

Characterization of Bimetallic Pd-Cu/ZnO/ZrO₂ Catalysts for Hydrogen Production by Methanol Partial Oxidation

Stephen J. Schuyten¹, J.M. Miller², J. Kropf³ and E.E. Wolf^{1*}

¹University of Notre Dame, Notre Dame, IN 46556 (USA)

²BP R&D Naperville Complex, BP, Naperville, IL 60566 (USA)

³Argonne National Laboratory, Chemical Engineering Div., Argonne, IL 60439 (USA)

*ewolf@nd.edu

Introduction

Production of hydrogen from high-energy liquid fuel such as methanol is a viable source of hydrogen for fuel cells. Both supported Pd and Cu/ZnO based catalysts are well known in the literature as catalysts for hydrogen producing methanol reforming reactions[1,2]. Previous work in our group identified the combination of both Pd and Cu active species for methanol partial oxidation enhanced activity greater than either element alone[3]. This work further identifies the structure and oxidation state of the Pd and Cu catalysts under *in-situ* and reaction conditions using a variety of characterization techniques.

Materials and Methods

Catalysts containing Cu, ZnO, ZrO₂, and/or Pd were prepared via co-precipitation using nitrate precursors and sodium carbonate, or a combination of co-precipitation and wet impregnation of Pd. Catalyst powders were analyzed via x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), CO and N₂O chemisorption, and BET surface area measurement. Powder XRD studies were performed in a Scintag X1 diffractometer using Cu-K α radiation. XPS was done using a Kratos XSAM 800 with a monochromatic Al-K α X-ray source operating at 1486.6 eV and a takeoff angle fixed at 90 degrees and a pressure less than 1x 10⁻⁸ torr. XAS experiments were conducted at the MRCAT beamline in the Advanced Photon Source (APS) at Argonne national laboratory. DRIFTS experiments were conducted in a Bruker Equinox 55 spectrometer using an in-situ diffuse reflectance cell (Harrick HVC) placed in "praying mantis" optics (Harrick DRA-3-3S). Finally, CO and N₂O chemisorption studies were done using pulse technique in conjunction with a thermal conductivity detector.

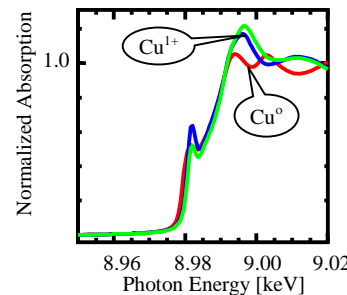
Results and Discussion

Table 1 summarizes results from activity, XRD, and adsorption studies. The addition of zirconia (catalysts 7310 and 7311) increases the BET surface area by a factor of three, the Cu surface area (as measured by N₂O adsorption) and CO adsorption. As expected, addition of 1%Pd does not significantly affect BET or Cu area. Interestingly, a decrease in CO adsorption is observed upon Pd addition to zirconia promoted catalysts. Incorporation of zirconia also has a significant effect on the Cu crystallite size calculated from the broadening of XRD lines from the scherrer equation, decreasing from ~200Å in unpromoted catalysts to approximately 65Å in catalysts containing zirconia. Little to no effect on Cu crystallite size was observed with addition of palladium. XPS results (not shown) used to determine the surface composition will be presented. The activity results presented in Table 1 are among the most active reported in the literature with the 7Cu/3ZnO/1ZrO₂-1% Pd being the most active.

Table 1. Summary of XRD and adsorption results

Catalyst ID #	Mole fraction (Pd % oxide)				BET area calcined	N ₂ O Cu area	CO adsorption	Cu crystal size (XRD) Å	Activity at 573K (MeOH)
	Cu	Zn	Zr	Pd	m ² /g	m ² /g-Cu	μmol/g		μmol/g-s
7300	7	3	0	0	20	14	41	200	11.3
7301	7	3	0	1	19	14	42	200	12.3
7311	7	3	1	1	63	37	42	60	16.4
7310	7	3	1	0	55	36	82	70	13.3

Studies using *in-situ* XAS and XRD techniques were used to determine the oxidation state of both Pd and Cu under reaction conditions. Figure 1 depicts the Cu near edge XAS spectra for pretreatment and reaction conditions. As calcined (not shown), the Cu shows distinct Cu²⁺, determined to be 100% CuO. After reduction in 4% hydrogen at 573K, the spectrum changes



matching that of Cu foil, indicating that all of the bulk and surface Cu is reduced. Upon introduction of a methanol partial oxidation reactant stream at 473K (3.8% CH₃OH and 1.9% O₂) the Cu completely oxidizes to Cu¹⁺. Results from *in-situ* XRD techniques (not shown) were used to determine the oxidation state of Pd under variable conditions. These studies show that palladium is in a reduced state under reaction conditions.

Figure 1. Cu XANES edge of catalyst 7311 under reducing (red line) and reaction (green) conditions

Results from DRIFTS on catalysts exposed CO and methanol DRIFTS (not shown) reveal adsorption sites for both copper and palladium on the surface of the catalyst. These characteristics have a strong dependence on temperature, revealing sites that are active at different temperatures.

Significance

This work presents results for the elucidation of structure and oxidation state of the bimetallic Pd and Cu based catalysts under *in-situ* and reaction conditions.

Acknowledgements

Funding from the International Copper Association and DOE contract number DE-AC02-06CH11357 for XAS studies is gratefully acknowledged.

References

1. Cubeiro, M.L. and Fierro, J.L.G. *Jor. of Catal.* **179**, 150-162 (1998).
2. Cheng, W.H. *Appl. Catal A: General* **130**, 13-30 (1995).
3. Schuyten, S.J. and Wolf, E.E. *Catal. Lett.* **106**, 7-14 (2006).