Chinese Journal of Catalysis 36 (2015) 595–602

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Article

Acetylation of alcohols and phenols under solvent-free conditions using iron zirconium phosphate

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ARTICLE INFO

Article history:
Received 24 November 2014
Accepted 26 December 2014
Published 20 April 2015

Keywords:
Iron zirconium phosphate
Nanoparticle
Acetylation
Alcohol
Phenol
Solvent-free condition
Solid catalyst

ABSTRACT

Iron zirconium phosphate (ZPFe) nanoparticles were found to function as an efficient catalyst for the acetylation of a wide range of alcohols and phenols using acetic anhydride, generating good to excellent yields under solvent-free conditions. The steric and electronic properties of various substrates had a significant influence on the reaction conditions required to achieve the acetylation. The catalyst used in the current study was characterized by inductively coupled plasma-optical emission spectrometry, X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy, and transmission electron microscopy. These analyses revealed that the interlayer distance in the catalyst increased from 7.5 to 9.3 Å when Fe^{3+} was intercalated between the layers, whereas the crystallinity of the material was reduced. This nanocatalyst could also be recovered and reused at least six times without any discernible decrease in its catalytic activity. This new method for the acetylation of alcohols and phenols has several important advantages, including mild and environmentally friendly reaction conditions, as well as good to 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 other 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, including Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Zn^{2+}, 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 shown 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 activities of ion-exchanged materials of this type, including the use of zinc zirconium phosphate (ZPZn) as a catalyst in the acetylation of alcohols and phenols and the use of copper zirconium phosphate (ZPCu) as a catalyst during the selective oxidation of alcohols [18–24].

The protection and deprotection of organic functional groups are important during multi-step organic syntheses. The particular functional group transformation chose is based on considering the simplicity of the reaction, as well as the ability to obtain high yields of the desired products and short reaction

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This work was supported by the Isfahan University of Technology (IUT), IR Iran.
DOI: 10.1016/S1872-2067(14)60280-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 4, April 2015

times, and to achieve a low cost process with an easy work-up [25,26]. The acetylation of alcohols, phenols, thiols, and amines is one of the most important and frequently used transformations in organic synthesis, especially in the synthesis of natural compounds, biologically active compounds, and polyfunctional molecules such as nucleosides, carbohydrates, chalcones, flavanones, naphthoquinones, pesticides, and steroids. Acetylated groups are also commonly found in cosmetics and food stuffs, as well as in solvents, perfumes, plasticizers, flavors, polymers, and pharmaceuticals [25–27]. One of the most common examples of a compound containing an acetylated group is acetylsalicylic acid (trademarked as Aspirin), which is produced by the acetylation of salicylic acid with acetic anhydride (AA) in the presence of an acid catalyst [28]. The acetyl group is one of the most inexpensive and commonly used protecting groups for –OH, –SH, and $–NH_2$ moieties because the resulting acetylated compounds are stable under a variety of reaction conditions and in contact with a wide range of reagents. Furthermore, the acetyl group can be readily introduced using inexpensive reagents and is easily removed by mild alkaline hydrolysis [29–31].

A number of different procedures have been developed for the acetylation of alcohols, phenols, amines, and thiols using both homogeneous and heterogeneous catalysts. These have included $V^{IV}(TPP)(OTf)_2$ [27], $La(NO_3)_3{\cdot}6H_2O$ [29], $B(C_6F_5)_3$ [30], NSPVPHS [31], $ZnCl_2$ [32], borated zirconia [33], ZnO_2 [34], $Ce(OTf)_3$ [35], $SiO_2–ZnCl_2$ [36], $H_3PW_{12}O_{40}$ [37], DMAP·HCl [38], $Cu(BF_4)_2$ [39], silica-bonded sulfamic acid [40], Cp_2ZrCl_2 [41], $[TMBSA][HSO_4]$ [42], [bmim][OTs] [43], $[MMPPA][HSO_4]$ [44], SaSA [45], SBNPSA [46], SuSA [47], P(4-VPT) [48], acylimidazolium acetate [49], polyvinylpolypyrrolidoniume tribromide [50], $ZnAl_2O_4@SiO_2$ [51], P_2O_5/Al_2O_3 [52], $[Hmim]HSO_4$ [53], yttria–zirconia [54], $CoCl_2$ [55], MWCNTs-C-PO_3H_2 [56], $NiCl_2$ [57], Ni/SiO_2 [58], DBSA [59], rice husk [60], anhydrous $NiCl_2$ [61], $LaFeO_3/SiO_2$ [62], and Fe/SBA-15 [63]. However, most of these catalysts have both advantages and limitations. Despite extensive interest in the development of new methods of acetylation, there is still a requirement to develop simple, efficient, inexpensive, widely applicable, reusable, and environmentally benign catalysts and procedures capable of promoting the acetylation process. With growing environmental concerns, one of the most promising ways to achieve these goals appears to be the use of environmentally friendly insoluble catalysts and/or solvent-free conditions. An insoluble catalyst may be readily recovered from the post-reaction mixture by simple filtration and potentially recycled and reused several times, making the process more economically and environmentally viable. Furthermore, reported examples have demonstrated that heterogeneous catalysts typically require less labor-intensive work-up procedures. Solvent-free synthetic methods are also valuable for both environmental and economic reasons [22,24]. With this in mind, and as part of ongoing work towards the development of efficient green catalysts for organic transformations [64,65] with a particular emphasis on the acetylation and acylation of aromatic compounds [52,53], we report herein the use of iron zirconium phosphate (ZPFe) as an efficient catalyst for the mild, simple acetylation of alcohols and phenols under solvent-free conditions. This new ZPFe catalyst was characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), N_2 adsorption-desorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

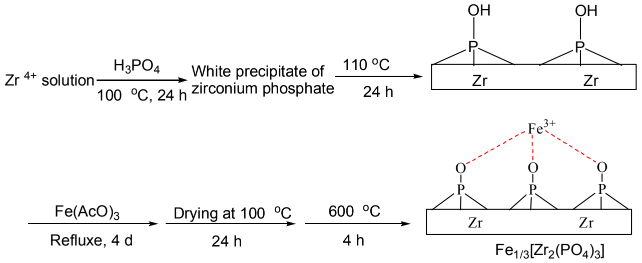
2. Experimental

2.1. *Catalyst synthesis*

All the reagents and solvents used in the current study were purchased from the 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 synthesized according to the following procedure. $ZrOCl_2{\cdot}8H_2O$ (5 g) was heated under reflux conditions 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. After filtration, the filter cake was 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 remaining solid was dried in an oven at 110 °C for 24 h [2]. ZPFe 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 $Fe(OAc)_3$ (100 mL, 0.1 mol/L) in water (providing an excess of Fe^{3+}). This mixture was then heated under reflux for 4 d. It is noteworthy that the acetate ion performed effectively as a base to keep the hydrogen ion concentration in the solution sufficiently low so as to achieve high loadings of the catalyst [8]. 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 below 80 °C [13]. The resulting slurry was filtered while hot to give a light yellow solid that was washed with distilled water until no Fe^{3+} ions could be detected in the filtrate (that is, 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, $Fe_{1/3}[Zr_2(PO_4)_3]$, as a pale yellow solid (Scheme 1).

2.2. *Catalyst characterization*

The chemical composition of the ZPFe catalyst was evaluated both before and after the catalytic reaction by ICP-OES using an Optima 7300 V ICP-OES spectrometer (PerkinElmer). Cata-



Scheme 1. Summary of the ZPFe preparation procedure.