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Bimetallic Au–Pd/MgO as efficient catalysts for aerobic oxidation of benzyl alcohol: A green bio-reducing preparation method

Guowu Zhan, Yingling Hong, Vernon Tebong Mbah, Jiale Huang*, Abdul-Rauf Ibrahim, Mingming Du, Qingbiao Li*

Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

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ABSTRACT

The oxidation of benzyl alcohol, with molecular oxygen at atmospheric pressure in an aqueous medium, is investigated using Au–Pd/MgO bimetallic catalysts to examine the effect of catalyst parameters (viz. preparation method, Au/Pd molar ratio, and calcinations temperature) and reaction conditions (viz. reaction temperature and oxygen flow rate) on conversion and selectivity. The bimetallic catalysts were prepared via two novel reduction methods with bio-reducing agents and were characterized by transmission electron microscopy, X-ray diffraction, diffuse reflectance UV–vis spectroscopy, and thermogravimetric analysis to understand synergistic interactions between Au and Pd. Under optimal conditions, the Au–Pd bimetallic catalysts, with a 1:1 molar ratio and 9.7 ± 1.3 nm particle size, exhibited remarkably enhanced catalytic activity (>52%) and selectivity (~100%) compared with their monometallic counterparts. Moreover, the activity of the catalysts was maintained after six recycles without agglomeration.

1. Introduction

Liquid phase oxidation of benzyl alcohol is of vital importance for both scientific and industrial fields because of the production of chlorine-free benzaldehyde [1]. Benzaldehyde, a versatile intermediate, is one of the most valuable aromatic aldehydes in organic synthesis ranging from perfumery, pharmaceuticals, cosmetics, dyestuff, and agrochemical industries. Currently, increasing environmental concerns necessitate the development of eco-friendly techniques for benzyl alcohol oxidation transformation [2,3]; accordingly, it is desirable to develop alternative processes and catalysts for the conversion of benzyl alcohol to benzaldehyde. The designs of alternative synthesis techniques that inject "greenness" into the three aspects of benzaldehyde production, specifically: (i) utilizing green oxidants, (ii) employing clean solvents, and (iii) designing environmentally benign catalysts with high activity and selectivity, is of supreme importance.

(i) *Oxidants*. Traditionally, benzyl alcohol oxidations are achieved by utilizing stoichiometric oxygen donors, such as chromium trioxide [4], ammonium permanganate [5], and tert-butyl hydroperoxide [6]. However, these stoichiometric oxygen donors are expensive, toxic, corrosive, and produce waste. Recently, the use of oxidants, such as aqueous H_2O_2 and molecular O_2, has attracted considerable attention because of economic and environmental concerns [7,8]. Molecular oxygen is the most desirable oxidant because it is cheap, safe, readily available, and above all, produces water as the sole byproduct.

(ii) *Solvents*. Conventionally, organic solvents, such as benzene, chloroform, toluene, acetonitrile, acetone, and xylene, are employed in alcohol oxidation [9–11]. However, toxicity and volatility are the major drawbacks for the utilization of organic solvents. Meanwhile, water has emerged as an effective reaction medium for the oxidation of benzyl alcohol because of its non-toxicity, easy handling, and abundance [12]. Moreover, Yang et al. have reported that water exhibits promotional functions by forming unique micro-droplets in their multiphase oxidation reaction system [13]. Accordingly, several researchers have reported the use of water as a solvent for benzyl alcohol oxidation in literature [14–16].

(iii) *Catalysts*. In an ideal green oxidation process, the catalyst should be environmentally benign. Homogeneous catalysts have been used in alcohol oxidation with excellent activity and selectivity [10,17]; however, practical and technical problems, such as difficulty in product separation and poor reusability, have hindered their industrial applications. Heterogeneous catalysts for the conversion of benzyl alcohol to benzaldehyde have been studied extensively for green chemistry. Noble metal catalysts (Ag, Ru, Pd, and Au-based substances [18,19]) and transition metal catalysts (Mn, Cu, Ni, Al, Mo, and V-based

* Corresponding authors. Tel.: +86 592 2189595; fax: +86 592 2184822.
E-mail addresses: cola@xmu.edu.cn (J. Huang), kelqb@xmu.edu.cn (Q. Li).

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