

KINETIC STUDY OF THE REVERSE WATER GAS SHIFT REACTION IN HIGH-TEMPERATURE, HIGH-PRESSURE HOMOGENEOUS SYSTEMS

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Introduction

The Water Gas Shift Reaction (WGSR), an important industrial reaction for the production of chemicals and/or hydrogen, is expected to play a key role in the integration of gasification technologies with a H₂ production/recovery unit. The effluent stream of the gasifier, mainly H₂, CO and CO₂ at high pressure (up to 30 atm) and temperature (up to 1000°C), will be directed to the water gas shift reactor along with steam where reaction (1) will take place, increasing the yield of hydrogen.



The WGSR is an exothermic, equilibrium-limited reaction that exhibits decreasing conversion with increasing temperature. Reviews of the catalyzed WGSR at temperatures below 600°C are available in the open literature¹. A catalyst is required under these conditions because of the lower reaction rate at low temperature. There has been renewed interest in the WGSR at extreme temperatures however, because of recent advances in high-temperature materials for hydrogen separation membranes. The permeation of hydrogen through the walls of a membrane reactor enables the attainment of high conversion of CO and steam to hydrogen and carbon dioxide².

Several papers have shown high reaction rates for the high-temperature (>875°C), non-catalytic water gas shift reaction. Graven and Long³ addressed both the forward (CO + H₂ reactants) and the reverse (CO₂ + H₂O reactants) water gas shift reaction in the temperature range 875-1050°C, reporting that the reaction occurs only in the gas phase, i.e. without any heterogeneous contribution. Their experimental results support the chain-reaction mechanism previously proposed. However, some of their results on the reverse WGSR were challenged by two later studies^{4,5}. Tingey⁴ and Kochubei and Moin⁵ found a lower value for the rate constant suggesting experimental errors in the work of Graven and Long due to the presence of traces of oxygen (an homogeneous catalyst) in the gas phase. Tingey studied the reverse water gas shift reaction over an extended temperature range (400-1200°C) and pointed out that at high-temperature (>800°C), the reaction would follow the chain-reaction mechanism but would follow a different mechanism at lower temperature. All of these studies were performed in a highly diluted reaction gas mixture at ambient pressure, without exploring the influence of pressure on the reaction rate and kinetics.

The utility of the high-temperature, non-catalytic WGSR is supported by these previous results showing high reaction rates at extreme temperatures. This report will address the kinetics of the reverse WGSR under conditions not studied previously, namely high-concentration streams, i.e. non-diluted streams, and high-pressures. These conditions are more appropriate to draw conclusions on the application of the WGSR directly to a gasification stream via a

membrane reactor. (The forward water-gas shift reaction will be examined in a subsequent study.)

Experimental

A flow system (CSTR reactor) was used for the kinetic studies. The Hydrogen Membrane Testing unit (HMT-1) at NETL was designed for study the water-gas shift reaction at high-pressure (up to 30 atm), high-temperature (up to 900°C) conditions. The unit has the capability of feeding a gas mixture to a high-pressure, high-temperature reactor composed of quartz or Inconel.

Hydrogen and carbon dioxide were fed by using electronic mass flow controllers. Tubing downstream of the reactor was heat-taped and insulated to avoid condensation of water. Reactor temperature was controlled with a thermocouple placed directly on the top of the reactor. Pressure was controlled with a pressure controller downstream the reactor.

The effluent of the reactor was analyzed with a gas chromatograph equipped with a TCD detector for quantification of H₂, CO, CO₂ and H₂O in the range of concentrations of interest.

The residence time of the reactants in the reactor was chosen to assure low conversions (less than 2 %), avoiding any significant effect of the forward reaction. Under these conditions, the rate can be modeled with the following power-law expression: $r = k[\text{H}_2]^\alpha[\text{CO}_2]^\beta$. Residence time was typically lower than 3 s. Reaction rates were evaluated from the CO₂ conversion, outlet CO₂ concentration, and residence time by using the CSTR design equation.

Results and discussion

Ambient pressure studies. In order to validate the experimental setup, kinetic experiments were carried out with an empty quartz reactor under the conditions reported in other studies^{3,4,5} (900°C, ambient pressure). Conversions were less than 0.1% in all cases and were in good agreement with the results of Tingey⁴ and Kochubei and Moin⁵. The energy of activation measured for the high-temperature (>875°C), ambient pressure experiments, $E_a = 75 \text{ Kcal/mol}$, was in agreement to the results reported in the literature (76 – 78 Kcal/mol^{4,5}). Kochubei and Moin⁵ had reported a surface effect by quartz at low temperatures (<850°C). Although this surface effect is relatively small, it would suffice to explain the lower value for the energy of activation reported by Graven and Long³ (56 Kcal/mol). In fact, for determining the Arrhenius parameters they used a packed reactor and some of their low temperature points may fall in the transition zone between homogeneous and surface-assisted reaction.

The effect of the walls on the reaction was tested for the Inconel reactor. Inconel is the material of choice for the reactor due to the harsh conditions (high temperature and pressure). For very small residence times (less than 0.5 s), conversions were very high (Figure 1). Moreover, these conversions were two orders of magnitude greater than the conversions observed with the quartz reactor (conversions with the quartz reactor were less than 0.1% under the same experimental conditions, i.e. temperature and residence time, than the Inconel reactor). This result implied that the metal walls of the Inconel reactor catalyzed the reaction. An increase in the Inconel surface area was achieved by packing the reactor with Inconel rings. As shown in Figure 1, the conversions were twice that observed with the empty Inconel reactor (Figure 1). However, the increase in the reaction rate may have been attributed to the enhanced mixing induced by the presence of packing. The replacement of Inconel packing with a similar surface area of quartz packing also induced an increase in the reaction rate. Nevertheless, the conversion was lower than that observed with the Inconel packing (34% for quartz packing versus 41% for Inconel packing). As the quartz surface is considered inert for this reaction^{3,5}, it appears that both catalytic and mixing

effects contributed to the dramatic increase in reaction rate. Figure 1 also illustrates that the reverse water-gas shift reaction was approaching the equilibrium conversion of 55% in the Inconel reactor even though the residence times were less than a second.

The Inconel packing (Inconel is 72% Ni, 17% Cr, 10% Fe) was examined by XPS after reaction. Results showed an increase in the concentration of chromium, and a depletion of nickel on the surface. The surface analysis also revealed a considerable amount of carbon deposits. Formation of carbon structures on Ni-Fe in gas phase reactions involving CO has been reported⁶. Further, chromium-based materials are used as catalysts for the “high-temperature” (400°C) WGS¹. Therefore, it appears that the chromium-rich Inconel surface was an active surface.

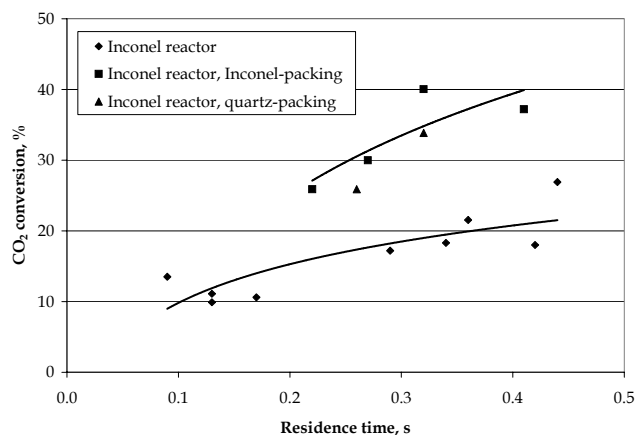


Figure 1. Reverse water gas shift reaction in an Inconel reactor. 900°C, ambient pressure, $[H_2]_0=[CO_2]_0$. Equilibrium conversion for these conditions is 55%.

High-pressure studies. The behavior of the high-pressure (16 atm), high-temperature (>700°C) was also investigated. An empty quartz reactor was used for the studies. A shift in the mechanism at a temperature around 800°C, consistent with the observations of Tingey⁴, was observed. The values for the rate exponents were very close to those reported previously (0.41 for H_2 , and 1.2 for CO_2 ; low-pressure exponents are 0.5 and 1.0 respectively), leading to the conclusion that the chain reaction mechanism is valid for high-pressure. However, the value for the energy of activation, 51 Kcal/mol, was much lower for the reaction carried out at high-pressure (Figure 2); the value of the pre-exponential factor was $1.8 \times 10^8 \text{ l}^{0.6} \text{ mol}^{-0.6} \text{ s}^{-1}$. An inhibiting effect (i.e. the rate at high pressure was slightly lower than that expected from the power-law model based on low-pressure data) at higher temperatures was also observed.

Even though the rate constant of the gas phase dissociation of hydrogen, which is the first step in the chain reaction mechanism, is pressure-dependent⁷, its effect would not explain the observed results. A surface effect was suspected and studied by adding quartz packing to the reactor. This inhibiting effect appeared to be increased by the presence of packing. Some authors⁸ have suggested a breaking of the chain on the walls under certain circumstances. We are currently exploring this behavior.

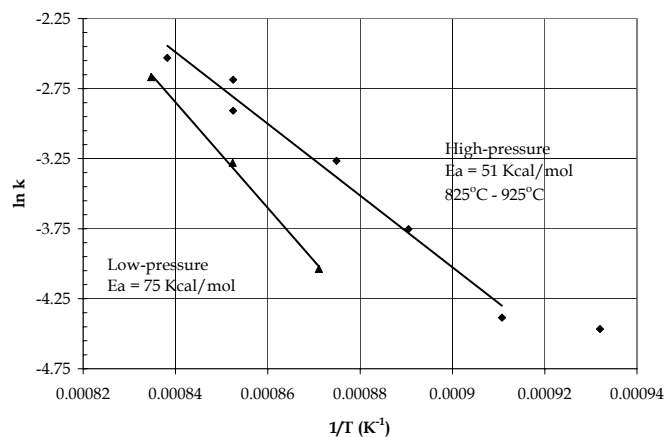


Figure 2. Arrhenius plot for the high-temperature, high-pressure (16 atm) and high-temperature, low-pressure (ambient) reverse water gas shift reaction.

Conclusions

The first experimental study of the high-pressure, high-temperature reverse water gas shift reaction was conducted. The findings of the study may be summarized as:

- Previous hypothesis on the reaction mechanism and homogeneous character of the low-pressure, high-temperature reverse water gas shift reaction were corroborated.
- A strong catalytic wall effect was found by using Inconel, evidenced by an enrichment of chromium and depletion of nickel at the surface.
- A significant reduction in the energy of activation for the high-temperature, high-pressure reverse water gas shift reaction was observed. Current research efforts are underway to explain this phenomenon.

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