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Article

Green catalytic oxidation of benzyl alcohol over Pt/ZnO in base-free aqueous medium at room temperature

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ABSTRACT

The selective oxidation of alcohol using molecular oxygen as an oxidant and water as a green solvent is of great interest in green chemistry. In this work, we present a systematic study of a Pt/ZnO catalyst for the selective oxidation of benzyl alcohol at room temperature under base-free aqueous conditions. Experimental observations and density functional theory calculations suggest that ZnO as a support can facilitate the adsorption of benzyl alcohol, which subsequently reacts with the activated oxygen species on the Pt catalyst, producing benzaldehyde. The resulting solid achieves a high conversion (94.1 ± 5.1% in 10 h) of benzyl alcohol and nearly 100% selectivity to benzaldehyde with ambient air as the oxidant. In addition, by introducing a small amount of Bi (1.78 wt%) into Pt/ZnO, we can further enhance the activity by 350%.

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1. Introduction

The catalytic oxidation of alcohol into aldehydes/ketones is of great importance at both the laboratorial and industrial levels, and is one of the most challenging reactions to conduct in green chemistry [1–6]. To achieve environmental and economic acceptability, significant effort has been devoted to the development of advanced catalysts that can use molecular oxygen as an environmentally friendly oxidant [7]. Traditionally, most studies are conducted in organic solvents or under solvent-free conditions, and the resulting mixtures of the organic substrates, products, solvents, and molecular oxygen can be quite dangerous [8]. Anhydrous conditions, in contrast, are impractical because water is formed during the reaction [9]. Considering that water is a safe, cheap, and environmental friendly solvent, it is highly desirable to develop efficient catalysts under aqueous conditions. Owing to their ability to activate molecular oxygen and the C–H bonds of alcohol, Pt nanoparticles are generally acknowledged as effective catalysts for alcohol oxidation reactions [10–12]. In addition, the high performance of such nanoparticles in water, the most promising green solvent, is also appealing [13,14]. However, the reaction must be carried out at relatively high temperatures (> 80 °C) [15,16] and oxygen pressures (> 0.1 MPa) [17] with the addition of bases (NaOH,

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K_2CO_3, etc.) [18], inevitably leading to severe problems such as undesirable side reactions, catalyst corrosion, and the requirement of an extra waste base treatment. From the viewpoint of green chemistry, it is of great interest to functionalize Pt catalysts for the selective oxidation of alcohol in the presence of atmospheric oxygen and the absence of a base at ambient pressure and room temperature.

Previous studies have mainly focused on the exploration of efficient structural or electronic modifiers for Pt nanoparticles [19–22]. Metal promoters, particularly Bi and Pb, have been demonstrated to drastically enhance the activity of Pt catalysts for alcohol oxidation by preventing an over-oxidation and poisoning of the Pt [23,24]. In contrast, relatively few studies have been devoted to the rational design of Pt catalysts based on a fundamental understanding of the elementary steps. Taking into account the fact that the adsorption and activation of molecular oxygen and alcohol are key steps in alcohol oxidation, it appears to us that the catalytic performance is able to be enhanced by introducing active components that facilitate the above important steps. Our previous study demonstrated that a partially reduced Bi_2O_{3-x} support can improve the activation of oxygen, which consequently enhances the catalytic performance of Pt nanoparticles for the selective oxidation of benzyl alcohol in a base-free aqueous medium with atmospheric oxygen as an oxidant [25]. To further prove this concept, effort should also be devoted to the fabrication and understanding of novel catalytic systems that can improve the activities of Pt nanoparticles by accelerating the alcohol adsorption and C–H activation.

Herein, we report a newly developed Pt/ZnO catalyst that enables efficient benzyl alcohol oxidation at room temperature under base-free aqueous conditions. Systematic experiments and density functional theory (DFT) calculations suggest that there is a synergistic effect between Pt and ZnO. Specifically, ZnO as a support can facilitate the adsorption of benzyl alcohol, which subsequently reacts with the activated oxygen species in a Pt catalyst to produce benzaldehyde. In addition, such activity showed an improvement of 350% with a small addition of Bi to the Pt/ZnO catalyst without any decrease in the selectivity.

2. Experimental

2.1. Materials

The materials used are as follows: deionized (DI) water, hexachloroplatinic acid (Sigma-Aldrich), sodium borohydride (Sigma-Aldrich), zinc oxide (Sinopharm Chemicals and Sigma-Aldrich), bismuth nitrate pentahydrate (Sinopharm Chemicals), and benzyl alcohol (Sinopharm Chemicals). All chemicals were used as received.

2.2. Preparation

Briefly, 1 g of ZnO powder was dispersed into 10 mL of DI water, followed by the addition of 2.66 mL of $H_2PtCl_6·6H_2O$ (19.2 mmol L^{-1}) into the above mixture under vigorous stirring at room temperature. Next, 2 mL of cold DI water containing 8 mg of $NaBH_4$ was then slowly dropped into the above mixture. The color of the solution changed from light yellow to grey very quickly, indicating the successful formation of Pt nanoparticles. The mixture was further stirred for 2 h before being centrifuged, and then washed three times using ethanol and DI water. The solid obtained was dried at 65 °C overnight in a vacuum oven, and labeled as a Pt/ZnO catalyst. The actual content of the Pt was determined to be 0.80 wt% using ICP-MS.

One gram of ZnO powder, 2.66 mL of $H_2PtCl_6·6H_2O$ (19.2 m mmol L^{-1}), and 48.5 mg of $Bi(NO_3)_3·5H_2O$ were mixed in 10 mL of DI water under vigorous stirring at room temperature. Then, 2 mL of cold DI water containing 8 mg of $NaBH_4$ was dropped into the above mixture. After stirring for 2 h, it was centrifuged, washed using ethanol and DI water three times, and then dried at 65 °C overnight in a vacuum oven. The as-synthesized solid was labeled as a Pt/Bi-ZnO catalyst. The actual contents of the Pt and the Bi were determined to be 0.80 wt% and 1.78 wt% using ICP-MS, respectively.

2.3. Characterizations

Wide-angle X-ray diffraction (WAXRD) patterns were recorded on a Rigaku Ultimate IV using Cu K_α radiation. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-1230 operated at 80 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a TECNAI G2 F20 operated at 200 kV. High-resolution X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. Nitrogen sorption data were obtained on a Micromeritics ASAP 2020 adsorption analyzer.

2.4. Catalytic reaction

In brief, 0.1 g of a catalyst, 0.2 mmol of benzyl alcohol, and 10.0 mL of H_2O were vigorously stirred together in a flask in the open air at room temperature (26 °C) in the dark. After several hours, 0.2 mL of the reactant was taken out with a plastic pipette, diluted with ethanol, and then analyzed using gas chromatography. Octane was utilized as the internal standard to quantify the reaction products. Because no byproducts such as benzoic acid or CO_2 were detected, the carbon balance = (moles of unconverted BA + moles of benzaldehyde)/moles of the total BA. The carbon balance was > 99%. For the Arrhenius plots, the catalytic reactions were conducted under identical reaction conditions except for the reaction temperature (35, 45, 55, and 65 °C). In O_2 partial pressure experiments, N_2 was employed as the balance gas. The partial pressure of O_2 was tuned by charging different amounts of N_2 and O_2 into the reaction flask using a mass flow controller. The total pressure for N_2 and O_2 was held at 1 bar.

The recycling tests were carried out as follows. After a catalytic reaction, the solid was separated from the mixture through centrifugation, followed by washing with DI water three times. The solid obtained was dried in an oven at 65 °C

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