Preparation and Characterization of Sulfonated Magnetic SiO₂ Microspheres as the Solid Acid Catalysts for Esterification

Ping Ke, Danlin Zeng, Jie Wu, Jiawei Cui, Xin Li, and Guanghui Wang

The State Key Laboratory of Refractories and Metallurgy, Hubei Key Laboratory of Coal Conversion and New Carbon Material, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

ABSTRACT: The sulfonated magnetic SiO₂ microsphere solid acid catalysts were prepared by the impregnation and grafting methods with iron oxide magnetic nanoparticles (Fe₃O₄ MNPs) as the magnetic cores. The catalytic properties of the magnetic SiO₂ solid acid catalyst were studied in detail. The characterization results showed that the SiO₂ was successfully coated on the Fe₃O₄ MNPs. Compared with the grafting method, impregnated solid acid exhibits higher catalytic performance, which reached an esterification rate of up to 99.00% when the reaction temperature was 105 °C, the molar ratio of n-butanol/adipic acid was 3:1, and the ratio of the catalyst (the mass of magnetic solid acid) to liquids (the total volume of n-butanol and adipic acid) was 2.95%. The magnetic solid acid exhibited great separation ability and reusability. After six times of recycle, the conversion of the grafted magnetic solid acid still attained 85.61% compared with that of the impregnated magnetic solid acid, which reduced to 81.35%, holding great potential for green chemical processes.

INTRODUCTION

The liquid acid catalyst is by far the greatly important area of catalysis in all sectors of chemical manufacturing due to its mild reaction conditions and simple processes. However, with the advancement of science and technology, people’s awareness of environmental protection has gradually improved, finding that the high toxicity and corrosive properties from liquid acid lead to a huge waste of energy and production of large amounts of waste products, which make it no longer adapt to the development of green chemistry. Recently, solid acid that is nontoxic, noncorrosive, high activity, and stable has attracted great interest among researchers, which make it possible to replace the liquid acids. Consequently, lots of experiments have been introduced for generating a variety of solid acid catalysts such as based on Ps-AlCl₃, SO₄²⁻/SnO₂, Sn-MFI, and clay, which have been widely used in many fields such as chemical synthesis, biomass conversion, adsorption, catalysis, and so forth. Moreno et al. synthesized the SO₄²⁻/SnO₂ solid acid catalyst for catalyzing the production of biodiesel from oleic acid and methanol. The characterization results showed that the SO₄²⁻/SnO₂ catalyst had a high specific surface area (87 m²/g), which enhanced its catalytic activity. However, the conventional supported solid acid catalysts were usually recovered by centrifugation or physical sedimentation, resulting in a low yield and failing to meet the needs of industrial continuous production. Compared with these catalysts, magnetic solid acids can be easily separated in the presence of an external magnetic field, particularly in viscous reaction solution. Recently, a series of magnetic solid acids were synthesized by the sulfonation method with various shell materials. However, many of the reported magnetic solid acids are unsatisfactory in acid-catalyzed reactions.

One way to overcome this problem of the magnetic solid catalyst is to use relatively stable SiO₂ nanoparticle as the carrier, which can protect the iron oxide magnetic core in the presence of the acidic solution. In this type of magnetic SiO₂ solid acid, the reactive centers are highly mobile, similar to the nonmagnetic catalyst, and at the same time, it has the advantage of recyclability. Generally, impregnation and grafting methods are often used for the solid acid preparation. For the former, the solid acid has a good catalytic effect, high utilization rate, and low cost, while for the latter, the acid radical is connected to the surface of the silicon-based material in the form of a covalent bond, which makes the acidic group more stable. Both impregnation and grafting are effective methods for improving the catalytic activity in which solid acid’s high recyclability can be represented. In this paper, iron oxide magnetic nanoparticles (Fe₃O₄ MNPs) were prepared by the hydrothermal method, and then the magnetic SiO₂ was prepared by using the former Fe₃O₄ as the magnetic core. The magnetic SiO₂ was used as the carrier to prepare the sulfonated magnetic SiO₂ solid acid by impregnation and grafting methods. The catalytic activity of the magnetic SiO₂ solid acid was investigated by the esterification of acetic acid and ethanol. The catalytic effect
and cyclic stability of the impregnation and grafting modification methods were also compared, aiming to achieve the high activity and recyclability of magnetic solid acids by comparing to the previously reported nonmagnetic solid catalysts.

**RESULTS AND DISCUSSION**

**Morphological Analysis.** The SEM and TEM images of Fe$_3$O$_4$ MNPs and magnetic SiO$_2$ samples are shown in Figure 1. Spherical Fe$_3$O$_4$ with uniform particle size and uniform

![Figure 1](image_url)  
**Figure 1.** SEM and TEM images of (a,c) Fe$_3$O$_4$ and (b,d) magnetic SiO$_2$.

distribution can be seen in Figure 1. It could be inferred that the Fe$_3$O$_4$ microspheres were composed of finer microspheres from the fine particles on the spherical surface. Compared with Fe$_3$O$_4$ microspheres, the magnetic SiO$_2$ particles exhibited a smooth surface, and the outer surface was coated with the SiO$_2$ microspheres.

Continuously reunited and growing Fe$_3$O$_4$ grains can be seen in Figure 1c, which formed the big nanoparticles on the Fe$_3$O$_4$ surface. At the same time, it can be clearly seen from Figure 1d that the SiO$_2$ particles were coated on the Fe$_3$O$_4$ particles. Additionally, the SiO$_2$ particles were uniformly distributed, which made the surface of the magnetic SiO$_2$ particles relatively smooth.

**X-ray Diffraction.** The XRD patterns of all as-prepared samples are shown in Figure 2. As shown in Figure 2, the characteristic peaks of Fe$_3$O$_4$ at 2$\theta$ = 18.5, 30.1, 35.5, 37.2, 43.2, 53.7, 57.1, 62.7, and 74.1$^\circ$ can be indexed as the diffractions of (111), (220), (311), (222), (400), (422), (511), (440), and (533), respectively, which are almost consistent with the diffraction peaks of the PDF standard powder diffraction card Fe$_3$O$_4$ (JCPDS 79-0419), indicating that the phase structure of Fe$_3$O$_4$ was the inverse spinel structure. Moreover, no obvious impurity peaks in the XRD pattern confirmed that the Fe$_3$O$_4$ showed a higher purity. It was interesting that the average size of Fe$_3$O$_4$ was calculated to be 17.9 nm, which inferred that Fe$_3$O$_4$ microspheres were composed of nanosized particles.

Comparative analysis found that magnetic SiO$_2$ and sulfonated magnetic SiO$_2$ solid acid showed a broad diffraction peak at 2$\theta$ = 23$^\circ$ besides the characteristic diffraction peak of Fe$_3$O$_4$, which belongs to the characteristic peaks of the amorphous structure of SiO$_2$, indicating that SiO$_2$ was successfully coated on the Fe$_3$O$_4$ MNPs. Meanwhile, it can be seen from the XRD pattern of the solid acid that the intensity of the diffraction peak of Fe$_3$O$_4$ in the impregnated solid acid was slightly weakened, which indicated that Fe$_3$O$_4$ may be reacted during the sulfonation process, resulting in the relatively lower content.

**Magnetic Analysis.** The hysteresis loops of all samples are shown in Figure 3. As can be seen, all of the samples showed no hysteresis loops, and the coercive force was almost zero, indicating that they were superparamagnetic, which was consistent with the previous conclusions of XRD analysis. Compared with the high saturation magnetization (67.02 emu/g) of Fe$_3$O$_4$, the saturation magnetization (15.36 emu/g) of magnetic SiO$_2$ was greatly reduced, which was caused by the thick layer of SiO$_2$ wrapped on the surface of Fe$_3$O$_4$. The saturation magnetization of the impregnated magnetic SiO$_2$ solid acid was 19.06 emu/g, slightly higher than that of the magnetic SiO$_2$, which may be caused by a slight drop of the SiO$_2$ shell during the sulfonation process.

Besides, the grafted magnetic SiO$_2$ solid acid exhibited a saturation magnetization of 37.83 emu/g, which was stronger than the saturation magnetization of the impregnated magnetic SiO$_2$ solid acid. This was caused by the apparent shedding of the SiO$_2$ shell on the surface of Fe$_3$O$_4$ during the grafting.
process, resulting in an increase in the relative content of Fe$_3$O$_4$.

Figure 4 shows the magnetic separation ability of the magnetic solid acid. It was found that the magnetic solid acid exhibited good separation ability regardless whether it was impregnated or grafted, which provided a strong basis for its high recyclability in the green industry.

**FT-IR Spectra.** The FT-IR spectra of all samples are shown in Figure 5. As shown in Figure 5, the broad bands at 3450 and 1640 cm$^{-1}$ were attributed to the stretching vibration peaks and bending vibration peaks of O–H$^{\ddagger}$ respectively. The characteristic band observed in the FT-IR spectrum of Fe–O–Fe at 580 cm$^{-1}$ was ascribed to the fundamental vibrational modes of Fe$_3$O$_4$. The characteristic bands around 470 and 953 cm$^{-1}$ were the vibrational band of the Si–O–Si bond and Si–OH bond, respectively, indicating that the outer surface of Fe$_3$O$_4$ was coated with SiO$_2$, which was caused by the large amount of hydroxyl groups on the surface of the silicon shell of Fe$_3$O$_4$. Furthermore, the band of 650 cm$^{-1}$ in the solid acid was assigned to the S–O stretching vibration, showing that –SO$_3$H were immobilized onto the surface of the magnetic SiO$_2$ after acid modification, which can also be confirmed by the initial acidity of the impregnated magnetic solid acid being 4.127 mmol/L and that of the grafted ones being 1.584 mmol/L.

**Catalytic Activity and Cyclic Stability.** The effects of reaction temperature, molar ratio of n-butanol/adipic acid, and catalyst (the mass of magnetic solid acid)/liquids (the total volume of n-butanol and adipic acid) on the esterification reaction are shown in Figure 6. It was found that different reaction factors showed a great influence on the esterification reaction. Figure 7 shows the conversion of grafted solid acid and impregnated solid acid as catalysts in six cycles.

As shown in Figure 6, in the initial 0.5 h of the reaction, the esterification rate increased significantly with the increase of reaction time. As the reaction time prolonged, the esterification rate gradually increased to a steady state at a slower rate. This was because the reactants established a contact equilibrium with the catalyst during the reaction progress, achieving a higher esterification rate. While the reaction continued, this led to adsorption or even side effects of the product on the catalyst surface, inhibiting the progress of the esterification reaction.

The molar ratio had a significant effect on the esterification of solid acid compared with other factors in this paper. As shown from Figure 6II, the esterification rate of solid acid in this paper first increased then gradually became flat, with the increase of the molar ratio of n-butanol/adipic acid. The amount of n-butanol was less as the molar ratio was low, resulting in a lower conversion rate. As the molar ratio increases, the amount of n-butanol increased correspondingly, which was beneficial to the positive movement of the esterification reaction, and thus, the conversion rate was increased; however, the reaction reached equilibrium as there was an excessive increase of the molar ratio, resulting in a constant conversion rate and flat reaction curve.

Compared with the optimal reaction conditions (Figure 6) and cyclic stability (Figure 7) of two different magnetic solid acids, it can be found that the highest esterification rate of the grafted magnetic solid acid was 89.12%, while the esterification rate of the impregnation magnetic solid acid was up to 99.00% when the reaction temperature was 105 °C, the molar ratio of n-butanol/adipic acid was 3:1, and the ratio of the catalyst/liquids was 2.95%, which was increased by 11.09%, indicating that the catalytic activity of the impregnated magnetic solid acid was higher than that of the grafted magnetic solid acid. It also can be seen that the impregnated magnetic solid acid decreased remarkably with the increase in the cycle times, and the conversion decreased to 81.35% after six cycle times, which can be attributed to the leaching of the −SO$_3$H absorbed on the outer surface during the reaction. It was confirmed by acidity detection of the impregnated catalyst after six cycle times, which showed that the amount of acid was greatly reduced from 4.127 to 1.856 mmol/g, which reduced by 55.03%. Meanwhile, the conversion of the grafted magnetic solid acid after the first cycle was 88.49%, and a small decline was observed for the next five cycles, which is mainly due to higher stability of the acid sites of the grafted catalysts. After six times of recycle, the conversion of the grafted solid acid still attained 85.61% with better stability, which can be confirmed by acidity detection of the grafted catalyst after six cycle times, showing that the amount of acid was slightly reduced from 1.584 to 1.203 mmol/g. Furthermore, the better thermal stability of the grafted catalyst from the thermogravimetric analysis (Figure 8), compared with the impregnated catalyst, also further supported the results of both conversion rates in
Figure 7. The stability of both was comparable to those of the reported solid acid catalytic systems, especially the grafted magnetic solid acid. Additionally, the catalytic properties of conventional solid acids were also studied, and a comparison with other solid acid catalysts under the same above conditions was analyzed as shown in Table 1. As can be seen, the solid acids exhibited high catalytic activity in the esterification reaction but still lower than those of the impregnated and grafted solid acids in this case, and the activity of the impregnated solid acid can be comparable to that of concentrated sulfuric acid. Combining Figures 4 and 7, it can be found that the solid acid prepared herein is not only easy to separate but also exhibits high catalytic activity and cyclic stability, thus showing a potential industrial application.
that the SiO$_2$ was successfully coated on Fe$_3$O$_4$ particles. The catalysts, the magnetic solid acid prepared in this paper had a simple magnetic recovery process, higher catalytic activity, and cyclic stability, which can be a highly effective solid acid catalyst for green chemical processes.

### EXPERIMENTAL SECTION

#### Materials

All chemicals including trisodium citrate, ferric chloride, urea, polyacrylamide, polyethylene glycol, ethanol, ammonia, tetraethyl orthosilicate (TEOS), sulfuric acid (98 wt %), 3-mercaptopropyl trimethoxysilane (MPTMS), toluene, methanol, hydrogen peroxide (H$_2$O$_2$, 30 wt %), adipic acid, n-butanol, cyclohexane, saturated saline were purchased from Sinopharm Chemical Reagent Co., Ltd. All other unlabeled chemicals were of analytical grade, and no further purification was required.

#### Preparation of Sulfonated Magnetic SiO$_2$ Solid Acid.

The steps for preparing the sulfonated magnetic SiO$_2$ solid acid are as follows. 8 mmol of trisodium citrate, 4 mmol of FeCl$_3$, and 12 mmol of urea were first dissolved in 80 mL of deionized water. Then 8 mmol of polyacrylamide and 0.4 mmol of polyethylene glycol were stirred and dissolved in deionized water. Next, the mixture was continuously reacted at 200 °C in a hydrothermal reaction kettle for 6 h, subsequently separated by an external magnet attraction, thoroughly washed with deionized water, and dried in a vacuum oven at 60 °C. Finally, the Fe$_3$O$_4$ MNPs were obtained by cooling and grinding.

Magnetic SiO$_2$ microspheres were prepared by a procedure previously reported. 1 mmol of Fe$_3$O$_4$ MNPs, 0.4 mol of ethanol, and 0.08 mol of deionized water were added into a three-neck flask. The solution was stirred until it was dispersed homogeneously. Then 0.08 mol of ammonia and 0.02 mol of TEOS were added dropwise, with subsequent stirring at 35 °C for 3 h. Next, the mixture was magnetically separated, thoroughly washed with deionized water, and dried in a vacuum oven at 60 °C to obtain the magnetic SiO$_2$ microspheres.

The sulfonated magnetic SiO$_2$ solid acid was prepared by impregnation and grafting methods as follows. For the former, SiO$_2$ microspheres and sulfuric acid were added into the mixture. Finally, the solid acid sample obtained by stirring and drying.

#### Characterization of the Samples.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed by a PHILIPS XL30 instrument with a working voltage of 200 kV and a JEOL 2100F instrument with a working voltage of 15 kV, respectively. The X-ray diffraction (XRD) patterns were recorded on a Phillips Xpert Pro powder diffraction system using Cu Kα radiation with a Ni filter over the range of 10° ≤ 2θ ≤ 80°. Magnetic properties were measured using a BHV-55 vibrating sample magnetometer (VSM) from Riken Electronics Co. Ltd., Japan. FT-IR spectra (4000−500 cm$^{-1}$) were recorded at room temperature on a Bruker VERTEX 70 FT-IR spectrometer using KBr in a ratio of 1:200.

### Table 1. Catalytic Performances of the Various Catalysts

| catalysts          | acidity (mmol/g) | conversion (%) | TOF (h$^{-1}$) |
|---------------------|-----------------|----------------|----------------|
| impregnated solid acid | 4.127           | 99.00          | 67             |
| grafted solid acid  | 1.584           | 89.12          | 59             |
| SO$_4$$^{2-}$/ZrO$_2$ | 3.643           | 70.82          | 42             |
| HZSM-5              | 1.216           | 57.18          | 34             |
| sulfuric acid       | 99.86           |                | 135            |

### CONCLUSIONS

The Fe$_3$O$_4$ MNPs were prepared as the magnetic core of the magnetic SiO$_2$ solid acid. The characterization results showed that the SiO$_2$ was successfully coated on Fe$_3$O$_4$ particles. The −SO$_3$H was also loaded on the catalysts after acid modification. The catalytic properties indicated that the impregnated magnetic solid acid showed a better catalytic activity (an esterification rate of up to 99.00%), while the grafted magnetic solid acid showed a better cyclic stability (the conversion attained 85.61%) after six times of recycle. Compared to the previously reported nonmagnetic solid catalysts, the magnetic solid acid prepared in this paper had
the modified acid—base titration referred to the literature. The 0.6 mL saturated saline was added into a mixed solution of 0.2 g of sulfonated magnetic SiO2 solid acid, 3.65 g of adipic acid, 4.6 mL of n-butanol, and 5 mL of cyclohexane in a 100 mL three-neck flask, subsequently stirred, and dissolved. Phenolphthalein was used as an indicator and titrated with 0.1 mol/L NaOH solution to determine the initial acid value and the reaction acid value, in which the calculation method was based on the Chinese national standard (GB/T16688-2008). The esterification rate was measured as follows

\[ X = \frac{c(NaOH) \times (V_1 - V_2) \times 56.11}{m} \]  

\[ Y = \left(1 - \frac{X_1}{X_2}\right) \times 100 \]

where \( X \) is the acid value, mg/g; \( Y \) is the esterification rate, %; \( c \) is the concentration of the standard NaOH solution, mol/L; \( V_1 \) and \( V_2 \) are the volumes of the NaOH solution consumed before and after the reaction, respectively, mL; \( X_1 \) and \( X_2 \) are the acid values before and after the reaction, mg/g; \( m \) is the mass of the reaction solution, g; and 56.11 is the conversion factor.

TOF (turn over frequency) was calculated by the data of the moles of converted reactant, the moles of acid sites, and the reaction equilibrium time, which reflected the intrinsic activity of the catalyst, and usually was measured as follows

\[ \text{TOF} = \frac{(\text{mole of converted reactant})}{(\text{moles of acid sites of catalyst} \times \text{reaction equilibrium time})} \]

The steps for catalyst recycling experiment are as follows: the catalyst sulfonated magnetic solid acid was recovered by magnetic separation when the reaction was completed. The recovered catalyst was washed with methanol and dried at 105 °C in a vacuum oven. The recovered catalyst was reused for the next cycle, and other steps were the same.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: zdanly@163.com.*

**ORCID**

Danlin Zeng: 0000-0003-0114-4607

**Notes**

The authors declare no competing financial interest.

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