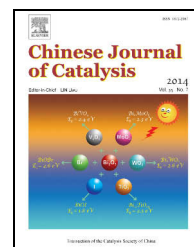


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## Article

# Zirconium phosphate nanoparticles as a remarkable solid acid catalyst for selective solvent-free alkylation of phenol

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## ABSTRACT

A facile synthesis of  $\alpha$ -zirconium phosphate (ZP) nanoparticles as an effective, eco-friendly, and recyclable solid acid catalyst is reported. Polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were used as organic matrix as dispersing agents and served as a template for the nanoparticles. Hydrogen bonds between ZP and PVA or PVP, along the polymer chains, appear to play an important role for improving the dispersion of in situ formed ZP. Following calcination of PVA/ZP or PVP/ZP, pure hexagonal ZP nanoparticles were obtained. The catalysts were characterized by nitrogen sorption, inductively coupled plasma optical emission spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, and transmission electron microscopy. Pyridine-FTIR and temperature-programmed desorption of  $\text{NH}_3$  suggest the presence of Brønsted acid sites. The acidic properties of the catalyst were studied in Friedel-Crafts alkylation of phenol by *tert*-butanol, producing 2-*tert*-butylphenol, 4-*tert*-butylphenol, and 2,4-di-*tert*-butylphenol. The alkylation reaction was performed in the presence of catalysts  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5/\text{SiO}_2$ ,  $\alpha$ -ZrP (prepared in the absence of the polymers), and various ionic liquids. The use of the hexagonal ZP nanoparticle catalyst afforded an excellent phenol conversion (86%) and selectivity towards 4-*tert*-butylphenol (83%) under optimized reaction conditions. The catalyst was easily recovered from the reaction mixture, regenerated, and reused at least four times without significant loss in the catalytic activity.

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## 1. Introduction

Alkylated phenols and their derivatives are important materials in both organic syntheses and chemical manufacturing. Mono-alkylphenols and di-alkylphenols are used as raw materials for the manufacture of diverse products such as resins, wire enamels, varnishes, printing inks, antioxidants, flame retardants, ultraviolet absorbers, fungicide, petroleum additives, and rubber chemicals [1–17]. Friedel-Crafts alkylation of phenol using *tert*-butyl alcohol (TBA) generally produces 2-*tert*-butylphenol (2-TBP), 4-*tert*-butylphenol (4-TBP), 2,4-di-*tert*-

butylphenol (2,4-DTBP), 2,6-di-*tert*-butylphenol (2,6-DTBP), and *tert*-butylphenol ether (TBPE), depending on the catalyst and reaction conditions. Based on previous studies, it is well known that moderate acid catalysts or high-temperature reactions lead to carbon-alkylated products, whereas weak acid catalysts produced TBPE as a major product. Product 2-TBP forms because of the presence of phenolic (–OH) groups on the aromatic ring that kinetically favor *o*-alkylation. However, because of steric hindrance, thermodynamically non-favored *o*-isomer 2-TBP readily isomerizes into the less hindered *p*-isomer (4-TBP), especially under moderate acidic media con-

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ditions. When strong acid catalysts are used in the alkylation reaction, 2,4-DTBP is the dominant product [17,18]. 2,4-DTBP is used in the manufacture of its triphosphite derivatives and benzotriazole, which are employed as a co-stabilizer for PVC or UV absorbers in polyolefins [12,13]. 2-TBP is used in pesticides, fragrances, and antioxidants [14]. High selectivity towards 4-TBP is preferred because this product imparts enhanced properties to the class of metallic detergents (phenates) that are used in lubricating oils [15]. Moreover, 4-TBP can be used in the manufacture of fragrances, phenol-formaldehyde resins, perfumes, antioxidants, ultraviolet absorbents, polymerization inhibitors, lube additives, oil field chemicals, and emulsifiers [1,8]. Therefore, investigation of this alkylation reaction has great commercial interest as well as academic. Generally, Brønsted- and Lewis acid-type catalysts, such as  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{BF}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ , and  $\text{HClO}_4$ , have been used in Friedel-Crafts phenol alkylation [19]. However, these homogeneous catalysts have major drawbacks such as considerable pollution production, high waste disposal costs, poor selectivity, and tedious work-up [7,20]. Gas phase alkylation of phenol has been investigated as an alternative because it can afford a high phenol conversion [9–11]. However, the process requires high temperature and pressure that lead to higher costs. Therefore, much attention has been devoted to heterogeneous solid acid catalysts as they have many merits, namely improved activity, high acid strength, enhanced selectivity, and easier post-reaction work-up [21]. The *tert*-butylation of phenol over various catalysts has been widely reported in the literature, and mainly involves heterogeneous catalysts such as clays and clay-based materials [4,22], heteropoly acids [16,23], cation-exchange resins [13], mixed oxides [11,14], zeolites [6], microporous mesoporous materials [2,3], molecular sieves [24], supercritical and near-supercritical water [1], ionic liquids [17,20], MCMs [7–10], sulfated zirconia [25], and iron-containing mesoporous aluminosilicate [26]. However, in some of these reported methods, low selectivity, by-product formation, long reaction times, organic solvents, and high temperature requirements remain the major disadvantages.

As a heterogeneous green solid acid catalyst,  $\alpha$ -zirconium phosphate (ZP),  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ , is one of the most important inorganic materials that has been prepared by various methods [27,28]. Crystalline ZPs are an important class of layered multi-functional materials with a well-ordered structure. The layered structure of ZPs consists of zirconium ions in a semi-planar arrangement, located slightly above and below the mean plane, and each  $\text{Zr}^{4+}$  ion is connected via the oxygen atoms of the phosphate groups from above and below the mean plane. 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, free  $-\text{OH}$  group, is oriented towards the interlayer region. These hydroxyl groups are responsible for the Brønsted acidity of ZP. Hence, each zirconium is octahedrally coordinated to six oxygens of six different phosphate groups [27–30]. The P–OH groups on the surface of ZP serve as adsorption sites for various organic functional groups (acidic, polar, and hydrophobic), thereby allowing control over the reactivity and selectivity of the reaction. Pre-

vious studies have shown potential applications of ZP in many fields [31–42]. ZP has attracted enormous interest as a low-cost, efficient, thermally stable, acidic, eco-friendly, and reusable catalyst both in organic syntheses and chemical manufacturing [34–38]. It is an important ion exchanger [31] with high water tolerance ability and ease of sedimentation [33]. Moreover, it is used in nuclear waste management [32], drug delivery, and immobilization of biological materials [39–42]. Recently, much attention has been focused on the development of preparation methods to produce different ZP nano compounds such as nanoparticles [35,36,43], nanoplates [28,41], and nanocomposites [44–46]. Polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) are both white, water-soluble, odorless, and nontoxic polymers. New PVA- and PVP-based precursor methods to produce nanocomposites and nanoparticles are available [44–50].

To the best of our knowledge, there are no literature reports on the use of ZP nanoparticles as a catalyst for the *tert*-butylation of phenol, and only a few studies on the solvent-free alkylation of phenol with TBA have been published [9,51,52]. Therefore, in continuation of our studies introducing efficient and green catalysts [53–58], herein we investigated the alkylation of phenol and some substituted phenols with TBA over ZP nanoparticles under solvent-free conditions. The reaction conditions, such as the amount of catalyst, reaction time, temperature, and molar ratio, were investigated in detail. Additionally, we investigated the alkylation process over catalysts  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5/\text{SiO}_2$ , and  $\alpha$ -ZrP (prepared in the absence of the polymers), and the results were compared with those obtained from the studies using ZPA and ZPP. In comparison with the other reported methods, the following advantages were achieved in the current study: (1) higher phenol conversion, (2) higher selectivity towards 4-TBP, and (3) ease of recovery of the product and catalyst.

## 2. Experimental

### 2.1. Catalyst synthesis

All chemicals and solvents were purchased from Sigma-Aldrich and Merck and used without further purification.

A 10% solution of PVA ( $M_w = 70000$ ) was prepared by dissolving PVA in deionized hot water (95 °C). The pH of the solution was adjusted to  $\sim 3$  by adding HCl. To prevent thermal decomposition and monitor the temperature of the PVA solution, a water bath was used. Then, 50 mL of a 1 mol/L solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was added dropwise to the precursor solution and heated at 60 °C for 2 h with constant stirring using a magnetic stirrer that affords better dispersion of the  $\text{Zr}^{4+}$  ions into the polymer chains. After a homogeneous solution was obtained, 50 mL of 2 mol/L  $\text{H}_3\text{PO}_4$  was added dropwise to the solution at 50–60 °C for 2 h, assisted by sonication. Upon addition of phosphoric acid,  $\text{Zr}^{4+}$  ions reacted with  $\text{PO}_4^{3-}$  ions almost immediately to form ZP. The resulting mixture was allowed to age for 6 h, and then the precipitate was filtered, washed with distilled water several times, and dried in an oven at 80 °C overnight. The obtained white fluffy precursor was

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