



# Hydrophobicity-enhanced magnetic solid sulfonic acid: A simple approach to improve the mass transfer of reaction partners on the surface of the heterogeneous catalyst in water-generating reactions

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## ABSTRACT

Two novel and environmentally benign organosulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts **1** ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Et-PhSO}_3\text{H}$ ) and **2** ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MeEt-PhSO}_3\text{H}$ ) were prepared and their surface hydrophobicity was assessed by esterification reaction of fatty alcohols. Also, their water-tolerance in two water-generating reactions was investigated, namely: synthesis of bis(indolyl)methane and the Biginelli reaction of benzaldehyde, methyl acetoacetate, and urea under solvent-free conditions. In these reactions, the catalyst **2** that was more hydrophobic and water-resistant showed higher catalytic activity and was characterized extensively by various techniques. This catalyst was successfully used in the Biginelli reaction of a series of aldehydes,  $\beta$ -keto esters, and urea/thiourea for the synthesis of a diverse range of pharmacologically active 3,4-dihydropyrimidin-2-one/thione (DHPM) derivatives. The catalyst **2** was easily separated by an external magnet and the recovered catalyst was reused in five cycles without any significant loss of activity.

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## 1. Introduction

During the last two decades, with the development of nanotechnology, numerous nanomaterials have been designed and created. Among them, hybrid organic–inorganic materials based on  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core–shell magnetic nanoparticles as special immobilizing carrier of the catalysts' active sites have shown significant contribution to the current researches [1,2]. This is due to their inherent properties such as biocompatibility, easy renewability and recovery by magnetic separation, thermal stability against degradation, large surface area and higher loading of active sites. The aforementioned advantages of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core–shell magnetic nanoparticles over the other heterogeneous catalysts have brought new opportunities for the design and synthesis of novel solid catalysts [1–3]. Although many investigations have been conducted on the synthesis and characterization of acidic magnetic nanoparticles [4–8], no attention has been paid to combining

hydrophobicity with acidity of materials for providing bifunctional  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core–shell magnetic nanoparticles bearing both sulfonic acid and terminal organic groups protruding on the silica surface of nanocomposites. Introduction of sulfonic acid and organic groups onto the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core–shell magnetic nanoparticles is interesting since the combination of both functionalities (acidic and hydrophobic) [9–13] allows creation of a less polar organic environment with a relatively strong acidity for acid-catalyzed reactions. In many acid-catalyzed reactions by silicious based solid acids, the water produced as a by-product is co-adsorbed on the silanol surface of the catalyst [14–22]; thus, the co-adsorbed water poisons the surface of the catalyst and produces more hydrophilic environment, reducing the performance of the catalyst in organic transformations (Scheme 1).

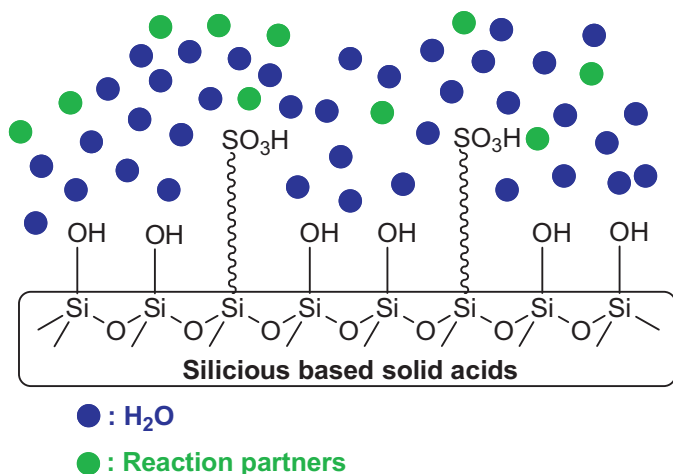
In addition to poisoning of the catalyst's surface in the presence of water molecules as the reaction by-product, the active acidic sites of the catalysts are also subjected to deactivation which inhibits the progress of reactions (Scheme 1) [14–22]. On the other hand, the polarities of the reactants and products, hydrophobic–hydrophilic balance on catalyst's surface, and the acidity of catalysts also have a considerable effect on the reactions' progress. Further research studies addressed the design, synthesis and utilization of the catalytic applications of other surface modified  $-\text{SO}_3\text{H}$  solid materials in order to optimize the performance of catalysts [19–26]. As far

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**Scheme 1.** Schematic representation of interaction between water and silanol surface and sulfonic acid active sites of solid acids in water-generating reactions.

as we know, there is not any report about surface hydrophobicity on sulfonic acid-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell magnetic nanoparticles; hence, this preliminary work represents the first and a unique example including a hydrophobic  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$  type magnetic material for catalysis in water-generating reactions; thus, offered a new approach to be researched and explored.

As part of our efforts in exploring novel heterogeneous catalysts for organic reactions [23–27], we have designed, prepared and characterized two novel water-tolerant and sulfonic acid organic–inorganic hybrid catalysts based on  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell magnetic nanoparticles:  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Et-PhSO}_3\text{H}$  (**1**, Scheme 2) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Me&Et-PhSO}_3\text{H}$  (**2**, Scheme 2); also, the acidity, hydrophobicity, water-tolerance and utility of these catalysts were investigated. In this context, we wish to show that in water-generating reactions involving both hydrophobic and hydrophilic reaction partners, catalyst **2** with hydrophobic character on the surface is much more active and much more robust than catalyst **1**.

## 2. Experimental

### 2.1. Chemicals and characterizations

All chemicals were purchased from Merck and Aldrich Chemical Companies. Melting points were determined on a Büchi melting point B-540 apparatus. NMR spectra were recorded at 400 ( $^1\text{H}$ ) and 100.6 ( $^{13}\text{C}$ ) MHz, respectively, on a commercial Bruker DMX-400 instrument using  $\text{DMSO-}d_6$  as solvent. IR spectra were recorded on an ABB Bomem Model FTLA 2000 spectrophotometer using KBr discs. The magnetic measurement of samples was carried out in a vibrating sample magnetometer (VSM) (4 in., Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. X-ray diffraction (XRD) patterns were recorded by an Xpert MPD, X-ray diffractometer using  $\text{Cu K}\alpha$  radiation. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (NETZSCH TG 209F1 Iris) with a heating rate of  $10^\circ\text{C min}^{-1}$ . SEM was carried out on a VEGA\TESCAN-LMU instrument. Transmission electron microscope, TEM (Philips CM-10) was also used to obtain TEM images. Elemental analyses for C, H and S were performed using a Heraeus CHN-O Rapid analyzer. The  $\text{N}_2$  and  $\text{H}_2\text{O}$ -sorption was carried out in a Belsorp-mini-BEL Japan, Inc. at 298 K (see ESI).

### 2.2. Preparation of materials

**Preparation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ .** The synthesis of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was achieved using the procedure described by Luo and co-workers [28]. This procedure involved a synthetic strategy based on the hydrolysis and condensation of tetraethoxysilane (TEOS) on the surface of  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles. In a typical preparation procedure, ferric chloride hexahydrate  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (11.0 g, 40.7 mmol) and ferrous chloride tetrahydrate  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  (4.0 g, 20.1 mmol) were dissolved in deionized water (250 mL) under nitrogen atmosphere with mechanical stirrer at  $85^\circ\text{C}$ . The pH value of the solution was adjusted to 9–11 using aqueous  $\text{NH}_3$  (25%). After continuous stirring for 4 h, the magnetite precipitates were washed with distilled water until the pH value descended to 7.0. The black precipitate ( $\text{Fe}_3\text{O}_4$ ) was collected with a permanent magnet at the bottom of the reaction flask. The silica coated core-shell magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$  MNPs) were prepared by an ultrasonic pre-mixing of a dispersion of the above black precipitate (2.0 g) with ethanol (400 mL) for approximately 30 min at room temperature. Then, aqueous  $\text{NH}_3$  (25%, 12 mL) and TEOS (4.0 mL) were slowly added successively. The resulting solution was mechanically stirred continuously for 24 h, after which the black precipitate product ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ) was collected by magnetic separation and washed with ethanol ( $3 \times 15$  mL) and dried under vacuum overnight at room temperature (Scheme 2).

**Preparation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Et-PhSO}_3\text{H}$  (**1**).** The surface functionalization of the silica coated magnetic nanoparticles with sulfonyl groups was carried out by adding 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPETS, 0.4 g, 1.23 mmol) to dry toluene (35 mL) containing silica-coated magnetic nanoparticles (1.0 g). The resulting mixture was stirred for 24 h and then washed with toluene ( $2 \times 15$  mL) and distilled water. Finally, the solid was suspended in  $\text{H}_2\text{SO}_4$  (1 M) solution for 2 h, washed several times with water and dried at room temperature under vacuum overnight to give the corresponding catalyst **1** (Scheme 2).

**Preparation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Me&Et-PhSO}_3\text{H}$  (**2**).** This procedure involved a synthetic strategy based on the co-condensation of CSPETS and trimethoxymethylsilane (TMMS) on the silica coated magnetic nanoparticles. In a typical preparation procedure, CSPETS (0.2 g, 0.62 mmol) and TMMS (0.2 g, 1.47 mmol) were added to dry toluene (35 mL) containing silica-coated magnetic nanoparticles (1.0 g). The resulting mixture was stirred for 24 h and then washed with toluene ( $2 \times 15$  mL) and distilled water. Finally, the solid was suspended in  $\text{H}_2\text{SO}_4$  (1 M) solution for 2 h, washed several times with water and dried at room temperature under vacuum overnight to give the corresponding catalyst **2** (Scheme 2).

### 2.3. Acidity of the catalysts (**1** and **2**)

The concentration of sulfonic acid groups was quantitatively estimated by ion-exchange pH analysis [8,28,29]. The catalyst (50 mg) was added to an aqueous solution of NaCl (1 M, 25 mL), and the resulting mixture was stirred for 3 days, after which titration by NaOH (0.05 M) was carried out on the above obtained solutions. The acid amount of **1** and **2** was determined to be 2.22 and  $0.70 \text{ mmol g}^{-1}$ , respectively.

### 2.4. General procedure for the one-pot preparation of 3,4-dihydropyrimidin-2-ones/thiones

A mixture of aldehyde (2 mmol), methyl acetoacetate (2 mmol), urea/thiourea (2.4 mmol) and catalyst **2** (7.1 mg, 0.5 mol %) (in the case of thiourea, 1 mol % of the catalyst was used) was stirred at  $100^\circ\text{C}$  for an appropriate time under solvent-free condition (Table 3). The progress of the reaction was monitored by thin layer

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