Applied Catalysis A, General 556 (2018) 64–72

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Dependence of H_2 and CO_2 selectivity on Cu oxidation state during partial oxidation of methanol on Cu/ZnO

Hao Chi[a], Christopher M. Andolina[a], Jonathan Li[b], Matthew T. Curnan[a], Wissam A. Saidi[c], Guangwen Zhou[b], Judith C. Yang[a,c], Götz Veser[a,d,*]

[a] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, 15216, USA
[b] Department of Mechanical Engineering, State University of New York, Binghamton, NY, 13902, USA
[c] Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA, 15261, USA
[d] Center for Energy, University of Pittsburgh, PA, 15261, USA

ARTICLE INFO

Keywords:
Methanol partial oxidation
Cu/ZnO catalyst
H_2 pRoduction
Reaction mechanism
X-ray photoelectron spectroscopy

ABSTRACT

Partial oxidation of methanol is a promising reaction for on-board production of high purity H_2 streams for fuel cell applications. In the present work, the influence of Cu oxidation state on the selectivity of POM catalyzed by Cu/ZnO was investigated via the use of a microreactor and X-ray photoelectron spectroscopy. A strong correlation between H_2 selectivity and the metallic copper (Cu°) content of the catalyst was observed, while, surprisingly, the CO_2 selectivity was not significantly affected by the catalyst oxidation state. Instead, CO_2 selectivity showed a strong correlation with O_2 partial pressure, which could be explained by differences in the energy barriers between CO desorption and CO_2 formation from CO* on Cu_2O surfaces calculated via first-principles calculations. Our results indicate that maintaining metallic Cu catalyst during methanol oxidation could maximize H_2 production for use in fuel cells or other clean energy applications.

1. Introduction

Pollution problems caused by the combustion of fossil fuels necessitate the search for cleaner and more sustainable fuels. Methanol is a promising candidate as a clean fuel due to its high energy density, easy storage, and transportation. Methanol can be used in direct methanol fuel cells to generate electricity or H_2 fuel cells to power mobile devices [1–3]. For use in H_2 fuel cells, a H_2-rich gas mixture can be obtained exothermically at relatively low temperatures (200–300 °C) through the partial oxidation of methanol (POM) [Eq. (1)] [4–7].

$$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2 \quad \Delta H^{\circ} = -192.2 kJ/mol \tag{1}$$

However, incomplete understanding of the POM reaction mechanism and catalyst design still hamper the practical utilization of POM. Cu-based catalysts have been used in methanol synthesis and methanol oxidation for decades [4,8]. Despite long-standing efforts towards developing Cu-based catalysts to address clean energy needs, we are still far from a rational design of Cu-based catalysts in terms of nanoscale structures, metal-support interfaces, as well as chemical states of the catalysts. Much effort has been invested in understanding the impact of Cu loading and the addition of metal promoters, in order to improve catalyst stability and catalytic performance [4,5,9–12]. However, the Cu active phase is still debated. Both Cu° and Cu^{1+} species have been speculated to be essential for hydrogen generation from methanol [6,13]. Moreover, other studies have suggested that, under similar conditions, Cu° is active for methanol oxidation to H_2 and CO_2, Cu^{1+} is active for H_2O and CO formation, and Cu^{2+} – as the least active species – only produces H_2O and CO_2 [5,10,14]. Recent work furthermore has shown that co-feeding product gas (H_2 and CO_2) to the reaction can modify the oxidation state of Cu and hence its catalytic performance. This work suggested that higher Cu° and Cu^{1+} content leads to higher H_2 selectivity [14]. However, mechanistic insight into the correlation between Cu oxidation state and POM reaction selectivity is still largely lacking.

In the present work, 30 wt% Cu/ZnO catalysts were synthesized and evaluated in POM. Methanol conversion, and H_2 and CO_2 selectivity were monitored as a function of the oxidation state of the active Cu phase in the catalyst, in order to elucidate correlations between these experimental observables with different O_2 feed conditions. X-ray photoelectron spectroscopy (XPS) was used to characterize the Cu oxidation states of the catalyst at various stages of the reaction. Based on the experimental observations, POM reaction pathways on Cu_2O and Cu surfaces are proposed, and key assumptions are probed using density functional theory (DFT) calculations in order to gain an improved

* Corresponding author at: Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, 15216, USA.
E-mail address: hac82@pitt.edu (H. Chi).

https://doi.org/10.1016/j.apcata.2018.02.028
Received 18 December 2017; Received in revised form 9 February 2018; Accepted 23 February 2018
Available online 24 February 2018
0926-860X/

atomistic understanding of the POM mechanism as a function of reaction conditions.

2. Experimental methods

2.1. Catalyst preparation

30 wt% Cu/ZnO nanoparticle (NP) catalysts were prepared by co-precipitation from an aqueous zinc and copper nitrate solution. Specifically, $Cu(NO_3)_2{\cdot}3H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (both > 99%, Sigma-Aldrich) were dissolved in deionized water (Milli-Q, 18.2 MΩ cm) to make a 1 M metal nitrate solution with a mass ratio of Cu:Zn = 3:7·Na_2CO_3 (> 99%, Sigma-Aldrich) was dissolved in deionized water to make 1 M solution as a precipitation agent. The mixed metal solution (50 ml) was added dropwise to 300 mL of deionized water at 70 °C under stirring. The pH was monitored by pH meter (OAKTON) and maintained at pH = 7 by adding Na_2CO_3 solution via a burette. The mixture was stirred at 70 °C for 2 h; during this time, the pH increased to ~8.4. The resulting blue precipitate was then separated by centrifugation and washed with deionized water until the pH was 7. The remaining paste was dried at around 90 °C in a vacuum oven overnight and calcined in air at 400 °C for 3 h.

2.2. Catalyst characterization

X-ray diffraction (XRD; Bruker D8) was used to check the catalyst crystal phase, using CuK_α radiation at a wavelength of 1.54 Å, a beam voltage of 40 kV, and a current of 40 mA. The pattern was recorded with a 2θ range from 20° to 90° and a scanning rate of 3.5° min^{-1}. After baseline subtraction and smoothing via fast Fourier transform (FFT), the particle sizes of Cu, CuO, and ZnO were calculated using the Scherrer formula.

Scanning electron microscopy (SEM, JEOL JSM-6510LV) was used to determine the catalyst morphology at low magnification (X3300) with a beam voltage of 15 kV. In order to increase the electron conductivity of the sample and avoid charging effects, a thin palladium film was sputter-coated onto the sample surface before measurement. The elemental composition was determined by using an energy dispersive X-ray spectroscopy (EDX) detector mounted on the SEM device.

High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) was used to observe catalyst morphology at the nanoscale with an accelerating voltage of 200 kV. The TEM sample was prepared by re-dispersing powder in an ethanol solution, dropping solution on a Cu type-B support grid (Ted Pella, Inc.) and vacuum drying. The size distributions of the resulting NPs were determined using TEM images from various areas on the grid. ImageJ 1.47d (National Institutes of Health, USA) was used to measure NP sizes and generate a histogram. In order to generate an elemental mapping from the high-resolution image, different crystal phases were identified from FFT processed images of lattice fringes of the crystals (Fig. S1A). By applying masks on a given lattice position in an FFT processed image and inverting those positions, spatial locations of Cu and ZnO were obtained and colored in red and blue, respectively.

2.3. Reactivity measurements

The conversion of methanol (> 99.8%, Fisher Scientific), as well as H_2 and CO_2 selectivities, were determined in an in-house manufactured microreactor made of an iron/chromium alloy coated with Au to avoid blind activity (as verified over the range of experimental conditions). The 30 wt% Cu/ZnO catalyst (2 mg) was packed inside the microreactor and methanol was introduced to the setup through a syringe pump at an injection rate of 0.127 cc/h. The entire setup was maintained at 200 °C via heating tape in order to avoid condensation of reactants or products. The molar ratio between O_2 (99.995%, Matheson) and methanol was controlled at 0.1, 0.3, and 0.5. Ar (99.995%, Matheson) was used as a carrier gas to maintain a fixed gas hourly space velocity (GHSV) of 3150 h^{-1}. Methanol molar concentration in the feed gas (MeOH, O_2, and Ar) was fixed at 62.5 mol%. The outlet gas composition which consisted of only H_2, H_2O, CO_2, CO and methanol was measured by a mass spectrometer (Pfeiffer Omnistar QMS 200), and the corresponding molar flow rates (ni) were calculated.

The experiments were run until steady state was attained (defined as no more than 10% change of measured concentrations over 10 min) which occurred within 1 h for all experiments shown. The selectivity (S) and conversion (X) of various gaseous products were calculated according to Eqs. (2)–(4):

$$X_{CH_3OH} = \frac{n_{CH_3OH,in} - n_{CH_3OH,out}}{n_{CH_3OH,in}} \times 100\% \quad (2)$$

$$S_{H_2} = \frac{n_{H_2}}{2 \times (n_{CH_3OH,in} - n_{CH_3OH,out})} \times 100\% \quad (3)$$

$$S_{CO_2} = \frac{n_{CO_2}}{n_{CH_3OH,in} - n_{CH_3OH,out}} \times 100\% \quad (4)$$

Since CO, CO_2, H_2, and H_2O were the only detectable products, CO and H_2O selectivities are simply the "mirror image" of CO_2 and H_2 selectivities (i.e. $S_{CO2} = 1 - S_{CO2}$ and $S_{H2O} = 1 - S_{H2}$). In order to check the accuracy of the reactivity measurements, the carbon molar balance was calculated and found to be within < 10% for all reported experiments [Eq. (5)].

$$n_{CH_3OH,in} = n_{CH_3OH,out} + n_{CO} + n_{CO_2} \quad (5)$$

2.4. Analysis of Cu oxidation state

X-ray photoelectron spectroscopy (ESCALAB 250XI, Thermo Scientific, Inc.) was used to determine the Cu oxidation states in the catalysts ex-situ after undergoing POM for various extents of time. After a specified time interval, the reaction was stopped by purging the system with Ar gas flow, and the sample was cooled to room temperature in Ar flow and stored under vacuum for transfer to XPS analysis. A fresh catalyst sample was used for measurement at each time interval. Cu $L_3M_{45}M_{45}$ Auger spectra were obtained for each sample with a monochromated, micro-focused Al Kα X-ray source (spot size = 200 μm; step size = 0.1 eV, pass energy = 50 eV). In order to identify and quantify Cu oxidation states from Cu Auger spectra, reference spectra of each copper oxidation state were collected from pure Cu NPs with similar particle size by the same instrument (Fig. S2). Each reference spectrum has a characteristic peak at an electron kinetic energy of 918.7 eV, 916.8 eV, and 917.6 eV for Cu, Cu_2O, and CuO, respectively. The quantification of Cu oxidation states via Cu Auger lines was implemented following Holse et al. [15]. A linear combination of three reference spectra was fitted to Cu $L_3M_{45}M_{45}$ Auger lines collected via XPS, and the relative amount of each oxidation state was determined from this fit. The errors in the relative ratios were determined at the 99% confidence level, or 3 standard deviations (3σ) of the mean relative ratio values.

2.5. First-principles calculations

First-principles DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [16–19] with the PW91 parameterization of the generalized gradient approximation (GGA) functional [20] and projector augmented wave (PAW) [21,22] pseudopotentials. Atomic structures and charge differences were visualized via the VESTA package [23,24]. The climbing image nudged elastic band ((CI-NEB)) method [25] was applied to calculate POM reaction energy barriers, applying five intermediate images between initial and final stable adsorption states. In order to account for the strong electronic correlation shown to affect the energetics of Cu_2O and related systems, [26,27] the rotationally invariant Dudarev implementation of the