Preparation of Core-Shell Structure Magnetic Carbon-Based Solid Acid and its Catalytic Performance on Hemicellulose in Corncobs

Xucheng Zhang,[a,b] Xuesong Tan,[a] Yan Xu,[c] Wen Wang,[a] Longlong Ma,[a] and Wei Qi [a,]*

Solid acid catalysts show good catalytic depolymerization behavior for lignocellulose. A stable core-shell structured magnetic solid acid catalyst (MSAC), $Fe_3O_4/C-SO_3H$, was prepared from glucose, concentrated sulfuric acid, and modified magnetic particles of Fe_3O_4, which was used as the core. The effects of the carbonization and sulfonation processes on the activity of the catalyst were investigated. The results showed that preparation conditions had great influence on the quantity of the acidic groups (sulfonic, carboxyl, and hydroxyl groups) and the stability of magnetic catalysts. The best preparation conditions for MSAC were 3 h of carbonization time, 450 °C as the carbonization temperature, 9 h of sulfonation time, and 90 °C as the sulfonation temperature. Its surface topography, functional group, chemical composition, and magnetic properties were characterized by analysis instrument. Furthermore, the catalyst was stably dispersed in the reaction system, quickly separated from the reaction system using an external field, and reused many times; 44.3% of xylose yield was obtained at 160 °C for 16 h. The catalyst was used repeatedly more than 3 times, and the recovery over 89%. The depolymerization of corncobs was achieved by magnetic catalyst, representing the depolymerization characteristics of real lignocellulose. This data can be used as a reference for the subsequent use of biomass resource.

Keywords: Carbon solid acid catalyst; Hydrolysis; Lignocellulose; Biomass; Catalytic activity; Magnetic

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INTRODUCTION

Fossil fuel shortages and climate change issues have raised new energy research and development to top national priorities. The solar, geothermal, wind, ocean, biomass, fusion, and other new energy sources have contributed proportionally to the world energy supply (Jacobson 2009; Long *et al.* 2013). Biomass energy has attracted interest because it is abundant, renewable, and environmentally friendly. Biomass energy is produced mainly from biomass such as agricultural straw, forestry, and solid wastes. Annually, 173 billion tons of substances are produced by photosynthesis on Earth, containing the energy equivalent of 10 to 20 times of the world's total energy consumption. However, the utilization of this energy resource is less than 3% (Qi *et al.* 2009).

The polysaccharide content of lignocellulose, the main source of biomass energy, can be converted into monosaccharides after saccharification. The monosaccharides can be used as the platform chemicals for producing fuel, gas, and bulk fermentation products through chemical and biological methods (Zhang *et al.* 2015).

Acids and enzymes are often applied to catalyze lignocellulose hydrolysis. Acid can corrode equipment and requires neutralization treatment after the reaction (Mosier *et al.* 2004). As for the enzymes, their high price, low reaction efficiency, and difficulties with recovery restrict their large-scale use (Wood and McCrae 1986; Lu and Mosier 2007). A solid acid catalyst is prepared *via* the loading of acid groups onto an inert carrier, which has the advantages of avoidance of corrosion equipment. It can be separated from the reaction system and is environmentally friendly (Hu *et al*. 2015). Amarasekara and Owereh (2010) used solid acid, which was prepared by strong acid (-SO_3H) ionic liquid and SiO_2 to catalyze the hydrolysis of cellulose in the [BMIM]Cl system, leading to a sugar yield of 67% (Amarasekara and Owereh 2010). However, the physical properties of biomass-based solid acid are similar to those of the hydrolytic residue of biomass, which gives rise to difficulties in the separation and recycling of the solid acid (White *et al*. 2009). A solid acid catalyst with magnetic characteristics has advantages in separation and recycling and has shown catalytic activity equal to that of a conventional solid acid catalyst (Berry and Curtis 2003). The MSAC can greatly simplify the recovery procedure and reduce the cost of the reaction compared with a conventional solid acid (Zhang *et al*. 2012). Ren *et al*. (2012) studied the catalytic properties of a MSAC in the cyclohexanone condensation reaction and found that a catalyst that was recycled six times still displayed good catalytic activity (Ren and Xu 2012).

Liu *et al*. (2012) used mesh oxidation asphalt to encapsulate Fe_3O_4 magnetic nanomaterials to form porous carbon membrane material. With further moderate activation and sulfonation, a core-shell structure of magnetic carbon-based solid acid was obtained by self-assembly technology, leading to over 80% esterification efficiency and above 90% repetition rate. However, there have been few studies on the application of magnetic catalyst to biomass depolymerization. Additionally, the cost of raw materials for the preparation of magnetic catalyst is high, and some preparation methods lead to poor mechanical strength and thermal stability of the catalyst (Verma *et al*. 2013; Xiong *et al*. 2014).

This study investigated a new magnetic core-shell structure solid acid catalyst to catalyze hydrolysis of lignocellulose. The effects of the preparation process on the catalytic activity were studied, and the characteristics of the catalyst were comprehensively analyzed. The recycling and deactivation of the core-shell structure solid acid catalyst was performed in a water thermal environment. Compared with the current catalysts in the literature, such as SBA-15 (Lai *et al*. 2011b) and HZSM-5 (Cai *et al*. 2012), the preparation of solid acid catalyst described in this study displays many advantages such as abundant sources and low-cost of biomass material. It was also found that a long-chain surfactant can give rise to a chemical reaction with biomass material on the surface of the Fe_3O_4, improve the stability of the core-shell structure, and increase the number of repeated uses of the catalyst. The hydrolysis properties of corncobs catalyzed by MSAC in this study was found to be greater than that of the model compounds. This work provides an important reference for hydrolysis saccharification technology of biomass material resources.

EXPERIMENTAL

Materials

The glucose reagent was purchased from Tianjin Damao Chemical Factory (Tianjin, China). The $FeCl_3•6H_2O$ (≥ 99.0%), $FeSO_4•7H_2O$ (≥ 99.9%), NaOH (≥ 96.0%), and H_2SO_4 (95.0% to 98.0%) reagents were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Anhydrous ethanol (≥ 99.7%) and glacial acetic acid (≥ 99.5%) were purchased from Tianjin Fuyu chemical Co., Ltd. (Tianjin, China). Sodium oleate (≥ 99.9%) was purchased from Sinopham Chemical Reagent Co., Ltd. (Beijing, China). Deionized water was used to prepare the catalyst. Corncobs were obtained from the Shandong province of China and were crushed and sieved with an 80 mesh sieve.

Preparation of Fe_3O_4 Particles

Seven grams of $FeCl_3•6H_2O$ and 4.8 g of $FeSO_4•7H_2O$ were dissolved in 200 mL of deionized water and placed in a water-bath with at the constant temperature of 65 °C, which was followed by rapid stirring and the addition of 55 mL of NaOH (2 mol/L) aqueous solution. After the addition of 40 mL anhydrous ethanol and standing for 10 min, black particles were formed. The reaction system was stirred again and heated to 80 °C. The pH of the reaction system was adjusted to around 5 with the addition of 45 mL of glacial acetic acid. Then the surfaces of magnetic particles were modified by an addition of 3.0 g sodium oleate. After 8 h, the sediment was collected using an external magnet, washed in anhydrous ethanol and deionized water, and calcined after being dried to obtain the Fe_3O_4 magnetic powder (Xuan *et al*. 2009; Lai *et al*. 2011a; Pourjavadi *et al*. 2012; Liang 2015).

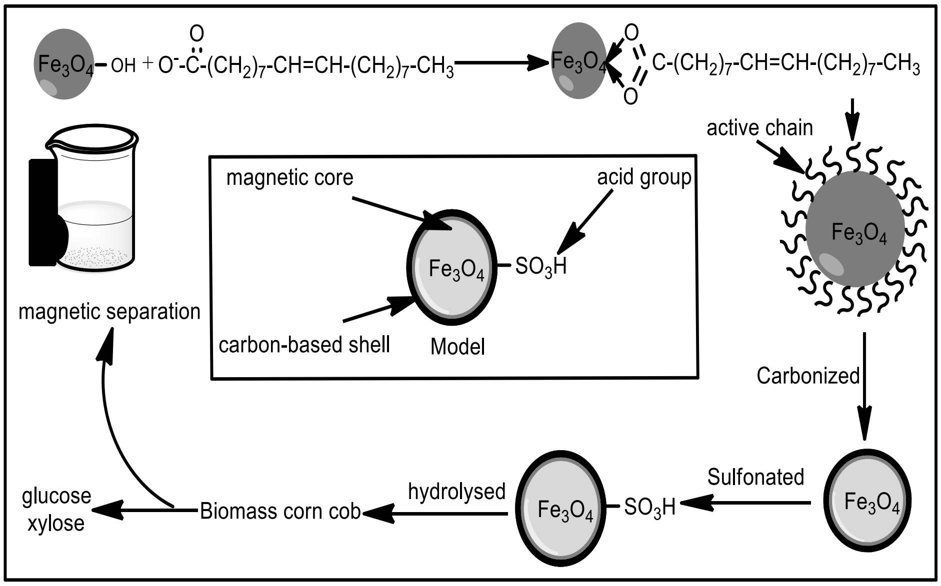

Fig. 1. Catalyst preparation and reaction process

Preparation of Carbon-based Solid Acid Catalyst

The synthesized magnetic Fe_3O_4 particles were fully ground and well mixed at a certain mass ratio with anhydrous glucose. They were carbonized (at 350 to 550 °C) under N_2 atmosphere for 2 to 6 h and cooled to room temperature. The Fe_3O_4/C magnetic carbon material was obtained and then sulfonated (at 60 to 160 °C) with sulfuric acid for 5 to 15 h. The sulfonated magnetic carbon material was recovered through filtration and washed with hot water (80 °C) until no SO_4^{2-} ion was detected. The $Fe_3O_4/C\text{-}SO_3H$ MSAC was dried for 12 h at 80 °C (Gill *et al*. 2007) (Fig. 1).

Characterization and Analysis

The functional groups of the catalysts were characterized by Fourier transform-infrared spectroscopy (FT-IR; Tensor27, Bruker, Karlsruhe, Germany), using samples mixed with KBr (the samples quality of 1 mg, and the KBr quality of 150 mg) in a full pellet after grinding. Crystal structures of the catalysts were analyzed by X-ray diffraction (XRD; X'PertPro MPD, Manufacturer, Almelo, Netherlands) using a Cu K_α radiation source in the 20 to 80° 2θ range with a scanning step length of 4 °/min. The catalyst morphologies were determined by transmission electron microscope (TEM; Hitachi HT7700, Tokyo, Japan) with the working voltage of 20.0 kV. The elementary compositions of the catalysts were tested by element analyzer test instruments (Vario EL cube; Elementar, Frankfurt, Germany), and the sample decomposition temperature was 950 to 1150 °C. Magnetic properties of catalysts were examined using a vibrating sample magnetometer (VSM; 7410, Lake Shore Company, Colchester, USA) for the sample particle hysteresis regression curve and Ms with an absolute accuracy of better than 2%. Specific surface areas of the catalysts were analyzed by automatic specific surface and pore size analyzer (BET; ASIQMO002-2, Quantachrome, Boynton Beach, USA) with a measuring range greater than 0.01 m^2/g (N_2). The thermal stabilities of the catalysts were characterized by thermo-gravimetric analyzer (TGA; TGAQ50, TA, New Castle, USA) with the heating rate of 20 °C/min.

The surface acid amounts of the catalyst were determined by an acid-base titration method, which included the amount of total acid and sulfonic acid as follows. First, 0.250 g of catalyst was added to 30 mL of NaOH solution (0.05mol/L), and the mixture was subjected to ultrasonic vibration for 60 min at room temperature, causing the full response of H^+ and OH^- on the catalyst surface. After centrifuging the mixture, 10 mL of solution was titrated with HCl (0.05 mol/L), and the magnetic solid acid total acid value was calculated. Moreover, 0.250 g of catalyst was added to 30 mL of NaCl solution (0.05 mol/L), and the mixture was subjected to ultrasonic vibration for 60 min at room temperature, causing the full H^+ and Na^+ response on the catalyst surface. After centrifuging the mixture, 10 mL of solution were titrated with NaOH (0.05 mol/L), and the magnetic solid acid and sulfonic acid values were calculated (Wang *et al*. 2011).

Catalytic Activity Test

The catalytic hydrolysis of raw corncobs was conducted in 100 mL of polytetrafluoroethylene with mechanical agitation in the high-pressure reaction kettle; corncobs (0.5 g), catalyst (1.0 g), and 50 mL of deionized water were added into the reaction kettle and heated to 160 °C for 16 h. The mixture was separated using a suction filter (PES, the diameter of 13 nm, pore diameter of 0.22 μm) after the reaction, and the liquid was analyzed for xylose content using high performance liquid chromatography (Waters 2698, Milford, USA; Shodex sugar SH-1011 chromatographic column, mobile phase of 5 L sulfuric acid, flow rate of 0.5 mL/min, column temperature of 50 °C). The yield of xylose was calculated as follows:

$$Xylose\ (\%) = \frac{moles\ of\ xylose\ in\ hydrolysate\ after\ hydrolysis}{moles\ of\ xylose\ in\ biomass\ before\ hydrolysis} \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Effects of Carbonization Process on Catalytic Activity

To study effects of carbonization on magnetic catalyst activity, the carbonization time and temperature were varied to examine the xylose yield of the biomass corncob hydrolysis reaction catalyzed by Fe_3O_4/C-SO_3H, as shown in Fig 2. In Fig. 2(a), preparation conditions of carbonization temperature (450 °C), sulfonation time (9 h) and temperature (100 °C) were fixed. When the carbonization time was increased from 0.5 h to 3 h, the xylose yield increased; however, when the carbonization time was too long, the sugar yield declined.

At 3 h the total amount of acid for catalyst was the highest, and the catalyst activity was the strongest. This result reflects that the carbonization time of carbon-based materials is affected by the H and O content. If carbonization time is short, the H and O content is higher, and the solid acid is not stable; after the sulfonation the sulfonic acid loading falls off dramatically, and catalytic activity is decreased. A long carbonization time results in a low H and O content and a reduction of the synergy between the hydroxyl and carboxyl groups, which is not conducive for the hydrolysis reaction (Taran *et al*. 2010).

As shown in Fig. 2(b), preparation conditions of carbonization time (3 h), sulfonation time (9 h) and temperature (100 °C) were fixed. Increasing carbonization temperature first increased and then decreased the sugar yield, with the highest yield obtained at 450 °C. This is mainly because the preparation of carbon-based solid acid to control the temperature within a certain range.

The temperature also has a great influence on the total amount of acid for the catalyst. 1.66 mmol/g of the total acid is optimal at 450 °C. At a low temperature, the carbide can lead to carbide materials and water solubility, preventing the formation of a stable solid acid catalyst. At high temperatures, full carbonization is achieved by reducing the hydrophilicity of the catalyst, which is unfavorable for hydrolysis (Delidovich and Palkovits 2016).

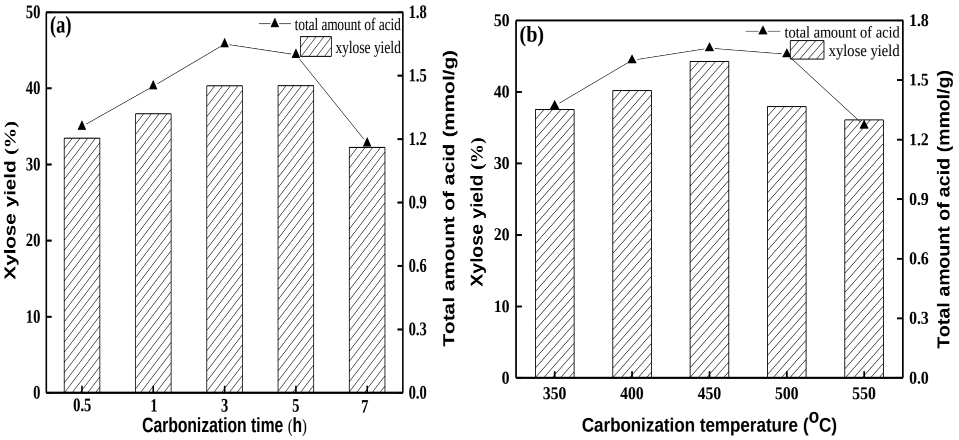

Fig. 2. Effects of carbonization process on catalytic activity

Effects of Sulfonation Process on the Catalytic Activity

To study the effects of sulfonation on magnetic catalyst activity, the sulfonation time and temperature were varied, and the xylose yield of the biomass corncob hydrolysis reaction catalyzed by $Fe_3O_4/C-SO_3H$ was examined, as shown in Fig. 3. In Fig. 3(a), preparation conditions of sulfonation temperature (100 °C), carbonization time (3 h) and temperature (450 °C) were fixed.

As the sulfonation time was increased from 5 h to 9 h, the total amount of acid for MSCA and the xylose yield continued to rise in Fig. 3(a). This result is mainly due to the increase in sulfonation time. The sulfonation reaction proceeded further toward completion, and the total amount of acid increased, leading to an increased sugar yield. However, possibly due to the relatively abundant oxidation reaction, a part of the hydroxyl group was oxidized into carboxyl groups, improving the catalyst acidity. However, for sulfonation times of more than 9 h, the xylose yield dropped noticeably. At this time the total acid of the catalyst also changed greatly, probably because the time was too long, causing some removal of the hydroxyl and carboxyl groups during the reaction. Due to the removal of the hydroxyl and carboxyl groups, the attraction of the catalyst for the raw materials is weaker, ultimately resulting in decreased catalytic efficiency (Aldana-Pérez *et al.* 2012).

In Fig. 3(b), preparation conditions of sulfonation time (9 h), carbonization time (3 h) and temperature (450 °C) were fixed, as the sulfonation temperature increased from 70 °C to 90 °C, the total amount of acid for MSCA increased, so the xylose yield increased. Mainly because when the temperature is too low, inadequate sulfonation leads to the lesser linking of the aromatic carbon ring with the sulfonic acid and low catalyst activity (Fig 3(b)).

When the temperature is too high, concentrated sulfuric acid can lead to the fracture of the condensed structure, damaging the structure of the catalyst and reducing the catalyst activity. And the total acid is reduced by 33.8% at 90 °C compared to 150 °C. Additionally, when the temperature is too high, the carbonization of carbon materials counteracts the sulfonation reaction (Lokman *et al.* 2016).

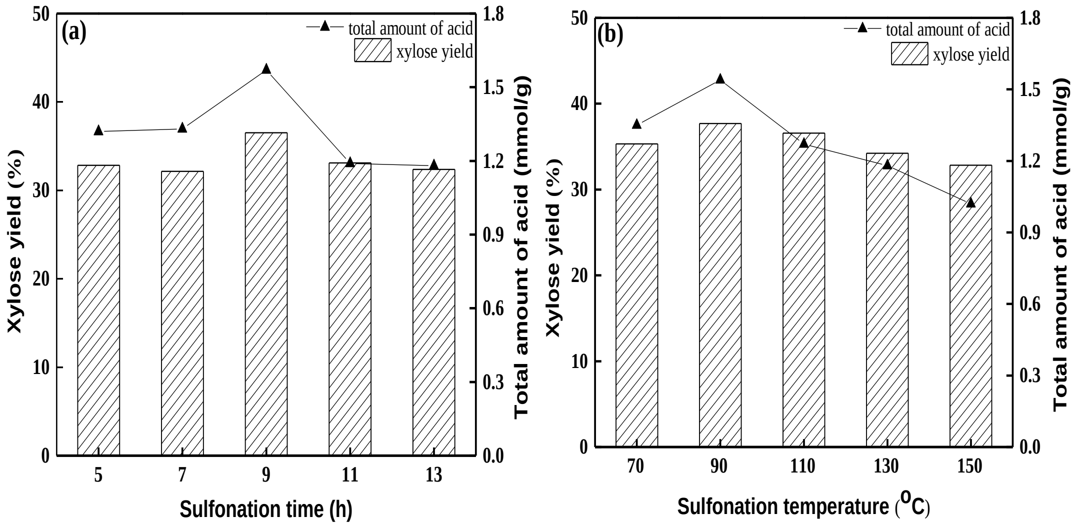

Fig. 3. Effects of sulfonation process on catalytic activity

In conclusion, the best preparation conditions for MSCA were selected as 3 h carbonization time, 450 °C as the carbonization temperature, 9 h sulfonation time, and 90 °C as the sulfonation temperature. These conditions were used for further study of catalyst characterization and recovery.

Characterization

The hysteresis loops of Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C-SO_3H are presented in Fig. 4. The three (a, b, and c) types of hysteresis loop were similar, with the saturation magnetization intensity values of 89.9 Am^2/kg, 29.9 Am^2/kg, and 7.8 Am^2/kg for Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C-SO_3H, respectively. This result illustrated that Fe_3O_4 superparamagnetism was not affected by the coating of the Fe_3O_4 surface with a carbon coating and sulfonation (Fei and Brosh 2014).

In the experimental process it was found that the catalyst does not lead to the particle reagglomeration phenomenon without magnetic attraction, and the catalyst can be well dispersed in the water. This is because the catalysts exhibit a magnetization only under an applied magnetic field and can be separated from the reaction system (Loyo *et al.* 2008).

Figure 5 shows the nitrogen adsorption/desorption isotherms of Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C-SO_3H. The specific surface areas were 4.3 m^2/g, 10.2 m^2/g and 39.1 m^2/g for Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C-SO_3H, respectively. While the carbon layer for magnetic particles, carbonization, and sulfonation decreased the saturation magnetization intensity, they also made it difficult for the catalyst to reassemble and reduce the particle size, increasing the catalyst specific surface area and leading to a better dispersion (Wang *et al.* 2014).

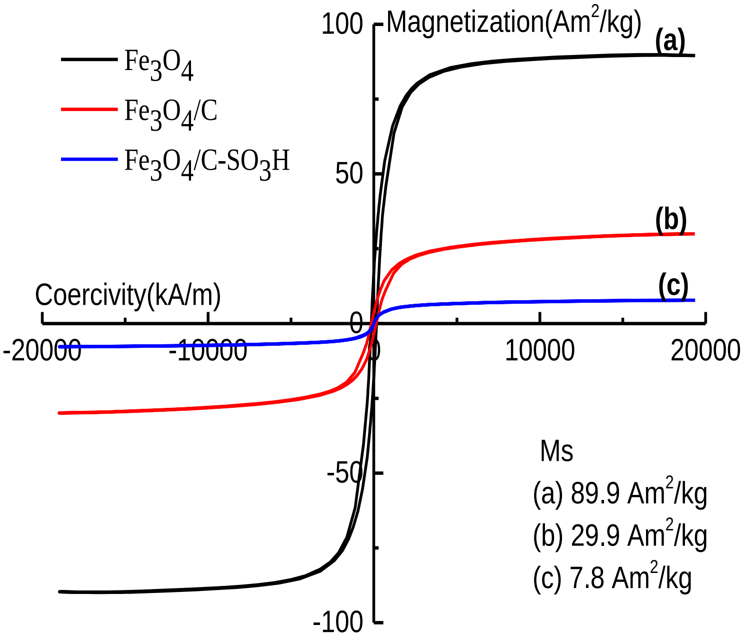

Fig. 4. Hysteresis loop of magnetic particles (Fe_3O_4), carbonized magnetic carbon (Fe_3O_4/C), and magnetic carbon-based solid acid (Fe_3O_4/C-SO_3H)

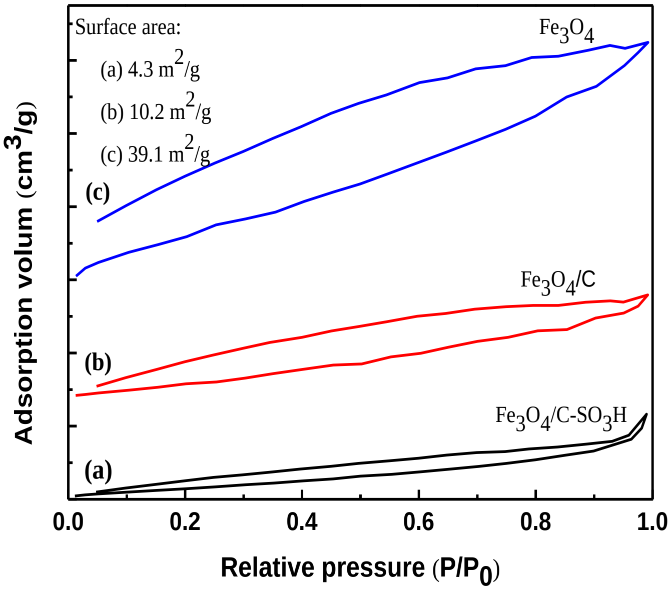

Fig. 5. Nitrogen adsorption/desorption isotherms of magnetic particles (Fe_3O_4), carbonized magnetic carbon (Fe_3O_4/C), and magnetic carbon-based solid acid (Fe_3O_4/C-SO_3H)

The microstructure of the Fe_3O_4 magnetic particles and the Fe_3O_4/C-SO_3H catalyst was observed by TEM. Figure 6(a) shows TEM images for the samples obtained by the coprecipitation method after the modification of the Fe_3O_4 magnetic particles, while Fig. 6(b) shows the TEM images for the Fe_3O_4/C-SO_3H catalyst.

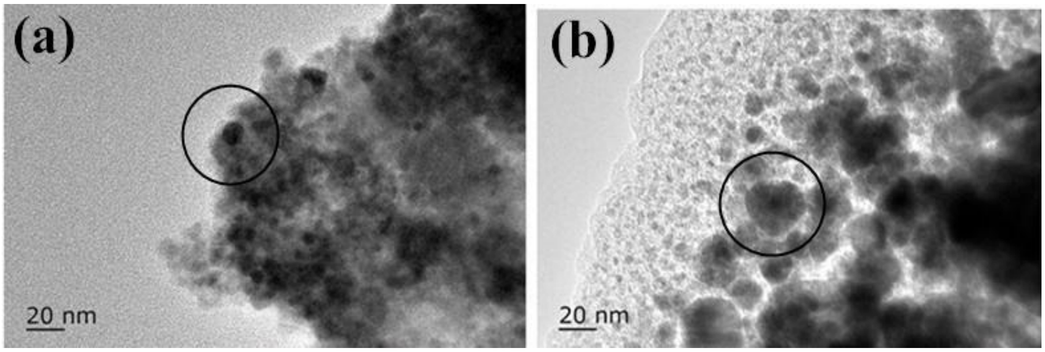

Fig. 6. TEM images for Fe_3O_4 magnetic particles and Fe_3O_4/C-SO_3H catalyst

Compared with Fig 6(b) and Fig 6(a), it can be seen that a layer of amorphous carbon was coated on the surface of Fe_3O_4 cores. The diameter for the Fe_3O_4 magnetic particles was approximately 16 nm for the spherical structures; Fe_3O_4 magnetic particles tend to reassemble into larger particles. In Fig. 6(b), Fe_3O_4 particles were carbon layer packages after carbonization, and Fe_3O_4/C-SO_3H maintained their spherical structures (with a diameter of approximately 20 nm) after sulfonation, mainly because of the magnetic nanoparticles coating the surface. This effect effectively improves the stability, prevents reagglomeration, reduces the particle size, and improves the catalytic activity (Okamura *et al*. 2006).

Figure 7 shows the XRD spectra of Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C-SO_3H; Fig. 7(a) shows that the samples exhibited the seven characteristic crystal diffraction peaks of Fe_3O_4 (2θ = 30.25°, 33.08°, 35.56°, 43.22°, 53.88°, 57.23°, and 53.88°). Figures 7(b) and 7(c) show that the 2 and 5 diffraction peaks of the spectral line became weaker, indicating that the coated polycyclic aromatic hydrocarbons were amorphous carbon (Wang *et al.* 2010). The 1, 3, 4, 6, and 7 diffraction peaks did not obviously change, showing that Fe_3O_4 was still present after carbonization and sulfonation. Thus, the catalyst maintained the excellent magnetic properties. This result demonstrated that the catalyst can be separated magnetically and recycled many times (Dawodu *et al.* 2014).

Figure 8 shows the FT-IR spectra of Fe_3O_4, Fe_3O_4/C, and Fe_3O_4/C–SO_3H; Fig. 8(a) shows that the sample exhibited absorption at 565 cm^{-1} and 602 cm^{-1} from the Fe-O stretching vibration in Fe_3O_4. In contrast, Fig. 8(b) shows that the absorption shifted to 575 cm^{-1} and 654 cm^{-1} after carbonization, and Fig. 8(c) shows that the absorption shifted to 582 cm^{-1} and 635 cm^{-1} after sulfonation. This data showed that the Fe_3O_4 telescopic characteristic peak was slightly offset and that the structure did not change after carbonization and sulfonation. Figure 8(c) shows that the absorption at 3387 cm^{-1} originated from the O-H stretching vibration. The absorption at 1694 cm^{-1} is a double bond stretching vibration area (C=C). The absorption at 1605 cm^{-1} is from C-H bending vibration; the absorption at 1210 cm^{-1} is the stretching vibration of all single bonds and some heavy atom double bonds from the S=O stretching vibration; the absorption at 1038 $cm^{-}1$ represents an ether bond. Thus, -SO_3H groups were loaded on the Fe_3O_4/C surface and contained a small amount of hydroxyl and carboxyl groups (Zhou *et al.* 2001; Suganuma *et al.* 2010; Shen *et al.* 2013).

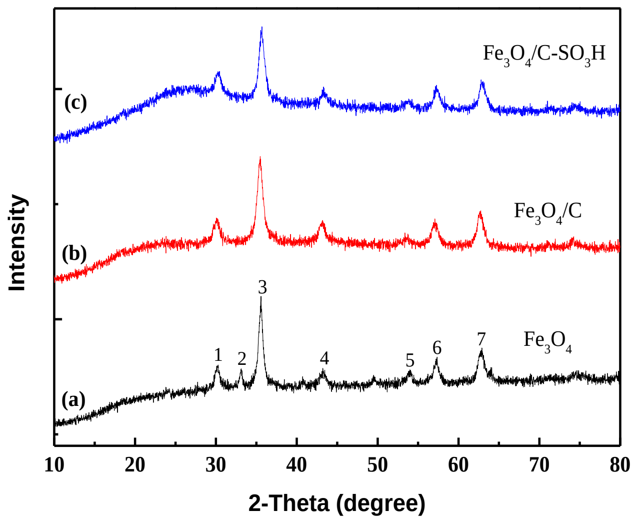

Fig. 7. XRD patterns of magnetic particles (Fe_3O_4), carbonized magnetic carbon (Fe_3O_4/C), and magnetic carbon-based solid acid (Fe_3O_4/C-SO_3H)

Table 1 shows the elemental composition of the magnetic catalyst. The calculated chemical formula of magnetic solid acid was $CH_{0.689}O_{0.443}S_{0.021}Fe_{0.124}$. Using the S element content, one can develop a theory for the amount of sulfonic acid groups for the concentration of 0.92 mmol/g, and the amount of sulfonic acid groups was measured as 0.64 mmol/g by the acid-base titration method. Not all of the S element was present as the -SO_3H group for magnetic solid acid because of the formation of the sulfone structure (R-SO_2-R') during sulfonation (Hara 2010).

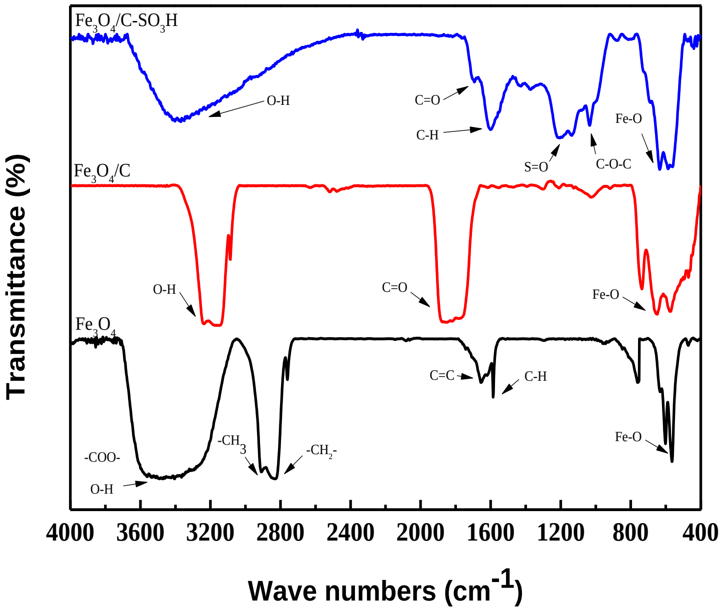

Fig. 8. FT-IR spectra of magnetic particles (Fe_3O_4), carbonized magnetic carbon (Fe_3O_4/C), and magnetic carbon-based solid acid (Fe_3O_4/C-SO_3H)

Table 1. Elementary Composition of the Catalyst (Fe_3O_4/C-SO_3H)

Catalyst	C (wt%)	H (wt%)	S (wt%)	N (wt %)	O (wt %)	Fe (wt %)
Fe_3O_4/C-SO_3H	41.70	2.29	2.75	0.03	29.06	24.16

Stability of Catalyst

The reusability of the Fe_3O_4/C-SO_3H catalyst was also examined. The catalyst was obtained by magnetic adsorption separation at the end of the reaction, washed, and used again after drying at 80 °C overnight. The number of recycling times, the amount of acid, and the relationship between recovery (*R*/ %) for the Fe_3O_4/C-SO_3H catalyst are presented in Table 2.

The recovery was slightly higher with increasing frequency, but the amount of the acid on the catalyst surface decreased gradually. After the first reaction, the catalyst decreased remarkably compared with fresh catalyst, with the total acid content decreased to 0.17 mmol/g. The decrease in catalyst acid was relatively small after several recycling reactions (0.08 mmol/g); nevertheless, the acidic groups on the surface decayed as the reaction progressed (Dora *et al*. 2012). This effect may explain the catalyst deactivation. The recovery was calculated as follows:

$$R(\%) = \frac{quality\ of the\ catalyst\ recovered\ by\ the\ magnet\ after\ each\ reaction}{quality\ of the\ catalyst\ added\ before\ each\ reaction} \times 100 \tag{2}$$

Table 2. Fe_3O_4/C-SO_3H Catalyst Acid Amount and Recovery Cycles

Reaction Time	Total Amount of Acid (mmol/g)	Amount of Sulfonic Acid (mmol/g)	Recovery (*R*/%)
1	1.66	0.64	89.02
2	1.49	0.51	89.43
3	1.41	0.49	89.11
4	1.30	0.47	89.62

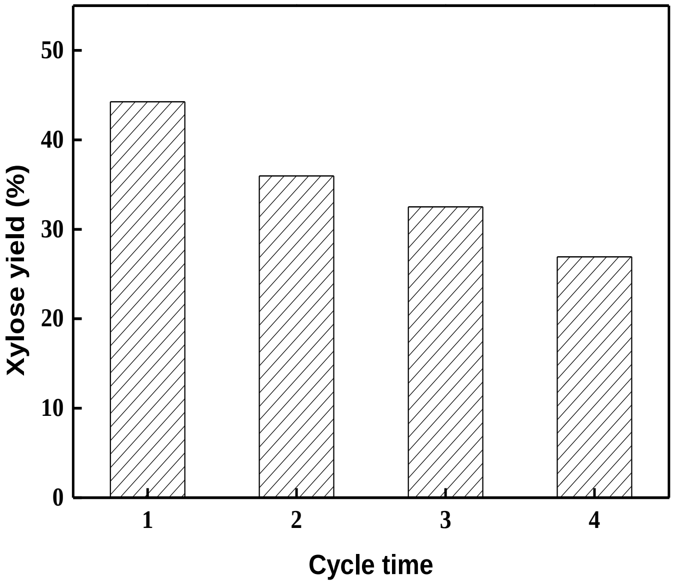

Fig. 9. Different cycle time of the Fe_3O_4/C-SO_3H catalyst

In the first cycle after the reaction, catalytic activity decreased obviously, with the xylose yield of the catalytic hydrolysis of the biomass decreasing from 44.3% to 36.0%; after the fourth cycle, xylose yield fell to 27.0%, showing that the catalyst retained some catalytic activity (Fig. 9). Figure 10 shows that the magnetic catalyst was rapidly separated from the hydrolysate residue and hydrolysis liquid in a magnetic field, thus demonstrating the implementation of magnetic catalyst recycling.

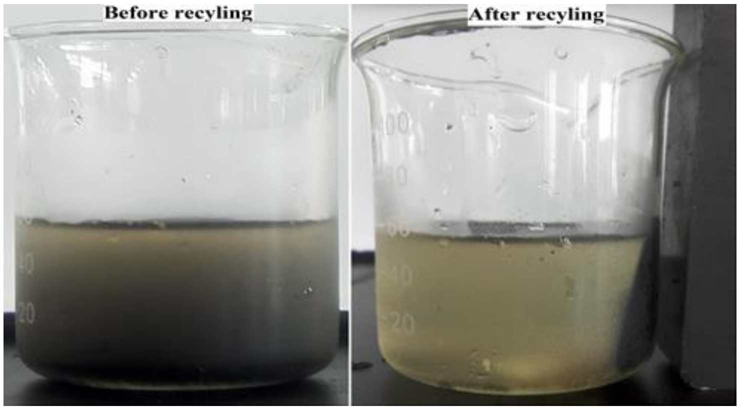

Fig. 10. Catalyst recycling schemes

Figure 11 shows the TG/DTG curves of Fe_3O_4/C-SO_3H MSAC. In the 25 to 200 °C region, quality decreased by 6.02 wt%, mainly because of the water and gas in the catalyst leading to effects such as the release of small molecules. In the 200 to 500 °C region, the quality was reduced by 10.85 wt% because of the weak coupling of the sulfonic acid groups of PAHS in the thermal decomposition with the increasing temperature (Bai *et al*. 2015). In the 500 to 800 °C region, the quality was reduced to 25.39 wt%; in the 500 to 700 °C region, mainly Fe_3O_4 and C elements were obtained. Above 700 °C, the Fe element appeared gradually as the main constituent with Fe_3O_4 and elemental C. The content of elemental Fe increased gradually with increasing temperature (Pereira *et al.* 2010). Overall, this solid acid showed good stability, similar to conventional solid acid.

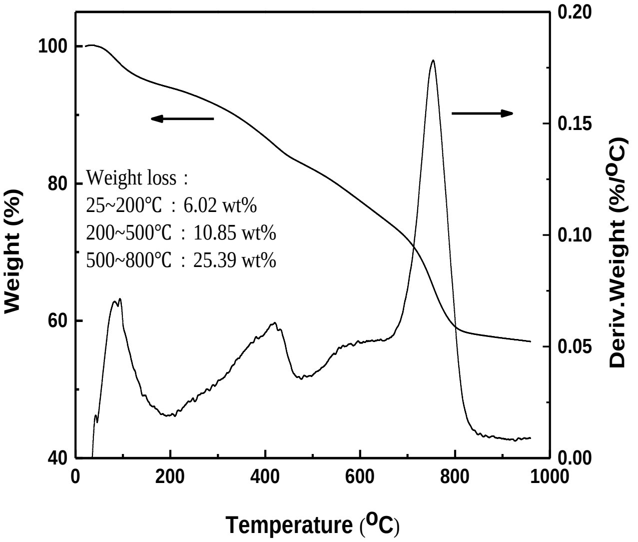

Fig. 11. TG/DTG curves of magnetic carbon-based solid acid (Fe_3O_4/C-SO_3H)

CONCLUSIONS

1. A core-shell structure magnetic $Fe_3O_4/C\text{-}SO_3H$ carbon-based solid acid was prepared through co-precipitation and modification of Fe_3O_4 magnetic particles, hydrothermal synthesis of the carbide magnetic Fe_3O_4/C composite material with glucose as a carbon source, and subsequent grafting of the sulfonic acid group. The addition of surfactant changed the Fe_3O_4 particle size by introducing oleate chains on the Fe_3O_4 particles, improving the stability of magnetic catalyst.
2. The effects of the carbonization and sulfonation on catalyst activity were investigated. The best conditions for MSAC preparation were 3 h carbonization time, 450 °C as the carbonization temperature, 9 h sulfonation time, and 90 °C as the sulfonation temperature.
3. The optimized conditions for MSAC characterization were as follows: saturation magnetization intensity values of 7.78 Am^2/kg, specific surface area of 4.26 m^2/g, particle diameter of approximately 20 nm, and 1.66 mmol/g of total acid. The chemical formula was $CH_{0.689}O_{0.443}S_{0.021}Fe_{0.124}$.
4. The MSAC was stably dispersed and 44.3% of xylose yield was obtained under 160 °C for 16 h in the reaction system, quickly separated from the reaction system using an external field, and reused many times. These results are of great significance for the commercial catalytic hydrolysis of lignocellulose.

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