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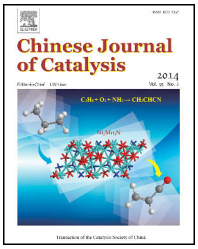

Article

Ferric hydrogen sulfate supported on silica-coated nickel ferrite nanoparticles as new and green magnetically separable catalyst for 1,8-dioxodecahydroacridine synthesis

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ABSTRACT

A new magnetically separable catalyst consisting of ferric hydrogen sulfate supported on silica-coated nickel ferrite nanoparticles was prepared. The synthesized catalyst was characterized using vibrating sample magnetometry, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy. This new magnetic catalyst was shown to be an efficient heterogeneous catalyst for the synthesis of 1,8-dioxodecahydroacridines under solvent-free conditions. The catalyst is readily recovered by simple magnetic decantation and can be recycled several times with no significant loss of catalytic activity.

1. Introduction

In recent years, magnetic nanoparticles (MNPs) have emerged as attractive solid supports for the immobilization of homogeneous catalysts [1,2]. This is because MNPs can be well dispersed in reaction mixtures without a magnetic field, providing a large surface that is readily accessible to substrate molecules. More importantly, after completing the reactions, the MNP-supported catalysts can be isolated efficiently from the product solution through simple magnetic separation, eliminating the need for catalyst filtration and centrifugation [3,4]. Among various MNPs, magnetite (Fe_3O_4) is the material most widely used for catalyst supports [5,6]. However, Fe_3O_4 is fairly reactive in acidic environments, and because it contains Fe^{2+}, which is readily oxidized, Fe_3O_4 MNPs are vulnerable to loss of magnetism. In contrast, nickel ferrite ($NiFe_2O_4$), which is a typical spinel-structured ferromagnetic oxide, has high thermal stability, moderate magnetization, and mechanical hardness [7,8]. Nickel ferrite therefore performs better than magnetite as a support for homogeneous catalysts. Currently, much attention is focused on the synthesis of magnetic core-shell structures by coating preformed MNPs with silica shells. Nanosized silica, which is non-toxic and can be grafted with various surface modifiers, has great potential in many applications [9]. Silica-gel-supported ferric hydrogen sulfate (SiO_2-FHS) has become a popular catalyst in organic synthesis [10,11]. Some of the advantages of using supported FHS rather than a homogeneous catalyst are easier recovery and recycling after reactions, and easier product separation. However, the separation and recovery of immobilized FHS are usually performed by filtration or centrifugation, which are not eco-friendly processes. The immobilization of FHS on silica-coated $NiFe_2O_4$ NPs

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($NiFe_2O_4@SiO_2$-FHS) can be used to produce a novel heterogeneous catalyst system that has both high separation efficiency and a relatively high surface area to maximize catalyst loading and activity. Based on these factors, we synthesized $NiFe_2O_4@SiO_2$-FHS as a novel nanomagnetically recoverable catalyst and assessed its catalytic activity in the synthesis of 1,8-decahydroacridines under solvent-free conditions.

Acridine and acridine-1,8-dione derivatives are polyfunctionalized 1,4-dihydropyridine derivatives. They have a wide range of pharmacological properties such as antimalarial [12], anticancer [13], cytotoxic [14], and antimicrobial [15] activities, and are widely prescribed as calcium β-blockers [16]. Also, 1,8-dioxodecahydroacridines have been used as laser dyes [17] and photoinitiators [18]. Many procedures for the synthesis of acridine derivatives containing 1,4-dihydropyridines by the reaction of dimedone, aldehydes, and different nitrogen sources in the presence of various catalysts have been reported [19–28]. Most of these methods suffer from disadvantages such as harsh condition, low yields, very high reaction temperatures, and expensive reagents. Based on our interest in the synthesis of heterocyclic compounds and in continuation of our previous work on the use of reusable catalysts in organic reactions [29–31], we report a new efficient and green method for 1,8-dioxodecahydroacridines synthesis using $NiFe_2O_4@SiO_2$-FHS as a catalyst (Scheme 1). To the best of our knowledge, this is the first report of the synthesis, characterization, and catalytic performance of $NiFe_2O_4@SiO_2$-FHS.

2. Experimental

All chemicals were available commercially and used without further purification. Melting points were recorded using an electrothermal 9100 melting point apparatus. Fourier transform infrared (FT-IR) spectra were obtained with a 4300 Shimadzu spectrometer using KBr disks. ^1H nuclear magnetic resonance (NMR; 500 MHz) spectra were recorded using a Bruker DRX500 spectrometer. X-ray diffraction (XRD) was performed using a PANalytical X'Pert Pro X-ray diffractometer. The surface morphology and particle size were studied using scanning electron microscopy (SEM; Hitachi S-4800). Transmission electron microscopy (TEM) was performed using a Hitachi H-7650 microscope at 80 kV.

2.1. *Preparation of catalyst ($NiFe_2O_4@SiO_2$-FHS)*

A solution consisting of $FeCl_3$ (160 mL, 1 mol/L) and $NiCl_2$ (40 mL, 1 mol/L) was poured as quickly as possible into a boiling alkaline solution (NaOH, 1000 mL, 1 mol/L) under vigorous stirring. The solution was then cooled and stirred continuously for 90 min. The resulting precipitate was purified four times by centrifugation (4000–6000 r/min, 20 min) and decantation. A layer of silica was coated on the surfaces of the $NiFe_2O_4$ NPs by first ultrasonically dispersing the NPs (8% w/w, 25 mL) in ethanol for 2 h at 60 °C. A concentrated ammonia solution was added, and the resulting mixture was stirred at 60 °C for 40 min. Tetraethyl orthosilicate (4.0 mL) was added, and the reaction mixture was continuously stirred at 60 °C for 24 h. The silica-coated NPs were collected using an external magnet, followed by washing three times with methanol and drying in a vacuum for 48 h. The resulting MNPs were calcined at 800 °C for 4 h. A round-bottomed flask was charged with FHS (1.0 g), and absolute ethanol (50 mL) was added. The mixture was stirred at room temperature for 30 min. $NiFe_2O_4@SiO_2$ (2.5 g) was then added to the solution, and the mixture was stirred for another 12 h. The mixture was filtered, and the residue was dried at 100 °C for 2 h. A brown homogeneous powder was obtained; it was stored in a desiccator.

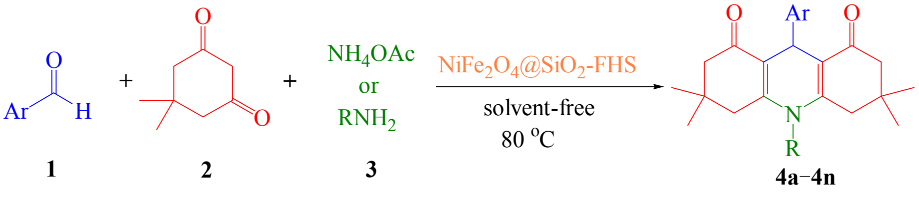
2.2. *Typical procedure for synthesis of 1,8-dioxodecahydroacridines **4a**–**4n***

A mixture of an aromatic aldehyde **1** (1 mmol), dimedone **2** (2 mmol), ammonium acetate or an aromatic amine **3** (1 mmol), and $NiFe_2O_4@SiO_2$-FHS (0.025 g, 2.4 mol%) was heated in an oil-bath at 80 °C for 15–30 min. During the procedure, the reaction was monitored using thin-layer chromatography. When the reaction was complete, the mixture was cooled to room temperature and chloroform was added. The catalyst was insoluble in chloroform and could be deposited on the side walls of the reaction vessel using an external magnet; the reaction solution was decanted to another vessel. The catalyst was then washed with chloroform and dried for reuse in the next run. The products were collected and recrystallized from ethanol to give compounds **4a**–**4n** in high yields.

2.3. *Selected ^1H NMR data*

3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-chlorophenyl)decahydroacridine (**4a**). ^1H NMR (500 MHz, $CDCl_3$): δ 1.00 (s, 6H, 2Me), 1.12 (s, 6H, 2Me), 2.19 (d, J = 16.3 Hz, 2H), 2.27 (d, J = 16.3 Hz, 2H), 2.29 (d, J = 16.7 Hz, 2H), 2.41 (d, J = 16.7 Hz, 2H), 5.07 (s, 1H, CH), 6.68 (s br, 1H, NH), 7.19 (d, J = 8.4 Hz, 2H, aromatic), 7.30 (d, J = 8.4 Hz, 2H, aromatic).

3,3,6,6-Tetramethyl-1,8-dioxo-9-(4-nitrophenyl)decahydroacridine (**4h**). ^1H NMR (500 MHz, $CDCl_3$): δ 1.00 (s, 6H, 2Me), 1.14 (s, 6H, 2Me), 2.19 (d, J = 16.5 Hz, 2H), 2.28 (d, J = 16.5 Hz,



R = C_6H_5, 4-MeC_6H_4, 4-$MeOC_6H_4$

Scheme 1. Synthesis of 1,8-dioxodecahydroacridines in the presence of $NiFe_2O_4@SiO_2$-FHS.