C. R. Chimie 17 (2014) 459–464

Contents lists available at SciVerse ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Polyphosphoric acid supported on silica-coated $NiFe_2O_4$ nanoparticles: An efficient and magnetically-recoverable catalyst for *N*-formylation of amines

Amir Khojastehnezhad [a,*], Mohammad Rahimizadeh [a], Farid Moeinpour [b], Hossein Eshghi [a], Mehdi Bakavoli [a]

[a] Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
[b] Department of Chemistry, Islamic Azad University-Bandar Abbas Branch, 7915893144, Bandar Abbas, Iran

ARTICLE INFO

Article history:
Received 27 April 2013
Accepted after revision 22 July 2013
Available online 25 September 2013

Keywords:
Amines
N-formylation
Magnetic recovery
Polyphosphoric acid
Silica-coated $NiFe_2O_4$

ABSTRACT

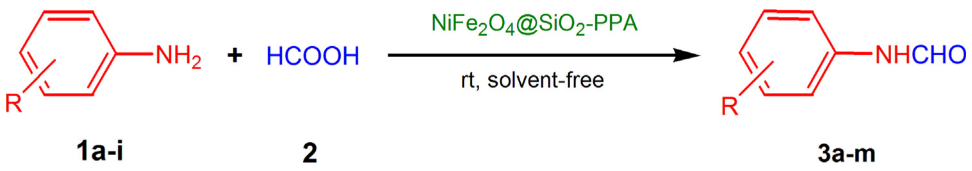
A rapid, green and simple method for the *N*-formylation of various aromatic amines with formic acid using polyphosphoric acid supported on silica-coated $NiFe_2O_4$ magnetic nanoparticles ($NiFe_2O_4$@SiO_2–PPA) under solvent-free conditions at room temperature has been developed. The magnetic catalyst can be easily removed by a simple magnet and reused at least three times without any loss of its high catalytic activity. In addition to its facility, this protocol enhances product purity and promises economic and also environmental profits.

1. Introduction

Nanoparticles can effectively improve the loading and the catalytic efficiency of immobilized catalysts due to their high surface area:volume ratios. Therefore, the use of nanostructured materials as supports for different types of catalyst immobilization remains an attractive field to the researchers [1,2]. Magnetic nanoparticles have obtained considerable interest in recent years [3–5]. The magnetic nature of these particles allows the easy recovery and recycling of the catalysts by an external magnet, which may optimize operational cost and improve product purity. Recently, magnetic nanoparticles, such as Fe, FePt, Fe_2O_3, Fe_3O_4, $ZnFe_2O_4$, $MnFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$, have been studied mostly for biomedical applications [6–11]. As Fe-based metallic nanoparticles are chemically not stable [12], therefore, iron oxides, in particular, spinel ferrites with a general formula (AB_2O_4), have attracted a great consideration. Ni ferrites are one of the most versatile magnetic materials as they have high saturation magnetization, high Curie temperature, chemical stability and relatively high permeability [13]. Due to the sensitivity of the magnetic nanoparticles and the strong surface affinity toward silica, these nanoparticles can be directly coated with amorphous silica. In spite of the recoverability of the silica-supported polyphosphoric acid (PPA), the slow recycling of catalyst by filtration and the unavoidable loss of some solid catalyst in the separation process are some of the drawbacks of the traditional heterogeneous PPA–SiO_2. Although the catalytic applications of silica-supported reagents for organic synthesis are well established, it is more interesting to introduce a novel version of PPA immobilized onto magnetic silica for more efficient catalyst recovery, especially from the green chemistry viewpoint. Due to the reasonable needs to clean and green recovery of the heterogeneous catalyst, especially acid catalyst, we decided to design a novel version of silica-supported polyphosphoric acid to ease the efficient

* Corresponding author.
E-mail address: akhojastehnezhad@yahoo.com (A. Khojastehnezhad).

1631-0748/$ – see front matter © 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.crci.2013.07.013



Scheme 1. *N*-formylation of amines in the presence of $NiFe_2O_4@SiO_2$–PPA.

recycling of this catalyst. In the present work, an efficient method for the preparation of PPA-functionalized silica-coated magnetic nanoparticles [$NiFe_2O_4@SiO_2$–PPA] is reported. The prepared composite was successfully used as the catalyst for the *N*-formylation of amines.

N-formylation of amines is a very important reaction in organic synthesis and medicinal chemistry. A variety of medicinally active compounds have formamides as their intermediates [14]. *N*-Formyl protection gained popularity in peptide synthesis [15], since *N*-formyl deprotection can easily be achieved without affecting the peptide bond, and it may serve as a precursor for isocyanide [16] and formamidine [17] synthesis. Reported literature methods for the *N*-formylation [17–21] use reagents, such as chloral, formic acid–DCC, formic acid–EDCI, formic acid–$ZnCl_2$, formic acid–PEG 400, formic acid esters, CMT, DMF–NaOMe, formic acid–thiamine hydrochloride, imidazole–DMF, $HClO_4$–SiO_2, and formamide–NaOMe. Most of these methods suffer from some disadvantages, such as harsh reaction condition, low yield, very high reaction temperature, expensive reagents, etc. Due to our interest in the synthesis of heterocyclic compounds and in continuation of our previous works on the applications of reusable catalysts in organic reactions [22–24], here, we report an efficient and green method for the *N*-formylation of amines using $NiFe_2O_4@SiO_2$–PPA as a catalyst (Scheme 1). To the best of our knowledge, this is the first report on the synthesis, characterization and catalytic performance of a $NiFe_2O_4@SiO_2$–PPA catalyst.

$NiFe_2O_4@SiO_2$ nanocrystallites were prepared according to the reported procedure by Massart et al. with minor modifications: fine particles are precipitated in an alkaline solution [25]. (Scheme 2).

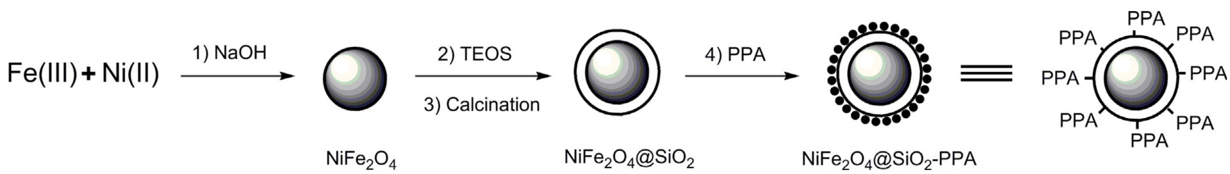
2. Experimental

2.1. Preparation of the catalyst ($NiFe_2O_4@SiO_2$–PPA) [25,26]

The solution of metallic salts ($FeCl_3$, 160 mL, 1 M and $NiCl_2$, 40 mL, 1 M) was poured as quickly as possible into the boiling alkaline solution [NaOH (1000 mL, 1 M)] under vigorous stirring. Then, the solution was cooled and continuously stirred for 90 min. The resulting precipitate was then purified by four-times repeated centrifugation (4000–6000 rpm, 20 min) and decantation. Coating of a layer of silica on the surface of the $NiFe_2O_4$ nanoparticles was achieved by (ultrasonically) premixing a dispersion of the nanoparticles (8% w/w, 25 mL) obtained with 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. Then, tetraethylorthosilicate (TEOS) (1.0 mL) was added to the reaction mixture and continuously stirred at 60 °C for 24 h. The silica-coated nanoparticles were collected by an external magnet, followed by washing three times with methanol and drying in vacuum for 48 h. After that, the resulting magnetic nanoparticles were calcined at 800 °C for 4 h. Polyphophoric acid (PPA) (2.2 g) was charged in the round-bottom flask, and $CHCl_3$ (100 mL) was added. After the mixture had been stirred at 50 °C for 1 h, $NiFe_2O_4@SiO_2$ (5.0 g) was added to the solution, and the mixture was stirred for another 4 h. The $CHCl_3$ was removed with a rotary evaporator and the resulting solid was washed with cold absolute ethanol, and dried in vacuo at 70 °C for 2 h. The amount of H^+ in the $NiFe_2O_4@SiO_2$–PPA, determined by acid–base titration, was 0.50 mmol/g.

2.2. Typical experimental procedure for N-formylation

A solution of 4-methylaniline (1.0 mmol), formic acid (1.5 mmol), and $NiFe_2O_4@SiO_2$_PPA (0.02 g, 1 mol%) was stirred at room temperature for 10–30 min. The progress of the reaction was monitored by TLC. Upon completion, ethyl acetate was added to the reaction mixture (the product is soluble in ethyl acetate) and $NiFe_2O_4@SiO_2$–PPA could be placed on the side wall of the reaction vessel with the aid of an external magnet, then the catalyst was washed and dried to be reused in the next run. The organic phase was washed with a saturated solution of $NaHCO_3$ (5 mL × 3), water, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting crude product was collected and give a white solid, yield 93%, mp: 52–54 °C, 3291, 1664 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.08–7.61 (m, 4H), 8.11 (s, 1H), 8, 15 (s, 1H).



Scheme 2. Preparation of polyphosphoric acid supported on $NiFe_2O_4@SiO_2$.