Fullerene Black: Relationship between Catalytic Activity in n-alkanes Dehydrocyclization and Reactivity in Oxidation, Bromination and Hydrogenolysis.

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Abstract
The reactivity of fullerene black in oxidation (by air oxygen or ions MnO$_4^-$ or Cr$_2$O$_7^{2-}$ in solution), bromination (by Br$_2$ or (C$_4$H$_9$)$_4$NBr$_3$) and hydrogenolysis (without hydrogenation catalyst) are studied. The dehydrocyclization of n-alkanes over fullerene black is realized via the monofunctional mechanism, i.e. the dehydrogenation and cyclization stages proceed on the same catalytic center. The addition of alumina to the catalyst transforms dehydrocyclization mechanism to bifunctional one, when fullerene black acts as dehydrogenation agent. Reactivity studies and ESR spectroscopy data for initial and annealed fullerene black show the presence in fullerene black structure of both non-conjugated multiple and dangling bonds. Non-conjugated bonds determine catalytic activity and reactivity of fullerene black. They are localized in amorphous part of fullerene black. Technological aspects of fullerene black as alkanes dehydrocyclization catalyst are discussed.

Introduction
Fullerene black is the main (80–90 wt %) part of condensed product of electric arc graphite vaporization. It represents a not containing fullerenes amorphous residue, which is insoluble in toluene, o-xylene or quinoline [1–23]. The reactivity of fullerene black is poorly studied; only its oxidation in air (or oxygen-containing mixtures) has been reported [1–10]. Fullerene black is oxidized at anomalously low temperatures as compared to other carbon materials. The temperature at which oxidation begins depends dramatically on the rate of temperature rise [11]. Fullerene black absorbs oxygen prior to its oxidation begins. Oxygen is adsorbed on structure defects and functional groups, which are decomposed with evolution of oxygen. Weight losses of fullerene black in an oxidation process are determined by an oxidation temperature in the isothermal heating. An analysis of kinetics of oxygen uptake shows that fullerene black contains several fractions and its oxidation is controlled by its topochemistry [1]. It has been shown that 3 wt % of fullerene black is oxidized at 115°C for 24 h on air with the molar ratio C/O in the residue 20.6. At 300°C for 24 h the residue after oxidation of 58 wt % of fullerene black contains 16.7 % of oxygen (C/O = 6.47), at 400°C for 22 h (20 wt %) contains 8.9 wt % of oxygen [3]. The standard energy of combustion of carbon-containing species decreases in the row: atoms C – C$_3$, C$_4$ clusters – C$_2$ clusters – fullerene black – fullerenes C$_{60}$, C$_{70}$ – giant fullerenes – fullerene onions – graphene sheet and multilayer graphite [23]. The standard energy of combustion of fullerene black is –36.0 ± 0.5 kJ/g. Nitric oxide oxidizes fullerene black at 1273°C with formation of mixture of N$_2$O, NO$_2$, N$_2$, CO, CO$_2$ [9]. ESR signal of fullerene black annealed in vacuum at 1000°C for 3 h does not broaden by oxygen, in contrast with amorphous carbon obtained by decomposition of sulphanilic acid in argon at 627°C [15, 16]. The content of fullerene materials and their stability at heating has been studied by diffusive IR Fourier reflective spectroscopy [12]. This method was also used for studying thermally induced oxidation of fullerenes C$_{60}$, C$_{70}$ and fullerene black [5]. The differences in reactivity of fullerene and common carbon materials are due to the presence of curved structures, that are peculiar for fullerene materials, and the fullerene black can be considered as a material with skeleton structure de-
fects [9]. The similar data has been obtained by $^{13}$C NMR spectroscopy [14]. X-ray diffraction has shown the presence of planar benzenoid structures and graphite in fullerene black [13]. The soot obtained by laser ablation of graphite [21] is more stable and structurally ordered.

We have revealed that completeness and other parameters of oxidation are determined by the rate of air supply and by the thickness of fullerene black layer. Therefore, the oxidation of a 10 mg sample was carried out under standartized conditions at the temperature increase 10 °C/min in a quartz cell of original design. In the present work, the thermogravimetry under standartized conditions and ESR are used as express-methods for study of earlier unknown transformations of fullerene black and for its certification as a catalyst of dehydrocyclization of alkanes. We have shown that non-conjugated multiple bonds, which are localized in an amorphous part of fullerene black and determine its reactivity, are essential for catalysis of alkanes dehydrocyclization.

**Experimental**

Samples of fullerene black were obtained as follows. A graphite rod (diameter 8 mm, length 200 mm) was vaporized at helium pressure 500 Torr and current 100 A. The condensed soot was subjected to exhaustive extraction from fullerenes by toluene in a Soxhlet apparatus. The solid residue after extraction was dried in vacuum at 150°C for 12 h.

The annealing of fullerene black was performed in a preliminary evacuated and sealed quartz ampoule under isothermal conditions for 50 h.

The thermogravimetric measurements were carried out by a Q-1500 D apparatus at forced air supply 10 cm$^3$/min, the sample weight 10 mg, the rate of temperature increase 10 °C/min in a quartz cell of original design.

ESR spectra were recorded on a SE/X-2544 spectrometer (Radiopan, Poznan).

The specific surface area was measured by the dynamic BET method by nitrogen on a Quantacrome device of Quantasorb Company (USA).

The methods of studying catalytic activity are described elsewhere [24, 25].

**Results and Discussion**

According to elemental analysis, initial fullerene black contains 95–97 wt % of carbon, about 1.5 % of hydrogen and 3–4 % of oxygen. Hydrogen and oxygen are probably present as non-removable water, because water was detected in absolute methanol after washing of fullerene black evacuated at 100°C for 10 h. The specific surface area (SSA) of fullerene black is 210–280 m$^2$/g depending on preparation conditions (for comparison, the SSA of fine-dispersed graphite is 6 m$^2$/g). The samples of fullerene black are characterized by the following parameters: the SSA = 278 m$^2$/g; oxidation point (T$_1$) is 270°C (as determined by TG curve); the temperature of maximal oxidation rate (T$_2$ on DTG curves) is 504°C and the temperature of oxidation end (T$_3$ on TG curve) is 630°C. These values for graphite and glassy carbon are much higher (Fig. 1, 2). Fullerene black consists mainly of amorphous carbon, which is oxidized at low temperatures. It can also include graphitized particles, which are detected by TG and DTG curves as a weight loss at 645–670°C, and graphite itself, which is detected at higher temperatures (Fig. 1, 2). Graphite itself, at concentrations more than 3 wt %, is revealed as the sharp line 002 of graphite on a X-ray diffraction pattern. The samples of fullerene black do not contain graphitized particles and graphite itself.

The ESR spectrum of initial fullerene black in vacuum represents a singlet line of width 0.19 mT and g-factor 2.0022 (Fig. 3). The line is close to Lorentzian in center, and has broad wings. The second integral of the ESR spectrum has allowed us to determine that fullerene black contains, depending on preparation conditions, $(2\div5)\times10^{20}$ spins per mole of carbon, i.e. 1 paramagnetic center (PC) per 1200–3000 carbon atoms.

![Fig. 1. TG curves of graphite (1), glassy carbon (2) and fullerene black before (3) and after annealing in vacuum for 50 h at 550°C (4), 650°C (5), 750°C (6), 850°C (7), 900°C (8). T$_1$ and T$_3$ marks relate to curve 3.](image-url)
At a temperature variation of the sample from 295 up to 142 the second integral S of ESR signal, as well as its intensity, is changed without variation of the linewidth. The dependence S~1/T has the maximum at 170 K, i.e. Curie’s law is not followed in the case of fullerene black. The deviations from Curie’s law for the ESR signal were also observed [15, 16] and were explained by coupling of spins. However, we have not observed satellites of ESR line and a line in a half magnetic field, which are expected for magnetic interaction of close spins.

Thermal treatment of fullerene black

The values of T1, T2 and T3 are increased with increasing annealing temperature of fullerene black (Fig. 1, 2). It corresponds to the decrease of the content of amorphous component of fullerene black and the increase of the content of graphitized particles, but not of graphite. The SSA of the samples is increased by two times after their annealing due to the decrease of the particles size. The ESR signal of a sample of annealed fullerene black is much broader than that of initial sample, g-factor is close to 2.00, the lineshape is close to Lorentzian. The spin concentration, determined by the second integral, is constant at all annealing temperatures (Fig. 3).

Oxygen adsorption

The influence of molecular oxygen on the ESR spectra of fullerene black before and after annealing was studied. After oxygen addition to initial sample in vacuum, the ESR line intensity is decreased (Fig. 4) without changes in linewidth and g-factor. Nitrogen and argon do not affect the ESR spectrum. The oxygen effect could be explained by the adsorption of oxygen molecules in the vicinity of paramagnetic centers of fullerene black that results in broadening PC spectra so that they are not observed. Only paramagnetic centers, in the vicinity of which there is no adsorbed oxygen molecules, give rise to the ESR signal of the sample. The dependence of ESR signal intensity I from oxygen pressure P is well described by the equation:

\[ I = \frac{I_1}{1 + \frac{P}{K_1}} + \frac{I_2}{1 + \frac{P}{K_2}} \]  

where \( I_1 \) and \( K_1 \), are the amplitudes of the ESR spectra and oxygen adsorption constants for two types of centers of oxygen adsorption, respectively. Their values are: \( I_1=166 \), \( I_2=21 \) and \( K_1=3.2 \) Torr, \( K_2=211 \) Torr (Fig. 4).

The adsorbed oxygen is not desorbed from the fullerene black samples by argon or nitrogen, but desorbed at evacuation, that points to a specific adsorption (but not a chemisorption) of oxygen. Organic solvents (benzene, toluene, oil, chlorobenzene and tetrahydrofuran) desorb adsorbed oxygen with increase of ESR signal intensity up to initial value. The high affinity of fullerene black to organics is confirmed also by its high adsorptive capacity with respect to organics. For instance, fullerene black sorbs organic solvents (petroleum crude, oils, and chlorobenzene) from aqueous emulsions with the adsorptive capacity of up to 4 grams per gram of fullerene black and can be used as an adsorbent repeatedly.
The effect of oxygen on the broad (5.3 mT) signal of fullerene black after annealing at 900°C differs drastically from that before annealing: ESR linewidth grows linearly with increasing the oxygen pressure (0.08553 mT/Torr) while the value of second integral remains constant. Because of the strong decrease of ESR signal amplitude under the influence of oxygen, this effect has been studied only at pressures from the range of 0–90 Torr.

The data on the oxygen effect allow to make some assumptions on the nature of paramagnetic centers in fullerene black before and after annealing. In initial fullerene black the paramagnetic centers, probably defects of dangling bonds type, are isolated one from other. Oxygen is attached in the vicinity of these centers and strongly broadens their ESR spectra. The small part of these PC (about 5%) is less accessible for oxygen.

Paramagnetic centers, occurred after annealing, are linked one to another probably by a system of conjugated bonds. Due to these bonds, the effect of adsorbed oxygen molecules averages over many paramagnetic centers and the broadening increases as the centers of oxygen adsorption are filled. The linear dependence of broadening on oxygen pressure is explained by small filling of the centers of the oxygen adsorption. The formation of conjugated bonds is confirmed by the increase of the number of graphitized particles detected by TGA (Fig. 1). Besides, the annealed fullerene black decreases considerably Q-factor of the cavity of ESR spectrometer that can be explained by high conductivity of these graphitized particles at microwave frequency.

**Oxidation of fullerene black**

High reactivity of fullerene black in oxidation by oxygen [1–10] implies an opportunity of its oxidation by inorganic agents under mild conditions. Experiments on fullerene black oxidation by permanganate and bichromate ions confirm this assumption. When oxidants CrO$_4^{2-}$ or MnO$_4^{-}$ are in contact with fullerene black in neutral or acidic media at ambient temperature the decrease in concentrations of the oxidants is observed that does not take place in contact with other carbon materials (graphite, shungite, glassy carbon, activated charcoal BAU) under the same conditions. The oxidation of fullerene black at ambient temperature in neutral medium is retarded after 2–3 h, probably due to a difficulty of oxidant diffusion as well as because of formation of water-insoluble oxides. The changes in concentrations of MnO$_4^{-}$ or CrO$_4^{2-}$ after 0.1 h of reaction permit to determine the reaction order with respect to oxidant (in both cases equal to 0.51) and the one with respect to fullerene black (0.91).

In boiling solution of the oxidant, the oxidation of fullerene black proceeds more readily, but is not completed after 10 h of boiling. In neutral medium both oxidants (CrO$_4^{2-}$ + H$_2$O and MnO$_4^{-}$ + H$_2$O) do not destruct fullerene black even on boiling. The study of fullerene black samples after neutral oxidation is complicated by the presence of water-insoluble MnO$_2$ or Cr$_2$O$_3$ in solid phase. In the oxidation by MnO$_4^{-}$-ion converting into MnO$_2$ easily removable by washing with HCl we observed the decrease of MnO$_4^{-}$-concentration with the simultaneous decrease (on the element analysis) in molar C/O ratio (Fig. 5) in the oxidized sample of fullerene black. After boiling for 10 h and removal of produced MnO$_2$ we have obtained the product with approximate (because of the presence of poor-removing water) molar C/O ratio 2.44. Only hydroxyl groups were evidenced by IR spectroscopy in these samples of fullerene black. Thus, it has been shown that fullerene black, similarly to alkenes, is oxidized via Wagner’s reaction without weight loss to form products of surface oxidation like alcohols. Other examples of oxidation of fullerene black without weight losses are unknown. In boiling chloric acid at 156°C, fullerene black loses 77% mass for 1 h. Reaction products of such a destruction were not studied [26].

Cr$_2$O$_7^{2-}$ or MnO$_4^{-}$ ions oxidize fullerene black destructively in acid medium (H$_2$SO$_4$, 1 mol/l) by continuous boiling with formation of poor-pressing and not precipitated at centrifuging (3000 g, 3 h) suspensions. In the course of the process the concentration of the oxidants is decreased, but the total metal (Cr or Mn) concentration remains constant, i.e. fullerene
black, both initial (hydrophobic) and after oxidation (hydrophilic), does not adsorb metal ions, in agreement with [9]. After oxidation during short time (1 h), we isolated a product containing hydroxyl, carbonyl and carboxyl groups.

**Bromination of fullerene black**

Fullerene black also interacts with bromine in dilute (up to $10^{-2} \text{ mol/l}$) solutions in acetic acid or in CCl₄. The bromination proceeds slowly at ambient temperature and is accelerated in the boiling solution. The halogen content does not exceed 17 wt % with more than 80 % of this amount being reached for 1 h. The bands corresponding to stretching vibrations of C–Br bonds are detected at 624 cm⁻¹ in IR spectra of fullerene black after bromination. Such a C–Br bond in the bromination product is rather strong, since this product is not a halogenating agent, in contrast with a product of chlorination obtained in [1]. The similar reaction proceeds also with (C₄H₉)₄NBr₃ that is not peculiar to the formation of intercalation compounds.

The sharp ESR signal of initial fullerene black decreases and slightly broadens (Fig. 6) with prolongation of reaction time and increase of bromine contents in the sample. Thus, the PC concentration in the product of bromination is 2–3 times less than in the initial sample of fullerene black.

Such features of reactivity are inherent mainly for hydrocarbons with C=C bonds. Such hydrocarbons interact with MnO₄⁻ + H₂O without destruction (Wagner’s reaction) to form glycols. Indeed, only the stretching vibrational bands of hydroxyl groups occur additionally in IR spectra of the samples of fullerene black after neutral oxidation. The hard oxidation of these hydrocarbons in acid medium by boiling results in cleavage of double bond with formation of ketones, carboxylic acids or CO₂. The samples of fullerene black after appropriate treatment exhibit the vibrational bands of hydroxyl, carbonyl and carboxyl groups in IR spectra and at more continuous treatment are oxidized destructively. Wagner’s reaction and interaction with bromine are test reactions for the presence of double bonds. The content of bromine and oxygen in the samples after appropriate treatment is not correspond to PC concentration, which is two order of magnitude less. In contrast with oxidation of alkanes [27, 28], the oxidation of fullerene black by inorganic oxidants does not require severe conditions and proceeds quickly enough.

**Hydrogenolysis of fullerene black**

Fullerene black was found to undergo destructive hydrogenolysis at high (more than 600°C) temperatures with formation of methane, ethane and ethene in the molar ratio 100:10:1. Hydrogenolysis is carried out in the absence of catalysts for hydrogen activation (the transition metals in concentrations more than $10^{-7}$ mass are not detected). At temperatures up to 600°C the hydrogenolysis proceeds with low rates. The contents of hydrocarbons in the output gases decreases in time, that definitely evidences that the reaction order on fullerene black is more than 0. For example, at 700°C and 0.1 MPa H₂ the weight loss of fullerene black was 50 % for the first 24 h, while for the next 24 h it was only 2 %. Sharp decrease of hydrogenolysis rate (during reaction time) can be explained by the presence of several fractions of amorphous carbon reported in [1]. In the pressure range 0.01–0.1 MPa the reaction of hydrogenolysis is the first-order with respect to hydrogen that is similar to inhibition of coking in the thermocatalytic pyrolysis.
of methane [29]. Fullerene black also dehydrogenates tetrалin (in bulk) and 9,10-dihydronaphthalene (in pentadecane) to naphthalene on boiling. The reaction with 9,10-dihydronaphthalene is used in fullerenes chemistry for producing stable fullerene hydrides (see, for example, [30]). We found that hydrogen chemisorption on fullerene black does not take place up to 350°C. After static treatment by hydrogen for 6 h at 400°C, ESR line amplitude of fullerene black increases by 4 times without changing in linewidth. This treatment at the temperature 100°C does not result in changeings in ESR line amplitude. This fact contradicts data reported in [1]. Equilibrium $C + 2H_2 \leftrightarrow CH_4$ is shifted to the right [31] at temperatures up to 700°C, but in case of graphite and diamond under such conditions is not achieved because of negligibly small reaction rate. We think that the hydrogenolysis of fullerene black found in this work is the first example of reaction of this type without any hydrogenation catalyst.

**Fullerene black catalytic activity in n-alkane dehydrocyclization**

Some features of fullerene black (the presence of multiple and dangling bonds, radical centers, capability to hydrogenolysis and dehydrogenation, high adsorption capacity towards organics) assume its catalytic activity in conversions of alkanes. Earlier we have observed the capability of fullerene black to activate C–H and C–C bonds [29]. Therefore, we assume that fullerene black has a catalytic activity in hydrocarbon processing.

Dehydrocyclization of alkanes is the necessary part of reforming process and, as the whole process, is directed to increase the octane number of a feed, in particular, due to a conversion of alkanes with low octane number, to aromatics having usually octane numbers about 100. The many hydrocarbon processings, including reforming and dehydrocyclization of alkanes, are accompanied by coke deposition on the catalyst surface. To avoid rapid coke formation and deactivation of the catalyst, a feed free from pentanes (coke precursors in this process) and diluted by hydrogen is usually employed [32]. During dehydrocyclization, hydrogen is produced. Therefore, feed dilution by hydrogen (about 4 moles per mole of hydrocarbon) decreases effectiveness of dehydrocyclization of alkanes only 15–20 % of which are converted under real conditions. Unconverted alkanes are low-octane ballast in reformate [32].

Fullerene black catalyzes conversions of $n$-alkanes $C_n$–$C_8$ with prevalent formation of benzene without a coke deposition and does not require feedstock dilution by hydrogen (Table 1).

$n$-Pentane is mainly subjected to cracking over fullerene black, but benzene is also produced. Methylocyclopentene has been detected in the products of $n$-pentane conversion. Conversion of $n$-pentane having 5 carbon atoms per molecule is difficult to be conceived by any other way, except for methylocyclopentene formation, its isomerization (with cycle expansion) to cyclohexane and subsequent dehydrogenation of the latter in benzene. It has been shown in additional experiments that cyclohexane is quantitatively (yield up to 96 %) converted to benzene at 550°C and 0.1 MPa. Izomerization is significant only for $n$-pentane and low for other alkanes (Table 1).

$n$-Hexane converts to benzene with intermediate formation of cyclohexane. $n$-Heptane and $n$-octane are also converted mainly to benzene probably by demethylation in the cyclization stage, since toluene demethylates to benzene under these conditions.

Samples of fullerene black annealed at temperatures of higher than 900°C for 50 h don’t exhibit catalytic activity in dehydrocyclization of $n$-alkanes [27, 28], dehydrogenation of cyclohexane and cyclization of hexane-1 and hexane-2. The simultaneous absence of both cyclization and dehydrogenation indicates that these stages are carried out on the same active centers (i.e. via the monofunctional mechanism) which are present in an unannealed sample of fullerene black. An annealed sample is oxidized by air oxygen much more difficulty, than initial one. This sample is practically not oxidized by inorganic oxidants and not brominated that points to the absence of non-conjugated multiple bonds, however, it contains PC (dangling bonds). These facts lead to conclusion that the active centers in initial fullerene black are non-conjugated multiple bonds.

After addition of neutral $Al_2O_3$ to fullerene black both the $n$-alkane $C_n$ conversion degree and the selectivity with respect to aromatic hydrocarbons $C_8$ increases (Table 1). $Al_2O_3$ alone is active only in cyclization and inactive in dehydrocyclization (Table 1) because of the absence of dehydrogenating function. This means that the dehydrogenation proceeds on fullerene black and the dehydrocyclization as a whole is realized over the mixed $Al_2O_3$-fullerene black-quartz catalyst [24, 25] via the bifunctional mechanism [32].

In alkane conversions on fullerene black cracking
Table 1
Conversion of \(n\)-pentane, \(n\)-hexane, \(n\)-heptane and \(n\)-octane (vapours saturated at 22°C in argon) over the catalysts based on fullerene black at 550°C and GHSV = 1000 h\(^{-1}\) (LHSV = 1 h\(^{-1}\) calculated for \(n\)-C\(_6\))

| Conversion products | Yield (%) at \(n\)-alkane conversion |
|---------------------|-------------------------------------|
|                     | \(n\)-C\(_6\)          | \(n\)-C\(_7\)          | \(n\)-C\(_8\)        | \(n\)-C\(_9\)        |
| FB+quartz (1:29 mass.) | FB+quartz (1:29 mass.) | FB+Al\(_2\)O\(_3\) + quartz (1:2:27 mass.) | Al\(_2\)O\(_3\) + quartz (1:1 mass.) | FB+quartz (1:29 mass.) |
| CH\(_4\)            | 1.8                      | 0.6                      | 0.8                      | 0.1                      | 0.1                      | 0.5                      |
| C\(_2\)H\(_6\)       | 1.9                      | 4.1                      | 3.8                      | 0.1                      | 0.6                      | 2.2                      |
| C\(_2\)H\(_6\)       | 1.9                      | 1.4                      | 2.4                      | 0.7                      | 0.2                      | 6.6                      |
| C\(_3\)H\(_6\)       | 1.1                      | 5.8                      | 5.0                      | -                        | 0.6                      | 1.2                      |
| C\(_3\)H\(_6\)       | 3.1                      | 8.0                      | 4.6                      | 0.5                      | 1.0                      | 2.8                      |
| C\(_4\) hydrocarbons | 3.9                      | 5.8                      | 2.9                      | 0.3                      | 3.9                      | 1.5                      |
| Hydrocarbon gases C\(_1\)-C\(_4\) | 13.7                  | 25.7                     | 19.5                     | 1.7                      | 6.4                      | 8.8                      |
| \(C_5\) alkanes      | 0.1                      | 6.6                      | 0.4                      | 0.3                      | 0.7                      | 1.1                      |
| \(C_5\) alkenes      | traces                   | 3.7                      | 0.1                      | 0.1                      | 0.5                      | 1.3                      |
| \(C_6\) alkanes      | 1.0                      | 2.7                      | 0.1                      | 0.3                      | 3.9                      | -                        |
| \(C_6\) alkenes      | 1.1                      | 6.2                      | 0.3                      | 0.15                     | 1.9                      | -                        |
| \(C_7\)              | -                        | -                        | -                        | -                        | 19.4                     | -                        |
| \(C_7\)H\(_6\) Benzene | 40.7                  | 25.8                     | 5.1                      | -                        | 42.2                     | 5.8                      |
| \(C_7\)H\(_8\) Toluene | -                      | 7.9                      | 69.4                     | -                        | 4.8                      | -                        |
| \(C_8\)H\(_{10}\) Xylenes + ethylbenzene | -            | -                        | -                        | -                        | 16.8                     | -                        |
| Aromatics total.     | 40.7                     | 33.7                     | 74.5                     | -                        | 63.8                     | 5.8                      |
| \(n\)-Alkane conversion degree | 56.8                  | 78.8                     | 95.0                     | \(\sim\) 2.5             | 96.3                     | 16.6                     |

GHSV—gas hourly space velocity; LHSV—liquid hourly space velocity; FB—fullerene black.

does not dominate (Table 1) and is largely represented by demethylation (benzene formation irrespective of chain length of initial alkane). Among the products of \(n\)-pentane cracking propene is the most abundant one, for \(n\)-hexane are butenes, \(n\)-heptane are hydrocarbons C\(_5\), \(n\)-octane are hydrocarbons C\(_6\), i.e. cleavage of initial C\(_n\) alkane with formation of C\(_2\) (ethene and ethane) and C\(_{n-2}\) hydrocarbons (\(\beta\)-elimination) is favoured. This testifies, alongside with yield of ethene higher than propene (Table 1), catalytic origin of cracking, but the contribution of cracking, similarly to thermal cracking, is decreased with reducing temperature.

Dehydrocyclization of \(n\)-alkanes on fullerene black is catalytic rather than stoichiometric reaction of the type C + C\(_6\)H\(_{14}\) \(\rightarrow\) CH\(_2\) + C\(_5\)H\(_6\) + 2H\(_2\), as the benzene amount produced at conversion of \(n\)-hexane without visible drop of activity exceeds the carbon amount. Indeed, after 48 h (longer testings were not performed) 0.544 mol of \(n\)-hexane are dehydrocyclized to 0.384 mol of benzene that requires consumption of 0.384 mol (4.608 g) of carbon, while the mass of alone carbonaceous material, fullerene black, in the mixed catalyst is equal to 0.1 g.

Technological aspects of fullerene black applications

Fullerene black is the effective catalyst for dehydrocyclization of alkanes, however it has several essen-
tial shortcomings. (1) Predominance of benzene in products irrespectively of chain length of initial alkanes explained by capability of fullerene black to C–C bond activation and by the monofunctional mechanism of dehydrocyclization over fullerene black. (2) Initial fullerene black has poor processability. This material has high specific surface area (up to 300 m²/g) and extremely low bulk weight (0.03–0.05 g/cm³). Fullerene black is practically not aggregated at pressures up to 3×10⁷ Pa (300 atm). Both these shortcomings can be easily overcome when a mixture of fullerene black with alumina is molded. The molded catalyst has bulk weight of 0.8 g/cm³ and good mechanical properties. Also the catalytic activity in dehydrocyclization of alkanes remains, and the contribution of demethylation (Table 1) decreases.

One usually stated that fullerene black has high cost. However this material is the waste of electric arc graphite evaporation used for producing fullerenes C₆₀ and C₇₀. On rather moderate counting the cost per 1 kg of fullerene black does not exceed 200 USD.

The important advantages of the catalyst based on fullerene black is the absence of coking, deactivation and therefore necessity of feedstock dilution by hydrogen, the absence of noble and transition metals, sulfur tolerance and the opportunity to utilize alkenes and pentanes which are removed from feedstock in practice. In the case of traditional reforming feed (hydrogenized straight run gasoline) at the temperature of 550°C and LHSV = 3 h⁻¹ the yield of aromatics comprises 76.3 % over the fullerene black based catalyst as compared to 56.1–56.9 % over the industrial catalyst.

Dehydrocyclization of alkanes over such catalyst also proceeds with intermediate formation of cyclohexane or its homologues (naphthenes having high octane number). Their yield can be increased. The raffinate of reforming process used now as a hydrocarbonaceous solvent or low octane number component of engine fuels and containing more than 99 % mass of alkanes and having octane number up to 20 can be subjected to dehydrocyclization. In the case of extractive gasoline the catalysate with octane number 78 has been obtained in one run from the feed having octane number 13.

Conclusion

Catalytic activity of fullerene black in dehydrocyclization of alkanes is determined by the preparation conditions. The optimal ones for fullerenes and catalytically active (and reactive) fullerene black are apparently different. The most active are the samples of fullerene black with low (270–280°C) oxidation point, not containing graphitized particles and graphite itself, having high (about 10²⁰ mol⁻¹) concentration of spins. Practically all products of electric arc vaporization of graphite (for example [33]) are able to activate C–C bond. Carbon materials of other origin (charcoal BAU, graphite, glassy carbon, and shungite) are practically not active in these processes. Fullerenes are sublimated under these conditions and fullerene cocoons (the epoxides of C₆₀) exhibit only cracking activity. Testing of samples of carbon material by TGA and ESR allows to predict their catalytic activity and reactivity and this test is error-free as our experience evidences.

There are both non-conjugated and dangling bonds in the network of fullerene black. But only the formers determine catalytic activity of fullerene black in dehydrocyclization of alkanes and reactivity.

Both samples of fullerene black annealed at temperature of higher than 900°C for 50 h and residues after oxidative baking (300°C, 8.5 h) or after hydrogenolysis (700°C, 24 h) don’t exhibit catalytic activity in dehydrocyclization of n-alkanes [27, 28]. These materials are oxidized by air oxygen much more difficultly, than initial fullerene black. They are practically not oxidized by inorganic oxidants and not brominated. These samples practically don’t contain amorphous carbon, which is reactive due to the presence of non-conjugated multiple bonds. This is amorphous carbon but not graphitized particles, graphite crystallites or residual amounts of fullerenes that seems to be the component of fullerene black, which determines its catalytic activity in dehydrocyclization of n-alkanes.

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