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Sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 nanocrystallites as a magnetically Brønsted acid for *N*-formylation of amines

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Dedicated to memory of Baradaraneh Dastvareh.

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A B S T R A C T

Treatment of aqueous formic acid (85%) with structurally diverse amines in the presence of a catalytic amount of sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 [HAp@-γ-Fe_2O_3] (0.9 mol.%) as a heterogeneous, reusable and highly efficient catalyst gave the corresponding formamides in good to excellent yields at room temperature. The magnetically catalytic system was recovered by-passing time consuming filtration operation by using an external magnet device. In addition to facility, this methodology, it also enhances product purity and promises economic as well as environmental benefits.

1. Introduction

Due to the high surface area:volume ratios, nanoparticles can effectively improve the loading and the catalytic efficiency of immobilized catalysts. Therefore the use of nanostructured materials as supports for different versions of catalyst immobilization is ever-increasing [1,2]. In addition, these particles can be dispersed into solvents, forming stable dispersions. In spite of the advantages of heterogenized catalysts, the tedious recycling of catalysts by filtration and the inevitable loss of some solid catalyst in the separation process, especially with air sensitive materials, are some of the drawbacks of the traditional procedures [3,4]. Therefore, there is more interest to introduce more efficient manners for catalyst recovery, especially from the standpoint of green chemistry.

Magnetic nanoparticles are receiving increasing interest in recent years [5–7]. The magnetic nature of these particles allows for easy recovery and recycling of the catalysts by an external magnetic field, which may optimize operational cost and enhance product's purity. However, an unavoidable problem associated with "naked" metallic or metal oxide nanoparticles is instability over longer periods of time due to high initial chemical activity, easy oxidation in air, loss of magnetism, dispersion and agglomeration due to the large surface area to volume ratio and the magnetic dipole–dipole attractions between particles. It was also found that pure Fe_3O_4 NPs were oxidized and easily lost their magnetism [8]. For many applications it is thus crucial to develop protection strategies to chemically stabilize the naked magnetic nanoparticles. It was reported that formation of a passive coating of magnetic NPs could prevent their aggregation in solutions and thus improve their chemical stability. The applied coating strategies can roughly be divided into two major groups: coating with an organic shell, including surfactants and polymers, or coating with inorganic components, including silica, carbon, precious metals and recently, calcium hydroxyapatite [9–16]. Calcium hydroxyapatite, the main component of bone and teeth, is of considerable interest in many areas because of ion-exchange ability, adsorption capacity and acid–base properties. It has been established that the CaHAp surface possess several kinds of P–OH groups acting as adsorption sites for various molecules such as H_2O, CH_3OH, CH_3I and CO_2. The number of surface P–OH groups determines various surface properties, for instance, acidity and basicity, affinity and catalytic activity. Due to good chemical stability, high surface area, easy synthesis hydroxyapatite coated magnetic nanoparticle has recently been used as heterogonous catalytic supports.

Solid acids catalysts have served as important functional materials in industrial processes. In particular, for reactions in which water participates as a reactant or product, only a few solid acids show acceptable performance. The development of new water-tolerant solid acids is expected to have a major impact in industrial applications as well as for scientific aspects. We have

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overcome this problem by designing a sulfonic acid functionalized hydroxyapatite-encapsulated-γ-Fe_2O_3 magnetic nanoparticles.

Formylation of amines is an important process in organic synthesis with the resulting formamide function being a crossroad intermediate. *N*-Formyl compounds have been widely used as precursor for formamidine and isocyanide preparations [17]. They are intermediates for mono-methylated amines from primary amines and are catalysts for allylation and hydrosilylation of carbonyl compounds [18,19]. In addition, the formyl group is a useful protecting group, because the selective deprotection process is possible in the presence of other groups like acetyl or benzoyl [20]. Furthermore, formamides are very proper reagents in the Vilsmeier reaction [21] and they have been used in the synthesis of pharmaceutically important compounds such as fluoroquinolines [22], 1,2-dihydroquinolines and substituted aryl imidazoles [23].

Numerous methods are available for the *N*-formylation of amines: *in situ* formed formic anhydride [24], acetic-formic anhydride [25,26], chloral [27], activated formic acid using DCC [28] or EDCI [29], activated formic esters [30–32], ammonium formate [33], solid supported reagents [34], aq. 85% formic acid with ZnO [35], and aq. formic acid in protic ionic liquid [36]. However, there are several factors in some of these methods which limited their applications. In many of these methods, the applicable reagents are toxic, expensive or out of accessible. Also long reaction times and by-products formation are other drawbacks of these protocols. Aqueous formic acid (85%) has previously been reported as a formylating agent under conventional heating. However, this method needs a Dean–Stark trap under reflux conditions in toluene and involves long reaction times. The *N*-formylation of anilines having electron-withdrawing groups was found to be difficult [37]. Regarding the green chemistry's goals, iron oxide magnetic nanoparticles open up new avenue to introduce an amazing and efficient system for facilitating catalyst recovery in different organic reactions. Therefore, we investigated a novel design for a powerful recoverable catalytic system to avoid the above-mentioned drawbacks.

2. Experimental

2.1. Synthesis of HAp-encapsulated-γ-Fe_2O_3 [Fe_2O_3@HAp]

Preparation of HAp-encapsulated-γ-Fe_2O_3 was according to the previously reported method. $FeCl_2 \cdot 4H_2O$ (1.85 mmol) and $FeCl_3 \cdot 6H_2O$ (3.7 mmol) were dissolved in deionized water (DW) (30 mL) under Ar atmosphere at room temperature and the resulting solution was added to a 25% NH_4OH solution (10 mL) with vigorous mechanical stirring (700 rpm). A black precipitate of Fe_3O_4 was produced instantly. In order to obtain small and uniform Fe_3O_4 particles, the drop rate of NH_4OH was controlled precisely by a constant dropper and the drop rate was 1 mL min^{-1}. After 15 min, 100 mL of $Ca(NO_3)_2 \cdot 4H_2O$ (33.7 mmol, 0.5 M) and $(NH_4)_2HPO_4$ (20 mmol, 3.0 M) solutions adjusted to pH 11 were added drop-wise to the obtained precipitate over 30 min with mechanical stirring. The resultant milky solution was heated to 90 °C. After 2 h, the mixture was cooled to room temperature and aged overnight. The dark brown precipitate formed was filtered, washed repeatedly with DW until neutral, and air-dried under vacuum at room temperature. The as-synthesized sample was calcined at 300 °C for 3 h, giving a reddish-brown powder.

2.2. Synthesis of sulfonic acid supported on HAp-encapsulated-γ-Fe_2O_3 [γ-Fe_2O_3@HAp-SO_3H]

To 1 g γ-Fe_2O_3@HAp, chlorosulfonic acid ($ClSO_3H$) 1 g was added drop-wise at room temperature over 15 min. After addition was complete, the mixture was mechanically stirred vigorously for 6 h until HCl gas evolution was stopped. Then the resulted magnetic nanoparticles were separated by an external magnet device and washed with DW until neutral and washed twice with diethyl ether (100 mL) then dried under vacuum at room temperature.

2.3. pH-analysis of [γ-Fe_2O_3@HAp-SO_3H]

To an aqueous solution of NaCl (1 M, 25 mL) with an initial pH 5.93, the [γ-Fe_2O_3@HAp-SO_3H] (500 mg) was added and the resulting mixture stirred for 3 h after which the pH of solution decreased to 1.74. This is equal to a loading of 0.9 mmol SO_3H g^{-1}. Additionally, this result confirmed by back-titration analysis of the catalyst.

2.4. Typical experimental protocol for the synthesis of formamides from amines

To a solution of amine (1.0 mmol) and aq. formic acid (1.2 mmol) was added [γ-Fe_2O_3@ HAp-SO_3H] (10 mg = 0.009 mmol of SO_3H, 0.9 mol.%) and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (see Table 1). The reaction mixture was then separated by an external magnet and the catalyst was washed and dried to reuse in the next run. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. All isolated products gave satisfactory spectral data (^1H NMR and ^{13}C NMR) and compared with those reported in literature.

2.4.1. Product data

1: White solid, mp 46–47 °C, literature [35] 46–48 °C, ^1H NMR (500 MHz, DMSO): 50:50 (*cis/trans*), 9.30 (brs, 1H, *trans*), 8.71 (d, 1H, *J* = 11.0 Hz, *trans*), 8.45 (brs, 1H, *cis*), 8.38 (s, 1H, *cis*), 7.10–7.56 (5H, Ar-H). ^{13}C NMR: 119.1 (CH), 120.6 (CH), 125.3 (CH), 125.6 (CH), 129.4 (CH), 130.2 (CH), 137.3 (C), 137.4 (C), 160.2 (C=O), 163.8 (C=O).

2: White solid, mp 78–80 °C, literature [41] 79–80 °C, ^1H NMR (500 MHz, DMSO): 20:80 (*cis/trans*), 8.33 (s, 1H, *cis*), 7.99 (br, 1, *cis*), 7.47 (d, 1H, *J* = 8.9 Hz, *trans*), 7.06 (d, 1H, *J* = 8.9 Hz, *trans*), 6.79 (d, 2H, *J* = 8.6 Hz), 6.69 (d, 2H, *J* = 8.6 Hz), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 55.9 (CH_3, *cis*), 56.0 (CH_3, *trans*), 114.6 (CH), 122.2 (CH), 140.4 (C), 153.3 (C), 159.3 (C=O), 163.4 (C=O).

3: Yellow solid, mp 194–195 °C, literature [35] 193–194 °C, ^1H NMR (500 MHz, DMSO): 80:20 (*cis/trans*), 10.80 (s, 1H, *cis*), 10.69 (d, 1H, *J* = 10.0 Hz, *trans*), 9.04 (d, 1H, *J* = 10.0 Hz, *trans*), 8.39 (s, 1H, *cis*), 8.20 (d, 2H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR: 116.8 (CH), 119.4 (CH), 124.9 (CH), 125.6 (CH), 143.2 (C), 144.4 (C), 160.0 (C=O).

4: Reddish solid, mp 129–131 °C, literature [35] 128–130 °C, ^1H NMR (500 MHz, DMSO): 100:0 (*cis/trans*), 8.26 (s, 1H), 8.10 (br, 1H), 7.51 (br, 1H), 6.88 (t, 1H, *J* = 8.0 Hz), 7.03 (d, 1H, *J* = 8.0 Hz), 7.16 (t, 1H, *J* = 8.0 Hz), 7.18 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, DMSO): 114.9 (CH), 119.5 (CH), 121.6 (CH), 124.5 (CH), 125.4 (C), 146.6 (C), 160.2 (C=O).

5: White solid, mp 50–54 °C, literature [35] 51–55 °C, ^1H NMR (500 MHz, DMSO): 50:50 (*cis/trans*), 8.60 (d, 1H, *J* = 8.0 Hz, *trans*), 8.52 (br, 1H, *trans*), 8.31 (d, 1H, *J* = 8.0 Hz, *cis*), 7.92 (br, 1H, *cis*), 7.42 (d, 2H, *J* = 8.3 Hz, *cis*), 7.13 (d, 2H, *J* = 8.3 Hz, *trans*), 7.10 (d, 2H, *J* = 8.3 Hz, *cis*), 6.98 (d, 2H, *J* = 8.3 Hz, *trans*), 2.31 (s, 3H, *trans*), 2.29 (s, 3H, *cis*). ^{13}C NMR (125 MHz, $CDCl_3$): 21.2 (CH_3), 21.3 (CH_3), 119.5 (CH), 120.6 (CH), 130.0 (CH), 130.6 (CH), 134.7–134.9 (CH), 135.5 (C), 159.8 (C=O, *cis*), 163.6 (C=O, *trans*).