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SHORT COMMUNICATION

KINETICS OF STEAM REFORMING OVER A Ni/ALUMINA CATALYST

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Abstract—Steam reforming of methane over a commercially available, nickel/alumina catalyst was experimentally studied. The reactor employed for the study was made of 7 mm i.d. quartz tube and catalyst particles were 0.84-1 mm in size. The amount of catalyst charge in the reactor was around 0.3 gram. Experiments were carried out varying the steam to methane ratio in the feed gas from 1 to 10 and reaction temperature from 823 to 1073 K. Nitrogen gas was used to control partial pressure of methane and steam. Using Marquardt method reaction rate derived from the experiments was fitted to

$$\text{reaction rate} = 1{,}527\ \exp(-14{,}820/RT)\ P^{1.014}_{CH_4} P^{-0.9577}_{H_2O}$$

Thus reaction order was close to one for methane and close to minus one for steam, respectively.

Key words: Steam Reforming, Ni/Alumina Catalyst, Marquardt Method

INTRODUCTION

Hydrogen is consumed in large quantities for the processing of heavy oil, synthesis of ammonia, oxo processes, etc. Although various technologies have been developed for the production of hydrogen, steam reforming of natural gas and naphtha is predominantly employed all over the world. Usually nickel based catalyst is used for steam reforming in industry and extensive studies have been made on the reaction mechanism and reaction rate of steam reforming of methane [Akers and Camp, 1955; Allen et al., 1975; Bodrov et al., 1964; Rostrup-Nielsen, 1984; Tomita et al., 1980]:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Reaction rate expression can be complicated to include adsorption and desorption on catalyst surface. But simple power law kinetic expression such as Eq. (3) is more convenient to use if product gases do not influence reaction rate:

$$\text{reaction rate} = k\ P^{m}_{CH_4}\ P^{n}_{H_2O} \tag{3}$$

It is generally known that the reacton is first order with respect to methane. However, reaction order with respect to steam reported in the literature varies form zero to minus one. For example Akers and Camp reported that steam reforming of methane over a Ni/Kieselguhr catalyst at 637-1180 °F was first order with methane [Akers and Camp, 1955]. Steam and product gases did not affect reaction rate in their experiments. However, Tomita et al. [1980] reported that reaction order with respect to steam was minus one over a calcium aluminate catalyst at temperatures 750°C to 950°C.

For power law kinetics expression assumption of a certain reaction order or trial and error approach had been employed by investigators to obtain reaction order. But it is also possible to obtain reaction order directly using optimization techniques such as Marquardt Method [Kuester and Mize, 1973]. With the data of Akers and Camp [1955] we have used their method and Marquardt method to obtain reaction order and activation energy. Calculation results are summarized in Table 1. We can see that Marqurdt method resulted in smaller value of standard deviation compared to the method of Akers and Camp [1955].

Table 1. Computation results from the method of Akers and Camp and Marquardt method

	Akers and Camp	Marquardt
Order of methane	1	0.97
Order of steam	0	−0.27
Activation energy(Kcal/g mole)	8.77	7.33
Standard deviation	0.7472	0.7072

In this study we carried out steam reforming of methane with a commercially available catalyst and obtained kinetic expression directly from experimental data using Marquardt method.

EXPERIMENTAL

A schematic diagram of the experimental set-up was shown in Figure 1. Methane (99.99% purity) and nitrogen (99.999% purity) from cylinder were fed to the reactor via mass flow controller. Nitrogen was used as a diluent to control partial pressure of methane and steam in the reactor. Distilled water fed from a syringe pump vaporized in the preheating section prior to injection into the reactor. The reactor, 0.58 meter long, was made of 7 mm i.d. quartz tube. It was mounted vertically inside a furnace and kept at atmospheric pressure. The temperature of the catalyst bed was measured with a 1/16 inch thermocouple. Reacted gases passed through a water trap cooled by dry ice. A couple of gas chromatography were used for the analysis of product gas

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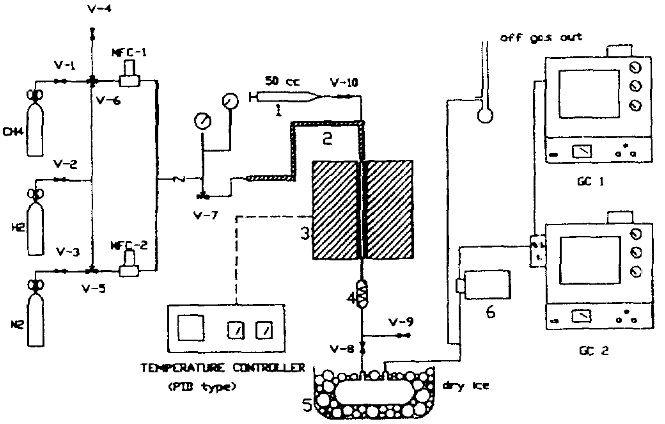

Fig. 1. Schematic diagram of the experimental setup for steam reforming of methane.

1. Syringe pump
2. Preheater
3. Furnace
4. Condenser
5. Water trap
6. Masterflex pump

Table 2. Stoichiometric table of steam reforming of methane

Species	Feed	Product
CH_4	1	1−X
H_2O	A	A−{X(2+B)/(1+B)}
CO	0	BX/(1+B)
CO_2	0	X/(1+B)
H_2	0	3X+{X/(1+B)}
N_2	E	E

composition. Blank test showed no evidence of reaction between steam and methane in the quartz reactor.

A nickel/alumina catalyst, manufactured by ICI, containing 21% Ni was used in this study. The ring-shaped catalyst with outer diameter of 16.3 mm (average) was crushed into particles of 0.84-1.0 mm. BET surface area of the catalyst determined with nitrogen was 11 m^2/g. The amount of catalyst charge in the reactor was around 0.3 gram. Before carrying out steam reforming reaction, catalyst particles were reduced in the reactor with hydrogen (17 cc/min) at 850°C for 12 hours. Reactivity of the catalyst could be sensitve to reduction temperature when reduction temperature was lower than reaction temperature. Hydrogen should be fed into the reactor until the admission of reactants. Otherwise it was found that reactivity of the catalyst to be poorer as mentioned by Rostrup-Nielsen [1984]. Steam reforming reaction were carried out varying reaction temperature, feed gas composition and weight of catalyst charge in the reactor. From the results of preliminary tests varying particle size and gas velocity through the reactor it was found that diffusional mass transfer did not affect significantly reaction rate in the range of experimental conditions.

RESULTS AND DISCUSSION

Mole fraction for each species could be obtained from stoichiometry as shown in Table 2 from methane conversion and feed composition.

Then rearranging the rate expression of Eq. (3) we can have

Table 3. Experimental conditions and results of stream reforming reaction

A	B	E	T (K)	t	Conversion
1.0	0.16	0.25	873	0.538	0.2
2.0	0.1	1.5	873	1.077	0.16
4.0	0.05	4.0	823	5.372	0.2
4.0	0.1	4.0	873	2.155	0.15
4.0	0.26	4.0	873	5.372	0.31
4.0	0.42	4.0	873	13.43	0.68
4.0	0.1	4.0	923	2.155	0.26
4.0	0.41	4.0	923	5.372	0.47
4.0	0.01	4.0	973	0.862	0.13
4.0	0.25	4.0	973	2.155	0.34
4.0	0.28	4.0	973	5.372	0.64
4.0	0.23	4.0	1073	0.862	0.21
6.0	0.01	2.0	873	2.155	0.1
6.0	0.06	2.0	823	2.155	0.07
6.0	0.19	2.0	973	2.155	0.27
6.0	0.35	2.0	1073	2.155	0.39
6.98	0.27	4.0	973	7.16	0.55
6.98	0.27	4.0	1073	3.58	0.47
6.98	0.187	4.0	973	3.58	0.32
6.98	0.17	4.0	873	17.9	0.51
6.98	0.25	4.0	973	6.09	0.51
6.98	0.36	4.0	1073	4.65	0.56
6.98	0.27	4.0	1073	2.87	0.43
6.98	0.3	4.0	1073	8.24	0.65
10.0	0.36	4.0	1073	11.46	0.76
10.0	0.36	4.0	1073	13.43	0.36
10.0	0.25	4.0	1073	5.372	0.56
10.0	0.07	4.0	923	13.43	0.46
10.0	0.18	4.0	923	21.49	0.65
15.0	0.0	4.0	973	13.43	0.47
15.0	0.0	4.0	973	5.372	0.22

$$\int(1+A+2X+E)^{m-n}(1-X)^{-m}\{A-(2+B)X/(1+B)\}^{-n}dX = k_0\exp(-E_a/RT)\int dt \qquad (4)$$

or

$$\frac{\int(1+A+2X+E)^{m-n}(1-X)^{-m}\{A-(2+B)X/(1+B)\}^{-n}dX}{k_0\ \exp(-E_a/RT)} - \int dt = 0 \qquad (5)$$

Our goal here was obtaining values of m, n, k_0 and E_a which minimize absolute value of Eq. (5) integrated over for all experimental data.

Experimental conditions and conversion of methane obtained for the experiments carried out in this study are summarized in Table 3.

Marquardt method of non-linear parameter estimation was used to determine m, n, E_a and k_0. After computation we obtained

$m = 1.104$
$n = -0.9577$
$E_a = 14.82$ Kcal/g mol
$K_o = 1{,}527$ g mol/g cat. hr

Thus reaction rate of steam reforming can be expressed as

$$\text{reaction rate} = 1{,}527\ \exp(-14{,}820/RT)\ P^{1.014}_{CH_4}P^{0.9577}_{H_2O} \qquad (6)$$

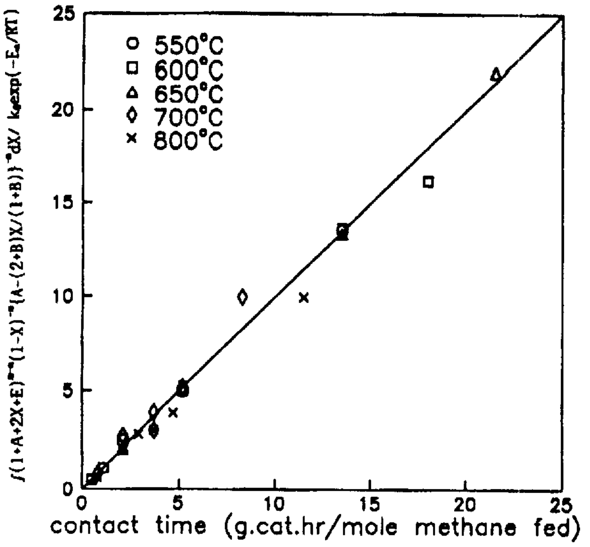

Fig. 2. Determination of reaction order and activation energy from modified integrated values and contact time.

Goodness of data fitting is demonstrated in Figure 2. Thus we can see Eq. (6) fits our experimental data fairly well and reaction order is close to one with respect to methane and minus one with respect to steam.

CONCLUSION

For the steam reforming reaction of methane over a Nikel/alumina catalyst Eq. (6), which was obtained from the experimental data with Marquardt method, fitted experimental data very well. Thus reaction order for methane was close to one and close minus one for steam.

NOMENCLATURE

A : molar ratio of steam to methane in input stream
B : molar ratio of CO to CO_2 in product gas
E : molar ratio of N_2 to methane in input stream
E_a : activation energy [cal/g mol]
k_1 : pre-exponential frequency factor [g mol/g cat. hr]
m : reaction order with respect to methane
n : reaction order with respect to steam
t : contact time [g cat./g mol hr]
T : reaction temperature [K]
X : conversion of methane

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