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# Magnetically separable porous carbon nanospheres using as solid acid catalysts

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A novel solid acid material, magnetically separable and SO<sub>3</sub>H-functionalized porous carbon nanosphere, was facilely synthesized by a simple activation route. The SiO<sub>2</sub> layer protected the magnetic core from dissolving during the process of activation with ZnCl<sub>2</sub>, and retained the highly magnetic property. The obtained materials were characterized by N<sub>2</sub> adsorption–desorption technology and transmission electron microscope, and the results indicated that this solid acid material possessed an excellent spherical morphology and a superior porosity with high surface area and large pore volume. The results of X-ray diffraction, fourier transform infrared spectra and energy dispersive X-ray spectra demonstrated the preservation of magnetic core and the successful modification of -SO<sub>3</sub>H functional groups. The solid acid activated at a low temperature (400 °C) showed the highest acidity of 1.98 mmol H<sup>+</sup>g<sup>-1</sup>, which was estimated by an indirect titration method. The high surface area, large pore volume and high acidity endued this solid acid material excellent catalytic performance for esterification and transesterification reaction. Besides, the solid acid catalyst possessed remarkable stability and recycling property.

#### 1. Introduction

Acid catalysts are essential for various chemical reactions in industry, including the fields of oil refining, petrochemicals and other hydrocarbon chemicals. Traditional homogeneous acid catalysts such as sulfuric acid, perchloric acid and other liquid acids are used extensively in industry for the production of industrially important chemicals. Although these liquid acid catalysts are inexpensive and highly efficient, it is difficult to separate them from the reaction mixture, resulting in abundant acid waste<sup>1–3</sup>.

Solid acid catalysts have shown great potential to replace liquid acid as reusable and environmentally-safe acid catalysts. Among them, carbon-base solid acids are considered as ideal catalysts for many chemical reactions owing to their chemical inertness and superior thermal stability. Particularly, sulfonated carbon materials are the most promising of solid acid developed for the production of biodiesel<sup>4</sup>. However, these sulfonated amorphous carbon-base solid acids are usually prepared by the sulfonation of incompletely carbonized biomass, such as glucose, sucrose, starch and biochar<sup>5–7</sup>. Consequently, these solid acids in general possess low surface area (< 2 m<sup>2</sup>g<sup>-1</sup>), poor porosity, relatively low acid density ranging from 0.37 to 1.34 mmol H<sup>+</sup>g<sup>-1</sup> and poor dispersion in liquid phase reaction mixture<sup>8</sup>.

To overcome these disadvantages and further improve catalytic performance,  $SO_3H$ -functionalized porous carbons (PCs) are used as fine powders in catalytic reactions.  $SO_3H$ -modified PCs with excellent catalytic performance have been successfully synthesized by different routes<sup>9-16</sup>. However, the hard-template prepared sulfonated PCs often suffer a high-temperature carbonization, and thus the surface of these materials possess limited oxygen-containing and hydrogen-containing functional groups, which seriously restricts the modification of  $-SO_3H$  groups, subsequently resulting in the low acidity and low activity<sup>11,14,16</sup>. Recently, we reported an approach to obtain PC solid acid with high acidity and impressive catalytic activity *via* the pretreatment of hard-template prepared mesoporous carbon with  $H_2O_2^{-10}$ . Another route to enhance the acidity of PC solid acids is to reduce the carbonation temperature and therefore retain an incompletely carbonized framework. Such strategy has been realized by a soft-template route, where the porous resin frameworks are self-organized with the assistance of triblock copolymers, such as Pluronic P123 and F127, and can keep the porous structure under a low temperature carbonization<sup>9,17</sup>. Despite these sulfonated PCs exhibit high catalytic performance, the separation of the fine powders from the catalytic systems is a great challenge.

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Design and synthesis of magnetically functionalized composites offer an alternative route for the separation of fine powders by an outer magnetic field. Magnetic nanoparticles with a wide range of compositions could be readily introduced into PC matrices. The conventional preparation of magnetic PCs is usually through either a direct synthesis approach or a post loading method<sup>18-2</sup> Normally, the magnetic nanoparticles can be well dispersed in case of a low content, resulting in a poor crystallinity and magnetic property. However, it also has some problems by improving the loading level to obtain highly magnetic property, such as the collapse of porous structure in the direct synthesis approach and the pore blocking in the post loading method. Therefore, it is extremely challenging to obtain strongly magnetic PC composite without pore blocking. Constructing a core-shell structure by covering carbon shell out onto the surface of magnetic core provides an opportunity to endow PC composites with strong magnetism and good monodispersity, as well as inter-connected pore structure. Consequently, these materials have attracted increasing attention in many applications, such as adsorption, separation, energy storage and conversion<sup>22,2</sup> Great progress in fabrication of magnetic core-shell PCs has been made by developing several synthesis strategies<sup>24-26</sup>. But, the tedious synthetic steps and low yields limit their wide applications. Moreover, little attention has been paid to simultaneously exploring and utilizing the high porosities of carbon matrices and the magnetic core-shell structure as active solid acid for industrial catalysis.

Herein, we reported a successful synthesis of magnetically separable and  $SO_3H$ -functionalized nanospherical PC solid acid catalyst,  $Fe_3O_4@SiO_2@PCS$ , which obtained *via* a facilely chemical activation of  $Fe_3O_4@SiO_2@C$  with  $ZnCl_2$ . The  $SiO_2$  layer between the magnetic core and carbon shell plays a key role for keeping the magnetic core from decaying by the strong acidity of  $ZnCl_2$  during the process of activation. The magnetic core-shell PC solid acid catalyst did not only possess high surface area and narrow pore size distribution, but also exhibited high acidity and excellently catalytic performance as well as a superb recycle. Such excellently magnetic separation ability and high acidity make this material as an efficient solid acid catalyst for the practical application of biodiesel production.

#### 2. Experimental

#### 2.1 Preparation of materials

**Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.** The dispersible Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized according to the method reported previously<sup>27</sup>. In a typical experiment, FeCl<sub>3</sub>·6H<sub>2</sub>O (3.25 g), trisodium citrate (1.3 g) and sodium acetate (NaAc, 6.0 g) were dissolved in ethylene glycol (100 mL) with magnetic stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave and the autoclave was heated at 200 °C for 10 h. The black products were washed repeatedly with deionized water and ethanol and oven-dried at 60 °C for more than 6 h.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres.** The core–shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres were prepared according to the previously reported method<sup>28</sup>. Briefly, 0.10 g of Fe<sub>3</sub>O<sub>4</sub> particles were treated with 0.1 M HCl aqueous solution (50 mL) by ultrasonication. After the treatment for 10 min, the magnetite particles were separated and washed with deioned water, and then homogeneously dispersed in the mixture of ethanol (80 mL), deioned water (20 mL) and concentrated ammonia aqueous solution (1.0 mL), followed by the addition of tetraethylorthosilicate (TEOS, 0.03 g). After stirring at room temperature for 6 h, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres were separated and washed with ethanol and water, and then dried at 60 °C for 6 h.

Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC microspheres. In a typical experiment, 4 g of glucose was dissolved in 40 mL of water to form a clear solution, and then 0.2 g Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres were dispersed in glucose solution. After vigorous stirring for 30 min, the suspension was transferred to a Teflon–sealed autoclave and maintained at 180 °C for 10 h. The products were separated and washed with deionized water and ethanol, and then dried at 60 °C for 6 h. The resulting materials were denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C. The dried Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C materials were impregnated in ZnCl<sub>2</sub> solution for 6 h, and dried at 110 °C for 12 h and then was activated in N<sub>2</sub> at different temperatures (400, 500 and 600 °C) for 1 h. After cooling down, the activated samples were thoroughly washed with distilled water and HCl solution (0.5 M). Finally, the materials were dried under vacuum at 80 °C for 10 h, which were denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C metarials were dried under vacuum at 80 °C for 10 h, which were denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC-*x*-*y* (*x* = 4, referring to the mass ratio of ZnCl<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C of 4:1; *y* = 4, 5 and 6, meaning the activation temperature is 400, 500 and 600 °C, respectively).

Subsequently, these Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC materials were sulfonated using concentrated sulfuric acid at 150 °C for 10 h in a Teflon–sealed autoclave. Then, these products were washed repeatedly with hot distilled water (> 80 °C) until the sulfate ions were no longer detected in the wash water (BaCl<sub>2</sub> precipitation test) and were dried at 80 °C for 10 h. The resulting materials were denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS.

#### 2.2 Characterizations

Nitrogen adsorption–desorption isotherms were carried out at -196 °C using a micromeritics ASAP 2020 analyzer. Before adsorption, the samples were out-gassed at 150 °C for 10 h. The specific surface area (S<sub>*BET*</sub>) was evaluated using the Brunauer–Emmett–Teller (BET) method, and the mesopore volume and micropore volume were calculated according to the Barrett–Joyner–Halenda (BJH) formula and *t*-plot method, respectively. The pore size distributions were calculated according to the Density–Functional–Theory (DFT) method. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Avatar 370 spectrometer using the stanndard KBr disk method. The morphology and core-shell structure were observed from a JEOL JEM–2100 transmission electron microscope (TEM) with an accelerating voltage of 200 KV. The energy dispersive X-ray (EDX) spectra were obtained using a Hitachi S–4800 field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer.

The number of acid sites was estimated by using an indirect titration method<sup>29,30</sup>, which involves an aqueous ion-exchange step of the catalyst H<sup>+</sup> ions with base of NaHCO<sub>3</sub>, followed by titration of the resulting solution with HCl aqueous solution (0.1 M). In a typical experiment, 30 mg of the catalyst was dispersed in 50 mL of  $5 \times 10^{-3}$  mol L<sup>-1</sup> NaHCO<sub>3</sub> solution, which was stirred for 24 h and separated by filteration. Then 5 mL of filtrate was taken out for titration with 0.1 M of HCl aqueous solution. Titration was performed three times and the average number was reported. The amount of acid groups in the solid acid catalysts was estimated by the NaHCO<sub>3</sub> consumed.

#### 2.3 Catalytic testing

Catalytic reactions were performed in a round bottomed flask equipped with a reflux condenser, magnetic stirrer and an oil bath maintained at a specified temperature. In the esterification of aliphatic acid (oleic acid, palmitic acid and stearic acid) and acetic acid with methanol or ethanol, aliphatic acid (0.01 mol), acetic acid (0.05 mol), and catalyst (0.1 g) were mixed in flask and the reaction was carried out at 70 °C for 5 h. For the transesterification of soybean oil with methanol, soybean oil (0.01 mol), and catalyst (0.3 g) were used at 150 °C for 6 h. The products in catalytic reactions were analyzed by gas chromatograghy (GC-2014C, shimadzu) with a flame ionization detector (FID), and methyl undecanoate was used as an internal standard.

#### 3. Results and discussion

#### 3.1 Characteristics of materials

Scheme 1 outlines the synthetic procedure of  $Fe_3O_4@SiO_2@PCS$  material, which begins with the synthesis of  $Fe_3O_4$  nanoparticles. First, uniform  $Fe_3O_4$  nanoparticles are coated with a thin layer of amorphous SiO<sub>2</sub> via a sol-gel approach to obtain nonporous  $Fe_3O_4@SiO_2$ . Second, glucose monomers polymerize on the surface of  $Fe_3O_4@SiO_2$  material under hydrothermal conditions at 180 °C, which is higher than the normal glycosidation temperature and results in aromatization and carbonization. Third, ZnCl<sub>2</sub> is used as a dehydrating agent to chemically activate the carbon layer to obtain the porous structure,  $Fe_3O_4@SiO_2@PC$ . Finally,  $Fe_3O_4@SiO_2@PC$  materials are sulfonated using concentrated sulfuric acid in Teflon autoclaves at a high temperature to form  $Fe_3O_4@SiO_2@PCS$  material.

To reveal the morphology and structure of materials, TEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C, and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS are shown in Fig. 1. As displayed in Fig. 1a, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> particles exhibit good dispersity and uniform spherical morphology. Particularly, the nonporous SiO<sub>2</sub> layer with a thickness of 40~60 nm forms a complete enveloping of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and it therefore plays a key role for keeping interior magnetic cores from decaying in the process of activation with ZnCl<sub>2</sub>. Additionally, this SiO<sub>2</sub> layer is indeed favorable to nucleation and growth of carbon outer layer<sup>31</sup>. Fig. 1b and 1c show the TEM images of

 $Fe_3O_4@SiO_2@C$  nanospheres. On the whole, carbon shell layer reveals spherical shapes with thickness of about 50~120 nm. After the activation of carbon shell with  $ZnCl_2$  and the following modification of sulfonation with concentrated sulfuric acid, the nanospherical morphology is retained and its initial core-shell structure can be directly observed in Fig. 1d, which indicates that the processes of activation and sulfonation do not destroy the structure and morphology of  $Fe_3O_4@SiO_2@C$  material.

To confirm the crystal structure of as-synthesized materials, XRD patterns of all samples were characterized (Fig. 2). The characteristic diffraction peaks of  $Fe_3O_4$  are present in all samples, which can be assigned to the (220), (311), (400), (511) and (440) planes of a pure cubic  $Fe_3O_4$ phase<sup>32</sup>.In comparison with pure Fe<sub>3</sub>O<sub>4</sub> sample, an additional broad diffraction peak at  $2\theta$  =  $20 \sim 30^{\circ}$  appears in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sample. This weak diffraction of amorphous silica verifies the successful coating of  $SiO_2$  layer onto the magnetic core. After the hydrothermal treatment of  $Fe_3O_4(a)SiO_2$  sample with glucose, an amorphous carbon shell is formed, which can be proved by the enhanced intensity of broad diffraction and the shift of center to low angle. No evident difference of the diffraction of magnetic core is found between  $Fe_3O_4$  and  $Fe_3O_4@SiO_2@C$ . suggesting the modification of SiO<sub>2</sub> layer and the carbon shell do not influence the crystal structure and grain size of  $Fe_3O_4$  phase. However, after the activation and further carbonization, the diffraction of Fe<sub>3</sub>O<sub>4</sub> become much sharper in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS, which imply that the process of activation improve the crystallization of  $Fe_3O_4$ . The grain size of  $Fe_3O_4$  in  $Fe_3O_4$  @SiO<sub>2</sub>@PC is estimated to be 20.6 nm, which is larger than 7.9 nm for the  $Fe_3O_4$ sample. Fig. 3 reveals the influence of  $SiO_2$  layer on the protection of magnetic  $Fe_3O_4$  core in the ZnCl<sub>2</sub> activation process. According to the activation mechanism, HCl would be released from the reaction of ZnCl<sub>2</sub> and the incompletely carbonized framework. This acidic gas could react with  $Fe_3O_4$  as lacking a compact and inert layer between  $Fe_3O_4$  core and carbon shell, which is verified by the XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@PC where the Fe<sub>3</sub>O<sub>4</sub> diffractions disappear. On the contrary, as coating a SiO<sub>2</sub> layer between  $Fe_3O_4$  core and carbon shell,  $Fe_3O_4$  cores can be well protected during the ZnCl<sub>2</sub> activation. Fig. 4 shows a direct comparison of the magnetism of Fe<sub>3</sub>O<sub>4</sub>@PC and  $Fe_3O_4@SiO_2@PC$ . Without an outer magnet, these two materials can be well dispersed in methanol to form a dark and stable suspension. As put a magnet close to these suspensions, the  $Fe_3O_4@SiO_2@PC$  sample is immediately attracted by the magnet. However, the  $Fe_3O_4@PC$ sample does not exhibit any magnetism because of the dissolution of  $Fe_3O_4$  by  $ZnCl_2$ .

FTIR spectra were used to further identify the successful coating of silica and carbon layers onto magnetic particles, and the presence of functional groups after sulfonation (Fig. 5). All of samples present the characteristic band of Fe-O appeared at 475 and 575 cm<sup>-133</sup>. Compared with  $Fe_3O_4$  sample, two additional adsorption bands at 950 and 1088 cm<sup>-1</sup> are found in  $Fe_3O_4$ @SiO<sub>2</sub> sample, which are ascribed to the characteristic stretching vibration of Si-O<sup>34</sup>, verifying the formation of the SiO<sub>2</sub> shell. In Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C material, the bands at 1710 and 1620 cm<sup>-1</sup> should be attributed to C=O and C=C stretching vibrations, respectively, and the results support the concept of aromatization of glucose during hydrothermal treatment<sup>35</sup>. The bands centered at 1000 ~ 1300 cm<sup>-1</sup> are related to the C-O stretching vibration and -OH bending vibration<sup>36</sup>. These absorptions overlap with the Si-O absorption at 950 and 1088 cm<sup>-1</sup>, and thus the latter become illegible. All these evidences identify that  $Fe_3O_4$  ( $aSiO_2$  are successfully coated by a carbon shell. After activation, the absorption peaks of C-O become illegible and even the characteristic absorption band of C=O at  $1710 \text{ cm}^{-1}$  disappear, which should be due to the chemical activation with ZnCl<sub>2</sub> by the release of H<sub>2</sub>O molecule<sup>37</sup>. After sulfonation treatment, the new absorption bands at 1108 and 1190 cm<sup>-1</sup> in the spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS are assigned to the symmetric stretching vibrations of S=O<sup>38</sup>, and another additional absorption band at 620 cm<sup>-1</sup> is attributed to the bending vibration of -OH groups hydrogen bonded to  $-SO_3H$  groups  $^{39,40}$ . The EDX analysis also shows a similar result (Fig. 6). Si and O elements are observed in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> sample, demonstrating the successful coating of SiO<sub>2</sub> layer. The finding of C element in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C sample also indicates that the  $Fe_3O_4@SiO_2$  nanospheres are successfully covered by a carbon shell. Furthermore, the signal of Fe in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC sample suggests the protection of magnetic core by  $SiO_2$  layer in the process of activation. In the meantime, the intensity of O signal becoming weak in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC is corresponding to the FTIR results. Finally, the S signal in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS sample gives the evidence of -SO<sub>3</sub>H groups modified on the carbon shell surface.

 $N_2$  sorption technology is used to investigate the porous properties of materials, as well as the effect of activation temperature and sulfonation on the pore structure (Fig. 7). With the enhancement of activation temperature, the  $N_2$  adsorption-desorption isotherms transform gradually to typical type IV curves with a clear hysteresis loop at relative pressure from 0.4 to 0.7, which suggest the pore of  $Fe_3O_4$  ( $\Omega SiO_2$ ) ( $\Omega PC$  evolve from micropore to mesopore. The specific surface area and pore volume also undergo a great change (Table 1). When the activation temperature is 400 °C, the pyrolysis reaction just commences, thereby producing some micropores and low micropore volume. This result should be ascribed to the inadequacy of heat energy produced at the low activation temperature for some substantial evolution of volatiles necessary for pore development. As the temperature is increased to 500 °C, the pyrolysis reaction is completely carried out, and the developed pore is mainly mesoporous. Mesopore size, mesopore surface area and total pore volume increase, however the BET surface area decreases because of the disappearance of micropores. With further enhancing the activation temperature to  $600 \, {}^{\circ}\text{C}$ . there are no evident changes in pore size, indicating that the pyrolysis reaction has finished at 500 °C. The decrease of mesopore surface area and mesopore volume should be due to a sintering effect at high temperature, where the shrinkage of framework and the realignment of carbon structure result in the reducing of pore areas as well as volume<sup>41</sup>. After sulfonation, the surface area, pore volume and pore size of these samples all decrease, and the result should be related to the presence of a large number of -SO<sub>3</sub>H groups. The decrement in surface area of  $Fe_3O_4@SiO_2@PCS-4-4$  is much more than those of  $Fe_3O_4@SiO_2@PCS-4-5$  and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-6, and the similar results can be detected in pore volume and pore size (Table 1), which suggest the much higher density of -SO<sub>3</sub>H groups modified on the surface of  $Fe_3O_4@SiO_2@PCS-4-4$ . The acidities of these materials listed in Table 1 are 1.98 mmolH<sup>+</sup>g<sup>-1</sup> for  $Fe_3O_4@SiO_2@PCS-4-4$ , 1.32 mmolH<sup>+</sup>g<sup>-1</sup> for  $Fe_3O_4@SiO_2@PCS-4-5$  and 1.14 mmolH<sup>+</sup>g<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-6, respectively. This phenomenon can be attributed to the different activation temperature. At low activation temperature, the pyrolysis reaction is incomplete and the surface of  $Fe_3O_4(a)SiO_2(a)PC-4-4$  still possesses numerous oxygen-containing and hydrogen-containing functional groups, which are favorable for the immobilization of -SO<sub>3</sub>H groups on carbon surface via forming covalent bonds or hydrogen bonds<sup>10</sup>.

#### 3.2 Catalytic performances for biodiesel preparation

In past decades, heterogeneous catalysts that functioned as efficient and stable catalysts for biodiesel production have attracted much attention. Among them, solid acid catalysts are promising candidates for preparation of biodiesel, because solid acids could simultaneously catalyze esterification and transesterification reactions.

In this paper, as-prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS catalysts were successfully tested in the esterfication of aliphatic acid (oleic acid, palmitic acid, stearic acid and acetic acid) with methanol or ethanol at 70 °C for 5 h. For comparison, the conventional homogeneous acid catalyst, sulfuric acid, was also examined under the identical conditions. From the results shown in Table 2, the yield of esters using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-6 catalyst are relatively low, only ca. 60 %, 70 %, 70 % and 55 % for methyl oleate, methyl stearate, methyl palmitate and ethyl acetate respectively, which should be ascribed to its low acidity. With the decrease of activation temperature, the acidity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS is obviously enhanced. Consequently, their catalytic performances for esterfication reaction are also improved. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 catalyst gives rise to a highest catalytic activity and the yields of esters of methyl oleatemethyl stearate, methyl palmitate and ethyl acetate reach ca. 81 %, 86 %, 82 % and 76 % within 5 h, respectively. In addition, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 catalyst also exhibits much higher catalytic performance for the esterfication reaction than those of other conventional solid Brønsted acid catalysts, such as niobic  $(Nb_2O_5 \cdot nH_2O)^{42}$ , Amberlyst-15 (sulfonated polystyrene)^{43} and Nafion acid NR 50 (perfluorosulfonated ionomer)<sup>44</sup>, and achieves about 80~85% catalytic efficient of surfuric acid under the same reaction condition. This result is attributed to its higher acidity than those of other solid acid catalysts. Although the reference acid catalyst, sulfuric acid, is catalytically effective to these esterification reactions, but it is difficult to separating from the reaction solution and unable to compete with many process advantages offered by the solid acid catalysts.

The reusability of catalyst is extremely vital to estimate the efficiency of solid acid catalysts, which contributes to reduce the cost of practical applications process. In case of carbon–base solid acid catalysts, the deactivation of catalytic activity is worth of notice<sup>45,46</sup>. In order to evaluate the reusability of catalyst, after each catalytic reaction the solid acid catalyst was magnetically

separated and washed repeatedly with ethanol and distilled water. The washed catalyst was dried at 80 °C and used for the next experiment. From the results shown in Fig. 8, no evident decrease in catalytic activity is observed even after five consecutive cycles, which indicates that  $Fe_3O_4@SiO_2@PCS-4-4$  possesses a good stability and reusability. Furthermore, for checking the stability of  $-SO_3H$  groups, the resulting mixture after catalytic reaction was washed with water to extract sulfate ions possibly leached from catalyst. The BaCl<sub>2</sub> precipitation test demonstrates no sulfate ions exist in the washed water, suggesting the stability of  $-SO_3H$  groups on the surface of catalyst.

The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS catalysts also show a good catalytic performance for the transesterification of soybean oil, as summarized on Table 3. Because of its the highest acidity, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 still shows a highest catalytic activity for the transesterification of soybean oil, and a *ca*. 80 % yield of esters at 150 °C for 6 h is obtained, which is much higher than *ca*. 60 % and 40 % yield of esters gained over Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-5 and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-6, respectively. Besides, its catalytic performance is also better than those of the conventional solid acids, such as silica-supported Nafion<sup>47</sup>, Amberlyst-15<sup>48</sup>, and so on<sup>49</sup>, and is about 85 % that of sulfuric acid under the same reaction condition. Fig. 9 depicts the results of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 catalyst reuse experiment for the transesterification. Even though after five consecutive runs, it still keep the original catalytic activity and the esters yield still reaches *ca*. 80 %. Consequently, these results suggest that the material presents great potential to be a stable and highly active solid acid catalyst for preparation of biodiesel.

#### 4. Conclusion

In summary, a magnetically separable of  $SO_3H$ -functionalized PC nanospheres solid acid material has been successfully prepared by the simple activation and sulfonation treatment. Under the protection of  $SiO_2$  layer, the  $Fe_3O_4@SiO_2@PCS$  still keep the structure of magnetic core after  $ZnCl_2$  activation, and this accelerates its magnetic separation in liquid reaction system. Meanwhile, the solid acid catalyst exhibits a high surface area, large pore volume and stable and high catalytic performance for esterification and transesterification reactions. Importantly, deactivation of the solid acid catalyst in the reaction system is inhibited and the solid acid can retain its initial activity after least five consecutive catalytic cycles. Consequently, this material has great potential in industry applications used as the solid acid catalyst due to its stability in catalytic activity and magnetic separation property.

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#### Notes

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Sample	$\mathbf{S}_{BET}^{a}$	$\mathbf{S}_{micro}{}^{b}$	$V_{meso}^{c}$	$V_{micro}{}^d$	$D^{e}$	Acidity <sup>f</sup>
	$(m^2g^{-1})$	$(m^2g^{-1})$	$(cm^{3}g^{-1})$	$(cm^{3}g^{-1})$	(nm)	$(\text{mmol H}^+\text{g}^{-1})$
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PC-4-4	3297.4	1082.2	1.16	0.45	1.62/2.18	
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PC-4-5	2918.4		1.66		2.73	
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PC-4-6	2426.4		1.57		2.73	—
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-4	1118.3	788.5	0.37	0.26	1.57/1.86	1.98
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-5	2310.1		1.29		2.70	1.32
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-6	2015.6	_	1.31	—	2.70	1.14

Table 1 Textural parameters of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS materials

<sup>a</sup> specific surface area estimated using BET method

 $^{b}$  micropore surface area calculated using the V-*t* plot method

<sup>c</sup> mesopore volume

<sup>d</sup> micropore volume

<sup>e</sup> pore size calculated using DFT method

<sup>f</sup> measured by acid-base titration

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Catalyst	Yield of ester (%)					
	Methyl oleate	Methyl stearate	Methyl palmitate	Acetic ester		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-4	81	86	82	76		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-5	65	74	76	60		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-6	60	70	70	55		

 Table 2. Comparisons of esterification of aliphatic acid with methanol or ethanol over different acid catalysts

Reaction conditions: catalyst 0.1 g; aliphatic acid 0.01 mol; acetic acid 0.05 mol; methanol 0.2 mol; ethanol 0.5 mol; reaction temperature 70 °C; reaction time 5 h;  $H_2SO_4$  3*wt*% of acid

98

95

 $\mathrm{H}_2\mathrm{SO}_4$ 

96

Catalast	Yield of esters (%)			
Cataryst	2 h	6 h		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-4	52	78		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-5	38	62		
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PCS-4-6	21	43		
$H_2SO_4$	65	89		

Table 3. Comporisons of transesterification of soybean oil by different acid catalysts

Reaction conditions: catalyst 0.3 g; soybean oil 0.01 mol; methanol 0.2 mol; reaction temperature 150 °C;  $H_2SO_4$ 3wt% of soybean oil



#### Scheme 1 Schematic illustrations of preparing Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS material

#### **Figure Captions**

- Fig. 1 TEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>(a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C (b, c) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS (d), and the insert is the single nanosphere of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS.
- Fig. 2 The XRD patterns of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS samples
- Fig. 3 The XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@PC and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC samples
- Fig. 4 The photographs of dispersed Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC (a) and Fe<sub>3</sub>O<sub>4</sub>@PC (b) in methanol and after being attracted by an outer magnet
- Fig. 5 FTIR spectra of all samples
- **Fig. 6** EDX spectra of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@C, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS nanospheres
- **Fig.** 7 N<sub>2</sub> adsorption–desorption isotherms (a) and pore size distributions (b) of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC-*x*-*y* before and after sulfonation
- Fig. 8 Recyclability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 catalyst for esterification of aliphatic acid (catalyst 0.1 g; aliphatic acid 0.01 mol; methanol 0.2 mol; 70 °C; 5 h)
- Fig. 9 Recyclability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PCS-4-4 catalyst for transesterification of soybean oil (catalyst 0.3 g; soybean oil 0.01 mol; methanol 0.2 mol; 150 °C; 6 h)

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