

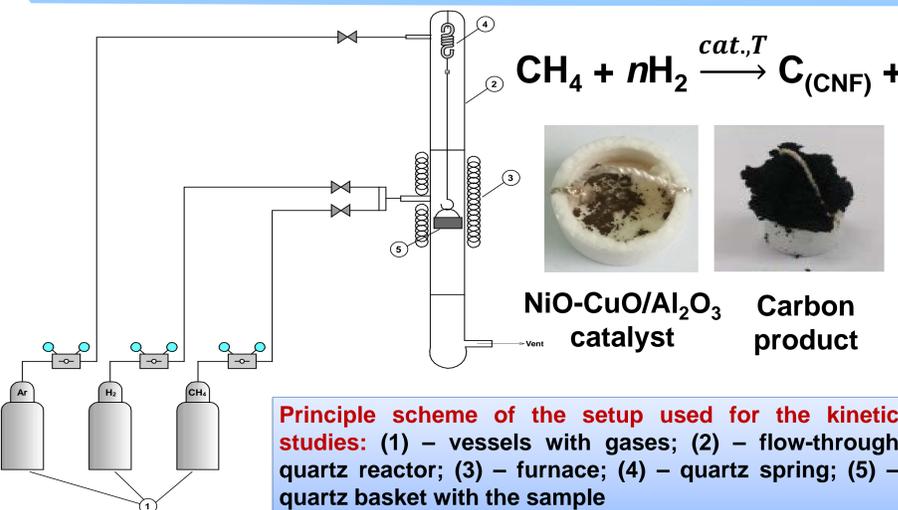


Coproduction of Hydrogen and Carbon Nanomaterials by Catalytic Decomposition of Methane-Hydrogen Mixtures: Experimental and Simulation Results

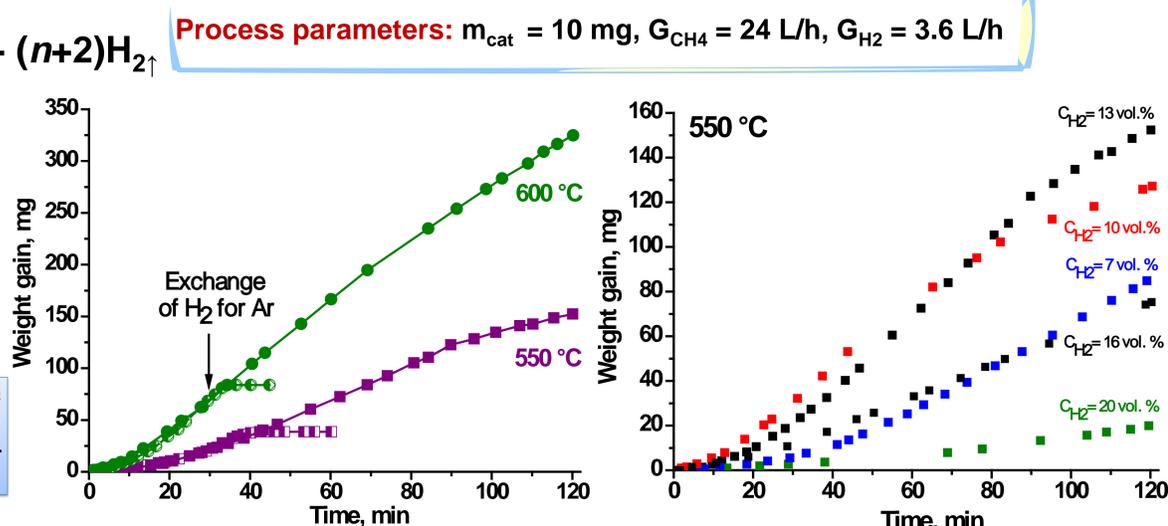
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Abstract

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 modelling was carried out using the non-stationary mathematical model.



Process parameters: $m_{cat} = 10 \text{ mg}$, $G_{CH_4} = 24 \text{ L/h}$, $G_{H_2} = 3.6 \text{ L/h}$



MATHEMATICAL MODEL

$$V_{mix} \frac{dC_i}{dt} = v_i r \times V_{cat} + G(C_{0i} - C_i), i = CH_4, H_2$$

$$V_{mix} \frac{dC_C}{dt} = v_C r \times V_{cat}$$

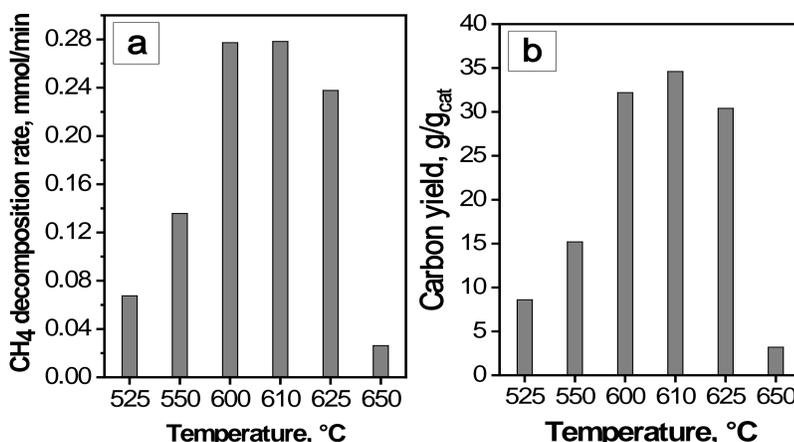
Initial conditions: $t = 0$; $C_i = C_{i,in}$, $i = CH_4, H_2$; $C_C = 0$

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

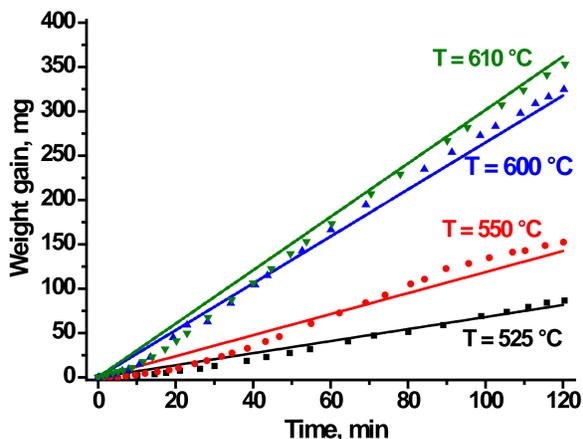
$$r = \frac{(k^+ \times P_{CH_4} - k^- / K_r \times P_{H_2}^2)}{(1 + P_{H_2}^{3/2} / K_r)^2}$$

where $k^+ = k_0^+ \times \exp(-E_a^+ / RT)$, $k^- = k_0^- \times \exp(-E_a^- / RT)$

$K_r = k_0^+ \times \exp(-E_a^r / RT)$, $E_a^+ = 91.2 \text{ kJ/mol}$, $k_0^+ = 5.088 \times 10^5 \text{ atm}^{3/2}$



- The addition of hydrogen into the reaction mixture provides the stable operation of the catalyst.
- The maximum carbon yield was reached with a hydrogen inlet concentration of 13 vol.%.
- The maximum carbon yield value of 34.9 g/g_{cat} was observed at the reactor temperature of 610 °C. A further increase in temperature decreases the carbon yield.



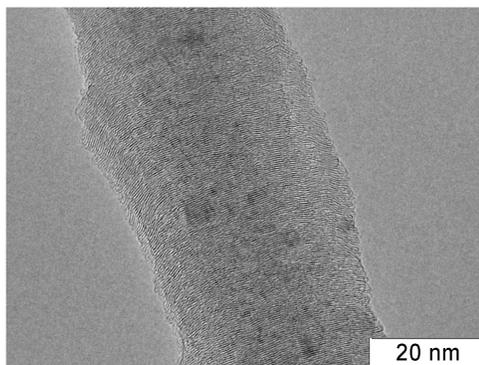
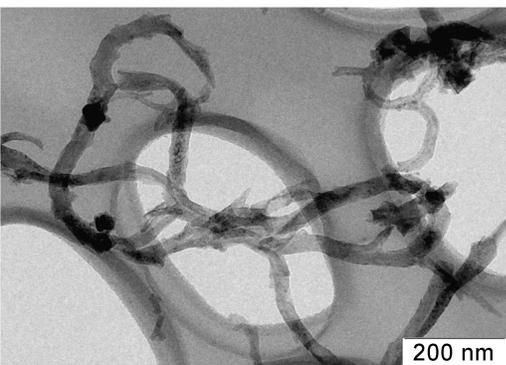
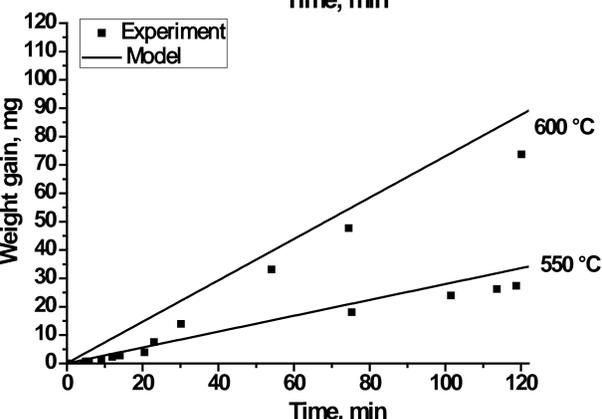
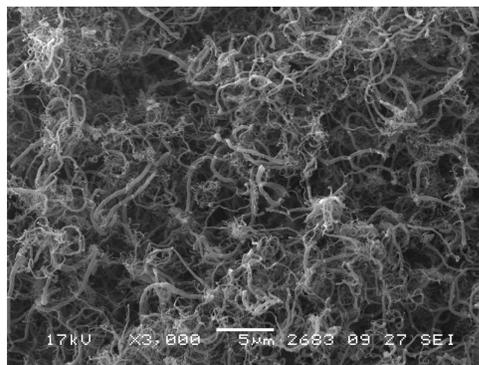
The mathematical modelling gives an appropriate coincidence of theory with experiment at the following values of the parameters:

$$E_a^+ = 53 \text{ kJ/mol},$$

$$k_0^+ = 41 \times 10^4 \text{ mol}/(\text{m}_{cat}^3 \cdot \text{s} \cdot \text{atm}),$$

$$E_a^- = 17 \text{ kJ/mol},$$

$$k_0^- = 35 \times 10^2 \text{ mol}/(\text{m}_{cat}^3 \cdot \text{s} \cdot \text{atm}^{1/2})$$



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 (V_{pore}). It was found that the SSA and V_{pore} 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/g_{cat} is observed for the temperature of 610 °C with a hydrogen inlet concentration of 13 vol.%. The simulation of the process was performed using the kinetic model based on the mechanism of the dissociative adsorption of methane on the nickel-copper catalyst. The defined kinetic constants for this model provide an appropriate fitting of the experimental points. It was found that the optimal value of residence time at 610 °C is equal to $3.23 \times 10^{-3} \text{ s}$.

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