Application of CuO$_x$-CeO$_2$ catalysts as selective sensor substrates for catalytic detection of CO in H$_2$ fuel

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Supporting Information

CuO$_x$-CeO$_2$ Catalyst Synthesis

CuO$_x$-CeO$_2$ catalysts were synthesized by the urea gelation technique. Precursors used were Cu(NO$_3$)$_2$ · 3H$_2$O (Alfa Aesar, ACS reagent), and (NH$_4$)$_2$Ce(NO$_3$)$_6$ (Alfa Aesar, 99.5%). These were dissolved in deionized water in appropriate proportions to a total molarity of approximately 0.5 M. A 7.5 M solution of urea (Alfa Aesar, 99.5%) one-third of the volume of the precursor solution was also prepared. Both solutions were heated to near their boiling points, and the urea solution was added steadily by buret to the precursor solution over a period of 10 minutes while stirring. The solution was then stirred and boiled gently for 2 more hours. At this point, the solution had become a gel and a fast color change from bright orange to dark green was noted. The dark green gel was then stirred and boiled for another 2.5 hours. The remaining material was washed twice by stirring vigorously in hot deionized water for 30 minutes and vacuum filtered. The catalyst was then dried overnight in an oven at 383 K and calcined in dry air at 923 K for 4 hours.

CuO$_x$-CeO$_2$ Activity Measurements

Catalysts used for this study were supported on a quartz frit in a vertical U-shaped quartz reactor (I.D. 10mm). Temperature measurements and control were done by a thermocouple resting in a well in contact with the catalyst bed. Reactor effluent was

analyzed by an Agilent MicroGC 3000, with a lower detection limit of water of approximately 2 ppm. Fractional conversion was calculated by disappearance as by [1].

$$X_{CO} = 1 - \frac{P_{CO,out}}{P_{CO,in}}$$ [1]

$P_{CO,out}$ is output CO partial pressure under reaction conditions and $P_{CO,in}$ is CO partial pressure in the reaction feed. Reaction selectivity was calculated by product formation, shown by [2], where $P_{CO2,out}$ and $P_{H2O,out}$ are CO_2 and H_2O partial pressures under reaction conditions. No other products were observed under reaction conditions.

$$S_{CO_2} = \frac{P_{CO_2,out}}{P_{CO_2,out} + P_{H_2O,out}} * 100$$ [2]

All measurements were made after first treating the catalyst in 10% O_2 balance He for 30 minutes at 773 K, then subjecting the catalyst to reaction conditions for 12-16 hours. After an initial deactivation period (~12 h), the catalyst activity was very stable over long time frames (>50 h).

Elemental Analysis by Atomic Absorption Spectroscopy (AAS)

Copper content of the CuO_x-CeO_2 catalyst in this work was determined by AAS using a Perkin Elmer AAnalyst 300 Spectrometer. A small amount of catalyst (16.56 mg) was dissolved in concentrated HCl then diluted to 250 mL in deionized water. Three standards were prepared (1, 5, and 10 mg/L) and a linear calibration was found. Cu concentration in the above solution was measured as 1.134 mg/L, corresponding to 4.5 % Cu (atomic basis) assuming $Cu_xCe_{1-x}O_2$ stoichiometry.

Surface Characterization by X-ray Photoelectron Spectroscopy (XPS)

XPS spectra of powdered catalyst samples were obtained using a Kratos Axis spectrometer. CasaXPS software was used for data analysis. Cu 2p and Ce 3d peaks were used for surface atomic concentration quantification. For each catalyst sample, spectra were obtained in two different regions to ensure homogeneity.

Characterization by X-ray Diffraction (XRD)

XRD patterns were obtained on powdered catalyst samples with a Scintag X2 Diffractometer. All samples were found to be free of crystalline copper or copper oxide species. Figure S1 shows results for the reported $CuCeO_x$ catalyst and CeO_2.
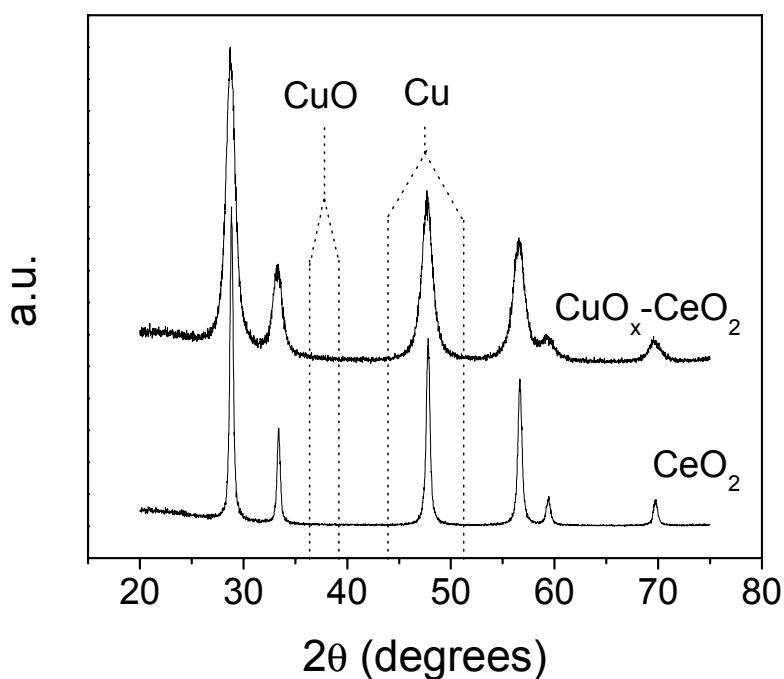

Figure S1. XRD pattern of CuO_x-CeO_2. Pattern matches well with CeO_2 sample prepared by the same methods. Sample is void of any crystalline CuO or Cu, as shown by the dotted lines.