# Application of $CuO_x$–$CeO_2$ catalysts as selective sensor substrates for detection of CO in $H_2$ fuel†

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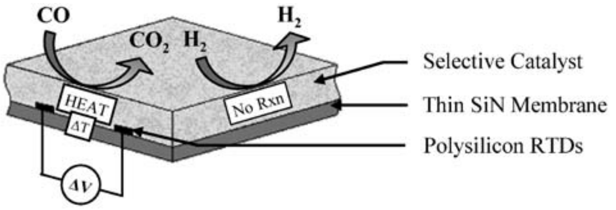
**The applicability and mechanism of $CuO_x$–$CeO_2$ as a catalytic microsensor substrate enabling 100% selective detection of low concentration CO in gas mixtures with $H_2$ is described.**

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. A selective catalyst for low level CO detection in $H_2$ is presented in this work. Sensors for on-line detection of CO in portable devices must be small in size, cost, and power consumption, and possess high sensitivity. These requirements have been 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]

A new sensor paradigm and capability is presented for using intrinsically selective catalysts coupled with MEMS thermal transduction. As shown in Scheme 1, a catalytic substrate selectively and exothermically oxidizes CO, providing a measurable temperature rise that is directly proportional to CO gas concentration and measured on chip using a resistive temperature device or similar signal transducer. The technical challenge giving rise to this high chemical specificity is the development of a catalyst that oxidizes CO, but not $H_2$, at process conditions; this is the focus of this communication.



**Scheme 1** Selective catalytic sensor operation.

$CuO_x$–$CeO_2$ 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] The presence of common reformate gases such as $H_2O$ and $CO_2$ has been reported to decrease CO oxidation rates with little deleterious effect on the selectivity of CO oxidation.[5] This work describes the potential of $CuO_x$–$CeO_2$ catalysts for the selective detection of CO at much lower concentrations in $H_2$.

$CuO_x$–$CeO_2$ catalysts (4.5 at% Cu as measured by atomic absorption) were synthesized by the urea gelation technique[5a] from $Cu(NO_3)_2{\cdot}3H_2O$ and $(NH_4)_2Ce(NO_3)_6$ precursors followed by calcination at 923 K. The BET surface area of the prepared catalyst is 115.8 $m^2\ g^{-1}$. Insertion of Cu into the $CeO_2$ lattice reportedly leads to the formation of an active and selective mixed metal oxide redox catalyst.[6] Neither Cu, CuO, nor $Cu_2O$ are observed by XRD, supporting favorable incorporation of Cu into the ceria structure, however a Ce : Cu atomic surface ratio of ∼7 : 1 (from XPS) suggests that some of the Cu is segregated to the catalyst surface. Reactions were carried out in a packed-bed reactor with high purity gases introduced and mixed upstream using mass flow controllers. Selectivity is reported as the $CO_2$ production rate divided by the sum of $CO_2$ and $H_2O$ production rates. Predicted sensor responses ($R_{CO}$ and $R_{H2}$) are calculated as a product of the measured oxidation rate with the molar heat of reaction. An Agilent microGC with Plot Q and molecular sieve columns

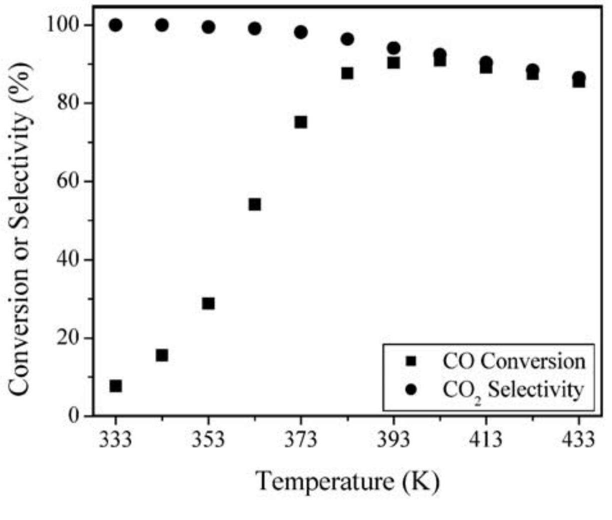


**Fig. 1** Steady state CO conversion and $CO_2$ selectivity over $CuO_x$–$CeO_2$ as a function of temperature. Reaction conditions: 50% $H_2$, 1% CO, 0.5% $O_2$, balance He, total flow = 100 sccm (100 $cm^3\ min^{-1}$), $W_{cat}$ ≈ 100 mg.

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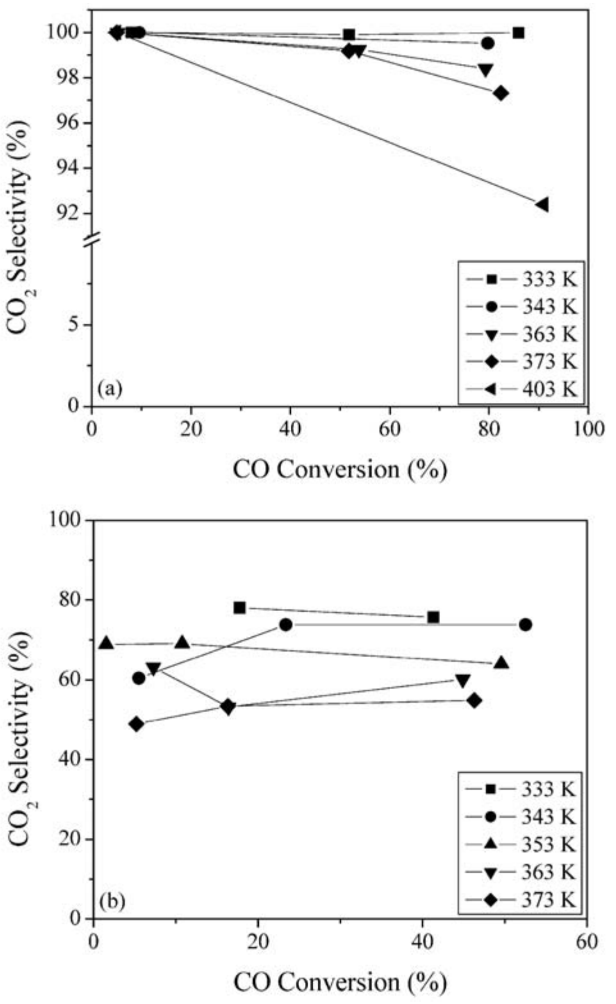

**Fig. 2** Steady state $CO_2$ selectivity as a function of CO conversion and temperature over $CuO_x$–$CeO_2$. Reaction conditions: (a) 50% $H_2$, 1% CO, 0.5% $O_2$, balance He. (b) 50% $H_2$, 100 ppm CO, 50 ppm $O_2$, balance He, total flow = 50–400 sccm, $W_{cat} \approx 2$–20 mg.

was used for product gas analysis with a lower limit on $H_2O$ of ~2 ppm.

Catalytic activity during oxidation of 1% CO in the presence of 50% $H_2$ (typical relative concentrations of a steam reformed $H_2$ source[7]) is shown in Fig. 1 as a function of temperature. As previously reported at these gas concentrations,[4,5a,8] the catalyst maintains 100% selectivity up to nearly 363 K.

Isothermal oxidation reactions with variable conversion were conducted to separate the convoluting effects of temperature and conversion on selectivity. Such kinetic measurements have not previously been reported for this system, yet they provide substantial insight into catalyst function, performance, and mechanism. Fig. 2 shows $CO_2$ selectivity over $CuO_x$–$CeO_2$ as a function of CO conversion and temperature during reaction with 50% $H_2$ in either 1% CO (a) or 100 ppm CO (b). With a 1% CO feed, 100% selectivity is achieved at low conversion (<10%) from 333–403 K and at 333 K, 100% selectivity is maintained from 0–90% conversion. Selectivity, however, decreases with both increasing temperature and increasing CO conversion at temperatures above 333 K. With a 100 ppm CO feed, 100% CO oxidation selectivity is not observed at any measured temperature or conversion; selectivity still decreases with increasing temperature, but is independent of CO conversion.

$H_2$ and CO oxidation rates are reported in Table 1 as a function of temperature and feed composition (single reactants *vs.* CO–$H_2$ mixtures). For both independent oxidation reactions (just CO or $H_2$ independently) and PROX reactions, CO oxidation rates are higher than $H_2$ oxidation rates at all temperatures. PROX selectivities are much higher (particularly at lower temperatures) than ideal selectivities calculated from independent CO and $H_2$ oxidation rates. Thus, factors in addition to the kinetic differences between CO and $H_2$ oxidation must contribute to this catalyst's ability to oxidize CO in $H_2$ with 100% selectivity.

From the results presented in Fig. 2 and Table 1 it is clear that the required 100% CO oxidation selectivity is achieved by operating (1) at lower temperatures where CO oxidation is appreciably more favorable than $H_2$ oxidation and (2) at high CO gas concentrations and/or low CO conversion (high CO conversion leads to a reduction in the effective CO pressure from inlet conditions). Both conditions are critical for achieving high CO oxidation selectivity and minimizing $H_2$ oxidation to $H_2O$. The high CO oxidation selectivity over $CuO_x$–$CeO_2$ appears to result from a combination of kinetic and adsorption factors. Conditions which should lead to an increase in CO coverage (lower temperature, higher CO gas concentration) provide high CO oxidation selectivities.

For sensors, it is critical to maximize selectivity to the target gas in order to avoid false positive responses. 100% selectivity (or an infinite CO/$H_2$ response ratio, $R_{CO}/R_{H2}$) is desirable. Table 2 shows the selectivity and predicted sensor response as the percentage that would be attributed to reaction with $H_2$.

**Table 1** Comparison of rates and selectivities from pure component oxidation reactions and PROX reactions

| | CO Ox. rate[e] (mol m$^{-2}$ s$^{-1}$) × $10^9$ | | $H_2$ Ox. rate[e] (mol m$^{-2}$ s$^{-1}$) × $10^9$ | | Selectivity[d] (%) | |
|---|---|---|---|---|---|---|
| Temp./K | CO only[a] | $H_2$ + CO[c] | $H_2$ only[b] | $H_2$ + CO[c] | Ideal | PROX |
| 333 | 0.6 | 1.5 | 0.2 | 0.0 | 75 | 100 |
| 353 | 1.8 | 2.0 | 0.6 | 0.4 | 75 | 83 |
| 363 | 5.5 | 3.8 | 2.0 | 0.9 | 73 | 81 |
| 373 | 11.1 | 4.0 | 2.9 | 1.4 | 79 | 74 |

[a] CO oxidation conditions: 200 ppm CO, 100 ppm $O_2$, balance He. [b] $H_2$ oxidation conditions: 25% $H_2$, 100 ppm $O_2$, balance He. [c] PROX reaction conditions: 25% $H_2$, 200 ppm CO, 100 ppm $O_2$, balance He. [d] Calculated by the $CO_2$ production rate divided by the sum of $CO_2$ and $H_2O$ production rates. [e] Differential rates reported (CO or $O_2$ conversion <10%).

**Table 2** $CO_2$ Selectivity and corresponding predicted $H_2$ response

| | $CO_2$ Selectivity (%) | | Predicted $H_2$ response[a] (%) | |
|---|---|---|---|---|
| CO Conc. (ppm) | 333 K | 353 K | 333 K | 353 K |
| 900 | 100[b] | 100[b] | 0 | 0 |
| 500 | 100[b] | 97 | 0 | 2 |
| 300 | 100[b] | 83 | 0 | 15 |
| 200 | 100[b] | 80 | 0 | 18 |
| 100 | 93 | 81 | 6 | 16 |
| 50 | 87 | 71 | 11 | 26 |

[a] Calculated as the heat evolved from $H_2$ oxidation divided by the sum of the heats evolved from both CO and $H_2$ oxidation × 100%. 25% $H_2$, stoichiometric $O_2$ (wrt CO), balance He (<10% conversion). [b] No $H_2O$ detected. Minimum $H_2O$ detection limit is ~2 ppm.

$CuO_x$–$CeO_2$ provides very high selectivities with no detectable contribution from $H_2$ ($R_{CO}/R_{H2} = \infty$) at CO concentrations down to <200 ppm and <500 ppm at operating temperatures of 333 K and 353 K, respectively.

Even assuming that water is formed at its minimum detection limit, with a CO concentration of 300 ppm where no $H_2$ oxidation is detected, the lower bound on $R_{CO}/R_{H2}$ is 30, and in as low as 50 ppm CO at 333 K, only 11% of the catalytic response is due to $H_2$ background, corresponding to a sensor response ratio ($R_{CO}/R_{H2}$) of 8. CO/$H_2$ response ratios on the order of 5–35, depending on substrate composition, gas composition (200–1000 ppm) and temperature, have been reported for resistive type semiconductor gas sensors.[9,10] Such results, however, are reported as ratios of $R_{CO}$ and $R_{H2}$ measured in separate experiments containing either CO or $H_2$ at equal molar concentrations, while the studies presented here are done under required detection conditions of CO mixed with a large $H_2$ excess ($R_{CO}/R_{H2}$ directly) and account for cross sensitivity and chemical interactions. Cross sensitivity to oxidizable gases other than $H_2$ can also be a concern, but preliminary studies show $CuO_x$–$CeO_2$ will not oxidize hydrocarbons such as acetone or ethanol at these temperatures; however, they will adsorb irreversibly and poison the catalyst. This is an important design consideration for these sensor systems, as some hydrocarbon contaminants must either be purified from the sample gas or degassed from the catalyst surface intermittently during operation.

For the first time, $CuO_x$–$CeO_2$ catalysts were demonstrated as a promising catalytic substrate for low level detection of CO in $H_2$ fuel for sensors using reaction calorimetry. False positive responses to $H_2$ can be avoided during detection of CO at concentrations as low as 200 ppm at 333 K. The catalyst's high selectivity results from a kinetic advantage of CO over $H_2$ oxidation along with a competitive adsorption mechanism with preferential adsorption of CO. Integration of this catalyst with MEMS temperature sensors will provide new capabilities in portable sensors for the selective quantitative detection of CO in $H_2$ while avoiding false positive responses.

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