

Fuel Cells (Application of $\text{CuO}_x\text{-CeO}_2$ catalysts as sensor substrates for catalytic detection of CO in H_2 fuel)

Christopher S. Polster and Chelsey D. Baertsch*
 Purdue University, West Lafayette, Indiana 47907 (United States)
 *baertsch@ecn.purdue.edu

Introduction

Proton exchange membrane fuel cells (PEMFCs) using H_2 fuel are a promising source of portable power for electronic devices and transportation [1]. However, as CO is a common poison for PEMFC electrodes and also a common contaminant in H_2 , it is critical to be able to detect and quantify CO contamination at low levels in concentrated H_2 fuel. Sensor requirements for on-line CO detection in portable devices include small size, low cost, low power consumption, and high sensitivity. These requirements can be met with microelectromechanical system (MEMS) signal transducers [2]. However, all current microsensor technologies use materials that are inherently unselective to CO, give rise to false positive responses in the presence of H_2 , and require arrays of sensors for gas identification [3].

We present a new sensor paradigm using an intrinsically chemically selective exothermic oxidation reaction coupled with thermal transduction on thin film temperature sensors for selective detection of CO at ppm levels in excess H_2 with negligible false response from H_2 . $\text{CuO}_x\text{-CeO}_2$ catalysts have been used in preferential oxidation (PROX) operations with very high (up to 100%) CO oxidation selectivity in process streams containing ~10,000 ppm CO or more in H_2 excess [4]. This work investigates the potential of $\text{CuO}_x\text{-CeO}_2$ as a sensor substrate for the selective catalytic detection of CO at lower levels in H_2 fuel.

Materials and Methods

$\text{CuO}_x\text{-CeO}_2$ (10 at% Cu) with BET surface area $115.8 \text{ m}^2/\text{g}$ was prepared by the urea gelation method [5]. X-ray diffraction and x-ray photoelectron spectroscopy confirm that Cu is dispersed within CeO_2 . Reactions are performed under isothermal conditions using a packed bed quartz reactor and a stoichiometric $\text{CO}:\text{O}_2$ feed ratio of 1:1. Reactor effluent is analyzed by gas chromatography (Agilent MicroGC 3000). CO conversion is calculated based on CO disappearance and CO_2 selectivity is calculated from products for maximum sensitivity. The water detection limit was determined to be approximately 2 ppm.

Results and Discussion

In an effort to isolate kinetic and surface coverage effects, CO and H_2 oxidation were studied both independently and together under PROX conditions as a function of temperature. Reaction selectivities are shown in Table 1. Independent selectivity is calculated using product formation rates during CO and H_2 oxidation reactions run separately. The high independent selectivity to CO_2 shows that CO oxidation rates are higher than H_2 oxidation rates at 60-100°C. During reaction with CO and H_2 together, the actual CO_2 selectivity is larger than the independent selectivity, indicating that preferential adsorption of CO may critically influence product selectivity in addition to temperature alone (kinetic effects).

It is necessary to investigate these preferential adsorption effects under sensing conditions. Figure 1 shows that CO_2 selectivity in a 10,000 ppm CO feed is a function of both

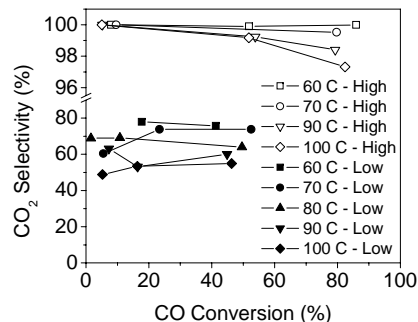


Figure 1. CO_2 selectivity as a function of conversion, temperature (60-100°C), and CO feed concentration (High – 10000 ppm, Low – 100 ppm). ($50\% \text{H}_2/1\% \text{O}_2/\text{He}$).

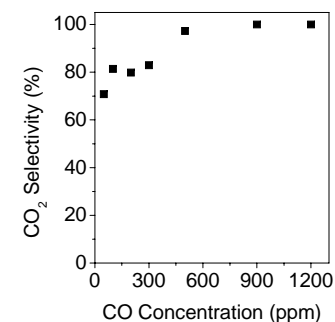


Figure 2. CO_2 selectivity as a function of CO feed concentration at 80°C and differential (< 10%) CO conversion. ($50\% \text{H}_2/1\% \text{O}_2/\text{He}$).

Table 1. CO_2 selectivity in H_2 compared to CO_2 selectivity calculated from individual CO and H_2 oxidation rates.

Temperature (°C)	Independent Selectivity (%)	Actual Selectivity (%)
60	88.4	100.0
70	90.9	100.0
80	92.4	99.5
90	92.5	99.1
100	90.0	97.8

CO conversion (or CO coverage) and temperature. For a 100 ppm CO feed, selectivity only depends on temperature. These results show that at low CO concentrations of importance for CO sensor applications, CO_2 selectivity is diminished from 100% to 80% at 60°C due to low CO coverage and increased adsorption and oxidation of H_2 . Figure 2 shows that very high selectivity (> 99%) can be maintained at 80°C with CO concentrations of 500 ppm or greater. Thus, these results demonstrate that $\text{CuO}_x\text{-CeO}_2$ catalysts will exhibit a sensitivity ratio ($S_{\text{CO}}/S_{\text{H}_2}$) of better than 100 with no false positive responses during operation at 80°C when exposed to multicomponent CO/H_2 fuels containing >500 ppm CO.

Significance

For the first time, $\text{CuO}_x\text{-CeO}_2$ catalysts with intrinsic chemical specificity for the selective oxidation of CO in H_2 , as a result of a combination of kinetic and surface effects, are demonstrated for use as catalytic sensing substrates. Integration of this catalyst with MEMS sensor technologies will provide new capabilities in portable sensors for the selective quantitative detection of CO in H_2 while avoiding false positive responses.

References

- Dyer, C.K. *J. Power Sources* 106, 31 (2002).
- Simon, I., Bársan, N., Bauer, M., and Weimar, U. *Sens. Actuators, B* 73, 1 (2001).
- Mishra, V.N., and Agarwal, R.P. *Microelectronics Journal* 29, 861 (1998).
- Sedmak, G., Hočevár, S., and Levec, J. *J. Catal.* 213, 135 (2003).
- Liu, Y., Fu, Q., and Stephanopoulos, M.F. *Catal. Today* 93-95, 241 (2004).