PECULIARITIES OF FORMATION OF GRANULATED POROUS FILAMENTOUS CARBON IN METHANE DECOMPOSITION ON Ni-CONTAINING CATALYSTS

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Introduction

One of the original ways for producing new carbon materials with an unusual nanostructure is a catalytic low-temperature decomposition of hydrocarbons in the presence of catalysts containing group 8 metals [1,2,3].

It was shown [4] that catalytic filamentous carbon (CFC) is produced in the form of porous granules on the Ni- containing catalyst on a pilot plant. In fact it is a new unusual class of granulated porous carbon materials.

Experiments show that this new mesoporous carbon has unusual properties and can be considered as a promising sorbent, catalyst, catalyst support, compound for various purposes, etc.

Technology studies show that the porous filamentous carbon manufactory will be simple and cheap [5].

In this paper the effect of the CH_4 + H_2 mixtures composition and temperature on carbon filaments formation and filament properties in methane decomposition on the Ni-containing catalyst as well as the peculiarities of carbon granule formation and catalyst deactivation are discussed.

Experimental

The catalysts containing 90 wt.% Ni were prepared by joint precipitation of nickel and aluminium hydroxides from the mixture of their salt solutions. The sediments were filtered, washed, dried at 120 °C and decomposed in nitrogen at 350 °C and the samples were reduced in hydrogen at 550 °C for 3 h.

Methane decomposition occurred in a perfectly mixed flow microreactor. Reactor was vertically vibrated with 1 mm amplitude and 50 Hz frequency. High-purity (no less than 99.99%) CH_4 and H_2 were used. Catalyst mass was 0.002 g. Experiments were carried out at 490-590 °C. Hydrogen concentrations were <2.5 ("pure" CH_4), 15, 30, and 40%.

CFC was sampled within a definite time after the process start-up and analyzed with a TEM JEM-100 CX microscope (10000-100000 magnification).

From the distributions obtained we calculated the average diameter of growth centers (GC) and filaments.

Results and Discussion

The photos in Figure 1 show the carbon granules (a) and their surface picture (b) obtained with a scanning electron microscope (6000 blow up). The filaments grow typically in a whiskerlike structure with a nickel microparticle of 50-150 nm at the top. We name these microparticles growth centers.

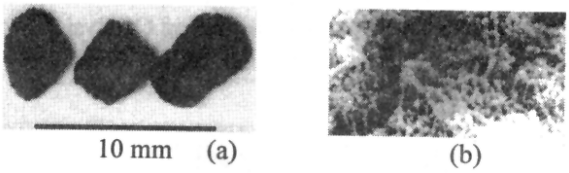


Fig.1. Carbon granules (a) and their surface picture (b).

During the granule growth the catalyst particle of 0.2-1 mm is converted to a carbon granule of 1-5 mm containing more than 99% of carbon. The porous carbon granule is formed by the weaving carbon filaments. The gaps between the filaments serve as pores. The inner surface of such particles is the surface of filaments.

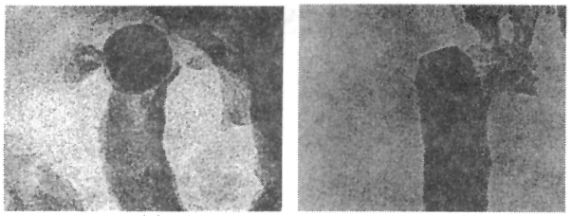
The process of carbon granule formation is rather unusual due to the filaments growth in the bulk of the catalyst particle. The particle is continuously destroyed and simultaneously sewed by growing filaments.

Influence of hydrogen concentration.

Experiments show that hydrogen concentration is one of the main parameters of the process observed. The lower is hydrogen concentration, the higher are the rates of carbon deposition and catalyst deactivation. At low hydrogen concentration (<2,5%) the maximum amount of CFC produced per unit catalyst mass until complete catalyst deactivation (y_c) (ca. 50 g/g cat) does not depend on the temperature. When hydrogen concentration is high (>10%), y_c can reach 150- 300 g/g cat.; the deactivation time increases from minutes to hours.

Electron microscope studies show two types of GC shape: spherical (Fig.2a) and faceted (Fig.2b). For example, GC corresponding to "pure" CH_4 at T=530 °C are spherical those related to 60%CH_4 + 40%H_2 at

T=550 °C are faceted. Probably the spherical particles are



(a) (b)

Fig.2. Growth center shape (80000 blow up): spherical (a), faceted (b)

liquid and the faceted ones are solid. It is a very unusual phenomenon because the nickel melting point under standard conditions is 1453°C. We observed that the more is the hydrogen concentration, the more is the mean GC diameter and the more is the portion of faceted particles.

Influence of temperature.

The rates of carbon formation and catalyst deactivation fall and y_c increases with the temperature decrease. For "pure" methane temperature does not affect y_c unlike the case when H_2 is present. Experiments show that the portion of the faceted GC increases as temperature falls. The analysis of the samples obtained in the $CH_4 + H_2$ media shows that, as temperature falls, the portion of large diameter GC and filaments grows. The temperature dependence of the CFC yield per GC unit volume and GC unit surface can pass through maxima.

Influence of GC size.

In "pure" methane the maximum CFC amount corresponds to the minimum GC size (0-20 nm). The GC diameter distribution of the CFC yield per GC unit surface area is less dependent on the GC sizes. This indicates that in "pure" methane the GC surface area is a key parameter in the CFC formation. It was found that the more is the GC size, the more is the portion of faceted GC.

Influence of CFC rate deposition.

As follows from the experimental data, an increase in the rate of deposition leads to y_c decrease and increase in the portion of spherical GC. One may assume that in the case of small particles the presence of carbon leads to the fall in melting point. In this case the increase in the rate of carbon deposition leads to the increase in the carbon content in nickel and therefore to the decrease in the temperature of transition from faceted (solid) to spherical (liquid) particles.

Some properties of granulated filamentous carbon.

Figure 3 presents the temperature dependencies of the average diameters of filaments in the CFC samples obtained 2 h after the process start-up in the $H_2 + CH_4$ media with various reagent concentrations. The above diameters decrease with temperature and grow with the H_2 concentration. Under the same conditions they differ by no more than 10%. With this regard one can conclude that the average diameter of filaments formed in a porous filamentous carbon grain is governed by concentration of H_2. Carbon purity depends on y_c and can reach 99,5%.

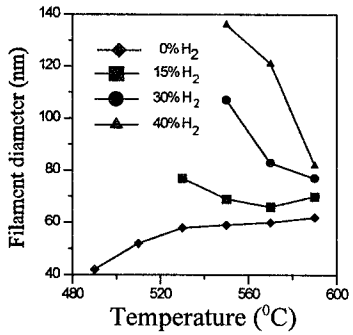


Fig. 3. Temperature dependence of the filament diameter.

Conclusions

There are complex relationships between the reaction medium composition, temperature, GC sizes and shape, on one hand, and between the rates of CFC formation, their texture and amount CFC per unit catalyst mass until its complete deactivation, on the other hand.

The results presented help one to understand the mechanism of CFC formation. They open a new way for mathematical simulation of the kinetics of carbon formation and catalyst deactivation in the process observed.

References

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