\text{O}_4\text{@Si/Ph}$ particles were effectively inactive and gave a fructose conversion of only 9.5%. Based on the same amount of acid groups, A-15 gave a fructose conversion of 60.1% and an HMF yield of 16.7%. Homogeneous *p*-toluenesulfonic acid showed a high efficiency for the transformation with a fructose conversion of 91.6% and an HMF yield of 56.4%. When $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ was used, the reaction gave a fructose conversion of 96.3% with a HMF yield of 55.2% following 3 h at 100 $^{\circ}\text{C}$. This result was higher than that achieved with A-15 and comparable to that of homogenous *p*-toluenesulfonic acid, and was also better than those reported for several solid sulfonic acid catalysts such as PS-PP- SO_3H , PC- SO_3H , and Nafion (15)/MCF [8,23,32]. Furthermore, the TOF value for this catalyst was up to 164.5 h^{-1} . The high efficiency of this catalyst may be attributed to the nanosize of the particles and their thin shells, which allowed for the acid sites to be effectively exposed on the outer surface of the particles. The $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ particles had a surface area nearly four times greater than that of A-15 (Table 1). Although several other research efforts have been devoted to effectively exposing the acid sites by functionalizing porous materials (i.e., PS-PP- SO_3H , PC- SO_3H , and Nafion (15)/MCF), mass transfer limitations generally cause problems in these systems because the active sites are on the inner pore surface. For the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ nanoparticles, the reactions occurred predominantly on the outside surface, which represents a favorable scenario for the substrate and the product, in terms of them being able to readily diffuse to and/or from the active sites, thus enhancing the conversion and preventing the occurrence of side-reactions involving the HMF at the acid sites.

Table 2

Conversion of fructose and yield of HMF over different acid catalysts.

Catalyst	Conversion (%)	Yield (%)	TOF (h^{-1})
$\text{Fe}_3\text{O}_4\text{@Si/Ph}$	9.5	trace	—
$\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$	96.3	55.2	164.5
A-15	60.1	16.7	49.8
<i>p</i> -toluenesulfonic acid	91.6	56.4	168.1
$\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}^a$	>99.0	82.3	254.0
$\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}^{ab}$	>99.0	78.9	243.5
$\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}^{ac}$	>99.0	79.5	245.4
PC- SO_3H^d	—	65.2	—
Nafion(15)/MCF ^e	84.4	78.6	28.2
PS-PP- SO_3H^f	27	20.3	0.69

Reactions were carried out with 0.02 g fructose and catalyst (acid amount: 0.12 $\mu\text{mol H}^+$) in 1 mL DMSO for 3 h at 100 $^{\circ}\text{C}$ in Ar.

^a 110 $^{\circ}\text{C}$.

^b Second recycle.

^c Third recycle.

^d Reaction conditions: 0.1 g fructose, molar ratio of fructose to acidic site at 10, 5 g DMSO, 110 $^{\circ}\text{C}$, 4 h [8].

^e Reaction conditions: fructose in DMSO (3 wt%, 12.5 g), 0.03 mmol H^+ , 90 $^{\circ}\text{C}$, 2 h [32].

^f Reaction conditions: 10 g fructose, 2 g catalyst (acidity: 1.8 mmol/g catalyst), MIBK/water (100 mL) = 3, 135 $^{\circ}\text{C}$, 4.5 h [23].

Fig. 6. (a) Effect of temperature on the fructose dehydration reactions over the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst in 3 h. (b) Time-on-stream profile at 110 °C.

A series of optimization experiments were conducted to determine the best reaction conditions for the dehydration of fructose over the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst (Fig. 6). Increasing the temperature led to a gradual increase in the fructose conversion, with a conversion of 99% being achieved at 110 °C after 3 h. Further increases in the temperature did not lead to further increases in the conversion, which effectively reached a plateau at 110 °C. Furthermore, the HMF selectivity increased from 16% at 80 °C to 82% at 110 °C, although further increasing the temperature to 120 °C led to a decrease in the HMF selectivity to 62%. These results indicated that the use of a high temperature would lead to by-products, such as furfural and acetic acid. Experiments to determine the effects of different reaction times were conducted at 110 °C. A reaction time of 3 h gave an HMF selectivity of 82%. Further extending the reaction time, however, led to HMF being converted to levulinic acid, formic acid, and humic acid under acid conditions, and a lower yield of HMF [33]. Following the optimization experiments, the reaction gave a fructose conversion of 99% and an HMF yield of 82.3% following 3 h at 110 °C (Table 2).

Furthermore, after the reaction, the magnetic $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst could be readily separated from the mixture by magnetic force. Figure 7 clearly shows that an aqueous suspension of the catalyst rapidly became transparent following the

Fig. 7. Images of the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst before (a) and after (b) the separation using magnetic force.

application of magnetic force. The used catalyst was then washed with hot water and ethanol several times before being dried at 100 °C to prepare it for use in the next run. The catalytic activities of the recycled $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst (after being recycled two times) were comparable to that of the fresh catalyst (Table 2). These results indicated that the $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$ catalyst was a relatively stable heterogeneous catalyst.

4. Conclusions

We have successfully synthesized a magnetic acid catalyst, $\text{Fe}_3\text{O}_4\text{@Si/Ph-SO}_3\text{H}$, consisting of an Fe_3O_4 core with a sulfonic acid functionalized silica shell using a nanocoating method, which allowed for the acid sites to be effectively exposed during the reaction and the catalyst itself to be readily separated from the reaction mixture upon completion of the reaction using magnetic force. This catalytic system showed higher activity than conventional solid sulfonic acid catalysts and comparable activity to homogeneous acid catalysts towards the dehydration of fructose to HMF. Furthermore, the catalyst could be easily separated by magnetic force and reused without any significant loss in activity.

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Graphical Abstract

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

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A magnetically recyclable acid catalyst consisting of an Fe_3O_4 core and a thin sulfonic acid functionalized silica shell has been prepared using a reverse microemulsion method and subsequently used for the dehydration of fructose to 5-hydroxymethylfurfural (HMF). This process gave a fructose conversion of approximately 99% and an 82% yield of HMF after 3 h in DMSO at 110 °C.

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磺酸官能化的磁性核壳结构的纳米材料用于果糖脱水制备5-羟甲基糠醛

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摘要: 通过反相微乳液法制备了以 Fe_3O_4 为核, 磺酸官能化的硅基材料为壳层的磁性酸性催化剂。首先制备纳米 Fe_3O_4 磁核, 然后涂层包覆苯基修饰的纳米级硅层, 最后进行苯基磺化修饰, 制得固体酸催化剂 $\text{Fe}_3\text{O}_4@\text{Si}/\text{Ph}-\text{SO}_3\text{H}$ 。在果糖脱水制备5-羟甲基糠醛反应中, 该催化剂表现出较好的催化活性, 优于传统催化剂A-15, 且与均相无机酸催化活性相当。当采用二甲基亚砜作溶剂, 在110 °C下反应3 h, 果糖转化率达到99%, 5-羟甲基糠醛收率为82%。另外, 该催化剂经磁法回收后可多次重复使用。

关键词: 磁性粒子; 纳米催化剂; 果糖脱水; 5-羟甲基糠醛; 磺酸

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