Synthesis of a Copper Zinc Oxide Catalyst using Pre-Coated Gamma Phase Alumina Supports

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Abstract

As part of the effort to operate a fuel cell with windshield wiper fluid, the need to study steam reforming catalyst deactivation became apparent. However, there wasn't enough information about commercial grade catalysts to be able to conduct a complete study, so an effort was made to develop our own methanol steam reforming catalyst which will be used to evaluate the effects of contaminants. Typically, research grade catalysts are most commonly created and evaluate in a powdered form, and in more limited cases the catalyst powder is wash coated onto a support structure. However, in this work an alpha phase support (pellet) was precoated with a high surface area gamma phase alumina powder, then the catalyst was applied. This approach allows for the catalyst to be evaluated under a more realistic conditions, while maintaining consistency offered by the precoated support. The catalyst was evaluated at reactor temperatures between 224 and 367°C. The fuel feed was a fixed molar steam to carbon ratio of 1.23 and a volumetric flow rate of 1 ml per minute. The catalyst performed well achieving ~56% conversion as low as 224°C and achieving full conversion at ~300°C, which is consistent with literature. Carbon monoxide selectivity ranged from 0.73% at 224°C and increased to 36.94% at 367°C. This work seeks to show how the base line catalyst was developed and its performance under realistic conditions.

Keywords

Use Methanol; Steam Reforming; Catalyst; Copper Zinc Oxide

Introduction

The goal of this work is to develop a basic methanol steam reforming catalyst which can be used to evaluate the effects of contaminates found in windshield wiper fluid. Methanol steam reforming is an endothermic reaction between methanol and water to produce carbon dioxide and hydrogen.

$$CH_3OH + H_2O => CO_2 + H_2$$
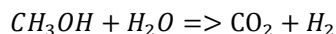
Methanol steam reforming has been an active research area for a past 40 years. Typically, research grade catalysts are most commonly created and evaluate in a powdered form, and in more limited cases the catalyst powder are wash-coated onto a support structure.

Argell [1] evaluated the effects of supports on a copper zinc oxide catalyst in powdered form. He achieved conversion at temperatures of 325°C. The catalyst had a molar copper to zinc ratio of 0.8:1. He found that the addition of zirconium oxide improved a catalyst resistance to redox cycles. Cecilia Mateos-Pedrero et al [2] evaluated how surface area and polarity of the support effected reformate composition. They achieved 97.7% conversion at 300°C with a WHSV = 0.95 hr^{-1}. They found that increasing the polarity ratio of ZnO carriers increased carbon dioxide selectivity. Cheng et al[3] evaluated the effects of magnesium doping of a copper zinc oxide catalyst at WHSV = 3.84 hr^{-1} using a powdered catalyst. He found 3-5% mg content improved hydrogen yields but decreased carbon dioxide selectivity. Chen used a molar copper to zinc ratio of 1:1. Jones et al [4] studied the influence of alumina nano particles methanol steam reforming. The reference catalyst preformed the best. It achieved full conversion at 283°C at LHSV at 2088 hr^{-1}. They used a molar copper to zinc ratio of 1:1.

Test Bed

A test stand was developed to evaluate catalysts. This test stand, shown in Figure 1 (without insulation), was built using existing components. The approach used to develop this test stand was based on a previous effort. The premixed reactants (methanol/water) are held in a 250ml flask with silicon stopper. A HPLC pump is used to draw the fuel/water mixture (S/C=1.23@ 1mlpm) from the tank and inject it into a vaporizer.

The vaporizer consisted of a cartridge heater (300W) nested inside a tube, filled with 1/8th inch dimeter stainless steel (304) ball bearings. The ball bearing served to increase the heat transfer area. The fuel water mixture temperature is directly measured after the vaporizer before being injected into the reactor.

Following vaporization, the reactants then flow into the heated reactor/ catalyst bed where they are converted into hydrogen and carbon dioxide. The tubular reactor is wrapped in 2ft off heat tape (300W). The catalyst (3.1mm pellets) are held in place with 1.5" of glass wool at either end of the reactor. The tubular reactor had an inner diameter of 0.68" and a length of 4". A thermocouple is placed inside the reactor, down the middle to provide catalyst bed temperatures. The 10 grams of catalyst were loaded into the reactor. The fuel was preheated to the same temperature as

the reactor. Under the conditions tested the reactor had a weight hourly space velocity of 5.19 hr^{-1}.
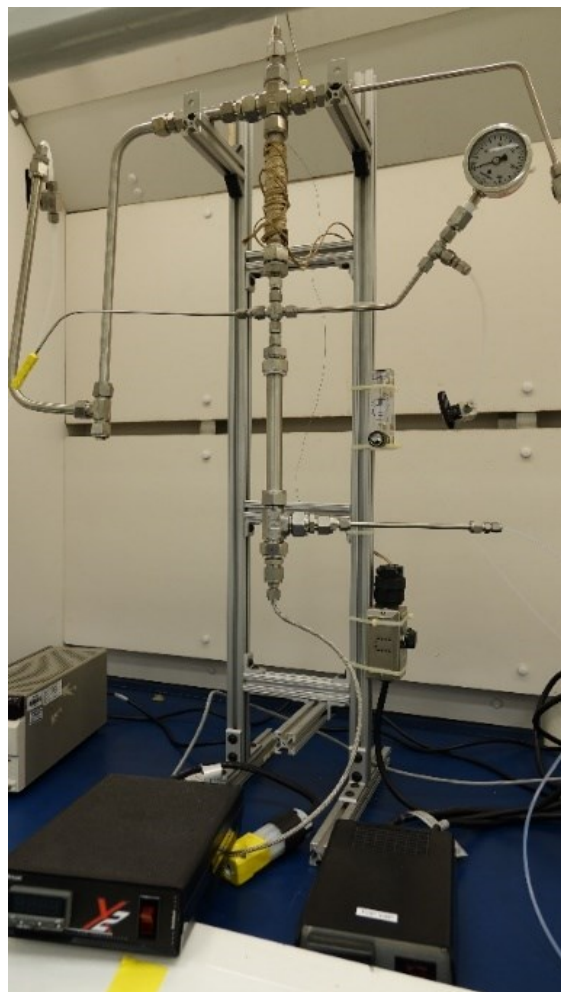
Figure 1. Test stand shown without insulation

The gasses are then cooled in a micro chiller before a sample is being processed in an online gas chromatograph (GC) Inficon Micro Fusion GC equipped with four channels. The condenser removes any potential water which would damage the capillary columns. It was configured with the refinery gas package, allowing detection of fixed gasses and hydrocarbon up to hexanes.

Process

An alumina coated pellets was selected as a support, as this material is compatible with the incipient wetness technique and provides excellent surface area as a catalyst support. The support had a high surface area of 247m^2/g and a total pore volume of 1.12 cm^3/g. The average diameter was 3.1mm. The baseline catalyst was chosen as copper nitrate and zinc nitrate were dissolved in distilled water. Based on literature a molar ratio of one part copper to one part zinc was chosen. The solution had a molarity of 1.61 mol/L. The support was then placed in a beaker and the dissolved catalyst was

dripped in. The mixture was then coated onto the pellets through incept wetness. The coated alumina supports were then dried for 12 hours at 110ºC, followed by calcination for an additional 12 hours at 350ºC. Figure 2 show the catalyst after calcination.

The catalyst was loaded into the reactor and reduced. The catalyst was then reduced within the reactor, with 5.19% hydrogen and a balance of argon at 250ºC at a flow rate of 0.1slpm for a period of 2 hrs. Following this the catalyst was allowed to cool to room temperature. After its reduced, the catalyst will turn black.


Figure 2. Catalyst prior to reduction

However, if the catalyst is exposed to oxygen for an extended period of time the catalyst begins to oxidize and will need to be reduced again. In typical applications, this is not an issue as the system typically remains sealed or limits the availability of oxygen to come into contact with the catalysts. To protect the catalyst at the end of every test all ports are sealed at the end of the experiment to prevent oxidation of the catalyst.

Results

The catalyst was evaluated at 1 mlpm of methanol water mixtures (59%$_{weight}$ methanol) at reactor temperatures of 224 to 367ºC. The maximum temperature was restricted to prevent catalyst sintering. The catalyst performed well as shown in Fig. 2. It was able to achieve full conversion between 280-300ºC.This is typical for the copper zinc oxide catalysts [1, 4] and indicates it will be a good representative baseline catalyst. The catalyst exhibited high hydrogen (73.8-76.8%) and carbon dioxide concentrations (16.5-23.0%), with low concentrations of carbon monoxide (0.0-9.6%). Higher temperatures suppressed hydrogen concentrations and promoted less favorable conditions

(higher carbon monoxide formation. This is believed to be either the result high temperatures promoting reverse water gas shift reaction or promotion of methanol cracking. Decreasing hydrogen concentrations and carbon dioxide concentrations, and increasing carbon monoxide concentrations support either assertion, as seen in Figure 3.

$$H_2 + CO_2 => CO + H_2O$$
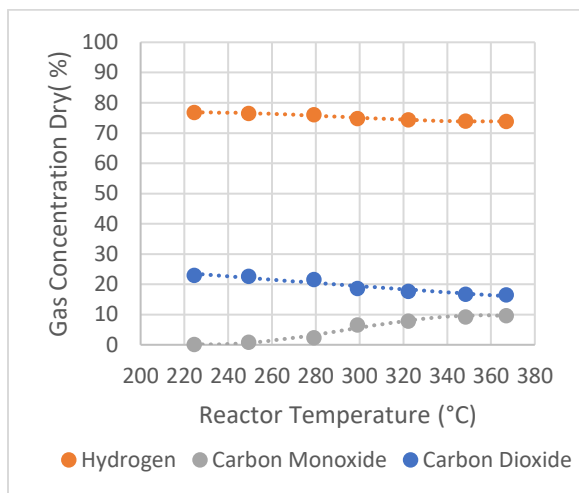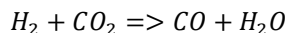
Figure 3. Reformate concentrations at reactor temperatures of 224-367ºC and a molar S/C ratio of 1.23

Figure 4 shows reforming efficiency and fuel conversion. Reforming efficiency is defined as the ratio of the energy content of the hydrogen (based on LHV) to the energy content of methanol (based on LHV) minus the enthalpy for steam reforming. Conversion is defined as the ratio of molar flow rates of carbon monoxide and carbon dioxide to the molar flow rate of methanol.

$$Conversion = \frac{Molar\ flowrate\ CO + CO_2}{Molar\ flow\ rate\ of\ CH_3OH}$$

$$Reforming\ Effiency = \frac{LHV\ (H_2)}{LHV\ CH_3OH - Heat\ SR}$$

Reforming efficiency ranged from low 60% to a high of 96.2% at 300ºC, which is typical for this catalyst. The catalyst performed well achieving ~56% conversion as low as 224°C and achieving full conversion at ~300°C, which is consistent with literature. As expected, higher reactor temperatures promoted greater conversion as a result of increased kinetic activity, which improved efficiency up until 300°C or full conversion. At reactor temperatures exceeding 300°C, the reforming efficiency decreased. This was a result of the decreasing hydrogen content, which was believed to be a result of the reverse water gas shift or the promotion of methanol cracking.
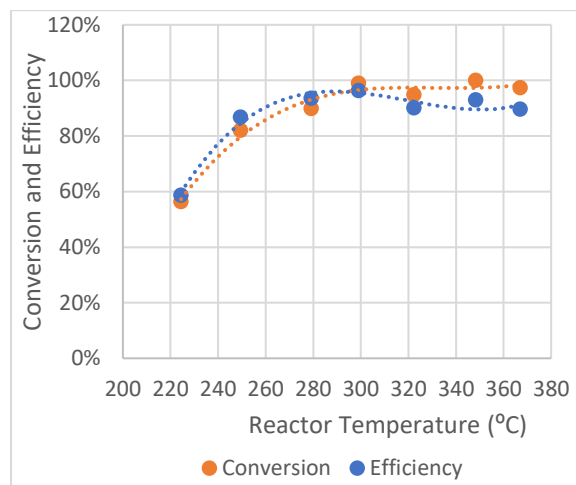
Figure 4. Conversion and efficiency at reactor temperatures of 224-367ºC and a molar S/C ratio of 1.23

Low temperatures favored higher selectivity towards carbon dioxide. At reactor temperatures of 224°C-249°C the carbon dioxide selectivity was greater than 94%. Increasing reactor temperature beyond this caused selectivity to rapidly drop, as more carbon monoxide formed. At full conversion (Reactor temperature of 300°C) carbon monoxide carbon dioxide selectivity was 73%. At reactor temperatures exceeding 348°C-367°C selectivity stabilized only varying between 63-64%. The change in selectivity at temperature above 300ºC is believed to be a result of increased active in the reverse water gas shift reaction.
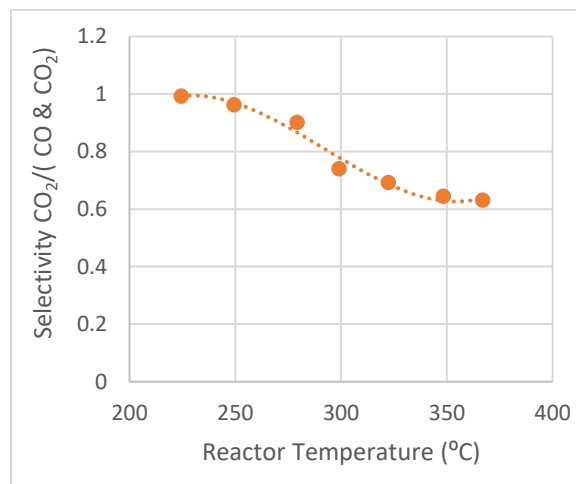
Figure 5. Carbon dioxide selectivity at reactor temperatures of 224-367ºC and a molar S/C ratio of 1.23

Conclusion

This approach demonstrated comparable efficiency to conventional methanol steam reforming catalyst, indicating that it will be a good surrogate for future work focusing on contamination. Full conversion was achieved at reactor temperatures 280-300ºC, which was comparable to what was identified in literature. This also indicated that using the

precoated support showed no adverse effects in reformate catalyst.

At full conversion, the reformate consisted of 74.7% hydrogen, 18.7% carbon dioxide and 6.6% carbon monoxide. Reforming efficiency achieved 96.2%. In a real system a water gas shift reactor would have also been included to reduce carbon monoxide concentrations. This should be sufficient for evaluating the effects of contaminants on methanol steam reforming.

At temperatures exceeding 300ºC there was a degradation in performance. It is believed that this could be the result of the reverse water gas shift or the promotion of methanol cracking over methanol steam reforming. As reactor temperature increased beyond 300°C the hydrogen and carbon dioxide concentrations, along with an increase in carbon monoxide concentrations. This could support either assertion.

References

1. J Agrell, H Birgersson, M Boutonnet, I Melián-Cabrera, R.M Navarro, J.L.G Fierro, "Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO2 and Al2O3", Journal of Catalysis, Volume 219, Issue 2, 2003, Pages 389-403
2. Cecilia Mateos-Pedrero, Hugo Silva, David A. Pacheco Tanaka, Simona Liguori, Adolfo Iulianelli, Angelo Basile, Adelio Mendes, "CuO/ZnO catalysts for methanol steam reforming: The role of the support polarity ratio and surface area", Applied Catalysis B: Environmental, Volumes 174–175, 2015, Pages 67-76
3. Zaizhe Cheng, Wenqiang Zhou, Guojun Lan, Xiucheng Sun, Xiaolong Wang, Chuan Jiang, Ying Li, "High-performance Cu/ZnO/Al$_2$O$_3$ catalysts for methanol steam reforming with enhanced Cu-ZnO synergy effect via magnesium assisted strategy", Journal of Energy Chemistry, Volume 63, 2021, Pages 550-557
4. Samuel D. Jones, Luke M. Neal, Helena E. Hagelin-Weaver, "Steam reforming of methanol using Cu-ZnO catalysts supported on nanoparticle alumina", Applied Catalysis B: Environmental, Volume 84, Issues 3–4, 2008, Pages 631-642