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Deactivation kinetics of methanol steam reforming catalyst for pure hydrogen generation

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ABSTRACT

Comprehensive studies on reaction kinetics and mechanisms of steam reforming of methanol (SRM) in early decades have confirmed that all three reactions (steam reforming, SR, water gas shift, WGS, and decomposition of methanol, D) involve simultaneously in the process. Because all methanol is not converted to H_2 and CO_2, the reverse water gas shift, RWGS, reaction won't be catalyzed and CO production will be stopped. The result of previous studies has presented that Cu particles are active sites for SRM reaction and selective to hydrogen production. The main drawback of using these catalysts is sintering of active Cu particles at desirable reaction temperatures. Deactivation kinetics of commercial Cu/ ZnO/Al_2O_3 catalysts were studied in a fixed bed reactor with 1:1 molar ratio of methanol-water mixture. The tests were carried out at different temperatures: 250, 280 , 310^0C for one week. The curves of the products yield were drawn at 250, 280 and 310^0C. In this work, effective reaction rate constant was calculated by determination of feed conversion throughout time on-stream and then were fitted with hypothetical model resulting from Fuentes expression including three adjustable parameters: K_S, K_F and S_S/S_0. Because of the main difference between adjustable S_S/S_0 in hypothetical sintering model and its real magnitude, Fuentes model is not efficient for fitting and processing of experimental data. For this reason, general deactivation model based on a_S/a_0 instead of S_S/S_0 was used for fitting of experimental data with a hypothetical model. Determination of copper surface area by N_2O adsorption on copper particles was done before and after runs. It is considered that this modified model is valid and useful for initial deactivation. In the temperature range of 250-310^0C reaction rate constant increases with increasing temperature.

KEYWORDS

Deactivation kinetic;
Steam reforming;
Methanol;
Hydrogen generation;
Cu-based catalyst.

INTRODUCTION

Fuel cell powered electric vehicles and power plants using hydrogen as fuel are currently being development in an effort to protect the environment and sustainable development[1]. Hydrogen is conventionally manufactured in large scale by the steam reforming of hydrocarbons such as methane or naphtha oil. For small and medium scale users, it is also generated from the steam reforming of methanol. Methanol posses some advantages relative to other hydrocarbons because of its low steam to carbon ratio, low reforming temperatures (250-300⁰C), high quality (sulfur <5ppm), high energy density, the possibility of using a petrol-like infrastructure for distribution and ease of handling[2,3,4]. Steam reforming of methanol is catalytic and endothermic reaction that can generate a product gas containing approximately 75% H_2 while maintaining a high selectivity towards CO_2. Comprehensive studies on reaction kinetics and mechanisms of steam reforming of methanol, SRM, in early decades have confirmed that all three reactions (steam reforming, SR, water-gas shift, WGS, and decomposition, D) involve simultaneously in the process[2,5]. Hence, the process can be described by the following reactions:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \text{SR} \tag{1}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{WGS} \tag{2}$$
$$CH_3OH \rightarrow CO + 2H_2 \quad \text{D} \tag{3}$$

The Cu-containing catalysts have showed particularly high activity and selectivity for the steam reforming of methanol. Unfortunately, a major concern in the use of steam reforming of methanol catalysts ($Cu/ZnO/Al_2O_3$) is the deactivation phenomena by sintering of Cu particles in initial hours of runs at desired cooperating conditions[5,6]. Loss of catalytic surface area due to crystalline growth in the catalytic phase (Cu-particles) or loss of support area due to support collapse and of catalytic surface area due to pore collapse on metal crystallite are typically referred to on sintering[7]. Thus, derivation of kinetic model of SRM on $Cu/ZnO/Al_2O_3$ that incorporates catalyst deactivation is an extremely useful tool for predicting age of catalysts and designing compressed fuel processors. This paper, will present results from an experimental study of deactivation kinetics of SRM and show the deactivation rate expression.

EXPERIMENTAL

Commercially available methanol steam reforming catalysts, BASF-V1766, were tested in tubular packed bed reactor was made of stainless steel (ASTM 316) with 85 cm height and inner diameter of 18mm at atmospheric pressure and three operating temperatures: 250, 280, 310⁰C for one week with a mixture of 64% by weight methanol in water fed at flow rate 2 ml/min. The catalyst was ground and sieved to eliminate internal diffusion resistance and to accelerate catalyst deactivation. The bed consisted of 8.2 g of 14-20 mesh catalyst particles mixed with 8.2 g 20-25 mesh inert α-alumina as a diluent. The criteria of Mears[8] were used to ensure that temperature gradients and axial dispersion were negligible. A detailed schematic of the laboratory test system is presented in figure 1.

The reactants were fed to the reactor with N_2 as a diluent and carrier. Prior to each experiment the catalysts were reduced with different proportion of H_2/N_2 mixture by a proper method in order to obtain complete conversion of the feed. The gas product stream composition was measured on-line using a gas chromatograph from Philips and liquid product was analyzed using a gas chromatograph from Shimadzue.

RESULTS

Catalytic activity measurements

The effect of reaction temperature on initial catalytic activity has shown in figure 2. Feed conversion, initial yield of H_2 and CO_2 will be enhanced with increasing reaction temperature. This is reasonable, because SRM is an endothermic reaction. The possible reaction between methanol and water can generate H_2, CO_2, CH_4 and CO as products[2,5,7]. But in our experimental results, There was no CO formation. Product distribution at different temperatures (250, 280, 310

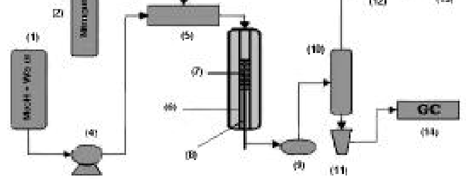

Figure 1: Laboratory test system

and 350^{0}C) has shown in figure 3. Both H_2 and CO_2 are produced approximately in stoichiometric amount (H_2/CO_2~3).

Methane production increased slowly with reaction temperature reaching 1.57(mole %) at 350 ^{0}C. But no CH_4 was detected at 250^{0}C. H_2 formation declined slowly with temperature, reaching to 70.1% at 350^{0}C from 73.4% at 250^{0}C. Our experimental results showed that only very low CO is produced at 350^{0}C (0.7% mole). Because all methanol is not converted to H_2 and CO_2 the RWGS reaction won't be catalyzed and CO production will be stopped.

Derivation of deactivation model for steam reforming of methanol on $Cu/ZnO/Al_2O_3$

In this study, three tests at 250, 280 and 310^{0}C and using an equimolar solution of methanol and water fed at flow rate 2 ml/min were carried out for derivation of deactivation model. We can assume that only reaction (1) occurs and ignore reaction (2) and (3) and this reaction is the first order and irreversible, therefore, We can write[6,9]:

$$\mathbf{r = K_e.P_{MeOH}} \quad (4)$$

Where K_e is an effective first order reaction rate constant and P_{MeOH} is the partial pressure of methanol. We can obtain K_e with writing mass balance equation for plug flow reactor.

$$\frac{W_{Cat}}{F_{MeOH}} = \int_0^{X_{MeOH}} \frac{dX_{MeOH}}{-r_{MeOH}} \quad (5)$$

and introducing eq 4 in eq 5, we obtain:

$$K_e = \frac{F_{MeOH0}}{W_{Cat}.P_{MeOH}}\left[-2Ln\left(1-X_{MeOH}\right)-X_{MeOH}\right] \quad (6)$$

Since we used the feed conversion during calculation of K_e, we replaced the total pressure (P=1atm) instead of P_{MeOH} and the molar flow rate of the feed (mol/min) instead of F_{MeOH0}. Therefore, we obtain:

$$K_e = \frac{F_{Feed0}}{W_{Cat}.P}\left[-2Ln(1-X_{Feed})-X_{Feed}\right] \quad (7)$$

Where W_{Cat} is the catalyst mass and X_{Feed} is the feed conversion. The unit of K_e is mol/(pressure)(time)(mass).

The hollow triangles in figures 4,5 and 6 show the variation of K_e versus time-on stream at 250, 280 and 310^{0}C. When increasing operating temperature, the time for decreased of K_e to constant level was decreased, on the other hand, the catalyst activity and K_e decreased more rapidly.

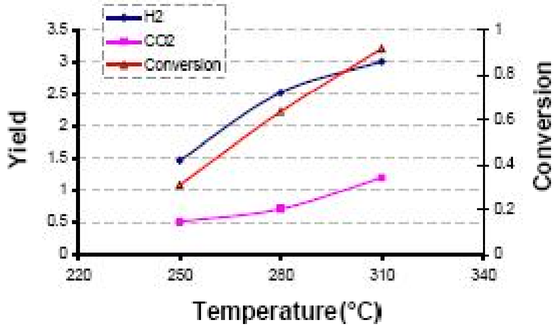

Figure 2: Effect of reaction temperature on initial feed conversion and initial yield of H_2 and CO_2(feed flow rate=2 ml/min)

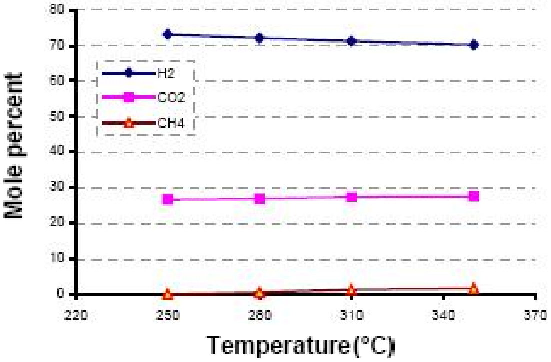

Figure 3: Product distribution at different temperatures (for 250, 280, 310 and 350^{0}C and feed flow rate=2 ml/min)

From figure 4,5 and 6 it is evident that operating temperature has an increasing effect on effective reaction rate constant, thus catalyst activity in the range of 250-310^{0}C. In addition, we can consider that because of the endothermic reaction, initial reaction rate constant is increased at higher temperatures.

Sintering reduces the metal surface area, thus decreasing catalytic activity throughout the bed. Sintering occurs rapidly until the catalytic activity reaches a new steady state level that is nonzero. It has been shown that the effects of temperature can be quantitatively determined by fitting of sintering kinetic data to general power law expression (GPLE). Rate of activity loss with time has been given by fuentes[7]:

$$-\frac{d(\alpha/\alpha_0)}{dt} = K_d\left[\alpha/\alpha_0 - \alpha_s/\alpha_0\right]^d \quad (8)$$

Where a_s/a_0 is the normalized steady state activity and K_d is a deactivation rate constant by sintering. GPLE equation fits sintering rate data for small integer values of d of 1,2 or 3. In our study, It was more convenient to fit all sintering data using the GPLE with d=1. After some algebra, using integration of eq 8 and applying the defined boundary condition:

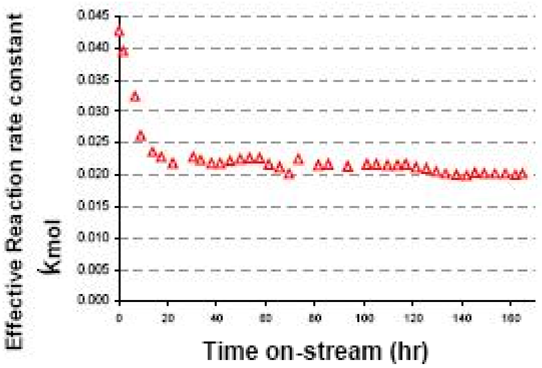

Figure 4: Effective reaction rate constant (K_e) versus time on-stream at 250^{0}C(feed flow rate=2ml/min)

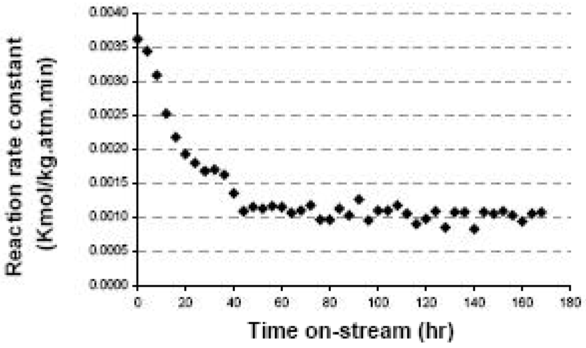

Figure 5: Effective reaction rate constant (K_e) versus time on-stream at 280^{0}C (feed flow rate=2ml/min)

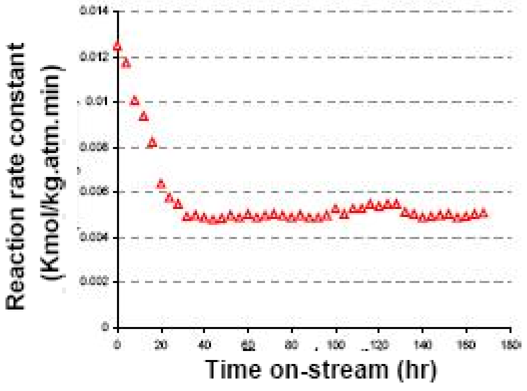

Figure 6: Effective reaction rate constant (K_e) versus time on-stream at 310^{0}C (feed flow rate = 2ml/min)

$$\alpha/\alpha_0 = \alpha_s/\alpha_0 + (1-\alpha_s/\alpha_0)\exp(-K_d.t) \qquad (9)$$

Assuming that lowering of effective reaction rate constant during time-on stream is proportional to the catalyst activity, we can write:

$$K_e = K_F(\alpha/\alpha_0) = \frac{F_{Feed0}}{W_{Cat}.P}\left[-2Ln(1-X_{Feed}) - X_{Feed}\right] \qquad (10)$$

Where the ratio a/a_0 is calculated from eq 9. All experimental data at different temperatures were fitted using eq 10. The adjustable parameters used to fit the experimental data were initial reaction rate constant (K_F), normalized steady state activity(a_s/a_0) and deactivation rate constant (K_d). Solid lines in figure 4, 5 and 6 indicate variation of K_e during time-on stream result from fitting of experimental data using mentioned hypothetical model.

From TABLE 1, when increasing the operating temperature, the normalized steady state activity is enhanced. On the other hand, operating temperature has an increasing effect on normalized steady state activity. To indicate dependency of a_S/a_0 (adjustable parameter result from deactivation model) on S_S/S_0(measured by applying N_2O adsorption), calculations including linear regression, logarithmic regression, exponential regression and power regression performed. The best expression based on a polynomial with an order of two(m=2).

$$\alpha_s/\alpha_0 = -1012(S_s/S_0)^2 - 0.6839(S_s/S_0) + 1.0189 \qquad (11)$$

This polynomial indicates that when declining the normalized surface area, the catalyst activity increases. Also, eq 12 indicates the functionality of S_S/S_0 with operating temperature in the range of 250-310^{0}C.

$$S_s/S_0 = -2.2066\ln(T) + 14.74 \qquad (12)$$

Surface area declined with temperature in spite of increasing the catalyst activity.

We may find that the temperature doesn't destructively affect on support- support, support- metal and metal-metal bonds in the range of 250-310^{0}C. Of course it is important to note that the duration of the runs was one week at any operating temperature. Thus, it was not possible to investigate the temperature effects during long time-on stream. Thus, it is considered that the derived deactivation model is valid during one week of operation or a little more.

Calculation of activation energy and pre-exponential factor

We used Arrhenieus theory to derivate pre-exponential factor and activation energy for the first order

TABLE 1: Comparison of experimental data with hypothetical deactivation model at different temperatures

Temp.(°C)	K_F ^{a}	K_F ^{b}	a_s/a_0	K_d (1/hr)	R^2
250	0.0036	0.0036	0.304	0.057	0.9678
280	0.0125	0.0126	0.390	0.067	0.9330
310	0.0428	0.0428	0.507	0.113	0.9562

Units: $K_{F\ and}$ $K_{F\ =}$ (Kmol/Kg_{Cat}.min.atm); (a) results from experimental data; (b) adjustable parameter result from hypothetical model

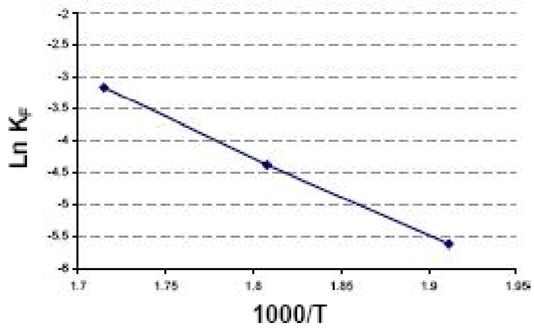

Figure 7: Ln K_F versus 1000/T

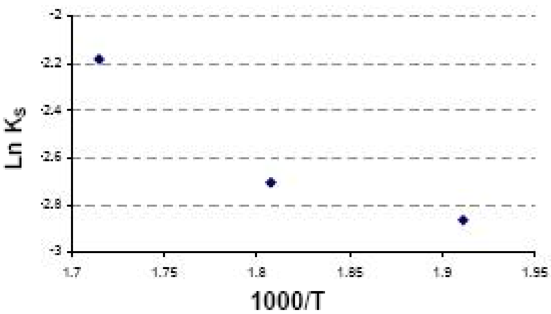

Figure 8: Ln K_S vs 1000/T

reaction (SRM). We obtained K_0 an E according to the Arrhenieus theory:

$$K_F = K_0 . e^{-E/RT} \quad (13)$$

The straight line in figure 7 yields the activation energy and pre-exponential factor. This can be seen from figure 7 in which Ln K_F is plotted against 1/T.

$$K_S = 38.62(l/hr)\cdot e^{-28.6(KJ/mol)/8.314\cdot T} \quad (14)$$

The slope of the curve line in figure 8 shows that the rate of deactivation by sintering is slow in the operating region (250-310°C).

CONCLUSION

1. Feed conversion, initial yield of H_2 and CO_2 will be enhanced with increasing reaction temperature. This is reasonable, because SRM is an endothermic reaction.
2. There was no CO formation. Thus, CO_2 selectivity is equal to 100% in the range of 250-310°C.
3. Both H_2 and CO_2 are produced approximately in stoichiometric amount (H_2/CO_2~3). Methane production increased slowly with reaction temperature. But no CH_4 was detected at 250°C. H_2 formation declined slowly with temperature, reaching to70.1%at 350°C from 73.4% at 250°C.
4. Our experimental results showed that only very low CO is produced at 350°C (0.7% mole). Because all methanol is not converted to H_2 and CO_2 the RWGS reaction won't be catalyzed and CO production will be stopped.
5. Operating temperature has an increasing effect on effective reaction rate constant, thus catalyst activity in the range of 250-310°C.
6. Temperature doesn't destructively affect on support-support, support-metal and metal-metal bonds in the range of 250-310°C.
7. The derivated deactivation model is valid during one week of operation or a little more.

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REFERENCES

[1] X.Zhang, P.Shi; J.Molecular Catalysis A Chemical, **3782**, 1-7 **(2002)**.

[2] Y.Choi, H.G.Stenger; Appl.Catal., **B38**, 259-269 **(2002)**.

[3] B.Lindstorm, J.Agrell, L.J.Petterson; J.Chemical Engineering, **4053**, 1-11 **(2002)**.

[4] B.Lindstorm, L.J.Petterson, P.G.Menon; Appl.Catal., **A234**, 111-125 **(2002)**.

[5] B.A.Peppley, J.C.Amphlett, L.M.Kearns, R.F. Mann; Appl.Catal., **A179**, 21-29 **(1999)**.

[6] D.G.Loffler, S.D.McDermott, C.N.Renn; J.Power Sources.

[7] C.H.Bartholomew; Studies in Surface and Catalysis, **88**, 1-18 **(1994)**.

[8] D.E.Mears, J.Catal., **20**, 127-13 **(1971)**.

[9] O.Levenspiel; 'Chemical Reaction Engineering', 3rd edition, John Wiley & Sons, **(1999)**.