R
BABI
2

MECHANISM AND RATE LIMITING STEP FOR THE CATALYTIC DECOMPOSITION OF METHANE TO HYDROGEN AND CARBON NANOTUBE

Sharif Hussein Sharif Zein[1], Abdul Rahman Mohamed[1], P. Sesha Talpa Sai[1] and Noor Asmawati Mohd Zabidi[2]

[1]School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, S.P.S, Pulau Pinang, Malaysia.
[2]Chemical Engineering Program, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia.

ABSTRACT

The main focus of this paper is to report a mechanism, a rate-limiting step, and a rate law consistent with experimental observation for the decomposition of methane to hydrogen and carbon nanotube over Ni/Mn based catalyst. An analysis of the rate equations was obtained for initial rate of reaction for different rate concentration steps. It is found that the rate equation when adsorption of methane on the surface as a rate controlling step showed linear relationship with concentration of methane. This observation is same as the one obtained from the analysis of data by the integral method. Hence, the assuming mechanism with adsorption of methane as rate controlling is consistent with the experimental observation.

Keywords: Mechanism, Methane Decomposition, Hydrogen, Carbon Nanotube.

1 INTRODUCTION

Natural gas containing primarily methane is a natural resource that rivals liquid petroleum in abundance. One of the major challenges is the development of direct process for conversion of natural gas to more value added chemicals. Carbon nanotubes and hydrogen are the most innovative material technologies of the twenty-first century because of their many desirable material properties. The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. In addition to that, hydrogen is one of the important industrial and potential chemicals. It is a clean fuel. The greatest incentive for its use as a fuel is the absence of objectionable combustion products. With increasing interest in fuel cells and progress in hydrogen storage technologies, the use of hydrogen as a source of clean fuel is likely to increase in the future (Armor, 1999). There is substantial interest in developing novel methods for production of hydrogen and carbon nanotube and one such process is the catalytic decomposition of methane (Steinberg, 1999; Monnerat et al., 2001; Takenaka et al., 2003 & 2004). Many experimental studies have been conducted to gain a better understanding of the kinetics of methane decomposition. The majority of the research has been focused on identification of the primary decomposition products and estimation of the activation energy for methane decomposition. (Alstrup et al., 1993, Dahl el., 2002).

Previously, it was obtained a high concentration of hydrogen (96%) and large amount of carbon nanotube in a single pass reaction for the decomposition of methane using Ni/Mn based catalyst (Zein et al., 2003). In this paper kinetic studies were carried out using Ni/Mn based catalyst for the catalytic decomposition of methane for the production of hydrogen and carbon nanotube. A mechanism, a rate-limitng step, and a rate law consistent with experimental observation for the decomposition of methane to hydrogen and carbon nanotube were discussed.

2 EXPERIMENTAL

The experiments were carried out at atmospheric pressure in a stainless steel fixed bed reactor system. A detail experimental procedure was discussed elsewhere (Zein et al., 2003). A total of 64 experiments were conducted with fresh catalyst in each run. One gram of catalyst was packed in the reactor. The experiment is repeated for different volumetric flow rates (100 to 450 mL/min) and temperatures (823 to 1173K). The product gases were analyzed using an on-line Gas Chromatograph. Spent catalysts were analyzed using a transmission electron microscope (Philips TEM CM12).

3 RESULTS AND DISCUSSION

The experimental program for obtaining the kinetics of the reaction consisted of runs at different mole ratios and temperatures with constant weight of the catalyst and the results are presented in Table 1. The conversion of methane versus time data was subjected to integral method for deriving a suitable rate law.

TABLE 1. Details of conversions obtained in the present study at various operating conditions

Temperature (K)	Volumetric Flow Rate (mL/min)					
	100	150	200	250	350	450
	Methane Conversion (%)					
823	15.82	11.42	7.04	6.52	-	-
873	27.41	20.65	16.55	14.03	7.03	-
923	41.56	33.81	27.43	24.87	16.21	9.87
973	53.99	45.10	37.21	31.58	24.99	17.88
1023	59.07	49.66	39.48	33.24	26.04	21.97
1073	70.54	59.63	49.02	35.10	24.43	21.07
1123	82.49	69.08	54.32	48.77	37.67	24.33
1173	92.03	76.88	65.87	53.46	47.01	34.68

For a first order reaction in packed bed reactor, the relation between conversion and weight time is as follows (Levenspiel, 1999):

$$k' t = (1 + e_A) \ln \frac{1}{1 - X_{out}} - e_A X_{out} \qquad (1)$$

For the present reaction, the above equation reduces as

$$k' t = 1.5 \ln \frac{1}{1 - X_{CH_4}} - 0.5 X_{CH_4} \qquad (2)$$

From the plots of the function on the right hand side of Equation (2) versus τ (w/v$_0$), shown typically in Figure 1 for a catalyst of weight of 1 gram, it follows that the data fall on a reasonably straight line through the origin. Hence the decomposition reaction is of first order.
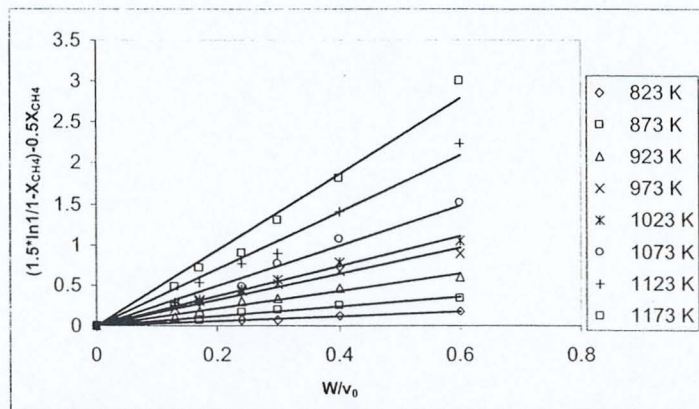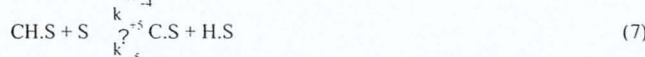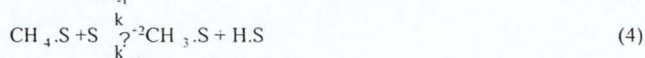
FIGURE 1. Plot of conversion as a function of weight time at different temperatures.

From the values of specific reaction rate constant, k', calculated from the slopes at different reaction temperatures, the activation energy obtained in the present study is 60 kJ/mol following Arrhenius equation. The plot is shown in Figure 4. Reported activation energies for methane decomposition without catalyst ranged from 356 to 402 kJ /mol (Holmen et., 1976; Steinberg, 1998; Dahl, 2002) and with catalyst from 90 to 236 kJ/mol (Alstrup, 1993; Kuvshinov, 1998; Muradov, 2000). Thus, the activation energy obtained in this study by using Ni/Mn based catalyst is considered to be the lowest activation energy reported in the literature for this reaction.

3.1 REACTION MECHANISM

The reaction mechanism and the identification of rate controlling steps are attempted in the present study following the mechanism proposed by Snoeck et al.(1997). They proposed the following mechanism for methane decomposition:

$$CH_4 + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} CH_4.S \tag{3}$$

$$CH_4.S + S \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} CH_3.S + H.S \tag{4}$$

$$CH_3.S + S \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} CH_2.S + H.S \tag{5}$$

$$CH_2.S + S \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} CH.S + H.S \tag{6}$$

$$CH.S + S \underset{k_{-5}}{\overset{k_{+5}}{\rightleftharpoons}} C.S + H.S \tag{7}$$

$$C.S \underset{k_{-6}}{\overset{k_{+6}}{\rightleftharpoons}} C_{Ni} + S \tag{8}$$

$$2H.S \underset{k_{-7}}{\overset{k_{+7}}{\rightleftharpoons}} H_2 + 2S \tag{9}$$

While equation 3 represents the adsorption of methane on the surface of the catalyst, equations 4 – 7 represent the surface reaction to form adsorbed methyl radicals and adsorbed hydrogen atoms on the catalyst surface. Equations 8 and 9 represent the deposition of carbon on the catalyst surface and the desorption of hydrogen from the catalyst surface respectively. For the mechanism shown in Equations 3 – 9, the rate-limiting step is identified as follows: It is assumed that one of the equations to be the rate limiting and then the rate law is formulated in terms of partial pressure of the methane and hydrogen. From the equation obtained, the variation of the initial reaction rate with the initial partial pressure of methane will be checked. If the theoretical rate varies with pressure in the same way as observed experimentally, it will be assumed that the mechanism and the rate limiting step are correct. A mechanistic interpretation for the growth of carbon on the catalyst was proposed in literature [17, 18]. Figure 2 supports the proposed mechanism for the growth of carbon nanotube on the catalyst. Methane decomposes on the front surface of certain active sites of the catalyst and the carbon so formed diffuses through the metal and precipitates at the rear surface. The driving force

which pushed the carbon diffusion was suggested to originate from the concentration gradient of dissolved carbon between the two interfaces i.e. the metal-gas interface to the metal-nanocarbon interface. Therefore, for high values of diffusivity, the concentration of carbon dissolved in nickel is almost uniform and small ($\therefore C_{Ni} \approx 0$).
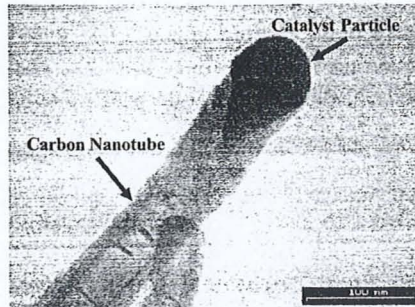

FIGURE 2. The transmission electron microscope image
of the carbon formation on the catalyst particle.

When the adsorption of methane is the rate-limiting step, the expression between rate of reaction and concentration of various species is:

$$-r_{CH_2} = \frac{C_T K_1 P_{CH_4}}{1 + K_7^{1/2} P_{H_2}^{1/2}}$$

(10)

Initially, the concentration of hydrogen is zero and equation (10) becomes:

$$-r_{CH_4,0} = C_T K_1 P_{CH_4}$$

(11)

If the methane decomposition is adsorption limited reaction, then the initial rate will be linear with the initial partial pressure of methane. This is what has been observed experimentally in the present study. However, the individual rate laws and individual initial rate plots with the other steps in the mechanism as rate limiting step will be derived and checked to confirm whether the methane decomposition reaction is really adsorption limited or not. When the removal of first hydrogen atom from molecularly adsorbed methane is rate-limiting step, it follows:

$$-r_{CH_4,S} = \frac{C_T K_1 k_{+2} P_{CH_4}}{\left(1 + K_1 P_{CH_4} + K_7^{1/2} P_{H_2}^{1/2}\right)^2}$$

(12)

Initially, $[H_2] = 0$ and hence equation (12) becomes:

$$-r_{CH_4,S,0} = \frac{C_T^2 K_1 k_{-2} P_{CH_4}}{\left(1 + K_1 P_{CH_4}\right)^2}$$

(13)

If the removal of first hydrogen atom from molecularly adsorbed methane limits the methane decomposition, the rate will increase at low initial partial pressures of methane and then decrease at high initial partial pressures of methane. This observation is not coherent with the experimental of the present study.

When the removal of second, third and fourth hydrogen atom from molecularly adsorbed methane is rate-limiting step, the expressions between rate of reaction and concentrations of various species, respectively, are as follows:

$$-r_{CH_4.S} = \frac{\left(\dfrac{C_T^2 K_1 K_2 k_{+3} P_{CH_4}}{K_7^{1/2} P_{H_2}^{1/2}}\right)}{\left(1 + K_1 P_{CH_4} + \dfrac{K_1 K_2 P_{CH_4}}{K_7^{1/2} P_{H_2}^{1/2}} + K_7^{1/2} P_{H_2}^{1/2}\right)^2} \qquad (14)$$

$$-r_{CH_2.S} = \frac{\left(\dfrac{C_T^2 K_1 K_2 K_3 k_{+4} P_{CH_4}}{K_7 P_{H_2}}\right)}{\left(1 + K_1 P_{CH_4} + \dfrac{K_1 K_2 P_{CH_4}}{K_7^{1/2} P_{H_2}^{1/2}} + \dfrac{K_1 K_2 K_3 P_{CH_4}}{K_7 P_{H_2}} + K_7^{1/2} P_{H_2}^{1/2}\right)^2} \qquad (15)$$

$$-r_{CHS} = \frac{\left(\dfrac{C_T^2 K_1 K_2 K_3 K_4 k_{+5} P_{CH_4}}{K_7^{3/2} P_{H_2}^{3/2}}\right)}{\left(1 + K_1 P_{CH_4} + \dfrac{K_1 K_2 P_{CH_4}}{K_7^{1/2} P_{H_2}^{1/2}} + \dfrac{K_1 K_2 K_3 P_{CH_4}}{K_7 P_{H_2}} + \dfrac{K_1 K_2 K_3 K_4 P_{CH_4}}{K_7^{3/2} P_{H_2}^{3/2}} + K_7^{1/2} P_{H_2}^{1/2}\right)^2} \qquad (16)$$

Initially, [H_2] is zero and the numerator and denominator of equation (14) to (16) approach infinity. Therefore, the limit of these expressions approaches to zero. Since the reaction rate cannot be zero, the removal of either second or third or fourth hydrogen atom from molecularly adsorbed methane cannot be the rate-limiting step.

When the deposition of carbon on the catalyst is rate limiting step, it gives:

$$-r_{C.S} = \frac{\left(\dfrac{C_T K_1 K_2 K_3 K_4 K_5 k_{+6} P_{CH_4}}{K_7^2 P_{H_2}^2}\right)}{\left(1 + K_1 P_{CH_4} + \dfrac{K_1 K_2 P_{CH_4}}{K_7^{1/2} P_{H_2}^{1/2}} + \dfrac{K_1 K_2 K_3 P_{CH_4}}{K_7 P_{H_2}} + \dfrac{K_1 K_2 K_3 K_4 P_{CH_4}}{K_7^{3/2} P_{H_2}^{3/2}} + \dfrac{K_1 K_2 K_3 K_4 K_5 P_{CH_4}}{K_7^2 P_{H_2}^2} + K_7^{1/2} P_{H_2}^{1/2}\right)} \qquad (17)$$

Initially, [H_2] is zero and the numerator and denominator of equation (17) approach infinity. Therefore, the limit of this expression gives:

$$-r_{C.S} = C_T k_{+6} \qquad (18)$$

Since, the reaction rate can not be $C_T k_{+6}$, the deposition of carbon on the catalyst can not be rate-limiting step.

When desorption of hydrogen from the surface is rate limiting step, it gives:

$$-r_{H.S} = -\frac{C_T^2 k_{-7} P_{H_2}}{\left(1 + K_1 P_{CH_4}\right)^2} \qquad (19)$$

Initially, [H_2] = 0 and equation (19) becomes:

$$-r_{H.S} = 0 \qquad (20)$$

Since the reaction rate cannot be zero, desorption of hydrogen from the surface cannot be rate limiting step.

An analysis of the above rate equations indicates that the rate equation when adsorption of methane on the surface as a rate controlling step showed linear relationship with concentration of methane. This observation is same as the one obtained from the analysis of data by both integral and differential methods. Hence, the assuming mechanism with adsorption of methane as rate controlling is consistent with the experimental observation. This can be expected as the surface reaction is unlikely controlled the rate because the reaction occurs at relatively high temperatures.

4 CONCLUSIONS

For the decomposition of methane to hydrogen and carbon using Ni/Mn based catalyst, it was found that the decomposition reaction is of first order with an activation energy of 60 kJ/mol. This activation energy is considered to be the lowest activation energy reported in the literature for this reaction. It was also found that the adsorption of methane on the surface is the rate-controlling step.

ACKNOWLEDGEMENTS

NOMENCLATURE

$C_{N i}$ = concentration of carbon dissolved in nickel
C_T = total concentration of sites
C_V = concentration of vacant sites
$k_{+1}, k_{-1}, k_{+2}, k_{-2}, k_{+3}, k_{-3}, k_{+4}, k_{-4}, k_{+5}, k_{-5}, k_{-6}, k_{-6}, k_{+7}, k_{-7}$ = Rate coefficients of the forward (+) and the reverse (-) reactions
k' = specific reaction rate constant (mL/g$_{cat}$ s)
$K_1, K_2, K_3, K_4, K_5, K_6, K_7$ = Equilibrium coefficients
$-r_{CH_4}$ = rate of methane decomposition (mol/g$_{cat}$ s)

P_{CH_4} = partial pressure of methane

S = surface active site
$?_0$ = entering volumetric flow rate
W = weight of catalyst
X_{CH_4} = conversion of methane
X_{out} = conversion at outlet

Greek Symbols

ε = fraction change in volume per mole of A reacted resulting from the change in total number of moles
τ = weight time (g. s/mL)

REFERENCES

Alstrup, I.; Tavares, M. T. Kinetics of carbon formation from CH$_4$ + H$_2$ on silica-supported nickel and Ni-Cu catalysts. *J. Catal.* **1993**, *139*, 513.

Armor, J. N. The multiple roles for catalysis in the production of H$_2$. *Appl. Catal. A: Gen.* **1999**, *76*, 159.

Dahl, J. K.; Barocas, V. H.; Clough, D. E.; Weimer, A. L. Intrinsic kinetics for rapid decomposition of methane in an aerosol flow reactor. *Int. J. Hydrogen Energy* **2002**, *27*, 377.

Ermakova, M. A.; Ermakov, D. Yu.; Chuvilin, A. L.; Kuvshinov, G. G. Decomposition of methane over iron catalysts at the range of moderate temperatures: the influence of structure of the catalytic systems and the reaction conditions on the yield of carbon and morphology of carbon filaments. *J. Catal.* **2001**, *201*, 183.

Holmen, A.; Rockstad, O. A.; Solbaklen, A. High-temperature pyrolisis of hydrocarbons. 1. Methane to acetylene. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15*, 439.

Kuvshinov, G. G.; Mogilnykh, Yu. I.; Kuvshinov, D. G. Kinetics of carbon formation from CH$_4$-H$_2$ mixtures over a nickel containing catalyst. *Catal. Today* **1998**, *42*, 357.

Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1999.

Monnerat, B.; Kiwi-Minsker, L.; Renken, A. Hydrogen production by catalytic cracking of methane over nickel gauze under periodic reactor operation. *Chem. Eng. Sci.* **2001**, *56*, 633.

Muradov, N. *Proceedings of the 2000 Hydrogen Program Review*; Report NREL/CP-570-28890; U.S. Department of Energy, U.S. Government Printing Office: Washington, DC, 2000.

Snoeck, J. W.; Froment, G. F.; Fowles, M. Kinetic study of the carbon filament formation by methane cracking on a nickel catalyst. *J. Catal.* **1997**, *169*, 250.

Steinberg, M. M. Fossil fuel decarbonisation technology for mitigating global warming. *Int. J. Hydrogen Energy* **1999**, *24*, 771.

Steinberg, M. Production of hydrogen and methanol from natural gas with reduced CO_2 emission. Int. *J. Hydrogen Energy* **1998**, *23*, 419.

Takenaka, S.; Kato, E.; Tomikubo, Y.; Otsuka, K. Structural change of Ni species during the methane decomposition and the subsequent gasification of deposited carbon with CO_2 over supported Ni catalysts. *J. Catal.* **2003**, *219*, 176

Takenaka, S.; Tomikubo, Y.; Kato, E.; Otsuka, K. Sequential production of H_2 and CO over supported Ni catalysts. *Fuel* **2004**, *83*, 47

Zein, S.H.S., Mohamed, A.R., Sai, P.S.T., Zabidi, N.A.M. (2003). The effect of Ni/Mn based catalyst synthesis on the activity and morphology of carbon nanotube from methane. In *Proc. Reg. Symp. Chem. Eng. (RSCE 1-3 Dec. 2003, Makati City)*, (Roces, S.A. and Aurestina, J. eds), De La Salle University-Manila, Philippines.

Zein, S.H.S., Mohamed, A.R., Zabidi, N.A.M. (2003). Hydrogen production from methane: current technology and utilization. *J. Industrial Tech.* SIRIM Berhad, Vol 12 (1) 2003, 67 – 79.

Zhang, T. T; Amiridis, M. D. Hydrogen production via the direct cracking of methane over silica-supported nickel catalysts. *Appl. Catal. A: Gen.* **1998**, *167*, 161.