Production of H_2 from Methanol by Supercritical Water Reforming: Strategies to Suppress Methanation

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Abstract

Hydrogen is produced by reforming of methanol in supercritical water tubular reactor. Both experimental results and equilibrium calculations show that as pressure increases, methanation of CO and CO_2 is favored which results in the loss of significant amount of H_2. It is therefore important to reduce the loss of H_2 by minimizing the methanation reactions. Here, three strategies for suppressing methane formation are proposed: (1) small residence time by having low reactor length or high feed flow rate, (2) addition of small amount of K_2CO_3 in the feed, or (3) utilization of the surface catalytic activity of the reactor made of Ni-Cu alloy. All three strategies resulted in the significant reduction in the methane formation and enhancement in the hydrogen production.
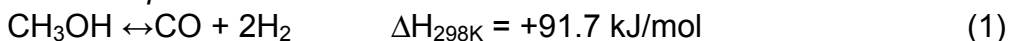
Introduction

Recently a considerable amount of research has been done in exploring the possibility of production of hydrogen from a variety of organic feedstock such as methane[1], methanol,[2, 3] ethanol[4], glucose and glycerol[5] in supercritical water. Methanol is a good choice as a feedstock for reforming because of its higher hydrogen-to-carbon ratio and absence of carbon-carbon bonds. High hydrogen-to-carbon ratio makes steam reforming of methanol energetically favorable while the absence of carbon-carbon bond reduces soot formation[6]. The advantages of carrying out reforming reactions in supercritical water have been well documented.[3] The density of supercritical water is higher than that of steam, which results in high space-time yield. Hydrogen is available at a high pressure, which can be stored directly, thus avoiding the problems associated with its compression. The hydrocarbons are completely soluble in supercritical water, which minimizes the formation of char or slug. This is particularly important in generation of hydrogen from heavy oils such as diesel.[7]
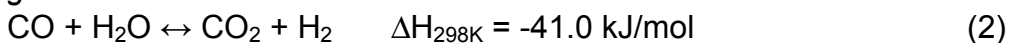
It is well known that methanol reforming takes place at high temperatures in the presence of catalysts such as Ni, Cu or Zn. In addition, the promoters such as Cr, Zn and Zr are used to promote the activity of the catalyst.[8] Taylor et al.[2] and Boukis et al.[3] have used a simple tubular reactor made of nickel alloy to carry out methanol reforming in supercritical water. In this reactor configuration the inside wall of the tubing provides catalytic surface area. The advantage of this configuration is the compactness and simplicity of design, which is utilized in this study.

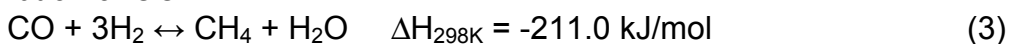The major reaction steps[3] involved in the methanol reforming are:
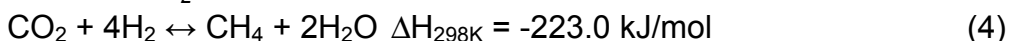
Methanol decomposition:

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad \Delta H_{298K} = +91.7 \text{ kJ/mol} \qquad\qquad (1)$$

Water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.0 \text{ kJ/mol} \qquad\qquad (2)$$

Methanation of CO:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_{298K} = -211.0 \text{ kJ/mol} \qquad\qquad (3)$$

Methanation of CO_2:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298K} = -223.0 \text{ kJ/mol} \qquad\qquad (4)$$

Reactions 1 and 5 are endothermic and hence are favored at higher temperature. The combined reaction of 1 and 2 is also endothermic. Reactions 3 and 4 involve a decrease in the number of moles in their stoichiometry making them favorable at higher pressures. Conversely, reactiosn 1 and 5 are favored at lower pressure. The major drawback of carrying out the reforming in supercritical water is that reaction 1 is not favored at higher pressures. Dependence of carbon formation on pressure is complicated. Based on our equilibrium calculations performed using Gibbs free energy minimization method (RGIBBS module) in ASPEN+ and Peng-Robinson equation of state, carbon formation was not observed. As pressure increases, CH_4 moles increase while H_2, CO and CO_2 moles decrease. A decrease in CO moles is advantageous for fuel cell applications.[9] A decrease in H_2, CO and CO_2 moles suggest that methanation of CO (reaction 3) and CO_2 (reaction 4) is favored at high pressure. Methanation of CO (reaction 3) results in a loss of 3 moles of H_2 while methanation of CO_2 (reaction 4) results in a loss of 4 moles of H_2. To enjoy the benefits of methanol reforming in supercritical water, which are mentioned before, it is important to prevent the loss of H_2 by minimizing methanation reactions. This paper examines the strategies for suppression of CH_4. The effect of various process parameters such as temperature, pressure, residence time, steam-to-carbon ratio and catalyst is studied.

Experimental Section

Apparatus

Methanol reforming was carried out in a tubular reactor made of Inconel 600 (Microgroup) having a composition of 73% Ni, 18% Cr, 9% Fe. The dimensions of the reactor were 0.125" OD and 0.085" ID. Three different lengths of the reactor (0.5, 1 and 2 m) were used in the study. Later reactor was replaced with a 1 m long tubing made of Ni-Cu alloy (Supelco) having the composition of 67% Ni, 33% Cu. The other dimensions of the tubing were kept the same. Aqueous methanol from the feed tank was pumped to the reactor after passing through a rupture disc using an HPLC pump (Waters 590). Feed tank was covered on the top to avoid the loss of methanol by evaporation. The reactor was heated using a tube furnace equipped with a temperature controller (Thermolyne 21100). Reactor temperature at the exit of the furnace was measured by using a type-K thermocouple with a tee arrangement. Both the

ends of the tube furnace were properly covered to avoid heat loss and thereby to achieve uniform temperature. The gas mixture exiting the reactor was cooled using an air-cooled heat exchanger. Pressure was measured by pressure gauge. Pressure was let down to ambient by means of a back pressure regulator (Straval). The gas-liquid mixture was separated in a glass phase separator having gas tight valves to prevent escape of gases. The gas flow was measured using a gas flow meter (Omega FMA 1600). A six-port injection valve (Valco) having a sample loop of size 100 μL was used for online sample injection. The gas composition was measured using a gas chromatograph (Varian 3700) equipped with a TCD and a 60/80 Carboxen-1000 carbon molecular sieve column (Supelco) having dimensions of 15' X 1/8". Helium was used as carrier gas. Gas chromatograph was calibrated using a standard gas mixture of known composition (BOC gases). Mass flow rate of the liquid coming out of the phase separator was measured using a balance. The carbon content was analyzed using a TOC analyzer (OI Analytical Model 700). Liquid was diluted appropriately to obtain the TOC readings within the range of the instrument.

Results and Discussion

K_2CO_3 doping

Kruse et al.[1] have reported an increase in hydrogen yield by addition of K_2CO_3 in the generation hydrogen from methane in supercritical water. We conducted experiments with the addition of 0.83 wt.% K_2CO_3 in the aqueous methanol feed (Figure 1). H_2 yield increased considerably with the addition of K_2CO_3. Onsager et al.[10] have reported hydrogen generation from water and CO in the presence of alkali metal formate salts, like K_2CO_3. We also conducted experiments with stoichiometrically equivalent amount of KOH (0.68 wt.%), which resulted in an increase in H_2 yield.

Ni-Cu alloy reactor

Cu is reported as a catalyst for steam reforming of methanol. Lindstrom et al.[8] have reported higher conversions and H_2-selectivities for catalysts with high Cu content. Hence experiments were conducted using Ni-Cu alloy reactor in this work. Figure 2 shows the effect of pressure on the molar gas yields for the experiments conducted at 600 °C and 1 ml/min. It can be seen that the increase in pressure has no effect on the gas yields. The H_2 yield is higher than the equilibrium yield at higher pressures. CH_4 yield is negligible at all pressures which prevents the loss of H_2 by methanation.

Conclusions

Methanol reforming in supercritical water favors the formation of CH_4, which is accompanied by a substantial loss of H_2. CH_4 formation can be reduced greatly by lowering the low residence time so that the equilibrium is not reached. Methanation can also be reduced by the addition of small amounts of K_2CO_3 or KOH in the aqueous methanol feed. Reactor made of Ni-Cu tubing prevents the formation of CH_4 even at higher pressures.
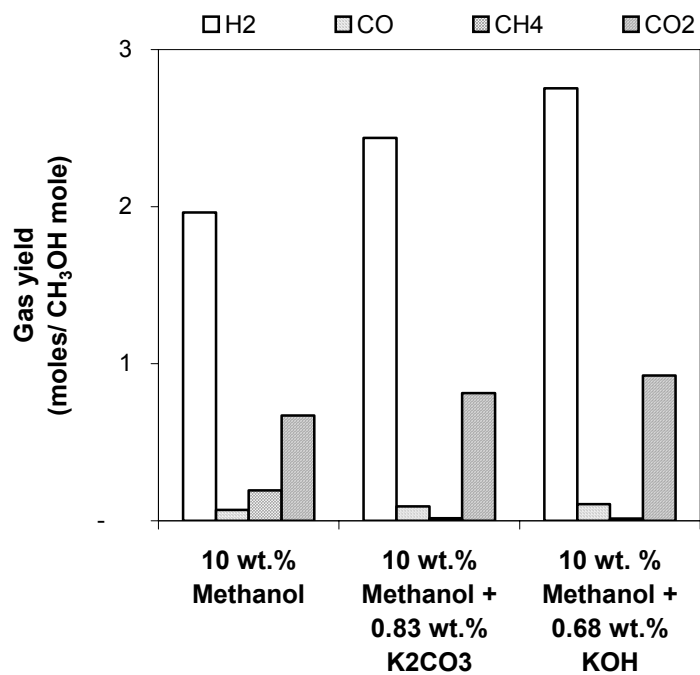
Figure 1: Effect of K_2CO_3 and KOH addition. Experimental conditions: 10 wt.% methanol, feed flow rate = 1 ml/min, 700 °C, reactor length = 2 m.
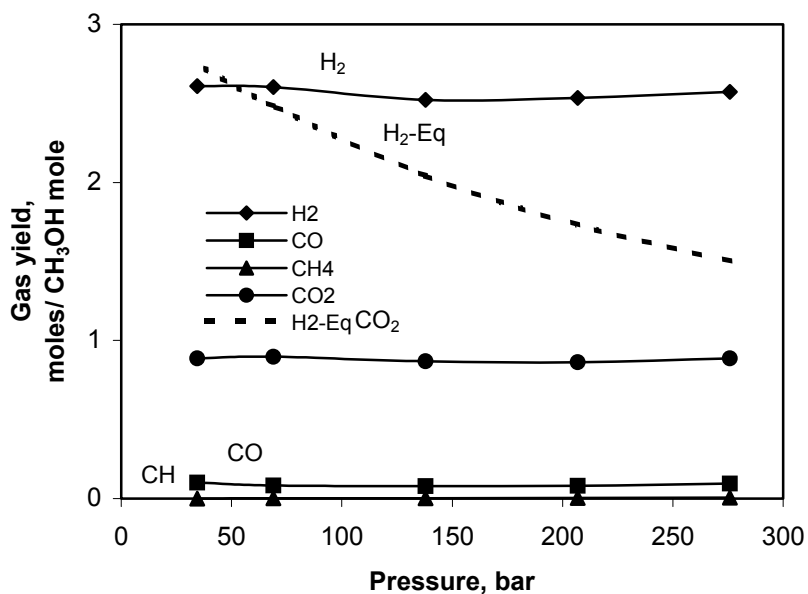

Figure 2: Effect of pressure on gas yield with Ni-Cu reactor. Experimental conditions: 10 wt.% methanol, feed flow rate = 1 ml/min, 600 °C, reactor length = 1 m.

References

[1] Kruse, Andrea; Dinjus, Eckhard. Hydrogen from methane and supercritical water.   Angewandte Chemie, International Edition (2003), 42(8), 909-911.

[2] Taylor, Joshua D.; Herdman, Christopher M.; Wu, Benjamin C.; Wally, Karl; Rice, Steven F. Hydrogen production in a compact supercritical water reformer. International Journal of Hydrogen Energy (2003), 28(11), 1171-1178.

[3] Boukis, N.; Diem, V.; Habicht, W.; Dinjus, E. Methanol Reforming in Supercritical Water. Industrial & Engineering Chemistry Research (2003), 42(4), 728-735

[4] Arita, Toshihiko; Nakahara, Koichi; Nagami, Kenzo; Kajimoto, Okitsugu. Hydrogen generation from ethanol in supercritical water without catalyst. Tetrahedron Letters (2003), 44(5), 1083-1086.

[5] Xu, Xiaodong; Matsumura, Yukihiko; Stenberg, Jonny; Antal, Michael Jerry, Jr. Carbon-Catalyzed Gasification of Organic Feedstocks in Supercritical Water. Industrial & Engineering Chemistry Research (1996), 35(8), 2522-2530.

[6] Pettersson, L. J.; Westerholm, R. State of the art of multi-fuel reformers for fuel cell vehicles: problem identification and research needs. International Journal of Hydrogen Energy (2001), 26(3), 243-264.

[7] Pinkwart, K.; Bayha, T.; Lutter, W.; Krausa, M. Supercritical reforming for fuel cells.   VDI-Berichte (2003), 1808(Kraftstoffe und Antriebe der Zukunft), 411-418.

[8] Lindstrom, B.; Pettersson, L. J. Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications. International Journal of Hydrogen Energy (2001), 26(9), 923-933.

[9] Amphlett, J. C.; Mann, R. F.; Peppley, B. A. On board hydrogen purification for steam reformation/PEM fuel cell vehicle power plants. International Journal of Hydrogen Energy (1996), 21(8), 673-678.

[10] Onsager, Olav-T.; Brownrigg, Marit Senum A.; Loedeng, Rune. Hydrogen production from water and CO via alkali metal formate salts. International Journal of Hydrogen Energy (1996), 21(10), 883-885.