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The regularities of the formation of carbon nanostructures from hydrocarbons based on the composition of the reaction mixture

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Abstract

This paper presents the results of research on the regularities of the formation of carbon nanofibrous materials, as well as the influence of the composition of the model mixture of hydrocarbons C_1–C_4 on the morphological features and textural characteristics of the resulting carbon nanofibres (CNF).

One of the most urgent issues faced by the oil and gas industry is how to increase the processing depth of associated petroleum gas (APG). In the Russian Federation alone, the annual economic losses from unutilised APG during processing are estimated at 2 billion dollars. It is known that the composition of APG can vary greatly, depending on the oil and gas field. In particular, the methane concentration, the main component of natural gas and associated gas, varies from 25 to 95 vol.%. In this study, we sought to identify the main factors that determine the morphology and structure of CNF, and to develop approaches in processing actual hydrocarbon mixtures to produce a carbon product with the desired or predictable characteristics. Such an approach can serve as a basis for resource-saving catalytic technology utilizing C_1–C_4 hydrocarbons that are currently disposed of as post-combustion flare gas.

The research results clearly demonstrate that the morphology and texture of the carbon materials obtained by the decomposition of hydrocarbon mixtures depend on the composition of the reaction gas. The key components in this case are methane and the resultant hydrogen: their relationship at a specific temperature determines the direction of the reversible reaction of carbon hydrogenation: $C + 2H_2 = CH_4$.

The decisive factor in the decomposition of hydrocarbons yielding carbon materials is the degree of deviation of the methanation reaction from equilibrium which can be influenced in two ways. The addition of hydrogen to the reaction gas promotes the driving force of the carbon hydrogenation reaction, resulting in defective high-surface carbon fibres. Increasing the concentration of methane in the reaction gas composition, in contrast, reduces the driving force of methanation until the process is suppressed, which promotes a more structured form of the CNF, without defects.

Keywords: Hydrocarbons; Decomposition; Nanofibres; Morphology; Methanation

1. Introduction

The synthesis of carbon nanofibres (CNF) and nanotubes (CNTs) on nickel-containing catalysts from raw hydrocarbons is of paramount practical importance [1–4]. This method, known by the acronym CCVD (Catalytic Chemical Vapour Deposition), along with valuable carbon nanomaterials, produces pure hydrogen, and has generated recent interest as a potential method for effectively processing natural gas based on methane and associated petroleum gas (APG) [5–8]. One of the most urgent issues faced by the oil and gas industry is how to increase the processing depth of associated petroleum gas (APG). In the Russian Federation alone, the annual economic losses from unutilised APG during processing are estimated at 2 billion dollars.

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It is known that in terms of its properties, methane differs significantly from all other representatives of the homologous series of hydrocarbons. An important property of the molecule CH_4 is its high stability [9,10]. It is known that the reaction of methane decomposition into carbon (graphite) and hydrogen is endothermic, whereas all other hydrocarbons decompose exothermically. Methane decomposition up to very high temperatures (900 °C or higher) is reversible, which implies the simultaneous presence in equilibrium conditions of both methane and hydrogen [11]. The equilibrium level of methane conversion increases with temperature, but this is almost always accompanied by a thermodynamic limit, which prohibits the attainment of 100% conversion of methane with the formation of CNF and hydrogen.

It is known that the composition of the reaction medium has a decisive influence on the morphology and structure of carbon fibres formed by the decomposition of hydrocarbons [12]. We should also note another important fact: the catalytic decomposition of any hydrocarbons C_2–C_n forming carbon and hydrogen will always generate side reactions in the hydrogenation of the carbon to form methane (methanation). Our previous studies have shown [13–15] that methanation plays a key role in the "loosening" of the packing of graphene layers in the body of the fibre, causing the formation of "feathery" nanofibres with a high specific surface area.

$$C + 2H_2 \rightleftarrows CH_4 \qquad (1)$$

In the temperature range of the decomposition of hydrocarbon mixtures under study (400–800 °C), the reaction (1) is reversible. This explains the occurrence of a driving force for the hydrogenation of carbon, which to some extent is manifested with the decomposition of all hydrocarbons except methane itself.

During the decomposition of a mixture of propane and butane, the formation of hydrogen takes place according to the reaction Eqs. (2) and (3).

$$C_3H_8 \rightarrow 3C + 4H_2 \qquad (2)$$

$$C_4H_{10} \rightarrow 4C + 5H_2 \qquad (3)$$

Thus, we can delineate several fundamentally important factors that together will determine the structural features of the resulting carbon materials:

1 the methane concentration in the composition of the hydrocarbon mixture (APG);
2 the conversion rate of raw hydrocarbon; and
3 the temperature for carrying out the process.

Some influence may also be wielded by other additives in the composition of natural gas (molecular nitrogen, carbon dioxide, etc.), hydrocarbon diluent, but their total concentration in the composition of APG rarely exceeds 10 vol.%, which means that their contribution is minor.

By increasing the degree of the conversion of raw hydrocarbon, the hydrogen concentration increases, thereby "launching" the methanation reaction, which in turn is reflected in the nature of the structuring (the number of defects) of the carbon fibres, and therefore, their textural and morphological characteristics.

2. Materials and methods

For the synthesis of CNF we used a nickel–copper catalyst with the following composition: 84 wt.% NiO + 13 wt.% CuO + 3 wt.% Al_2O_3. The catalyst was prepared through the mechanochemical activation of nickel oxide (II), copper oxide (II) and aluminium hydroxide, combined in the corresponding ratio. Mechanochemical activation was carried out in an AGO-3 planetary mill (grinding medium – steel balls with a diameter of 8 mm, the acceleration of the grinding medium – 390 m/sec^2, activation time – 15 mins).

Before beginning the experiment on the synthesis of CNF the catalyst was reduced in the hydrogen stream at 550 °C for 15 minutes. The reduction led to the formation of dispersed particles of Ni–Cu alloy, which subsequently played a role of the active centres for the carbon fibre growth [15–17]. Aluminium oxide in an amount of 3 wt.% serves the function of a structural promoter, preventing the sintering of alloyed metal particles [15].

To investigate the dependence of the morphology and texture properties of the carbon material on the composition and degree of conversion of raw hydrocarbon, experiments were conducted in a horizontal flow-through quartz reactor. The specially-designed reactor allowed us to carry out a so-called "discrete load" of the catalyst – in several different consecutive points (up to five) along the length of the reactor.

The experimental reactor was a horizontal 1.4 m tube made of quartz, with two main entry–exits at the ends, as well as 9 add-ons, used for sampling the gas phase along the length of the reactor while the hydrocarbons were in the decomposition process.

A schematic of the reactor with the reaction insert for the discrete catalyst load is presented in Fig. 1. The catalyst was discretely loaded into the reactor by 4 equivalent samples.

The catalyst was placed at the liner surface in separate samples (5 mg each, with 15–20 cm increments) so that the sample was situated in the reactor zones at approximately the

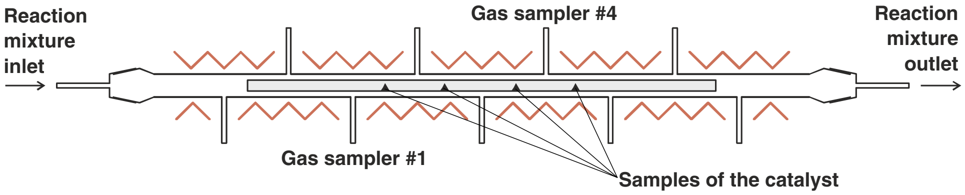

Fig. 1. Scheme of a horizontal quartz reactor with a discrete catalyst loading.