Applied Catalysis A: General 485 (2014) 74–83

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Iron exchanged tungstophosphoric acid supported on activated carbon derived from pinecone biomass: Evaluation of catalysts efficiency for liquid phase benzylation of anisole with benzyl alcohol

Chowdari Ramesh Kumar[a,b], N. Rambabu[a], K.C. Maheria[a,c], A.K. Dalai[a,*], N. Lingaiah[b]

[a] *Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada S7N 5A9*
[b] *Catalysis Laboratory, Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, Telangana, India*
[c] *Department of Applied Chemistry, S.V. National Institute of Technology, Ichchhanath, Surat 395007, Gujarat, India*

ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form 23 July 2014
Accepted 28 July 2014
Available online 7 August 2014

Keywords:
Activated carbon
Benzylation
Heteropoly tungstate
Keggin ion
Pinecone

ABSTRACT

A series of iron-exchanged heteropoly tungstate (TPA-Fe) supported on activated carbon produced from pinecone biomass, have been investigated as catalysts for the benzylation reaction. Catalysts were characterized by FT-IR, XRD, Laser Raman, BET surface area, and ammonia TPD analysis. FT-IR, XRD, and Raman data revealed retention of the Keggin ion on activated carbon-supported catalysts. The catalytic activity of these catalysts was evaluated for liquid phase benzylation of anisole with benzyl alcohol. The catalytic activity was significantly dependent on the dispersion of TPA-Fe on activated carbon. The effect of TPA-Fe loading on activated carbon was studied ranging from 40 to 80 wt%. The catalyst with 70 wt% loading of TPA-Fe showed higher benzylation activity, which is related to variation in acidity of the catalysts. Thermal stability and structural properties of the catalysts were studied by treating the catalyst at different calcination temperatures. The benzyl alcohol conversion and selectivity towards benzylated products were also dependent on the anisole to benzyl alcohol molar ratio, reaction temperature, and catalyst concentration/loading. To know the effect of the benzylating agent, the reaction was carried out using benzyl chloride, benzyl alcohol, and dibenzylether. The preferential order for conversion of the benzylating agent was observed as benzyl chloride > benzyl alcohol > dibenzylether. This study indicated that biomass derived activated carbon is suitable support to disperse Keggin type heteropoly acid for the benzylation reaction.

1. Introduction

Alkylation of aromatic compounds is a very important reaction since diphenylmethane and substituted diphenylmethane compounds are versatile chemical feedstocks for a wide range of industrial products such as benzophenone, substituted benzophenone, 2-/4-nitrodiphenylmethane, diamines of diphenylmethane and diphenylmethanes which are used as monomers for poly carbonate resins, aromatic solvents, pharmaceuticals, dyes, perfumes [1]. Synthesis of these compounds frequently involves electrophilic aromatic substitution reactions. The conventional acid catalysts like HCl, H_2SO_4, $AlCl_3$, $ZnCl_2$, and $FeCl_3$ are required in stoichiometric ratio to carry out such reactions [2]. The use of these catalysts leads to many limitations concerning handling, safety, corrosion, and waste disposal. The development of efficient methods for recovery and reuse of the catalysts is very important in chemistry. One solution is to heterogenize the homogeneous catalysts by supporting them onto solid supports, thus providing facile recovery from the reaction mixture and the possibility of reusing them. Furthermore, Active components supported on a solid material, the surface area increases effectively and subsequently enhance the reactivity of the catalysts.

Heteropoly acid (HPA) compounds are known to be active catalysts for many acid catalyzed reactions. HPA compounds have attracted increasing interest due to their high acidity, redox properties, pseudo-liquid behaviour, physico-chemical properties, and catalytic activity. HPAs have very strong Brønsted acidity, approaching the super acid region, high stability, and high proton

---

* Corresponding author at: University of Saskatchewan, 57 Campus Drive, Saskatoon, SK, Canada S7N 5A9. Tel.: +1 306 966 4771; fax: +1 306 966 4777.
E-mail address: ajay.dalai@usask.ca (A.K. Dalai).
URL: http://www.engr.usask.ca/ dalai (A.K. Dalai).

http://dx.doi.org/10.1016/j.apcata.2014.07.034
0926-860X/© 2014 Elsevier B.V. All rights reserved.

mobility. The Hammett acidity ($H_0 = -13.2$) of tungstophosphoric acid is much stronger than 100% sulfuric acid ($H_0 = -11.94$). Heteropoly compounds with a Keggin structure are the most studied in the polyoxometalate class because they possess relatively high thermal stability and high intrinsic acidity [3,4]. Among the Keggin type HPAs, tungstophosphoric acid (TPA) is the usual catalyst of choice because of its high acidic strength and relatively high thermal stability. The main disadvantages of HPAs include their low surface area and high solubility in polar solvents, especially in aqueous solutions [5]. HPAs can be made into heterogeneous catalyst by exchanging their protons with metal ions such as Cs^+ [6], Ag^+ [7], $Sn^{4+/2+}$ [8,9], and Sm^{3+} [10] or by supporting them onto suitable supports like silica [11], zirconia [12], niobia [13], titania [14], tin oxide [15], and zeolite [16]. Activated carbons are also recommended for impregnation of heteropoly acids due to their high surface area (>1000 m^2/g), their ability to entrap certain amounts of heteropoly acid, and due to thermal stability in a wide range of p^H [17].

Activated carbons with a high surface area and porous structure have attracted increasing interest due to their novel catalytic applications. Agricultural and forest waste materials are increasingly popular for use in lightweight hybrid materials/biocomposites, chemical and food industries, as well as in the area of catalysis. Commercial activated carbons are generally prepared from coal, wood, peat, and coconut shells [18]. The demand for novel and more efficient, low-cost, and locally available renewable materials as alternative precursors in activated carbon production has led researchers to use many agricultural and forest waste materials such as fruit stones [19], pyrolyzed coffee residues [20], pine bark [21], nutshells [22] and olive stones [23] as precursors for production of activated carbons. The pinecone is a common biomass in North America and it can be converted into activated carbon using different activation methods. Huge quantities of pine trees and cones are produced throughout the world, especially in pine plantations for paper and pulp industries. Pinecones are generally discarded or burned in winter for heat generation after seed collection. The utilization of seedless waste pinecones is great potential for the production of value added products such as activated carbon.

Chimienti et al. [24] reported the impregnation of Keggin type TPA and STA on carbon for the isopropanol dehydration reaction using up to 50%. Their results indicated an increase in catalyst activity with increased loading up to 30%. Timofeeva et al. [25], used filamentous type carbons as supports for Dawson and Keggin type tungstophosphoric acid and tested the activity of the synthesized catalysts in a reaction of 2,6-ditert-butyl-4-methylphenol with toluene. Their results showed that the activity of supported catalysts had increased due to an increase in activity of surface protons of the catalysts. Degirmenci et al. [26] used activated carbon-supported silicotungstic acid and caesium salt of silicotungstic acid catalysts for synthesis of ethyl-tert-butyl ether. Park et al. [27] reported the effect of coke-capture in a Pd lattice on coking resistance in carbon-supported tungstophosphoric acid catalysts for dehydration of glycerol into acrolein reaction. To the best of our knowledge, the synthesis of Fe-exchanged TPA supported on AC and the detailed characterization of these catalysts and their application to benzylation reactions has not been studied.

The objective of the present work was the preparation of iron salt of tungstophosphoric acid supported on activated carbon derived from pinecone biomass and the investigation of its activity for liquid phase benzylation of anisole with benzyl alcohol. The effects of the benzylating agent on benzylation of anisole and catalytic activity of the optimized catalyst compared with the activity of tungstophosphoric acid supported on activated carbon were also studied. Reaction parameters such as catalyst weight, reaction temperature, and molar ratio were optimized.

2. Materials and methods

The following analytical grade chemicals were used for catalyst preparation and benzylation of anisole reaction: iron nitrate (Sigma–Aldrich, Canada), 12-tungstophosphoric acid (Sigma–Aldrich, Canada), Benzyl alcohol (EM Science, Canada), dibenzylether and phosphoric acid (Alfa-Aesar, Canada), 4-methoxydiphenylmethane (Matrix Scientific, Columbia), Anisole (Alfa-Aesar, Canada). Ammonia balanced with helium, hydrogen, air, and nitrogen gases were procured from Praxair Canada.

2.1. Production of activated carbon

Pinecone activated carbon was prepared according to the procedure available in the literature [28]. Pinecones were collected from the University of Saskatchewan campus, Canada. The cones were repeatedly washed with hot distilled water to remove adhering dirt and soluble impurities and dried at overnight. The cleaned and dried pinecones were grounded and sieved to particle size >350 μm for the production of activated carbon. Activated carbon was prepared in a two-step process. In the first step, 20 g of pinecone powder was impregnated with 60 g of 85 wt% H_3PO_4 (weight ratio 1:3). The mixture was stirred and kept overnight in a 100 °C oven. In the second step, H_3PO_4 impregnated pinecone material was placed in a fixed-bed reactor and heated under inert atmosphere of nitrogen. Initially, the temperature was raised to 150 °C at a heating rate of 10 °C/min and maintained at this temperature for 1 h. Then, the temperature was increased at the same ramping rate to reach the desired activation temperature of 500 °C and maintained at the same temperature for 2 h. Thereafter, it was allowed to cool to room temperature, followed by repeated washing with distilled water until it was free of any residual phosphoric acid (up to p^H 6.8–7.0), and the product was then dried at 110 °C for 24 h. This product was denoted as activated carbon (AC).

2.2. Preparation of the iron salt of tungstophosphoric acid

The iron-exchanged 12-tungstophosphoric acid catalyst was prepared with a nominal Fe^{3+}:TPA ratio of 1:1. TPA was dissolved in distilled water and the calculated amount of $Fe(NO_3)_3 \cdot 9H_2O$ was added to this solution and the resultant mixture was kept at 60 °C, with continuous stirring. At this stage, the solid particles grew slowly in size and yellow colour precipitates were obtained. The resultant mixture was stirred for 2 h and the excess water was evaporated on a rotary evaporator. The dried catalyst was kept for further drying in hot air oven and finally calcined at 300 °C for 2 h. This catalyst was denoted as TPA-Fe.

2.3. Preparation of iron salt of tungstophosphoric acid supported on activated carbon

Synthesis of supported metal salt of tungstophosphoric acid prepared by the method reported in the literature [29]. A series of AC-supported variants of TPA-Fe (40–80 wt%) were prepared by the impregnation method with a nominal Fe^{3+}:TPA ratio of 1:1. The typical procedure for the preparation of 40 wt% $H_3PW_{12}O_{40}$/Fe-AC catalyst is as follows: in a 100 ml round bottom flask, 1.14 g of activated carbon (AC) was stirred in 10 ml of distilled water. 50 mg of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in distilled water and subsequently added drop-wise to the activated carbon with vigorous stirring. The required amount of aqueous solution of TPA was added drop-wise to give 40 wt% TPA-Fe on AC and the reaction mixture was stirred for a further 2 h. The excess water was removed by rotary evaporator, followed by drying the obtained powder overnight in a hot air oven at 100 °C and then calcined at 300 °C for 2 h under nitrogen flow. The obtained catalyst is denoted as 40TF-AC. Similarly,