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Preferential oxidation of carbon monoxide on CoO_x/ZrO_2

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Abstract

The preferential oxidation (PROX) of carbon monoxide to carbon dioxide in excess H_2 is one of the strategies for obtaining high purity H_2 streams, especially for PEM fuel cells. A CoO_x/ZrO_2 catalyst was synthesized and studied for the PROX reaction under various reaction conditions and indicated that in the temperature window of interest (80–200 °C), this catalyst had potential for obtaining high conversions of CO with high O_2 selectivity to CO_2. Increases in the GHSV and the CO/O_2 ratio led to lower CO conversion but higher O_2 selectivity to CO_2. High temperature operation led to a decrease in CO oxidation activity and the formation of methane, which was attributed to partial reduction of CoO_x/ZrO_2. The catalyst performance was examined using steady-state and transient temperature-programmed reaction (TPRxn) experiments. Temperature-programmed reduction (TPR) and time-on-stream studies were used to examine the catalyst stability in reducing conditions. DRIFTS studies during CO TPD and *in situ* PROX were used to examine surface species on ZrO_2 and CoO_x/ZrO_2.

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1. Introduction

Proton exchange membrane (PEM) fuel cells have recently garnered much research attention for mobile energy applications due to several factors, including their potential for high efficiency and environmentally friendly operation [1,2]. The electrocatalysts used in hydrogen-powered PEM fuel cells on the anode side, however, require high purity hydrogen streams and can be poisoned by trace amounts of carbon monoxide [3–8]. Hydrogen production from hydrocarbon sources such as coal and natural gas may include steam reforming followed by high and low temperature water gas shift reactors. These streams, however, may still contain a substantial level of CO (0.2–2%) which must be further reduced to ∼10–100 ppm in order to avoid poisoning of the fuel cell catalysts [8–11]. Purification of H_2 streams can be achieved by methods such as pressure-swing adsorption, Pd membrane separation, catalytic methanation, and catalytic preferential oxidation (PROX) of CO. Of these methods, PROX is a possible solution and offers the potential for the lowest cost and ease of implementation, without the parasitic loss of H_2 which occurs during catalytic methanation [2,8].

In the PROX reaction, high activity and selectivity in the same temperature window are essential. For on-board applications, the desired operating temperature should ideally lie between the exit temperature of a low temperature water gas shift reactor (200–250 °C) and operating temperature of a PEM fuel cell (∼80 °C) [12]. Scheme 1 shows the network of the important reactions that should be monitored during PROX studies. The oxidation of CO to CO_2 is the desired route, while the H_2 combustion reaction is the key undesired competitive reaction, especially at higher temperatures. While methanation eliminates CO, it does so at the expense of H_2. The Boudouard reaction also eliminates CO, but the deposition of coke is well known to decrease catalytic activity, so this reaction should be avoided. Water gas shift activity would also help eliminate CO and produce additional H_2.

In addition to the wealth of literature on CO oxidation, much work has been conducted on the PROX reaction. Early work on PROX by Oh and Sinkevitch investigated several noble metals supported on alumina as well as various transition metal based catalyst compositions and platinum was found to be among the best candidate materials [13]. Noble metal catalysts, especially platinum and gold, have been among the most studied systems [14–22]. Platinum has generally been considered to be more active, while gold catalysts provide higher O_2 selectivity to CO_2 [14]. Some studies have also

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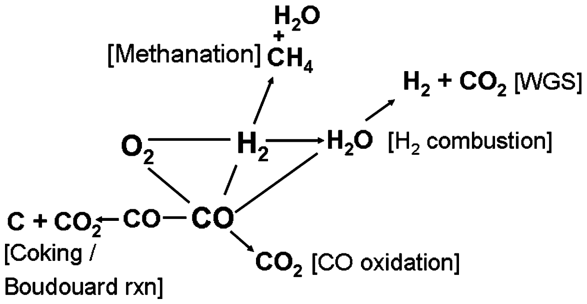

Scheme 1. Diagram of key reactions in the PROX network.

examined lower cost transition metals for the PROX reaction.

Mechanistic studies on CO oxidation in excess O_2 were carried out and showed cobalt to be an active metal for the reaction, though carbonate formation could lead to decreased activity at temperatures below 100 °C [23]. Other studies have shown strong promotional effects of Co and Fe to Pt/Al_2O_3 catalysts, leading to substantial activity gains for the PROX reaction [24–27]. Studies without Pt, using solely Co, indicate that Co_3O_4 is active for CO oxidation but that bulk cobalt oxide may reduce to metallic Co^0 under an excess H_2 atmosphere [28,29]. These studies indicate that a highly oxidized form of cobalt that exhibits strong interaction with a defect-forming support and allows CO activation could lead to high activity for the preferential oxidation of CO in excess H_2.

Additional studies for PROX on bulk transition metal oxides found that operation at high temperatures could lead to a reduction to lower valency oxides or to metallic phases, which could in turn lead to increased activity for H_2 combustion and methane formation. Of the metal oxides that were tested, cobalt oxide was the most active and also showed high selectivity over a broad temperature window [30]. To further examine CoO_x-based catalysts, a series of cobalt catalysts on various metal oxide supports have been prepared in our laboratories. We have found that high CO oxidation activity could be obtained on cobalt-based catalysts [31–33] and that a ZrO_2 support provided higher rates of CO conversion than other metal oxide supports. In the present work, a CoO_x/ZrO_2 catalyst is examined for its activity for the PROX reaction and the influence of GHSV, O_2/CO ratio, and stability in reducing conditions are explored.

2. Experimental

2.1. Catalysts synthesis

The incipient wetness impregnation technique was used to synthesize a catalyst consisting of 10 wt% cobalt on ZrO_2. An aqueous solution of the cobalt nitrate precursor, $Co(NO_3)_2\cdot 6H_2O$ (Aldrich), was used to impregnate a ZrO_2 support provided by Saint Gobain (Lot 2000920047). Three impregnation steps were performed on the catalyst, with a 4 h drying period between steps in an oven at 110 °C. After the final impregnation, the catalyst was placed in the oven overnight. After drying, the sample was transferred to a calcination furnace and heated at a rate of 10 °C/min to 500 °C in air and held here for 3 h. The catalyst used in this study has been previously characterized by XPS, XRD, TPR, and laser Raman spectroscopy and the results indicated that after calcination, Co_3O_4 formed on the monoclinic ZrO_2 support [32,33].

2.2. Catalyst reaction testing

Activity measurements were performed using a stainless steel tube (1/4 in. O.D.) fixed bed reactor. The reactor furnace was controlled by an Omega CN49000 temperature controller and K-type thermocouple in direct contact with the quartz wool plug upstream of the catalyst bed. All tubing and connections were made of Swagelok stainless steel fittings. Brooks 5850E mass flow controllers were used to control the gas flow rate. The gas hourly space velocity and reactant concentrations were varied among experiments and a GHSV = 39,000 h^{-1}, corresponding to 200 mg catalyst and 50 cm^3(STP)/min, was used for most experiments. The samples were pretreated in 10% O_2 in balance Ar at 300 °C for 30 min before experiments. Analysis of the feed and effluent gas streams was conducted using a HP 5890 gas chromatograph equipped with molecular sieve and Porapak Q separation columns and a TCD and an FID with a methanizer. Activity measurements were taken at 30 and 60 min and averaged. Time-on-stream studies were performed using a Varian 4900 Micro-GC with TCD and Poraplot Q columns and TCD detectors. The conversions of CO (X_{CO}) and O_2 (X_{O_2}) as well as the O_2 selectivity to CO_2 (S_{CO_2}) are defined as follows:

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

$$X_{O_2} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}},$$

and

$$S_{CO_2} = \frac{[CO_2]_{out} - [CO_2]_{in}}{2([O_2]_{in} - [O_2]_{out})}.$$

Temperature-programmed reaction (TPRxn) studies utilized a Cirrus RGA quadrupole mass spectrometer to monitor the reactor effluent. Before the experiment, the sample was pretreated at 300 °C for 30 min in 10% O_2/He, and was then cooled to room temperature under He flow. The total gas flow rate was 30 cm^3(STP)/min and 100 mg of CoO_x/ZrO_2 was loaded into the reactor. The temperature was increased at 5 °C/min from room temperature to 300 °C, and held for 30 min. The feed composition was 1% CO, 1% O_2, 60% H_2, and balance He.

2.3. Catalyst characterization

N_2 physisorption was conducted on a Micromeretics ASAP 2010 at 77 K and the BET surface area of the ZrO_2 was determined to be 48 m^2/g and the CoO_x/ZrO_2 catalyst had a surface area of 41 m^2/g.

Temperature-programmed reduction (TPR) experiments were performed on an in-house constructed system equipped with a TCD detector to measure H_2 consumption. A water trap removed moisture from the TPR effluent stream before

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