



Promising nanostructured gold/metal oxide catalysts for oxidative coupling of benzylamines under eco-friendly conditions



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ABSTRACT

Designing Au nanocatalysts supported on nanosized metal oxides has drawn much attention due to remarkable nanoscale influenced metal-support interactions and their favorable role in heterogeneous catalysis. This work reports development of Au nanocatalysts dispersed on nanosized CeO₂ and CeO₂-ZrO₂ supports for solvent- and base-free oxidative coupling of benzylamines into *N*-benzylbenzaldimines using O₂ as a green oxidant. The physicochemical characterization of nanocatalysts has been undertaken using HRTEM, UV–vis DRS, XRD, Raman, BET, TG-DTA, AAS, and XPS techniques. HRTEM images reveal the formation of nanosized CeO₂ and CeO₂-ZrO₂ supports with an average diameter of ~10 and 7 nm, respectively. HRTEM images also indicated that Au/CeO₂-ZrO₂ catalyst has smaller Au nanoparticles (~2.1 nm) compared with that of Au/CeO₂ catalyst (~3.7 nm). Raman and XPS studies showed that the addition of ZrO₂ to CeO₂ leads to abundant oxygen vacancies and higher concentration of Ce³⁺, respectively. The Au/CeO₂-ZrO₂ catalyst exhibited a higher efficiency in benzylamine conversion (~95%) followed by Au/CeO₂ (~78%), CeO₂-ZrO₂ (~51%), and CeO₂ (~39%). The Au/CeO₂-ZrO₂ catalyst was also found to effective for oxidative coupling of various benzylamines, and moderate to good product yields were obtained. The presence of smaller Au particles (2.1 nm) and improved surface-defect properties of nanoscale CeO₂-ZrO₂ support are found to be key factors for high performance of Au/CeO₂-ZrO₂ catalyst. Additionally, the reaction temperature is one of the important factors for the performance of catalysts. Remarkably, ~99.6–99.9% selectivity for *N*-benzylbenzaldimines was found in the amine oxidation, which highlights the significance of present work in the selective oxidation catalysis.

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1. Introduction

Catalysis using supported gold nanoparticles (Au NPs) is currently one of the most attractive research areas due to its wide significance in the chemical industry [1,2]. Indeed, bulk gold had long been considered as catalytically 'inactive' metal [3]. However, the pioneering discoveries of Haruta and Hutchings have been demonstrated that smaller sized gold nanoparticles dispersed on suitable metal oxides exhibit a remarkable catalytic performance in the oxidation of carbon monoxide and hydrochlorination of ethyne, respectively [3,4]. Consequently, the Au nanocatalysts have been widely used in many reactions of both environmental and industrial importance, such as CO oxidation, oxidation of alcohols, chemoselective hydrogenation, C–C and

C–N coupling reactions, H₂O₂ production, water–gas-shift reaction, combustion of volatile organic compounds and oxidation of olefins [5–15]. In particular, the oxidative coupling of benzylamines into *N*-benzylbenzaldimines using nano-Au catalysts has received tremendous attention due to the many useful applications of imines [16–18]. For example, *N*-benzylbenzaldimines are important building blocks for the synthesis of dyes, polymers, agrochemicals, fine chemicals, anti-inflammatory and anti-cancer agents [19,20]. Owing to the C=N double bond, *N*-benzylbenzaldimines can also be used in a number of transformations, such as hydrogenation, cycloaddition, and nucleophilic addition reactions.

Stoichiometric amounts of chromate, permanganate, 2-iodoxybenzoic acid, and *N*-tert-butylphenylsulfonimidoyl-chloride are typically used oxidants for the oxidation of organic compounds [21,22]. However, the use of stoichiometric (hazardous) oxidants is unfavorable from the perspective of sustainable chemical industry. On the other hand, the catalytic efficiency of several Au catalysts has been tested for the oxidation of benzylamines using molecular

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oxygen (O_2) as the oxidant [17,23–25]. O_2 is an abundant and eco-friendly oxidant that generates only water as the by-product in the benzylamine oxidation, hence O_2 is an efficient alternative to stoichiometric (hazardous) oxidants [18]. However, the major limitations in the above Au-catalyzed benzylamine oxidation reactions is the use of harmful organic solvents and bases, which generates large amounts of toxic chemical waste and requires a tedious workup procedure for separating the Au catalysts from the reaction mixture as well as for analyzing the reaction products. Therefore, developing greener and more efficient methodologies that can be performed under solvent- and base-free conditions using O_2 as the oxidant are highly desirable toward a sustainable organic chemistry.

It is now a well-known fact that the nature of metal oxide supports plays a pivotal role in modifying the structure-activity properties of nano-Au catalysts [26]. The metal oxides can be classified into reducible or active supports, such as TiO_2 , CeO_2 , Fe_2O_3 , and MnO_2 , and inert supports, such as SiO_2 , MgO , and Al_2O_3 . It has been reported that Au nanoparticles supported on reducible metal oxides exhibit a higher catalytic performance compared with that of Au nanoparticles supported on inert metal oxides [27,28]. The reason is that reducible metal oxides provide active sites for the adsorption of oxygen, generating active oxygen species for the oxidation reactions [29–31].

Cerium oxide (CeO_2) is one of the widely used active supports for the Au nanoparticle-catalyzed reactions [27,31–34]. This significance has been aroused due to unique properties of CeO_2 , such as abundant oxygen vacancies and remarkable redox properties ($Ce^{3+} \leftrightarrow Ce^{4+}$). In addition, the particle size of CeO_2 plays a key role in enhancing the efficiency of Au catalysts. It has been shown that nano- CeO_2 supported Au catalyst exhibits better activity compared with that of bulk CeO_2 supported Au catalyst in the oxidation of carbon monoxide and oxidation of alcohols [32,34]. It is therefore believed that by enhancing the textural (e.g., surface area) and redox properties of ceria, the catalytic efficiency of Au catalysts can be improved. The doping of metal ions (e.g., Zr^{4+}) into the CeO_2 is one of the promising ways to modify its physicochemical properties [7,35–37]. Doped ceria materials exhibit smaller particle size, higher specific surface area, and more number of oxygen vacancies compared with bare ceria, which is attributed to the co-operation effect of the cerium and dopant. Particularly, oxygen vacancies play a favorable role in the adsorption and activation of gaseous phase oxygen in order to interact with the reactant molecules in the oxidation reactions [38,39].

The present study has been undertaken against the above background. Nanoscale CeO_2 and CeO_2 - ZrO_2 ($Ce/Zr = 1/1$) supports were synthesized using a modified co-precipitation method. Au nanoparticles are dispersed onto the nanoscale CeO_2 and CeO_2 - ZrO_2 supports using a deposition-precipitation method. The physicochemical properties of the nanocatalysts were systematically analyzed using X-ray diffraction (XRD), thermogravimetric-differential thermal analysis (TG-DTA), BET surface area, atomic absorption spectroscopy (AAS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, UV-vis diffuse reflectance spectroscopy (UV-vis DRS), and high resolution transmission electron microscopy (HRTEM) techniques. The catalytic efficiency of the nanocatalysts was studied for the oxidative coupling of various benzylamines. The catalytic experiments have been conducted under solvent- and base-free conditions using O_2 , a greener and more efficient methodology toward a sustainable chemistry. To the best of our knowledge, this is first report on the catalytic performance of Au/ CeO_2 and Au/ CeO_2 - ZrO_2 catalysts for the solvent- and base-free oxidative coupling of benzylamines using molecular oxygen. Great efforts have been made to correlate the catalytic activity results with the characterization studies.

2. Experimental

2.1. Materials and methods

Nanoscale 50% Zr-doped CeO_2 was synthesized using a modified co-precipitation method from ultra-high dilute aqueous solutions, which is crucial for synthesizing nanoscale CeO_2 -based metal oxides [40,41]. The employed precursors are $NH_4Ce(NO_3)_4 \cdot 6H_2O$ (Aldrich, AR grade), $ZrO(NO_3)_2 \cdot xH_2O$ (Fluka, AR grade). Extremely dilute aq. NH_3 solution (2.5 v/v%) was used as the precipitating agent. In a typical procedure, the required amounts of metal precursors are dissolved in Milli-Q water under mild stirring conditions. The precipitant was added slowly to the above mixture solution over a period of 1 h until the pH of the solution reached to ~ 8.5 . The obtained precipitates were decanted, filtered off, washed with Milli-Q water, and oven dried at 393 K for 12 h. The sample was then calcined at 773 K for 5 h in air at a heating rate of 5 K/min. Nanoscale CeO_2 support was also synthesized using the same preparation method.

Homogeneous deposition precipitation method was used to synthesize 1 wt.% Au catalysts. In brief, to prepare the Au/ CeO_2 - ZrO_2 catalyst the adequate amounts of $HAuCl_4 \cdot 4H_2O$ (Alfa Aesar, 99.9%) and urea (urea:Au = 100 mole ratio) are dissolved in Milli-Q water and the solution was then heated to 343 K. The required amount of CeO_2 - ZrO_2 support was added to the Au solution and the stirring was continued for 12 h at the same temperature. The solution was then cooled to room temperature, filtered off, and washed with Milli-Q water until no traces of chloride ions were detected by $AgNO_3$ test. Finally, the sample was oven dried at 373 K for 12 h and calcined in air at 573 K for 4 h (1 K/min). The Au/ CeO_2 catalyst was also synthesized by adopting the same method.

2.2. Catalyst characterization

Powder XRD analysis was performed using a Rigaku diffractometer with $Cu K\alpha$ radiation (0.15418 nm) and a scintillation counter detector. Scherrer equation and standard cubic indexation method were used to determine the average crystallite size of CeO_2 and its lattice parameter in the synthesized catalysts, respectively. The TG-DTA analysis was carried out on a Mettler Toledo TG-SDTA instrument. The samples were heated from ambient temperature to 1073 K with a heating rate of 5 K min^{-1} under the flow of N_2 .

HRTEM studies were made on a JEOL JEM-2100F instrument equipped with a slow-scan CCD camera and an accelerating voltage of the electron beam 80 kV. The preparation of samples involves sonication in acetone for 10 min, followed by deposition of a drop on the copper grid supporting a perforated carbon film and allowed to dry. The Au content of the catalysts was estimated using the AAS technique. For this, Spectra AA-220 spectrophotometer at a wavelength of 242.8 nm was used. The UV-vis DRS measurements were performed over the wavelength range of $\lambda = 200$ –750 nm using a GBS-Cintra 10e UV-vis NIR spectrophotometer with an integration sphere diffuse reflectance attachment. Sample was diluted in a KBr matrix by pelletization.

N_2 -adsorption/desorption isotherms of the catalysts were obtained on a Micromeritics ASAP 2010 instrument at liquid N_2 temperature (77.25 K). Prior to analysis, the samples were degassed at 423 K for 16 h. XPS studies were conducted using a Thermo K-5 Alpha XPS instrument with $Al K\alpha$ radiation (photon energy = 1486.6 eV) at a pass energy of 50 eV. The core level binding energies (BEs) were charge corrected with respect to carbon (C 1s) peak at 284.8 eV. Raman analysis was performed using PerkinElmer-Raman Station 400F (785 nm laser, spot size of 100 μm) spectrometer equipped with a liquid N_2 cooled charge coupled device detector and a confocal microscope. The samples

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