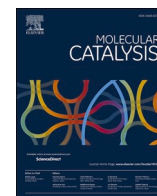




Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

Heterogeneous recyclable copper oxide supported on activated red mud as an efficient and stable catalyst for the one pot hydroxylation of benzene to phenol

Subhashree Mishra^a, Rajaram Bal^{b,*}, R.K. Dey^{a,*}^a Department of Chemistry, Central University of Jharkhand, Ranchi, 835 205, India^b CSIR-Indian Institute of Petroleum (IIP), Dehradun, 248 005, India

ARTICLE INFO

Keywords:

Catalyst
Heterogeneous
Hydroxylation
Phenol
Red-mud

ABSTRACT

Phenol is a key intermediate in chemical industry. The present research work reports facile synthesis of a new copper supported activated red mud as a heterogeneous catalyst for oxidative conversion of benzene to phenol. The process is simple and efficient for one pot hydroxylation reaction using H_2O_2 as an oxidant. The catalyst was characterized using FTIR, XRD, TEM, XPS and BET surface area analyzer. Catalyst reducible properties were studied using H_2 -TPR technique. The one-pot hydroxylation reaction, carried out at 75°C under optimum reaction conditions in presence of catalytic material, shows conversion of benzene to phenol with 84.5 % and 87.1 % selectivity and conversion efficiency, respectively. The proposed mechanism emphasizes upon cooperative effect of residual and embedded metal ions in solid catalyst matrix as the contributing factor for efficient conversion and selectivity. The reusable properties of the material, tested up to 5th consecutive cycles of batch operation, indicate retention of selectivity (83.9 %) as well as conversion efficiency (86.7 %), suitable for future commercial development adhering to the principle of green chemistry.

1. Introduction

The fundamental understanding of structural and chemical factors to study specific catalyst performance is important in view of number of variable factors such as catalytic activity, selectivity and durability. Development of new catalysts and catalytic technologies to transform benzene into phenol is currently attracting genuine scientific interest among researchers all over the world. The reason is attributed to the fact that phenol is a key intermediate in chemical industry for diverse production of number of key products/chemicals/intermediates such as resins, fungicides, pesticides, preservatives, pharmaceuticals, caprolactam and adipic acid [1]. At present, production of phenol accounts for 10 million metric tons [2]. Phenol is commercially synthesized from benzene following three steps cumene process, where compression of benzene and propylene is carried out at 30 bar pressure and at 250°C temperature in presence of phosphoric acid catalyst [3]. The reaction also involves formation of cumene-hydroperoxide as intermediate and monitoring of requisite parameters to avoid any kind of industrial hazards. The conversion of benzene to phenol also regarded as an energy intensive process [3,4]. The low selectivity of phenol also resulted in less

yield of phenol with generation of equivalent molar quantity of acetone as a side product indicating that the reaction suffers from lower atomic efficiency. Direct hydroxylation of benzene (HoB) to form phenol requires introduction of hydroxyl group in the benzene moiety and the conversion process is regarded as one of the most difficult task to achieve technically. In this context increasing global demand of phenol urgently requires a suitable alternative material/method/technology that can facilitate one-step hydroxylation of benzene. Development of alternative pathway can be helpful in reducing the need of currently adopted 3-step process with quantitative reduction of hazardous intermediates and chemicals.

Use of heterogeneous catalyst in hydroxylation of benzene is advantageous due to ease of separation/recovery of solid catalytic material from the process. In addition, regeneration and reusability of catalyst make the process more environmentally acceptable in view of generation of less amount of hazardous waste leading to greener pathway and lesser pollution [5–12]. It is to be noted that the stability of benzene and high reactivity of phenol are two key factors which makes the conversion of benzene to phenol more challenging one. Among various explored catalytic materials, carbon based materials are widely explored

* Corresponding authors.

E-mail addresses: raja@iip.res.in (R. Bal), ratan.dey@cuja.ac.in (R.K. Dey).<https://doi.org/10.1016/j.mcat.2020.111310>

Received 23 July 2020; Received in revised form 5 November 2020; Accepted 7 November 2020

2468-8231/© 2020 Elsevier B.V. All rights reserved.

