ARTICLE IN PRESS

ELSEVIER

Porous structured CuO-CeO₂ nanospheres for the direct oxidation of cellobiose and glucose to gluconic acid

Prince Nana Amaniampong [a,1], Quang Thang Trinh [b], Kaixin Li [a], Samir H. Mushrif [a], Yu Hao [c,*], Yanhui Yang [a,*]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
[b] Cambridge Centre for Advanced Research and Education in Singapore (CARES), Nanyang Technological University, 1 Create Way, Singapore 138602, Singapore
[c] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ABSTRACT

Porous-structured CuO-CeO₂ nanospheres were synthesized using a hydrothermal method and were tested as catalysts for the direct oxidation of cellobiose to gluconic acid. Catalytic reaction along with catalyst characterization results and ^{18}O-oxygen isotope labeled experiments revealed that the surface lattice oxygen of CuO in CuO-CeO₂ nanospheres was consumed during the oxidation of cellobiose. This provides a direct evidence of our previous work (Amaniampong et al., Angew. Chem. Int. Ed. 54 (2015) 8928–8933). Characterization results further suggested that the lattice oxygen in CeO₂ did not participate in the oxidation; nonetheless, the addition of CeO₂ to CuO enhanced the surface area of the catalyst composite which was crucial for the reaction. The spent catalyst upon re-oxidation regained its activity. In addition, isotope labeled deuterium oxide (D₂O) experiments suggested that hydrogen exchange between the solvent and the substrate (glucose) are not involved in the mechanistic formation of gluconic acid and confirmed the solvent had no direct influence in the formation of gluconic acid.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Metal oxide catalysts are promising for oxidation processes, due to their lower costs and higher stability, as compared to noble metals. The synthesis and characterization of transition metal oxides with controlled shape, size, structure and uniform dimension have attracted considerable interest because of their unique physico-chemical properties and potential in catalysis [1,2]. Among these, copper oxide (CuO) was reported to be suitable for various catalytic applications [3–6], and the property of CuO has been documented in literature [7] to be closely related to its microstructures, particularly its morphology, crystal size and orientation. Rajesh et al. reported that CuO/Al₂O₃ was even more active than Pt/Al₂O₃ for the complete oxidation of ethanol [8]. Larsson and Anderson attempted CuOₓ/Al₂O₃ for the incineration of CO, ethanol and ethyl acetate and found an excellent catalytic performance [9,10]. CuO was also

the most active metal oxide of those explored for the catalytic incineration of toluene with γ-Al₂O₃ as support [11]. Copper-modified or copper promoted by ceria has been reported to exhibit enhanced catalytic performance than copper only in the total oxidation of carbon monoxide, catalytic wet oxidation of phenol and water gas shift reactions [12–14]. The enhanced activity of the copper oxide promoted by cerium oxide can be attributed to the structural enhancement and improved thermal stability of the copper-cerium mixed oxide [15].

The activation of C—H bond was reported to be a key step in oxidation reactions [16,17]. There has been considerable interest in the oxidation of saturated hydrocarbons involving C—H bond activation to manufacture valuable products such as the production of oxygenates *via* the partial oxidation of light alkanes [18] through the activation of C—H bonds by under coordinated metal lattice oxygen sites, with a concerted mechanism in which the metal center inserted into the C—H bond, and cleaved it. The production of olefins *via* dehydrogenation or oxidative dehydrogenation mechanisms over transition metal oxides has also become attractive [19]. Recently, great interest in the valorization of renewable resources has led to extensive investigation on the catalytic oxi-

dation of sugars and other carbohydrates. In spite of the great interest in these processes, partially conflicting opinions regarding their underlying mechanisms, were reported in the literature concerning several details of the mechanism of oxidation over oxide catalysts. For instance, the selective oxidation of glucose to gluconic acid, and the liquid phase oxidation at the alcoholic C—OH and carbonylic C=O bonds have been reported to occur *via* dehydrogenation mechanism [20,21]. In our previous study [6], oxidation of glucose, cellobiose and cellulose was performed on a CuO catalyst, in the form of nanoleaves, with excellent yield towards gluconic acid. Using quantum mechanical calculations, it was revealed that the surface lattice oxygen of CuO activated the formyl C—H bond in glucose and incorporated itself into the glucose molecule to oxidize it to gluconic acid.

Herein, CuO-CeO$_2$ nanospheres with a porous structure were synthesized by a hydrothermal treatment, using urea as a precipitating agent without the aid of surfactant to achieve a Ce-Cu binary precursor and subsequent calcination of the precursor. The as-synthesized CuO-CeO$_2$ nanospheres were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscope (HR-TEM), transmission electron microscope (TEM), H$_2$ temperature-programmed reduction (H$_2$-TPR), N$_2$ adsorption-desorption techniques and scanning electron microscope (SEM). The catalytic performance for the selective oxidation of cellobiose and glucose was examined to study the correlation between the catalytic performance and the interaction at the Ce-Cu interface. It was anticipated that, high oxygen mobility and redox properties of ceria oxide my further promote the catalytic properties of copper oxide in these reactions due to the additional active sites generated from oxygen vacancies at the Cu-Ce interfaces. Isotope labeling experiments with ^{18}O (oxygen) were carried out to study the reaction mechanism and also to further confirm the findings in our previous study that, indeed it was the lattice oxygen in CuO that incorporated into glucose to form gluconic acid [6]. Deuterium labeled water (D$_2$O) experiments were also carried out to investigate the role of solvent.

2. Experimental

2.1. Catalyst preparation and characterization

CuO-CeO$_2$ nanospheres were prepared by a hydrothermal method based on a previously reported two-step route [22]. In a typical synthesis process, Ce(NO$_3$)$_3$·6H$_2$O (1 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (1 mmol) were dissolved in 50 mL of deionized water, followed by adding 8 mmol of urea dropwise. The transparent solution attained after stirring the precursor solution, was transferred to a Teflon-lined autoclave and then heated at 180 °C for 100 min, resulting in the precipitation of the precursors. The precipitate was centrifuged, washed several times with deionized water and ethanol. After drying at ambient atmosphere, the precursor was finally calcined in air at 600 °C for 4 h. For the spent catalyst regeneration, a specified amount of the CuO-CeO$_2$ catalyst recovered after reaction were thoroughly washed with DI water and ethanol and dried at 60 °C. The dried catalyst was then placed in a tube furnace and charged with O^{18}-labeled oxygen and calcined at 400 °C for 4 h.

Crystallographic analysis for the tested were performed by means of XRD measurements in 2θ mode on a Bruker AXS D8 diffractometer with Cu$_{K\alpha}$ (λ = 0.154056 Å) radiation at 40 kV and 20 mA. XPS was performed on a Thermo Escalab 250 spectrometer. The binding energy was calibrated using C1 s (284.6 eV) as a reference. The as-synthesized CuO-CeO$_2$ morphology was also studied by SEM (JEOL JSM 6700F field emission), TEM and HR-TEM (JEOL JEM-2100F). H$_2$-TPR was carried out in a quartz fixed-bed reactor

equipped with TCD. In each run, approximately 50 mg of the catalyst was pretreated at 300 °C under a flow of He (30 mL min^{-1}), and then heated to 700 °C with a ramp of 10 °C min^{-1} in the stream of 5 vol% H$_2$/Ar (40 mL min^{-1}). Surface area analysis was determined by nitrogen physisorption on a Micromeritics TrisStar apparatus. The specific area was calculated using the Brunauer-Emmett-Teller (BET) equation. Raman measurements were performed on an inVia reflex confocal microprobe Raman system (Renishaw Company). Excitation with radiation of 514.5 nm was provided with an Ar$^+$ laser.

2.2. Catalyst testing

Catalytic experiments were carried out using 0.050 g of CuO-CeO$_2$ catalyst and 0.205 g of cellobiose, unless otherwise stated. A stainless-steel autoclave reactor, equipped with a Teflon liner (50 mL) was employed to perform the oxidation of cellobiose. Typically, cellobiose, the catalyst and deionized water (15 mL) were loaded into the reactor. The reactor was purged several times with high-purity nitrogen, (unless otherwise stated) to eliminate any traces of residue air present in the reactor. Reactions were allowed to proceed at desired set temperatures with constant stirring at 800 rpm. After the reaction was completed, an Agilent 1100 HPLC with a RID − 6A refractive index detector and a Hi-Plex H column (300 × 6.5 mm) were used to analyze the reaction products, with a mobile phase of 0.01 M H$_2$SO$_4$ buffer at a 1 mL min^{-1} flow rate. For the isotopically labeled experiments, D$_2$O was used as solvent and O^{18}-labeled oxygen was used for the spent catalyst regeneration. Noteworthy, the detected amount of formic acid reported in our study is the solubilized fraction of it, although the volatized amount of formic acid at the analyze condition is small according to its corresponding Henry's law coefficient [23].

3. Results

3.1. Structural characterization

CuO-CeO$_2$ composites were obtained after calcining the Ce-Cu binary precursors synthesized by the hydrothermal process. The morphology and microstructure of as-synthesized CuO-CeO$_2$ were investigated by SEM, TEM and HR-TEM analysis. The low magnification SEM image in Fig. 1a reveals that the samples consists of spherical particles of 200–300 nm in diameter. The porous nature of the as-synthesis CuO-CeO$_2$ is shown in Fig. 1b (high magnification SEM). The spent CuO-CeO$_2$ catalyst (Fig. 1c and d) is also sphere-like, indicating that the morphology of the fresh catalyst is not destroyed after the catalytic reaction. Fig. 2 displays the TEM and HR-TEM images of the as-synthesized and spent CuO-CeO$_2$ nanospheres. The TEM images (Fig. 2a) confirms our above deduction that, the nanospheres consist of nanoparticles. These small nanoparticles consisting of the nanospheres have a diameter of *ca.* 10 nm. HR-TEM image shown in Fig. 2b of the CuO-CeO$_2$ nanospheres give lattice spacing of 0.156 and 0.234 nm, corresponding to (111) planes of cubic CeO$_2$ phase and (111) planes of monoclinic CuO phase, respectively [24,25]. The HR-TEM analysis reveals that the nanospheres are mainly composed of mixed crystallites, preferentially exposing the disordered crystal phases of CuO and CeO$_2$ crystals. The TEM analysis of the spent catalyst (Fig. 2c) confirms the sphere-like morphology of the spent CuO-CeO$_2$ catalyst as revealed by the SEM analysis. The HR-TEM image in Fig. 2d also shows the presence of Cu (111) with lattice fringe of 0.206 nm, and CeO$_2$ (111) with lattice fringe of 0.156 nm. Surface area analysis (BET) is performed to further investigate the porous structure and surface area of the as-synthesized CuO-CeO$_2$ nanospheres. The specific surface area estimated from the BET