Carbon Dioxide Conversions in Microreactors

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Abstract

The sequestration and utilization of carbon dioxide in microreaction systems has significant potential applications in the chemical processing industry as well as space applications. With the advent of more stringent government mandates for reduced CO_2 emissions, chemical processing plants must find new ways to remove and process CO_2 from their product streams. In addition, NASA's In Situ Resource Utilization program is seeking novel methods for conversion of atmospheric CO_2 to fuels during manned missions to Mars. Two possible methods for these conversions include Sabatier methanation and the reverse water-gas shift (WGS) reaction. The applicability of these reactions in microreactors is discussed.

Introduction

Carbon dioxide makes up the majority of carbon-containing emissions from the commercial chemical industry. When combined with vehicular emissions, the resulting atmospheric carbon dioxide concentrations have been associated with the so-called Greenhouse Effect. In response to this possible source of global climate change, legislators have enacted laws that limit carbon dioxide emissions from industrial point sources. The chemical industry is therefore seeking out novel methods to sequester and utilize carbon dioxide in waste streams as these laws become increasing stringent. Several possible processes are viable for carbon dioxide conversions, among them the Sabatier reaction and the reverse WGS reaction.

In the Sabatier reaction, carbon dioxide is catalytically activated in the presence of hydrogen, which fully hydrogenates the adsorbed carbon species to methane, with accompanying water formation:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (1)$$

This reaction is moderately exothermic, $H° = -165$-kJ/mol. The National Aeronautics and Space Administration (NASA) is also interested in this reaction for use in future manned Mars missions. As we bring terrene hydrogen to Mars, we envision that advance robotic missions will establish a miniature chemical plant to convert the Martian carbon dioxide atmosphere into methane and water for fuel and astronaut life support systems.

The stoichiometric reverse water-gas shift reaction, which typically operates close to equilibrium, is mildly endothermic, $\Delta H° = 41.2$-kJ/mol:

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

This process is commonly used to tailor the hydrogen concentration of mixed syngas streams in industrial operations. Due to its reversibility, however, maximum conversions and selectivities are typically governed by equilibrium. Typical water-gas shift catalysts are used but at higher temperatures.

Background

Microchemical reactors take advantage of dramatically reduced heat- and mass-transfer limitations, which are minimized at the micron scale. By physically reducing the characteristic path lengths for these processes, extremely

high transport rates are realized. This results in highly efficient, ultra-compact systems that exhibit performances superior to conventional systems, with one to two orders of magnitude reductions in hardware volume and/or weight (Tonkovich 1998, 1999). Thus, microchemical systems (comprising microreactors and microthermal units) find applications in advanced transportation power systems, portable or local power generation, as well as defense and space applications.

One such application is the generation of hydrogen gas from hydrocarbon fuels, for use in polymer electrode membrane (PEM) fuel-cell power systems (Tonkovich 1998). This type of power system is currently considered the most promising option for electric-powered vehicles, and nearly every major automobile manufacturer is currently conducting extensive research and testing of these systems. Components of this type of systems have been successfully developed and tested at Pacific Northwest National Laboratory, where an integrated automotive fuel vaporizer and hydrogen combustor has been demonstrated (Tonkovich 1999).

For a catalytic process to be successfully used in a microchemical reactor, the reaction must exhibit intrinsically rapid kinetics that is detectable at very short residence times. Thus, the first step in evaluating a process for use in a microchemical system is to conduct catalytic experiments using millisecond residence times. The ultimate goal of this initial experimentation is to identify possible novel catalysts that are more active than conventional commercial catalysts. Because of the reduced resistances to heat and mass transfer, microreactors can realize the full activity of such catalysts, where conventional systems cannot.

Experimental

Catalytic activity experiments were conducted using 70–100 mesh powdered catalysts in 4-mm-diameter packed beds, typically 5- to 10-mm in height, housed in an isothermal tube furnace. Reactant gases were supplied with electronic mass flow controllers. The product stream passes through multiple ice bath condensers and then to an on-line gas chromatograph (GC) that monitors carbon dioxide, carbon monoxide, hydrogen, methane, and nitrogen (sometimes used as a diluent). Thermocouples positioned above and/or below the catalytic bed allow for temperature monitoring. Residence times down to about 5-ms are achievable in these systems. All experiments were conducted at atmospheric pressure.

For each experiment, catalysts are reduced in 10- to 20-vol% hydrogen in nitrogen for 1 to 2 hours, depending on the composition. After reducing, the catalyst is heated to reaction temperatures under nitrogen flow followed by introduction of reactant gases. At each temperature, the product stream composition is allowed to reach a steady-state value before continuing on to a different temperature. In this way, activity graphs showing conversion and product selectivites are generated as a function of temperature and/or residence time.

Results

Sabatier Methanation

For the production of methane from carbon dioxide via the Sabatier reaction, three ruthenium-based catalysts were tested for activity at temperatures from 110° to 350°C at residence times as low as 20 ms. The catalysts are identified as 1RU, 3RU and 5RU, corresponding to 1 wt% Ru/G1-80 (United Catalysts), 3 wt% Ru/TiO_2 (Degussa) and 5 wt% Ru/ZrO_2 (Engelhard), respectively.

The performance of these three catalysts as a function of residence time at 250°C is shown in Figure 1. As this figure shows, all three catalysts exhibit similar conversion activity over the range of residence times examined. For all catalysts, the conversion at a residence time of 20 ms was about 55%. As the residence time was increased, the conversion increases rapidly. At residence times greater than about 100 to 200 ms, the conversion reaches nearly 90%, with further increases in residence time having only a slight effect. The equilibrium conversion at this temperature is also shown, and, as can be seen, this conversion is not achieved at any residence time. This figure also shows the selectivity of the 3-RU catalyst toward methane formation. At all residence times, most of the product consisted of methane, with the selectivity reaching 100% at a residence time of 100 ms and greater, which is the equilibrium selectivity at 250°C.

Figure 2 shows the activity of the same catalysts as a function of temperature at two different residence times. Again, all three catalysts exhibited similar activity. At temperatures below about 250°C, conversion remained below 50%, but at higher temperatures, the conversion rapidly maximized to about 85%. Further increases in temperature had no effect. The equilibrium conversion as a function of temperature is also shown, and it is apparent that near-equilibrium conversion is achieved at 350°C. Although not shown, the selectivity towards methane for catalyst 3RU was 100% at all temperatures due to the longer residence times used here. This is in agreement with equilibrium calculations over this temperature range.
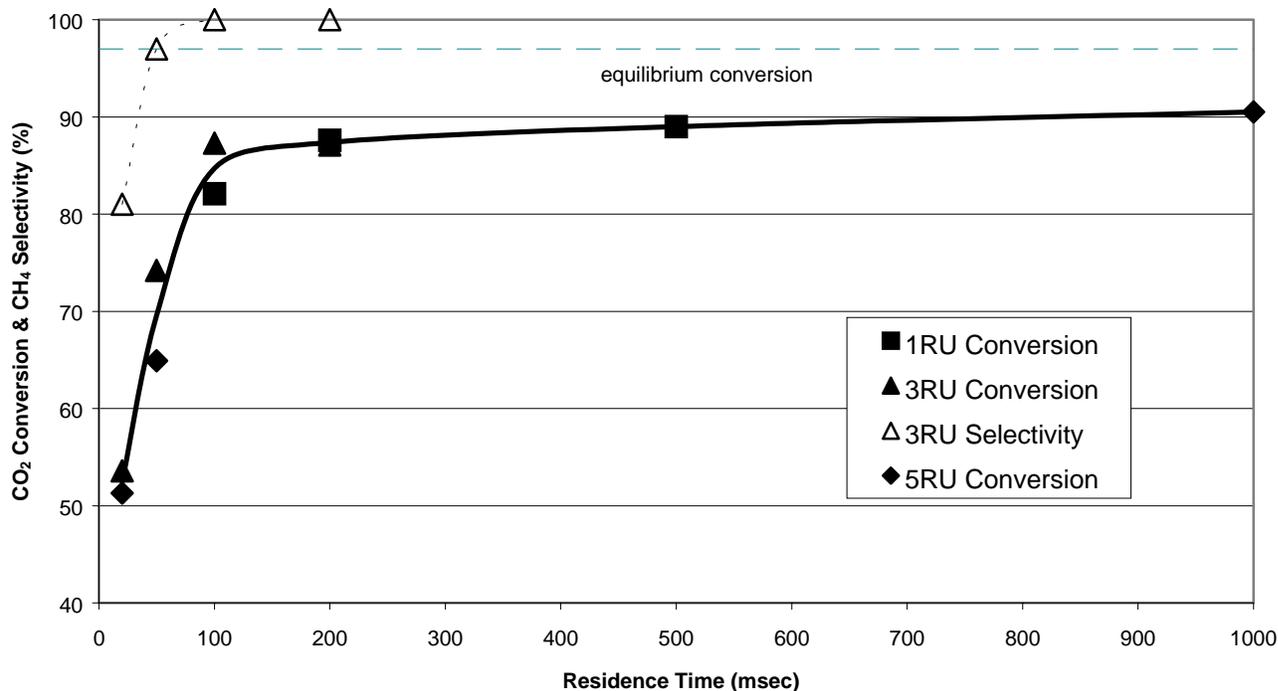

Figure 1. Similar Activity of Three Catalysts During Sabatier Methanation at 250°C

Reverse Water-Gas Shift Reaction

The intrinsic kinetics of the reverse water-gas shift (RWGS) reaction was examined at very short residence times in an attempt to avoid sequential reaction through the forward reaction. The catalyst employed was prepared in our laboratories. This catalyst was tested at residence times from 5 to 64 ms. For residence times below 32 ms, the feed had to be diluted with nitrogen to achieve the short residence time feed rates.

Figure 3 shows the effect of residence time on the carbon dioxide conversion and selectivity to carbon monoxide at 540°C. Note that, to achieve a very high flow rate, the feed stream was diluted for the 5-ms data point. Inspection of this figure shows that, at this temperature, near-equilibrium conversions of about 30% were achieved at nearly all contact times. Of particular interest, however, is the considerably high selectivity of the products toward carbon monoxide. At these very short residence times, the equilibrium selectivity was surpassed. However, there was not a significant difference in this selectivity at residence times between 32 and 64 ms. Although the selectivity was much higher at 5-ms residence time, a direct comparison with the undiluted points cannot be made.
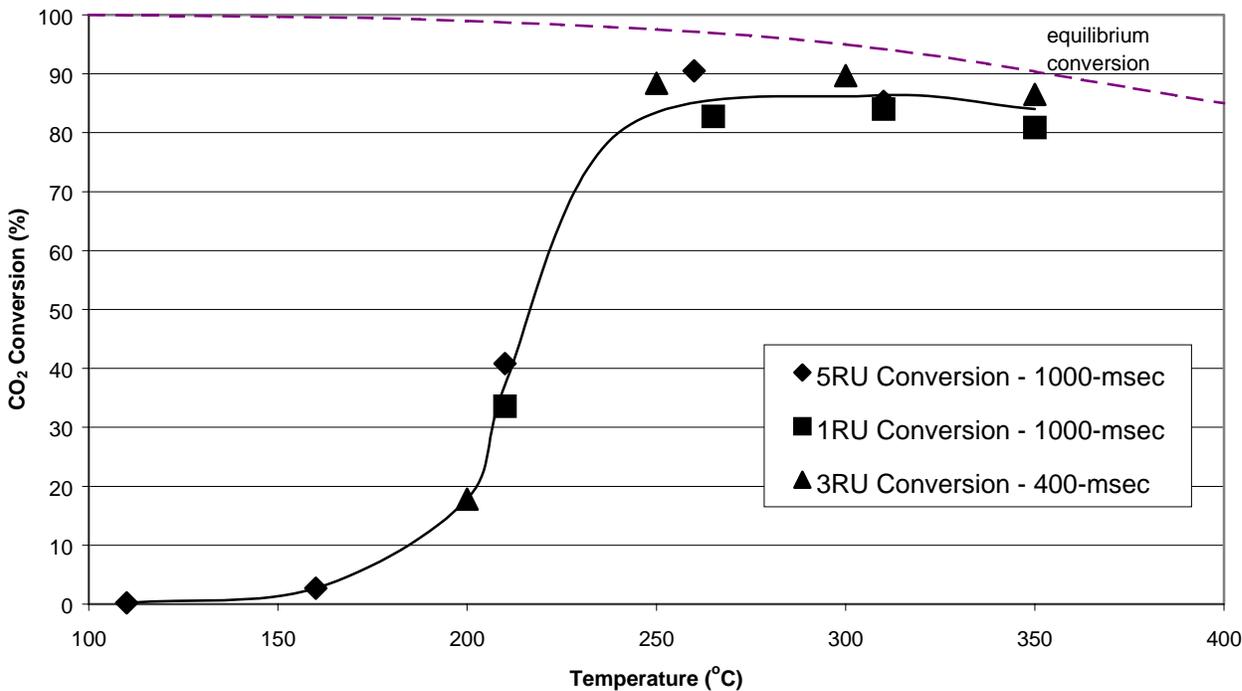
Figure 2.   Similar Performance at Longer Residence Times for Three Catalysts over a Range of Temperatures During Sabatier Methanation

The effect of temperature on the RWGS reaction was examined at residence times of 32 ms. Figure 4 shows the results of this study, where equilibrium conversion and CO selectivity are again shown for comparison. The conversion of carbon dioxide remains nearly zero until about 300°C, when it steadily rises to its near-equilibrium value of about 30% around 525°C. At all temperatures, production of carbon monoxide occurs at greater than equilibrium levels due to the short residence time used. Only at the highest temperature examined, 550°C, does this selectivity begin to approach the equilibrium prediction. Although not shown, the only product formed besides carbon monoxide is methane, so at lower temperatures, it is formed exclusively.

Summary and Conclusions

The results of this work show that both of the processes under examination here, the Sabatier and RWGS reactions, have intrinsic kinetics that is fast enough to use these conversions in microchemical reaction systems. Methanation through Sabatier seems to require a minimum residence time of about 100 ms to achieve a near-equilibrium conversion of 90% with nearly 100% selectivity to methane. However, production of carbon monoxide via RWGS can be conducted at residences times well below 50 ms, although in this case an equilibrium conversion of about 30% is reached when operating around about 500°C. Nonetheless, in this process, CO selectivities far in excess of equilibrium can be achieved at all temperatures. In addition, the Sabatier reaction has the additional benefit of reaching optimum catalytic performance at about 250°C, compared to about 550°C for RWGS. From the perspective of microtechnology, the Sabatier reaction requires hardware volumes (directly proportional to residence time) roughly 2- to 10 times larger than RWGS.
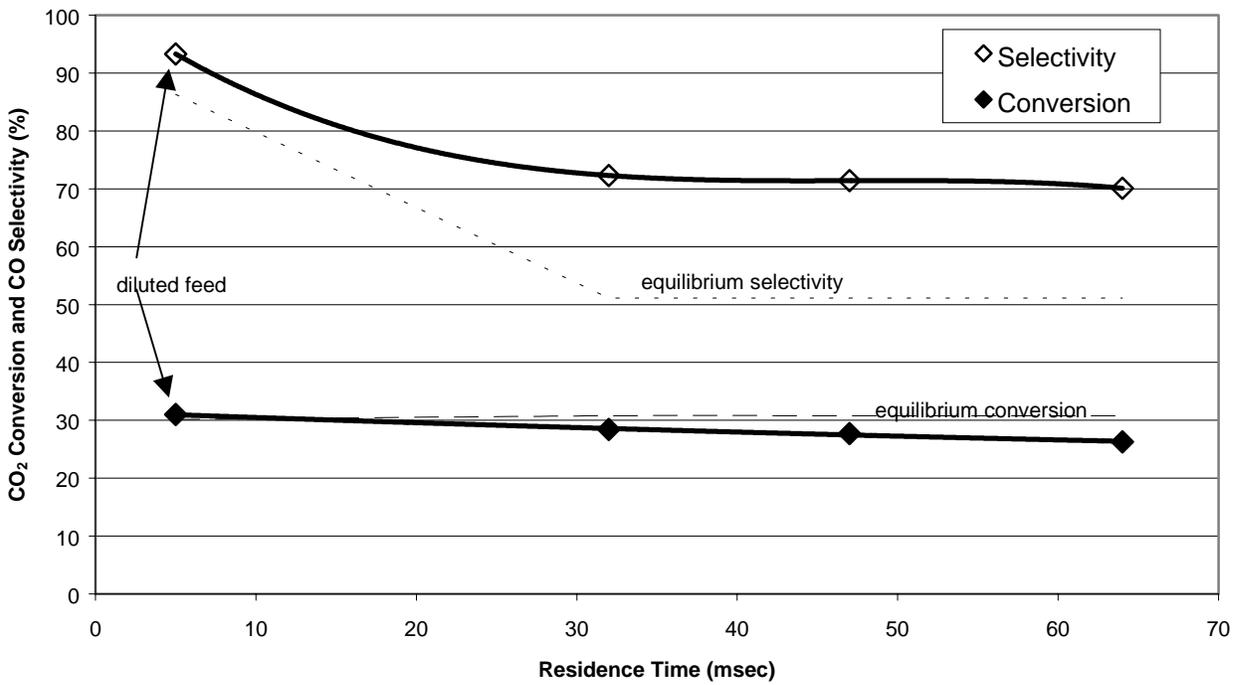
Figure 3. Near Equilibrium Conversion and High CO Selectivity for RWGS Reaction at Very Short Residence Times (540°C)
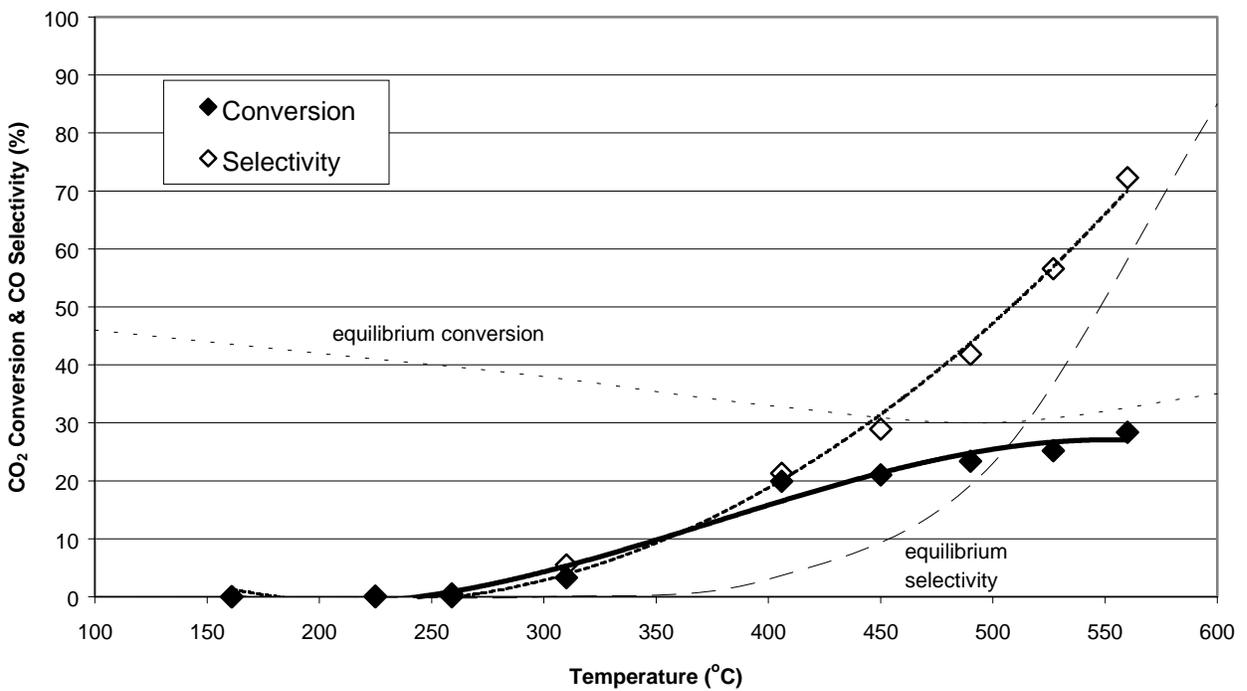

Figure 4. Nonequilibrium CO Selectivity and Near-Equilibrium Conversion of CO_2 During RWGS Reaction at 32-ms Residence Time

References

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