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Porous carbon materials prepared from C_1–C_3 hydrocarbons

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Abstract

The inexhaustibility of various solid porous carbons produced from C_1–C_3 hydrocarbons, which may be used as catalyst supports, adsorbents and so on is reported. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Porous carbon materials; C_1–C_3 hydrocarbons; Sibunit; Carbon molecular sieve; Catalytic filamentous carbon; Micropore-size distribution

There are two utmost ways of C_1–C_3 hydrocarbons transformation to different forms of solid carbon: *homogeneous* mechanisms that proceed in gaseous phase at T>1000°C and *heterogeneous* mechanisms that proceed at lower temperatures on the surface of various solids. It is a predominant opinion that carbon black and its intermediates in form of pyrocarbon (PyC) are only produced by homogeneous mechanisms. However, deposition of PyC on the carbon surface is not a simple physical deposition of gaseous reaction products. This fact was mentioned, for example, by Kiselev and Krylov [2]. This problem was studied more carefully by Hoffman et al. [3]. They showed that the irreversible chemisorption C_1–C_4 of alkanes and alkenes takes place on the pure surface of graphitized carbon black at the temperature as low as 573 K. These chemisorbed hydrocarbons are decomposed at higher temperatures to evolve the typical pyrolysis products, i.e., carbon, hydrogen, and a number of light hydrocarbons of the composition other than that of the primarily adsorbed species. That is why we have to consider PyC deposition even on the carbon surface as a heterogeneous catalytic process.

Hoffman et al. [3] stated that this catalytic reaction occurs on the active sites, which are localized on the "edge" graphite planes (*hko*), formed during the graphite gasification or on the defects of the basal graphite planes (0 0 2) of the non-burnt graphitized carbon black. The accessibility of these active sites is strongly influenced by the shape, size, and orientation of the chemisorbed molecules.

It is not our aim to discuss the complexity of *chemical* transformations. In this report we will concentrate on general physicochemical mechanisms of texture formation.

The first typical example is the production carbon composite materials by PyC deposition on a granulated carbon black. Such materials, named *Sibunits*, are obtained by C_1–C_4 pyrolysis at 850–950°C [1,4]. Basic processes of the Sibunit structure formation are shown schematically on Fig. 1. Pre-granulated carbon black (Fig. 1(a)) is covered by a fixed amount of PyC (Fig. 1(b)), which usually ranges from 1 to 5 g per gram of the initial carbon black. This is the stage of condensation or chemical vapor deposition (CVD). In

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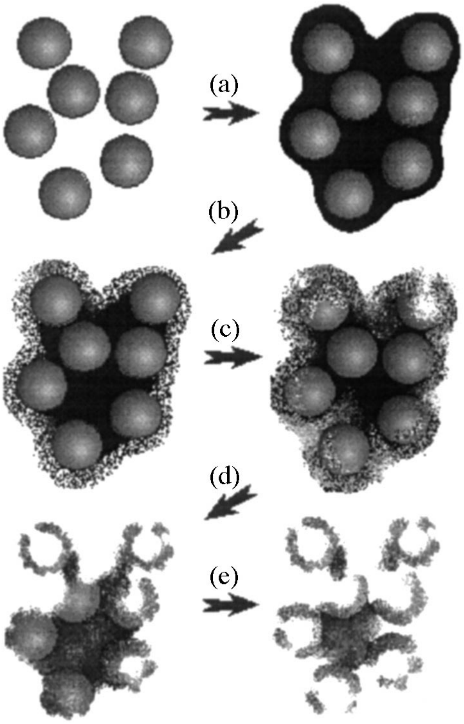

Fig. 1. Sibunit formation scheme.

the kinetic operation conditions the deposited PyC have lamellar structure. Then the activation stage is usually conducted in flowing water steam at 700–850°C (Fig. 1(c)–(e)). During this stage a part of carbon is removed by gasification. At first the most defected parts of PyC are gasified. But when the system of the formed pores reaches the carbon black, the preferential gasification of the latter starts. This causes by the more structural disordering of carbon black compared to PyC. As a result, a sponge-like system including meso- and macropores whose dimensions depend on the dispersion of the initial carbon black is formed. When the carbon black is burnt out almost completely (Fig. 1(e)), the obtained granules lose their mechanical strength and destroy into shell-like fragments.

This general scheme of Sibunit production allows all structural and textural properties to be controlled over a very wide range. For example, the macropore size can be varied in a range 10^2–10^4 nm via adjusting dispersion of the initial carbon black and conditions of treatment and granulation. The size and volume of mesopores (2–100 nm) are controlled by using fine-dispersed carbon black, varying the amount of deposited PyC and its burn off extent. The size and volume of micropores (0.4–2 nm) is controlled by the quantity of PyC and its burn off extent. As a result, the specific surface area can be varied from 0.1 to 800 m^2/g, the pore volume from 0.1 to 2.0 cm^3/g. A distinctive feature of Sibunits is formation of supermicropores only of more than 1 nm in size but not ''true'' micropores typical of conventional active carbons. Smaller pores appear only at the first stages of activation. Their volume is maximized when the burn off degree $\gamma=0.1$ and then it decreases rapidly. Pores with the predominated size of 1–2 nm are formed at the stage of PyC lattices gasification. They correspond to burning-off of individual graphene packets of the most defective structure. Carbon black burning-off follows meso- and macro-pores formation.

A distinctive feature of Sibunits is high resistance to attrition and mechanic crushing, values of which at a limited activation degree are much superior to those for conventional porous carbon materials, produced by traditional methods. This is a new family of porous carbon materials [4].

The deposition of PyC at the external surface of microporous activated carbon granules is used to synthesize another family of porous carbon materials, the so-called carbon molecular sieves (CMS). CMS are similar to zeolites in separation performance. But their internal space is formed by the lattice of pores of different size. In this case the materials behave as sieves due to percolation effects in big lattices [5]. Additionally the effective size of the porous space entrance can be controlled by covering the external surface of granule (or big interior aggregates) with a thin layer of PyC. As a result, the percolation effects and the extra coverage may be used to control molecular-sieving behavior. CMS of this kind with the effective size of limiting pores of 3, 4, 5, 6 and 7 Å are described in literature [1].

Another large family of porous carbon materials is produced by C_1–C_3 decomposition on metal catalysts, for example on Fe, Co, Ni and their alloys. In this case the carbon usually deposits in a filamentous shape, so this family may be called catalytic filamentous carbon (CFC). Formation of CFC is due to the catalytic decomposition of the gaseous precursor that proceeds at one edge of a metal particle to produce the chemi-

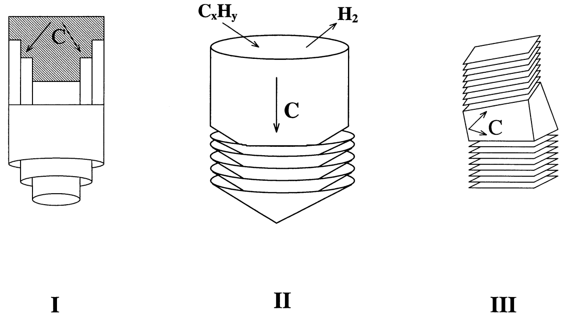

Fig. 2. Different forms of catalytic filamentous carbon.

sorbed carbon, which is dissolved in metal and deposited as a graphite-like phase on the other edge of the crystal [6]. Carbon diffusion from the formation zone through the bulk of metal to the deposition one arises from the difference in chemical potentials at these zones. Some characteristic examples of CFC morphology are presented in Fig. 2.

It is interesting to note that most of transition metal carbides form very stable, hard and high-melting compounds. This is due to the filling of the octahedral voids between the closely packed metal atoms with carbon atoms (radius 0.77 Å). Carbon atoms in such systems are not bonded with one another and bear a negative charge, but metal atoms are bonded. It explains their electric conductivity. But Fe, Co, and Ni atoms are smaller in size than other transition metals. As a result they are pushed too strongly by carbon atom, and the stability of the configurations decreases with the metal atomic radius R_{Me} (Table 1). Low stability of metals of this group follows from endothermic enthalpy of formation, H_{298}, and low equilibrium constants, K_{298}. Variations in the catalytic activity, for example for the reaction of methane conversion, correlates with the thermostability: Cr-based catalysts reveal a low activity, Fe-based ones are active at T>800°C, and Ni-based ones at as low as 550–650°C.

As a result, insertion of carbon, at least into Ni and Co catalysts, induces distortions in the original metal lattice and weakening of the metal–metal bonds. Such carbides can exist at the temperatures of CFC formation as unstable solid solutions only under the conditions of continuous supply of carbon. It is a brilliant example of dissipative systems, that "live" only in conditions of non-stop mass- and energy transfer from surrounding. Stopping of this transfer results in its self-destruction. The composition and structure of these solid solutions are strongly dependent on partial pressures of the carbon-containing gas and hydrogen, as well as on temperature and the catalyst particle size.

Now we will discuss the general scheme of CFC formation during CH_4 decomposition on high percentage Ni catalysts at 600–650°C. It is presented in Fig. 3 [1,4]. At first the Ni particles are saturated with carbon. The process is accompanied with their recon-

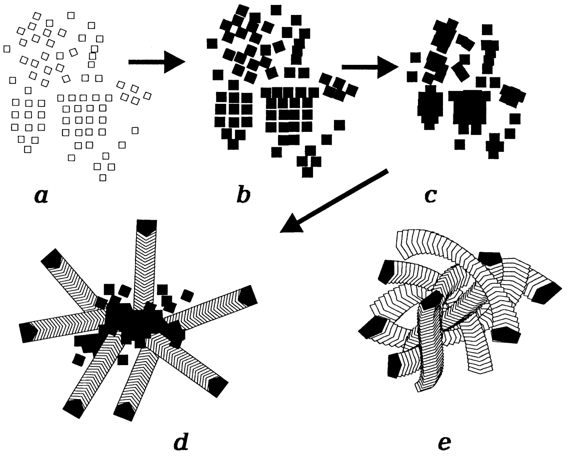

Fig. 3. Scheme of catalytic filamentous carbon growth.

Table 1
Atomic radii, R_{Me}, melt temperature, T_{melt}, entalphy of formation, H_{298}, and equilibrium constants, K_{298} of several transition metal carbides

Carbide	TiC	VC	Cr_3C_2	Mn_2C	Fe_3C	Co_3C	Ni_3C	Mo_2C	W_2C
R_{Me} (Å)	1.47	1.34	1.27	1.26	1.26	1.25	1.24	1.39	1.39
T_{melt} (°C)	3257	2450	1890	—	1650	<300	<300	2522	2870
H_{298} (kJ/mol)	−191	−109	−111	−25	−6	40	36	−39	−50
log K_{298}	31.7	17.3	15.1	−0.96	−3.5	−1.1[a]	−11.2	5.1	6.7

[a] By T.P. Gröbner [12], the rest H_{298} and K_{298} by I. Barin [13].

struction and partial conglomeration. (Fig. 3(a)–(c)). Distinct faces (1 1 0), (1 0 0), and (1 1 1) of the nickel metal are formed during the reconstruction, the following CH_4 decomposition proceeds on the (1 0 0) faces and, partially, on (1 1 0) face. The chemisorbed carbon diffuses through the particle and extrudes as graphite-like layers at the face (1 1 1). Non-stop carbon extrusion makes active particles moving in the ''rocket-like'' manner. Active metal particles are situated at the tips of the ''rockets'', and their ''tails'' consist of the growing carbon filaments (stage *d*). Continuous growth of numerous filaments is accompanied by their interlacing into a close clew constituted by randomly interlaced filaments (stage *e*). Carbon yield on such catalysts achieves 300 g per gram of the initial catalyst. This corresponds to a total ash content up to 0.3%. The porosity of the obtained agglomerates is 60–70%, surface area 100–300 m^2/g and average pore radius 10–15 nm. More detailed morphology depends on temperature, initial hydrocarbons, experimental conditions, etc.

Some words about the relation between structure of the formed filaments and metal catalyst composition: Fig. 2 shows three main structural types of CFC. In all these cases CFC consists of the carbon layers (graphenes) with a turbostratic packing. But the morphology of filaments is determined by the active metallic particles shape at the region of carbon releasing. For Fe and Co catalysts graphenes usually rolled up into coaxial cylinders, called a bulk structure of type I. In the case of Ni catalysts graphenes form up the cone-shaped bulk structures of type II, and in the case of Cu/Ni alloys the bulk structure of type III with flat graphene packing forms. The last case probably corresponds to an internal alloy bulk catalysts segregation with formation of active zones, enriched with Ni and inert zones, enriched with Cu. The presence of active zones leads to simultaneous growth of a few filaments from the single particle with a characteristic ''octopus'' morphology.

Let us devote the final part to the problem of ratio between contributions of *basal* (0 0 1) and *edge* (h k o) graphite planes to total specific surface area. Actuality of this problem relates to the active sites responsible for chemisorption, catalysis, anchored components of supported catalysts, etc. [1–4]. From the classical work by Abramson [8], the surface enthalpy of opened edge planes is almost 40 times as high as that of the graphite basal plane (6.1 and 0.155 J/m^2, respectively). To solve this problem Hoffman et al. [3] studied the C_1–C_4 hydrocarbons, H_2 and O_2 chemisorption on clear and activated by gasification graphitized carbon black. But the surface of CFC is the ideal model for such an investigation because the surface for CFC of types II and III seems to be formed completely with open edges, and in case of type I – from basal graphite planes only.

However the detailed study provided by high resolution transmission microscopy (HRTEM) and scanning tunneling microscopy (STM) by Shaikhutdinov et al. [9], SIMS data, obtained by Ivanov et al. [10], and results by Fenelonov et al. [7] show that the surface structure for types II and III is significantly reconstructed. The reconstructed zone expands into the bulk by 1–2 nm [10]. The surface is covered predominantly by deformed fragments of the graphite *basal* planes in form of closed-layer structures. It is a result of spontaneous reconstruction to provide the surface energy minimization. It is impossible to disappoint the nature. Almost 40-fold difference in the surface energy between the open edges and basal planes [8] provides a sufficient driven force for such a reconstruction.

So the structure of filaments surface differs from the bulk structure. In the case of bulk structure of type II, when bulk graphenes are oriented at some angles to the filament axis, the surface tends to be covered by steps and terraces formed by fragments of the basal planes [9]. When bulk graphenes are oriented normally to the filament axis (bulk structure of type III), the closed-like structures are formed on the surface when the neighbor or next-neighbor graphene layers are linked like a kind of ''nanocaps'' [9]. But in all these cases some minor portion of surface still keeps the open graphite edge planes. This is seen, for example, from several independent gas chromatographic studies, discussed in [7]. These studies show abnormally high adsorption of hydrocarbons reduced to the total surface in the region of very low adsorptive concentrations. These values are higher by 5–6 orders of magnitude than those on graphitized carbon black.

We studied adsorption isotherms of benzene, heptane and nitrogen on these CFC [7] and concluded that types CFC II and CFC III have very low micropore volume (<0.01 ml/g). The relation of this volume to the surface area, calculated by subtraction of micro-

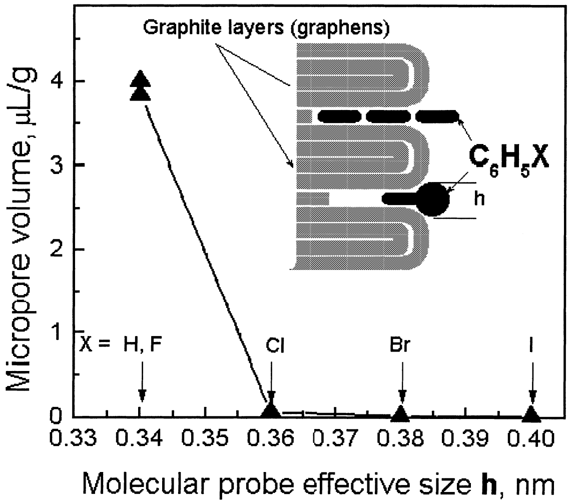

Fig. 4. Dependence of accessible micropore volume V_μ for different test molecules.

pore contribution in adsorption for every type of CFC varies in a very narrow range. For example for CFC III it is 1.9×10^{-5}–2.2×10^{-5} ml/m^2. To determine the size of this micropores we used a modified molecular probes method, based on gaseous-chromatography studies of monohalogenated benzene derivatives from fluorine to iodine [11]. Note that technique [11] eliminates the activated diffusion which is the main imperfection of traditional variants of this method. In [11] it was shown that the space of such micropores, V_μ (μl/g), is available for benzene and F-benzene (effective molecular size D_m=0.34 nm; V_μ=4.0 and 3.84, respectively), restricted for Cl-benzene (D_m= 0.36 nm; V_μ=0.06) and practically unavailable for Br- and J-benzene (D_m=0.38 and 0.40 nm; V_μ=0.012 and 0.01, respectively). So micropore size is close to the average interlayer distance $d_{0\,0\,2}$=0.341–0.343 nm, measured by XRD. That is why such micropores can be represented as slits between graphene layers of various lengths (Fig. 4).

The depth of such microslits (SIMS data) varies between 1 and 2 nm. If one knows the values of volume and width of these plane microslits, it is possible to estimate the part of surface area, covered with these defects. This part varies in the range 2–7% of the total surface area, the lower estimation corresponds to ~2 nm and the highest to ~1 nm depth of microslits.

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