Applied Catalysis B: Environmental 218 (2017) 621–636

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Thermal catalysis vs. photocatalysis: A case study with $FeVO_4$/g-C_3N_4 nanocomposites for the efficient activation of aromatic and benzylic C—H bonds to oxygenated products

Subhajyoti Samanta, Rajendra Srivastava*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab, 140001, India

ARTICLE INFO

Article history:
Received 24 March 2017
Received in revised form 28 May 2017
Accepted 16 June 2017
Available online 17 June 2017

Keywords:
$FeVO_4$
g-C_3N_4
Oxidation
Hydroxylation
Visible light photocatalysis

ABSTRACT

Three semiconductor metal vanadates $FeVO_4$, $BiVO_4$, and $LaVO_4$ were synthesized. To improve the thermal catalytic and photocatalytic activity of highly efficient metal vanadate $FeVO_4$, nanocomposites of $FeVO_4$ and graphitic C_3N_4 were prepared. Nanocomposites were prepared via thermal annealing method by varying the composition of $FeVO_4$ and g-C_3N_4. Catalysts were characterized by a series of complementary combination of powder X-ray diffraction, thermogravimetric analysis, N_2 adsorption-desorption, scanning/transmission electron microscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, diffuse reflectance ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, photoluminescence, and photoelectrochemical techniques. Catalysts were investigated in the liquid phase oxidation of benzene, phenol, hydroquinone, naphthalene, anthracene, toluene, ethyl benzene, di-phenyl methane, and *p*-xylene under conventional thermal condition and visible light irradiation condition. Kinetic and thermodynamic parameters (such as k, E_a, ΔH, ΔG, and ΔS) were calculated for the benzene hydroxylation by varying the reaction parameters under thermal catalytic condition. In order to confirm the active species responsible for the thermal catalytic and photocatalytic processes, UV–vis, fluorescence, cyclic voltammetry, and radical scavenging experiments were carried out with the help of suitable probe molecules. Based on the results obtained, reaction mechanism was proposed, and the structure-activity relationship was established. The catalyst was magnetically separated and recycled with negligible loss in the activity which is important for the sustainable heterogeneous catalysis. The developed catalytic process has the potential for the sustainable synthesis of a wide range of industrially important fine chemicals. Such a unique and detailed investigation of comparative study between thermal catalysis and photocatalysis using $FeVO_4$/g-C_3N_4 nanocomposite will be highly useful to design optimum catalyst for an appointed catalytic reaction.

1. Introduction

Activation of aromatic and benzylic C—H bonds to oxygenated products is an attractive route to synthesize a wide range of important fine chemicals such as phenol, benzoquinone, acetophenone, etc. Phenol is widely used in the synthesis of phenol resin, bisphenol-A, caprolactam, etc. Further, benzaldehyde and acetophenone are extensively utilized to produce a wide range of synthetic intermediates through C═O group transformation. Similarly, quinones are important precursors for the synthesis of many valuable chemicals that exhibit cardiovascular, antitumor, antibacterial, antigerminative, and antiprotozoal activities [1–3]. In conventional practice, syntheses of these compounds are not straight forward. For example, phenol is industrially produced from surplus cumene as a petroleum feedstock by Hock process, in which cumene is oxidized to cumene hydroperoxide by air in aqueous Na_2CO_3 followed by the acid treatment to produce equivalents amount of phenol and acetone [4]. Benzaldehyde is produced by the side-chain chlorination of toluene followed by saponification of the resulting dichloromethyl group [5]. However, this process leads to produce benzaldehyde (which is contaminated with the chlorinated by-products) that do not meet FDA protocols. Moreover, benzaldehyde can also be produced by the vapour phase oxidation of toluene with oxygen [6,7]. The vapour phase process is operated at high pressure and temperature which is too harsh to improve the selectivity of the benzaldehyde. Acetophenone is produced by the oxidation of ethylbenzene in the homogeneous catalytic process

---

* Corresponding author.
E-mail address: rajendra@iitrpr.ac.in (R. Srivastava).

http://dx.doi.org/10.1016/j.apcatb.2017.06.043

using cobalt acetate or cobalt cycloalkane carboxylate as catalyst, manganese and/or bromide species as promoters, acetic acid as a solvent and molecular oxygen or air as an oxidant [8]. Corrosive nature of acetic acid, difficulty in the solvent, and catalyst recovery, and explosion hazards associated with the solvent and dioxygen discourage this industrial process. Furthermore, benzoquinone can be prepared by the oxidation of hydroquinone [9,10].

One can easily think that these compounds can be prepared by the direct functionalization of aromatic hydrocarbons by the catalytic oxidation of C—H bonds to form oxygenated products under mild reaction condition using H_2O_2 as a safe oxidizing agent. Various metal oxide and zeolite based catalysts have been developed for these reactions [11–15]. Microporous titanosilicate is one of the most studied catalysts for the hydroxylation and epoxidation reactions involving small organic molecules [11,12]. Researchers have developed mesoporous titanosilicate and zirconosilicate for reactions involving large organic molecules [13–15]. Vanadium containing mesoporous silicate and polyoxometalates have also been developed for the aromatic C—H activation [16–18]. Further, Fe-based Fenton reagent is well known for the hydroxylation reaction. Therefore, efforts have been made to develop Fe-based heterogeneous catalysts for C—H activation [19–21]. Howevere, low yield of the product was obtained using Fe/V/Ti based metallosilicates using TBHP or H_2O_2. It is difficult to incorporate a large amount of metal in zeolite/silica framework, which is one of the prime reason for the low catalytic activity. Furthermore, the mild acidic nature of zeolite framework is responsible for the low selectivity of the desired product, especially in the epoxidation reaction. This problem can be solved if Fe/V/Ti-based catalyst is supported on a neutral support such as carbon or related materials. In this study, we demonstrated the application of C_3N_4 as support material, which is being explored as a versatile support for the heterogeneous catalysis [22,23]. It is worthy to note that C_3N_4 based materials are being developed due to their excellent photocatalytic activity [24–31]. Photochemical dissociation of H_2O_2 can produce various oxygenated free radicals. Such free radicals are known to catalyze oxidation reactions and the degradation of organic pollutants found in water bodies [32–35].

Mixed metal oxides containing two or more metals are widely used as commercial catalysts for various industrial processes. Since V and Fe have been found to be good metals for the catalytic oxidation, therefore one may anticipate that oxide of these metals could be interesting for C—H activation also. $FeVO_4$ has been studied for a few oxidation reactions such as methanol oxidation [36,37]. $FeVO_4$ also exhibited impressive results in the gas sensing [38,39]. The role of $FeVO_4$ as a heterogeneous catalyst is less explored. However, in the recent time, significant efforts are being made to develop $FeVO_4$ based photocatalysts [40,41].

In the present study, metal vanadates ($FeVO_4$, $BiVO_4$, and $LaVO_4$) were investigated in the liquid phase oxidation of aromatic compounds for the synthesis of phenol, hydroquinone, benzoquinone, 1, 4-napthoquinone, 9, 10-anthraquinone, benzaldehyde, acetophenone, *4*-methyl benzaldehyde, and benzophenone using H_2O_2 under mild reaction condition. For further improvement in the catalytic activity, $FeVO_4$ and g-C_3N_4 based nanocomposites were prepared and investigated in the synthesis of above mentioned compounds. The detailed kinetic investigation was carried out by varying the reaction parameters such as substrate concentration, catalyst amount, H_2O_2 amount, and temperature. H_2O_2 efficiency and thermodynamic parameters such as activation energy (E_a), change of – enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) were calculated. Time-dependent UV–vis study was performed to investigate the active species involved in the oxidation reaction. Further, reactions were performed in the presence of radical scavenger to verify the intermediate radical species involved in the reaction.

$FeVO_4$ and g-C_3N_4 have good visible light absorption capacity and good photocatalytic activity. In this study, $FeVO_4$/g-C_3N_4 nanocomposite catalysts were investigated in the C—H activation at ambient temperature under visible light irradiation and the results were compared with the data obtained under thermal catalytic condition. The unique aspect of this study is to demonstrate the difference in the catalytic activity of $FeVO_4$ and $FeVO_4$/g-C_3N_4 nanocomposites under conventional thermal catalysis and photocatalysis. Catalysts exhibited better activity under photocatalytic condition when compared to thermal catalysis. Involvement of radical species in the photoassisted reaction was confirmed by fluorescence spectromenter with radical trapping experiments using terephthalic acid as a probe molecule. Involvement of hydroxyl radical species was also confirmed using cyclic voltammetry. Catalyst was easily separated using magnet and recycled with negligible loss in the activity during thermal catalysis and photocatalysis. Catalytic investigations reveal that $FeVO_4$/g-C_3N_4 (3:7) exhibited the highest catalytic activity among all the catalysts investigated in this study with good recovery and excellent recyclability. The excellent catalytic activity of $FeVO_4$/g-C_3N_4 (3:7) nanocomposite under themal catalytic and photocatalytic conditions can be attributed to the dual metal catalysis by Fe^{+3} & V^{+5}, optimum dispersion of $FeVO_4$ nanospheres on g-C_3N_4 matrix, optimum physical adsorption and photo-physical processes like photoadsorption, photodesorption, and efficient charge separation. The key features of the present study is that the same material ($FeVO_4$/g-C_3N_4 nanocomposite) is able to catalyze same set of reactions under thermal condition as well as under visible light illumination which will encourage catalysis researchers, materials chemists, and green & sustainable chemists to develop novel catalysts for the synthesis of a wide range of fine chemicals.

2. Experimental

2.1. Materials

All chemicals were of AR grade and used as received without further purification. $Fe(NO_3)_3.6H_2O$, NH_4VO_3, melamine, and ethanol were obtained from Loba Chemie Pvt. Ltd. India. Benzene, phenol, hydroquinone, naphthalene, anthracene, toluene, ethyl benzene, *p*-xylene, and diphenyl methane were purchased from Spectrochem India Pvt. Ltd. Hydrogen peroxide and acetonitrile were obtained from Merck Chemicals, India.

2.2. Catalyst preparation

2.2.1. Synthesis of $FeVO_4$

$FeVO_4$ was prepared by following the reported procedure [42]. In a typical synthesis, 80 mL of 0.3 M NH_4VO_3 and 80 mL of 0.3 M $Fe(NO_3)_3{\cdot}6H_2O$ were mixed in a beaker and stirred until a yellow precipitation appeared. Reaction mixture was transferred into a Teflon-lined stainless steel autoclave and kept in an oven at 180 °C for 3 h. Autoclave was cooled to ambient temperature and the reaction mixture was centrifuged. Solid product was washed with deionized water followed by ethanol, and dried in vacuum at 60 °C for 6 h. Finally, the resulting sample was calcined at 550 °C for 24 h. Details of synthesis procedure for $BiVO_4$ and $LaVO_4$ are provided in supporting information section.

2.3. Synthesis of g-C_3N_4

Graphitic carbon nitride was synthesized by heating 10 g of melamine in a cylindrical crucible (closed with a lid) at 550 °C for 4 h at a heating rate of 5 °C/min in a programmable furnace [24].