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Article

Fe₃O₄ nanoparticles as an efficient and reusable catalyst for the solvent-free synthesis of 9,9-dimethyl-9,10-dihydro-8*H*-benzo-[*a*]xanthen-11(12*H*)-ones

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ABSTRACT

A simple and efficient method for the synthesis of 9,9-dimethyl-9,10-dihydro-8*H*-benzo-[*a*]xanthen-11(12)-one derivatives (DDBXs) was developed by the condensation reaction of various substituted aryl aldehydes with 2-naphthol and dimedone using Fe₃O₄ magnetic nanoparticles (MNPs) as a heterogeneous catalyst under solvent-free conditions at 90–110 °C. The experimental procedure is very simple, the products are formed in high yields and the catalyst is easily separated by applying an external magnetic field.

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1. Introduction

SXanthenes and benzoxanthenes are biologically important drug intermediates since they can act as antibacterial [1] and antiviral compounds [2]. These heterocycles also show interesting properties in laser technology [3], dyes [4] and pH-sensitive fluorescent materials [5]. There are numerous methods for the synthesis of these compounds by application of homogenous catalysts such as tetra-*n*-butylammonium fluoride (TBAF) [6], BF₃/Et₂O [7], ceric ammonium nitrate (CAN) [8], cyanuric acid [9], *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluenesulfonamide) [10], HClSO₃ [11], HClO₄-SiO₂ [12], InCl₃ [13], I₂ [14], NaHSO₄/SiO₂ [15], peroxysulfuric acid (Caro's acid)/SiO₂ [16], proline triflates [17], *p*-toluenesulfonic acid (PTSA) [18], sulfamic acid [19], Sr(OTf)₂ [20], 12-tungstophos-

phoric acid (TPA: H₃PW₁₂O₄₀) [21], and Zr(HSO₄)₄ [22]. Many of these methods have limitations such as long reaction time, harsh reaction conditions and tedious work-up procedures. Among the most promising ways to synthesize xanthenes and benzoxanthenes, solvent-free reactions have attracted the most attention for economic reasons and pollution reduction.

However, homogeneous catalysts are difficult to apply in industrial processes because of environmental concerns and difficult work-up procedures. Thus, heterogeneous catalysts such as HClO₄/SiO₂ [23], mesoporous silica [24], TiO₂ nanoparticles [25], zeolite [26] and Fe₃O₄ MNPs [27] have been applied for organic syntheses despite most suffering from a lack of surface area and difficulties in the catalyst separation [28]. Among them, Fe₃O₄ MNPs not only have a relatively high surface area (up to 400 m²/g), but are also capable of being easily collected

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Scheme 1. A schematic representation for the synthesis of different benzoxanthrenes.

by a magnet because of their magnetic properties. In addition, Fe_3O_4 MNPs have high thermal and mechanical stability [29,30].

In this paper, we have developed a new and efficient method for the synthesis of DDBXs by treatment of aryl aldehydes with 2-naphthol and dimeredone under solvent-free conditions at 90–110 °C in the presence of Fe_3O_4 MNPs (Scheme 1).

2. Experimental

2.1. Chemicals and instruments

All analytical grade reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. IR spectra were recorded on a Bruker IFS-66 FT-IR spectrophotometer. The elemental analysis was performed with a Thermo Finnigan Flash-1112EA microanalyzer (Italy). Magnetic separation was done by a super magnet with 1.4 T magnetic field ($10 \times 5 \times 4$ cm). The morphology of particles was observed on a Philips XL-30 scanning electron microscope (SEM) and Leo 960 transmission electron microscope (TEM). Specific surface areas were measured by the N_2 adsorption technique using a Micrometris ASPS 2010 analyzer. ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300 MHz. The XRD were obtained on a STOE diffractometer with $\text{Cu } K_\alpha$ radiation.

2.2. General procedure

2.2.1. Preparation of Fe_3O_4 MNPs

The Fe_3O_4 MNPs were synthesized according to the previously reported procedure [28]. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10.8 g, 40 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.0 g, 20 mmol) were dissolved in de-ionized water (100 mL), degassed with N_2 for 15 min and heated to 80 °C. A solution of NH_4OH (32%, 15 mL) was then added dropwise and the solid was separated after 15 min by a magnet and washed with NaCl solution (0.1 mol, 100 mL).

The MNP formation was confirmed by XRD, specific surface area measurements, SEM, TEM and EDAX microanalysis.

2.2.2. Preparation of DDBXs

In a typical reaction, Fe_3O_4 MNPs (12 mg, 5 mol%) were added to a mixture of 2-naphthol (0.144 g, 1.0 mmol), aldehyde (1.0 mmol) and dimeredone (0.168 g, 1.2 mmol) under solvent-free conditions and the mixture was heated to 110 °C. After completion of the reaction, the catalyst was separated from the solution using a magnet. The product was then separated by filtration, washed with CH_2Cl_2 and the crude product recrystallized from aqueous EtOH (90%) to yield the pure

product, which required no further purification.

All products are known and were characterized by comparison of their physical and spectral data with authentic samples.

2.3. Reusability of the catalyst

The reusability and stability of Fe_3O_4 MNPs as a catalyst were studied in several subsequent runs. After each run, the catalyst was separated from the solvent by a strong magnet and washed with MeH_2Cl_2 , EtOH and MeCOMe, then dried under vacuum at room temperature for 4 h before reusing in the subsequent reaction.

3. Results and discussion

3.1. Synthesis and characterization of Fe_3O_4 MNPs

To investigate the phase of these MNPs as well as the purity, the XRD pattern of this catalyst was recorded (Fig. 1) and compared with the JCPDS (Joint Committee on Powder Diffraction Standards) card No. 85-1436. The pattern shows peaks at $2\theta = 31^\circ$, 35° , 43° , 54° , 57° and 64° that are attributed to (220), (311), (400), (422), (511) and (440) and confirm formation of the crystalline cubic spinel structure of the Fe_3O_4 MNPs. Since no other phase peaks could be detected in the XRD pattern, this indicates high purity in the Fe_3O_4 MNPs.

The purity of Fe_3O_4 MNPs was further investigated by EDAX microanalysis (Fig. 2). It can be seen from the microanalysis that there are no impurities and only Fe and O are detected.

Since the size and morphology of the Fe_3O_4 MNPs are important in their catalytic efficiency, SEM and TEM micrograph images of these particles were recorded (Fig. 3). It can be seen that spherical MNPs (35–50 nm in diameter) were obtained

Fig. 1. The XRD pattern of Fe_3O_4 MNPs.

Fig. 2. The EDAX microanalysis of Fe_3O_4 MNPs.

under an ultrasound power.

For further investigation, the size distribution of the prepared nanoparticles was obtained using a Manual Microstructure Distance Measurement program. As shown in Fig. 4, the average size of Fe_3O_4 MNPs produced by this method is 50–60 nm. The size of nanoparticles was calculated from the Scherrer equation and the average crystallite size was 15–19 nm.

Another important parameter in catalytic performance is the specific surface area. The single point BET (Brunauer-Emmett-Teller) analysis showed a surface area of $342 \text{ m}^2/\text{g}$ for the Fe_3O_4 MNPs.

Fig. 3. (a) SEM, and (b) TEM micrographs of Fe_3O_4 MNPs.

Fig. 4. Particle size of Fe_3O_4 MNPs.

3.2. Synthesis of DDBXs

3.2.1. Optimization of reaction conditions

To optimize the reaction conditions, the solvent-free reaction of aldehydes with 2-naphthol and dimedone were carried out at 90–110 °C in the presence of Fe_3O_4 MNPs under various conditions. Increasing the reaction time as well as the amount of catalyst did not improve the yield. Optimum conditions were achieved at 5 mol% Fe_3O_4 MNPs and 1 h reaction time (Table 1, entry 2).

3.2.2. Synthesis of benzoxanthenes

DDBXs were prepared at the optimized reaction conditions by reacting 2-naphthol with different aryl aldehydes and dimedone in the presence of Fe_3O_4 MNPs (5 mol%) under solvent-free conditions for 1–2 h at 90–110 °C with good to excellent yields (80%–95%) (Table 2).

3.2.3. Selected spectroscopic data of some DDBXs

9,9-Dimethyl-12-phenyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (**g**, Table 2, entry 7). M.p. 149–152 °C (lit: 151–153 °C) [32]; ^1H NMR (200 MHz, CDCl_3): δ = 6.9–8.0 (aromatic protons), 4.8 (1H of CH), 2.5 (2H of CH_2 , adjacent to the carbonyl group), 2.15 (2H of CH_2), and 1.15 (6H, 2 CH_3).

9,9-Dimethyl-12-styryl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (**e**, Table 2, entry 5). M.p. 62–64 °C (lit: not determined) [30]; ^1H NMR (200 MHz, CDCl_3): δ = 6.9–8.0 (aromatic protons), 6 (2H of double bond), 4.5 (1H of CH), 2.5 (2H of CH_2 , adjacent to the carbonyl group), 2.2 (2H of CH_2), and 1.15 (6H, 2 CH_3).

The NMR spectra are represented in the Supplementary Materials and the proposed mechanism for this reaction is shown in Fig. 5.

Table 1

Optimization of the reaction conditions at 110 °C.

Entry	Amount of MNPs (mol%)	Reaction time (min)	Yield (%)
1	2.5	60	83
2	5	60	94
3	5	30	71
4	5	90	94
5	10	60	94

Table 2
Synthesis of DDBXs.

Entry	R	Product	Time (h)	Temp (°C)	Yield (%)	m.p. (°C)	Entry	R	Product	Time (h)	Temp (°C)	Yield (%)	m.p. (°C)
1	4-F-C ₆ H ₄		1	110	94	189–191 (190–193 [31])	7	C ₆ H ₅		1	110	94	149–152 (151–153 [32])
2	3-Cl-C ₆ H ₄		1	110	92	172–173 (172–173 [31])	8	4-MeO-C ₆ H ₄		1	100	83	202–204 (204–205 [32])
3	4-Me-C ₆ H ₄		1	110	80	201–203 (203–205 [31])	9	4-NO ₂ -C ₆ H ₄		1	100	89	177–179 (178–180 [32])
4	4-HO-C ₆ H ₄		1	110	95	207–209 (207–209 [31])	10	3,4-di (MeO)C ₆ H ₃		2	100	91	196–198 (201–204 [33])
5	Ph-CH=CH		2	90	85	62–64 (Not determined [31])	11	3-F-C ₆ H ₄		1	110	93	223–228 (230–232 [34])
6	4-Cl-C ₆ H ₄		1	110	93	179–181 (180–182 [32])	12	3-PhO-C ₆ H ₄		2	100	90	152–154 (151–152 [12])

3.3. Reusability

As catalyst reusability is very important from both economic and environmental points of view, the catalytic reusability of

Fig. 5. The plausible mechanism for preparation of DDBXs.

Fe₃O₄ MNPs was investigated in several subsequent runs. The results show that the catalyst could be reused for more than 16 successive runs without any significant decrease in conversion (Fig. 6). The high reusability of the catalyst can be explained by its high thermal and mechanical stability and vast surface area owing to an extremely high porosity.

Fig. 6. The reusability of Fe₃O₄ MNPs in successive runs.

Graphical Abstract

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9,9-dimethyl-9,10-Dihydro-8H-benzo-[a]xanthen-11(12)-one derivatives were synthesized by the condensation reaction of different substituted aryl aldehydes with 2-naphthol and dimedone in the presence of Fe₃O₄ magnetic nanoparticles (MNPs) as a heterogeneous catalyst under solvent-free conditions at 90–110 °C.

4. Conclusions

We have demonstrated a new application of Fe₃O₄ MNPs as an efficient catalyst for the synthesis of xanthene derivatives. This cost-effective catalyst has the advantages of high product yields and simple work-up procedures as well as high thermal and mechanical stability.

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