



Cs_xH_{3-x}PW₁₂O₄₀ nanoparticles dispersed in the porous network of Zr-pillared α-zirconium phosphate as efficient heterogeneous catalyst for synthesis of spirooxindoles

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ARTICLE INFO

Article history:

Received 19 June 2017

Received in revised form 8 December 2017

Accepted 12 December 2017

Keywords:

Phosphotungstic acid

α-ZrP

Spirooxindole

UV-vis-DRS

HRTEM

ABSTRACT

Layered α-zirconium phosphate (α-ZrP) was prepared by reflux method using ZrOCl₂·8H₂O and H₃PO₄ as precursor. The α-ZrP material was pillared with Zr-oxyhydroxy nanoclusters to prepare Zr-pillared α-zirconium phosphate (ZZP). An enhancement in interlayer spacing, surface area and porosity was noticed as a result of Zr-pillaring. The cesium exchanged phosphotungstic acid (Cs_xH_{3-x}PW₁₂O₄₀) nanoparticles were dispersed in the porous matrix of ZZP material to prepare Cs_xH_{3-x}PW₁₂O₄₀-ZZP nanocomposite systems. The nanocomposites were characterized using XRD, FTIR, UV-vis-DRS, TGA-DTA, XPS, N₂ sorption, TPD, FESEM and HRTEM techniques. The expansion in layer structure of α-ZrP upon pillaring and its subsequent retention in the composite material was noticed from XRD. UV-vis and FTIR study indicated structural integrity of the Cs_xH_{3-x}PW₁₂O₄₀ nanoclusters in the ZZP interlayer. The surface area of the composite materials was in the range of 80–130 m² g⁻¹. The composite materials contained significantly higher amount of medium and strong acidic sites compared to the ZP and ZZP materials. Microscopic study suggested the presence of hierarchical nanospheres with diameter between 150 and 200 nm. The presence of well dispersed Cs_xH_{3-x}PW₁₂O₄₀ nanoparticles with size between 8 and 15 nm was confirmed from HRTEM study. The nanocomposite materials were used as efficient heterogeneous catalyst for synthesis of spirooxindoles by multicomponent one pot condensation of isatin, malononitrile, naphthol/1,3-diketones. Structurally diverse spirooxindole derivatives were synthesized in high yield and purity in short span of time using the Cs_xH_{3-x}PW₁₂O₄₀-ZZP nanocomposites as catalyst under mild conditions.

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1. Introduction

Zirconium phosphates (ZrP) are a class of versatile materials used in many advanced applications such as proton conducting membrane, ion exchanger, solid state gas sensor, adsorbent and as substrate for immobilization of biological materials [1–3]. These materials possess surface acidic functionality which are water tolerant, thermally stable and hence are suitable for application in acid catalyzed organic transformations [4]. Among different structural forms of zirconium phosphates, α-zirconium phosphate is the most widely investigated material in catalysis [1,2]. In recent years, efforts have been devoted to prepare engineered catalytic materi-

als by modification of the interlayer space and layer composition of the ZrP material. Several organomodified ZrP materials have been reported in literature and studied for selective drug delivery and catalysis [1,3]. The other important characteristics of ZrP material are the exfoliation of the layers in polar solvents and presence of exchangeable interlayer protons. These properties have been exploited to ion exchange the protons with surfactant molecules, inorganic cationic nanoclusters as well as bulky organic moieties to form expanded structures with porosity and high surface area [2,5–10]. The pillared α-ZrP materials prepared by intercalation of inorganic cationic clusters of Al, Ti, Cr, Fe-Cr, Zr and Si into the interlayer space are a class of promising materials for catalysis [8–17]. The intercalation of these inorganic nanoclusters imparts structural rigidity and significantly improves the surface area and pore volume of α-ZrP. The pillared materials also exhibit enhanced surface acidity which is reflected in their higher catalytic activity

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for acid catalyzed reactions [8–15]. In addition to their application as heterogeneous acid catalyst, the pillared α -ZrP materials due to their high surface area and uniform porosity have been used as support for catalytically active phases. For example, the alumina pillared α -ZrP material has been used as an efficient support for the Ni-Mo hydrodesulfurization catalyst [16] and Cu catalyst for reduction of NO with propane [17]. Although there are reports on the catalytic application of the pillared α -ZrP material, there is no study dealing with the catalytic application of these materials for synthesis of biologically important molecules. In this work, we have used the porous matrix of Zr-pillared α -ZrP material as carrier for catalytically active $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ nanoparticles and studied their catalytic application for synthesis of biologically important spirooxindoles.

The metal insoluble salts of heteropoly acids (HPAs) obtained by partially exchanging the labile protons of HPA with large monovalent ions such as Cs^+ , NH_4^+ , K^+ , Ag^+ are attractive materials for application in heterogeneous catalysis [18–23]. These materials possess improved physicochemical characteristics such as high surface area, evolved porosity and enhanced acidity compared to the parent HPA. In recent years, the Cs^+ exchanged phosphotungstic acid ($\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$) has been studied widely as a promising heterogeneous catalyst for acid catalyzed reactions. The $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ material exhibits superior catalytic activity for Beckmann rearrangement, alkylation/acylation reactions, hydration of olefins, hydrocracking of extra-heavy oil, transesterification reactions, esterification of fatty acids and biodiesel synthesis [19–24]. These materials are known to exhibit composition dependent surface properties. Particularly, the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ material with $x = 2.0$ – 2.5 , display higher catalytic activity than the parent $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [20,21]. The catalytic utility of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ materials has been further enhanced by dispersing them on high surface area support [24–27]. The $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ material dispersed over catalytically active functional supports such as ZrO_2 , SnO_2 have been studied recently for unsymmetrical ether synthesis and carbonolysis and etherification of glycerol [25–27]. A synergistic effect between the acidic sites of the support and the active phase has been invoked to explain the higher catalytic activity of the supported system.

Indole has been widely discovered as a pharmacophore, which represents many natural isolates of diverse biological activity [28]. In the past, several natural products containing indole nucleus particularly 3-substituted indoles and spirooxindoles have been isolated [28,29]. The heterocyclic spirooxindole ring is found in a number of pharmaceutical compounds including horsfiline, alstonisine, coerulecine, spirotryprostatins A and elacomine [30]. It has also been observed that spirooxindole compounds containing substituted fused 4H-chromenes display a wide range of useful biological properties, including spasmolytic, diuretic, anticoagulant, anticancer, and antianaphylactic activities [31–33]. In view of the therapeutic properties and biological relevance, the synthesis of these compounds has received considerable attention from synthetic chemists. The most effective route for synthesis of spirochromene derivatives involves the catalytic multicomponent condensation of isatin, active methylene compound, and 1,3-dicarbonyl compounds [34]. Several catalytic protocols have been developed in the recent past for the synthesis of these biologically important compounds which include the use of InCl_3 , sodium stearate, sulfamic acid, triethylbenzylammonium chloride (TEBA), $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -imid-PMA, amino-functionalized SBA-15, ZnS nanoparticles, nano MgO and guanidine functionalized magnetic Fe_3O_4 nanoparticles as catalyst [33–40]. However, many protocols use homogeneous catalysts at elevated temperatures giving moderate to good yield of the product. Although the investigated heterogeneous catalytic protocols offer advantages in terms of reusability of the catalyst, some protocols involve complex catalytic

system requiring multiple steps and costly chemicals for their synthesis. Keeping in mind the merits and demerits of the developed methods; we feel that there is scope to develop novel heterogeneous catalytic protocol for synthesis of spirooxindole under mild conditions. In this work, we have used $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ nanoparticles dispersed in the porous matrix of Zr-pillared α -ZrP material as efficient catalyst for synthesis of structurally diverse spirooxindole derivatives.

2. Materials and methods

Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), phosphoric acid (H_3PO_4), phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and cesium carbonate (Cs_2CO_3) were procured from Hi media Chemicals Pvt. Ltd., India. All chemicals used in this study were of AR grade (>99.9% purity) which was used directly in the experiments without further purification. Deionized water prepared in the laboratory was used for material synthesis.

2.1. Preparation of α -zirconium phosphate (ZP)

The α -zirconium phosphate material was prepared using the procedure described in the literature [7,8]. Briefly, 10 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was added to 100 ml of 12 M H_3PO_4 solution and refluxed at 100 °C for 24 h. The obtained white precipitate was filtered, washed repeatedly with hot water to remove Cl^- ions and centrifuged at 5000 rpm. The solid material was subsequently dried in a hot air oven at 90 °C for 24 h to obtain the ZP material.

2.2. Preparation of Zr-pillared α -zirconium phosphate (ZPP)

2.2.1. Preparation of Zr-pillaring solution

A 0.1 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution was prepared by dissolving the required amount of the salt in deionized water. The solution was subsequently refluxed for 24 h to prepare the pillaring solution.

2.2.2. Pillaring process

2 g of ZP was dispersed in 200 ml of 0.1 M *n*-butylamine solution and stirred for 24 h to prepare a well dispersed exfoliated colloidal suspension. Required amount of Zr-pillaring solution (ZP: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ molar ratio 1:30) was then added dropwise (50 ml h^{-1}) to the colloidal suspension and refluxed at 100 °C for 24 h under constant stirring. After completion of the intercalation process, the solid material was recovered by centrifugation at 5000 rpm and washed repeatedly with hot water to remove the amine and chloride ions. The solid material was subsequently dried in a hot air oven at 80 °C for 12 h and calcined at 350 °C for 2 h to obtain the ZPP catalyst.

2.3. Preparation of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ dispersed over Zr-pillared α -zirconium phosphate (CPxZPP)

The 20 wt% $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ supported over ZPP material was prepared by ion exchange of H^+ with Cs^+ ions followed by wet impregnation. In a typical procedure, 2 g of ZPP material was dispersed in 20 ml water by sonication for 20 min. To this aqueous dispersion, 0.4 g of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was added and stirred for 2 h. Stoichiometric amount of 0.5 mmol Cs_2CO_3 solution was then added dropwise to this suspension and stirred for 6 h at room temperature. The temperature was then raised to 90 °C and was heated continuously under stirring to remove the excess water. The resulting material was dried in air at 120 °C for 6 h followed by calcination at 350 °C for 2 h to obtain the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}/\text{ZPP}$ material. Using this procedure 20 wt% $\text{Cs}_1\text{H}_2\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_2\text{H}_1\text{PW}_{12}\text{O}_{40}$ supported over ZPP material were prepared. These supported materials

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