Trade Science Inc.

December 2007
Volume 2 Issue 3

CHEMICAL TECHNOLOGY
An Indian Journal

Full Paper

CTAIJ 2(3) 2007 [94-99]

Study of methanol steam reforming kinetics on BASF-V1766 commercial catalyst

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Received: 28th November, 2007 ; Accepted: 3rd December, 2007

ABSTRACT

High purity hydrogen production is an integral part of a modern fuel cell package. Steam reforming of methanol has become commercially viable process fro hydrogen production. Experiments have been carried out to study the kinetics of the methanol steam reforming over a commercial catalyst BASF V1766 containing 50%(wt) CuO and 30%(wt) ZnO in an integral reactor under conditions of no diffusion limitation. Preliminary experiments were carried out to obtain the catalyst size and feed space velocities for exclision of mass and heat transfer resistances. The experiments demonstrated that both H_2 and CO_2 are formed as primary products, and the rate of methane disappearance is proportional to the partial pressure of methanol, H_2 and CO_2 even at low product concentrations. In all experiments carried out there was no CO formation and thus CO_2 selectivity is 100% in the range of 523.15 to 583.15K. The following power law kinetic expression for the reforming reactions was developed and parameters were obtained by nonlinear regression fit to the experimental data.

$$-r_{MeOH} = k_0 \exp(\frac{-E}{RT}) P_{MeOH}^{0.59} P_{H_2O}^{0.42} P_{H_2}^{-0.22} P_{CO_2}^{-0.05}$$

The kinetic model developed was compared with previous works and the difference in the amount of Cu/Zn in the catalyst was a contributory factor to the observed differences between the present and previous studies.

KEYWORDS

Methanol steam reforming;
Kinetic model;
Hydrogen;
Integral reactor;
Power law.

INTRODUCTION

Methanol steam reforming on solid catalysts is the well-established commercial process for the production of hydrogen especially in fuel cell applications. The simulation and optimal design of the commercial process requires information on the intrinsic kinetics.

A considerable effort has been put into investigations of the kinetics of methanol steam reforming since the early 1970s[1,2]. Methanol steam reforming is a quite complex process. It not only involves the transfer and diffusion of reactants and products between the bulk phase and catalyst surface as well as within the catalyst, but also reactions occurring simultaneously in parallel or in series. Since reported studies of the kinetics of the methanol–steam reaction were carried out with catalysts of different compositions prepared by various methods and of different particle size, and over wide ranges of temperature and pressure, it is not surprising that different mechanisms and kinetics have been suggested. The reasons for this are two-fold (1) the change of catalyst composition changes not only the values of the parameters of the kinetic model, but also the structure of the kinetic model via changes in the mechanism; (2) the effects of the diffusion limitation in some experiments often result in misunderstanding of the kinetic mechanism[3]. This makes it impossible to develop generalized kinetics, which can be applied to different catalysts with only a change in parameters to suit each catalyst.

The kinetics of methanol steam reforming in the literature has been discussed involving two mechanisms; the decomposition-Water Gas Shift ñúõ(WGS) reaction and the methyl formate intermediate reaction scheme. In the decomposition-WGS reaction scheme [4-7], the overall reaction for methanol steam reforming is considered to occur through methanol decomposition, followed by the water gas shift reaction, in which CO_2 and H_2 are produced from CO formed in the decomposition step. Additionally it is assumed that the active sites for methanol decomposition are distinct from the sites at which the steam reforming and WGS reactions take place.

$$\mathbf{CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2}$$
$$\mathbf{CH_3OH \leftrightarrow CO + 2H_2}$$
$$\mathbf{CO + H_2O \leftrightarrow CO_2 + H_2}$$

In the methyl formate intermediate scheme[8,9] the WGS reaction, along with the production of CO through methanol decomposition, is ruled out. Instead, methyl formate is proposed as the only stable intermediate and by-product present

$$\mathbf{2CH_3OH \rightarrow CH_3OCHO + 2H_2}$$
$$\mathbf{CH_3OCHO + H_2O \rightarrow HCOOH + CH_3OH}$$
$$\mathbf{HCOOH \rightarrow CO_2 + H_2}$$

Effect of addition of zirconia to the copper based catalyst has been studied by Breen and Ross[10] who carried out methanol steam reforming experiments using various catalyst with different mass compositions of Cu-Zn, Cu-Zr, Cu-Zn-Zr, Cu-Zn- Al and Cu-Zn-Zr-Al. The authors found that an increase in the copper content of Cu/ZrO2 catalysts increased the conversion and the selectivity whereas the activity decreased for a Cu/ZrO2 catalyst(30/70wt%) at temperatures above 618.15K. The best results over the entire temperature range were obtained over the $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst. It was also noted that addition of zinc to Cu/ZrO_2 catalysts increases the copper dispersion, as well as the activity. Furthermore, Cu-Zn-Zr catalysts were more active than Cu-Zn-Al catalysts, indicating that zirconia is a more effective support for copper and zinc than alumina. The addition of alumina to Cu-Zn-Zr increased the stability

We know that from the point of view of design, simulation and optimization of an industrial reformer, detailed product compositions and effects of operational conditions on desired product yield should be determined. The objective of this work is to study the intrinsic kinetics of the steam reforming of methanol, over a commercial $Cu/ZnO/Al_2O_3$-ZrO_2 catalyst in an integral reactor. Within a wide range of temperature and pressure and steam/methanol, H_2/methanol and CO_2/methanol ratios, the effects of these parameters on reaction have been investigated experimentally in the absence of inter/intra particle concentration and temperature gradients. Hence, extensive effort has been taken to determine the mechanism and the kinetics for steam reforming under conditions of no mass/heat transfer and diffusion limitations.

EXPERIMENTAL

A schematic diagram of the experimental equipment used is given in figure 1. It consists of three sections:

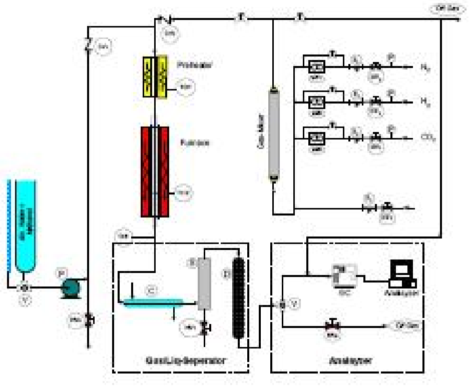

Figure 1: Schematic diagram of experimental setup

feed, reaction and analysis section. The feed section contains gas supplies for H_2, CO_2 and carrier gas N_2 and liquid supplies for H_2O and CH_3OH. After pressure reduction from the gas cylinder by means of a regulator, a mass flow controller at a desired value controlled the flow rate of each gas. Liquids were delivered from storage tanks by means of diaphragm pumps. After mixing, the gas and liquid feeds flowed into the preheater-evaporator in which the feed mixture was heated. The integral reactor and evaporator used in the present experiments were made from stainless steel tubes 1.8 cm I.D. enclosed by an electric resistance heater. A straight section, 890 mm long, served as both evaporator-preheater and the reactor. 5 thermocouple was placed in a thermocouple well of 6 mm O.D. which was located along the axis of the reactor. The thermocouples were connected to temperature indicators and temperature controllers to monitor and control the preheating and reaction temperatures. After condensation of the steam and methanol and drying of the gas mixture, the effluent gas and liquid were sent to the analysis section. The analysis section contained the gas chromatograph (GC, Shimadzu and HP 5890 for liquid and gas respectively). The GCs with a thermal conductivity detector (TCD) were used to analyze the methanol, water, H_2, CO_2 and carrier gas N_2. The carrier gas for the GC used was helium.

Catalyst and its pretreatment

A $Cu/ZnO/Al_2O_3$ catalyst (methanol steam reforming catalyst) of cylindrical type was provided by BASF. The physical properties of the catalyst are listed in TABLE 1. To avoid diffusional effects within the catalyst pellet, particle size of 1.5 mm was used in the experiments as explained later. The amount of catalyst loaded was 2 gr for the methanol steam reforming experiments. Once loaded, the catalyst was reduced according to the following procedures (1) the catalyst was heated up to a fairly uniform temperature of 443.15 to 453.15 K at a rate of no more than 50 K/hr followed by the addition 0.5 to 1.0 Vol.% of reducing gas H_2; (2) while maintaining the inlet temperature of 448.15K the hydrogen concentration was raised to 1.5 to 2 Vol.% making sure the catalyst bed temperature did not exceed 493.15K; (3) after the equilibration of bed temperature and outlet H_2 concentration reaching 90 % of its inlet value then the inlet feed temperature was raised to 478.15K (4) the hydrogen concentration was raised stepwise to 10 to 15 Vol.% as a post-reduction to ensure complete reduction of the catalyst. The catalyst was then ready for the reaction experiments. In all experiments the total reactor pressure was kept at atmospheric.

TABLE 1: BASF V1766 catalyst physical property

Specifications	Values
Bulk density	1500 to 1600kg/m^3
Surface area (based on BET analysis)	60 to 80m^2/gr
Pore volume (based on N_2 isotherm analysis	0.2 to 0.25ml/gr
Crush strength	35 to 45 N/tablet
CuO wt %	50 %
ZnO wt %	30 %
Al_2O_3-ZrO_2 wt %	20 %

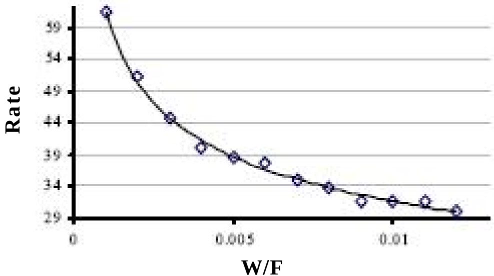

Figure 2: Conversion vs. catalyst particle size

Preliminary experiments

Prior to the formal experiments, preliminary experiments were carried out to exclude any limitations by intra/inter particle diffusion, and also to determine a space velocity at which film resistances are negligible. Figure 2, 3 and 4 show the variation of methanol conversion at different conditions. It was found that there were no significant changes in values of the methanol conversion for all particle sizes in the selected range. This result indicated that both the intraparticle diffusion limitation and that of film resistance is negligible for particles in the range 0.25 to 1.5 mm and MeOH molar rates between 0.08 to 3 mol/hr. Consequently, for the main experiments, catalyst particles of 1.5 mm were used.

One of the important steps in experimental kinetics investigation and reactor design is a proper choice of space velocity (S.V.). In the present work also at fixed W_{cat}/F_{MeOH} and different temperatures, MeOH conversion was measured in different catalyst bed lengths. From figure 3 it's evident that S.V=25000hr^{-1} (corresponding to residence time=0.144sec and bed

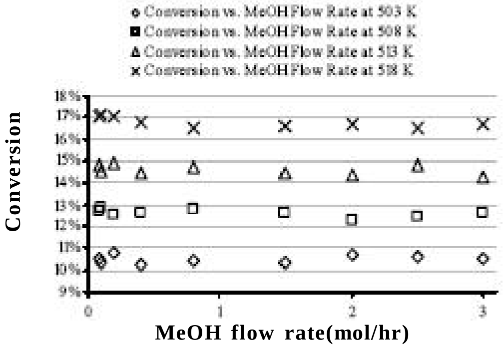

Figure 3: Conversion vs. Space Velocity at different temperatures

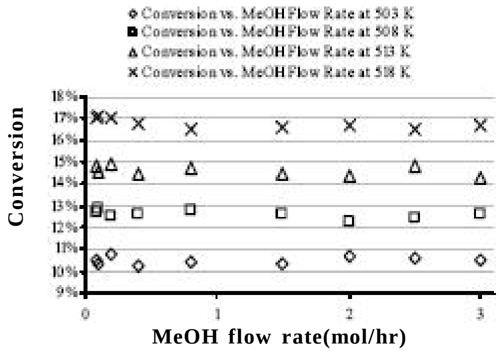

Figure 4: Conversion vs. MeOH molar flow rate at different temperature

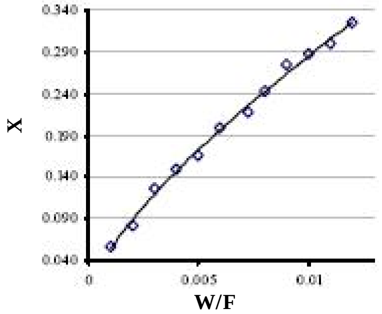

Figure 5: Conversion vs. W_{Cat}/F_{MeOH} at reference conditions

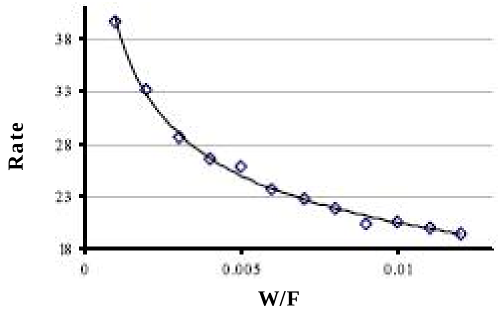

Figure 6: Rate vs. W_{Cat}/F_{MeOH} at reference conditions

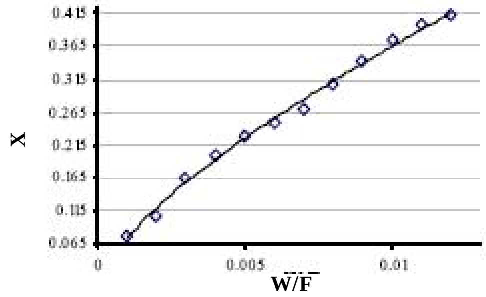

Figure 7: Conversion vs. W/F at reference conditions except with methanol concentrations varied between 0.25 to 3mol/h)

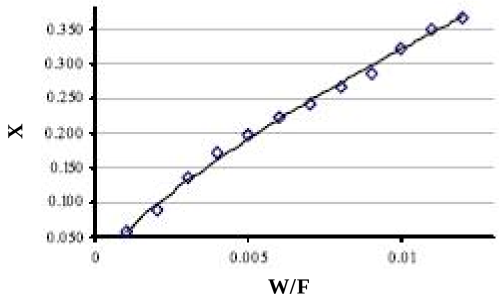

Figure 8: Conversion vs. W/F at reference conditions except with water concentrations varied between 0.2 to 3.5 mol/h)

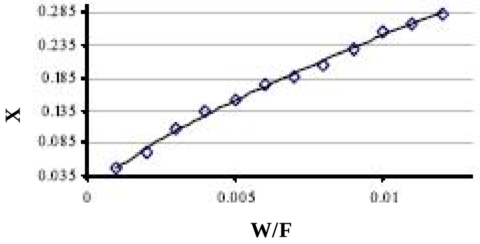

Figure 9: Conversion vs. W/F at reference conditions except with H_2 concentrations varied between 0.1 to 2mol/h)

length=6cm) is the optimum choice.

RESULT AND DISCUSSION

The thermodynamic relationships for methanol steam reforming limit any kinetic study to a rather narrow temperature range[11]. Also the equipment design limits reaction pressure and total flow rate. To account for effects of the slow deactivation on the experiments, the reference conditions chosen for methanol steam reforming were P_{tot}=101.1kPa, W_{cat}/F_{MeOH}=0.001-0.012kghr/mol, a molar ratio of $H_2O/H_2/CO_2/CH_3OH$

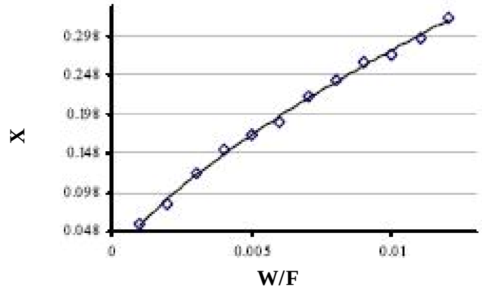

Figure 10: Conversion vs. W/F at reference conditions except with CO_2 concentrations varied between 0.083 to mol/h)

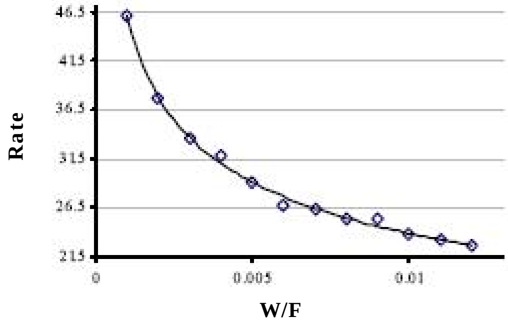

Figure11: Rate vs. W/F at 508K

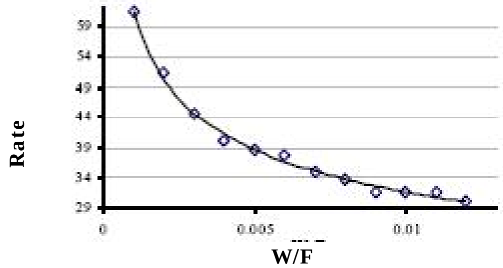

Figure 12: Rate vs. W/F at 518K

=1.4/0.5/0.25/1 and T=503K. Nitrogen was used as carrier gas. Tests under reference conditions were carried out prior to runs at specified conditions.

Also to account for effects of changes in feed composition and reaction temperature on methanol conversion, a series of experiments were carried out with the following conditions as the base conditions: **$H_2O/H_2/CO_2/CH_3OH$=1.4/0.5/0.25/1, W=0.002kg catalyst, nitrogen as carrier gas and W_{cat}/F_{MeOH} 0.001, 0.002, 0.003, …, 0.012kg·hr/mol.**

Figures 5 and 6 show methanol conversion and methanol consumption rate versus W/F respectively.

The effects of temperature and ratio of Steam: Hydrogen: Carbon dioxide: Methanol on methanol conversion

Typical methanol conversions versus contact time (W/F) for different steam/methanol, hydrogen/methanol, carbon dioxide/methanol ratios and temperatures are shown in figures 7 to 12. For convenience both methanol conversion and methanol consumption rate versus W/F are presented in a separate graph in each case. From the figures, one can see that methanol and water concentrations have positive effect on methanol conversion (and consumption rate), but hydrogen and carbon dioxide have inverse effects. Temperature increase also has positive effect on conversion and consumption rate.

CONCLUSION

1. Based on the experimental results the following rate equation for the catalyst BASF V1766 containing 50 % (wt) CuO and 30 % (wt) ZnO has been determined in this study.

$$-\mathbf{r}_{\mathbf{MeOH}} = \mathbf{k}_0 \exp\left(\frac{-\mathbf{E}}{\mathbf{RT}}\right)\mathbf{P}_{\mathbf{MeOH}}^{0.59}\mathbf{P}_{\mathbf{H_2O}}^{0.42}\mathbf{P}_{\mathbf{H_2}}^{-0.22}\mathbf{P}_{\mathbf{CO_2}}^{-0.05}$$

In which k_0= 773220854 (mol/hr·kg·atm$^{0.74}$) and E=62810 (J/mol).

Samms and Savinel[12] have obtained the following rate equation for the catalyst BASF K3-110 containing 40 % (wt) CuO and 40 % (wt) ZnO.

$$-\mathbf{r}_{\mathbf{MeOH}} = \mathbf{k}_0 \exp\left(\frac{-\mathbf{E}}{\mathbf{RT}}\right)\mathbf{P}_{\mathbf{MeOH}}^{0.03}\mathbf{P}_{\mathbf{H_2O}}^{0.39}\mathbf{P}_{\mathbf{H_2}}^{-0.23}\mathbf{P}_{\mathbf{CO_2}}^{-0.23}$$

In which k_0= 2.2932×10^{10}(mol/ hr·kg·atm$^{0.74}$) and E=74164 (J/mol).

Jiang et al.[8,9] obtained the following rate expression for methanol steam reforming for the BASF S3-85 catalyst containing 40 % (wt) CuO and 50 % (wt) ZnO.

$$-\mathbf{r}_{\mathbf{MeOH}} = \mathbf{k}_0 \exp\left(\frac{-\mathbf{E}}{\mathbf{RT}}\right)\mathbf{P}_{\mathbf{MeOH}}^{0.26}\mathbf{P}_{\mathbf{H_2O}}^{0.03}\mathbf{P}_{\mathbf{H_2}}^{-0.2}$$

The catalyst K3-110 has 40%(wt) CuO and 40%(wt) ZnO composition in comparison with catalyst BASF V1766 which has 50%(wt) CuO and 30%(wt) ZnO composition. Comparing rate equations and also composition differences it can be concluded that catalyst V1766 is more active in methanol usage and also less sensitive to CO_2 presence and therefore overall this catalyst is more active in H_2 production.

1- CO_2 concentration has an effect on the reforming reaction as concluded by Samms and Savinel [12] and contrary to the finding by Jiang et al.[8,9].

2- It is generally accepted that metallic copper is the active species in methanol steam reforming [8,9] and therefore catalyst V1766 with the highest copper concentration has the highest conversion.

3- The role of ZnO in Cu/ZnO based catalysts is discussed by Chinchen et al.[13] as to enhance the dispersion of copper at the surface. Other authors[14-16] have proposed that the activity of the catalyst is influenced by the morphology and the structural disorder of the copper particles, or by incorporation of copper into ZnO. Therefore catalyst with the highest ZnO concentration has better stability. But this shortcoming for the catalyst V1766 is compensated with the addition of zirconia as supported by the experimental findings of Breen and Ross[10]

4- Feed conversion, yields of H_2 and CO_2 increase with increasing reaction temperature and this is expected, as the reforming reaction is an endothermic reaction.

5- in all experiments carried out there was no CO formation and thus CO_2 selectivity is 100 % in the range of 523.15 to 583.15K.

6- Both H_2 and CO_2 are produced approximately at stoichiometric amounts($H_2/CO_2 \sim 3$). Methane production increased slowly with reaction temperature. But no CH_4 was detected at 523.15 K. H_2 formation declined slowly with temperature, reaching 70.1% at 583.15 K from 73.4% at 523.15 K.

7- Experiments results showed that in the range of 523.15 to 583.15K negligible deactivation occurring in the catalyst for the duration that all experiments were carried out.

ACKNOWLEDGMENTS

The author would like to thank Dr. A.Irandokht, Mr. H.Bonyad

REFERENCES

[1] P.G.Ashmore; 'Catalysis and Inhibition of Chemical Reactions', Butterworths, London, **140**, 141 **(1963)**.
[2] W.H.Heffner, A.C.Veverlea, G.T.Skaperdas; Advances in Chemistry Series, 318-331 **(1965)**.
[3] M.V.Twigg; 'Catalyst Handbook', 2nd Edition, Wolfe Publishing Ltd., U.K., **(1989)**.
[4] E.Santacesaria, S.Carra; Appl.Catal., **5**, 345 **(1983)**.
[5] B.A.Peppley, J.C.Amphlett, L.M.Kearns, R.F.Mann; Appl.Catal.A., **179**, 21 **(1999)**.
[6] S.P.Asprey, B.W.Wojciechowski, B.A.Peppley; Appl.Catal.A., **179**, 51 **(1999)**.
[7] J.C.Amphlett, K.A.M.Creber, J.M.Davis, R.F.Mann, B.A.Peppley, D.M.Stokes; Int.J. Hydrogen Energy, **19**, 131 **(1994)**.
[8] C.J.Jiang, D.L.Trimm, M.S.Wainwright, N.W.Cant; Appl.Catal.A., **97**, 145 **(1993)**.
[9] C.J.Jiang, D.L.Trimm, M.S.Wainwright, N.W.Cant; Appl.Catal.A., **93**, 245 **(1993)**.
[10] J.P.Breen, J.R.H.Ross; Catal.Today, **51**, 521 **(1999)**.
[11] J.C.Amphlett, M.J.Evans, R.A.Jones, R.F.Mann, R.D.Weir; Can.J.Chem.Eng., **59**, 720-727 **(1981)**.
[12] S.R.Samms, R.F.Savinnel; J.Power Sources., **112**, 13-29 **(2002)**.
[13] G.C.Chinchen, K.C.Waugh, D.A.Whan; Appl.Cat., **25**, 101 **(1986)**.
[14] P.L.Hansen, J.B.Wagner, S.Helveg, J.R.Rostrup-Nielsen, B.S.Clausen, H.Tops; Science, **295**, 2053 **(2002)**.
[15] J.B.Bulko, R.G.Herman, K.Klier, G.W.Simmons; J.Phys.Chem., **83**, 3118 **(1979)**.
[16] B.S.Clausen, J.Schiøtz, L.Grabaek, C.V.Ovesen, K.W.Jacobsen, J.K.Norskov, H.Topsoe; Top.Catal., **1**, 367 **(1994)**.