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Article

Selective suppression of toluene formation in solvent-free benzyl alcohol oxidation using supported Pd-Ni bimetallic nanoparticles

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ABSTRACT

The solvent-free oxidation of benzyl alcohol was studied using supported Pd-Ni bimetallic nanoparticles. Compared with monometallic Pd, the addition of Ni to Pd was found to be effective in suppressing the nondesired product toluene, thereby enhancing the selectivity towards benzaldehyde. This result was attributed to a dual effect of Ni addition: the weakening of dissociative adsorption of benzyl alcohol and the promotion of oxygen species involved in the oxidation pathway.

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1. Introduction

Selective oxidation of alcohols to corresponding aldehydes or ketones is of fundamental importance in functional group transformation in both laboratorial and industrial applications. Traditionally, alcohol oxidations are performed by using stoichiometric and toxic permanganate or chromate as oxidants. From the viewpoint of green chemistry, the liquid-phase oxidation of alcohols with molecular oxygen or air as oxidants under mild solvent-free reaction conditions is highly desirable.

Over the past few years, a variety of heterogeneous catalysts have been developed for this transformation [1,2]. Among the reported catalysts, supported palladium has been recognized as one of the best catalysts owing to its excellent activity [3–7]. Although supported palladium catalysts can be very active for the oxidation of benzyl alcohol, which is a model reaction for selective oxidation, the selectivity towards the desired product benzaldehyde is difficult to control. Previous investigations on the solvent-free oxidation of benzyl alcohol using palladium catalysts have demonstrated the formation of many products, including (a) benzaldehyde, benzoic acid, and benzyl benzoate from oxidation, dehydrogenation, and esterification, respectively (b) benzene from decarbonylation, (c) dibenzyl ether from dehydration, (d) dibenzyl acetal from condensation, and (e) toluene from disproportionation or hydrogenolysis of benzyl alcohol [8–10]. Among these products, toluene is the major byproduct under solvent-free conditions, which can lower the selectivity towards the oxidation product [6,7]. To switch off

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toluene formation and achieve high aldehyde selectivity, one widely adopted approach is to use intrinsically basic or modified supports. Sankar et al. [9] reported MgO- and ZnO-supported catalysts did not produce any toluene. They interpreted that the basicity of the supports inhibited the cleavage of the C–O bond of benzyl alcohol that gives rise to toluene generation. Furthermore, N-doped mesoporous carbon [11], amino-group-functionalized TUD-1 and CNT [12,13], and alkali-treated titanate nanobelts [14] also showed enhanced selectivity towards the desired oxidation product owing to the basic sites grafted on the surface of the supports. Another approach to suppress toluene formation involves the use of supported bimetallic or trimetallic catalysts. Pd-Au bimetallic nanoparticles are most frequently used, which improve the overall selectivity compared with monometallic Pd [15]. However, a considerable amount of toluene is inevitably formed when it comes to a higher reaction temperature or conversion [9,16]. Recently, He et al. [17] demonstrated that the addition of Pt to the Pd-Au alloy catalysts could significantly minimize toluene formation. However, the full complexity of ternary alloys can be missed because the composition of such catalysts varies systematically with particle size.

It is generally accepted that bimetallic catalysts exhibit superior catalytic performance to monometallic catalysts owing to the synergetic interactions between the metals [18–20]. In terms of selectivity control, the introduction of a less active metal to a more active metal may selectively nullify some active sites for side reactions [21]. In the case of Pd-Au bimetallic catalysts, the catalytically more active Pd is perturbed by the inferior activity of Au, which makes Pd more atomic-like and suppresses the formation of byproducts [22]. Additionally, analogous Pd-M (M = Co, Cu, Zn, Ga, Ag, Sn, Pb, Bi) catalysts have been used in many Pd-catalyzed reactions and has resulted in enhanced selectivity [23–29]. For example, Pd-Ag and Pd-Cu bimetallic nanoparticles dramatically increased the selectivity towards the target alkenol in the semi-hydrogenation of alkynol reported by Yarulin et al. [24]. In an attempt to prevent the formation of nonselective reaction products, especially toluene, in solvent-free benzyl alcohol oxidation, we adopted a bimetallic catalysis strategy by alloying Pd with nonprecious transition metals instead of other noble metals such as Au and Pt. Herein, we report that a Pd-Ni bimetallic catalyst displayed high selectivity and overall productivity to the corresponding aldehyde.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of EP-FDU-12

The EP-FDU-12 support was synthesized as reported in the literature [30]. Typically, 0.50 g of Pluronic F127, 0.60 g of 1,3,5-trimethylbenzene (TMB), and 1.25 g of KCl were dissolved in 50 mL of HCl (1 mol/L) at 14 ± 0.1 °C. After stirring for 1 h, 2.08 g of tetraethyl orthosilicate (TEOS) was added to this solution. After stirring at 14 °C for 24 h, the mixture was transferred into an autoclave and heated at 140 °C for 24 h. The product was obtained by filtration and dried at room temperature in air. The organic templates were removed by annealing at 350 °C.

2.1.2. Synthesis of Pd nanoparticles

Pd nanoparticles (PdNPs) were synthesized according to a reported method [31]. In a typical synthesis, 112 mg of palladium acetate was mixed with 3.3 mL of oleic amine with stirring at 50 °C to form a clear solution. Oleic acid (3.2 mL) was then added and the mixture was kept at 50 °C for 1 h. Then, 386 mg of tetrabutylammonium borohydride (TBAB) dissolved in 2 mL of $CHCl_3$ was added in one portion. The mixture was heated for 1 h before it was cooled to room temperature. The PdNPs were precipitated by the addition of 15 mL of ethanol. The precipitate was separated by centrifugation and washed with ethanol. Finally, the precipitate was dried in a vacuum oven overnight. The size of the PdNPs was examined by transmission electron microscopy (TEM) and determined to be 2.83 ± 0.27 nm.

2.1.3. Synthesis of supported Pd-Ni bimetallic nanoparticles

The synthesis of supported Pd-Ni bimetallic nanoparticles (BMNPs) was similar to our previous study with some modifications [32]. First, the required amount of nickel nitrate and 500 mg of mesoporous silica (EP-FDU-12) were added to 5 mL of ethanol. The mixture was stirred until the ethanol evaporated to form a powder, which was further dried under vacuum oven overnight. The as-obtained solid powder was added to a predetermined volume of a chloroform solution of PdNPs. After 24 h of stirring, the solid product was centrifuged and dried in air. Finally, the powder was calcinated under 5% H_2/95% Ar at 500 °C for 4 h. The loading mass of Pd was 1 wt% for all the samples. For comparison, supported monometallic Pd and Ni nanoparticles were prepared in a similar manner to the above procedure by omitting the deposition of nickel nitrate and PdNPs, respectively.

2.2. Characterizations

The TEM images were recorded on a Hitachi HT-7700 operated at 80 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectrometry (EDX) analysis were performed on a Tecnai G2 F20 operated at 200 kV. The sample was embedded in epoxy resin and then microtomed into a sub-100-nm ultrathin film at room temperature. These thin film samples floated on water or other solvents and were collected by a copper mesh with a polymer microgrid for HAADF-STEM imaging and elemental line scanning. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. All binding energies were referenced to the C 1*s* peak at 284.8 eV of the surface adventitious carbon. Diffuse reflectance Fourier transform infrared spectra of adsorbed CO (CO-DRIFT) were obtained on a Bruker Vertex 70 spectrometer equipped with a

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