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Short communication

Microwave-assisted Fe_3O_4 nanoparticles catalyzed synthesis of chromeno[1,6]naphthyridines in aqueous media

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ABSTRACT

Fe_3O_4 nanocatalyst was prepared by co-precipitation method and characterized by XRD, FT-IR, TEM, VSM and BET analyses. The particles have an average size of 7 nm and possess highly open mesopores, moderate surface area, and uniform morphology with superparamagnetic behavior. Activity of catalyst was probed through the synthesis of chromeno[1,6]naphthyridines in water under microwave irradiation (MW) and it was about 7-fold higher as compared to conventional method. Nanocatalyst plays a dual role of catalyst as well as susceptor, and enhances the overall capacity to absorb MW. Fe_3O_4 NPs easily recovered by simple magnetic separation and recycled at least 5 times.

1. Introduction

The applications of iron-based materials as catalysts in organic synthesis have attracted a lot of attention during the last decade [1]. Iron is most widely recommended due to its low cost, abundance, environmentally benign and non-toxic nature [2,3] for industrial scale synthesis of fine chemicals [4]. Iron oxides have been frequently used as catalysts and supports in bulk industrial processes, usually at high temperature and pressure [5]. However, Fe has a great deal to offer at the nanoscale, including potent magnetic and catalytic properties [6]. The strategy of magnetic separation of magnetic nanoparticles is typically more effective than filtration or centrifugation as it prevents loss of the catalyst. Furthermore, Fe_3O_4 nanoparticles have showed potential applications in many other fields [7,8].

Chromenes and 1,6-naphthyridines are associated with a wide spectrum of biological activities [9–11]. Consequently, integration of chromene moieties with naphthyridines in a single molecular-framework may increase their biological and fluorescence properties [12]. While a considerable number of naphthyridines fused with five-membered rings has been described in literature [13,14], corresponding derivatives condensed with six-membered heterocycles have been less investigated [15,16]. There are also few synthetic methods available in literature for the synthesis of chromeno[1,6] naphthyridines [17–20].

A vigilant scrutiny described that most of the methodologies endure some setbacks owing to their limited utility i.e. usage of corrosive catalysts [17], multistep process [18], high temperature, long reaction time, non-compatible solvent [19], low yields and unavailable starting materials [20]. Although, some strategically sound modifications have been documented [21] for upliftment of reaction condition, but somewhere down the line it still lack the versatility. The employed catalytic systems are more often non-recoverable [21], thus plummeting the turn over frequency (TOF), which is significant from an industrial point of view. As a result, the development of new synthetic methods for this purpose remains an attractive goal.

The use of nanomaterial as efficient catalysts in aqueous medium has attracted considerable interest [22,23]. The coupling of nanocatalyst with aqueous medium and MWs can offer an astonishing synergistic effect with superior potential than these components in solitude [24]. In continuation of our efforts towards the development of newer nanocatalytic processes [25–27], herein, we wish to report the synthesis of magnetically recoverable Fe_3O_4 nanoparticles and their catalytic applications in the synthesis of chromeno[1,6]naphthyridines in water.

2. Experimental

General part including used instruments is provided in ESI.

2.1. Catalyst preparation

A mixture of ferric chloride (2.7 g) and ferrous chloride (0.99 g) in a fixed molar ratio of 2:1 (Fe^{+3}:Fe^{+2}) in 30 mL of ethylene glycol was

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introduced in a 50 mL heavy walled pear-shaped two necked flask with non-standard tapered outer joint. The flask was attached to a 12 mm tip diameter probe and the reaction mixture was sonicated at ambient temperature for the specified period at 50% power of the processor and in a 4 s pulse mode. After proper sonication of the mixture, sodium acetate was added and sonication was continued until a fine dispersion was seen. This assembly was then subjected to an oil bath where the temperature was increased to 190 °C. For uniform heating of the broth, oil was constantly stirred. After 6 h of stirring, the temperature was lowered to room temperature and the nanoparticles were separated magnetically and washed repeatedly with isopropanol followed by centrifugation at 8000 rpm for 20 min. Drying in a vacuum oven at 60 °C for 2 h gave a brown colored fine powder.

2.2. Catalyst activity measurement

Aromatic aldehyde (1 mmol), malononitrile (2 mmol), 2-hydroxyacetophenone (1 mmol) and 5 mol% of Fe_3O_4 NPs in water (10 mL) were introduced in a 50 mL round-bottom flask. The flask was placed in the microwave cavity and subjected to irradiation for an appropriate time at 70 °C using a power of 400 W. On the completion of reaction, Fe_3O_4 NPs were separated by using external magnet and crude product was purified by crystallization from ethanol.

3. Results and discussion

3.1. Synthesis and characterization of catalyst

Fe_3O_4 NPs have been synthesized via co-precipitation method [28] with excellent catalytic properties and high stability. The morphology, behavior and structure of Fe_3O_4 nanoparticles were characterized by XRD, FT-IR, TEM, VSM and BET analyses. In FT-IR, the adsorption band of the Fe–O bonds in tetrahedral sites was observed at 606 cm^{-1}. In XRD patterns, characteristic peaks appeared at $2\theta = 30.15, 35.48, 43.2, 56.83$ and 62.64 which correspond to the major planes (220), (311), (400), (511) and (440) respectively, confirmed the inverse spinel structure. TEM image showed that average diameter of Fe_3O_4 NPs is about 7 nm with a square shaped morphology. The excellent magnetically controllable behavior of Fe_3O_4 NPs was investigated by VSM. The hysteresis loops exhibit a superparamagnetic behavior with the saturation magnetization of about 67 emu/g (Fig. 1).

In the N_2 adsorption–desorption isotherm sample showed a typical type IV isotherm with 'a' type hysteresis loop. The isotherm accounts for the relatively ordered mesopores and the hysteresis loop. The BET surface area for the Fe_3O_4 NPs is 39 m^2g^{-1} with pore dimensions of 3.6 nm (Fig. 2).

3.2. Assessment of catalytic activity

We began our study by evaluating the efficiency of MW (400 W) at 70 °C for 60 min for the model reaction of 3-phenoxybenzaldehyde (1.0 mmol), malononitrile (2.0 mmol) and 2-hydroxyacetophenone (1.0 mmol) in aqueous medium without using any catalyst. Under these conditions the reaction did not proceed. In order to optimize the reaction conditions, different iron catalysts in water were examined (Table 1).

When $FeCl_2 \cdot 4H_2O$ was used as a catalyst the product were obtained in low yields. When $FeCl_3 \cdot 6H_2O$ was used, the yield was still lower, whereas with $Fe(NO_3)_3 \cdot 9H_2O$ the yield of 4 h is 36% with no reusability of catalyst (Table 1). However, reaction occurred smoothly in the

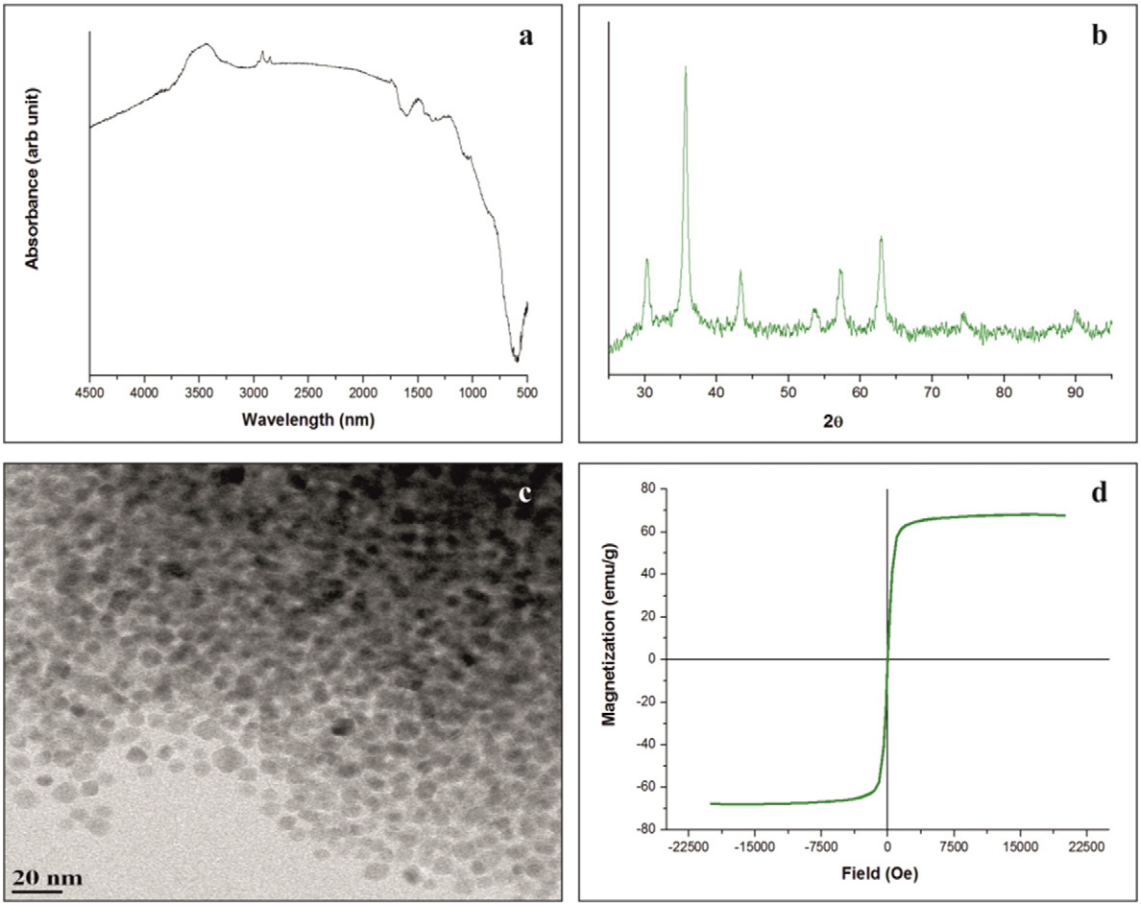

Fig. 1. (a) FT-IR spectra, (b) XRD pattern, (c) TEM image and (d) magnetic hysteresis loops of Fe_3O_4 NPs.