View Article Online
View Journal

RSC Advances

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

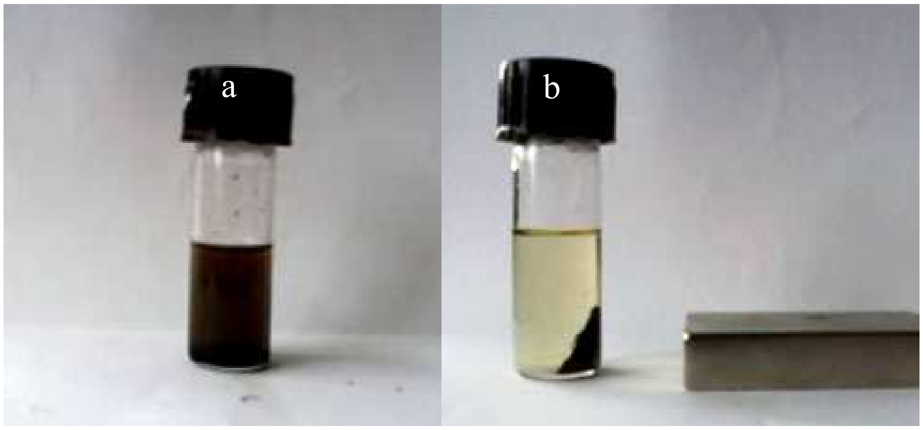
Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/advances
Registered Charity Number 207890

Graphical Abstract

$$C_{15}H_{31}COOH+CH_3OH \xrightleftharpoons{\text{magnetic catalysts}} C_{15}H_{31}COOCH_3+H_2O$$



a: without, b: with the external magnetic field.

Water-tolerant heteropolyacid on magnetic nanoparticles as efficient catalysts for esterification of free fatty acid

Xixin Duan[a, c,*], Jing Zhao[a], Wei Shi[a], Xia Zhang[a], Xiaohong Wang[a,*], Shiwu Li[b,*]

[a] Key Lab of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun 130024, P. R. China

[b] Traffic College, Jilin University, Changchun 130025, P. R. China

[c] Faculty of Chemistry and Biology, Beihua University, Jilin 132013, P. R. China

Fax: 0086-431-85099759; E-mail: wangxh665@nenu.edu.cn

Abstract: Heteropolyacids (HPAs) supported on magnetic nanoparticles (MNPs) have been prepared by a simple acid-base interaction between functionalized magnetic nanoparticles and HPAs. The surface of the catalyst had been modified by organic groups to protect the catalytic sites from destroy by water. The hybrid SiO_2-MNPs-HPW consists of a core of magnetic iron oxide MNPs, silica shell, amino-silica and organic groups on the surface, which catalyzed the esterification of palmitic acid with methanol to give 90.4% FFA conversion within 2 h and high TOF of 4.95×10^2 h^{-1} under mild reaction conditions. The good catalytic performance was good among the other solid acid catalysts, demonstrating the advantage of the small size of catalyst particles in reducing mass-transfer limitation and providing better accessibility of the catalyst sites on the surface of carriers for the substrates. The catalysts are easily separable from the reaction mixture under a magnetic field and showed high stability and recyclebility, with no significant loss of productivity after five cycles of esterification.

Keywords: Heteropolyacids; esterification; magnetic separation; water-tolarence.

1. Introduction

Biodiesel recognized as ‘a green fuel’ is one of the alternative renewable fuel composed of fatty acid methyl ester (FAME), typically derived from transesterification of triglycerides (TG) in vegetable oils or animal fats or through esterification of free fatty acids (FFAs). [1-3] The major drawbacks of transesterification of crude oils are the FFAs in feedstocks leading to the low efficiency for base catalysts. A simple and efficient approach to improve the process is to first esterify FFAs with methanol to their alkyl esters using an acid catalyst, and then transesterify triglycerides into FAME. [4, 5] Homogeneous acid catalysts such as sulfuric acid are known for the esterification of FFA but suffer from many drawbacks such as corrosion, pollution, complex downstream neutralization, difficult separation, and no reusability of the catalysts. [3] Solid acid catalysts have served as important functional materials for green and recyclable catalysts. However, the reported heterogeneous acid catalysts have been thus far unsatisfactory for the esterification of FFA, because of the low densities and low accessibility of the acid sites, easy deactivation, low thermal stability, low catalytic activity and high cost. Moreover, owing to the formation of water as by-products, many of the acid catalysts generally become deactivated or decomposed during the esterification processes, leading to highly acidic and corrosive wastes. Thus, development of solid acid catalysts with high accessibility to the acid sites, water-tolerance is crucial to obtain satisfactory product yields in esterification of FFAs. [6]

As continuing efforts towards the investigation of waste cooking oil as a potential biodiesel feedstock, [7] we are interested in developing novel heterogeneous acid catalysts based on heteropolyacids (HPAs) with high activity, stability, and recyclability for the esterification of FFA from waste cooking oils. By now, there are some reports on the esterification of FFA catalyzed by solid HPA catalysts. For example, Prof. Guo’s group synthesized a series water-tolerant HPAs catalysts loading on mesoporous Ta_2O_5 or ZrO_2 [8] for esterification and transeterification reactions, while the hgihest conversion of FFA is about 99% at 24 h and 65 ºC with acid/ethanol of 1: 9. J. A. Dias and co-workers designed $H_3PW_{12}O_{40}$ loading on ZrO_2 as esterification catalyst with an optimum reaction performance (88% of oleic acid conversion at 20 wt% loading, 100 ºC, 4 h reaction and 1:6 of acid:ethanol molar ratio). [9] A. Patel et al. reported $H_3PW_{12}O_{40}$ supported by SBA-15(the loading of $H_3PW_{12}O_{40}$ as high as 28.5%) as catalysts for esterificatio of FFA, by which 92% conversion of oleic acid was obtained at 40 ºC, 4 h reaction and 1:40 of acid: methanol molar ratio. [10] Nevertheless some efforts had been paid, but the low activity of current solid acid catalysts is the main problems, which is mainly caused by the diffusional limitation of porous materials, or the low acid loading and mass transfer limitation of the large size carriers. [11] However, another problem of HPA in catalysis is the high solubility in polar media, which made POMs physically absorbed on a support leach into reaction solution. Therefore, the attempt to heterogenization of HPAs has been one area of research that has seen increasing interest. There are several methods for synthesis of stable materials for leaching of HPAs in polar medium, such as capsulation of HPAs in solid matrix and application of a support modified with functional groups such as carboxylic groups, lactam, amide, imide or amino-groups for the anchoring of POMs. [12-20] Amino-modified silica materials are widely used for immobilization of POMs. In spite of the decreasing of acidity after chemically anchoring of HPAs to the amino-modified support, these HPA/NH_2-support systems can be used as catalyst for different acid type reactions, showing easy handling, water-tolerant properties. But in these materials, HPA molecules were embedded on the porous of silica resulting in low efficiency and requirement of high ratio of alcohol to acid.

To overcome these, our group choose magnetic nanoparticles (MNPs) as the carriers to prepare nano-size solid catalyst containing HPAs and hydrophobic group on the surface. Magnetic nanoparticles are available from cheap materials via simple synthesis and easily tunable by structural surface modifications, and also allow for the convenient and efficient recovery of nanocatalysts under a magnetic field, thus facilitating catalyst recycling. [21] Three examples of MNPs supporting HPA catalysts are known: MNPs supported HPAs via non-covalent interaction as reusable acid catalysts for Friedel–Crafts reaction with HPA loading 0.55 mmol/g; [22] HPA/chitosan/Fe_3O_4 shell-core materials with acid content of 0.13 mmol/g for acid catalytic reaction; [23] HPAs supported on silica functionalized Fe_3O_4 through sol/gel method. [24] These catalysts are efficient for other catalytic reaction except for esterification reaction with moderate or low HPA loadings. We have focused on the engineering of cheap and stable HPA acid catalyst for an esterification reaction. Herein, we report novel core–shell structured iron oxide MNPs with SiO_2 as shell, HPA and organic groups as core, which acts as a highly active, water-tolerant, stable, and easily recyclable nano-size solid acid catalyst for the high-yielding esterification of FFAs with methanol.

2. Experimental

2.1. Preparation of catalysts

$H_3PW_{12}O_{40}$ (HPW) was prepared according to Ref. [25] and identified by IR spectroscopy, ICP-AES and ^{31}P NMR spectrum. Preparation of Magnetic Fe_3O_4 nanoparticles were prepared by a co-precipitation method. [26] MNPs functionalized by silica (SiO_2-MNPs) were fabricated according to Ref. [27]

2.1.1 Preparation of Magnetic Fe_3O_4 nanoparticles

Preparation of Magnetic Fe_3O_4 nanoparticles were prepared by a co-precipitation method [26] as follows: 10.3 mL of 1M HCl and 25 mL of purified, distilled water were mixed. 8.65 g of $FeCl_3 \cdot 6H_2O$ and 3.18 g of $FeCl_2 \cdot 4H_2O$ (ratio of Fe(II)/Fe(III) = 1/2) were dissolved in the solution with vigorous stirring. The above solution was dropped into 250 mL of 1.5 M NaOH solution under vigorous stirring for 1 h. Precipitate was separated by maganitic and washed with purified deoxygenated water repeatedly to pH = 7.0, then dried at room temperature.

2.1.2 Preparation of the SiO_2-MNPs-1-HPW

The obtained SiO_2-MNPs (0.25 g) were suspended in 200 mL of anhydrous ethanol containing 0.5 mL of aminopropyl trimethoxy silane (APTES) under dry nitrogen atmosphere. The mixture was refluxed for 12 h and then aged for another one night. The resulting solid was magnetically separated, washed with ethanol three times to remove the unreacted residue of silylating agent and then dried under vacuum at 353 K. APTES-functionalized SiO_2-MNPs (SiO_2-MNPs-1) were obtained with yield of 0.34 g and suspended in hydrochloric acid (pH = 4) to acidify the amino group to ammonia group. To the above mixture, HPW solution (1 g/10 mL) was added and stirred for 4 h to confirm the loading effect of HPW on SiO_2-MNPs-1. Then the mixture was separated by magnetic separation and washed with deionized water three times, then dried under vacuum at 353 K to give SiO_2-MNPs-1-HPW material with the yield of 0.51 g.

2.1.3 Preparation of hydrophobic hybrids SiO_2-MNPs-2-HPW

The prepared procedure is as the same as SiO_2-MNPs-1-HPW, only the mixture of 1 mL octyltrimethoxysilane (OTMS) and 0.5 mL APTES were used instead of APTES only.

2.1.4 Preparation of SiO_2-MNPs-HPW

SiO_2-MNPs-HPW was synthesized as follows: Tetraethoxysilane (TEOS) was dissolved in ethanol, then an aqueous $H_3PW_{12}O_{40}$ solution was added to the above solution with the molar ratio of the $H_3PW_{12}O_{40}$: H_2O: TEOS: EtOH 0.04: 13.4: 1: 2. The mixture was stirred vigorously for 1 h at room temperature to form HPW silica solution. Then 1 g of SiO_2-MNPs was added to 10 g of HPA silica sol with vigorous stirring at 45 °C for 3 h to form hydrogel. The hydrogel was cooled to room temperature and then dehydrated for one day. The gels were further dried in vacuum at 150 °C for 2 h.

2.2. Catalytic experiments

The esterification of palmitic acid with methanol was carried out in a 50 mL three-necked round bottomed flask with mechanical stirring at atmospheric pressure and 338 K. In a typical experiment, palmitic acid (5.12 g), anhydrous methanol (6.4 mL) and certain amounts of catalyst were mixed and refluxed for some time. After reaction, magnetic separated the catalyst for reuse. The residual methanol was gathered using rotary evaporator at 323 K. The conversion of free fatty acid into ester was estimated by measuring the acid value of the product and the yield of the product was measured by gas chromatography.

2.3. Instrument

FTIR spectra (4000-400 cm^{-1}) of different catalysts were recorded as KBr discs on a Nicolet Magna 560 IR spectrometer. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a PE 2400 CHN elemental analyzer. The ^{31}P MAS spectrum was recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head whose X channel was tuned to 162 MHz for ^{31}P, using a magnetic field of 9.39 T at 297 K. X-ray diffraction (XRD) patterns were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The yield of monoester was determined on Shimazu GC-14C fitted with a HP-INNOWAX capillary column and flame ionization detector and HP-INNOWAX capillary column (30 m × 0.32 mm; 0.50μm film). The oven temperature was set at 220 °C and the temperature of the detector and injector were set at 250 °C and 250 °C, respectively. The conversion was calculated on a GC using ethyl laurate as an internal standard.

2.4 Analytical analyses

The acid values (AV) of were measured following standards of PRC: GB/T14489.3-93, calculated by the following equation (AV):

$$\mathrm{AV}\ (\mathrm{mg\ KOH\ g^{-1}}) = (V_{KOH} \times C_{KOH} \times 56.1)\ /m_{acid} \qquad (1)$$

V_{KOH} : the volume of KOH standard solution (mL),

C_{KOH} : KOH standard solution concentration (mol L^{-1}).

AV: the number of milligrams of KOH needed for the neutralization of 1 g free fatty acids. The AV reduction efficiency (a) was calculated by the following equation:

$$a = (AV_r - AV_E)/AV_r \times 100\% \qquad (2)$$

AV_r : the acid values in raw material (mg KOH g^{-1})

AV_E : the acid values after esterification (mg KOH g^{-1}).

3 Results and discussion

3.1. Preparation strategy of SiO_2-MNP-1-HPW and SiO_2-MNP-2-HPW

The common strategy for preparation of MNP-supported HPAs is through the well-applied “acid–base” strategy. Since MNPs are acid sensitive, they were first protected with a 1-2 nm thickness silica layer. The obtained SiO_2-MNP was then treated with the commercial (3-aminopropyl) triethoxysilane in refluxing ethanol to afford SiO_2-MNP-1 (Scheme 1), which the surface of silica was functionalized by aminoropropyl groups. The next step involves reaction of amine groups of SiO_2-MNP-1 with $H_3PW_{12}O_{40}$ to yield SiO_2-MNP-1-HPW through the electrostatical interaction of protonation of amine groups and HPAs. Following the same procedure, SiO_2-MNP-2 was also prepared only using the mixture of APTES and OTMS, which the surface of the silica was modified by aminoropropyl groups and octyl groups. The immobilization of SiO_2-MNP-2-HPW was achieved by stirring of a mixture of SiO_2-MNP-2 and $H_3PW_{12}O_{40}$.

Scheme 1

3.2. Characterization of catalysts

HPW was identified by ICP-AES (H: 0.03%, P: 1.06%, W: 76.4%, O: 22.4%) and ^{31}P NMR spectrum (Fig. S1). IR spectra (Fig. S2) shows four characteristic peaks of Keggin structure at 1080, 9979, 887 and 814 cm^{-1}, which are attributed to the asymmetric vibrations P-O_a, W-O_d, W-O_b and W-O_c, respectively. The above results indicated that HPW was in high purity.

The loadings of HPW on SiO_2-MNP-HPW, SiO_2-MNP-1-HPW and SiO_2-MNP-2-HPW measured by ICP-AES were 34.8, 30.3, and 29.2%, respectively. The contents of N and Si in SiO_2-MNP-1-HPW and SiO_2-MNP-2-HPW were 0.64%，0.60%，21.3% and 32.9%, respectively.

The IR spectra of different complexes including Fe_3O_4, SiO_2-MNP-1-HPW, and SiO_2-MNP-2-HPW were shown in Fig. 1. The infrared spectra of SiO_2-MNP-1-HPW (Fig. 1b) and SiO_2-MNP-2-HPW (Fig. 1c) in the 1080 cm^{-1}, 984 cm^{-1}, 893 cm^{-1}, 804 cm^{-1} are consistent with parent HPW, which suggested that HPW maintained integrity Keggin structure in hybrid complexes. The bands at 580 cm^{-1} and 1200-1100 cm^{-1} should be attributed to Fe-O and Si-O-Si, respectively. The bands at 3378-3370 cm^{-1} which are attributed to N-H stretching vibration proved the presence of aminopropyl silane. The bands at 2920 cm^{-1} and 2860 cm^{-1} were attributed to the C-H stretching vibration of CH_3 and the C-H stretching vibration of CH_2, respectively, which demonstrated that the organic group of octyltrimethy has been introduced into the hybrids. [28]

Fig. 1

The magnetic core was analyzed by XRD and the observed diffraction pattern at 18.3°, 30.1°, 35.5°, 43.1°, 56.9°, 62.6°, and 74.0°, respectively, is consistent with the JCPDS no. 851436 for magnetite (Fig. 2a). The XRD spectrum of silica coated Fe_3O_4 (Fig. 2b) gives the same diffraction peaks with that of Fe_3O_4. The diffraction peaks of SiO_2-MNP-1-HPW and SiO_2-MNP-2-HPW (Fig. 2c, 2d) could be indexed to $H_3PW_{12}O_{40}$ (JCPDS no. 76-1815) with one peak at 8°.

Fig. 2

The SEM image of Fe_3O_4 (a) and TEM of SiO_2-MNP-1-HPW (b) were shown in Fig. 3. It could be known that the size of Fe_3O_4 microspheres were around 30 nm. When functionalized by organic group and HPW, the size was around 45 nm and SiO_2-MNP-1-HPW has core-shell structure. The thickness of silica layer was about 15 nm.

Fig. 3

3.2. Catalytic activity

In our previous studies, [7] it was found that the heteropolyacids were efficient catalysts for esterification of FFAs or transterification of triglycerides. However, only a few solid HPA acids are known to demonstrate acceptable performance in the presence of water [8, 29] including SiO_2 supported HPAs and Ta_2O_5 supported HPAs. Try our best to evaluate the MNP supported HPAs in esterification of FFAs is meaningful for the solid acid catalysis, not only for reusable FFA esterification but also alternative for other acid catalytic reactions.

The catalytic activity for different catalysts had been done including HPW, SiO_2-MNPs, SiO_2-MNP-HPW, SiO_2-MNPs-1-HPW, and SiO_2-MNPs-2-HPW (Table 1). It can be seen that the conversion of palmitic acid was only 41.7% catalyzed by SiO_2-MNP due to the absence of acid sites. The FFA conversions were enhanced catalyzed by SiO_2-MNP-HPW, SiO_2-MNPs-1-HPW, and

SiO_2-MNPs-2-HPW attributed to the immobilization of HPAs on SiO_2-MNPs. To evaluate the catalytic activity per mole of HPW, the catalytic activity decreased in range of SiO_2-MNPs-2-HPW > SiO_2-MNPs-1-HPW > SiO_2-MNP-HPW > HPW. When considering the reaction turnover frequency (TOF) based on acidic protons of the catalyst, the activity decreased in the same trend, while the amount of acidic protons was measured by titration method. [30] The results show that HPW is homogeneous catalyst with high FFA converision, but the activity is restricted by the absence of water-tolerant property. SiO_2-MNPs-HPW is only grafting HPW on MNPs, there is no interaction between HPW and supports resulting in the leaching problem. Moreover, HPW was enbedded by silica, and the substrates were hindered to access the HPW sites with low activity. HPW was solidified on the surface of SiO_2-MNPs-1-HPW through the acid-base interaction of NH_3^+ and HPW, therefore the leaching of HPW was avoided. From Table 1, the octyl-grafted catalyst SiO_2-MNPs-2-HPW showed a high activity of 2.12×10^2 h^{-1}, which was attributed to the tolerance to water produced during the esterification reaction. To our knowledge, the activity of SiO_2-MNPs-2-HPW is the highest observed in solid acid catalysts. This point could also be observed in the experiment of the reaction time (Fig. 4).

Table 1

One can be seen from Fig. 4 conversion of FFA depends on methods of HPAs immobilization in solids, amount of octyl- and amino-groups in solids. For SiO_2-MNPs-HPW and SiO_2-MNPs-1-HPW, the highest conversions of FFA were obtained at 4 h for 84.5%, and 10 h for 91.4%, respectivley. Further increasing the reaction time could decrease the FFA conversion. This trend might be attributed to the adsorption of reagents by the catalysts. Therefore, the adsorption of ester and water on the catalysts had been done. The results showed the ester decomposition under the reaction conditions. It is known that esterification of fatty acid is reversible reaction, which water might caused the ester to decompose catalyzed by acid catalyst. For SiO_2-MNPs-2-HPW, the conversion kept increase as enhancement of the reaction time with highest conversion of 98.4% at 10 h. This results also confirm that grafting of organic group on the surface of the support could remove the water molecules from the catalyst. [28]

Fig. 4

The molar ratios of methanol/acid of esterification reaction is very important parameters in real application. The previous reports used HPA loading on the pore of the SiO_2 or Ta_2O_5 carriers, which might hinder the reaction due to the diffusion to the catalytic acitive sites resulting in high usage of methanol. Our strategy is to loading HPW on the surface of the magnetic nanoparticles overcoming the limitation of diffusion (Fig. 5). From the difference activity of SiO_2-MNPs-HPW and SiO_2-MNPs-1-HPW at different molar ratio of methanol and FFA, it can be seen that at low molar ratio of 4:1, the conversions of FFA were lower by SiO_2-MNPs-HPW than by SiO_2-MNPs-1-HPW. When increasing of molar ratio to 1:8, the conversion of FFA increased by two catalysts. However, the significant increase by SiO_2-MNPs-1-HPW was observed attributing to the easy access of substrates to catalytic sites. Therefore, the lower molar ratio of methanol to acid is required by SiO_2-MNPs-1-HPW, by which the drawbacks of diffusion to pore structure could be overcome. From Fig. 5, it also can be seen that increase of molar ratio could enhance the FFA conversion.

Fig. 5

The other problem of solid acid catalysts in esterification or transesterification is the sensitivity to water from feedstocks and the by-product of esterification reaction, which could easily cause the deactivation and lead to phase segregation to influence the activity of the catalysts. Most inorganic solid acid catalysts do not work in water, while the exceptions include H-ZSM-5, and a hydrophobic zeolite, which are also believed to have hydrophobic surfaces. Therefore, inorganic solid acid catalysts with water-tolerant property are required to develop. Compared to SiO_2-MNPs-1-HPW, more the octyl groups were grafted on the surface of silica. Therefore, SiO_2-MNPs-2-HPW was further modified by grafting of organic group around the HPW, which provides hydrophobic surroundings available for elimination of water molecules from the catalyst leading to water-tolerant property. [29] In order to assess the water-tolerance of SiO_2-MNPs-2-HPW, some extra water had been added to the mixture under the same conditions and the result was given in Fig. 6. In addition, SiO_2-MNPs-1-HPW also had been tested for its water-tolerant property.

Fig. 6

It can be seen that the effect of water on the catalytic activity is related to water content and the different components of catalysts. As for SiO_2-MNPs-1-HPW, the water content gives a significant influence on the conversion of FFAs, while the conversion decreased to half as the water content of 0.4 wt% and the FFA conversion decreased to 6.5% in presence of 1 wt% of water. As using SiO_2-MNPs-2-HPW, the conversion was slightly reduced to 80.6% when the water content was below 0.4 wt%. The high amount of water of 1 wt% did not influence the FFA conversion sharply. When 1% of water was added, the conversion was significantly reduced to 33.9%. Therefore, the grafting of octyl on the surface of MNPs would protect the HPW from being destroy by water molecules. In addition, SiO_2-MNPs-2-HPW is relatively more tolerant of water than other solid acid catalysts such as H_2SO_4,[31] SO_4^{2-}/ZrO_2.[32]

Acting as heterogeneous catalysts, the regeneration of SiO_2-MNPs HPA hybrids is of practical, economic importance. The regeneration is easily achieved by magnetic separation by the external magnetic field and reused only by calcinating at 373 K for 2 h (Fig. 7). As presented in Fig. 8, SiO_2-MNPs-1-HPW and SiO_2-MNPs-2-HPW demonstrated excellent stability and reusability, maintaining 97.7% and 95.7% conversion throughout five reaction cycles. As the catalysts are stable, there is no regeneration step needed to restore the acid capacity of the catalyst, thus decreasing the cost of catalyst production and hence the cost of biodiesel production.

Fig. 7

Fig. 8

4. Conclusions

Active, stable, water-tolerant and recyclable magnetic nano-size HPA catalysts have been developed, for the first time, as efficient catalysts for the esterification of FFA with methanol. A novel acid catalyst SiO_2-MNPs-2-HPW consisting of a core of magnetic iron oxide MNPs, silica shell, amino- silica and organic groups on the surface was was fabricated. SiO_2-MNPs-2-HPW catalyzed the esterification of palmitic acid with methanol at 8.2 wt% loading to give 90.4% FFA conversion within 2 h and high TOF of 4.95×10^2 h^{-1} at lower methanol to acid ratio. The catalytic performance was good among the other solid acid catalysts, demonstrating the advantage of the small size of catalyst particles in reducing mass-transfer limitation and providing better accessibility of the catalyst sites on the surface of carriers for the substrates. Moreover, the organic groups on the surface of the supports provide the resistence to water molecules, allowing the esterification reaction occurs under the conditions in the presence of high content of water. The catalysts are easily separable from the reaction mixture under a magnetic field and showed high stability and recyclability, with no significant loss of productivity after five cycles of esterification.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20871026), "the Fundamental Research Funds for the Central Universities" (10JCXK011) and the major projects of Jilin Provincial Science and Technology Department (20100416).

References

1 M. E. Borges and L. Díaz, Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review, *Renew. Sust. Energ. Rev.*, 2012, **16**, 2839-2849.

2 M. Tariq, S. Ali and N. Khalid, Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review, *Renew. Sus. Energy Rev.,* 2012, **16**, 6303-6316.

3 M. K. Lam, K. T. Lee and A. R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review, *Biotechnol. Adv.*, 2010, **28**, 500-518.

4 A. Baig and F. T. T. Ng, A single-step solid acid-catalyzed process for the production of biodiesel from high free fatty acid feedstocks, *Energy Fuels*, 2010, **24**, 4712-4720.

5 Zillillah, G. W. Tan and Z. Li, Highly active, stable, and recyclable magnetic nano-size solid acid catalysts: efficient esterification of free fatty acid in grease to produce biodiesel, *Green Chem.*, 2012, **14**, 3077–3086.

6 E. Lotero, Y. Liu, D. E. Lopez, K. D. Suwannakarn, A. Bruce and J. G. Goodwin, Synthesis of biodiesel via acid catalysis, *Ind. Eng. Chem.Res.*, 2005, **44**, 5353-5363.

7 J. Li, X.Wang, W. Zhu and F. Cao, $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ nanotubes with double acid sites as heterogeneous catalysts for the production of biodiesel from waste cooking oil. *ChemSusChem.*

2009, **2**, 177-183.

8 L. L. Xu , Y. H. Wang, X. Yang, X. D. Yu and Y. H. Guo, Preparation of mesoporous polyoxometalate-tantalum pentoxide composite catalyst and its application for biodiesel production by esterification and transesterification, *Green Chem.,* 2009, **11**, 314-317.

9 C. F. Oliveira, L. M. Dezaneti, F. A. C. Garcia, J. L. de Macedo, J. A. Dias, S. C. L. Dias and K. S. P. Alvim, Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia, *Appl. Catal. A: Gen.,* 2010, **372**,153-161.

10 V. Brahmkhatri and A. Patel, 12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids, *Appl. Catal. A: Gen.,* 2011, **403**, 161-172 .

11 Zillillah, G. W. Tan and Z. Li, Highly active, stable, and recyclable magnetic nano-size solid acid catalysts: efficient esterification of free fatty acid in grease to produce biodiesel, *Green Chem.,* 2012, **14**, 3077-3086.

12 M. J. Verhoef, P. J. Kooyman, J. A. Peters and H. van Bekkum, A study on the stability of MCM-41-supported heteropoly acids under liquid- and gas-phase esterification conditions, *Micropor. Mesopor. Mater.*, 1999, **27**, 365-371.

13 P. Van Der Voort and E. F Vansant, Silylation of the silica surface a review, *J. Liq. Chromatogr. Related Technol.* 1996, **19**, 2723-2752.

14 W. Kaleta and Nowinska, K. Immobilisation of heteropoly anions in Si-MCM-41 channels by means of chemical bonding to aminosilane groups, *Chem. Commun*. 2001, **0**, 535-536.

15 A. Tarlani, M. Abedini, A. Nemati, M. Khabaz and M. M. Amini, Immobilization of Keggin and Preyssler tungsten heteropolyacids on various functionalized silica, *J. Colloid Inter. Sci.* 2006,

303, 32-38.

16 S. S. Wu, J. Wang, W. H. Zhang and X. Q Ren, Preparation of Keggin and Preyssler heteropolyacid catalysts on amine-modified SBA-15 and their catalytic performances in esterification of n-butanol with acetic acid, *Catal. Lett.*, 2008, **125**, 308-314.

17 S. S. Wu, P. Liu, Y. Leng and J. Wang, Heteropolyacids anchored on amino-functionalized MCM-41 via condensation as reusable catalysts for esterification. *Catal. Lett.*, 2009, **132**, 500-505.

18 A. S. Dias, M. Pillinger and A. A. Valente, Mesoporous silica-supported 12-tungstophosphoric acid catalysts for the liquid phase dehydration of D-xylose, *Micropor. Mesopor. Mater.*, 2006, **94**, 214-225.

19 H. Liu, N. H. Xue, L. M. Peng, X. F. Guo, W. P. Ding and Y. Chen, The hydrophilic/hydrophobic effect of porous solid acid catalysts on mixed liquid phase reaction of esterification, *Catal. Commun.*, 2009, **10**, 1734-1737.

20 H. Q. Guo, G. Yan, M. Q. Chen and S. R. Liu, Assembling of 12-Tungstophosphoric Acid into Amino-Modified SBA-15 and its Catalytic Performance, *Adv. Mater. Res.*, 2012, **465**, 224-228.

21 V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J. M. Basset, Magnetically recoverable nanocatalysts, *Chem. Rev.,* 2011, **111**, 3036-3075.

22 X. Zheng, L. Zhang , J. Li , S. Luo and J. Cheng, Magnetic nanoparticle supported polyoxometalates (POMs) via non-covalent interaction: reusable acid catalysts and catalyst supports for chiral amines, *Chem. Commun.*, 2011, **47**, 12325-12327.

23 A. Kong, P. Wang, H. Zhang, F. Yang, S. Huang and Y. Shan, One-pot fabrication of magnetically recoverable acid nanocatalyst, heteropolyacids/chitosan/Fe_3O_4, and its catalytic performance,

Appl. Catal. A: Gen., 2012, **417-418**, 183-189.

24 M. M. Farahani, J. Movassagh, F, Taghavi, P. Eghbali and F. Salimi, Magnetite-polyoxometalate hybrid nanomaterials: Synthesis and characterization, *Chem. Eng. J.,* 2012, **184**, 342-346.

25 R. C. Deltcheff, M. Fournier, R. Franck and R. Thouvenot, Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum(VI) and tungsten(VI) compounds related to the Keggin structure, *Inorg. Chem.,* 1983, **22**, 207-216.

26 J. S. Choi, H. K. Youn, B. H. Kwak, Q. Wang, K. S. Yang and J. S. Chung, Preparation and characterization of TiO_2-masked Fe_3O_4 nano particles for enhancing catalytic combustion of 1,2-dichlorobenzene and incineration of polymer wastes, *Appl Cataly B: Environ.,* 2009, **91**, 210-216.

27 Y. H. Deng, C. C. Wang, X. Z. Shen, W. L. Yang, L. Jin, H. Gao and S. K. Fu, Preparation, characterization, and application of multistimuli-responsive microspheres with fluorescence-labeled magnetic cores and thermoresponsive shells, *Chem. Eur. J.*, 2005, **11**, 6006-6013.

28 S. Mohapatra, N. Pramanik, S. Mukherjee, S. K. Ghosh and P. Pramanik, A simple synthesis of amine-derivatised superparamagnetic iron oxide nanoparticles for bioapplications, *J. Mater. Sci.,* 2007, **42**, 7566-7574.

29 K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara and S. Yamanaka, Water-tolerant, highly active solid acid catalysts composed of the Keggin-type polyoxometalate $H_3PW_{12}O_{40}$ immobilized in hydrophobic nanospaces of organo modified mesoporous silica, *Angew. Chem., Int. Ed.,* 2007, **46**,

7625-7628.

30 M. Di Serio，R. Tesser，M, Dimiccoli, F. Cammarota, M. Nastasi and E. Santacesaria, Synthesis of biodiesel via homogeneous Lewis acid catalyst, *J Mol Catal A: Chem.*, 2005, **239**, 111-115.

31 D. Kusdiana and S. Saka, Effects of water on biodiesel fuel production by supercritical methanol treatment, *Bioresour. Technol.,* 2004, **91**, 289-295.

32 J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho and P. Jenvanitpanjakul, Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts, *Chem. Engin. J.,* 2006, **116**, 61-66.

Figure Captions

Fig. 1 IR spectra of (a) Fe_3O_4, (b) SiO_2-MNP-1-HPW and (c) SiO_2-MNP-2-HPW.

Fig. 2 XRD patterns of (a) Fe3O4, (b) SiO2-MNP, (c) SiO2-MNP-1-HPW and (d) SiO2-MNP-2-HPW.

Fig. 3 The SEM image of (a) Fe3O4 and (b) TEM image of SiO2-MNP-1-HPW.

Fig. 4 Kinetic data of esterification of palmitic acid with methanol over SiO2-MNP-HPW systems. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC.

Fig. 5 The effect of methanol/acid molar ratio on the ester conversion over different catalysts. Reaction conditions: amount of catalyst 8.2 wt%, 65 ºC for 2 h.

Fig. 6 Effect of water on activity of SiO_2-MNPs-1-HPA and SiO_2-MNPs-2-HPA. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC for 2 h.

Fig. 7 Photographs of magnetic separation after the esterification of palmitic acid with methanol, a: without, b: with the external magnetic field.

Fig. 8 Catalytic cycles of SiO_2-MNPs-1-HPA and SiO_2-MNPs-2-HPA recycling in esterification of palmitic acid with methanol. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC for 2 h.

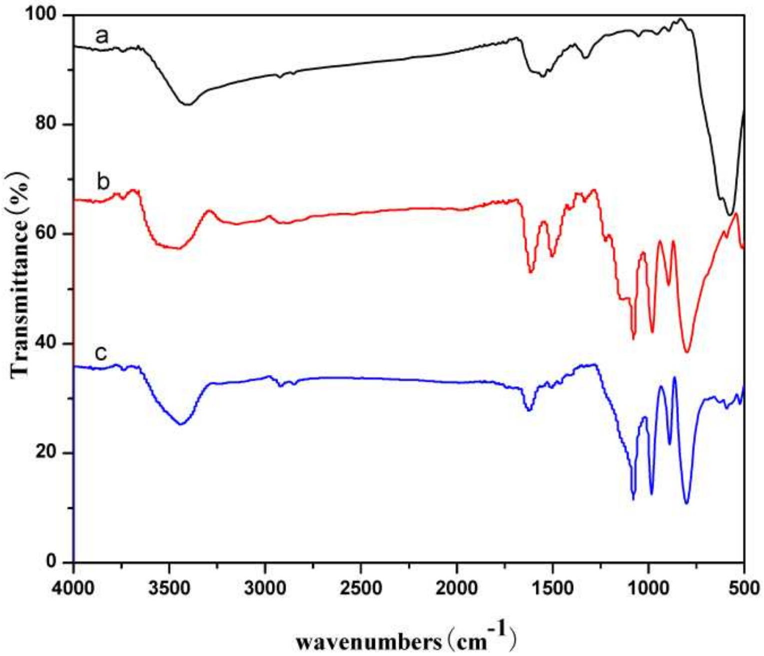


Fig. 1 The IR spectra of (a) Fe_3O_4, (b) SiO_2-MNP-1-HPW and (c) SiO_2-MNP-2-HPW.

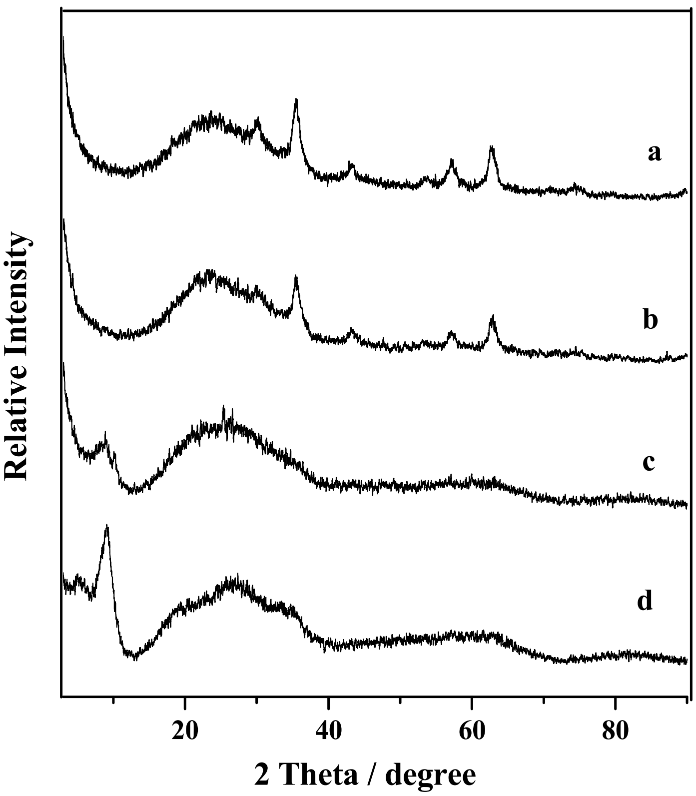


Fig. 2 XRD patterns of (a) Fe_3O_4, (b) SiO_2-MNP, (c) SiO_2-MNP-1-HPW and (d) SiO_2-MNP-2-HPW.

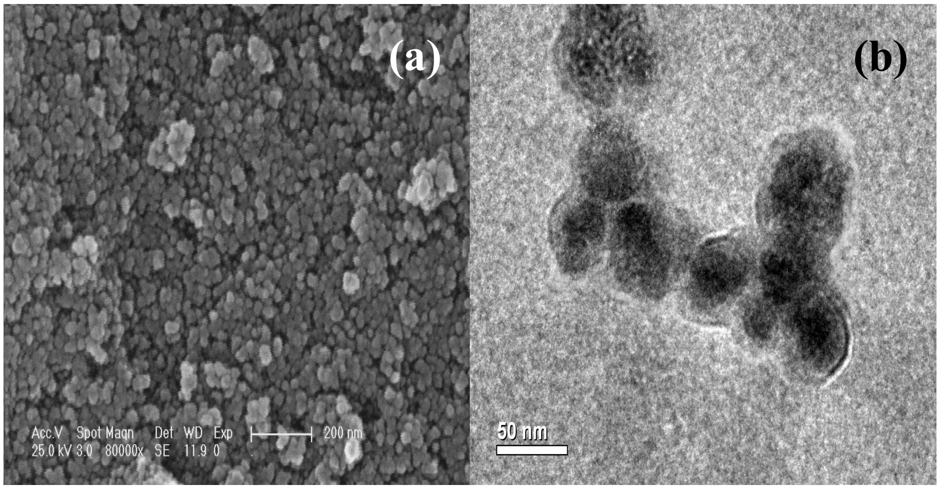


Fig. 3 The SEM image of (a) Fe_3O_4 and (b) TEM image of SiO_2-MNP-1-HPW.

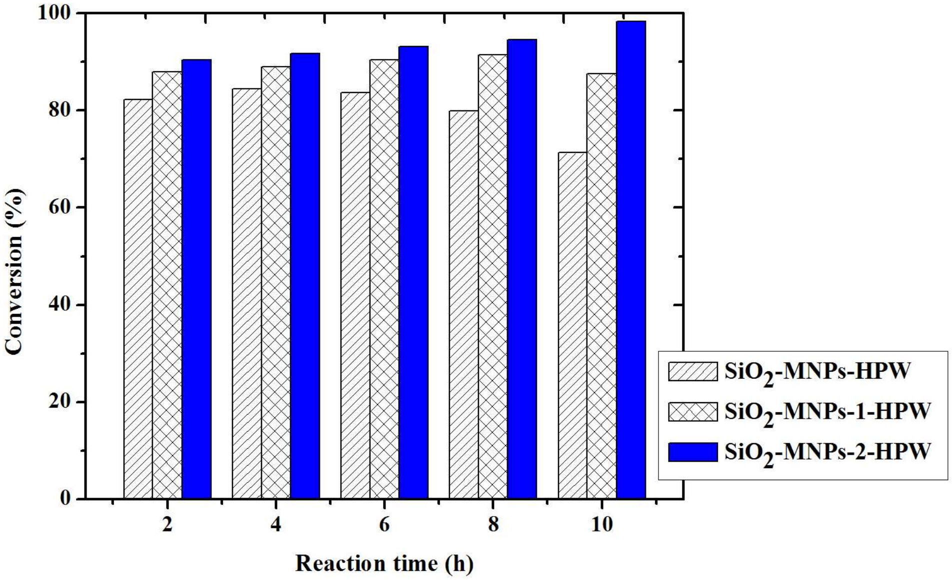


Fig. 4 Kinetic data of esterification of palmitic acid with methanol over SiO2-MNP-HPW systems. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC.

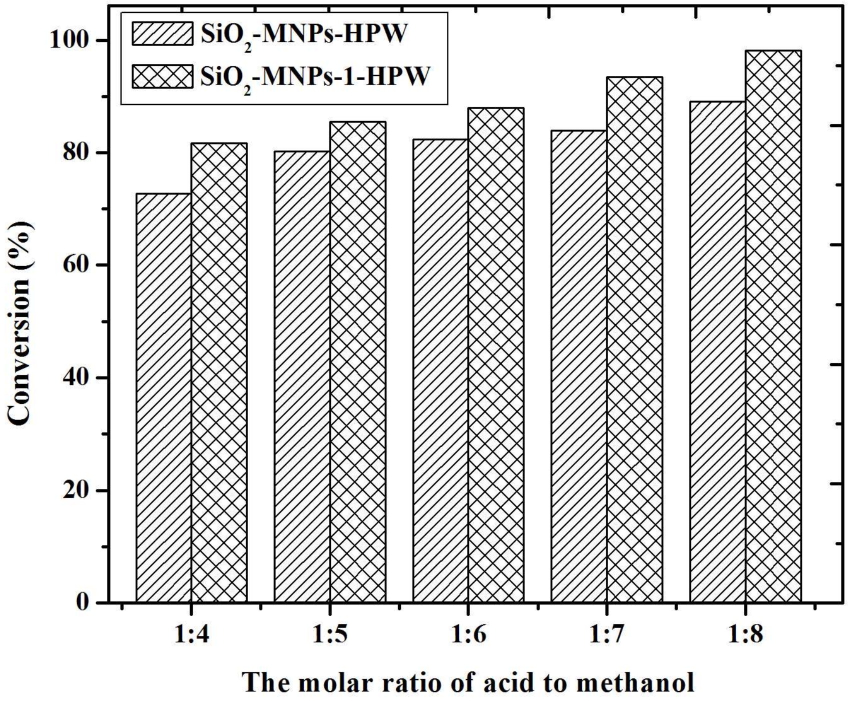


Fig. 5 The effect of methanol/acid molar ratio on the ester conversion over different catalysts. Reaction conditions: amount of catalyst 8.2 wt%, 65 ºC for 2 h.

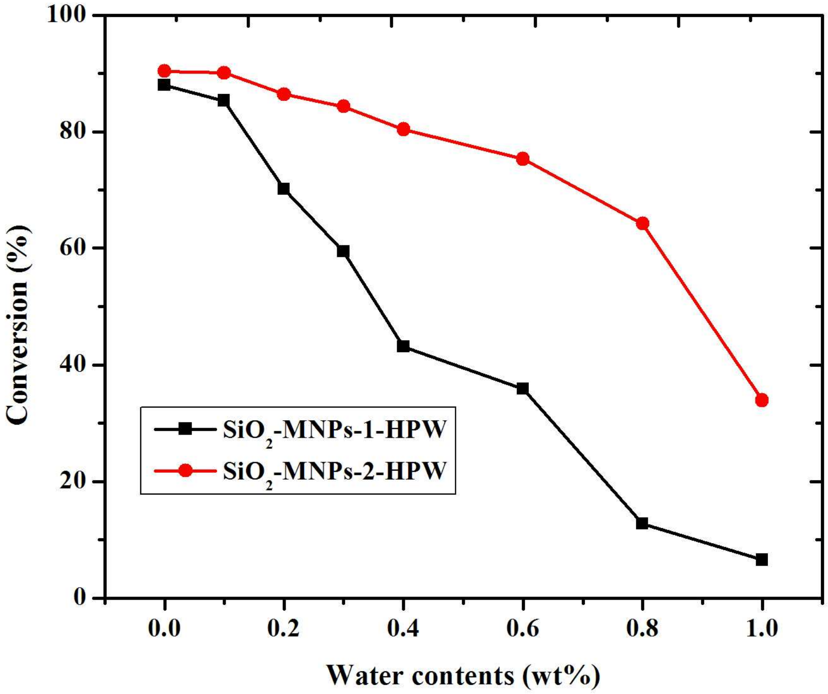


Fig. 6 Effect of water on activity of SiO2-MNPs-1-HPA and SiO2-MNPs-2-HPA. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC for 2 h.

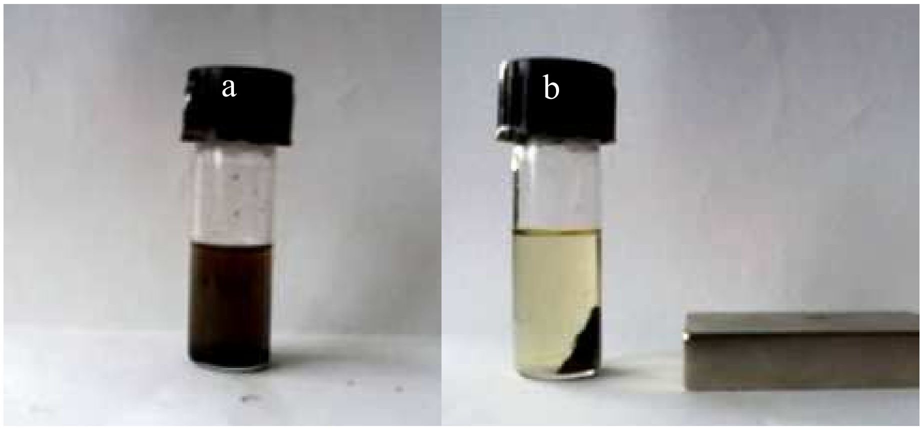


Fig. 7 Photographs of magnetic separation after the esterification of palmitic acid with methanol, a: without, b: with the external magnetic field.

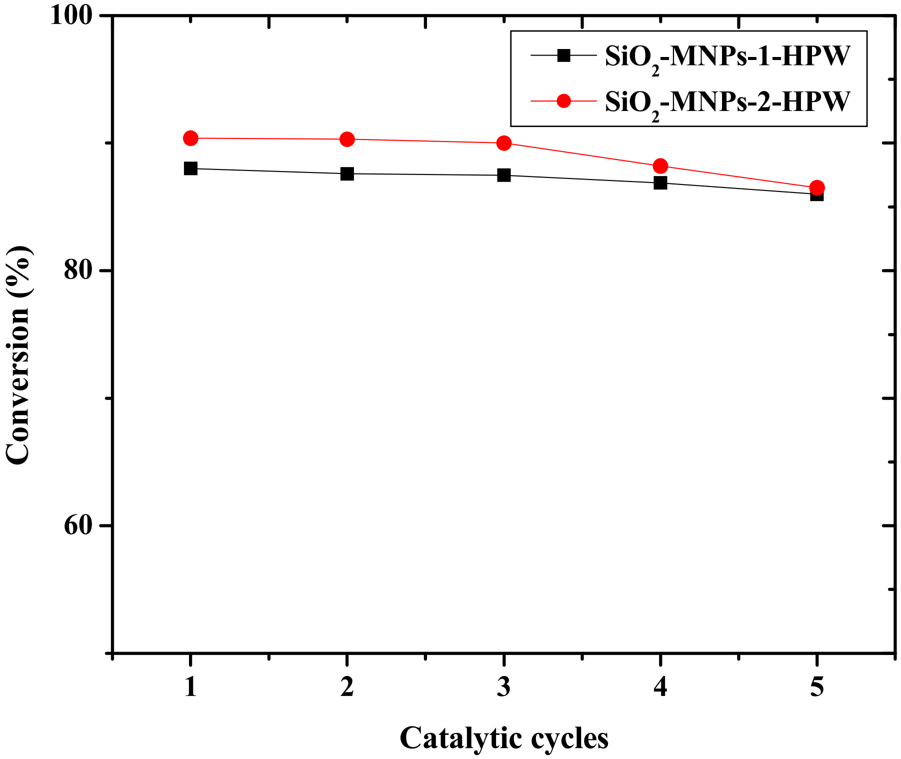
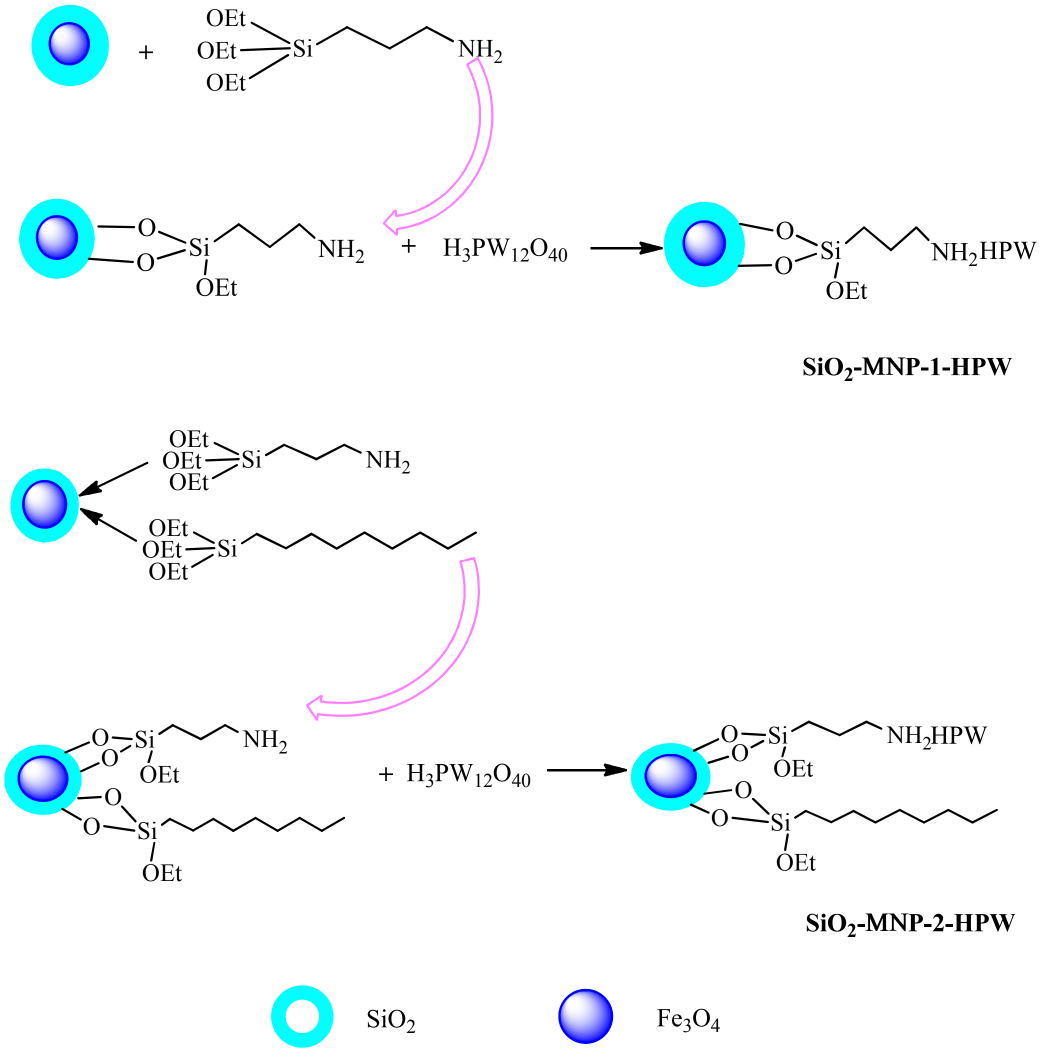


Fig. 8 Catalytic cycles of SiO_2-MNPs-1-HPA and SiO_2-MNPs-2-HPA recycling in esterification of palmitic acid with methanol. Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC for 2 h.



Scheme 1 Preparation strategy of SiO$_2$-MNP-1-HPW and SiO$_2$-MNP-2-HPW.

Table 1 Esterification of palmitic acid with methanol over different catalytic systems based on HPA.

Catalysts	Acid content mmol/g	Conversion (%)	TOF ^{a}(h^{-1})	TOF ^{b}(h^{-1})
$H_3PW_{12}O_{40}$	0.893	84.1	0.58×10^2	0.65×10^2
no catalyst	—	40.6	—	—
SiO_2-MNP	—	41.7	—	—
SiO_2-MNP-HPW (first cycle)	0.579	82.3	1.62×10^2	2.8×10^2
SiO_2-MNP-HPW (second cycle)	—	78.1	1.54×10^2	2.66×10^2
SiO_2-MNP-1-HPW (first cycle)	0.453	88.0	1.99×10^2	4.39×10^2
SiO_2-MNP-1-HPW (second cycle)	—	87.6	1.98×10^2	4.37×10^2
SiO_2-MNP-2-HPW (first cycle)	0.429	90.4	2.12×10^2	4.95×10^2
SiO_2-MNP-2-HPW (second cycle)	—	90.3	2.12×10^2	4.95×10^2

Reaction conditions: molar ratio of methanol to acid 6:1, amount of catalyst 8.2 wt%, 65 ºC for 2 h.

$$\mathrm{TOF}^{a} = \frac{\text{number of moles of FFA reacted}}{\text{number of moles of HPW} \times \text{reaction time}}$$

$$\mathrm{TOF}^{b} = \frac{\text{number of moles of FFA reacted}}{\text{number of moles of acid protons} \times \text{reaction time}}$$

Supplementary data

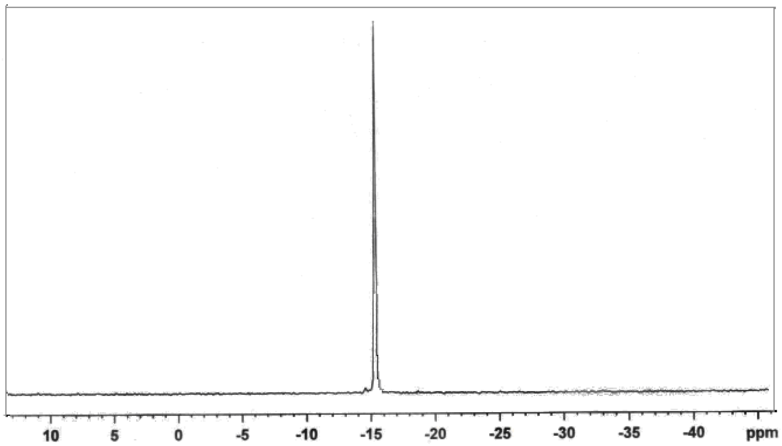


Fig. S1 The ^{31}P NMR spectra of $H_3PW_{12}O_{40}$

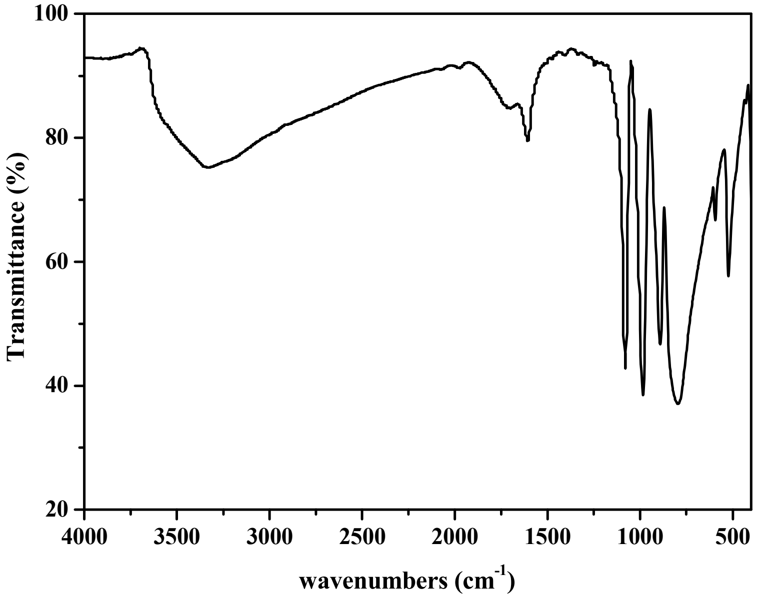


Fig. S2 IR spectrum of $H_3PW_{12}O_{40}$