Cellulose (2013) 20:127–134
DOI 10.1007/s10570-012-9839-5

ORIGINAL PAPER

Magnetic core–shell Fe_3O_4@C-SO_3H nanoparticle catalyst for hydrolysis of cellulose

**Changbin Zhang · Huayu Wang · Fudong Liu ·
Lian Wang · Hong He**

Received: 12 September 2012 / Accepted: 1 December 2012 / Published online: 11 December 2012

Abstract Catalytic hydrolysis of cellulose over solid acid catalysts is one of efficient pathways for the conversion of biomass into fuels and chemicals. High catalytic activity and easy separation from reaction media are two important factors for evaluating the performance of the solid acid catalysts for the cellulose hydrolysis. In this study, we report a core–shell Fe_3O_4@C-SO_3H nanoparticle with a magnetic Fe_3O_4 core encapsulated in a sulfonated carbon shell, as recyclable catalyst for the hydrolysis of cellulose. The sulfonated carbon shell shows a good activity, presenting 48.6 % cellulose conversion with 52.1 % glucose selectivity under the moderate conditions of 140 °C after 12 h reaction. Importantly, the magnetic Fe_3O_4 core makes the catalysts easily separated from reaction mixtures by using the externally applied magnetic field. In addition, the Fe_3O_4@C-SO_3H nanoparticle catalyst shows a high stability in the activity and magnetization during recycling tests, suggesting it a promising solid acid catalyst for the hydrolysis of cellulose.

Keywords Biomass · Hydrolysis · Magnetic catalyst · Carbon based solid acid · Sulfonation

Introduction

Increasing energy crisis and environmental concern on global climate change have stimulated the development of fuel production based on renewable resources, such as starch, cellulose, and lignin. Among them, cellulose is non-digestible by human beings and also by far the most abundant renewable biomass (Rinaldi and Schüth 2009). Therefore, the efficient use of cellulose is generally considered as one of promising ways for solving the energy problem. Cellulose is a polysaccharide made of D-glucose, which is linked via β-1, 4-glycosidic bonds, resulting in its insolubility in common solvents. In addition, the presence of the extensive hydrogen bonding networks in the cellulose crystals makes the cellulose structure so robust that the direct conversion of cellulose is a challenging task (Fan et al. 1987; Nishiyama et al. 2002).

Much attention has been focused on the degradation of cellulose with dilute acids, enzymes, and supercritical water (Mok et al. 1992; Zhang and Lynd 2004; Saka and Ueno 1999; Sasaki et al. 2000). However, some major drawbacks of these traditional methods such as corrosion, separation problem, harsh reaction conditions, etc., limit their practical utility. Heterogeneous catalysis has the advantages of easy separation, easy handling and wide range of reaction conditions, and therefore attracts many researchers. Hydrogenolysis of cellulose on the supported metal catalysts has been widely investigated (Fukuoka and Dhepe 2006; Deng et al. 2009; Ji et al. 2008; Luo et al. 2007). The

---

C. Zhang · H. Wang · F. Liu · L. Wang · H. He (✉)
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, Beijing 100085, China
e-mail: honghe@rcees.ac.cn

noble metal catalysts, such as Pt/Al_2O_3 (Fukuoka and Dhepe 2006), Ru/CNT catalyst (Deng et al. 2009), have been found to be the most efficient catalysts for the cellulose hydrogenolysis into sugar alcohols in a water medium under high pressure H_2 atmosphere. Although the cellulose hydrogenolysis can effectively convert the cellulose, this reaction needs the high-pressure hydrogen gas and/or generally employs the noble-metal catalyst, therefore not so safe operation and/or cost-effective.

Catalytic hydrolysis of cellulose into glucose or saccharides using solid acid catalysts is another efficient reaction for cellulose conversion. Various of solid acid catalysts, such as the sulfonated carbon materials (Toda et al. 2005; Nakajima and Hara 2012; Van de Vyver et al. 2010; Pang et al. 2010; Onda et al. 2008; Suganuma et al. 2008), ion-exchange resins (Rinaldi et al. 2008), heteropolyacids (Tian et al. 2010) and transition-metal oxide (Takagaki et al. 2008; Nakajima et al. 2011), etc., have been found active for the hydrolysis of cellulose. In particular, the sulfonated carbon catalysts were widely studied since Hara et al. (Toda et al. 2005) reported it effective for biodiesel production from vegetable oil. Many efforts were made to improve the activity of carbon materials. The high activity have been achieved by introducing other component to carbon catalyst or by increasing the sulfonation temperature to improve the acid density (Van de Vyver et al. 2010; Pang et al. 2010), etc. Van de Vyver et al. improved the glucose yield to 50 % at 61 % conversion of cellulose using the sulfonated silica–carbon nanocomposites after 24 h reaction at 150 °C (Van de Vyver et al. 2010). Pang et al. reported the most active solid carbon acid catalyst so far and they achieved the 94.4 % cellulose conversion with 74.5 % glucose yield under same reaction reaction using the CMK-3 catalyst sulfonated at 250 °C (Pang et al. 2010). Although the sulfonated carbon catalyst is active for the hydrolysis of cellulose, its speration from the reaction mixture is still a challenge during the practical application. The catalyst is generally recovered by the filtration or centrifugation methods (Deng et al. 2009; Van de Vyver et al. 2010; Onda et al. 2008; Li et al. 2012), which are dependent on special apparatus and time-consuming. More recently, a magnetic sulfonated mesoporous silica catalyst was reported for the hydrolysis of biomass, indicating that the magnetism separation could be a feasible way to separate the catalytic material from the reaction residues (Lai et al. 2011).

In this study, we synthesized a magnetic sulfonated carbon nanoparticle with core–shell structure (Fe_3O_4@C-SO_3H) as environmental-friendly and recyclable catalyst for the hydrolysis of cellulose. The sulfonated carbon shell demonstrates a good activity. The magnetic Fe_3O_4 core makes the materials easily separated from reaction mixtures by using the externally applied magnetic field. In addition, the Fe_3O_4@C-SO_3H nanoparticle catalyst shows a high stability in the activity and magnetization during recycling tests.

Materials and methods

Catalyst preparation

The typical procedures for carbon catalyst synthesis as follows: glucose (1.8 g), $FeCl_3$ (0.97 mol) and urea (6.0 g) were dissolved in 40 mL of water under vigorous stirring. After being stirred for 1 h, the solution was transferred and sealed in a 100 mL Teflon-sealed autoclave. The autoclave was kept at 180 °C for 14 h before cooled naturally. The products were separated by magnet, and washed with deionized water and ethanol several times to neutral solution, then dried at 40 °C in an oven under vacuum for 12 h. Sulfonation of the Fe_3O_4@C nanoparticles were performed in a sealed glass container using 16 mL concentrated sulfuric acid per gram of Fe_3O_4@C nanoparticles at 60 °C for 24 h (Xing et al. 2007). After cooling and magnet separation, the sulfonated solid was washed thoroughly with hot deionized water (80 °C) until no SO_4^{2-} was detected in the solution. Finally, the sulfonated Fe_3O_4@C nanoparticles were separated from solution by magnet and then dried at 100 °C overnight. The as prepared catalyst is denoted as Fe_3O_4@C-SO_3H.

Characterization of catalyst

A computerized Rigaku D/max-RB Diffractometer (Cu Kα radiation, 0.154056 nm; Rigaku, Tokyo, Japan) was used to obtain the XRD pattern. Scans were taken over a range of 2θ angles from 10° to 90° at a speed of 4°/min. Transmission electron microscopy (TEM) were taken with a Hitachi H-7500 electron microscope at an accelerating voltage of 80 kV. The crystalline structure and elemental analysis of the nanoparticles were characterized by a JEOL JEM-2010 field emission high-resolution electron transmission microscopy (HR-TEM) equipped with EDS at an accelerating voltage of 200 kV. Raman spectra were recorded on a UV resonance Raman spectrometer (UVR DLPC-DL-03). A continuous diode pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation with the source power of 80 mW. XPS were recorded on a scanning X-ray microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al Kα radiation. Binding energies of elements were calibrated using C 1 s peak (BE = 284.6 eV) as standard. FT-IR spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N_2 cooled MCT detector. The sample (about 30 mg) was finely ground and placed in a ceramic crucible. All spectra were measured with a resolution of 4 cm^{-1} and accumulating 100 scans. A background spectrum was subtracted from each spectrum. The number of acid sites was calculated by an acid–base titration method. First, NaOH aqueous solution (0.01 mol/L, 20 mL) was added to a catalyst (0.04 g). Then the mixture was stirred for 2 h at room temperature. After magnet separation, several drops of phenolphthalein solution were first added to the solution and then this solution was titrated with HCl (0.01 mol/L) aqueous solution to neutrality. Magnetization measurements were carried out by VSM using a magnetometer (VSM 7307, Lake Shore, USA) at room temperature.

Activity test of materials

Prior to the hydrolysis reaction, the cellulose (Avicel®, microcrystalline Merck, Germany) was pretreated by ball-milling at room temperature for 4 days with ZrO_2 balls and a speed of 100 rpm. The hydrolysis of cellulose was carried out in a stainless-steel autoclave lined with Teflon (100 mL) in air without stirring. For each reaction, 0.05 g of cellulose, 0.15 g of catalyst and 10 mL of water were put into the reactor. The solid acid catalyst to cellulose ratio was 3 which is much higher than that of the enzymatic cellulose hydrolysis (Zhu et al. 2009). Here the ball-milling pretreatment and high catalyst to cellulose ratio were mainly aimed to overcome the bad mass transfer between the cellulose and solid catalyst and also to achieve the high product yields. The reaction proceeded at 140 °C for 12 h. After the reaction, the catalyst was recovered by magnet and the liquid reaction mixture was centrifuged and filtered. The filtered solution was subjected to high-performance liquid chromatography analysis (HPLC, RI detector, Waters 2414) equipped with a Sugar-Pak-1 column (6.5 × 300 mm) using water as a mobile phase. Cellulose conversions were determined by the change in cellulose weight before and after the reaction, with an uncertainty of ±3 % in this work. The yields of hydrolysis products, such as the glucose and oligosaccharides were calculated from the below equations:

Glucose yield (%) = (mol of glucose produced by the hydrolysis)/(total mol of glucose monomer in cellulose) × 100.

Oligosaccharides yield (%) = (mol of glucose monomer in oligosaccharides)/(total mol of glucose monomer in cellulose) × 100.

Results and discussion

Catalyst characterization

Figure 1 shows the TEM (a, b, c) and HRTEM (d) images of the Fe_3O_4@C-SO_3H catalyst with the SAED result (insert in d) of the Fe_3O_4 core. TEM images (Fig. 1a, b, c) clearly showed that the as prepared particle has a core–shell structure; the size of Fe_3O_4 core is around 100–200 nm and the thickness of carbon shell is at around 10 nm. HR-TEM image of core (Fig. 1d) indicated that the interlayer spacing for the core is about 0.48 nm, which is close to the value for the (111) planes of the Fe_3O_4. The electron diffraction (ED) pattern of core (insert in Fig. 1d) further showed that the Fe_3O_4 core is in crystalline state. Our present results demonstrate that the Fe_3O_4@C-SO_3H nanoparticles could survive the sulfonation process with sulfuric acid at 60 °C and keep their well defined core–shell structure. The bulk structures of samples were next studied by XRD (Fig. 2). All detected sharp diffraction peaks could be indexed as Fe_3O_4 (JCPDS card No. 19-629), which is in well agreement with the HR-TEM and ED analysis.

In order to study the surface structure of the Fe_3O_4@C-SO_3H catalyst, the Raman, XPS and FTIR measurements were carried out and the results are

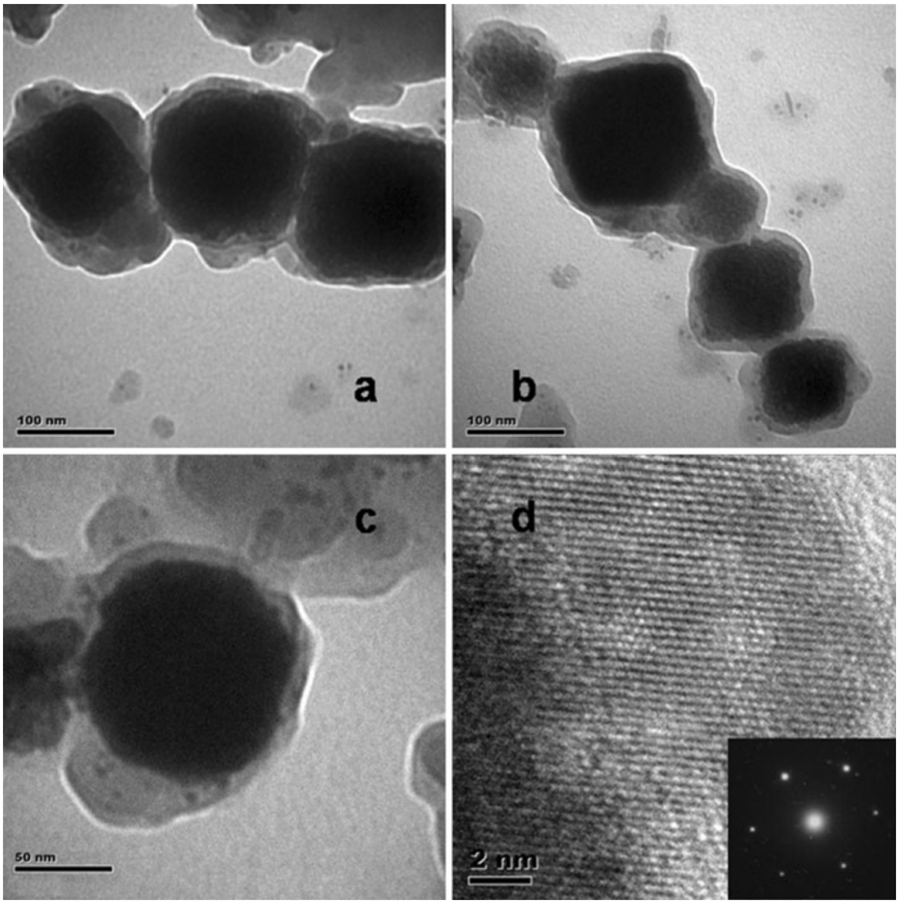

Fig. 1 TEM (**a**, **b**, **c**) and HR-TEM (**d**) images of Fe_3O_4@C-SO_3H catalyst and the SAED result (insert in **d**) of Fe_3O_4 core

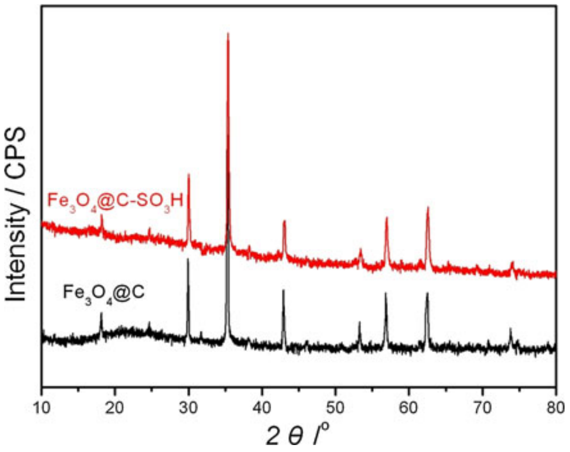

Fig. 2 XRD patterns of Fe_3O_4@C catalysts before and after sulfonation

shown in Figs. 3, 4 and 5, respectively. Raman spectrum (Fig. 3) showed two main peaks centered at 1,357 and 1,566 cm^{-1}, which were assigned to the D-band and G-band of amorphous carbon, indicating the carbon shell is in amorphous state (Ferrari and Robertson 2001; Hu et al. 2003). XPS results (Fig. 4) presented the sharp C1 s peak but no $Fe2p_{3/2}$ peak at 710.2 eV was detected whether the samples was sulfonated or not due to the cover of carbon shell. From XPS spectrum of the sulfonated sample, a clear S $2p_{3/2}$ peak appeared, indicating that the SO_4^{2-} group is successfully grafted on the Fe_3O_4@C surface after sulfonation. FTIR spectra (Fig. 5) showed a new peak at 1,039 cm^{-1} due to the vibration of S = O group on the sulfonated samples, further confirming the successful grafting of the SO_4^{2-} group (Zhou et al. 2001).

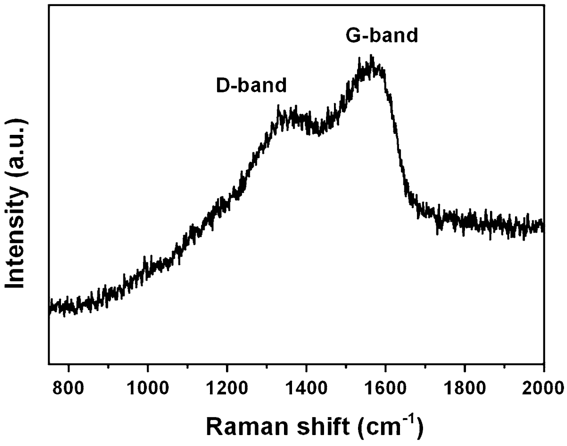

Fig. 3 Raman spectrum of the core/shell Fe_3O_4@C-SO_3H catalyst

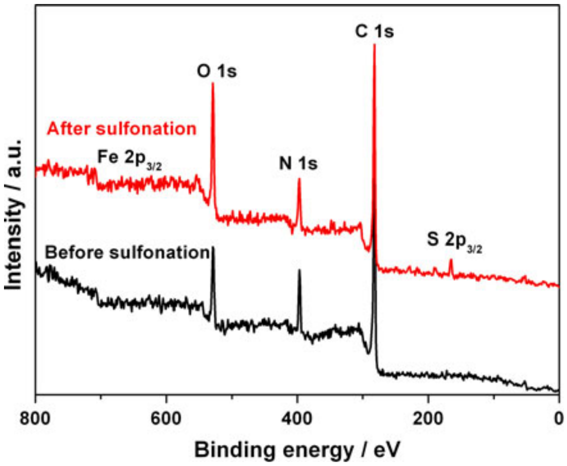

Fig. 4 XPS spectra of the Fe_3O_4@C particles before and after sulfonation

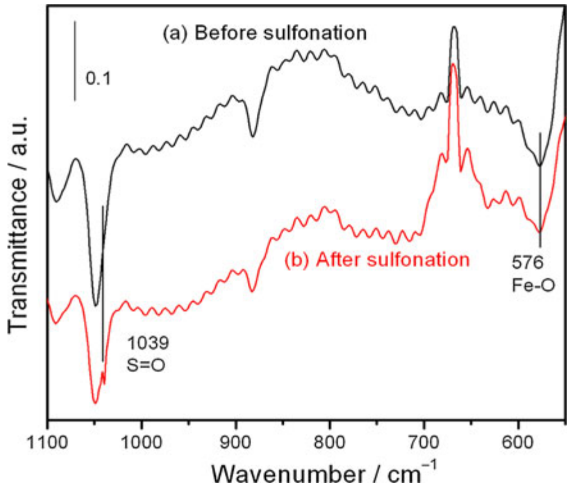

Fig. 5 FT-IR spectra of Fe_3O_4@C catalysts before and after sulfonation. **a** Fe_3O_4@C; **b** Fe_3O_4@C-SO_3H

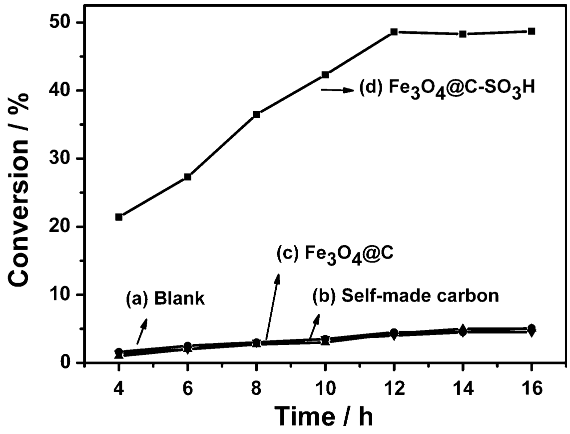

Fig. 6 Experimental results of cellulose conversion over Fe_3O_4@C-SO_3H catalyst. Reaction conditions: 10 mL H_2O, 0.05 g cellulose, 0.15 g catalyst, 140 °C, **a** blank; **b** self-made carbon; **c** Fe_3O_4@C; **d** Fe_3O_4@C-SO_3H

Activity test for hydrolysis of cellulose

The Fe_3O_4@C-SO_3H catalyst was then tested for hydrolysis of cellulose. The cellulose conversions over different samples are shown in Fig. 6. Blank test only presented less than 5 % cellulose conversion within 16 h reaction. The unsulfonated carbon and Fe_3O_4@C samples showed the similar results to that of blank test. When the Fe_3O_4@C sample was sulfonated to Fe_3O_4@C-SO_3H, the activity was greatly enhanced, presenting a high capacity for the hydrolysis of cellulose. It was observed that the cellulose conversion was around 20 % after 4 h reaction, and then gradually increased to the highest level of 48.6 % with reaction time prolonged to 12 h. The distributions of products of the cellulose hydrolysis over the Fe_3O_4@C-SO_3H catalyst as function of reaction time are summarized in Table 1. The products were the mixture including various oligosaccharides from cellohexose to glucose and some amount of unknown products. The carbon balance was calculated based on the total organic carbon (TOC) analysis and the results showed that no gas-phase product is produced. Among the products, the glucose showed the highest yield and selectivity. When the cellulose conversion reached 48.6 % after 12 h reaction, the glucose yield was 25.3 % with a high selectivity of 52.1 %.

Table 1 Distribution of products for the hydrolysis of cellulose over Fe_3O_4@C-SO_3H catalyst

Reaction time (h)	4	8	12
Cellulose conversion (%)	21.4	36.5	48.6
Product yield (%)			
Cellohexose	2.3	–	3.5
Cellopentaose	–	–	–
Cellotetraose	–	3.0	–
Cellotriose	1.5	2.8	2.2
Cellobiose	1.2-	2.2	3.7
Glucose	8.1	17.6	25.3
Unknown products	8.3	10.9	13.9

Reaction conditions: 10 mL H_2O, 0.05 g cellulose, 0.15 g catalyst, 140 °C, 12 h

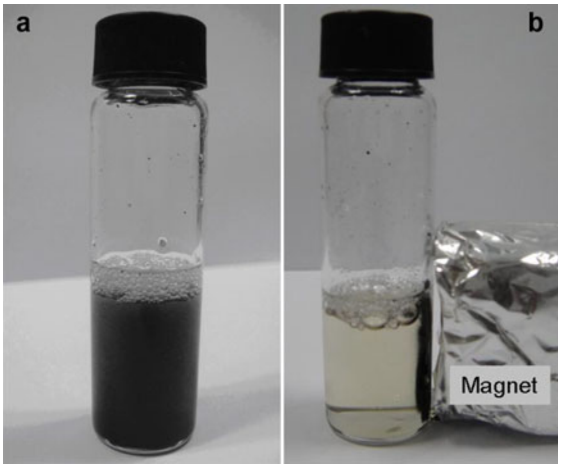

Fig. 7 Magnetic property and the separation of Fe_3O_4@C-SO_3H acid catalyst. **a** Without magnet, **b** with magnet

Although the as prepared Fe_3O_4@C-SO_3H catalyst showed a lower activity than the reported sulfonated carbon catalysts (Onda et al. 2008; Van de Vyver et al. 2010; Pang et al. 2010), the catalyst has the advantage of easy separation from reaction mixture. After the activity test, the Fe_3O_4@C-SO_3H catalyst could be separated from solution by using the externally applied magnetic field due to its magnetic Fe_3O_4 core. As shown in Fig. 7, before the magnetic field was present, the Fe_3O_4@C-SO_3H catalyst well dispersed in reactant solution. When a magnetic field was applied to one side of glass bottle containing the reactant, products and acid catalyst, the magnetic catalyst was quickly accumulated tightly against the side of glass bottle and then could be very easily separated in 1 min.

Recycling experiments

The recycling experiments were performed to test the stability of the Fe_3O_4@C-SO_3H catalyst. The recycling procedures are as follows. After the first run at 140 °C for 12 h, the catalyst was first recovered by magnet and then washed with deionized water, followed by dryness at 40 °C in an oven under vacuum for 12 h. Next, fresh cellulose and water were added to the recovered catalyst and then the second run started. Similarly, the third run was also performed using the same procedure. The Fe_3O_4@C-SO_3H catalyst showed a relatively high stability, which is in accordance to the reported results (Onda et al. 2008; Van de Vyver et al. 2010; Pang et al. 2010). The cellulose conversions only slightly dropped from the 48.6 to 46 and 45 % with the first, second and third run, respectively.

After the second and third run, the acid densities of Fe_3O_4@C-SO_3H catalysts were measured by NaOH titration and examined by XPS for the surface acid density. It is clear from the Table 2 that the activity test results in the slight losses of acid densities from the 1.30, 1.15 to 1.10 mmol/g with the fresh, after the first and second run, respectively, possibly due to the leaching of surface carboxylic and/or SO_3H groups (Onda et al. 2008). XPS spectra (Fig. 8) showed that S $2p_{3/2}$ peak at 168 eV slightly dropped with the run times, confirming the leaching of partial SO_3H groups. Therefore, the loss of acid density during the tests should account for the slight activity decrease of the Fe_3O_4@C-SO_3H acid catalyst. The pH of the supernatant after the cellulose hydrolysis was measured and the pH = 4.5 was obtained. Further experiment by putting the fresh cellulose into the separated solution after the first run revealed that the cellulose conversion was only around 3 % after the reaction at 140 °C for 12 h, providing strong evidence that the hydrolysis reaction mainly takes place on the solid catalyst surface (Pang et al. 2010).

Samples were finally characterized in terms of magnetization at room temperature. Figure 9 shows the field dependent magnetization (M (H) curves) of the sample before and after the first test. The fresh sample presented the saturation magnetization (Ms) value of about 26 emu g^{-1}, indicating a satisfactory magnetization for nanoparticle separation. After the first test, the saturation magnetization slightly dropped to 23 emu g^{-1}, possibly due to the leaching of trace

Table 2 Acidity density of Fe_3O_4@C-SO_3H catalyst during the catalytic runs

Catalyst	Acid density/(mmol g^{-1})
Fresh	1.30
After first run	1.15
After second run	1.10

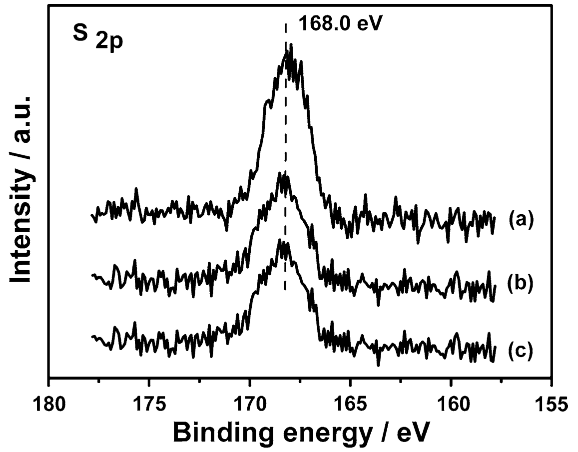

Fig. 8 XPS spectra of S_{2p} of Fe_3O_4@C-SO_3H catalyst **a** fresh catalyst; **b** after the first run; **c** after the second run

amount of Fe_3O_4 impurity contained in carbon shell. The second run did not result in the further decease of magnetization (Ms) value. The present results show that the magnetic Fe_3O_4 core in Fe_3O_4@C-SO_3H catalyst is very stable because the carbon shell could prevent the elution of the Fe_3O_4 core during the reaction, which keeps the material magnetic and easy separation from the solution.

Conclusions

In summary, we successfully synthesized a magnetic core–shell Fe_3O_4@C-SO_3H acid catalyst for catalytic hydrolysis of cellulose. As prepared catalyst showed a high activity with a 48.6 % cellulose conversion and 52.1 % glucose selectivity under the conditions of 140 °C after 12 h reaction. In addition, the Fe_3O_4 core makes the catalyst to be easily recovered by externally applied magnetic field. The Fe_3O_4@C-SO_3H catalyst also had a relatively high stability in both activity and its magnetization, indicating it a promising solid acid catalyst for the hydrolysis of cellulose.

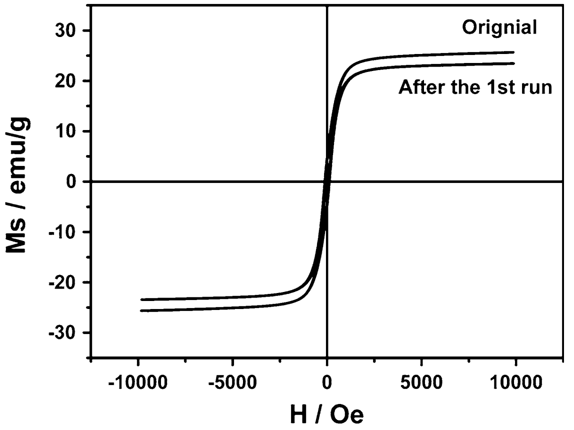

Fig. 9 Field-dependent magnetization curves of Fe_3O_4@C-SO_3H before and after the first test

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (20177117), the Program of the Ministry of Science and Technology of China (2012AA062702 and 2010AA064905).

References

Deng WP, Tan XS, Fang WH, Zhang QH, Wang Y (2009) Conversion of cellulose into sorbitol over carbon nanotube-supported ruthenium catalyst. Catal Lett 133:167–174

Fan LT, Gharpuray MM, Lee YH (1987) Cellulose hydrolysis. Springer, Berlin

Ferrari AC, Robertson J (2001) Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. Phys Rev B 64:075414

Fukuoka A, Dhepe PL (2006) Catalytic conversion of cellulose into sugar alcohols. Angew Chem Int Ed 45:5161–5163

Hu G, Cheng MJ, Ma D, Bao XH (2003) Synthesis of carbon nanotube bundles with mesoporous structure by a self-assembly solvothermal route. Chem Mater 15:1470–1473

Ji N, Zhang T, Zheng MY, Wang AQ, Wang H, Wang XD, Chen JG (2008) Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. Angew Chem Int Ed 47:8510–8513

Lai D, Deng L, Guo Q, Fu Y (2011) Hydrolysis of biomass by magnetic solid acid. Energy Environ Sci 4:3552–3557

Li C, Zheng M, Wang A, Zhang T (2012) One-pot catalytic hydrocracking of raw woody biomass into chemicals over supported carbide catalysts: simultaneous conversion of cellulose, hemicellulose and lignin. Energy Environ Sci 5:6383–6390

Luo C, Wang S, Liu HC (2007) Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. Angew Chem Int Ed 46:7636–7639

Mok WS, Antal MJ, Varhergyi G (1992) Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose. Ind Eng Chem Res 31:94–100

Nakajima K, Hara M (2012) Amorphous carbon with SO_3H groups as a solid Brønsted acid catalyst. ACS Catal 2:1296–1304

Nakajima K, Kitano M, Hara M (2011) $Nb_2O_5 \cdot nH_2O$ as a heterogeneous catalyst with water-tolerant Lewis acid sites. J Am Chem Soc 133:4224–4227

Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron X-ray and neutron fiber diffraction. J Am Chem Soc 124:9074–9082

Onda A, Ochi T, Yanagisawa K (2008) Selective hydrolysis of cellulose into glucose over solid acid catalysts. Green Chem 10:1033–1037

Pang J, Wang A, Zheng M, Zhang T (2010) Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. Chem Commun 46:6935–6937

Rinaldi R, Schüth F (2009) Design of solid catalysts for the conversion of biomass. Energy Environ Sci 2:610–626

Rinaldi R, Palkovits R, Schüth F (2008) Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids. Angew Chem Int Ed 47:8047–8050

Saka S, Ueno T (1999) Chemical conversion of various celluloses to glucose and its derivatives in supercritical water. Cellulose 6:177–191

Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Dissolution and hydrolysis of cellulose in subcritical and supercritical water. Ind Eng Chem Res 39:2883–2890

Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M (2008) Hydrolysis of cellulose by amorphous carbon bearing SO_3H, COOH, and OH groups. J Am Chem Soc 130:12787–12793

Takagaki A, Tagusagawa C, Domen K (2008) Glucose production from saccharides using layered transition metal oxide and exfoliated nanosheets as a water-tolerant solid acid catalyst. Chem Commun 44:5363–5365

Tian J, Wang J, Zhao S, Jiang C, Zhang X, Wang X (2010) Hydrolysis of cellulose by the heteropoly acid $H_3PW_{12}O_{40}$. Cellulose 17:587–594

Toda M, Takagaki A, Okamura M, Kondo JN, Hayashi S, Domen K, Hara M (2005) Biodiesel made with sugar catalyst. Nature 438:178

Van de Vyver S, Geboers J, Dusselier M, Schepers H, Vosch T, Zhang L, Van Tendeloo G, Jacobs PA, Sels BF (2010) Selective bifunctional catalytic conversion of cellulose over reshaped Ni particles at the tip of carbon nanofibers. ChemSusChem 3:698–701

Xing R, Liu N, Liu Y, Wu H, Jiang Y, Chen L, He M, Wu P (2007) Novel solid acid catalysts: sulfonic acid group functionalized Meso-structured polymers. Adv Funct Mater 17:2455–2461

Zhang YP, Lynd LR (2004) Toward an aggregated understanding of enzymatic hydrolysis of cellulose: noncomplexed cellulase systems. Biotechnol Bioeng 88:797–824

Zhou W, Yoshino M, Kita H, Okamoto K (2001) Carbon molecular sieve membranes derived from phenolic resin with a pendant sulfonic acid group. Ind Eng Chem Res 40:4801–4807

Zhu Z, Sathitsuksanoh N, Zhang Y-HP (2009) Direct quantitative determination of adsorbed cellulase on lignocellulosic biomass with its application to study cellulase desorption for potential recycling. Analyst 134:2267–2272