CATALYTIC PRODUCTION OF HYDROGEN GAS BY METHANOL REFORMING

Erdogan Gulari, and J. Chris Brown

Department of Chemical Engineering
University of Michigan
2300 Hayward St.
Ann Arbor, MI 48109

Introduction

Recently, there has been a big move forward to find alternative methods to the current propulsion system in automobiles. These alternative methods need to preserve oil and provide more environmentally friendly exhaust than the current internal combustion system. One such, potentially viable alternative, is the use of PEM fuel cell system. Fuel cells turn hydrogen gas into useful electric power with an efficiency that is not limited by thermodynamics. Due to current infrastructure and safety concerns, hydrogen gas cannot be stored on-board. It is proposed that hydrogen be produced on-board as needed from liquid hydrocarbons. Methanol reforming is a proposed method of producing hydrogen gas on-board. This method has a couple of advantages: unlike oil, liquid methanol can be readily produced from biomass, it is easily adaptable to current infrastructure, it is easily transported and stored, and finally it has more hydrogen density than hydrogen gas.[1,2] The methanol must be converted to hydrogen gas without the production of harmful gases such as CO, because they deactivate the PEM fuel cells. There are three main reactions that extract H_2 from methanol. The first reaction is decomposition of pure methanol.

$$CH_3OH \rightarrow 2H_2 + CO \quad (1)\ \text{DEC} \qquad \Delta H^o_{298} = +90.7\, kJ/mol$$

There are two issues concerning this reaction. The first is this is an endothermic reaction, thus heat must be provided to sustain the reaction. Second, the carbon monoxide is harmful to the fuel cells, so some downstream processing must be done to eliminate the CO. This can be done with the water-gas shift reaction.

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (2)\ \text{WGS} \qquad \Delta H^o_{298} = -39.4\, kJ/mol$$

The next method of producing H_2 gas from methanol is the steam reforming of methanol. This involves the sum of reactions 1 & 2 combined into one step as given in eq. 3:

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2 \quad (3)\ \text{SRM} \quad \Delta H^o_{298} = +49.4\, kJ/mol$$

This reaction is also endothermic and requires heat. However, steam reforming also produces some CO as a byproduct. The last major reaction is partial oxidation of methanol (POM). It proceeds as follows:

$$CH_3OH + \frac{1}{2}O_2 \leftrightarrow 2H_2 + CO_2 \quad (4)\ \text{POM}$$

$$\Delta H^o_{298} = -192.2\, kJ/mol$$

This is reaction is exothermic and can provide heat to the SRM and DEC reactions.[3,4]

Experimental

Catalyst Preparation. Various formulations of Pd/CeO_2-Al_2O_3 and Pt/CeO_2-Al_2O_3 catalyst were prepared for testing. The Al_2O_3 supported catalysts were made by either conventional impregnation or sol-gel techniques. The CeO_2/Al_2O_3 was always made by sol-gel and was used as a support for the impregnated metal. It was prepared as follows; The aluminum isopropoxide was added to a beaker of water at 80°C. After 30 minutes of stirring, nitric acid was added. This will result in a fibrillar sol. Cerium (III) oxide was added to the sol at room temperature and then the mixture is mixed and aged until gelation occurred. The gel was then dried overnight at 100°C. The resulting sol-gel was then crushed in sieved at 100 mesh. Next the required amounts of Pt (from H_2PtCl6) or Pd (from $Pd(NO_3)_2$) was impregnated in the CeO_2/Al_2O_3. A few catalysts, such as Pt/Al_2O_3 were made by the single step sol-gel process (i.e. the metal precursor was incorporated into the gel). In this case, the Pt or Pd precursor was added immediately after the Ce in the sol-gel process, instead of impregnation at the end. All catalysts were dried at 373 K for 24 hrs, and calcined at 773 K for another 24 hrs. The catalysts were reduced under the conditions of: 20/80 hydrogen/helium 100 ml/min gas at 573 K.

Activity testing. The reforming of methanol was conducted using an ordinary, vertical fixed bed reactor under atmospheric pressure. A Pyrex glass tube was used as the bed. The system was charged with 60 mg of catalyst. The catalyst was held in place by a glass wool plug. The reactions took place at temperatures ranging from 433-673 K. The thermocouple tip was positioned to touch the top of the catalyst. The liquid, either pure methanol or a water-methanol mixture, was vaporized and then combined with the carrier gas, helium. The total flow rate ranged from 43,000-120,000 $ml^{-1}\ h^{-1}\ g\text{-}cat^{-1}$. The products were then separated by a HP 5710A GC with a Carbosphere 80/100 10 ft. column. The products were analyzed using a thermal conductivity detector.

Results and Discussion

Catalytic activity for methanol decomposition. Each catalyst was tested at a space velocity of 43,000 $ml^{-1}\ h^{-1}\ g\text{-}cat^{-1}$ with 14% methanol and 86% helium. The methanol conversion graphs are shown in Figures 1 & 2. The 2 wt.% Pt/Al_2O_3 sol-gel performed the worst with a 100% conversion occurring at 405°C. The presence of CeO_2 has a significant effect. The 2 % Pt-5% CeO_2/Al_2O_3 exhibited much better activity with the conversion near 100% happening around 360°C.

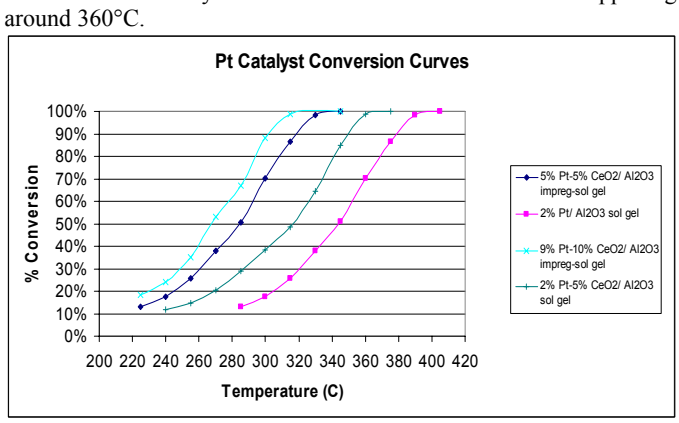

Figure 1. The decomposition curves for the Pt-based catalyst

A higher loading of Pt also has a positive effect on lowering the maximum conversion temperature. The 5% Pt catalyst performed better than the 2% while the 9% Pt catalyst was the best. The palladium catalysts performed similarly.

The 10% Pd-10%CeO_2/Al_2O_3 prepared by impregnation/sol-gel (315°C 99.8% conv.) showed higher activity than the 5% Pd-10% CeO_2/Al_2O_3 prepared by imp/sol-gel(330°C 100% conv). The preparation techniques had little effect on the 5% Pd-10% CeO_2/Al_2O_3. An imp/sol-gel and a single step sol-gel catalyst of the same formulations were made and they behave similar under the

decomposition reaction. They both reached maximum conversion at 330°C. There is also very little activity difference between the Pd

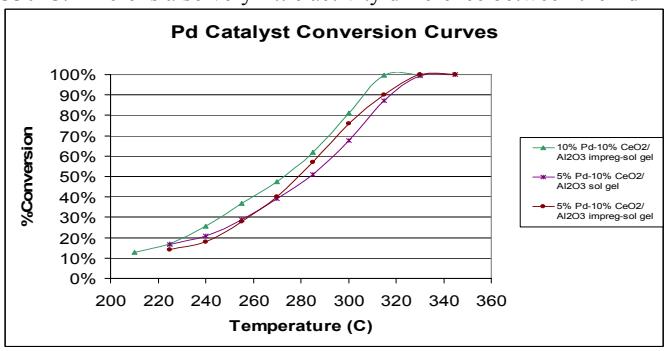

Figure 2. Decomposition curves for the Pd-based catalyst.

and the Pt catalyst. Their complete conversion temperatures are roughly the same for comparable formulations. For all of the catalysts tested the selectivity to H_2 is very high. It is over 98.3 % except for the 2% Pt/Al_2O_3 sol-gel which produces a selectivity of 91.8%.

Catalytic activity for steam reforming of methanol. The steam reforming of methanol was tested next. Two formulations of catalyst were tested; the 9% Pt-10% CeO_2 /Al_2O_3 and the 5% Pd-10% CeO_2 /Al_2O_3 both impregnation. The system was run under the condition of 115,000 ml^{-1} h^{-1} $g\text{-}cat^{-1}$ with 50% helium. The rest of the feed was made of water and the methanol. The ratio of water to methanol ranged from 1:1 and 2:1. Since the steam reforming is a combination of the decomposition followed by the water-gas shift reactions, the results will be presented in that manner. The conversion rate for the DEC and WGS will be expressed. For the Pd-based catalyst, the water seems to have very little effect on the complete conversion temperature. The curves are very similar and reach 100% conversion around 330°C. This is comparable for the no water case. For the second reaction, WGS, the conversion curves appear much different. There is no measurable steam-reforming or WGS occurring.

In the case for the Pt based catalyst, the conversion curves appear a bit different. The water does have an effect on the 100% conversion temperature. The presence of water definitely lowers that temperature. Without water the temperature is 315°C, while for the systems with water the 100% conversion temperature is approximately 290°C. The conversion curves for all the experiments containing water look virtually identical, so the amount of water seems to have little effect on the methanol conversion rates. In Figure 3, the conversions for the water-gas shift reactions are displayed. The conversion is based on the initial amount of

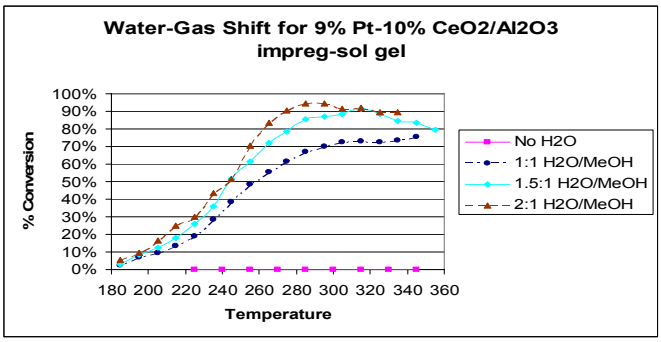

Figure 3. Water-Gas shift or SRM conversion for the Pt-catalyst

methanol. The maximum conversion depends on the amount of water initially. The 1:1 ratio reaches a maximum conversion of 75%, whereas the 1.5:1 has a maximum conversion of 92% and the 2:1 ratio has a maximum of 95%. The temperature at which the maximum conversion occurs also depends on the initial amount of water. The higher the amount of water, the lower the temperature of which the maximum conversion occur. For the 2:1 case, this temperature is 285°C, while for 1:1 case it is 345°C. The 1.5:1 case falls in between with a temperature of 315°C. The water also has an effect on the selectivity of CO_2 produced. The selectivity to CO_2 is higher for higher water to MeOH ratios. The selectivity reaches above 90% for the 1.5 and 2 H_2O:MeOH ratios and the began to level out at around 93% at temperature above 290°C.

Catalytic Activity in the Presence of Oxygen. In this set of experiments, the conditions were similar to SRM experiments except different amounts of oxygen were added. The only catalyst used is the 9% Pt-10% CeO_2 /Al_2O_3 catalyst. The conditions were the same as the reaction for 1.5:1 H_2O:MeOH runs except the appropriate amount of oxygen was added. The maximum conversion temperature is affected by the amount of oxygen present at the beginning. The 20% and 32% O_2 runs had the lowest temperature at 255°C and no O_2 had the highest at 315°C. The 6% and 10% fell in between at 305°C and 295°C, respectively. They all reached a maximum conversion of 100%.

The oxygen also had an effect on the WGS reaction. The maximum conversion is affected by the amount of oxygen present. This can be seen in Figure 4. The 32% O_2 reached the highest maximum

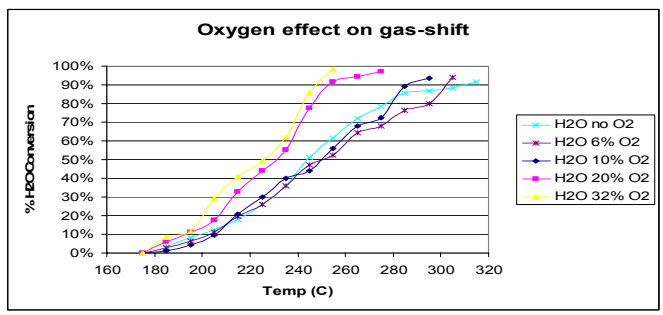

Figure 4. POX of methanol for Pt-based catalyst

conversion at 99%, while the run without oxygen reached a maximum 92%. It seems that the more oxygen present, the higher the conversion. This is not exactly true for 6% and 10% runs. The 6% and 10%, both, have a maximum conversion of 94%. The biggest effect oxygen has on the WGS reaction is at the temperature at which this maximum temperature occurs. This temperature is 255°C for the 32% O_2, which is the lowest such temperature. The no O_2 run produced the highest such temperature at 315°C. The others three fall in between this two runs. They follow the trend of the higher the oxygen content, the lower the maximum conversion temperature. The more oxygen present, the higher the selectivity to CO2. At 20 and 32% O2, the selectivity reaches very near 100% and levels out at this level for higher temperatures. In contrast, when there is no water present the maximum selectivity of CO2 reaches 92%.

References

(1) S. Velu, K. Suzuki, T. Osaki, *Chem. Commun.*, **1999**, 23, 2341.
(2) T. Takahashi, M. Inoue, T. Kai, *Appl. Catal. A-Gen.*, **2001**, 218 1-2, 189.
(3) L. Alejo, R. Lago, M. A. Pena, J. L. G. Fierro, *Appl. Catal. A-Gen.*, **1997**, 162 1-2, 281.
(4) H. Jan, I. S. Kim, H. S. Choi, *J. Power Sources*, **2000**, 86 1-2, 223.