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α-Fe_2O_3 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-Fe_2O_3 nanopowder at much lower temperature and its catalytic activity for the one-pot preparation of 3,4-dihydropyrano[*c*]chromenes. The combustion derived α-Fe_2O_3 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-Fe_2O_3 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.

Keywords: α-Fe_2O_3 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, malononitrile and 4-hydroxycoumarin have been developed in the presence of a variety of catalysts such as diammonium hydrogen phosphate [3], $H_6P_2W_{18}O_{62}\cdot 18H_2O$ [4], TBABr [5], and K_2CO_3 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, inexpense, 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-Fe_2O_3 on synthesis of 3,4-dihydropyrano[*c*]-chromenes, to the best of our knowledge is concerned the use of α-Fe_2O_3 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-Fe_2O_3 nanoparticles were of analar grade ferric nitrite ($Fe(NO_3)_3{\cdot}9H_2O$) and oxalyl dihydrazide fuel (ODH; $C_2H_6N_4O_2$). 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 $Fe(NO_3)_3{\cdot}9H_2O$ and ODH; $C_2H_6N_4O_2$ 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-Fe_2O_3 with ODH can be written as follows:

$$2Fe(NO_3)_3 + C_2H_6N_4O_2 + 5O_2 \rightarrow Fe_2O_3 + 2CO_2 + 3H_2O + 5N_2 \quad 10.0\,\text{molofgasesliberated/molof}Fe_2O_3 \qquad (1)$$

The phase of the as-formed α-Fe_2O_3 nanopowder has been characterized by PXRD in a Philips diffractometer operating with Cu-K_α radiation (λ = 1.54056 Å). In Fig. 1, all the PXRD peaks can be indexed as hexagonal phase of α-Fe_2O_3 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 m^2/g, determined by a Quanta Chrome Corporation, NOVA1000 Gas Sorption Analyzer. The infrared spectroscopy of the as prepared nanocrystalline α-Fe_2O_3 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.

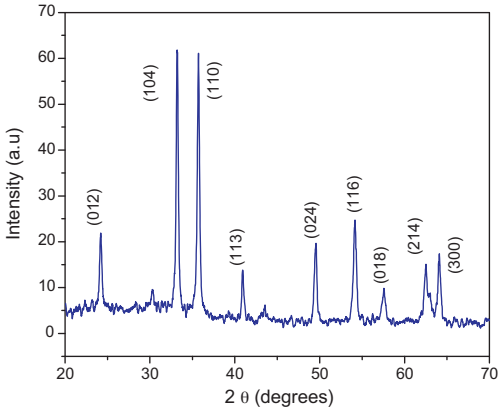

Fig. 1. PXRD of as-formed α-Fe_2O_3.