

Hydrogen Production via Methanol – Steam Reforming using Catalysts containing a Hydrotalcite Phase Structure

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Abstract

Steam reformation of methanol is an actively studied process for supplying hydrogen rich fuel gas to proton-exchange membrane (PEM) fuel cells. The purpose of the present investigation is to improve activity and thermal stability of our optimized Cu/Zn/Al formulation. Cu/Zn/Cr, Cu/Zn/Cr/Al, Cu/Zn/Ce, Cu/Zn/Ce/Al, Cu/Zn/La and Cu/Zn/La/Al were prepared at different calcination temperatures. The catalysts were thoroughly characterized and activity studies were run at 250°C with 1:1 methanol/steam using a pulse reformer. Characterization results indicate that the hydrotalcite skeletal structure is still intact in catalysts calcined up to 300°C. The activity of the Cu/Zn/Cr catalyst calcined at 300°C of the calcination series was significantly higher than for any other catalyst series in the study with very little deactivation during the duration of the run. Activity studies using a high pressure reactor also showed superior activity for the Cu/Zn/Cr catalyst with analysis of the spent catalyst indicating very little structural damage.

1. Introduction

With growing support for environmental issues, there is incentive to develop an efficient, clean electric power system to operate stationary power plants and vehicles such as cars, buses and submarines. The increased interest is caused both by a search for an alternative energy source for the decreasing supply of fossil fuels and the increasingly stringent regulations for emission levels that are coming into effect in many parts of the world. A promising system actively being developed is the hydrogen fed Proton Exchange Membrane (PEM) fuel cell. The many benefits include a significant increase in energy efficiency and reduction of emissions by as much as 90%; specifically reducing CO₂ emissions by 40%[1]. A liquid fuel is the desirable form for transport and storage of hydrogen. Steam reformation of methanol is the most widely studied system for production of hydrogen rich gas to be utilized at the anode of a PEM fuel cell as compared to hydrocarbon reformation and steam reformation of ethanol[2,3]. Methanol, as a reactant in steam reformation, is a relatively inexpensive renewable fuel that produces less environmentally harmful products than the internal combustion of conventional petroleum fuel. We have developed an improved CuO/ZnO/Al₂O₃ catalyst for methanol steam reforming. Our latest formulation gives higher activities than commercial catalysts for the range of temperatures and time on line investigated [4,5].

Experience with our optimal catalyst showed that enhanced activity was correlated with the presence of hydrotalcite structure, therefore other elements that can be incorporated in a hydrotalcite structure may also show high activity and possibly higher thermal stability. Also, structures that resisted sintering would lower the rate of deactivation of a proposed catalyst. Cerium, Chromium and Lanthanum were incorporated in some catalyst formulations. These elements have potential to form hydrotalcite structures with Cu and Zn with or without Al present. Lanthanum has also been used to improve thermal stability of catalysts. The principle is that the small sized La atoms fit between the atoms in the phase structure and act as a physical block to inhibit sintering. Modified catalysts of Cu/Zn/Ce, Cu/Zn/Ce/Al, Cu/Zn/Cr, Cu/Zn/Cr/Al, Cu/Zn/La and Cu/Zn/La/Al were prepared at different calcination temperatures.

2. Experimental

2.1 Catalyst Preparation

The catalyst was prepared by a coprecipitation method using a dilute mixed Cu, Zn, X (X=Al,Ce,Cr,La) - nitrate solution and a solution of Na₂CO₃. The two solutions were simultaneously added to distilled water with vigorous stirring, using pumps whose flow rates were adjusted to keep the pH of the resulting mixture precisely at 7.0. The precipitate was filtered, washed, reslurried, then filtered again before drying at 110°C for 16 hrs. The precursor was crushed into smaller particles, then calcined in air at the specified temperature (300, 400, 550 or 650°C) for 6 hrs.

2.2 Catalyst Characterization

The catalyst series were characterized using thermal gravimetric analysis (TGA), x-ray powder diffraction (XRD) for phase structure analysis, N₂ adsorption for total surface area and CO chemisorption for copper surface area. Copper dispersion was calculated from the results of copper content and copper surface area. Surface studies were carried out using diffuse reflectance infrared fourier transform spectroscopy (DRIFTS).

TGA analyses were done using a TA Instruments Thermograph Model 2050 controlled by a Thermal Analyst 3000 computer. The He flow rate was 100 ml/min. The temperature was increased at 10°C/min. The first derivatives of the TGA curves (%Mass vs. Temperature) were calculated and used to determine the decomposition profile for the precursor phase structure.

XRD powder patterns were obtained using a Scintag diffractometer. Scans were taken at a 2θ step size of 0.03° between 10 and 60° using Cu-Kα₁ (nickel filtered) radiation. Cu and Zn crystallite sizes were calculated from the line broadening of the CuO(111) and ZnO(101) lines respectively using the Debye-Scherrer Method.

2.3 Study of Catalyst deactivation

The high pressure test reactor used for part of the activity studies was a fully automated tubular fixed-bed reactor. The catalyst was pelletized and screened to obtain a particle size distribution of 20-25 mesh. A

1.0 g sample of the catalyst material was diluted in α - Al_2O_3 of identical mesh size to ensure that uniform plug flow and isothermal operation were achieved.

The catalyst was activated at 240°C in 1:1 molar methanol-steam vapour. The liquid hourly space velocity (LHSV) was 47 h^{-1} assuming a catalyst bulk density of 1.2 kg L^{-1} . After two hours of conditioning at 240°C a steady-state conversion was achieved and the catalyst was considered to be fully activated. The temperature of the reactor was then increased to 280°C and operated continuously for the duration of the test.

The pulse reformer consisted of a reactor containing 15 mg of catalyst and 200mg of alpha alumina. Twenty five, 10 microlitre pulses of 1:1 methanol/water were passed through the catalyst bed in a stream of UHP helium at a flow rate of 35 ml/min . The reaction temperature was 250 C. The product gas was separated on a Porapak Q column in a Gow Mac Gas Chromatograph using a TCD detector.

3. Results and Discussion

3.1 Aluminum Containing Series

Cu/Zn/Al precursor, prepared using the optimal preparation procedure, was calcined in air at specified temperatures (300, 400, 550 and 650°C) for 6 hrs. The calcined catalysts were thoroughly characterized and activity studies were carried out. TGA results indicated that residual hydrotalcite was present for catalysts calcined at temperatures of 400°C or below. The hydrotalcite phase partially reformed in catalysts that were placed in water except for the catalyst calcined at 650°C. Very little hydrotalcite

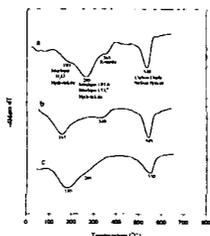


Figure 1. First derivative of TGA curve for Cu/Zn/Al a) precursor; b) catalyst calcined at 300°C; c) after reconstitution of b).

reformed for the catalyst calcined at 550°C. In an environment of 1:1 steam/methanol it is conceivable that the hydrotalcite structure would have the ability to be in dynamic equilibrium with its reaction environment. CuO and ZnO were observed as very weak peaks for the catalyst calcined at 400°C. These peaks grew larger as the calcination temperature of the catalyst increased with appearance of ZnAl_2O_4 for the catalyst calcined at 650°C. An XPS study of the catalyst series clearly showed the change from the full hydrotalcite structure to an oxycarbonate followed by formation of oxide. There was strong correlation between high catalyst activity and presence of the hydrotalcite phase, either as the fully developed phase structure, as seen in the precursor, or as a partially decomposed (dehydroxylated) phase as observed in the catalysts calcined at 300°C and 400°C. The activities, with respect to methanol-steam reforming of the precursor and catalysts calcined at 300°C and 400°C were similar and significantly higher than for the

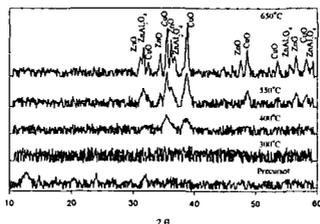


Figure 2. XRD profiles for Cu/Zn/Al catalyst series calcined at various temperatures.

catalysts calcined at higher temperatures which contained significantly less residual hydrotalcite structure. Presence of hydrotalcite in the catalyst structure appears to be imperative in obtaining a catalyst with optimum activity.

3.2 Lanthanum and Cerium Containing Series

The TGA curves for the Cu/Zn/La, Cu/Zn/La/Al, Cu/Zn/Ce and Cu/Zn/Ce/Al catalyst series were very similar. A large proportion of the precursor consisted of the hydrotalcite phase with some rosasite as observed by the presence of their respective characteristic decomposition temperatures. A very large peak was observed in the 1st derivative of the TGA curves at approximately 500°C which was due to decomposition of surface carbon oxides. TPD (temperature programmed desorption) experiments in which

samples of the desorbing gases were analysed by mass spectrometry for each range of temperature, confirmed the assignment of the peaks from the 1st derivative of the TGA curves.

For these catalyst series, the precursors were XRD amorphous. A broad peak was observed between 34° and 36° 2θ for the catalysts calcined at 300°C which became more intense for the catalysts calcined at 400°C. Peaks for CuO and ZnO were observed for catalysts calcined at 550°C and 650°C. The activities of the Cu/Zn/La and Cu/Zn/Ce series were similar to the Cu/Zn/Al series as were the rates of deactivation. The precursor and catalysts calcined at 300°C and 400°C had the highest activities.

3.3 Chromium-Containing Catalysts

From TGA and TPD results the presence of a hydrotalcite structure was confirmed in precursors for both the Cu/Zn/Cr and Cu/Zn/Cr/Al formulations. The broad overlapping decomposition temperature range for the intralayer OH and interlayer CO₃²⁻ was shifted to a lower temperature centred at 210°C for the Cu/Zn/Cr/Al precursor and 190°C for the Cu/Zn/Cr precursor. Upon placing samples calcined at 300°C in water, reconstitution of the hydrotalcite was observed as with the other formulations. Very little surface carbon oxide species were present on the Cr catalyst series compared to any other catalysts studied. Also, the decomposition temperature for the surface carbon oxide species was shifted to a lower temperature of 440°C for the Cu/Zn/Cr precursor compared to 540°C for the Cu/Zn/Cr/Al precursor. In the XRD profiles,

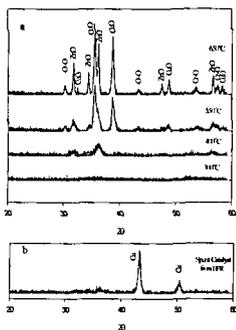


Figure 3. XRD profiles for a) Cu/Zn/Cr series calcined at various temperatures; b) spent Cu/Zn/Cr catalyst calcined at 300°C. The catalyst was removed from the high pressure reactor after 7 days at 280°C.

shown in Figure 3, the catalyst calcined at 300°C was XRD amorphous, as well as the precursor whose XRD profile is not shown. Very broad peaks attributed to zincite (ZnO) were observed for the catalyst calcined at 400°C. The ZnO crystallites were much smaller in the Cu/Zn/Cr catalyst than in the Cu/Zn/Cr/Al catalyst. Tenorite (CuO) was not observed until 550°C. CuO appears to be highly dispersed (XRD amorphous). Chromium oxide appeared only in the catalysts calcined at 550°C and 650°C.

The low quantity of surface carbon oxides observed by FTIR indicates that Cr containing catalyst formulations are less basic than the other catalysts studied. Bands due to OH groups and hydrogen bonding between the interlayer hydroxy groups and carbonates of hydrotalcite were present.

The activity of the Cu/Zn/Cr catalyst calcined at 300°C was higher than the Cu/Zn/Al catalyst with very little deactivation during the duration of the run. The activity study of the Cr series is shown in Figure 4. The activities of the Cu/Zn/Cr/Al series was similar to that of the Cu/Zn/Al series except that the catalyst calcined at 550°C also had a high activity as the same series of catalysts calcined at lower temperatures.

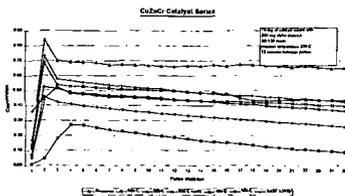
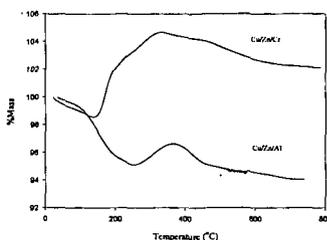


Figure 4. Deactivation study of the Cu/Zn/Cr series using a pulse reformer. Reaction was carried out at 250°C With 1:1 methanol/steam and pulses every 12 minutes.

4. Characterization of Spent Catalysts

4.1 Cu/Zn/Al

Characterization of the spent Cu/Zn/Al catalyst was carried out on the catalyst calcined at 300°C since it was the catalyst in the series with the highest activity. The XRD profile showed the presence of relatively large crystallites of zincite. No tenorite was observed, so if any CuO was present it was



amorphous or XRD invisible. Metallic Cu was observed in the XRD profiles and was evidently stable to air at room temperature. The very low weight loss of the spent catalysts in comparison to the fresh catalysts, observed in the TGA, indicated that very little hydroxycarbonate phases had remained intact after

Figure 5. TGA curves for the spent Cu/Zn/Cr and Cu/Zn/Al catalysts calcined at 300°C. The Cu/Zn/Cr catalyst was run at 280°C for 170 hours while the Cu/Zn/Al catalyst was run at 240°C in a high pressure reactor. The reactant feed was 1:1 methanol steam.

completion of the reaction run. A weight loss of 7% was observed compared to 18% for the fresh catalyst. The initial decrease in the TGA scan of the spent catalyst coincided with those found for the precursor hydroxalcalite representing decomposition of interlayer H₂O and intralayer OH/interlayer CO₃²⁻. The structure of the spent catalysts was considerably changed compared to the fresh catalyst. A gain in mass was observed beginning at 230°C (Figure 5) in the TGA curve. The mass increase was the result of formation of CuO from Cu metal during heating in air.

4.2. Cu/Zn/Cr

The Cu/Zn/Cr spent catalyst that was characterized was calcined at 300°C and run in the high pressure reactor for 170 hours at 280°C in a 1:1 ratio of methanol/steam reactant flow. The XRD profile of the spent Cu/Zn/Cr catalyst is shown in Figure 3b. Cu metal was the only phase observed. Crystallite size was determined using the Debye-Scherrer method and was found to be 19 nm. ZnO was not observed in the spent Cu/Zn/Cr. TGA analysis, shown in Figure 5, indicated that stable Cu metal began oxidizing at 190°C. A mass increase of more than 5% was observed.

5. Conclusions

The most active catalyst formulation was Cu/Zn/Cr. The catalyst calcined at 300°C gave the highest activity of any catalyst. In all cases, the catalyst calcined at 300°C gave higher activities than catalysts in the same calcination series. The Cu/Zn/Cr catalyst calcined at 300°C showed very little deactivation in the activity studies for reactions run in the pulse reformer and the high pressure reactor. Analyses of the spent catalysts gave very interesting results. For the Cu/Zn/Al catalyst, relatively large ZnO and Cu metal crystallites were observed by XRD. Whereas with the Cu/Zn/Cr spent catalyst, only crystallites of Cu metal were observed. The ZnO remained well dispersed during the test reaction using the high pressure reactor. Also, the Cu metal appeared to be more active in the Cu/Zn/Cr spent catalyst as observed in Figure 5 where oxidation of Cu metal during the TGA run occurred at a much lower temperature and in much greater abundance than for the Cu/Zn/Al spent catalyst. These findings help to identify the differences in the Cu/Zn/Cr catalyst, calcined at 300°C and may indicate why this catalyst has significantly higher activity and thermal stability.

References

1. P. Patil, P. Zegers, J. Power Sources 49 (1994) 169.
2. B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Methanol-Steam Reforming on Cu/ZnO/Al₂O₃, Part I: The Reaction Network, Appl. Catal., submitted for publication.
3. B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Methanol-Steam Reforming on Cu/ZnO/Al₂O₃, Part 2: A Comprehensive Kinetic Model, Appl. Catal., submitted for publication.
4. B.A. Peppley, "A Comprehensive Kinetic Model of Methanol-Steam Reforming on Cu/ZnO/Al₂O₃ catalyst". Ph.D. Thesis, Royal Military College of Canada, Kingston, Ontario, Canada, (1997).
5. R.O. Idem and N.N. Bakhshi, Chem. Eng. Sci. 51 (1996) 3697.