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PREFERENTIAL OXIDATION OF METHANOL AND CARBON MONOXIDE FOR GAS CLEANUP DURING METHANOL FUEL PROCESSING

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ABSTRACT

Methanol fuel processing generates hydrogen for low-temperature, PEM fuel cell systems now being considered for transportation and other applications. Although liquid methanol fuel is convenient for this application, existing fuel processing techniques generate contaminants that degrade fuel cell performance. Through mathematical models and laboratory experiments, chemical processing is described that removes CO and other contaminants from the anode feed stream.

INTRODUCTION

Future electric vehicles offer promise for ultra low emission transportation technology. World-wide progress continues in traction batteries and other electric drive components. As part of these efforts, a methanol-powered/air fuel cell system is also under investigation. Fueled by liquid methanol, this system drives a low-temperature hydrogen-air PEM (proton exchange membrane) fuel cell stack to operate in a battery/fuel cell hybrid mode.

Supported jointly by the United States Department of Energy and General Motors Corporation, the fuel cell engine project includes components for generating hydrogen using on-board steam-reforming.(1) Liquid methanol and water are reacted on heterogeneous catalysts to form a hydrogen-rich stream for the anode (fuel) input. This hydrogen feed, derived from the primary conversion step, is contaminated with unreacted methanol, CO, and other constituents that degrade fuel cell performance. Potential contaminants are removed in a sequential gas cleanup section designed to convert low levels of contaminants to fuel-cell-tolerant compounds.(2)

Methanol is readily converted to hydrogen by reaction of liquid methanol fuel. Methanol steam reforming is typically represented as a combination of the methanol decomposition reaction and the shift reactions.

$$CH_3OH = 2H_2 + CO \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

These reactions, when summed, result in the usual methanol steam reforming reaction:

$$CH_3OH + H_2O = 3\,H_2 + CO_2 \qquad (3)$$

Amphlett et al.(3) have discussed various proposed reaction mechanisms and models for methanol processing. Useful mixed metal oxide catalysts operate with hydrogen-dosed surfaces, dominated by Zn-H and -OH bonding. Several possible mechanistic routes have been suggested, though all are more complex than those suggested in Reactions 1 and 2.(4) Reaction 3 is invariably conducted under water-rich conditions, so the hydrogen product is accompanied by water and CO, frequently in concentrations close to those predicted by the equilibrium situation shown as Reaction 2. Depending upon reaction conditions and temperature, CO is generated in concentrations of 0.5 to 4% CO.(5) These high CO concentrations within the anode feed for low-temperature (80-100°C) PEM stacks result in severe performance loss. (The size of the voltage loss is a function of temperature, catalyst formulation and loading, and other factors.)

Anode feed contaminated with methanol is also detrimental. Methanol can block

anodic reacting sites. Moreover, methanol tends to dissolve in the membrane separator with possible harmful consequences. Fortunately, equilibrium unreacted methanol concentrations tend to be sufficiently low, 170 to 615 ppm for usual reacting conditions; thus, equilibrium methanol breakthrough values are normally not a concern. However, long residence time reactors are required to achieve equilibrium conditions. In practice, appreciable unreacted methanol is frequently reported as part of the fuel processing output stream.

Several technical approaches exist for CO removal from hydrogen-rich streams. Reduction to methane is technically feasible, though the presence of CO_2 in the mixture complicates processing. CO can also be oxidized to CO_2. This process approach requires reaction control to force CO oxidation preferentially to hydrogen oxidation. Here, we describe this second approach, based on the preferential reactivity of CO over that of hydrogen during oxidation processing. The implications of conducting this cleanup step in a mixture contaminated both by methanol and CO are also addressed.

TECHNICAL APPROACH—MODELING

A mathematical model for the conversion reactor predicts the outlet composition based on reactor inlet conditions for the preferential oxidation of CO and CH_3OH in a gas stream containing approximately 66% H_2. This one-dimensional model assumes plug flow within an adiabatic, steady-state tubular reactor. The oxidation reactions of CO, methanol, and hydrogen and the *reverse* shift reaction, the reaction between CO_2 and hydrogen to generate additional CO, are treated as irreversible, global catalytic reactions. The forward-shift reaction is not considered because the conditions of interest are far from equilibrium and, thus, favor the reverse-shift reaction.

The reaction rate expressions were written in forms of the Langmuir-Hinshelwood equation:

$$R_{CO} = -k_{CO}\frac{C_{CO}C_{O_2}}{\left(1+K_{ad}C_{CO}\right)^2} \quad (4)$$

$$R_{H_2} = -k_{H_2}\frac{C_{O_2}}{\left(1+K_{ad}C_{CO}\right)^3} \quad (5)$$

$$R_M = -k_M\frac{C_{CH_3OH}C_{O_2}}{\left(1+K_{ad}C_{CO}\right)^2} \quad (6)$$

$$R_{RS} = -k_{RS}\frac{C_{CO_2}C_{H_2}}{\left(1+K_{ad}C_{CO}\right)^2} \quad (7)$$

where the reaction rate coefficients

$$k_i = A_i \cdot \exp\left(\frac{-E_i}{RT}\right) \quad (8)$$

are written in the Arrhenius form. Note that the surface coverage of CO

$$K_{ad} = A_{ad} \cdot \exp\left(\frac{E_{ad}}{RT}\right) \quad (9)$$

is assumed to preferentially dominate over other species at the partial pressures and temperatures used during this conversion. The mass balance for each species i is given by

$$\frac{d(uC_i)}{dz} = r_i \quad (10)$$

where u is the bulk-gas velocity, and r_i is the net molar production rate of each species determined by summing the formation and destruction rates. The mass balance equations for the species are

$$\frac{d(uC_{CO})}{dz} = R_{CO} - R_{RS} \quad (11)$$

$$\frac{d(uC_{CO_2})}{dz} = R_{RS} - R_M - R_{CO} \quad (12)$$

$$\frac{d(uC_{O_2})}{dz} = \frac{1}{2}R_{CO} + \frac{1}{2}R_{H_2} + \frac{1}{2}R_M \quad (13)$$

$$\frac{d(uC_{H_2O})}{dz} = -R_{H_2} - R_{RS} \quad (14)$$

$$\frac{d(uC_M)}{dz} = R_M \quad (15)$$

The energy balance for the tubular plug flow reactor is written as

$$c_p C_t \frac{d(uT)}{dz} + \sum_i \Delta H_i R_i = 0 \quad (16)$$

where changes in u are determined from the ideal gas law and c_p is the specific heat of the gas mixture determined from

$$c_p = \sum_i \frac{C_i}{C_t} c_{p,i}(T) \quad (17)$$

and $c_{p,i}(T)$ is the specific heat of species i evaluated at the local temperature.

This system of ordinary differential equations was integrated using a fourth-order Runge-Kutta method. Boundary conditions are required at the inlet of the reactor for temperature, pressure, flow rate, and molar compositions. Integration over the length of the reactor generates profiles of the temperature, velocity, and molar composition along the reactor.

E_{CO} / R	12600
E_{ad} / R	961
E_{H_2} / R	1708
E_{RS} / R	18100
E_M / R	3970

Table 1. E_i/R (K) for the Arrhenius rate coefficient expressions.[6,7,8]

TECHNICAL APPROACH—EXPERIMENTS

Adiabatic preferential oxidation experiments were conducted to simulate anticipated process conditions and to test model predictions. This test apparatus (Figure 1) forms a gaseous mixture (called synthetic reformate) of H_2, CO_2, CO, H_2O, and CH_3OH. Individual gas flow rates were metered with mass flow controllers, while liquid flow rates were metered using HPLC pumps. Synthetic reformate typically contained 69.5% H_2, 23.2% CO_2, and 6.4% H_2O, which corresponds to a reformer injection feed of ~1.3 moles of water per mole of methanol. Concentrations of CO, CH_3OH, and injected oxygen were varied over the experimental ranges of interest.

Gas-stream inlet temperatures were varied using a tubular heat exchanger, and the outlet pressure was controlled. Experiments were done using proprietary catalyst samples and geometries prepared by the AC Rochester Division of General Motors. A Hewlett-Packard 5890 gas chromatograph was used to monitor CO, CH_3OH, and O_2 concentrations. Periodic

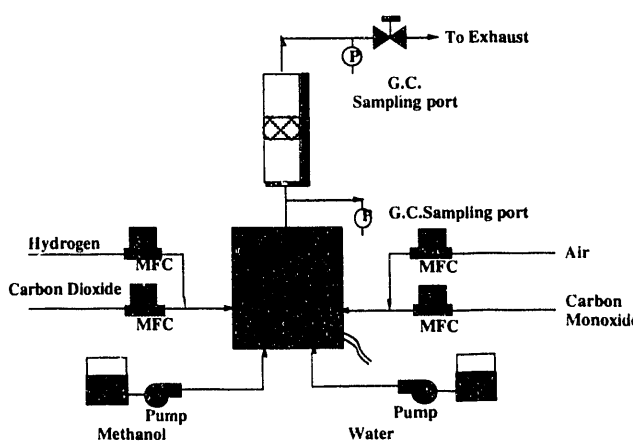

Figure 1: Preferential Oxidation Experiment: Instrument generates synthetic reformate dosed with quantities of CO and CH_3OH for gas cleanup processing.

GC calibration demonstrated sensitivities to 5 ppm CO, 200 ppm CH_3OH, and 5 ppm O_2.

RESULTS AND DISCUSSION

The reaction rates shown at the end of the previous section require five pre-exponential factors and five activation energies, as well as energetics for CO adsorption. Initially, activation energies were assumed to be catalyst dependent, and literature values previously determined for platinum (Table 1) were used. Furthermore, measured (literature) values for the pre-exponential factors were initially incorporated in the model, but they were later adjusted to match the experimental data.

Figure 2 shows the model results for the concentration of CO along a specific monolith channel. A reformate sample, along with 1% oxygen, is introduced in this calculation. This sample uses an inlet temperature of 200°C. The inlet CO concentration is 2,500 ppm (0.25%). The CO is quickly reacted in the first catalyst section and is, essentially, completely converted in a short reaction zone (short residence time). Continuous oxygen consumption occurs, however, as a result of the CO and hydrogen conversions. Heat is released, and the temperature increases. These conditions lead to the formation of additional CO, which results from the reverse shift reaction, in the end section of the monolith channel. In this example the exit CO concentration is actually double that of the entrance concentration. This reverse-shift conversion occurs because of a longer residence time at an elevated temperature through most of the reaction zone. Controlling the inlet temperature, the monolith catalyst length, the oxygen concentration, or the catalyst type and loading enables increased effectiveness in removing CO. For example, if the actual catalyst length, under the conditions shown in Figure 2, is 0.2 in., then essentially all of the CO will be converted to CO_2.

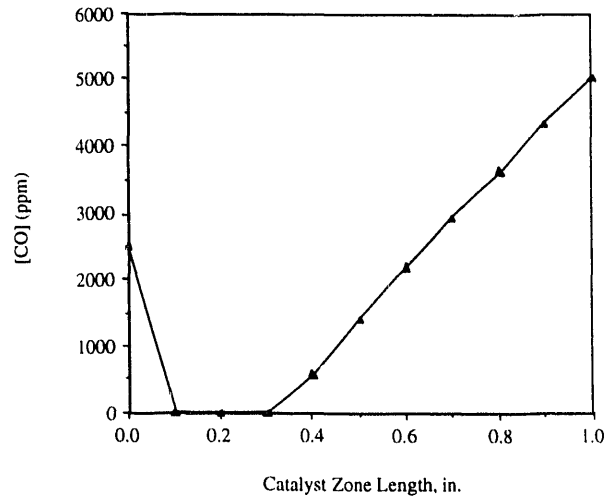

Figure 2: Model results of CO concentrations in short reaction geometry: CO is first removed, then additional CO is generated along the reaction channel.

Figure 3 compares the model results and experimental measurements for the separate oxidation of CO and methanol. These experiments were done using the conditions shown in Figure 3, with inlet concentrations of 2600 ppm (CO) or 2300 ppm (CH_3OH), an inlet temperature of 170°C, and a flow rate of 4.32 l/min. Data are shown as contaminant concentrations from the exhaust of the 1-in. monolith as a function of inlet oxygen concentration. During the traverse through the catalyst sample, most of the oxygen is consumed. The CO is efficiently removed using an oxygen/CO feed ratio of ~2; effective methanol removal requires an oxygen/CH_3OH ratio of ~4. Higher oxygen feed concentrations result in conditions that accelerate the reverse shift reaction, again leading to the possible generation of CO under poorly designed reaction conditions. In this adiabatic approach, temperature increases continuously along any flow channel as long as oxygen is present. Methanol conversion is accelerated by higher reaction temperatures. As shown in Figure 3, the model adequately predicts the conversion results.

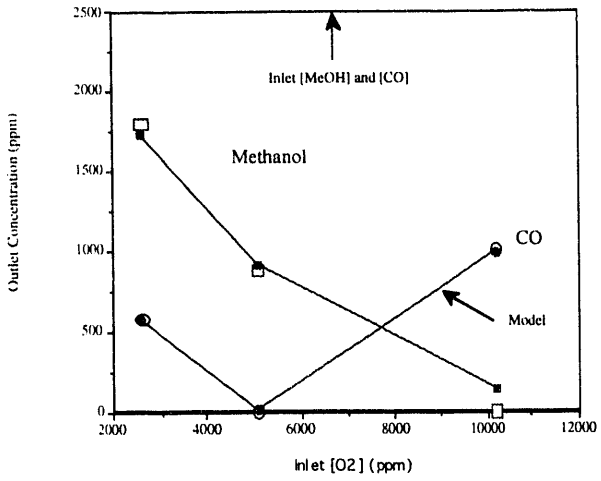

Figure 3: Comparison of modeling and experimental results on CO and CH_3OH preferential oxidation.

CONCLUSIONS

Low-temperature electrochemical engines (PEM) operating with reformate fuel require gas cleanup following the primary hydrogen generation step. Our results focus on oxidative removal through a preferential oxidation step. Modeling and experimental results confirm that both CO and CH_3OH can be effectively removed to levels that do not degrade PEM fuel cell stack performance. However, because of the sensitivity of the reformate mixture to generating additional CO through CO_2 reduction (reverse shift), reaction control is required to assure continuous, effective CO removal.

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