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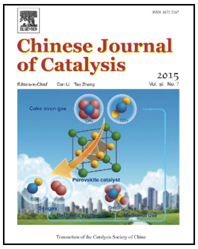

Article

Selective oxidation of alcohols over nickel zirconium phosphate

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ABSTRACT

Nickel zirconium phosphate nanoparticles were found to function as efficient catalysts for the selective oxidation of a wide range of alcohols to their corresponding ketones and aldehydes using H_2O_2 as an oxidizing agent and without any organic solvents, phase transfer catalysts, or additives. The steric and electronic properties of various substrates had significant influence on the reaction conditions required to achieve acetylation. The results showed that this method can be applied for the chemoselective oxidation of benzyl alcohols in the presence of aliphatic alcohols. The catalyst used in the current study was characterized by ICP-OES, XRD, NH_3-TPD, Py-FTIR, N_2 adsorption-desorption, SEM and TEM. These analyses revealed that the interlayer distance in the catalyst increased from 0.75 to 0.98 nm when Ni^{2+} was intercalated between the layers, whereas the crystallinity of the material was reduced. The nanocatalyst could also be recovered and reused at least seven times without any discernible decrease in its catalytic activity. This new method for the oxidation of alcohols has several key advantages, including mild and environmentally friendly reaction conditions, short reaction time, excellent yields and a facile work-up.

1. Introduction

α-Zirconium phosphate (ZP) is one of the most important compounds in inorganic chemistry, and the layered structure of this material has led to its use in a variety of different fields [1–3]. ZP behaves as a unique ion exchanger because of its exceptionally poor aqueous solubility, high thermal stability, resistance to radiation and abrasive properties [4,5]. The H^+ of the P–OH moiety in ZP can be exchanged for various ions, resulting in an enlargement of the interlayer distance [6–9]. Several studies pertaining to the successful exchange of this proton with various divalent and trivalent cations have been presented in the literature [10–14]. It has also been reported that ZP possesses excellent selectivity towards Pb^{2+}, Zn^{2+}, and Fe^{3+} as an ion exchanger [15–17]. Furthermore, ZP has been reported to exhibit antibacterial activity when loaded with Cu^{2+}, Zn^{2+}, or Ce^{3+} [5,6,13,14]. There have also been several reports concerning the catalytic activity of ion-exchanged materials of this type, including the use of zinc zirconium phosphate (ZPZn) and copper zirconium phosphate (ZPCu) as catalysts in the acetylation of alcohols and phenols and the use of potassium iron zirconium phosphate as a catalyst in Friedel-Crafts benzoylation reactions [18–24].

The selective oxidation of alcohols into the corresponding carbonyl compounds is of importance in research because the corresponding aldehydes, ketones and carboxylic derivatives serve as important and versatile intermediates for the synthesis of various chemicals, vitamins, drugs and fragrances [25–27]. For example, benzaldehyde (BzH) is a typical product of alcohol oxidation and a starting material for the preparation

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of intermediates for dyestuffs, agrochemicals, perfumery and pharmaceuticals [27–29]. From economic and environmental viewpoints, there have been many recent publications emphasizing environmentally benign methods for the oxidation of alcohols, using molecular O_2 or aqueous H_2O_2 as the oxidant, in the presence and/or absence of solvents such as $CuSO_4$ [25], $CuBr_2$ [26], AMPA [28], MPA/V_2O_5-Al_2O_3 [29], TEMPO-IL/CuCl [30], $Ni_3[Fe(CN)_6]_2$ [31], (Pd/Fe@C) [32], silica-gel-TEMPO-NO_x [33], $CoTM_4PyP$-MT [34], $Zn_4(P_2W_{15}O_{56})^{16-}$ [35], $(TEAH)H_2PW_{12}O_{40}$ [36], Zn-Co-LDH [37], $RuCl_3{\cdot}3H_2O$ [38], $H_4SiW_{12}O_{40}/SiO_2$ [39], AuRu/AC [40], oxidovanadium(V) complexes [41], Ag/SBA-15 [42], DHPDMDO [43], $H_2WO_4/[C_8mim][NTf_2]$ [44], SF-3-APTS–Fe(TClPP) [45], $NaBrO_3$/[bmim]Br [46], KBr/Oxone [47], WO_4@PMO-IL [48], Cu-NHC-TEMPO complexes [49], Cu/AlO(OH)$_x$ [50], $Na_4H_3[SiW_9Al_3{\cdot}(H_2O){\cdot}3O_{37}]$ [51], copper/imidazolium/TEMPO [52], $Ca(ClO)_2/Al_2O_3$ [53], PVPTB [54], Au/UiO-66 [55], PSFC [56], Au/Al_2O_3 [57], $PMo_{11}M$ (M = Co, Mn, Ni) [58], Mn(salen)OAc [59], BPFC [60], $KMnO_4$-aluminum silicate [61], MnTPPS-silica [62] and PVP-H_2O_2 [63]. Homogeneous catalysts have drawbacks in terms of their corrosive nature, pollution of the product with catalyst, tedious catalyst separation and post-synthesis disposals, and recovery from the effluents. However, the design of a new catalyst, which gives excellent conversion with maximum selectivity for organic transformation, is one of the challenges in the field of catalysis. With growing environmental concerns, one of the most promising ways to achieve these goals seems to be the use of green and insoluble catalysts or of ecofriendly solvent-free conditions. H_2O_2 is a green and very clean oxidant for liquid phase oxidations because it provides a high content of active oxygen species where water is the only byproduct. This oxidant is much cheaper and safer than most other organic and inorganic oxidants and is also readily available. When an insoluble catalyst is used, it can be easily recovered from the reaction mixture by simple filtration and recycled and can be reused several times, making the process more economically and environmentally viable. Furthermore, reported examples have demonstrated that heterogeneous catalysts typically require easier work-up procedures. With this in mind, and as part of ongoing work towards the development of efficient green catalysts for organic transformations [64,65] with particular emphasis on the oxidation of alcohols [23], we report herein the use of nickel zirconium phosphate (ZPNi) as an efficient catalyst for the mild and convenient selective oxidation of alcohols as characterized by ICP-OES, XRD, BET, NH_3-TPD, Py-FTIR, SEM and TEM.

2. Experimental

2.1. *Catalyst synthesis*

All the reagents and solvents used in the current study were purchased from Merck Chemical Company and used without further purification. The catalyst was prepared according to previously published procedures, with minor modifications [2,8–10]. As an initial step, ZP was prepared according to the following procedure. $ZrOCl_2{\cdot}8H_2O$ (5 g) was heated at reflux in a solution of H_3PO_4 (50 mL, 12 mol/L) for 24 h. The resulting mixture was cooled to ambient temperature to give a suspension, which was filtered and then washed with a solution of H_3PO_4 (0.1 mol/L) until the filtrate was free of chloride ions. The filter cake was then washed several times with distilled water until the pH of the filtrate was neutral. The solid was collected and dried in an oven at 110 °C for 24 h.

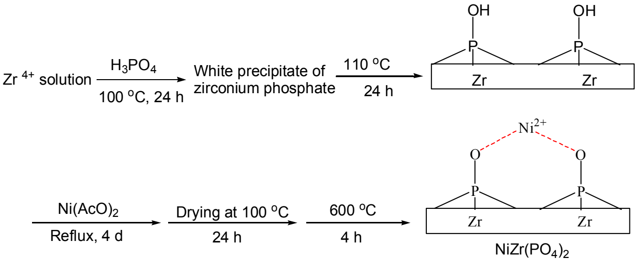
ZPNi was prepared through an ion exchange reaction [8–10]. Briefly, ZP (3 g) was dispersed in deionized water (50 mL) at 50 °C and the resulting suspension was treated with a solution of $Ni(OAc)_2$ (100 mL, 0.1 mol/L) in water (excess amount of Ni^{2+}). This mixture was then heated at reflux for 4 d. It is noteworthy that the acetate ion performed effectively as a base to keep the hydrogen ion concentration in solution sufficiently low to achieve high loadings of the catalyst [24]. A complete exchange between the cations and the hydrogen ions of the P–OH groups could not be achieved in less than 3 d or at temperatures below 80 °C [13]. The resulting slurry was filtered hot to give a light green solid, which was washed with distilled water until no Ni^{2+} ions could be detected in the filtrate (i.e., until the filtrate was colorless). The solid product was then dried at 100 °C for 24 h before being calcined at 600 °C for 4 h to give the final product, ZPNi, as a pale green solid (Scheme 1).

2.2. *Catalyst characterization*

The chemical composition of the ZPNi catalyst was evaluated at different stages of the reaction (i.e., before and after the catalytic reaction) using an Optima 7300 V ICP-OES spectrometer (PerkinElmer). The samples were ground into a fine powder and analyzed by XRD on a Philips X'pert X-ray diffractometer. The specific surface areas of the samples were determined from their N_2 adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method on a Quantachrome ChemBET 3000 instrument. Each sample was degassed at 400 °C for 2 h before being analyzed to remove any adsorbed species from their surfaces. The BET surface areas of the materials were estimated from their N_2 adsorption-desorption isotherms. The surface morphologies of the ZP and ZPNi materials were studied by SEM on a Philips XL scanning electron microscope (Philips). TEM images of ZPNi were obtained on a CENTRA 100 TEM system (Zeiss).

2.3. *General experimental procedure for the oxidation reaction*

ZPNi (0.5 mol%) was added to 5-mmol substrate in a 25-mL two-necked flask. The mixture was heated in an oil bath to 50



Scheme 1. Procedure for the preparation of ZPNi.