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Short Communication

Environmentally benign synthesis of polyhydroquinolines by Co_3O_4–CNT as an efficient heterogeneous catalyst

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ABSTRACT

A novel and eco-friendly synthesis of polyhydroquinolines is efficiently catalyzed by Co_3O_4–CNT nanocomposites. This recyclable catalytic system provides a simple strategy to generate a variety of polyhydroquinolines under mild conditions. Utilization of easy reaction condition, recyclable nanocatalyst, reduced environmental impacts and simple work-up make this methodology an interesting option for the eco-friendly synthesis of polyhydroquinolines.

1. Introduction

Polyhydroquinolines have attracted considerable interest because they possess various important pharmacological properties [1]. Polyhydroquinolines have found commercial utility as an important class of Ca^{+2} channel blockers as exemplified by therapeutic agents such as Nifedine, Nitrendipine and Nimodipine [2]. These examples clearly demonstrate the remarkable potential of polyhydroquinolines as a source of valuable drugs. In view of the importance of polyhydroquinoline compounds, many classical methods were reported in literature for the synthesis of polyhydroquinolines such as conventional heating [3] microwave technology [4], ultrasound irradiation [5] light induced procedure [6], various types of catalysts [7–12], grinding [13] and by refluxing in water [14]. Each of the above methods has its own merits, while some of the methods are plagued by limitations of poor yields, toxicity of solvents, critical product isolation procedures, restrictions for large scale applications, expensive catalysts, difficulty in recovery of high boiling solvents, excessive amounts of catalysts and generation of large amounts of toxic wastes in scaling up for industrial applications leading to environmental issues. Therefore, the discovery of novel and efficient catalysts is of prime importance to synthesize polyhydroquinoline compounds for further improvement toward milder reaction conditions and higher yields.

It is important to develop metal oxides nanoparticles as heterogeneous catalysts in organic reactions, because of their interesting structure, high catalytic activities and improved selectivity [15,16]. In general, heterogeneous nanocatalysts offer higher surface area and lower coordinating sites, which are responsible for the higher catalytic activity. On the other hand, among all metal oxides, the tricobalt tetraoxide (Co_3O_4) can be considered as a one of the best examples to understand the catalytic activity based on the variable particle size [17–19]. However, the specific surface area of the pure Co_3O_4 is not high enough for the practical applications. In addition, Co_3O_4 cannot be recycled easily, and the leaching cobalt cations in the reacting liquid-phase can lead to secondary pollution [20].

Stability of the nanoparticles is an important issue and supported metal nanoparticles as catalytic systems have potential to show greater efficiency. Recently, interest in carbon nanotubes (CNTs) as nanocatalyst supports has been increasing because of their unique morphologies and various potential applications [21–23]. CNTs as excellent supports possess a high surface area for high dispersion of nanocatalysts, well-defined porosity of structure for maximum reactant contact, excellent crystallinity or low electrical resistance to facilitate electron transport during chemical transformations and good interaction between the nanosized catalysts and the carbon support [23]. Co_3O_4 supported on CNTs are attracting significant attention owing to their wide applications as Schottky-junction diode [24], electrochemical capacitors [25], Li-ion battery anode applications [26], and nanocatalyst [27]. Combination of Co_3O_4 and CNTs with excellent electron transfer rate and large specific surface area is expected to provide a chance for improvement of the durability and performance of pure Co_3O_4 particles. We devised an effective and novel Co_3O_4–CNTs catalyzed synthesis of polyhydroquinolines in an efficient reaction (Scheme 1). However, there are no reports on the use of Co_3O_4–CNT nanocomposites for the synthesis of polyhydroquinolines under mild condition.

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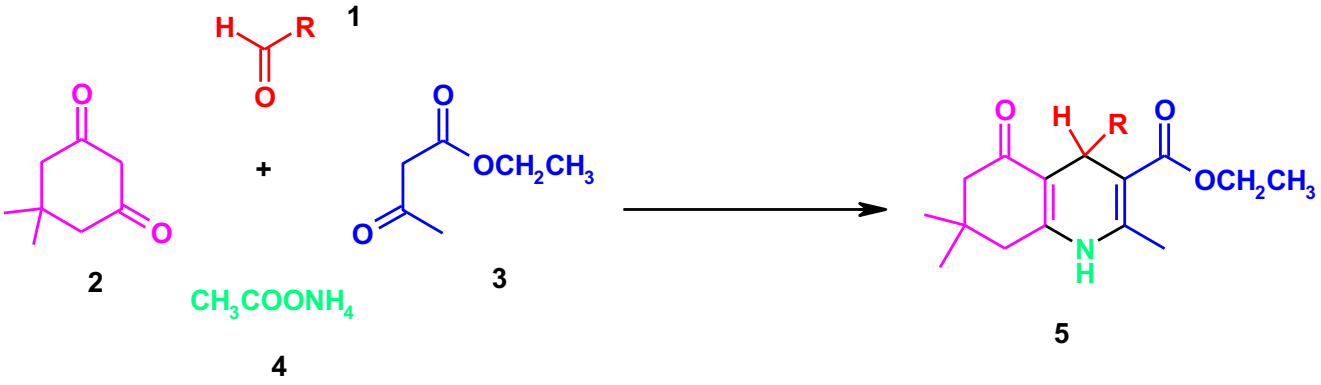


Scheme 1. One-step synthesis of polyhydroquinolines using Co_3O_4–CNTs.

2. Experimental

2.1. Materials and apparatus

Chemical reagents were obtained from the Merck Chemical Company. MWNTs with surface area of 136 m^2/g and 10–20 nm in diameter were supplied from Neutrino Company, Iran. Melting points (°C) were determined on an Electro thermal MK3 apparatus using an open-glass capillary and are uncorrected. FTIR spectra were recorded as KBr pellets on a Perkin–Elmer 781 spectrophotometer and on an Impact 400 Nicolet FTIR spectrophotometer.^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Bruker DPX-400 spectrometer. X-ray diffraction analysis was carried out on a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK, radiation, $\lambda = 1.5406A°$), at a scanning speed of 2° min^{-1} from 10° to 100° (2θ). The TEM images were recorded using a Philips CM10 transmission electron microscope operated at a 100 kV accelerating voltage.

2.2. Preparation of Co_3O_4–CNT nanocomposites

Oxidized CNTs were prepared by purification in a ratio of 3:1 70% nitric acid and 98 sulfuric acid at 50 °C under ultrasonication for 6 h. Composite material of Co_3O_4–CNT was prepared according to reported procedures in the literature [25]. In short, 0.5 g $Co(NO_3)_2 \cdot 6H_2O$ was dissolved into 40 mL n-hexanol to form a red solution. 70 mg of oxidized CNTs was dispersed in the red solution by sonication for 2 h. Then, this solution was refluxed at 140 °C for 10 h. After cooled to ambient temperature, the products were washed with cyclohexane repeatedly to remove any impurities and dried. The black powder was filtered and washed with ethanol and dried at 100 °C to obtain the Co_3O_4–CNT nanocomposite (Scheme 2).

2.3. General procedure for the synthesis of 2-ketomethylquinolines

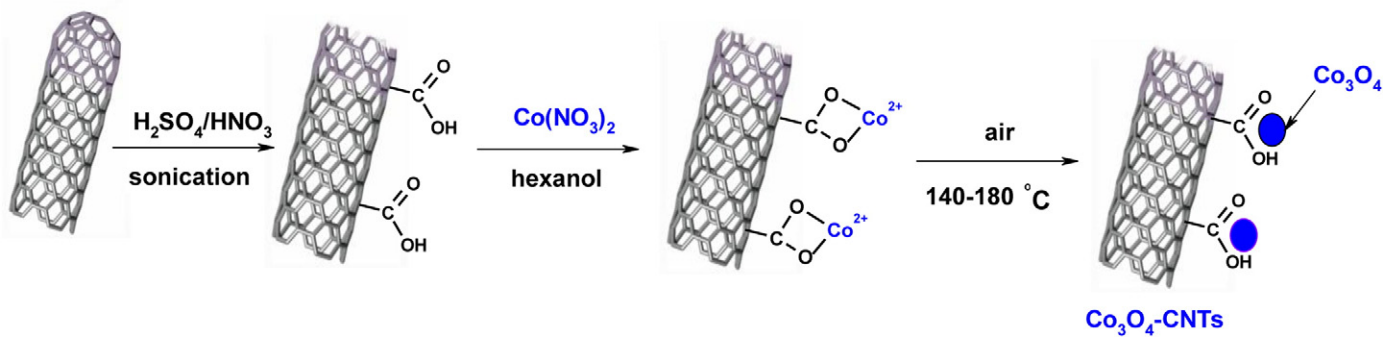
Benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.5 mmol) and Co_3O_4–CNT (0.03 g) were successively charged into a 50 mL round-bottomed flask and the contents were refluxed in EtOH (5 mL) for an appropriate period while the product formation was monitored by TLC (petroleum ether–EtOAc; $v/v = 7:3$). Upon completion, the nanocatalyst was recovered by simple filtration. Then, the ethanol was evaporated under reduced pressure to yield the crude product, which was then purified by recrystallization from hot ethanol and water to afford pure polyhydroquinolines.

3. Results and discussion

In this research, Co_3O_4–CNTs were prepared according to the schematic 2. The positive cobalt ions in the hydrophobic *n*-hexanol solution are adsorbed to the surface of the acid treated CNTs through electrostatic attraction and then in situ decomposes into Co_3O_4 according to the following process [25]:

$$3Co(NO_3)_2 \xrightarrow[140-180^{\circ}C]{air,\ n-hexanol} Co_3O_4\downarrow + 6NO_2\uparrow + O_2\uparrow$$

The XRD patterns of CNTs and Co_3O_4–CNTs composites are presented in Fig. 1. The diffraction peaks at 18.63, 35.17, 43.55, 54.22, 60.08 and 65.19 correspond to (1 1 1), (3 1 1), (4 0 0), (3 3 1), (4 2 2) and (5 1 1) reflections, respectively, which they are correlated with Co_3O_4 in spinel structure (JCPDS card No. 74-1656). This confirms the crystalline nature and phase purity of Co_3O_4 nanoparticles. Also, a peak is clearly observed near 26.22, which is typical for CNTs [28]. The XRD result clearly indicates that Co_3O_4 nanoparticles were decorated on the surface of CNTs.



Scheme 2. Schematic illustration of decoration of the CNTs with Co_3O_4 nanoparticles.