

Liquid phase bromination of phenol

II. Over heteropoly acid (HPA)-impregnated zirconium phosphate (ZrP)

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Received 3 November 2005; received in revised form 15 February 2006; accepted 17 February 2006

Available online 29 March 2006

Abstract

Heteropoly acid (HPA)-impregnated zirconium phosphate (ZrP) was prepared by an incipient wetness impregnation method by varying the wt.% of HPAs like phosphotungstic acid (PWA), phosphomolybdic acid (PMoA), silicotungstic acid (SiWA) and silicomolybdic acid (SiMoA). All the samples were characterized by X-ray diffraction studies, FTIR, determination of acid sites and TG-DTA. The catalytic activities of all the samples were evaluated by carrying out the liquid phase bromination of phenol using KBr and hydrogen peroxide. The reaction products were analysed by GC through a capillary column. From the product analysis it was found that PWA/ZrP shows the highest conversion. Even so SiWA/ZrP heated at 110 °C shows the highest *para*-selectivity (in the range of 32–41%), higher than any other HPA/ZrP. The selectivity increases with an increase in the activation temperature up to 400 °C and thereafter it remains constant. The reaction proceeds through the formation of Br⁺ (bromonium ion) which attacks the phenol ring, forming different brominated products.

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Keywords: Heteropoly acid-impregnated zirconium phosphate; Bromination; Potassium bromide; Hydrogen peroxide; *Para*-selectivity

1. Introduction

Selective bromination of organic compounds is investigated in view of the importance of the brominated products in organic synthesis [1]. The ring bromination of aromatics is catalysed by Lewis acids such as the chlorides of aluminium, zinc and iron [2]. Lambert et al. [3] reported the bromination of benzene and toluene using an NBS–H₂SO₄–H₂O system. This method is not suitable for industrial bromination of aromatic compounds due to need to a stoichiometric amount of catalyst, the formation of polybrominated products and the difficulty in separation of catalyst from the final product. Traditional methods of aromatic bromination involve the use of nonselective hazardous acidic reagents such as mineral acids and metal halides, which can lead to separation difficulties and unacceptable levels of toxic, corrosive or waste materials.

The classical direct bromination of aromatic compounds suffers from being wasteful in the bromine employed; one half ends up as hydrogen bromide. Broadly speaking this is an environmental as well as economic problem. Oxybromination [4–7] using HBr as bromine source and H₂O₂ as an oxidant was thought to be one solution to overcome the above difficulties. The replacement of highly toxic, corrosive and harmful HBr or similar reagents by nontoxic and more selective reagents is very desirable from an environmental point of view. A novel heterogeneous catalytic system to generate electrophilic bromine from an easily available bromine source and H₂O₂ as an oxidant for oxybromination as a possible alternative to overcome the limitations described in the above methods.

Heteropoly acids and their acidic salts having the Keggin structure are known to be excellent acid catalysts [8–11]. Heteropoly acids are polyoxometalates made up of heteropoly anions having metal-oxygen octahedral as the basic structural unit [12]. They can be represented by the general formula: [XM₁₂O₄₀]^{x–8}, where X is the central heteroatom (Si⁺⁴, P⁺⁵, etc.), *x* is its oxidation state, and M is the metal ion (W⁺⁶, Mo⁺⁶, V⁺⁵, etc.). The negative charges can be compensated by hydrogen ions or by wide variety of cations (e.g. HPA salts).

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One of the main drawbacks of the Keggin-type HPA is their low specific surface area (1–10 m²/g) [13,14], which limits their applications in gas–solid phase reactions. The catalytic activity of supported HPA depends on the HPA loading, the pretreatment conditions and the type of the support material. Acidic or neutral substances such as: SiO₂ [15,16], active carbon [17,18], acidic ion-exchange resin [19] and TiO₂ [20,21] are suitable as supports. Also, the thermal stability of HPA is influenced by the support [22,23]. Oxidative bromination of a range of aromatics with HBr in the presence of oxygen catalysed by a heteropoly acid [24] and regioselective oxybromination of phenols with HBr gas catalysed by H₅PMo₁₀V₂O₄₀ (HPA-2) are also reported [25].

The present work deals with the liquid phase bromination of phenol over heteropoly acid (HPA)-impregnated zirconium phosphate (ZrP) as catalyst, KBr as brominating agent and hydrogen peroxide as oxidant.

2. Experimental

2.1. Material preparation

The heteropoly acids were prepared by following the literature [26]. The HPA supported ZrP was prepared by an incipient wetness impregnation method. The catalysts were activated at various temperatures for further study.

2.2. Physico-chemical characterization

The X-ray powdered diffraction patterns were taken on a Philips PW 1710 diffractometer with automatic control. The patterns were run with monochromatic Cu K α radiation with a scan rate of 2° min⁻¹.

The FTIR spectra were taken using a Nicolet Instruments Corporation instrument (Model: Magna 550) in a KBr matrix in the range of 400–4000 cm⁻¹.

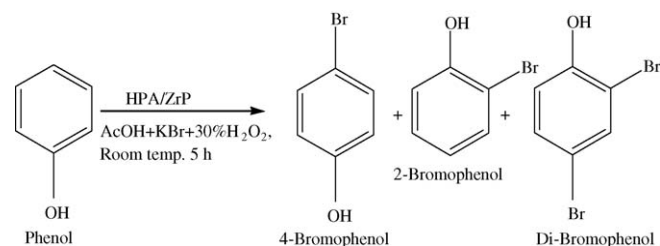
The strong and Bronsted acid sites of all the samples were determined by the spectrophotometric method [27] by irreversible adsorption of pyridine (PY) and 2,6-dimethyl pyridine (DMPY).

TG–DTA analyses of samples dried at 110 °C were carried out using a Thermal Analyzer (Universal V2.5H TA Instruments). The thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed in N₂ using 12–13 mg samples at a heating rate of 10 °C/min.

2.3. General procedure for bromination of phenol

A 100 ml two-necked round bottomed flask was charged with 200 mg HPA/ZrP, substrate (phenol = 2 mmol) and KBr (2.2 mmol) in acetic acid (4 ml). Thirty percent H₂O₂ (2.2 mmol) was then added drop-wise to the reaction mixture and the contents were allowed to stir at room temperature (Scheme 1) [28].

After 5 h of the reaction, the catalyst was filtered and washed with ether, followed by the washing with sodium bicarbonate. The organic layer was extracted with ether and dried over



anhydrous sodium sulfate. The products were analysed with a Shimadzu GC (GC-17A) through a capillary column.

3. Results and discussion

3.1. Physico-chemical characterization

Fig. 1 shows the XRD pattern of 15 wt.% of different HPAs (PWA, PMoA, SiWA and SiMoA) impregnated ZrP dried at 110 °C. It can be observed that the impregnated products are crystalline. The peaks indicated in blank squares indicate the peaks due to zirconium phosphate. The other peaks are mainly coming from the Keggin molecules. Some peaks of HPA overlapped with that of zirconium phosphate. This may be due to the interaction of HPA with that of the support. Fig. 2 shows the effect of activation temperature on the 15 wt.% SiWA/ZrP. One can notice that, with increase in the activation temperature, the crystallinity was increased. From this we can infer that the

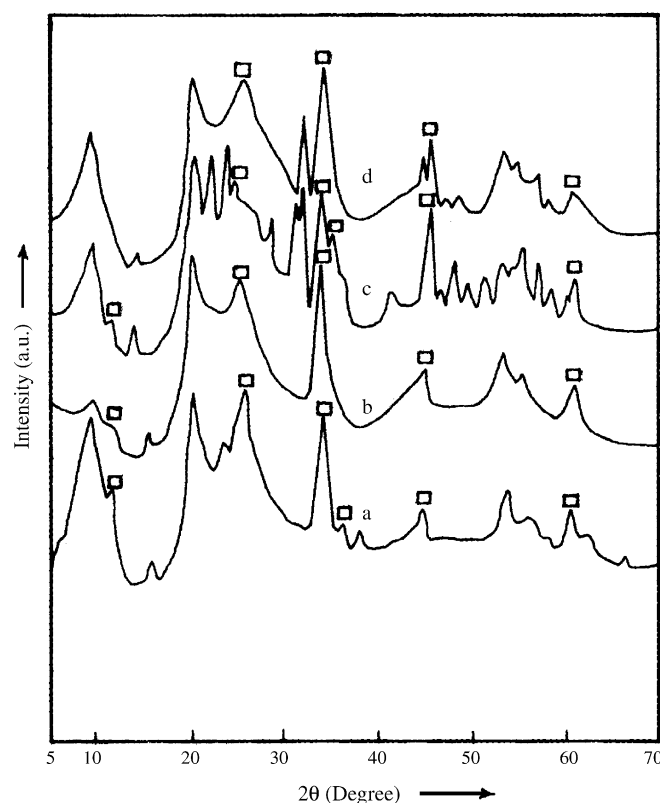


Fig. 1. XRD patterns of 15 wt.% samples of: (a) PWA/ZrP; (b) PMoA/ZrP; (c) SiWA/ZrP; (d) SiMoA/ZrP, dried at 110 °C.

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