Catalysis Communications 29 (2012) 53–57

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Efficient conversion of aldehydes and ketones into oximes using a nanostructured pyrophosphate catalyst in a solvent-free process

Abdelhakim Elmakssoudi [a], Karima Abdelouahdi [b], Mohamed Zahouily [a,c,*], James Clark [d], Abderrahim Solhy [a,*]

[a] MAScIR Foundation, VARENA Center, Institute of Nanomaterials& Nanotechnology, ENSET, Av. De l'Armé Royale, Madinat El Irfane 10100-Rabat, Morocco
[b] Centre National pour la Recherche Scientifique et Technique (CNRST), Division UATRS, Angle Allal Fassi/FAR, B.P.8027, Hay Riad, 10000 Rabat, Morocco
[c] Laboratoire de Catalyse, Chimiométrie et Environnement, URAC 24, Faculté des Sciences et Techniques, Université Hassan II, Mohammedia B. P. 146, 20650, Morocco
[d] Green Chemistry Centre of Excellence, University of York, York YO10 5DD, UK

ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form 9 September 2012
Accepted 13 September 2012
Available online 20 September 2012

Keywords:
Heterogeneous catalysis
Nanostructured pyrophosphate
Clean synthesis
Oximes
Microwave
Conventional heating

ABSTRACT

A nanostructured pyrophosphate ($Na_2CaP_2O_7$) was synthesized by controlling the speed of its calcination, and then characterized by several methods including TGA, X-ray diffraction, FTIR, SEM, TEM and the determination of the surface area by the BET method. However, several aldehydes and ketones were efficiently and rapidly converted into the corresponding oximes by treatment with hydroxylamine hydrochloride in a solvent-free process under microwave irradiation using this nanostructured pyrophosphate as catalyst. The yields of the products were very high and the time required for their preparation was very short compared to conventional heating experiments and the catalyst was efficiently re-used.

1. Introduction

One of the most important challenges for the modernization of organic synthesis is the preparation of active, selective, robust, and low-cost catalysts. Thus, the development of nanostructured catalysts for fine chemical production is currently a subject of increasing interest [1–4]. The second approach to achieve this target is to explore alternative reaction conditions and reaction media with minimal by-products [5]. Specifically, microwaves (MW) are an important alternate source of energy, which can accelerate reactions by the selective absorption of MW energy by polar molecules. The short reaction time and the expanded reaction range offered by MW assisted synthesis are suited to meet the increased demands in industry, particularly the pharmaceutical industry [6–8].

On the other hand, a large number of pharmaceutical oximes contain a group attached to a variable structure [9,10]. Furthermore, oximes are widely used as intermediates in fine organic synthesis [11–13]. The classical method for preparing them is the reaction of an aldehyde or ketone with hydroxylamine hydrochloride [14]. Several methods for their preparation have been reported in the literature including the use of formic acid [15], pyridine-chloroform [16], ethanol-pyridine [17], sulfuric acid [18], and NaOH with or without solvent [19–22]. However, the hazardous nature of these reagents results in many limitations. In order to avoid these limitations, many alternative strategies have recently been developed using solid catalysts such as alumina [23], silica gel [24], basic Al_2O_3 [25], resin (Amberlyst A-21) in ethanol [26], CaO [27], $FeCl_3$ [28], TiO_2/SO_4^{2-} without solvent [29], supported-POM [30], and Na_2SO_4 under ultrasound irradiation [31–33]. Recent literature has reported that high yields of hydroxyiminocycloalkanes could be achieved by either treating corresponding ketones with hydroxylamine or treating its salts in ionic liquids that contain sodium acetate or sodium bicarbonate [34]. Zang et al. have synthesized these products by the action of an ionic liquid under ultrasound irradiation [35]. More recently, Liao et al. have used the Pd/CNTs (carbon nanotubes) in the hydrogenation of nitrocyclohexane to cyclohexanone oxime [36].

Furthermore, many studies have been published describing the synthesis and use of the pyrophosphate ($Na_2CaP_2O_7$) in various fields, particularly in heterogeneous catalysis [37]. Bennazha et al. were able to synthesize and characterize a series of pyrophosphates by adopting a dry technique [38]. Recently, we have developed a method to tailor the nanostructure of this pyrophosphate by focusing on reactant crashing and the speed of calcination. This nanostructured pyrophosphate has been used with great success to catalyze the synthesis of 2-amino-chromenes [39]. In this paper and in the continuity of our work we wish to report a new, simple,

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[*] Corresponding authors. Tel.: +212 661379886; fax: +212 530279827.
E-mail addresses: m.zahouily@mascir.com (M. Zahouily), a.solhy@mascir.com (A. Solhy).

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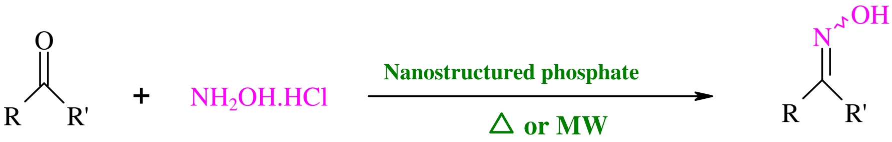
http://dx.doi.org/10.1016/j.catcom.2012.09.017



Scheme 1. Nanopyrophosphate catalyzed the synthesis of oximes under solvent-free conditions under microwave irradiation or conventional heating.

and green method for the solvent-free synthesis of oximes under microwave irradiation and via conventional heating using a nanostructured pyrophosphate ($Na_2CaP_2O_7$) catalyst (Scheme 1).

2. Experimental

2.1. Materials and apparatus

All commercial reagents were purchased from Aldrich Chemical Company and were used without further purification. Thermogravimetric analyses (TGA) were conducted under air in a TA Instrument Q500 apparatus with a 10 °C/min ramp between 25 and 1000 °C. X-ray diffraction (XRD) patterns of the catalyst were obtained at room temperature on a Bruker AXS D-8 diffractometer using Cu-K_α radiation in Bragg–Brentano geometry (θ–2θ). Fourier transform infrared (FT-IR) spectra of samples in KBr pellets were measured on a Bruker Vector 22 spectrometer. Scanning electron microscopy (SEM) pictures were recorded on a FEI Quanta 200 microscope after carbon metallization. The TEM micrographs were obtained on a Tecnai G2 microscope at 120 kV. Specific surface areas were determined from the nitrogen adsorption/desorption isotherms (at −196 °C) and measured with a Quantachrome Autosorb-1 automatic analyzer, using the BET equation at $p/p_0 = 0.98$. The microwave used was a StratSynth (Milestone S.r.l.); the wavelength of the microwave varied between 1 mm and 1 m, with a frequency that varied between 300 GHz to 300 MHz. NMR spectra were recorded on a Bruker ARX 300 spectrometer. Melting points were determined using a Stuart SN5228 apparatus.

2.2. Catalyst preparation

The synthesis of the pyrophosphate ($Na_2CaP_2O_7$) in nanopowder form was carried out using Na_2CO_3, $CaCO_3$ and $NH_4H_2PO_4$ in a 1:1:2 molar ratio respectively (purity of starting materials greater than 99%). These materials were mixed together in an agate mortar and heated progressively from 100 to 450 °C (Fig. S1 in Supplementary Data). Another sample has been prepared by adopting the conventional method described previously [38]. Thus, the same reagents were ground together and heated progressively to fusion (950 °C) in a porcelain crucible for 24 h with intermittent cooling and regrinding. The difference between these two methods is at the grinding velocity and the temperature of calcination.

2.3. General procedure for the synthesis of oximes

1 mmol of aldehyde or ketone and 2 mmol of hydroxylamine hydrochloride were mixed with 0.1 g of the nanostructured pyrophosphate ($Na_2CaP_2O_7$), and the mixture was heated classically at 80 °C or placed in a glass tube in a microwave reactor and then irradiated at 400 W (80 °C). After completion, CH_2Cl_2 was added, and the reaction mixture was filtered. The solution obtained was evaporated under reduced pressure. Further purification was accomplished by column chromatography on silica gel (200–300 mesh, eluted with petroleum ether or a mixture of petroleum ether and ethyl acetate). The products were identified by their melting points, ^1H NMR, and IR spectroscopies. The recovered nanostructured pyrophosphate was washed with acetone and calcined at 500 °C for 1 h before re-use.

3. Results and discussion

The synthesis of $Na_2CaP_2O_7$ was carried as it was described above (Section 2.2). In order to obtain a homogeneous single phase product, additional grinding and progressive heating steps were carried out. The details of the synthesis process of this catalyst and the adopted manner to control the nanostructuring are described in Figure S1. We note that the only difference with the method described in our previous work [39], is the velocity of heating and the affinity of the reagents mixture. The nanocrystal-size of the final product does depend not only on the quality of the starting products but also on the precision of the weighing and grinding. Thermogravimetric analysis (TGA) of a mixture of these three reagents showed that the thermal behavior of this blend was suitable to form the desired pyrophosphate (Figure S2 in ESI). Three major mass losses were observed and represented approximately 52% of loss, then these corresponded to the dehydration reaction (20%), the loss of NH_3 (17%) and CO_2 (5%) as well as the crystallization of this material (10%). X-ray diffraction (XRD) of $Na_2CaP_2O_7$ showed that this system crystallized in the

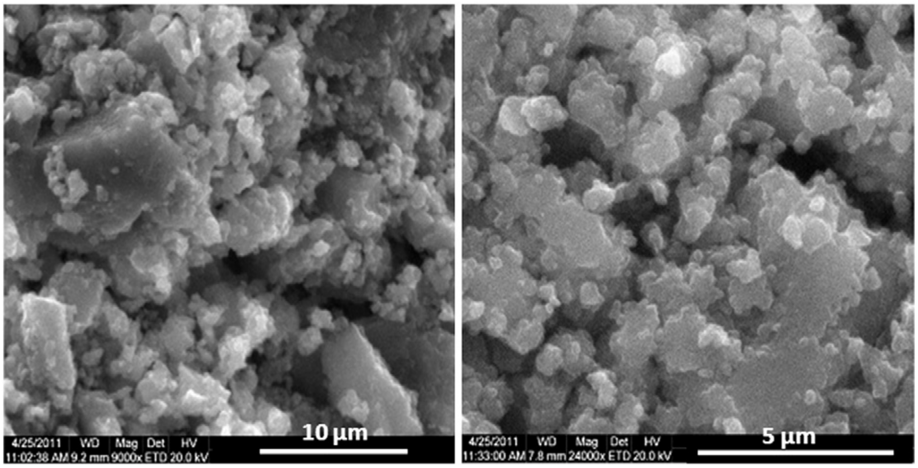


Fig. 1. SEM of $Na_2CaP_2O_7$.