A Study of the C + H_2 Reaction, Taking into Account H_2 Chemisorption

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Introduction

In previous communications we reported the mathematical models for the C+H_2O and C+O_2 Reactions [1,2]. We showed that the rate-conttrolling steps of the above mentioned reactions were chemisorption of H_2O and disintegration of oxygen surface complexes respectively. In this paper we report a mathematical model for the C+H_2 reaction, taking into account H_2 chemisorption.

Theoretical Analysis

The apparent rate of the C+H_2 reaction is determined in the kinetic area, taking account of the variation in the gas volume:

$$-P\frac{dx}{dt} = kF_k P_{H_2} \qquad (1)$$

where P is the total pressure in the system, x is the proportion by volume of unconverted H_2, K is the experimental rate constant, F_k is the external specific surface of the carbon (m^2/m^3) and P_{H_2} is the partial pressure of H_2.

If chemisorption of H_2O is taken into account, the apparent rate of reaction is given by

$$-P\frac{dx}{dt} = K' F_K \theta_x \qquad (2)$$

where K' is the theoretical rate constant and θ_x is the fraction of the carbon surface occupied by H_2, given by the Langmuir Equation

$$\theta_x = \frac{b\, P_{H_2}}{K_a P_{H_2} + K_d} \qquad (3)$$

where K_a, K_d are rates of chemisorption and desorption of H_2 respectively, b= K_a/K_d. The simultaneous solution of equations (2) and (3) leads to:

$$-P\frac{dx}{dt} = K' F_k\, b \frac{P_{H_2}}{1 + b\, P_{H_2}} \qquad (4)$$

When chemical reaction takes place the apparent rate of C+H_2 process can be described as the difference between adsorption and desorption rates:

$$-\frac{dx}{dt} = F_k\,(K_a\,(1-\theta_x) - K'_d\theta_x) \qquad (5)$$

From (1) and (5)

$$\theta_x = \frac{(K_a - K)\, P_{H_2}}{K_a P_{H_2} + K'_d} \qquad (6)$$

where K'_d is the rate constant of H_2 desorption taking account of the chemical reaction

From (1), (2) and (3) :

$$-P\frac{dx}{dt} = \frac{K^2}{K'} F_k P_{H_2} \frac{1+b\, P_{H_2}}{b} \qquad (7)$$

from $K'_d = K_a + K'$ and $b=K_a/K_d$; $b_1 = K_a/K'_d$:

$$K_a = K'\frac{b\, b_1}{b_1 - b}\ ;\ K'_d = \frac{K'\, b}{b_1 - b} \qquad (8)$$

For the determination of b_1 from (1), (2), (5) and (6) one can find:

$$-P\frac{dx}{dt} = KF_k b P_{H_2} \frac{\frac{K'}{K} b_1 - 1}{b_1 - b} \cdot \frac{AP_{H_2} + 1}{1 + b_1 P_{H_2}}\ ;$$

$$A = \frac{b_1\,(b_1 - 2b)}{b(\frac{K'}{K} b_1 - 1)} \qquad (9)$$

Using proposed mathematical model and experimental data following kinetic parameters of the C+H_2 reaction were obtained[3].

T°K	K'	K_a	K_d	$K_{d'}$	b	b_1
			P = 0,13 Mpa			
1133	$2,28_{10}{-6}$	$4,02_{10}{-4}$	$6,87_{10}{-6}$	$4,59_{10}{-6}$	58,44	87,51
1173	$3,96_{10}{-6}$	$4,75_{10}{-3}$	$1,18_{10}{-5}$	$7,91_{10}{-6}$	400,00	599,98
1213	$5,74_{10}{-6}$	$1,61_{10}{-2}$	$1,72_{10}{-5}$	$1,15_{10}{-5}$	933,47	1400,30
			P = 2,00 Mpa			
1133	$1,06_{10}{-3}$	$2,14_{10}5$	$4,25_{10}{-3}$	$3,19_{10}{-3}$	$5,00_{10}7$	$6,70_{10}7$
1173	$2,07_{10}{-3}$	$3,60_{10}5$	$8,49_{10}{-3}$	$3,40_{10}{-3}$	$4,20_{10}7$	$6,03_{10}7$
1213	$3,13_{10}{-3}$	$4,10_{10}4$	$9,34_{10}{-3}$	$6,22_{10}{-3}$	$3,05_{10}4$	$4,59_{10}4$

References

1. A.S.Fedoseev, "A Study of the Kinetics of the $C+H_2$ Reaction Taking into account H_2 Chemisorption", Extanded Abstracts, Sixth London International Carbon and Graphite Conference, Society of Chemical Industry, London, p.p. 109-111. 1982

2. A.S.Fedoseev, "Mathematical Modelling of the $C+O_2$ Reaction", Extanded Abstracts, Carbon-84, International Conference on Carbon, Bordeaux, France, 1984

3. K.J.Hüttinger, P.Schleicher, "Kinetics of Hydrogasification of Coke Catalysed by Fe, Co and Ni", Fuel,V.60,NII,p.p.1005-1012 1981