

## Hydrogen Production From Methanol: Experiments And Mechanistic Kinetic Modeling

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### Introduction

Hydrogen will play a major role in the future as a carbon free energy carrier. Its use in vehicles via PEM fuel cells offers no toxic emissions and higher efficiencies compared to internal combustion engines, however efficient and safe storage of hydrogen with high energy density is still facing some technical problems. One promising solution is, on board production of hydrogen using organic liquids, among them methanol offers several advantages for the hydrogen production via steam reforming of methanol (SRM) [1].



In the present study kinetic model of steam reforming of methanol over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst has been developed by Langmuir-Hinshelwood approach to predict the methanol conversion as well as hydrogen production and CO formation, which is useful for the accurate design of reformer. The reaction mechanism was studied and a kinetic analysis was undertaken to determine the rate constants and the activation energies for the model reactions. The H<sub>2</sub> yield was improved by developing appropriate catalyst and optimizing process parameters.

### Materials and Methods

The details of catalyst preparation and characterization have been reported in our earlier publication [2]. SRM reaction was carried out at an atmospheric pressure using fixed-bed reactor. The average particle size 0.6 mm was selected for all the kinetic experiments. Preliminary runs were also carried out to achieve the negligible film diffusion effect on kinetic data. The plug flow conditions were maintained by keeping L/Dp ≥ 50 and D/Dp ≥ 30. The kinetic data were collected by varying contact-time (W/F) 3-15 kg<sub>cat</sub> s mol<sub>methanol</sub><sup>-1</sup>, temperature 493-573 K and steam to methanol (S/M) molar ratio 1-1.8 at atmospheric pressure. All the kinetic data were collected ensuring there was no deactivation of catalyst.

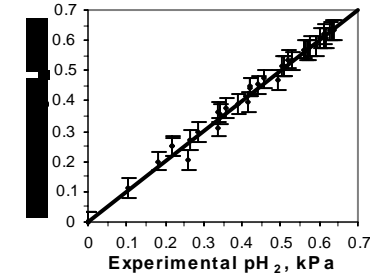
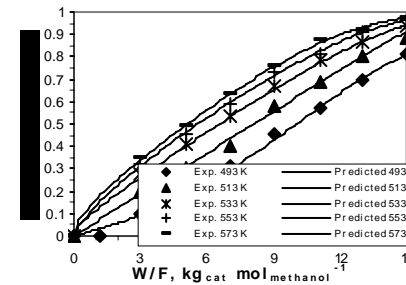
### Results and Discussion

The catalyst with composition Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>:10/5/85 wt% prepared by wet impregnation method with BET surface area 158 m<sup>2</sup> g<sup>-1</sup> was the most active; hence further detailed study has been done for it. Two distinct active sites, one for the oxygen or carbon containing species and another for H<sub>2</sub> on the surface of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst are taken, which is also proposed by Peppley et al. [3]. In addition to the SRM reaction (Eq.1) reverse water gas shift reaction (rWGS) is also considered for the kinetic modeling. There are eleven elementary reactions proposed including rate determining reactions. The elementary reactions were written in terms of known concentrations with equilibrium constants were lumped to reduce the no of parameters. The final rate expressions derived are as following:

$$r_{SRM} = \frac{k_r K_{O^{(1)}} K_{CH_2O^{(1)}} \left( \frac{P_{CH_3OH} P_{H_2O}}{P_{H_2}^2} \right) \left[ 1 - \left( \frac{P_{H_2}^3 P_{CO_2}}{K_r^* P_{CH_3OH} P_{H_2O}} \right) \right]}{\left[ 1 + \frac{K_{CH_2O^{(1)}} P_{CH_3OH}}{P_{H_2}^{1/2}} + \frac{K_{OH^{(1)}} P_{H_2O}}{P_{H_2}^{1/2}} + \frac{K_{O^{(1)}} P_{H_2O}}{P_{H_2}} + \frac{K_{CH_2O^{(1)}} P_{CH_3OH}}{P_{H_2}} + K_{HCOO^{(1)}} P_{H_2} P_{CO_2} \right]^2 C_T^2}$$

$$r_{rWGS} = \frac{k_{rw} \left( K_{HCOO^{(1)}} P_{H_2}^{1/2} P_{CO_2} \right) \left[ 1 - \left( \frac{P_{H_2O} P_{CO}}{K_{rw}^* P_{H_2} P_{CO_2}} \right) \right]}{\left[ 1 + \frac{K_{CH_2O^{(1)}} P_{CH_3OH}}{P_{H_2}^{1/2}} + \frac{K_{OH^{(1)}} P_{H_2O}}{P_{H_2}^{1/2}} + \frac{K_{O^{(1)}} P_{H_2O}}{P_{H_2}} + \frac{K_{CH_2O^{(1)}} P_{CH_3OH}}{P_{H_2}} + K_{HCOO^{(1)}} P_{H_2} P_{CO_2} \right]^2 C_T^2}$$

Kinetic parameters of the multi-response nonlinear mechanistic kinetic model were estimated using a nonlinear least-square regression by fitting the expression to experimental data.



**Figure 1.** Experiment and predicted methanol conversion at different temperatures. **Figure 2.** Parity plot of hydrogen rate conversion at different temperatures.

### Significance

A kinetic model developed for SRM over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> can predict the methanol conversion and, hydrogen and CO formation for a wide range of operating conditions, which is quite useful for the design of hydrogen (produced on-board by methanol reforming) based PEM fuel cell vehicles. The concentration of CO in the product gas was less than 0.8% and was always well below the equilibrium CO concentration of the reverse WGS, in support of the reaction sequence of methanol steam reforming followed by the rWGS.

### References

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3. Peppley, B.A., Amphlett, J.C., Kearns, L.M., and Mann, R.F., Appl. Catal. A 179, 31 (1999).