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Enhanced hydrogen selectivity via photo-engineered surface defects for methanol steam reformation using zinc oxide–copper nanocomposite catalysts

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ABSTRACT

Methanol steam reformation (MSR) to produce hydrogen (H_2) gas using copper on zinc oxide (Cu/ZnO) supported catalysts is attractive due to the simple and low cost preparation process of the catalyst. H_2 yield from MSR is proportional to total catalyst loading which can be tuned during catalyst preparation. By creating UV-c light induced surface defects on ZnO nanorods, we have shown improved copper (Cu) nano-particle distribution on the ZnO nanorods leading to better H_2 yield. Increase in Cu nanoparticle adsorption is achieved by in situ reduction of Cu ions by photo-generated electrons, facilitated by ZnO surface defects that act as high energy sites favorable for Cu ion adsorption and their subsequent growth into nanoparticles. The modulated Cu/ZnO catalyst increases H_2 selectivity by 57% along with a corresponding increase in CO content, which can be controlled by adjusting H_2O:MeOH ratio in the precursor solution.

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1. Introduction

Production of hydrogen using steam reformation of methanol (MSR) is attractive due to its high hydrogen to carbon (H/C) ratios and zero sulfur content, yielding high energy density at lower operating temperatures. Incorporation of selected catalysts in MSR can enhance the efficiency of the process, which is strongly correlated to catalyst loading and surface energy. Increase in the loading and free energy at the catalyst surface can lower operating temperatures, the importance of which is highlighted by the considerable research being carried out to develop catalysts which maintain high catalytic activity operating at even low temperatures [1]. Among the various catalysts (including commercial catalysts) used in MSR, higher activity and hydrogen selectivity of Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ has propelled the application of Cu-Zn binaries and ternaries as favorable for hydrogen production [2–4].

Zinc oxide (ZnO) has an inherent ability to crack methanol molecules and as such has been widely used as a promoter and/or a support material for MSR [4,5]. Native crystal defects in ZnO, especially surface oxygen vacancies have been reported to enhance the adsorption and dissociation of small molecules such as methanol, water and formate species [6,7]. Nanostructured rods of ZnO can be grown via a low temperature hydrothermal process, wherein zinc nitrate (Zn(NO$_3$)$_2$) and hexamethylene tetramine (hexamine, C$_6$H$_{12}$N$_{14}$) in a growth solution react to form c-axis oriented one-dimensional nanorods or nanowires [8]. At temperatures below 100 °C hexamine hydrolyzes, leading to a controlled release of hydroxyl ions, which upon reacting with Zn^{2+} ions form ZnO crystals [9,10]. ZnO growth along the c-axis leads to anisotropic structures, the morphology of which can be controlled by moderate changes in growth conditions [10]. By growing rod shaped nanostructures of ZnO to maximize surface area followed by engineering defects on its surface, we can actively control and enhance the catalytic activity of ZnO.

Incorporation of copper nano-particles on ZnO nanorods (Cu/ZnO) further enhances catalytic activity as it promotes synergistic catalytic activation of a bimetallic system and enhances selectivity to hydrogen production by reducing the over potential associated with methanol reformation [11–13]. It has been reported that pure metallic copper is not active to methanol reforming, but a combination of copper and zinc oxide leads to MSR catalytic reactions [14]. Since the surface of Cu nano-particles on ZnO provides a site for methanol decomposition, Cu loading and surface free energy become important in determining the catalyst's performance.

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These parameters are sensitive to growth techniques but have been shown to be controllable to a reasonable degree [15–18]. A commonly followed method of incorporating metal nano-particles on catalyst supports is impregnation, whereby active phases from an ionic solution are deposited on solid supports through the physical contact of the metal ionic solution with the support [19]. Thermal treatment is normally applied to enhance the diffusion of ions to deposit and aggregate on the substrate surfaces upon drying of the solvents [19,20]. Impregnation generally leads to a low degree of control of particle size distribution, resulting in the uncontrolled agglomeration of particles and often reducing the specific surface area of the resulting catalysts [21,22]. In situ adsorption/reduction is an alternative deposition technique which gives better control on the amount and uniformity of precursors pinned on catalyst supports [19,20]. Several modifications to in situ adsorption/reduction methods have been reported by various groups [18,23–25]. In one of our previous reports, we have shown that upon exposure to UV light, ZnO surface wettability is enhanced by the incorporation of photo-induced surface defects [25,26]. The increase in ZnO crystal non-stoichiometry under UV exposure increases the surface free energy and hence the density of sites favorable for metal ion deposition, which can lead to a uniform distributed growth of metal nano-particles on ZnO, enhancing MSR catalytic activities [25,27]. Thus, the deposition of Cu ions on the ZnO NR surface can take place either via direct photo-reduction of the ions, or by agglomeration of the hydrated Cu ions on the UV light induced surface defects and their subsequent growth into nano-particles.

In this work, we have grown zinc oxide nanorods on high surface area porous ceramic (cordierite) support using hydrothermal technique. Cu ions were incorporated on ZnO nanorods using in situ adsorption/reduction method, where the nanoparticles grow by the agglomeration of free Cu ions. Using photo-mediated defect engineering of ZnO nanorods, we show enhanced catalyst loading and distribution on the supports. Control experiments were conducted on ZnO supports without defect engineering for comparison. Prepared Cu/ZnO catalysts were examined for the catalytic activities in methanol steam reforming reactions in a packed tubular reactor operating at temperatures up to 350 °C. The synthesized catalysts were characterized and the MSR reactions carried out are discussed in this work.

2. Experimental

2.1. Materials

All the chemicals used for synthesis of the catalysts were of analytical grade and used as-received without further purification. Chemicals used in this work include: zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ethanol ($C_2H_5OH$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and methanol (CH_3OH), all from Merck; copper nitrate hemipentahydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) from Univar and hexamethylene tetramine ($C_6H_{12}N_4$) from Sigma–Aldrich.

2.2. Preparation of Cu/ZnO catalysts

The catalysts were prepared on porous cordierite substrates (procured from Zhongtian Co., Ltd.) by depositing a ZnO seed layer prior to nanorod growth. The seed layer was deposited by dipping the ceramic substrates in a 2 mM zinc acetate solution in ethanol, followed by thermal decomposition of zinc ions in air at 350 °C to form zinc oxide nanoparticles. ZnO nanorods were then grown epitaxially from the seed layer through a hydrothermal process at 95 °C for 10 h using zinc nitrate and hexamethylene tetramine as the precursors of zinc ions and hydroxyl ions, respectively [10]. As strong hydrolysis reactions on porous ceramic surfaces influence the zinc oxide nanorod growth, pH of growth solution was
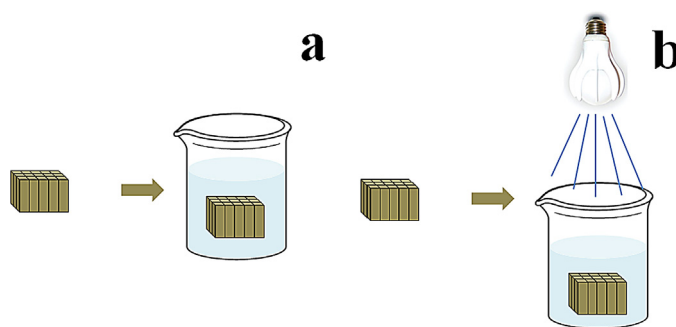

Fig. 1. Cu deposition schemes by defect engineering on ZnO nanorods using UV-c light showing (a) control experiment and (b) in situ treatment.

controlled between 6.2 and 6.4 prior to the growth stage [28]. UV mediated defect engineering was carried out for four different time durations (5, 15, 60 and 90 min), during which the ZnO nanorods on cordierite were dipped into 30 mM $Cu(NO_3)_2 \cdot 2.5H_2O$ (copper nitrate dihydrate) precursor solution and simultaneously exposed to 12 W lamp emitting primarily 4.9 eV UV-c (254 nm wavelength) radiation from a distance of 6 cm (Fig. 1b). Control samples were prepared by dipping them into the precursor solution without UV excitation for 5, 15, 60 and 90 min durations (Fig. 1a). After the completion of the deposition process, all samples were rinsed thoroughly with deionized water followed by calcination at 300 °C for 3 h.

2.3. Characterization of the catalysts

Each catalyst were investigated using field emission scanning electron microscope (FESEM; JEOL, JSM-6301) working at 20 kV. The length and diameter of the nanorods were determined by considering a sample of 60 nanorods (taken from 3 SEM images) on each substrate following which an image analyzer (ImageJ software) was used for the measurements. X-ray diffraction patterns were collected using a Philips PANalytical X'Pert PRO (45 kV, 45 mA) with step angle of 0.02° and 0.5 s of count time. Specific surface area (S.S.A.) of the catalysts were determined by gas adsorption technique (BET; Quantachrome, Autosorb-1C) by outgassing the catalysts at 300 °C for 5 h followed by nitrogen gas adsorption at 77 K. The metal contents were determined (Cu and Zn loading) using inductively coupled plasma-optical emission spectrometer (ICP-OES; Optima, 7300 HF version). XPS measurements were carried out using Omicron Nanotechnology XPS system using a monochromatic Al K_α radiation ($h\upsilon = 1486.6$ eV) at 10^{-10} mbar base pressure. The source voltage and emission current were 20 kV and 20 mA respectively. Deconvolution of the peaks were performed by Casa XPS software (Fairley, N. CASA XPS, version 2.0).

2.4. Steam reformation of methanol

Experiments for the steam reforming of methanol were carried out at atmospheric pressure in a packed electrically heated tubular reactor of 20 mm diameter with a 20 cm long heating zone. The tubular heater comprised of two inter-connected hollow resistively coupled cylindrical heaters (800 W each), 7 cm in diameter and 10 cm in length. 2.5 cm thick aluminum ingots were sandwiched between the tubular heater and the reactor for better heat transportation. Reforming process was performed at temperatures between 250 °C and 350 °C. Cu/ZnO catalyst on cordierite substrates and commercial copper–zinc–aluminum (CuZnAl) catalysts obtained from Sud Chemie (for comparison) were crushed into tiny particles (less than 1 mm in size) using a mortar and 0.5 g of the crushed catalyst was packed in the reactor. Prior to methanol