Preferential Oxidation of CO to CO_2 in H_2-Streams Over Cobalt-based Catalysts for PEM Fuel Cells

Matthew M. Yung*, Zhongkui Zhao, Umit S. Ozkan

The Ohio State University, Columbus, OH 43210

*yung.14@osu.edu

Introduction

Fuel processing for fuel cell applications is an area of great interest due to the promise of higher efficiencies and lower emissions that fuel cells offer. For PEM fuel cells, the purity of the hydrogen feed stream is an area of concern, because even very low concentrations of CO can poison the fuel cell's Pt-based anode catalysts. Hydrogen feed streams produced from steam reforming of methane followed by the water-gas shift reaction commonly contain substantial amounts of CO (0.5-2%) [1]. In order to avoid poisoning of the fuel cell anode, CO concentrations generally need to be reduced to less than 10 ppm. The challenge is not, however, merely the removal of CO but rather the selective removal of CO. The streams to be purified will contain high concentrations of hydrogen, which can react with the available oxygen in the undesired combustion reaction and/or with CO in the undesired methanation reaction. The value of these fuel streams lies in their hydrogen content, so any parasitic losses of H_2 due to the methanation reaction with CO or by combustion with O_2, will result in an overall decrease in the process efficiency.

Materials and Methods

Transition metal oxide catalysts have shown high activity for CO oxidation [2]. Cobalt based catalysts have been prepared using equal-volume impregnation of aqueous nitrate solutions to obtain 10wt% on commercially obtained m-ZrO_2, t-ZrO_2, TiO_2, Al_2O_3, CeO_2, and SiO_2 supports. Additional catalysts were also prepared by a sol-gel method to examine the effect of the synthesis technique on the activity and material properties. Steady-state activity measurements were recorded from 25-300°C using a gas chromatograph equipped with molecular sieve 5A & Porapaq columns, a methanizer, and TCD & FID detectors. Typical reactant concentrations were 2500-5000ppm O_2, 2500-5000ppm CO, and 5-40% H_2 in Ar or He at 1 atm and 39,000 h^{-1}. Structural and mechanistic characterization studies were performed using BET surface area measurements, laser Raman spectroscopy (LRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction / oxidation / desorption / reaction (TPR, TPO, TPD, TP-rxn), and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry. Time-on-stream studies and the effects of other components in the feed where also examined.

Results and Discussion

Catalysts that are capable of reducing CO concentrations from 5000 ppm to below 10 ppm and are active in the desired temperature range (<150°C) at space velocities ranging from 20,000 to 78,000 h^{-1} have been developed. The choice of support was shown to have a significant impact on the activity and affected the nature of the supported cobalt species. As has been previously reported [3], the presence of Co_3O_4 led to high CO oxidation activity.
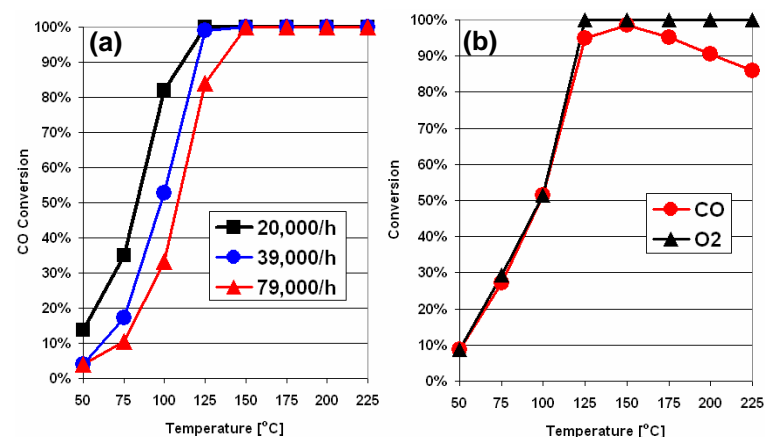
Figure 1. Steady-state reaction results on 10%Co/ZrO_2. (a) CO conversion at different GHSV on with 5000ppm CO, 5000ppm O_2, and 10% H_2. (b) Conversion of CO and O_2 with stoichiometric O_2/CO in the feed: 2500ppm O_2, 5000ppm CO, and 10% H_2. in Ar at 39,000 h^{-1}.

High activity and selectivity were observed on Co/ZrO_2 catalysts. The steady-state reaction results, Figure 1 (a), show the conversion of CO at various GHSV on 10%Co/ZrO_2. By 150°C, the CO conversion was 100% across all of the studied space velocities. This indicates that the necessary activity to minimize fuel cell catalyst poisoning can be achieved within the desired temperature range for fuel cell applications over a broad range of space velocities. The experiment conducted with a stoichiometric ratio of CO-to-O_2 in the feed, Figure 1(b), showed that the CO and O_2 conversion were nearly identical below 175°C, corresponding to high O_2 selectivity (>90%) to CO_2 at all but the highest temperature. Above 200°C, the decrease in CO conversion corresponds to a loss of selectivity due to the combustion of H_2.

Significance

Highly selective CO oxidation catalysts could eliminate concerns regarding the poisoning of Pt fuel cell catalysts, helping to advance this technology.

References

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