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Facile Preparation of Ionic Liquid Functionalized Magnetic Nano-Solid Acid Catalysts for Acetalization Reaction

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Abstract The facile two-step preparation procedure of a novel magnetic nano-solid acid catalyst is described, which includes grafting an ionic liquid onto Fe_3O_4 nanoparticles, followed by the sulfonation of phenyl groups in the ionic liquid. The catalytic performance of this novel material has been systematically studied in the acetal formation of benzaldehyde and ethylene glycol. The experimental results testify this catalyst possesses high catalytic activity with a yield of 97% under mild reaction conditions. Furthermore, the catalyst is readily separated using a permanent magnet and it is reusable without any significant decrease in catalytic activity.

Keywords Magnetism · Solid acid catalyst · Nanoparticle · Ionic liquid · Functionalization

1 Introduction

Homogenous acid catalysts including corrosive protic acids [1, 2], Lewis acids such as $AlCl_3$, $FeCl_3$ [3, 4] are widely applied in the large-scale synthesis of industrial bulk chemicals as well as the production of fine chemicals. However, it is urgent to replacing highly corrosive, hazardous and polluting acid catalysts with eco-friendly and renewable solid acid catalysts for meeting green chemistry demands, which may be a challenge of green chemistry and green engineering [5, 6]. Recently, the facile recovery and reuse of homogeneous catalysts by covalent tethering to heterogeneous support are extensively investigated, which become an important field of catalytic research [7, 8]. Nanoparticles as heterogeneous catalyst supports have received increasing attention because when the diameter of the particles decreases to the nanometer scale, ample external surface area emerged, which allows a high dispersion of the active species and provides a large amount of the active and accessible centers [9]. Moreover, magnetic nanoparticles (MNPs) offer an added advantage of the separation and eliminate the filtration step for recycling catalyst after completion of the reaction [10]. However, nano-scale magnetic solid acid materials were few reported although MNPs-supported basic ionic liquids [11], amino group [12], composite hydroxide materials [13] had been prepared. Recently, several different sulfonic acids grafted onto silica-coated magnetic nanoparticle supports were reported by Jones and coworkers [14], and the synthesis of these catalysts was more complex and expensive. It is still attractive to prepare efficient magnetic solid acid catalysts using the cheap raw material and simple method in the synthetic chemistry.

Herein, we have prepared a magnetic nano-solid acid catalyst via grafting an ionic liquid onto Fe_3O_4 nanoparticles followed by sulfonation of phenyl groups in the ionic liquid. This catalyst exhibited high catalytic activity in the acetalization reactions, and can be easily separated after completion of the reaction and reused without any significant reduction of catalytic activity.

2 Experimental

2.1 Preparation of Materials

2.1.1 Grafting an Ionic Liquid onto MNPs

Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation method [15]. 0.18 M $Fe(NO_3)_3$ solution of

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400 mL and 0.12 M $FeSO_4$ solution of 400 mL were added in 1,000 mL four-neck rounded bottom flask at room temperature, and then 25 wt% $NH_3 \cdot H_2O$ solution of 96 mL was quickly added to the mixture solution at 313 K under mechanical stirring vigorously in N_2 protecting. After 15 min, the mixtures were heated to 333 K and held for 5 min to form stable nanoparticles (Fe_3O_4) at the same temperature. The resultant black precipitates (Fe_3O_4 nanoparticles) were separated by using a permanent magnet, washed with deionized water and dried in vacuum at 353 K for 8 h.

The grafting an ionic liquid onto MNPs were carried out by the procedures as follows, a 1,000 mL three-necked round-bottomed flask equipped with a condenser, a thermocouple, and mechanical stirrer were charged with freshly prepared Fe_3O_4 nanoparticles of 6.0 g, 3-chloropropyltrimethoxysilane (CPTMO) of 29.8 g, 47.2 g triphenylphosphine (PPh_3) and 480 mL dried toluene. The mixtures were kept for 48 h under reflux with continuous stirring at 383 K. The final product was collected by magnetic decantation, washed with ethanol, and dried in vacuum at 353 K overnight (denoted as MNPsSi-PPh_3).

2.1.2 *Sulfonation of MNPsSi-PPh_3*

The sulfonation of MNPsSi-PPh_3 was completed by the method of vapour-phase sulfonation as described [16]. The sulfonation was performed in a Teflon-lined autoclave where MNPsSi-PPh_3 powders of 3 g were contacted with the vapor from 50 mL 50 wt% SO_3/H_2SO_4 at 353 K for 72 h. The sulfonated samples were washed with hot deionized water (>353 K) to remove any physically adsorbed species until the sulfate ions were not detected in the upper layer solution. After the separation, the samples were dried at 373 K overnight in air (denoted as MNPsSi-PPh_3-SO_3H).

2.2 Characterization

The X-ray diffraction (XRD) patterns of all samples were recorded with a Rigaku Corporation D/MAX2200PC diffractometer using Cu-Kα radiation ($\lambda = 0.1541$ nm), and the data were collected from 10° to 70° (2θ) with a scan speed of 6°/min. Transmission electron microscopy (TEM) images were taken on a JEOL-JEM-2010 transmission electron microscope using an accelerating voltage of 200 kV. Magnetic properties were measured at room temperature using a vibrating sample magnetometer (VSM). Fourier transform infrared (FT-IR) spectra were recorded on a Nexus-870 Fourier-transform spectrophotometer using KBr pellet technique with a measuring range 400–4,000 cm^{-1}.The amount of Si, P and S in the synthesized samples was quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a thermo elemental PERKIN-ELMERPLASMA-2000 spectrometer. The amount of acid sites was quantified by acid–base titration.

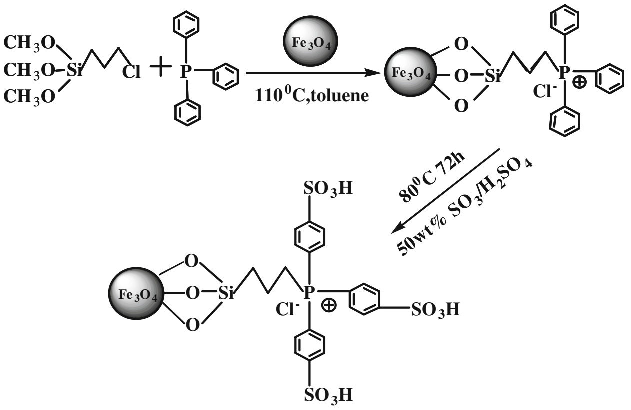
2.3 Catalytic Reactions

The acetalization reaction of benzaldehyde (PhCHO) with ethylene glycol (EG) was carried out in a 100 mL three-necked flask, 0.06 g catalysts were added to a mixture of 30 mmol PhCHO, 90 mmol EG and 185 mmol cyclohexane. The reaction was conducted with vigorous magnetic stirring under reflux for 2 h. The products were confirmed by GC–MS. The reaction conversion was monitored by gas chromatography (GC) analysis in reference to a toluene internal standard.

3 Results and Discussion

3.1 Synthesis of Materials

Scheme 1 shows the schematic representation of the synthetic pathway for MNPsSi-PPh_3-SO_3H solid acid catalysts by a two-step chemical modification. In the synthesis, the formation of ionic liquids and its grafting on Fe_3O_4 nanoparticles are achieved by one-pot method using inexpensive and routine chemicals (CPTMO and PPh_3). Moreover, the sulfonation of MNPsSi-PPh_3 can be easily accomplished by contacting the samples with the vapor from fuming sulfuric acid in a closed autoclave. In comparison with the methods reported by Jones and coworkers, the whole synthesis procedure of MNPsSi-PPh_3-SO_3H is simple and inexpensive, and it is suitable for the large-scale production of magnetic solid acid catalyst. Besides, the ionic liquids can be tightly grafted on the surface of Fe_3O_4



Scheme 1 The synthesis process of MNPSi-PPh_3-SO_3H solid acid catalysts

and the linked PPh_3 provide a chance to obtain more acid sites by the sulfonation. The changeable cation group may be used for further modification of catalyst.

3.2 X-Ray Diffraction

Figure 1 shows the large-angle XRD patterns of these samples. The XRD pattern of Fe_3O_4 clearly showed six reflection peaks and confirmed the formation of a cubic spinel ferrite structure, and the crystallite size was calculated from the Scherrer formula and found to be an average diameter of about 11.3 nm (Fig. 1a). The same six reflection peaks appeared in the XRD patterns of the synthesized samples of MNPsSi-PPh_3-SO_3H (Fig. 1b). No obvious change of the average particle size was observed, which suggested that the Fe_3O_4 crystallite phase was still maintained in the MNPsSi-PPh_3-SO_3H nanoparticles.

3.3 Transmission Electron Microscopy

The nanoparticle size and morphology of Fe_3O_4 nanoparticles, MNPsSi-PPh_3-SO_3H were investigated by TEM. As shown in Fig. 2a and b, Fe_3O_4 nanoparticles (Fig. 2a) displayed an approximate spherical shape with the particle size range from 8 to 13 nm and slight agglomeration, in agreement with the results of XRD. Figure 2b shows the TEM image of the synthesized samples MNPsSi-PPh_3-SO_3H, although aggregated phenomenon of some nanoparticles was also observed, the particle diameters of the nanoparticles still remained in the range of 8–13 nm. It indicated that the two-step chemical modification of the Fe_3O_4 was not caused the significant increase of the particle size, and the advantages of magnetic nanoparticles can be maintained.

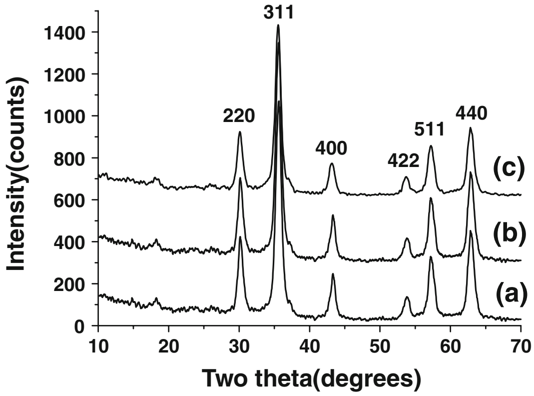


Fig. 1 Large-angle XRD patterns of (*a*) Fe_3O_4 nanoparticles, (*b*) the synthesized samples of MNPsSi-PPh_3-SO_3H, (*c*) the synthesized samples after five cycle reusage

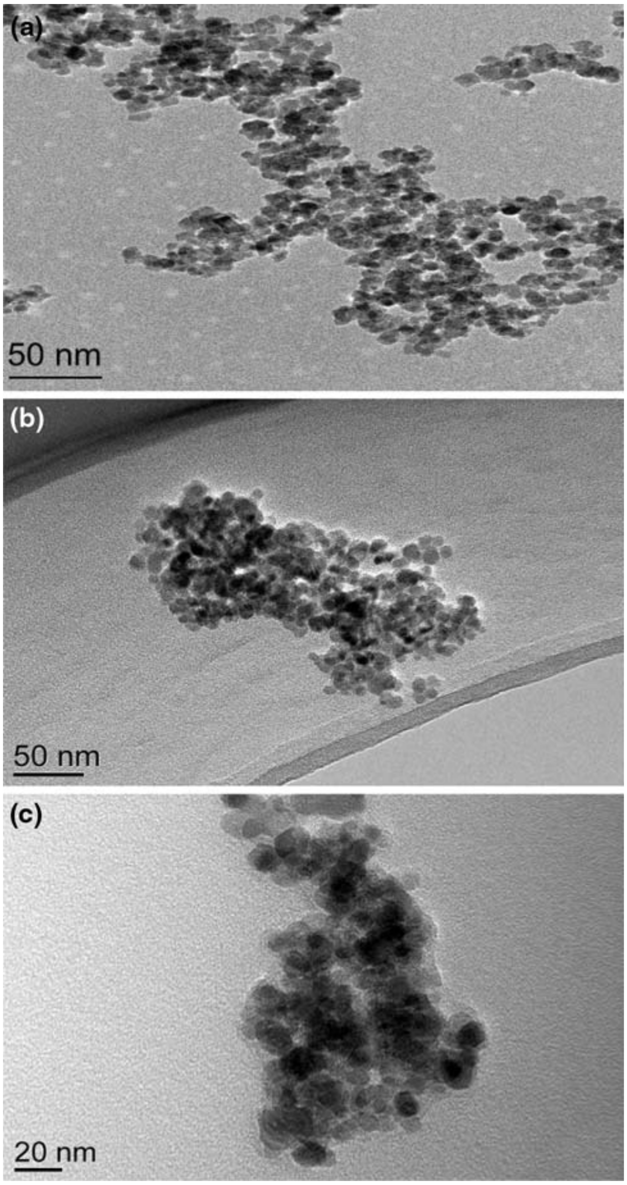


Fig. 2 TEM images of **a** Fe_3O_4 nanoparticles, **b** the synthesized samples of MNPsSi-PPh_3-SO_3H, **c** the synthesized samples after five cycle reusage

3.4 Magnetic Properties

The magnetic properties of these samples were characterized by vibrating sample magnetometer (Fig. 3). All of the samples were suitable for supporting materials in separation owing to their superparamagnetic properties. The saturation magnetization of Fe_3O_4 nanoparticles (Fig. 3a) and MNPsSi-PPh_3-SO_3H (Fig. 3b) was 47.0 and 45.1 emu/g, respectively. A slight decrease of the saturation magnetization of the MNPsSi-PPh_3-SO_3H was due to the successful grafting of ionic liquids on the surface of Fe_3O_4 nanoparticles.

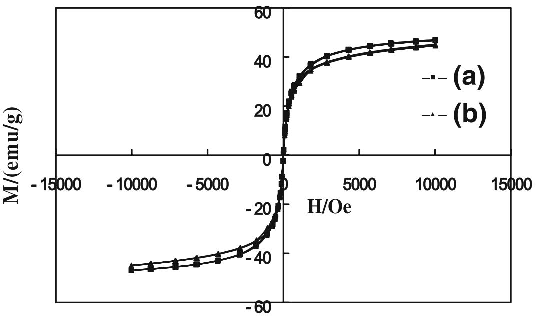


Fig. 3 Magnetization curves at room temperature of (*a*) Fe_3O_4 nanoparticles and (*b*) MNPsSi-PPh_3-SO_3H

3.5 Fourier Transform Infrared Spectroscopy

Figure 4 shows the FT-IR spectra of the Fe_3O_4 nanoparticles, MNPsSi-PPh_3, and MNPsSi-PPh_3-SO_3H. FT-IR spectrum of the MNPs showed similar spectrum to Fe_3O_4 materials as described in literature [17]. In comparison to Fig. 4a, a strong peak near 1,100 cm^{-1} (corresponding to the Si–O stretch) and the relatively weak peaks at 2,800–3,000 cm^{-1} (ascribed to the stretching vibrations of C–H) were observed in the FT-IR spectra of MNPsSi-PPh_3 (Fig. 4b), which implied that CPTMO was bonded to Fe_3O_4 nanoparticles. The distinguished feature in the FT-IR spectra of MNPsSi-PPh_3-SO_3H was the appearance of a new peak at 1,032 cm^{-1}, which was assigned to the symmetric stretching vibration of S=O group (Fig. 4c). These results were in agreement with the chemical component of the materials prepared.

3.6 ICP-AES Analyses and Acid–Base Titrations

ICP-AES analyses testified that Si, S, P had been supported on Fe_3O_4 nanoparticles. The molar ratio of Si, P determined was 6.29: 1, higher than theoretic value in an ionic liquid. The result implied that CPTMO without forming the ionic liquid tag may be also supported on the surface of Fe_3O_4 nanoparticles. Although CPTMO can not be further sulfonated, it resulted in the formation of an inert barrier on the surface of Fe_3O_4 nanoparticles and may inhibit the loss of the ferrite. The molar ratio of S, P was 1.14: 1 in the MNPsSi-PPh_3-SO_3H samples, suggesting that three phenyl groups of PP_3 were partly functionalized by –SO_3H group.

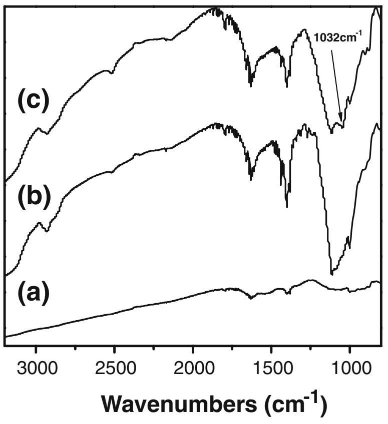


Fig. 4 FT-IR spectra of (*a*) Fe_3O_4 nanoparticles, (*b*) MNPsSi-PPh_3, (*c*) MNPsSi-PPh_3-SO_3H

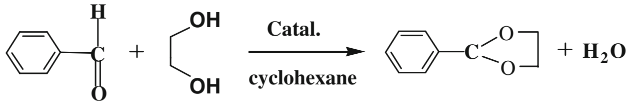
Acid–base titrations were used to measure acid capacity that is the quantity of catalytically active ingredients of samples as described in the literature [18]. In a typical measurement, the samples of 0.5 g were suspended in 0.02 M KCl solution of 50 mL and then was stirred for 20 min and titrated with 0.01 M KOH in the presence of phenolphthalein. The results revealed that the samples of MNPsSi-PPh_3-SO_3H possessed 0.51 mmol/g acid amount. Under the same sulfonation conditions, the acidity from the direct sulphonation of Fe_3O_4 nanoparticles was not observed. However, for the sulfonation of CPTMO modified Fe_3O_4 nanoparticles, the acid–base titration results revealed 0.02 mmol/g acid amount. Generally, the sulfonation of CPTMO modified Fe_3O_4 nanoparticles was difficult in this synthesis condition, which had a negligible contribution to the total acid amount of MNPsSi-PPh_3-SO_3H materials.

3.7 Catalytic Studies

Acetals are widely used in carbohydrate synthesis and organic synthesis reactions of carbonyl protection in the synthesis of the fine chemicals and pharmaceutical industries [19–21]. The acetalization reaction (Scheme 2) of benzaldehyde with ethylene glycol as a test reaction was carried out to investigate the catalytic properties of the prepared magnetic solid acid materials.

3.7.1 Effect of the Reaction Conditions

The different reaction conditions had the remarkable effect on the yield of acetal in the acetalization reaction (Fig. 5). As shown in Fig. 5a, the yield of acetal increased with the increment of the catalyst mass, and the highest yield (97%) of acetal was obtained when the amount of catalyst used was 0.06 g. With further increasing of the catalyst mass, the yield of acetal decreased. The results indicated that the suitable amount of catalyst used was important in this



Scheme 2 Schematic illustration for the acetalization reaction of benzaldehyde with ethylene glycol

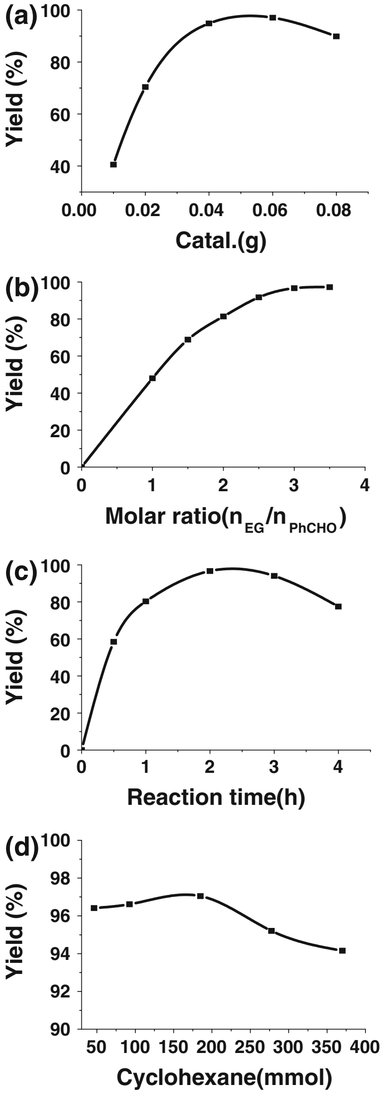


Fig. 5 The effect of the reaction conditions on the yield of acetal: the amount of MNPsSi-PPh_3-SO_3H (**a**), molar ratio of EG/PhCHO (**b**), reaction time (**c**) and cyclohexane (**d**). **a** Reaction conditions: n_{EG}:n_{PhCHO} = 3:1; cyclohexane: 185 mol; reflux temperature: 354 K; reaction time: 2 h. **b** Reaction conditions: the catalyst: 0.06 g; cyclohexane: 185 mmol; reflux temperature: 354 K; reaction time: 2 h. **c** Reaction conditions: the catalyst: 0.06 g; n_{EG}:n_{PhCHO} = 3:1; cyclohexane: 185 mmol; reflux temperature: 354 K. **d** Reaction conditions: the catalyst: 0.06 g; n_{EG}:n_{PhCHO} = 3:1; reflux temperature: 354 K; reaction time: 2 h

acetalization reaction, and the excess acid amount may promote the occurrence of the reverse reaction.

The molar ratio of EG/PhCHO played an important role for the yield of acetal in the acetalization reaction (Fig. 5b). The results showed that the yield of acetal was directly proportional to the molar ratio of EG to PhCHO and the conversion of PhCHO can be improved by increasing the amount of EG. When the molar ratio of EG/PhCHO was 3:1, the best yield obtained was 97%. Further raising the amount of EG, the increase in yield was negligible.

The optimal reaction time to get the highest yield was 2 h under the optimum conditions (including the appropriate amounts of EG, PhCHO, and catalyst). The decrease in the yield of acetal observed in prolonged reaction time was due to the hydrolysis of the product acetal (Fig. 5c).

Because a great quantity of water was produced in the acetalization reactions of PhCHO with EG, the cyclohexane was used as an agent entraining water in order to rise the yield of acetal. The effect of the amount of the cyclohexane used on the yield was studied. The experimental results in Fig. 5d illustrated that when cyclohexane of 185 mmol was added in the reactive system, the most of water produced in the reaction was entrained and the highest yield was obtained.

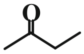
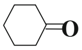
3.7.2 The Acetalization or Ketalization of Three Different Aldehyde or Ketone with EG

Under the optimal reaction conditions, the acetalization or ketalization of the EG with different aldehyde (or ketone) were performed. The results were showed in Table 1. The conversion of propionaldehyde, butanone and cyclohexanone was 96, 95 and 94%, respectively. It indicated that the magnetic solid acid catalysts prepared possessed an excellent performance in the acetalization or ketalization of the carbonyl.

3.7.3 Recycling of the Catalyst

Reusability of the catalyst was an important character and a performance criterion of any industrial process. In this method reported herein, the catalyst can be separated by simple magnetic decantation by using a permanent magnet at the end of reaction and reused after washing with ethanol and then drying in vacuum at 323 K for 8 h. After the fifth

Table 1 The acetalization or ketalization of different aldehyde or ketone with EG

Entry	Substrate	Yield (%)[a]	Conversion (%)	Selectivity (%)
1		96	96	100
2		95	95	100
3		94	94	100

[a] Yield = Conversion × Selectivity

Reaction conditions: the catalyst: 0.06 g; n_{EG}:$n_{\text{aldehyde or ketone}}$ = 3:1; cyclohexane: 185 mmol; reflux temperature: 354 K; reaction time: 2 h

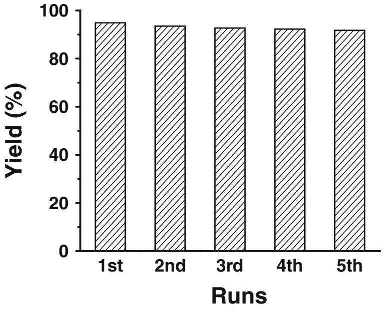


Fig. 6 The reusability of MNPsSi-PPh$_3$-SO$_3$H in the acetalization reactions of PhCHO with EG. Reaction conditions: the catalyst: 0.06 g; n_{EG}:n_{PhCHO} = 3:1; cyclohexane: 185 mmol; reflux temperature: 354 K; reaction time: 2 h

cycle, the acid amount of the catalyst was still maintaining 0.40 mmol/g and the yield was only slightly decreased, indicating that the catalyst possessed an excellent reusability under the reaction conditions (Fig. 6).

The crystal structure and the appearance of the samples after five cycle reusage were also investigated by XRD and TEM. The results were shown in Figs. 1c and 2c. Compared with those of MNPsSi-PPh$_3$-SO$_3$H (Figs. 1b, 2b), the X-ray diffraction patterns, the appearance and the average particle diameters of the samples after five cycle reusage revealed no obvious changes (Figs. 1c, 2c), which indicated that this material may be a more stable catalyst for the acid catalyzed reaction.

4 Conclusions

In conclusion, a magnetic nano-solid acid catalyst, MNPsSi-PPh$_3$-SO$_3$H, is prepared by a simple method, and possesses an excellent performance in the acetalization of the carbonyl under mild reaction conditions, and it can be reusable without significant loss in catalytic activity. This kind of novel magnetic nano-solid acid catalyst may be wide applied in acid-catalyzed reactions.

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