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Short Communication

Efficient clay supported Ni^0 nanoparticles as heterogeneous catalyst for solvent-free synthesis of Hantzsch polyhydroquinoline

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ABSTRACT

A green and efficient multicomponent one-pot synthesis of Hantzsch polyhydroquinoline was achieved by the condensation of aldehydes, dimedone, ethylacetoacetate and ammonium acetate at room temperature using environmentally benign modified Montmorillonite supported Ni^0-nanoparticles as catalyst. The well dispersed Ni^0-nanoparticles having a high surface to volume ratio have promising features for the reaction such as easy removal of the catalyst, solvent-free, shorter reaction time, high product yields (about 95%) and easy work up procedure. There is no significant effect of electron withdrawing or donating nature of substituent on aldehydes in the formation of polyhydroquinoline derivatives.

1. Introduction

4-Substituted 1,4-dihydropyridine (DHP) nucleus comprises a large family of medicinally important compounds such as Ca^{2+} channel blockers and some of the representative compounds of this class possess acaricidal, insecticidal, bactericidal and herbicidal activities [1]. 1,4-Dihydropyridine possesses a variety of biological activities, such as, vasodilator, bronchodilator, anti-atherosclerotic, antitumor, geroprotective, hepatoprotective and antidiabetic agent [2–5]. Photocatalytic oxidation of these compounds to pyridine derivatives constitutes the principal metabolic pathway in biological systems [6]. Therefore, oxidative aromatization of DHPs has been a subject of great interest of organic and medicinal chemists.

Realizing the importance of polyhydroquinoline derivatives, several synthesis methods have been reported, like conventional heating [7], refluxing in acetic acid [8] and microwave irradiation [9] and ultrasound [10]. Different other approaches for the syntheses of polyhydroquinoline derivatives using various catalysts, such as TMSCl [11], ionic liquids [12,13], L-proline [14], polymers [15], $Yb(OTf)_3$ [16], $Sc(OTf)_3$ [17], $HClO_4$–SiO_2 [18], cerric ammonium nitrate [19], heteropoly acid [20], p-TSA [21], HY-zeolite [22] and Mont. K10 [23] have also been reported and some of the methods are associated with several shortcomings such as long reaction times, expensive reagents, harsh reaction conditions, low-product yields and the use of large quantity of volatile organic solvents.

In recent years, heterogeneous catalysts are gaining more importance due to environmental and economic factors. The efficiency can be improved by using nanosized catalysts because of their small size and large surface to volume ratio. It has been observed that Ni^0-nanoparticles as catalysts offer great attention for a wide range of applications in organic transformations such as chemo-selective oxidative coupling of thiols [24], reduction of aldehydes and ketones [25–27], hydrogenation of olefins [28] and support for hydrogen adsorption [29]. Recently, the progress in the field of solvent-free reactions is gaining significance because of their high efficiency, operational simplicity and environmentally benign processes. The multi-component reactions are powerful tools in the modern drug discovery process and allow fast, automated and high throughput generation of organic compounds. The possibility of performing multi-component reactions under solvent-free conditions with a heterogeneous catalyst could enhance their efficiency from an economic as well as an ecological point of view.

Herein, we would like to report Hantzsch polyhydroquinoline derivative synthesis catalyzed by modified Montmorillonite supported Ni^0-nanoparticles under solvent-free conditions, using aromatic aldehyde, dimedone, ethylacetoacetate and ammonium acetate. This method not only preserves the simplicity, but also consistently gives the corresponding products in good to excellent yields. The modified clay support has paved the way for better dispersion of the Ni^0-nanoparticles which results in higher catalytic activity.

2. Experimental

2.1. Materials and method

Naturally occurring Montmorillonite contains impurities like silica sand, iron oxide, etc. and were purified by dispersion cum sedimentation technique [30] to collect the <2 μm fraction. The reagents were

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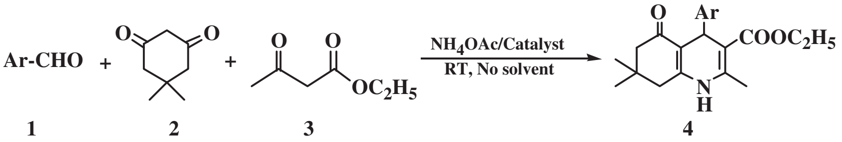

Scheme 1. Modified Montmorillonite supported Ni^0-nanoparticle catalyzed synthesis of polyhydroquinone under solvent-free condition.

purchased from Acros Organic, Aldrich, Spectrochem and Merck and used as received from the supplier without further purification.

2.2. Preparation of clay supported Ni^0-nanoparticles

The preparation of modified Montmorillonite and supported Ni^0-nanoparticles was carried out as reported earlier [31]. In a synthetic methodology, a known amount of acid treated clay was taken in a 100 ml beaker to which 10 ml (0.05 mM) aqueous solution of Ni $(CH_3COO)_2$ was added under vigorous stirring condition. The stirring was continued for 5–6 h followed by evaporation to dryness in rotary evaporator. The dry composite thus obtained was dispersed in 50 ml ethylene glycol in a double necked round bottom flask and refluxed for 6 h under nitrogen atmosphere to form an in situ solid product of Ni^0-nanoparticles. The materials were recovered, washed with methanol until it was free from ethylene glycol and dried at about 40 °C for 12 h. The Ni loading in the supported catalysts was determined by AAS analysis and found to be 4.85 wt.%.

2.3. Characterization

The modified clay support and supported Ni^0-nanoparticles were characterized by using PXRD, surface area analyzer and transmission electron microscopy (TEM) studies [32]. The powder XRD was recorded in Rigaku Ultima IV machine with Cu Kα radiation ($\lambda = 1.5409$ Å). The textural properties measured by using Autosorb-1 (Quantachome, USA) and transmission electron microscopy (TEM) image were recorded on a JEOL JEM-2011 electron microscope.

2.4. Synthesis of Hantzsch polyhydroquinoline derivatives

To a mixture of aromatic aldehyde (1 mmol), dimedone (1 mmol), ethylacetoacetate (1 mmol), and ammonium acetate (1.5 mmol) in a 10 ml round bottom flask, modified Mont. supported Ni^0-nanoparticle catalyst (25 mg) was added [Scheme 1]. The mixture was homogenized and stirred at room temperature for 20–25 min, the progress of the reaction was monitored by thin layered chromatography. After completion, 10 ml dichloromethane was added to the reaction mixture; the catalyst was removed by filtration and washed with dichloromethane and acetone. Then, the liquid portion was extracted with ethyl acetate and water to remove any unreacted ammonium acetate; the organic layer was dried over sodium sulfate and concentrated in vacuum to afford the crude products. The pure product was obtained by recrystallization from ethanol.

3. Results and discussion

The XRD patterns of modified Montmorillonite (AT-Mont.) along with parent clay are shown in Fig. 1. The significant structural modification of Montmorillonite was reflected in their relative intensity and location of basal spacing (d_{001}). The parent Montmorillonite clay exhibited an intense basal peak at $2\theta = 7.06°$, corresponding to basal spacing of 12.5 Å. When the clay is activated with mineral acid under controlled conditions for different time periods, the intensity due to basal spacing (d_{001}) decreases. From the XRD [Fig. 2], the characteristic peaks at $2\theta = 44°$, 51.8° and 76° marked by their indices (111), (200) and (222) indicate the formation of Ni^0 in the nanoparticles. The TEM study [Fig. 3] also reveals the formation of well dispersed Ni^0-nanoparticles of size less than 10 nm on modified Montmorillonite.

The supported Ni^0-nanoparticles were investigated as a catalyst in the synthesis of polyhydroquinoline derivatives i.e. condensation of benzaldehyde, dimedone, ethylacetoacetate, and ammonium acetate in the presence of catalytic amount of Ni^0-nanoparticles under solvent-free conditions at room temperature, which afforded product 4a in 95% yield [Table 1]. Such reaction occurs with a wide range of aromatic aldehydes carrying either electron-donating or electron withdrawing substituents in the ortho, meta, and para positions [Table 1]. The products were established by comparing their melting points and the spectral data for selected compounds. A possible explanation for the better yield in solvent-free conditions is that the eutectic mixture having uniform distribution of the reactants brings the reacting species in close proximity to react than in solvent.

To investigate the effects of solvent, the condensation reaction of benzaldehyde, dimedone, ethylacetoacetate, and ammonium acetate in various organic solvents at room temperature using 4.85 wt.% Ni^0-nanoparticles as the catalyst was carried out. About 75% of the expected

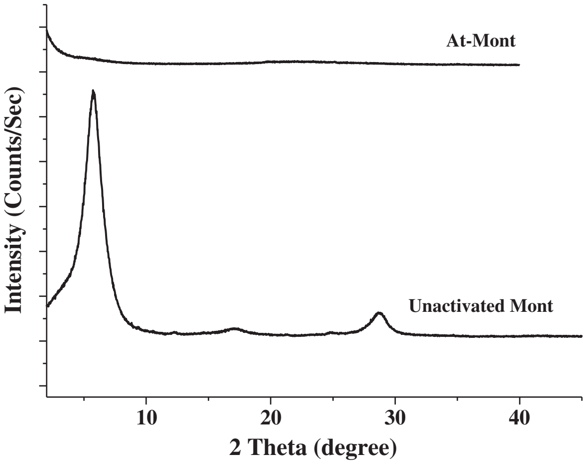

Fig. 1. Powder XRD pattern of unactivated and acid treated Montmorillonite (At-Mont.).

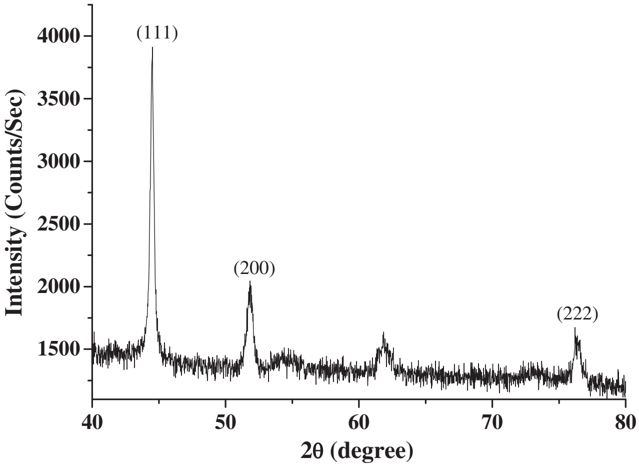

Fig. 2. Powder XRD pattern of Ni^0-nanoparticles supported on modified Montmorillonite.