Catalyst Development for the Reforming Process of Liquid Hydrocarbons

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Introduction

Fuel cells are fast becoming a desirable source of electricity to power automobiles and light-duty trucks. They are currently used in some small stationary applications and have the potential to power residential and commercial buildings. Fuel cells, powered by hydrogen, have the potential to be the cleanest and most efficient source of electricity for use by the automotive industry. Our goal is to develop a process that will use a liquid hydrocarbon fuel as the hydrogen source in an on-board fuel cell. A problem in current reforming processes is the quantity of carbon monoxide (CO) produced. Carbon monoxide acts as a poison upon contact with the proton exchange membrane (PEM) fuel cell (Pt based) catalyst. The objective of our research is to reduce the quantity of carbon monoxide produced during reforming to near-zero levels.

Published investigations [1] have indicated that copper-based catalysts may be the optimum catalyst for use in the reforming of liquid hydrocarbons, such as methanol and petroleum-based fuels. Our earlier investigations of a selective copper-based catalyst and various modifications agree with these scientific studies and experiments. However, our initial studies were done using only methanol as a feed, while other studies have used water and methanol as a feed with a ratio between 1.0 and 1.3. In fact, our system demonstrated higher methanol conversion over an extended period of time than what was recorded in other experimental studies and research [2]. This led us to our current investigative studies, which involve using water and methanol with a volume ratio of 1.0. Our studies have indicated that methanol conversion is approximately the same as that reported in the literature [1], however, we observed higher hydrogen yields.

Experimental

The catalysts were prepared by sequential precipitation. 4.62 g $Zr(NO_3)_2O$, 1.50 g $Al(NO_3)_3{\cdot}9H_2O$, and 1.53 g $Y(NO_3)_3{\cdot}6H_2O$ were dissolved in 125 ml distilled water. The solution was heated in a 1500 ml beaker to about 70°C on a hot plate with magnetic stirring for 10 minutes. 33.34 g $Cu(NO_3)_2{\cdot}3H_2O$ in 250 ml distilled water was added dropwise to the solution while a pH of 7 was maintained using Na_2CO_3 solution. A pH meter was used to monitor pH while adjustments were made by adding the Na_2CO_3 with a dropper as needed. After approximately 20 minutes, 10.14 g $Zn(NO_3)_2{\cdot}6H_2O$ in 125 ml distilled water was added dropwise over a 15 minute interval to the solution. The pH was maintained at 7 using the same Na_2CO_3 solution. The product was recovered by filtration using a Büchner funnel and aspirator. The product was washed three times with distilled water. The sample was dried at 120°C over night followed by calcination in air at 350°C for 6 hours.

All reactions were conducted in a 0.5 inch od x 0.375 inch id (1.27 cm od x 0.95 cm id) x 10 inch (25.4 cm) 304 stainless steel reactor. The inside wall of the reactor was coated with Restek Corporation's Silcocteel® coating. The catalyst was supported in the reactor between quartz-wool plugs and the reactor was operated in an up-flow configuration. A gold-plated thermocouple in the center of the catalyst bed was used to control the temperature of reaction to ±0.5°C. Brooks proportional ratio mass-flow controllers were used to feed the gases to the reactor. An Isco high-pressure syringe pump controlled feeds of liquids to the reactor. The feeds were preheated to approximately 130°C prior to entering the reactor and the products of reaction were heated to approximately 150°C between the exit of the reactor and the cold trap, which was maintained at –4°C.

Reaction conditions were as follows: 1.0000 grams of catalyst were placed in the reactor supported between deactivated-quartz wool plugs such that the tip of the thermocouple was located in the middle of the catalyst bed. The reactor was purged with helium at 5 mL/min for at least 2 hours. The temperature of the reactor was increased to either 150 or 255 °C. Methanol flow was begun, at a weight hourly space velocity of 1 hr^{-1}, after the catalyst had reached the desired temperature.

Products of reaction were directly sampled and analyzed by an online dual-column gas chromatograph (GC). The GC, a Hewlett-Packard 5890 Series II, was equipped with a 6 ft x 0.125 od 80/100 Porapak Q and a 20 ft x 0.125 od 60/80 Molecular Sieve 5A (both obtained from Supelco). The GC was held at a constant temperature of 100°C during elution. Argon was used as the carrier gas having an average linear velocity, at 30°C, of 30 mL/min for the Molecular Sieve column and 50 mL/min for the Porapak Q column. The Molecular sieve column was used to separate the light gaseous products while the Porapak Q column was used to identify unreacted liquid hydrocarbons. Both columns were equipped with back-flushing capability. Dual thermal conductivity detectors (TCD's) were employed to detect the separated components.

Results and Discussion

Reforming of methanol was done using methanol only and then using methanol and water with a 1:1 volume basis. Reforming of methanol only was run at various reaction temperatures. Table I list the data from a series of those methanol-reforming reactions.

TABLE I Results of Methanol Reforming Reactions

Catalyst	Temp. (°C)	CH_3OH Conversion	H_2 (%)	CO_2 (%)	CO (%)
Cu/Zn/Zr/Al/Y*	150	21.2	8.9	91.1	0.0
Cu/Zn/Zr/Al/Y*	255	72.2	91.1	8.9	0.0
Cu/Zn/Zr/Al/Y**	255	49.1	77.6	16.6	5.8
Cu/Zn/Ce/on ã-Al_2O_3	255	85.1	47.2	22.5	29.3
Cu/Zr/ on ã-Al_2O_3	255	80.9	53.5	40.6	5.9
Cu/Zn/Zr/ on ã-Al_2O_3	255	90.5	45.5	35.2	19.3

* 69/17/10/2/2 mole percent. ** 8/2/64/13/13 mole percent.

As is shown in Table I, methanol conversion increases with reaction temperature. For the Cu/Zn/Zr/Al/Y (69/17/10/2/2 mole

percent) catalyst at 150°C, methanol conversion was approximately 21%. The majority of product detected by the GC was carbon dioxide. When the reaction temperature was increased to 255°C, conversion of methanol increased initially to 80%. The product selectivity also increased, with hydrogen comprising approximately half of the detected product.

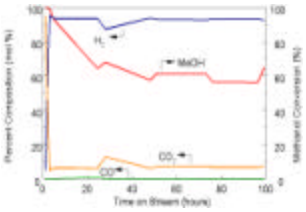

Figure 1 Results of methanol conversion over Cu/Zn/Zr/Al/Y catalyst as a function of time.

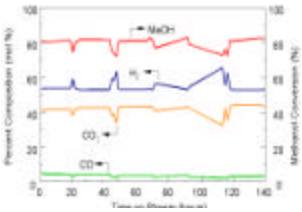

Figure 2 Results of methanol Cu/Zr on ã-Al_2O_3 catalyst as a function of time.

Figure 1 shows an extended conversion run for the Cu/Zn/Zr/Al/Y (69/17/10/2/2 mole percent) catalyst. As is shown in Figure 1, conversion of methanol at 255°C decreased with time on stream. This is due to coke formation during the reaction.

When compared to the literature values [1], our catalyst gave similar results. Conversion of methanol was low at 150°C and increased with increasing temperature. Conversions of methanol at 250°C were greater than 50% in both cases. Differences arise when the product slate is examined. Our catalyst produced larger quantities of carbon dioxide than those reported in the literature.

Of importance is that carbon monoxide was not detected at either reaction temperature in our investigation or in the literature with the Cu/Zn/Zr/Al/Y catalyst.

Figure 2 shows an extended conversion run for the Cu/Zr on ã-Al_2O_3 (7/3/90 mole percent) catalyst. As is shown in Figure 2, conversion of methanol at 255°C is relatively stable with time on stream as are the products produced. This catalyst did exhibit CO production at 255°C, however coking was much less than that observed with the Cu/Zn/Zr/Al/Y catalyst.

The same group of catalysts was run using a 1:1 volume methanol/water feed and a reaction temperature of 250°C. The results of reactions of methanol and water are listed in Table II. As is shown in Table II, conversion of methanol for all the catalysts except the low surface area Cu/Zn/Zr/Al/Y were greater than 99%. Product selectivity for the experiments using water and methanol as a co-feed exhibited lower carbon monoxide levels than the experiments with methanol alone..

Figure 3 shows an extended conversion run for a 1:1 methanol/water reaction over the Cu/Zn/Zr/ on ã-Al_2O_3 (12/2.5/2.5/83 mole percent) catalyst. As is shown in Figure 3, conversion of methanol at 255°C remains constant with time on stream. Of importance is that carbon monoxide was almost nonexistent at either reaction temperature in our investigation with the Cu/Zn/Zr/ on ã-Al_2O_3 catalyst. Note that carbon monoxide was not observed in the methanol/water reactions when it was observed for the methanol only reactions.

When using methanol and water as a co-feed and the higher temperature of 250°C, methanol conversions increased by another 50%.

TABLE II Results of Methanol/Water Reforming Reactions

Catalyst	Temp. (°C)	CH_3OH Conversion	H_2 (%)	CO_2 (%)	CO (%)
Cu/Zn/Zr/Al/Y*	250	100	59.0	35.8	4.3
Cu/Zn/Zr/Al/Y**	250	21.2	7.9	4.8	0.0
Cu/Zn/Ce/on ã-Al_2O_3	250	99.0	57.6	38.5	3.7
Cu/Zr/ on ã-Al_2O_3	250	99.4	43.2	30.4	1.1
Cu/Zn/Zr/ on ã-Al_2O_3	250	99.7	60.9	38.0	0.98

* 69/17/10/2/2 mole percent. ** 8/2/64/13/13 mole percent.

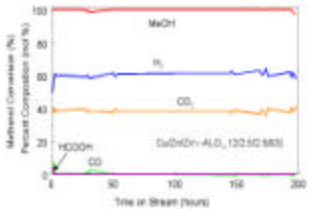

Figure 3 Results of methanol/water conversion over Cu/Zn/Zr on ã-Al_2O_3 catalyst as a function of time.

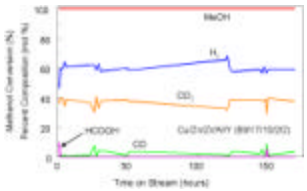

Figure 4 Results of methanol/water conversion over Cu/Zn/Zr/Al/Y catalyst as a function of time.

Figure 4 shows an extended conversion run for a 1:1 methanol/water reaction over the Cu/Zn/Zr/Al/Y (69/17/10/2/2 mole percent) catalyst. As is shown in Figure 4, conversion of methanol at 255°C is relatively stable with time on stream as are the products produced. This catalyst did exhibit CO production at 255°C, however coking was not observed.

Table III Catalyst Surface Area

Catalyst Composition (mole %)	Surface Area (as prepared) (m^2/gm)	Surface Area (after reaction) (m^2/gm)	Surface Area (after reaction w/H_2O) (m^2/gm)
Cu/Zn/Zr/Al/Y 69/17/10/2/2	92	55	57
Cu/Zn/Zr/Al/Y 8/2/64/13/13	21	16	
Cu/Zr/ ã-Al_2O_3 12/5/83	200	188	
Cu/Zn/Zr/ ã-Al_2O_3 12/2.5/2.5/83	198	187	186
Cu/Zn/Ce/ ã-Al_2O_3 12/2.5/2.5/83	194	195	194

Table III shows the surface area of the catalyst as prepared, after 150 of reaction with methanol reforming, and after 150 hours of

methanol/water reforming. As is shown in Table III, both catalyst preparations of Cu/Zn/Zr/Al/Y exhibit a loss of surface area after reaction due to coking. The three catalysts supported on ã-Al_2O_3 retain more than 90% of there as prepared surface area. These catalysts were also the most stable of all the catalysts that we tested.

Conclusions

We have synthesized several catalysts that are capable of reforming methanol at moderate temperatures. The main products of reaction are hydrogen and carbon dioxide. Our results agree well with those reported in the literature [1]. We observed higher selectivity of H_2 with our catalysts without the need for the water-gas shift reaction. However, by employing the WGS reaction we detect a decrease in the selectivity of CO and CO_2. A direct correlation between the catalyst's surface area, methanol conversion, and catalyst stability is also observed.

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Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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