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Short Communication

(α-Fe_2O_3)-MCM-41-SO_3H as a novel magnetic nanocatalyst for the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives

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ABSTRACT

The new (α-Fe_2O_3)-MCM-41-SO_3H catalyst was prepared directly through the reaction of chlorosulfonic acid with silica-coated nanoparticles (α-Fe_2O_3)-MCM-41 and used as a magnetically recyclable catalyst for an efficient one-pot synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives. The catalyst with 10 wt% of loaded iron oxide nanoparticles could be recovered from the reaction mixture by an external magnet and reused without significant decrease in activity even after 5 runs. This new prepared catalyst exhibited better activities to other commercially available sulfonic acid catalysts.

1. Introduction

Acidic catalysts are widely used in a variety of organic transformations, such as aldol condensations, hydrolysis, acylations, and nucleophilic additions. However, use of soluble or liquid acids (homogeneous catalysts) has been inhibited in manufacturing synthesis because of difficulty in their waste neutralization, separations, reactor corrosion, and reusability [1].

The recovery and reusability of the catalyst are the two most important features for many catalytic processes. Hence, one efficient way to overcome the problem of homogeneous catalysts is the heterogenization of active catalytic molecules, creating a heterogeneous catalytic system. In contrast, the recovery of the most heterogeneous catalysts from the final reaction systems requires a filtration or centrifugation step and/or a tedious workup. For this purpose, by applying magnetic supports and an external magnet the catalysts can be easily recovered and subsequently reused in another cycle without significant decrease in their activity.

MCM-41 is an ordered mesoporous material which has only mildly acidic sites [2,3]. In order to promote their acidic character, sulfonic acid groups have been covalently bonded to these supports by various methods such as, oxidation of attached thiols [4], hydrolysis of sulfonic acid chlorides [5], sulfonation of supported phenyl groups [6], ring opening of perfluorosulfonic acid sultones [7,8], and immobilization of perfluorosulfonic acid triethoxysilanes [9]. It should be mentioned that covalent anchoring of various molecules on silica surfaces is based on the presence of silanol groups [10].

Hence, for the first time the present work illustrates the immobilization of sulfonic acid groups on silica coated magnetic nanoparticles for its use as recyclable, solid acid catalyst for the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives.

Over the past few years, naphthyridine derivatives have received considerable attention because of their wide range of biological and pharmaceutical activities, such as antitumor, anti-inflammatory, and antifungal properties [11–13]. These compounds are very useful in the treatment of hypertension, myocardial infarction, hyperlipidemia, cardiac arrhythmia, and rheumatoid arthritis [14–16].

In view of these useful properties, and since we were interested in the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives, a literature survey revealed that there are only a few reports for the synthesis of these compounds. El-Subbagh et al. have reported the synthesis of 1,6-naphthyridine derivatives through the two component reaction of α,β-unsaturated ketones and cyanoacetamide in butanol [12]. Recently, Shu-Jiang Tu et al. [17] reported the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives through three component reaction between α,β-unsaturated ketones, aniline, and malononitrile using microwave irradiation in the presence of acetic acid as catalyst.

However, these methods are time-consuming and use a lot of toxic solvents and reagents. Thus, the development of a green, simple, efficient, and general method for the synthesis of these widely used organic compounds, from readily available reagents, remains one of the major challenges in organic synthesis.

Therefore in this work, magnetic nanoparticles which have been embedded in MCM-41 and subsequently functionalized with chlorosulfonic

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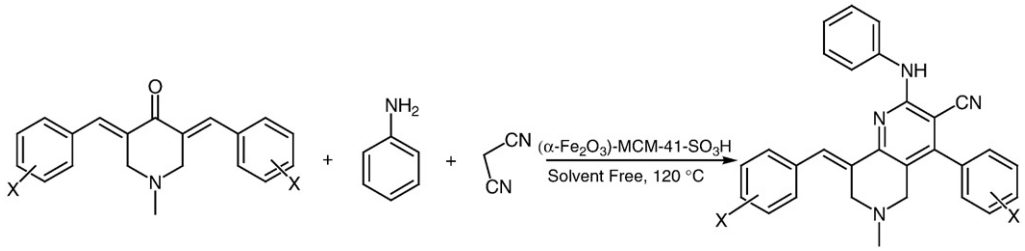


Scheme 1. (α-Fe_2O_3)-MCM-41-SO_3H as a magnetic catalyst for the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives.

acid [(α-Fe_2O_3)-MCM-41-SO_3H] have been used as new acidic catalyst for the one-pot synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives under solvent free conditions (Scheme 1).

2. Experimental

Melting points were recorded on a Buchi B-540 apparatus. IR spectra were recorded on an ABB Bomem Model FTLA200-100 instrument. ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-300 spectrometer, at 300 and 75 MHz, using TMS as an internal standard. Chemical shifts (δ) were reported relative to TMS, and coupling constants (J) were reported in hertz (Hz). Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer with 70-eV ionization potential. X-ray powder diffraction (XRD) was carried out on a Philips X'Pert diffractometer with CuKα radiation. The pore structure of the prepared catalyst was verified by the nitrogen sorption isotherm ([5.0.0.3] Belsorp, BEL Japan, Inc.). Transmission electron microscope (TEM) was recorded on a Philips CM-10 instrument on an accelerating voltage of 100 kV.

2.1. Catalyst preparation

A solution with molar composition of 3.2 $FeCl_3$:1.6 $FeCl_2$:1 CTABr:39 NH_4OH:2300 H_2O was used for preparation of naked Fe_3O_4 nanoparticles at room temperature. Typically, 2 g of iron (III) chloride ($FeCl_3 \cdot 6H_2O$) and 0.8 g of iron (II) chloride ($FeCl_2 \cdot 4H_2O$) were dissolved in 10 mL of distilled water under N_2 atmosphere. The resulting solution was added dropwise to a 100 mL solution of 1.0 M NH_4OH solution containing 0.4 g of cetyltrimethylammonium bromide (CTABr) to construct a colloidal suspension of iron oxide magnetic nanoparticles. The magnetic MCM-41 was prepared by adding 20 mL of the magnetic colloid to a 1 L solution with the molar composition of 292 NH_4OH:1 CTABr:2773 H_2O under vigorous mixing and sonication. Then sodium silicate (16 mL) was added, and the mixture was allowed to react at room temperature for 24 h under well-mixed conditions. The magnetic MCM-41 [(Fe_3O_4)-MCM-41] was filtered and washed with alcoholic ammonium nitrate. The surfactant template was then removed from the synthesized material by calcination at 450 °C for 4 h to give the [(α-Fe_2O_3)-MCM-41].

2.2. Preparation of (α-Fe_2O_3)-MCM-41-SO_3H

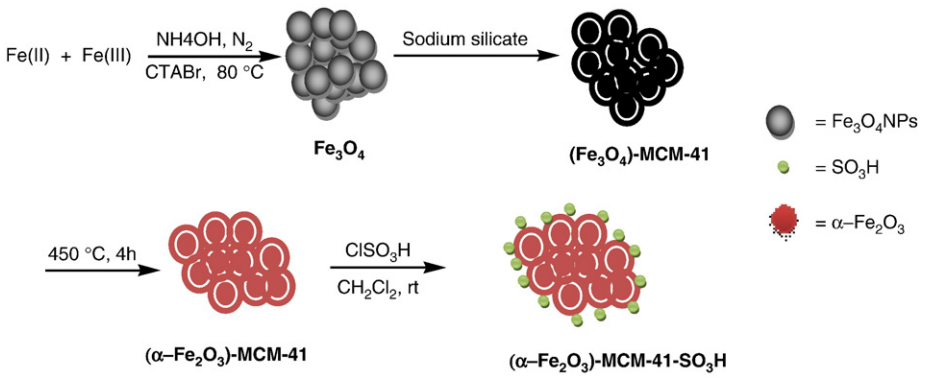
To (α-Fe_2O_3)-MCM-41 (1 g), chlorosulfonic acid (1 g, 9 mmol) in 5 mL dichloromethane was added dropwise at room temperature during 30 min. After completion of the addition, the mixture was mechanically stirred for other 30 min until HCl was removed from reaction vessel. The mixture was then filtered and washed with CH_2Cl_2 to give (α-Fe_2O_3)-MCM-41-SO_3H as brown powder. The amount of sulfonic acid groups of (α-Fe_2O_3)-MCM-41-SO_3H which were determined by acid–base titration was found to be (0.56 SO_3H per g).

2.3. General procedure for the synthesis of 3,5-dibenzylidenepiperidin-4-one [12]

In a 50-mL reaction vial, a mixture of the 4-piperidone (10 mmol), the appropriate aldehyde (20 mmol), 10% NaOH (1 mL) and 95% EtOH (30 mL) was stirred at room temperature for 0.5–2 h. The separated solid was collected by filtration and for further purification was recrystallized from ethanol.

2.4. General procedure for the synthesis of N-aryl-2-amino-1,6-naphthyridine derivatives

To the mixture of 3,5-dibenzylidenepiperidin-4-one (0.33 mmol), aniline (0.33 mmol), and malononitrile (0.33 mmol) was added (α-Fe_2O_3)-MCM-41-SO_3H (40 mg); it was then stirred at 120 °C for an appropriate period of time (Table 4). After completion of the reaction (monitored by thin-layer chromatography, TLC; petroleum ether and EtOAc, 1:1), the ethanol was added to the reaction mixture and the catalyst was collected with an external magnet. Then, the mixture was filtered and the



Scheme 2. Preparation of (α-Fe_2O_3)-MCM-41-SO_3H.