



Hexagonal zirconium phosphate nanoparticles as an efficient and recyclable catalyst for selective solvent-free alkylation of phenol with cyclohexanol



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ARTICLE INFO

Article history:

Received 18 January 2014

Received in revised form 24 May 2014

Accepted 27 May 2014

Available online 4 June 2014

Keywords:

Hexagonal zirconium phosphate

Nanoparticles

Solvent-free

Solid acid catalyst

Cyclohexylphenol

ABSTRACT

A facile synthesis of hexagonal α -zirconium phosphate (ZP) nanoparticles as an effective, eco-friendly and recyclable solid acid catalyst was studied. Polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were used as the organic matrix which were the dispersing agents and acted as a template for the nanoparticles. It seems H-bonds between ZP and PVA or PVP along polymer chains lead to a better dispersion of in situ formed ZP. Pure ZP nanoparticles with hexagonal shape were obtained after calcination of PVA/ZP or PVP/ZP. The catalysts were characterized by several physico-chemical techniques such as BET, ICP-OES, XRD, FT-IR, SEM and TEM. The TPD-NH₃ analysis suggests the presence of a reasonable amount of Brønsted acid sites. The acidic properties were studied in the alkylation of phenol with cyclohexanol under solvent-free conditions which produced 2-cyclohexylphenol (2-CP), 4-cyclohexylphenol (4-CP) and 2,4-dicyclohexylphenol (2,4-DCP). This alkylation reaction was also performed over P₂O₅/Al₂O₃, P₂O₅/SiO₂, α -ZrP (prepared in the absence of the polymers) and various ionic liquids using cyclohexanol and cyclohexene as the alkylating agents. When the hexagonal ZP nanoparticles were used as the catalyst, under optimized reaction conditions, excellent conversion of phenol and selectivity toward 4-CP were obtained. The catalyst was recovered easily from the reaction mixture, regenerated and reused at least four times without significant loss in its catalytic activity.

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1. Introduction

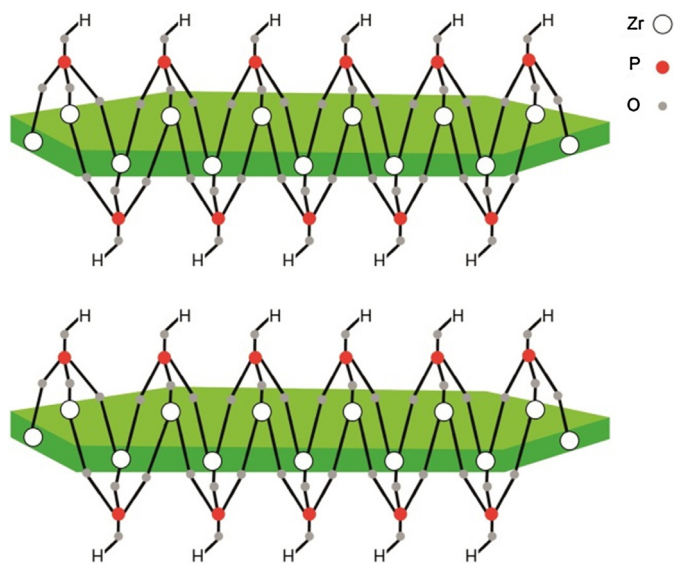
Alkylation of phenols is one of the most important aromatic reactions, both in organic synthesis and chemical manufacturing. The alkylphenols are widely used as precursors in detergents, pesticides, additives for fuels, herbicides, polymers, phenolic resins, antioxidants, lubricants, fragrances, thermoplastic elastomers and paints [1–4]. Cyclohexylphenol is one of the very interesting alkylated phenol compounds. Cyclohexylation of phenol produces 2-cyclohexylphenol (2-CP), 4-cyclohexylphenol (4-CP), 2,4-dicyclohexylphenol (2,4-DCP), 2,6-dicyclohexylphenol (2,6-DCP) and cyclohexylphenyl ether (CPE), depending on both the catalyst and the reaction conditions. Based on previous researches, it is well known that C-alkylation requires stronger acid sites than those for O-alkylation [2–6]. In the cyclohexylation of

phenol, the crucial point is the regioselectivity. 4-CP is widely used as an intermediate in the manufacture of colorants for plastics, biocides, dyes and 2-CP is an important intermediate in dyestuff and 2-phenylphenol preparation as a disinfectant [3–6]. This reaction has been performed over various catalysts such as zeolites [7,8], cationic ion-exchange resins [6], 12-tungstophosphoric acid [9], cesium salt of dodecatungstophosphoric acid [4], HZSM5 [10], La₂(HPO₄)₃, BaSO₄ and SrSO₄ [11], silica-supported BF₃ [12], and acidic ionic liquids [13]. Traditionally, concentrated H₂SO₄ and H₃PO₄ [14,15] were used for cyclohexylation of phenol, but these homogeneous catalysts are not desirable as they are hazardous, corrosive and highly-polluting, and thus their usage leads to serious environmental problems. Moreover, in almost all these methods, lack of positional selectivity toward 4-CP, as the most desirable product have been reported. Hence, there is much interest for the development of more efficient and eco-friendly methods.

As a heterogeneous green solid acid catalyst, α -zirconium phosphate (ZP), Zr(HPO₄)₂·H₂O, is one of the most important inorganic materials which has been prepared by various methods [16,17]. Crystalline ZP is an important class of layered multi-functional materials with well-ordered structure. The layered structure of ZP

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Scheme 1. Schematic structure of hexagonal α -zirconium phosphate.

consists of zirconium ions in a semiplanar arrangement, located slightly above and below the mean plane, while each Zr^{4+} ion is connected through the oxygen atoms of phosphate groups from above and below. Three of the four oxygen atoms in the phosphate groups are bonded to three different zirconium atoms. The fourth oxygen atom of the phosphate groups that bonds to a proton, the free $-OH$ group, is pointing into the interlayer region (Scheme 1) [16–18]. These hydroxyl groups are responsible for ZP Brønsted acidity. The P-OH groups on the surface of ZP could be assumed as hooks in which various organic functional groups could adsorb on (acidic, polar, and hydrophobic), allowing to control both the reactivity and selectivity of the reaction.

Previous researches have shown potential applications of ZP in many fields [19–31]. ZP has attracted enormous interests as a low cost, efficient, thermally stable, acidic, eco-friendly and reusable catalyst [23–27]. It is an important ion exchanger [19,20] with high water tolerance ability and easy sedimentation [22] which also was used in nuclear waste management [20,21], drug delivery and immobilization of biological materials [28–31]. Recently, much attention has been focused on the development of new preparation methods to produce different ZP nanocompounds such as nanoparticles [24,25,32,33], nanoplates [17,30] and nanocomposites [34–36]. Polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) are both white, water-soluble, odorless and nontoxic polymers. There are some new PVA and PVP based precursor methods to produce nanocomposites and nanoparticles [33–40]. To the best of our knowledge, there is no report available in the literature for using ZP nanoparticles as catalyst for cycloalkylation of phenol and not much work has been reported on the alkylation of phenol using cyclohexanol. Therefore, in continuation of our researches to find efficient and green catalysts [41–44], we have investigated cycloalkylation of phenol by cyclohexanol over ZP nanoparticles under solvent-free conditions. The reaction conditions such as the amount of catalyst, reaction time, temperature and mole ratio were investigated in detail. Also, we have investigated this alkylation over a series of ionic liquids, P_2O_5/Al_2O_3 , P_2O_5/SiO_2 and α -ZrP (prepared in the absence of the polymers). This alkylation reaction was performed with both cyclohexanol and cyclohexene as the alkylating agents and results were compared with those obtained from ZPA and ZPP.

2. Experimental

2.1. Catalyst synthesis

All chemicals and solvents were purchased from Merck Chemical Company and used without further purification. The detailed procedure for the preparation of the catalyst can be found in the literature [33]. Typically, a 10% solution of PVA ($M_w = 70,000$) was prepared by dissolving PVA in deionized hot water ($95^\circ C$). By adding HCl, the pH value was adjusted about 3. 50 ml of a 1 M solution of $ZrOCl_2 \cdot 8H_2O$ was added dropwise to precursor solution and heated at $60^\circ C$ for 2 h with constant stirring using a magnetic stirrer. To the resulting homogeneous solution, under ultrasonication, 50 ml of a 2 M H_3PO_4 solution was added dropwise at $50\text{--}60^\circ C$ for 2 h. The resulting mixture was allowed to age for 4 h then the precipitate was filtered, washed several times with distilled water and then dried in an oven at $80^\circ C$ overnight. The obtained white colored fluffy precursor was ground and calcined at $550^\circ C$ for 4 h to decompose the organic matrix. The final product, the desired pure hexagonal α -zirconium phosphate ($Zr(HPO_4)_2 \cdot H_2O$) nanocrystals, was identified as ZPA.

A 10% solution of PVP ($M_w = 40,000$) was prepared by dissolving PVP in deionized water. The same procedure described above was performed to produce ZP nanoparticles. The final product was identified as ZPP. The detailed procedure for the preparation of the α -ZrP can be found in the literature [17]. P_2O_5/Al_2O_3 [45], P_2O_5/SiO_2 [46], 1-H-3-methyl-imidazolium bisulfate ([Hmim]HSO₄) [47], morpholinium bisulfate ([morH]HSO₄) [48], N-(4-sulfonic acid) butyl triethyl ammonium hydrogen sulfate ([TEBSA]HSO₄) [49] and 3-carboxypyridinium hydrogen sulfate ([Hcpy]HSO₄) [50] were prepared according to previously reported procedures by our research team (supplementary information). The gas chromatography–mass spectroscopy (GC–MS) analyses were performed by the Agilent 5975C spectrometer.

2.2. Catalyst characterization

On the basis of N_2 adsorption–desorption isotherms at liquid nitrogen temperature, the specific surface area was determined by BET [51] with a Quantachrome ChemBET 3000 (Fig. 1). Prior to analysis, each sample was degassed at $400^\circ C$ for 2 h to remove any adsorbed species on the surface. Total acidity of the samples was determined by temperature-programmed desorption of ammonia (TPD-NH₃) with a Quantachrome ChemBET 3000. Before the adsorption of ammonia, the samples were pre-treated in He at $250^\circ C$ for 30 min and then at $350^\circ C$ for 1 h and cooled to $100^\circ C$. Then ammonia was adsorbed on the samples for 1 h. The TPD-NH₃ was carried out between 100 and $880^\circ C$, at $10^\circ C \text{ min}^{-1}$, and analyzed by a thermal conductivity detector (TCD) for continuous monitoring of the desorbed ammonia. Typical curves of the release of NH₃ from ZP under different conditions are shown in Fig. 2. The Zr and P contents were obtained using inductivity coupled plasma-optical emission spectroscopy (ICP-OES) on PerkinElmer ICP-OES 7300 DV spectrometer. The results are discussed in Section 3. The FT-IR spectroscopic measurements were carried out using a JASCO FT/IR (680 plus) spectrophotometer (Fig. 3). The spectra were recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$ using a KBr technique. The crystallinity of ZPA and ZPP after calcination at $550^\circ C$ were measured by a Philips X'pert X-ray powder diffractometer. The samples were scanned in 2θ range of $5\text{--}50^\circ$ (Fig. 4). The morphology of the samples was investigated using a Philips XL scanning electron microscope (SEM). Transmission electron microscope (TEM) images were collected using a LEO912-AB microscope.

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