

Atom economical benzylation of phenol with benzyl alcohol using 20 % (w/w)Cs_{2.5}H_{0.5}PW₁₂O₄₀ supported on mesocellular foam silica (MCF) and its kinetics

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ABSTRACT

Traditionally benzylation of phenol is carried out with benzyl chloride which is corrosive and difficult to handle, and the resultant reaction is not atom economical. Benzyl alcohol is an alternative to benzyl chloride which is safe and easy to handle. Benzyl phenols are industrially important products particularly in plastic, rubber and petroleum industries. In present study, cesium salt of dodecatungstophosphoric acid (Cs_{2.5}H_{0.5}PW₁₂O₄₀, Cs-DTP) supported on mesocellular foam (MCF) silica was used as catalyst among others. The activity of prepared catalyst, 20% (w/w) Cs-DTP/MCF was compared with Amberlyst-15, montmorillonite clay K10, S-ZrO₂ and unsupported Cs-DTP catalyst. The supported catalyst showed better performance because of even distribution of acidic sites on MCF. The effect of reaction parameters were studied in detail and it was found that reaction follows second order kinetics. The activation energy was found to be 15.94 kcal/mol. The catalyst was found reusable.

1. Introduction

Mesoporous silica has always been an interesting topic for researchers worldwide because of its wide application in various fields such as catalysis, packing material for better separation of analytes in HPLC [1] drug carrier [2], preparation of semiconductor nano wires [3] adsorbent [4] sensor [5,6] and many more. Mesoporous silica has wide applications in catalysis but as such mesoporous silica does not show any catalytic activity based on solely silanol groups. Hence it plays a major role as a support as well as inclusion of various metals which leads to the formation of a variety of catalysts having either acidity [7,8], basicity [9,10] or redox [11,12] properties. In some cases, modification of mesoporous silica by organo-amines as well as organo thiol groups [13,14] has also been reported. This type of modification provides better anchoring of the catalytic sites.

Mesoporous silicas are prepared by use of various organic templates like cationic surfactants [15] organic fatty amines [16] and nonionic poly (ethylene oxide) monoethers [17]. The effect of these templates had shown remarkable effect on the structure and porosity of the resultant mesoporous silica. Mesocellular silica foam (MCF), is a modified form of SBA-15, where mesitylene was used as a pore expander along with non-ionic surfactant P-123 block co-polymer [18] which increased not only the pore diameter of MCF but also resulted in the formation of 3D ultra cage spherical structure. The 3D ultra cage structure of MCF

made it better support for larger molecules like enzymes [19], ionic liquids [20], metal oxides [21], heteropoly acids [22] as well as to make mesoporous graphitic carbon nitride [23].

Heteropolyacids (HPA) have been studied extensively as catalyst both in homogeneous and heterogeneous forms. Alkaline metal salts of heteropoly acids have replaced plain heteropoly acids with the advantage of insolubility in organic solvents. However, because of ultra-fine size of the particles, metallic salts of heteropoly acids were found difficult to separate from the reaction mass. Hence they were used in the form of supported catalysts [24]. Different type of supports have been used for HPAs and their metallic salts like acidic clay K-10 [25,26], MCM-41 [27], HMS [28], SBA-15 [29], metal oxides like ZrO₂ [30] and TiO₂ [31]. These catalysts have been successfully implemented in various organic transformations like alkylation, acylation and condensation reactions.

Benzylation of phenol is one of the important alkylation reactions. The importance of the reaction is due to the application of the products benzyl phenols in various functional areas like production of antioxidants, rubbers and plastics, and other useful intermediates. Pai et al. [32] reported use of benzyl chloride as a benzylation agent, wherein the time for completion of reaction was very high whereas Yadav et al. [33] suggested benzyl alcohol is a better alkylating agent than benzyl chloride. Apart from these studies, the major drawback of benzyl chloride is difficult handling and generation of HCl as a co-product

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which is not environment friendly. Hence benzyl alcohol is an alternative to benzyl chloride as it is easy to handle and the co-product is water; the atom economy of the reaction is also very high which makes it a suitable reagent. Halligudi et al. have worked extensively on benzylation of phenol using tungstophosphoric acid supported on various supports [31,34,35]. Lingaiah et al. reported tin exchanged tungstophosphoric acid as an efficient catalyst for benzylation of phenol [36]. However, neither of these reports have carried out detailed kinetic studies of the reaction nor shown the surface mechanism of the reaction. In the present report, we have used MCF as a support for cesium salt of tungstophosphoric acid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ abbreviated as Cs-DTP) and used in benzylation of phenol. Its activity was compared with the commercial catalyst like clay K-10 and ion exchange resin Amberlyst-15 and bulk Cs-DTP. The prepared catalyst was characterized before and after use by various techniques and effects of reaction parameters were studied in detail.

2. Experimental section

2.1. Materials

Pluronic P-123 (MW-54000) and tetraethoxysilane (TEOS) were purchased from Sigma Aldrich. Methanol, HCl (35% aq. solution), mesitylene, ammonium fluoride, CsCl and dodecatungstophosphoric acid (DTP) (all were procured from S.D.fine chem., Mumbai, India) and n-hexadecane from Himedia, Mumbai.

2.2. Catalyst synthesis and characterization

2.2.1. Synthesis of mesocellular foam silica (MCF)

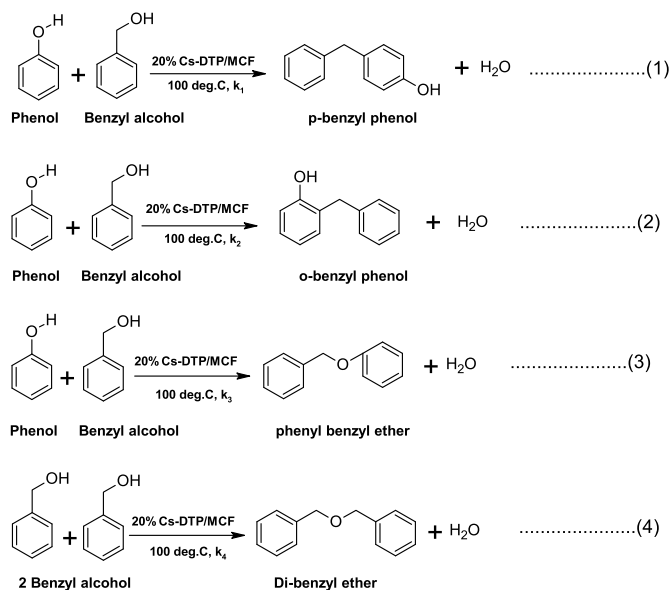
MCF was prepared by the procedure followed in the literature [18]. Four g triblock copolymer P123 was dissolved in 10 ml 35% (w/w) HCl dissolved in 65 ml DI water. After complete dissolution of polymer in acidic solution, 3.4 ml of mesitylene was added and the resulting solution was kept at 40 °C with vigorous agitation. After 2 h, 9.2 ml of tetraethoxysilane was added and the resultant mixture was stirred for 5 min and kept on aging for 20 h at 40 °C for slow hydrolysis of tetraethoxysilane. After completion of 20 h aging, 46 mg of ammonium fluoride dissolved in 5 ml of DI water was added to the solution and stirred for 15 min. The resulting solution then was kept for further aging at 100 °C for 24 h. The obtained material was then filtered and washed with water and ethanol to get rid of all acid and polymer. The material was then dried and calcined at 600 °C in air for 6 h.

2.2.2. Synthesis of bulk $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (bulk Cs-DTP)

The bulk Cs-DTP ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) was prepared by using CsCl as a precursor as per procedure reported in literature [37]. During addition of CsCl solution to dodecatungstophosphoric acid solution, a white precipitate of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst was formed which was dried and calcined at 300 °C for 3 h. This catalyst is referred to as 'bulk Cs-DTP' onwards.

2.2.3. Synthesis of 20% (w/w) $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /MCF

The supported catalyst was prepared by incipient wetness technique. The procedure was similar to the one described in literature [28]. Eight g of previously dried MCF silica was weighed accurately. 0.2808 g CsCl was dissolved in small amount of water followed by 18 ml of methanol (volume approximately equivalent to the pore volume of MCF). CsCl solution was added in small portions of 1 ml to the MCF and the material was mixed with glass rod continuously. On complete addition, the mixture was kept for drying at 120 °C for 3 h. Further impregnation of dodecatungstophosphoric acid (DTP) on above material was carried out by adding 18 ml of methanolic solution containing 2 g of DTP. The procedure was the same as above and the catalyst dried at 120 °C for 3 h and calcined further at 300 °C for 3 h.



Scheme 1. Benzylation of phenol.

2.3. Catalyst characterization

XRD patterns of prepared catalysts were determined using Bruker X-Ray diffractometer with Cu-K α radiation ($\lambda = 1.540562$ nm). Textural characteristics of prepared catalysts were determined by nitrogen adsorption-desorption procedure on Micromeritics ASAP 2010 instrument at an adsorption temperature 77 K. FTIR spectral comparisons were done on Perkin-Elmer instrument. SEM images and elemental composition of 20% (w/w) $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /MCF were recorded on FEI quanta 200 instrument. TEM images of catalysts were captured on JEOL for further clarification of porous nature of MCF support as well as supported catalyst. Ammonia-TPD of catalyst samples was done by AutoChem II 2920 instrument using 10% NH_3 in He.

2.4. Reaction procedure and analysis of reaction mixture

Experiments were done in flat bottom glass reactor of 50 ml capacity containing four baffles. For agitation, a pitched blade stirrer was used at specific speed (controlled by an electric motor). The thermostatic oil bath was used to control the temperature of the system. In a typical

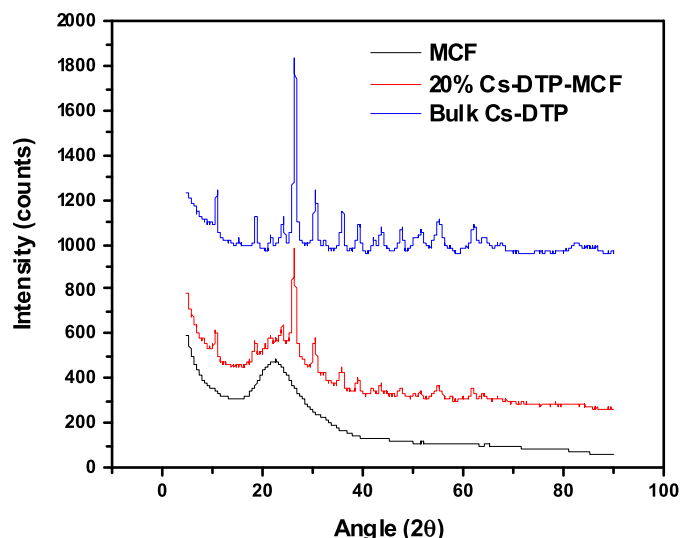


Fig. 1. XRD of MCF, 20% (w/w) Cs-DTP/MCF and Cs-DTP bulk catalyst.

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