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Kinetics of carbon formation from CH_4–H_2 mixtures over a nickel containing catalyst

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Abstract

The experimental data, corroborating the effect of CH_4–H_2 mixture compositions and temperature on the formation of catalytic filamentary carbon (CFC) in methane decomposition over a highly loaded Ni-containing catalyst, are presented. We propose a model of the catalyst deactivation: carbon blocks the surface of a CFC growth center (GC). Using this model, we have derived the equation for calculating the deposition rate of CFC and its maximum quantities which may form during the time of complete catalyst deactivation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic filamentary carbon; Methane decomposition; Catalyst; Deactivation; Kinetics

1. Introduction

At present, the process of catalytic filamentary carbon formation in hydrocarbon decomposition over Ni-containing catalysts is treated as a nontraditional way for producing novel carbon materials [1–3].

The kinetic regularities of the CFC formation on lower loaded Ni-containing catalysts (<30 wt% Ni) were studied in [4–7], whereas the catalyst deactivation was examined in [5,8].

A particular group of publications studies the process of CFC formation in the CH_4 decomposition over the highly loaded nickel catalyst [3]. Here, the CFC forms porous carbon granules (2–5 mm), comprising almost 99 wt% of filamentary carbon, which exhibit a higher degree of graphitization [9] and unique adsorption properties [10].

Unfortunately, the kinetics of granular CFC formation over highly loaded Ni catalysts is insufficiently studied. The data available [10,11] relate to a variable CH_4–H_2 reaction medium composition under experimental conditions, therefore, they cannot be used for deducing kinetic equations describing the processes of CFC deposition and catalyst deactivation.

2. Experimental

The catalyst composition and its preparation procedure are described elsewhere [12].

The experimental data were obtained in the methane decomposition in a flow vibrofluidized bed catalyst microreactor of ideal mixing. CH_4 and H_2 were almost 99.92% pure. The H_2 concentration was kept constant in the reactor throughout one run, and it varied from 0% to 40% with each experiment.

3. Results and discussion

Figs. 1 and 2 present the curves of the CFC deposition rate versus time in pure methane and a mixture of

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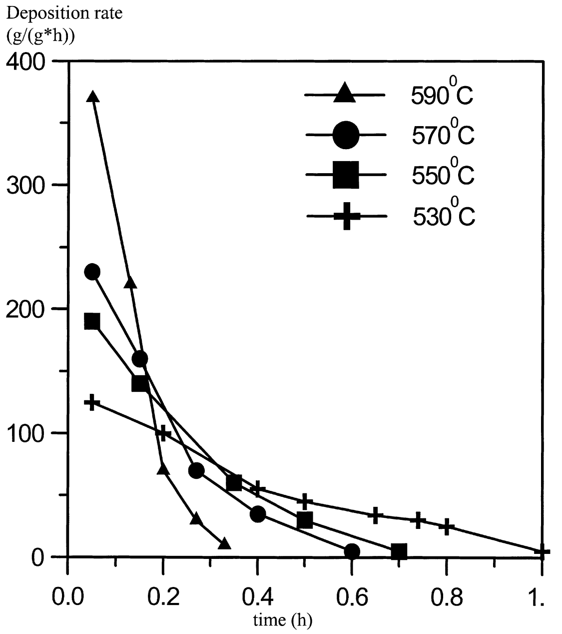

Fig. 1. The rate of CFC formation in pure CH_4 vs. time.

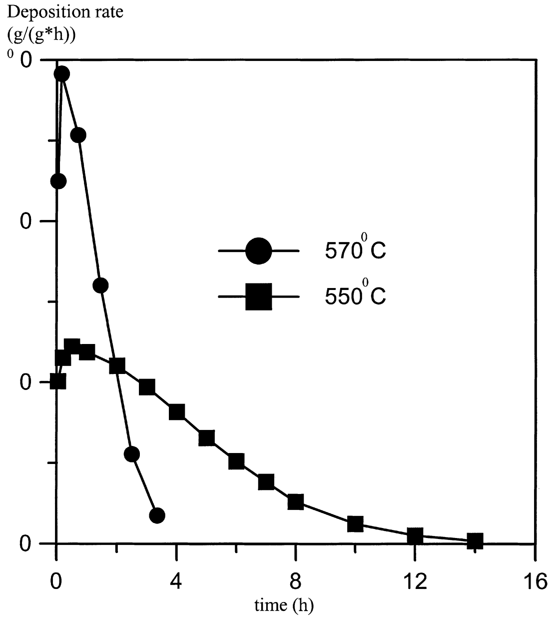

Fig. 2. The rate of CFC formation in the 85% CH_4+15% H_2 medium vs. time.

CH_4+H_2 (15%), respectively. In the presence of H_2, the rate of deposition first increases and then drops to 0. This dependence persists even if the H_2 concentration comes to 40%. The final process step, characterized by a relatively slow catalyst deactivation, significantly differs from that described in [11] when the H_2 concentration was not kept constant in the ideal mixing reactor.

In contrast to the experiment [5], where the catalyst lost its activity almost immediately in the reaction mixture containing 100% of CH_4, our catalyst has ensured a rather high overall yield of CFC (about 50 g/g_{cat} h) under the same conditions.

The data obtained (some are presented in Figs. 1 and 2) permitted one to establish how the maximum rate (during the time of catalyst deactivation) of CFC deposition depends on the temperature and concentrations of H_2 and CH_4 in the reaction medium as well as to describe this dependence using the Langmuir–Hinshelwood equation, allowing for hydrogen dissociative adsorption on the nickel site of growth of CFC [5]:

$$r_{\max} = k(P_{CH_4} - P_{H_2}^2/K_e)/(1 + K_H P_{H_2}^{0.5})^n, \qquad (1)$$

where $r_{\max}$ is the maximum rate of CFC formation with time (g/g_{cat} h);

$$K_e = 5.088 \times 10^7 \exp(-91200/(RT)), \qquad (2)$$

$$k = 2.83 \times 10^8 \exp(-97000/(RT)), \qquad (3)$$

$$K_H = 9.883 \times 10^{-9} \exp(108300/(RT)), \qquad (4)$$

where K_e is the equilibrium constant for the CH_4=$2H_2$+C[kPa] reaction, k the constant for CFC formation (g/g_{cat} h kPa), K_H the equilibrium constant for hydrogen adsorption ($kPa^{0.5}$), P_{H_2} the partial pressure of hydrogen in reactor (kPa), P_{CH_4} the partial pressure of methane in reactor (kPa), R the universal gas constant 8.314 J/(mol K), and T is the temperature (K).

In [5], the best agreement between the calculated and experimental results was observed for n=7; therefore, we also set n equal to 7 in the experimental data processing. The largest discrepancy between the experimental results and the data calculated by Eq. (1) comes to 7%. Using Eq. (2), we have obtained the values of K_e which are very close to those of [13] and far exceed the values of [14,15]. The activation energy of the methane decomposition over the nickel catalyst attains 97 kJ/mol, which is very close to 88, 90 and 96.1 values obtained in [5,7,8], and exceeds that observed in [16], 75 kJ/mol.

If one assumes a carbon blocking of the GC surface as a mechanism of the catalyst deactivation, then

$$\mathrm{d}C/\mathrm{d}t = r = r_{\max} a^n, \tag{5}$$

where a is the portion of active sites, C the amount of CFC formed (g/g_{cat}), r the rate of CFC formation (g/g_{cat} h), n the number of active sites involved in the limiting stage upon CFC formation, and t is the time (h).

Considering the dependence $r=f(t)$, we have found that relations an $\sim C(t)$ [8] and an $\sim\exp(-P_{CH_4^*} t/P_{H_2})$ [5], used to describe the experimental data (Figs. 1 and 2) are not true. It was found that the rate of a decrease in time is proportional to the CFC formed and to the square of its maximum formation rate:

$$\mathrm{d}a/\mathrm{d}t = -r_{\max}^2 C k^*, \tag{6}$$

where k^* is constant for deactivation rate of catalyst active sites $(g_{\mathrm{cat}})^3$ h/g^3.

Assuming that $a=1$ at $r=r_{\max}$, Eqs. (5) and (6) can be supplemented with the following initial conditions:

$$C|_{t=tm} = C_{\max} \tag{7}$$

and

$$a|_{t=tm} = 1, \tag{8}$$

where $C_{\max}$ is the amount of CFC deposited by the time, when the rate of its formation becomes maximum (g/g_{cat}) and t_{m} is the time when the rate of CFC formation is maximum (h).

Applying Eqs. (5) and (6), one has:

$$\frac{1}{nk^* r_{\max}^{1/n+2}} \left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)^{-1+1/n} \frac{\mathrm{d}^2 C}{\mathrm{d}t^2} = -C. \tag{9}$$

Allowing for Eq. (5), Eq. (9) can be rewritten as

$$r^{1/n}\mathrm{d}r = -nk^* r_{\max}^{1/n+2} C\,\mathrm{d}C. \tag{10}$$

Then, integrating both parts of Eq. (10), one obtains the dependence for the CFC rate formation:

$$\mathrm{d}C/\mathrm{d}t = r = \left[-\frac{n+1}{2} k^* r_{\max}^{1/n+2}(C^2 - C_{\max}^2) + r_{\max}^{1+1/n}\right]^{n/(n+1)}. \tag{11}$$

Maximum CFC quantity is determined by integrating both sides of Eq. (10) from $r_{\max}$ to 0 and from $C_{\max}$ to C_{maxb}, respectively:

$$C_{\mathrm{maxb}} = \left(\frac{2}{k^*(n+1) r_{\max}} + C_{\max}^2\right)^{1/2}, \tag{12}$$

where C_{maxb} is the maximum CFC amount formed (g/g_{cat}).

Assuming $n=7$, and neglecting the CFC formed before the maximum rate of deposition is obtained, Eqs. (11) and (12) can be rewritten as

$$\frac{\mathrm{d}C}{\mathrm{d}t} = r = (-4 r_{\max}^{15/7} C^2 k^* + r_{\max}^{8/7})^{7/8}, \tag{13}$$

$$C_{\mathrm{maxb}} = \tfrac{1}{2}(r_{\max} k^*)^{-1/2}. \tag{14}$$

The initial condition for Eq. (14) will be

$$C|_{t=0} = 0. \tag{15}$$

$k^*=f(T)$ can be approximated by the following equation:

$$k^* = 2.73 \times 10^{-13} \exp(99270/(RT)). \tag{16}$$

Using Eqs. (13) and (14), we have obtained a good agreement (not less than 7%) between the calculated and experimental data presented in Figs. 1 and 2 and the experimental results corresponded to the 30% and 40% hydrogen concentrations.

The efficiency of the kinetic dependences is supported by comparing the experimental results, obtained in the carbon formation at constant methane flow rate and Ni catalyst deactivation in the ideal mixing reactor, to the data of the mathematically simulated process performed using these dependences.

4. Conclusions

1. Rate of CFC formation in the absence of catalyst deactivation is limited by dissociative adsorbtion of methane and can be described by the Langmuir–Hinshelwood equation which accounts for the competitive dissociative adsorbtion of H_2.
2. For the particular composition and reaction temperature, rate of decrease of the active site portion on the growth center surface is proportional to the amount of CFC formed per mass catalyst unit and square of the maximal rate of CFC formation with time under these conditions.

3. Maximum amount of CFC, formed for the particular composition and reaction medium temperature, is inversely related to maximum rate of CFC formation under these conditions.
4. Comparison of the obtained kinetic dependences and experimental results indicate their close agreement. Using the obtained kinetic dependence for calculation of CFC formation during Ni-catalyst deactivation in the reactor with ideal mixing we have shown a good agreement between calculated and experimental results.

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