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α -Fe₂O₃ nanoparticles: An efficient, inexpensive catalyst for the one-pot preparation of 3,4-dihydropyrano[*c*]chromenes

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Abstract

This paper describes the combustion synthesis of α -Fe₂O₃ nanopowder at much lower temperature and its catalytic activity for the one-pot preparation of 3,4-dihydropyrano[*c*]chromenes. The combustion derived α -Fe₂O₃ nanopowder was characterized by powder X-ray diffraction (PXRD), Braunauer, Emmett and Teller (BET) surface area, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Highly efficient, three-component condensation of aromatic aldehyde, malanonitrile and 4-hydroxycoumarin catalyzed by α -Fe₂O₃ nanoparticles at room temperature is described. The method offers an excellent alternative to the synthesis of 3,4-dihydropyrano[*c*]chromenes. The reactions are rapid, clean, and the products with good yield and high purity. © 2010 Published by Elsevier B.V. on behalf of Chinese Chemical Society.

Keywords: α -Fe₂O₃ nanopowder; One pot three-component condensation; Aromatic aldehyde; Malanonitrile; 4-Hydroxycoumarin

3,4-Dihydropyrano[*c*]chromenes and its derivatives are very useful compounds in various fields of chemistry, biology and pharmacology. Some of these compounds exhibit spasmolytic, diuretic, anticoagulant, anti-cancer, and anti-anaphylactic activity [1]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, Parkinson's disease, Huntington's disease, AIDS associated dementia and Down's syndrome for the treatment of schizophrenia and myoclonus [2]. Recently, one-pot procedures for the synthesis of 2-amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile from aromatic aldehyde, malonitrile and 4-hydroxycoumarin have been developed in the presence of a variety of catalysts such as diammonium hydrogen phosphate [3], H₆P₂W₁₈O₆₂·18H₂O [4], TBABr [5], and K₂CO₃ under microwave irradiation [6]. However, many of these methods are associated with several disadvantages such as long reaction time, drastic reaction conditions, very expensive reagents, low yields and tedious work-up procedures. The main disadvantage is that the catalyst is destroyed during the work-up procedure and cannot be recovered and reused. Therefore, it is important to find a simple, inexpensive, recoverable and reusable catalyst for the synthesis of 3,4-dihydropyrano[*c*]chromenes. Iron oxide nanoparticles are of considerable interest because of the

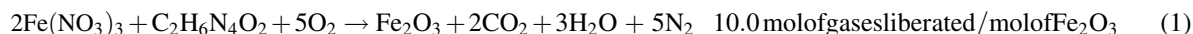
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valuable applications such as magnetic storage, medicine, and as catalyst [7,8]. Over the years researchers have employed in synthesis of iron oxide nanoparticles using different synthesis techniques such as sol–gel processes [9], chemical precipitation [10,11] forced hydrolysis [12] and other methods [13–16]. In the present work, an attempt has been made to study catalytic activity of α -Fe₂O₃ on synthesis of 3,4-dihydropyrano[*c*]-chromenes, to the best of our knowledge is concerned the use of α -Fe₂O₃ nanoparticles as a catalyst in the synthesis of 3,4-dihydropyrano[*c*]-chromenes has not been reported yet. Instantaneous combustion synthesis is an important powder processing technique generally used to prepare oxide ceramics [17]. It involves several advantages like fast heating rates, short reaction time, besides producing foamy, homogeneous and high surface area nanocrystalline products. It has also the advantage of doping desired amounts of dopant ions in solution medium and ‘low processing temperature’ leading to uniform crystallite size at superfine dimensions. High purity and homogeneity can be achieved at temperature as low as 300 °C as against 1470 °C needed to synthesize these materials *via* combustion route.

1. Experimental

The initial ingredients used for the preparation of α -Fe₂O₃ nanoparticles were of analar grade ferric nitrite (Fe(NO₃)₃·9H₂O) and oxalyl dihydrazide fuel (ODH; C₂H₆N₄O₂). The ODH fuel was prepared in our laboratory by the reaction of diethyl oxalate and hydrazine hydrate as described in the literature [18]. An aqueous solution containing stoichiometric amounts of ferric nitrite Fe(NO₃)₃·9H₂O and ODH; C₂H₆N₄O₂ were taken in a Petri dish of approximately 300 mL capacity. The excess water is allowed to evaporate by heating over a hot plate until a wet powder is left out. Then the Petri dish is introduced into a pre heated muffle furnace maintained at 300 ± 10 °C. The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products such as oxides of nitrogen and carbon. The combustion propagates throughout the reaction mixture without further need of any external heating, as the heat of the reaction is sufficient for the decomposition of the redox mixture. Finally, a voluminous and foamy reddish product has been obtained. Assuming complete combustion, the theoretical equation for the formation α -Fe₂O₃ with ODH can be written as follows:



The phase of the as-formed α -Fe₂O₃ nanopowder has been characterized by PXRD in a Philips diffractometer operating with Cu-K_α radiation ($\lambda = 1.54056 \text{ \AA}$). In Fig. 1, all the PXRD peaks can be indexed as hexagonal phase of α -Fe₂O₃ which are consistent with the values in the literature (Joint Committee on Powder Diffraction Standards (JCPDS card No.: 33-0664)). The average crystallite size of the product was estimated from the Debye–Scherrer’s equation and found in the range 30–40 nm. The surface morphology of the powders is examined by scanning electron microscope (SEM), using a JEOL (JSM-840A). The circular shaped primary particles are agglomerated and size in the order 0.2–1.0 μm (Fig. 2). The surface area of the powder sample was 35.0 m²/g, determined by a Quanta Chrome Corporation, NOVA1000 Gas Sorption Analyzer. The infrared spectroscopy of the as prepared nanocrystalline α -Fe₂O₃ was examined using a Perkin-Elmer spectrometer (spectrum 1000) with KBr pellets, the band at 450 and 537 cm⁻¹ were ascribed to Fe–O stretching vibrations.

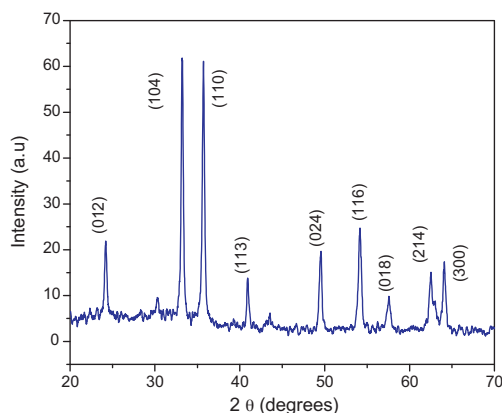
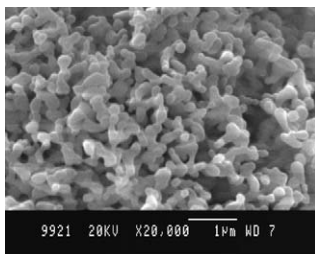


Fig. 1. PXRD of as-formed α -Fe₂O₃.

Fig. 2. SEM picture of as-formed α -Fe₂O₃.Table 1
Optimization of reaction conditions for the synthesis of **4a**.^{a,b}

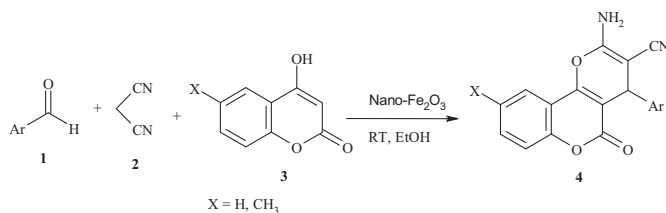
Entry	Catalyst	Quantity (wt%)	Solvent	Time (min)	Yields (%) ^c
1	Fe ₂ O ₃	5	C ₂ H ₅ OH	60	62
2	Fe ₂ O ₃	10	C ₂ H ₅ OH	30	93
3	Fe ₂ O ₃	15	C ₂ H ₅ OH	30	90
4	Fe ₂ O ₃	10	CH ₃ OH	60	60
5	Fe ₂ O ₃	10	CH ₃ CN	60	55
6	Fe ₂ O ₃	10	DCM	60	40
7	Fe ₂ O ₃	10	THF	60	35

^a Reagents: **1a** (1 mmol), **2** (1.2 mmol), **3** (1 mmol), solvent (20 volume).^b All reactions were carried out at room temperature condition.^c Yield refers to isolated product.

2. Results and discussion

Initially, the reaction of benzaldehyde (**1**, 1 mmol) malanonitrile (**2**, 1.2 mmol) and 4-hydroxycoumarin (**3**, 1 mmol) was chosen as a model reaction for the optimization of solvent effect and catalyst amount (Table 1, entries 1–7). Reaction in acetonitrile, dichloromethane (DCM) and tetrahydrofuran (THF) solvent gave low product yields even after 60 min (Table 1, entries 5–7). Although the yields were moderate in case of ethanol and methanol (Table 1, entries 1 and 4). We found ethanol and 10 wt% of α -Fe₂O₃ catalyst an efficient reaction medium in terms of reaction time as well as yield under room temperature (Table 1, entry 2). It is noteworthy to mention that in the absence of catalyst, no product was found even after 5 h. These results indicate that the catalyst exhibits a high catalytic activity in this transformation. Encouraged by these results and to explore the catalytic activity of nano catalyst, a variety of aldehyde with electron donating and withdrawing substituent was used for the highly selective synthesis of 3,4-dihydropyrano[*c*]chromenes in the presence of α -Fe₂O₃ under similar experimental conditions. However, the variations in the yields were very little and both substituted aromatic aldehydes such as 4-nitro and 2-nitro as well as heterocyclic aldehydes like 2-pyridine carboxaldehyde and gave the desired products in excellent yields (Scheme 1 and Table 2).

Reusability of the catalyst was examined employing the reaction between **1a**, **2** and **3** to obtain **4a** under identical reaction conditions. The catalyst was easily recovered from the mixture by filtration. The catalyst was washed with distilled water and ethanol repeatedly, and dried for 2–3 h under vacuum before re-use. The recycled catalyst was used five times to obtain 2-amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromenes without appreciable decrease in the yield 93, 90, 89, 85 and 82% respectively for 1–5 cycles. After every reaction, the catalyst was recovered from the reaction mixture



Scheme 1.

Table 2

Synthesis of 2-amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromenes in the presence of α -Fe₂O₃ [19].

Entry	Ar	X	Product	Time (min)	Yield (%) ^a	Mp (°C)
1	4-Pyridyle	H	4a	30	87	182–184 ^b
2	8-Quinoline	H	4b	30	83	218–220 ^b
3	3-CH ₃ OC ₆ H ₄	CH ₃	4c	30	86	266–268 ^b
4	2,4-(CH ₃ O) ₂ C ₆ H ₃	CH ₃	4d	30	84	225–227 ^b
5	4-O ₂ NC ₆ H ₄	CH ₃	4e	30	94	152–153 ^b

^a Yields are related to isolated pure products.^b Novel compounds.

by filtration and regenerated as described above. In conclusion this procedure offers several advantages including mild reaction conditions, cleaner reaction, and satisfactory yields of products, as well as simple experimental and isolating procedure, which makes it a useful and attractive protocol for the synthesis of these compounds.

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- [17] J.J. Kingsley, K.C. Patil, *Mater. Lett.* 6 (1988) 427.
- [18] G. Gran, *Anal. Chim. Acta* 14 (1956) 150.
- [19] General procedure for the synthesis of dihydropyrano[*c*]chromenes: a mixture of aldehyde (**1**, 1 mmol), malanonitrile (**2**, 1.2 mmol), 4-hydroxycoumarin (**3**, 1 mmol) and α -Fe₂O₃ (10 wt%) in (20 vol.) absolute ethanol was stirred at room temperature for 30 min, the progress of the reaction was monitored by TLC analysis. After the completion of reaction, the reaction mass was filtered, then washed with THF, the mother liquor containing the product was reduced to one fourth the volume and the pure product precipitated was filtered and dried to afford title compound good to excellent yield. Products {using 4-methoxy, 4-nitro, 3-nitro, 4-chloro, 2,4 and 2,3-dichlorobenzaldehydes (yields 86–93%) [Lit. 3,4]} are known compounds and their physical data, IR, and ¹H NMR spectra were essentially identical with those of authentic samples. Other products (**4a–4e**), which are new, were characterized by IR, ¹H NMR and LCMS analysis. Compound **4a**: brown solid, IR (KBr): ν max = 3386, 3132, 1728, 1685, 1645, 1586, 1438, 1246, 817 cm⁻¹; ¹H NMR: (400 MHz, DMSO-*d*₆): δ 4.96 (s, 1H), 7.22–7.23 (d, 1H), 7.48–7.52 (t, 2H), 7.72–7.77 (m, 3H), 7.87–7.89 (d, 1H), 8.01–8.02 (d, 1H); MS: m/z = 318 (M⁺). Compound **4b**: Creamish solid, IR (KBr): ν max = 3402, 3224, 1665, 1519, 1434, 1338, 1234, 1068, 813 cm⁻¹; ¹H NMR: (400 MHz, DMSO-*d*₆): δ 4.52 (s, 1H), 7.31–7.33 (t, 2H), 7.48–7.54 (m, 4H), 7.72–7.77 (m, 1H), 7.90–7.92 (m, 1H), 8.51–8.52 (m, 1H); MS: m/z = 368 (M⁺). Compound **4c**: White solid, IR (KBr): ν max = 3479, 3321, 3197, 2923, 2198, 1704, 1665, 1585, 1377, 1257, 821 cm⁻¹; ¹H NMR: (400 MHz, DMSO-*d*₆): δ 2.43 (s, 3H), 3.72 (s, 3H), 4.41 (s, 1H), 6.78–6.83 (m, 3H), 7.21–7.25 (t, 1H), 7.35–7.38 (d, 3H), 7.52–7.55 (m, 1H), 7.71 (s, 1H); MS: m/z = 361 (M⁺). Compound **4d**: Cream solid, IR (KBr): ν max = 3460, 3325, 3213, 2927, 2194, 1697, 1670, 1380, 1130, 779 cm⁻¹. ¹H NMR: (400 MHz, DMSO-*d*₆): δ 2.43 (s, 3H), 3.69 (s, 3H), 3.73 (s, 3H), 4.58 (s, 1H), 6.42–6.45 (m, 1H), 6.52–6.53 (d, 1H), 6.97–6.99 (d, 1H), 7.17 (s, 2H) 7.34–7.36 (d, 3H), 7.50–7.53 (m, 1H), 7.71 (s, 1H); MS: m/z = 390 (M⁺). Compound **4e**: Yellow solid, IR (KBr): ν max = 3477, 3336, 2198, 1758, 1685, 1586, 1410, 1190, 1185, 1058, 817 cm⁻¹; ¹H NMR: (400 MHz, DMSO-*d*₆): δ 2.43 (s, 3H), 4.66 (s, 1H), 7.36–7.38 (d, 1H), 7.53–7.59 (t, 4H), 7.72 (s, 1H), 8.17–8.19 (d, 2H); MS: m/z = 375 (M⁺).