Coproduction of Hydrogen and Carbon Nanomaterials by Catalytic Decomposition of Methane-Hydrogen Mixtures: Experimental and Simulation Results

Shelepova E.V., Maksimova T.A., Bauman Yu.I., Mishakov I.V., Vedyagin A.A.
Boreskov Institute of Catalysis, Pr. Ak. Lavrentieva, 5, Novosibirsk, Russia, 630090

Abstract
The existing hydrogen production technologies are associated with a number of hardship and disadvantages. The process of methane catalytic pyrolysis permits one to obtain the hydrogen along with nanostructured carbon at significantly lower temperatures than thermal pyrolysis of methane. The efficiency of the catalytic decomposition of methane-hydrogen mixture over the NIO-CuO/Al2O3 catalyst was studied using the reactor with McBain balances. The kinetic model based on the dissociative adsorption of methane was used for the mathematical modeling. The defined kinetic constants for this model provide an appropriate fitting of the experimental points. In order to optimize the process parameters for catalytic decomposition of methane-hydrogen mixture, the mathematical modeling was carried out using the non-stationary mathematical model.

MATHEMATICAL MODEL

\[
V \frac{dc_i}{dt} = V_i \cdot \frac{dc_{cat}}{dt} + G \cdot (c_{bi} - c_i), i = CH_4, H_2
\]

Initial conditions: \( t = 0; c_i = c_{bi}, t = CH_4, H_2; c_c = 0 \)

The kinetic model based on the dissociative adsorption of Methane is described by the following equation:

\[
r = k^* \times P_{CH_4} \times \frac{K_{cat}(c_a)^{3/2}}{(1 + P_E)^2},
\]

where \( k^* = k_1 \times e^{-E_1/RT}, k = k_2 \times e^{-E_2/RT} \)

\( K_{cat} = K_{cat}(c_a)^{3/2} \)

\( E_1 = 91.2 \text{ kJ/mol}, K_0^* = 5.088 \times 10^5 \text{ atm}^{3/2} \)

The mathematical modeling gives an appropriate coincidence of theory with experiment at the following values of the parameters: \( B^* = 53 \text{ kJ/mol}, \) \( k_1 = 4.1 \times 10^6 \text{ mol}^{-1} \text{ cm}^{-3} \cdot \text{s}, \) \( E_1 = 17 \text{ kJ/mol} \)

The product is represented by carbon filaments varied in length and diameter. The carbon nanofibers are well-packed ones and belong to a stacked (or “pile of plates”) structural type. These filaments possess the bimodal structure composed of thin (20-100 nm in diameter) and thick (150-350 nm in diameter) fibers. Characterization of the carbon samples by low-temperature nitrogen adsorption allows estimating their specific surface area (SSA) and pore volume (Vpore). It was found that the SSA and Vpore values lie within ranges of 120-170 m²/g and 0.16-0.18 cm³/g, correspondingly.

Conclusions
In the present work, the efficiency of the catalytic decomposition of methane-hydrogen mixture over the NIO-CuO/Al2O3 catalyst was studied. The maximum CNF value of 34.9 g/gcat was observed at the reactor temperature of 560 °C and a hydrogen concentration of 13 vol.%. The maximum carbon yield value of 34.9 g/gcat was observed at the reactor temperature of 610 °C. A further increase in temperature decreases the carbon yield.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390054-1). Characterization of the samples was performed using the equipment of the Center of Collective Use “National Center of Catalysis Research”. The authors are grateful to Ayupov A.B. for the useful results and discussion.