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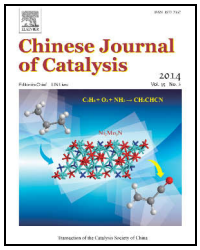

Article

Preparation and characterization of nano-CaO based on eggshell waste: Novel and green catalytic approach to highly efficient synthesis of pyrano[4,3-*b*]pyrans

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ABSTRACT

Nano-CaO was prepared by calcination of ball-milled chicken eggshell waste. This novel, bioactive, heterogeneous catalyst, which had high catalytic activity and reusability, was used in the green synthesis of pyrano[4,3-*b*]pyrans via condensation of various aromatic aldehydes, malononitrile, and 4-hydroxy-6-methyl-2*H*-pyran-2-one at 120 °C under solvent-free conditions. The reaction proceeded to completion within 5–45 min in 93%–98% yield. The nano-CaO was fully characterized by scanning electron microscopy, X-ray powder diffraction, infrared spectroscopy, X-ray fluorescence spectroscopy, and thermal gravimetric, surface area, and elemental analyses.

1. Introduction

Recently, there has been increasing interest in the development of clean technology to replace the use of hazardous reagents and catalysts with relatively environmentally benign compounds. Additionally, "green chemistry" emphasizes the optimization of synthetic methodologies to reduce pollution, costs, and tedious work-ups [1–3]. This new challenge has led to a growing interest in the use of natural and bio compounds for organic and inorganic application. Eggs, an abundant natural food source, are consumed worldwide because they contain essential amino acids, vitamins, and minerals. Chicken eggshell is totally biodegradable, recyclable, and biocompatible, with good osteoconductivity [4]. It consists of more than 90% $CaCO_3$ and has emerged as a novel bone substitute in its natural form [5–8]. This natural solid waste is non-hazardous, and is commonly disposed of in landfills without any pretreatment because it has no traditional uses [9]. The eggshell structure is mesoporous, with the ability to form a nanoporous structure [10]. Substrates with nanostructures, dense nanopores, and high surface areas have found many application in biosensors, proteomics, light-emitting diodes [4,11–14], and tissue engineering [15–17]. We previously reported the first ultrasonic-assisted preparation of nano-$CaCO_3$ based on eggshell waste, and its use as a heterogeneous catalyst in the green synthesis of 2-aminochromenes [16]. Eggshells have previously been used to synthesize nanoparticle apatite, hydroxyapatite nanopowders, and nano-$CaCl_2$, but these require sintering or the use of acidic and hazardous solvents to make porous scaffolds [18–20]. In this paper, we report a green, simple, and cheap approach to making nano-CaO based on chicken eggshell waste. We also characterized the nano-CaO structure and investigated its use as a catalyst in the green synthesis of pyrano[4,3-*b*]pyrans.

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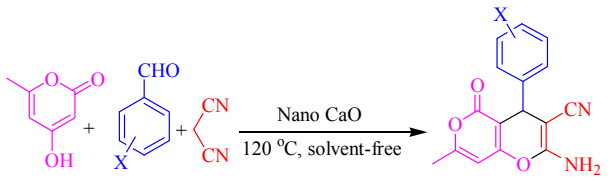

Scheme 1. Synthesis of 2-amino-7-methyl-5-oxo-4-phenyl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitrile derivatives.

It is known that many pyran derivatives exhibit a wide spectrum of pharmacological and biological activity [21–23]. Moreover, they have been shown to have important medicinal properties such as antimicrobial [24], antiviral [25,26], antiproliferative [27], antitumor [28], anticancer [29], anti-HIV, antituberculosis, anti-inflammatory, and antifungal activity [30–35]. Despite their wide range of pharmacological and industrial application, the synthesis of pyrano[4,3-*b*]pyrans has received little attention. Recently, members of this important class of pyran derivatives have been synthesized via one-pot multicomponent condensation reactions of aryl aldehydes, malononitrile, and 4-hydroxy-6-methyl-2*H*-pyran-2-one in the presence of different reagents. Various reagents such as KF-Al_2O_3 [36], [bmim]BF_4 [28], piperidine [37], and NH_4OAc [38] have been used to accomplish this transformation. However, in spite of their potential utility, all of these methods suffer from one or more disadvantages, such as unsatisfactory yields, very prolonged reaction time, and the use of organic solvents. So, in a continuation of our efforts to develop new green chemistry methods [39,40], we decided to explore the green synthesis of 2-amino-7-methyl-5-oxo-4-phenyl-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitrile derivatives in the presence of nano-CaO based on eggshell waste as a novel and green biocatalyst, under solvent-free and thermal conditions (Scheme 1).

2. Experimental

2.1. Materials and Instruments

All chemicals were of analytical grade, purchased from Merck, and used as received. Melting points were determined using a Gallenkamp melting-point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded at 500 (^{1}H) and 125.77 (^{13}C) MHz using a Bruker DRX-500 Avance spectrometer. Fourier-transform infrared (FT-IR) spectra were obtained using a MATSON 1000 FT-IR spectrophotometer. X-ray diffraction (XRD) was performed using a D8 Bruker diffractometer (40 kV and 40 mA) with Cu K_α radiation (λ = 0.154 nm) to analyze the crystal structure of the milled powders. The XRD patterns were recorded in the 2θ range 20°–80° with a step size of 0.01°. The mean size and size distribution of the eggshell powder were measured using a dynamic laser light scattering apparatus (FRITSCH Analysette 22 NanoTec Laser Particle Sizer). The chemical composition of the catalyst was determined using X-ray fluorescence (XRF) spectroscopy (Microanalyser Unisantis XMF-104, Germany) operated at 40 kV and 300 mA, with Mo radiation. Thermogravimetric analysis-differential thermal analysis (TGA-DTA) experiments were carried out using an STA 409 PC Luxx thermal analysis instrument (NETZSCH, Germany) under a flow of nitrogen. The sample mass used was about 20 mg, and the temperature ranged from 25 to 900 °C, with a rising rate of 10 °C/min. The film cross-section morphology was examined using field-emission scanning electron microscopy (FESEM) after fracturing in liquid nitrogen. Dried samples were coated with gold ions using an ion coater for 150 s. The surface structure was visualized using FESEM (Hitachi S4160) at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were obtained using a LEO912-AB (LEO, Germany) transmission electron microscope with an accelerating voltage of 120 kV. Particles were deposited on carbon foil supported by a copper grid. Energy-dispersive X-ray analysis (EDX) was performed using an Oxford instruments EDX detector (UK) with an accelerating voltage of 10.0 kV. Milling was carried out in a planetary ball-mill using a hardened chromium steel vial (250 mL) at room temperature in an argon atmosphere. The ball-to-powder mass ratio and the rotation speed of the vial were 10:1 and 350 r/min, respectively.

2.2. Catalyst preparation

Empty chicken eggshells were collected from household waste and washed with warm tap-water. The adhering membranes were separated manually. The eggshells were then washed with distilled water and dried at 120 °C for 1 h. The eggshells were milled in a planetary ball-mill for 2 h, and the eggshell powder was calcined at 900 °C for 1 h. The resulting material was denoted by nano-CaO.

2.3. General procedure for synthesis of pyrano[4,3-b]pyrans

A mixture of 4-chlorobenzaldehyde (0.14 g, 1 mmol), malononitrile (0.07 g, 1 mmol), and 4-hydroxy-6-methyl-2*H*-pyran-2-one (0.126 g, 1 mmol) was stirred thoroughly at 120 °C under solvent-free conditions in the presence of a catalyst amount of nano-CaO (0.1 g) to afford the corresponding pyrano[4,3-*b*]pyran in excellent yield. After completion of the reaction (thin-layer chromatography), hot EtOH was added and the reaction mixture was stirred for 5 min. Then the solid catalyst was filtered from the soluble products and washed with hot EtOH. After cooling, the crude products were precipitated. Pure pyrano[4,3-*b*]pyrans were obtained in high yields without further purification. All compounds were known in the literature [28,36–38] and the NMR and IR spectra of the products were in agreement with earlier data [28,36–38].

Spectra data of two selected compounds are as following.

2-amino-7-methyl-5-oxo-4-(4-chlorophenyl)-4*H*,5*H*-pyrano [4,3-*b*]pyran-3-carbonitrile (Table 2, Entry 2): pale-yellow crystals, mp 227–229 °C. IR (KBr, cm^{-1}): 3383, 3324, 3195, 2201, 1710, 1674, 1645, 1597, 1488, 1445, 1414, 1384, 1261, 1141, 1092, 1015, 981, 854, 830, 807, 777, 511. ^{1}H NMR (400.2 MHz, DMSO, δ): 2.23 (s, 3H, CH_3), 4.33 (s, 1H, CH), 6.29 (s, 1H, =CH), 7.23 (d, 2H, J = 8.4 Hz, ArH), 7.26 (s, 2H, NH_2), 7.38 (d, 2H, J = 8.4 Hz, ArH). ^{13}C NMR (400.2 MHz, DMSO, δ): 19.8, 36.2,