

## Methane Pyrolysis over Carbon Catalysts

S.D. Kushch<sup>1\*</sup>, V.E. Muradyan<sup>1</sup>, P.V. Fursikov<sup>1</sup>, Eu.I. Knerelman<sup>1</sup>

V.L. Kuznetsov<sup>2</sup> and Yu.V. Butenko<sup>2</sup>

<sup>1</sup>Institute of Problem of Chemical Physics RAS,

18 Institutsky prospect, Chernogolovka, Moscow Region, 142432, Russia

<sup>2</sup>Boreskov Institute of Catalysis SB RAS, 5 Lavrentieva str., 630090 Novosibirsk, Russia

### Abstract

Methane pyrolysis at the temperature range of 550-1000°C in gas flow reactor with fixed bed of mixed catalysts based on carbon materials of various structure (fullerene cocoons, fullerene black, vacuum black, cathode deposit, onion-like carbon, glassy carbon, carbon fibers, mineral shungite and graphite) has been studied. Methane pyrolysis products, including stoichiometric amount of hydrogen are C<sub>3</sub>-C<sub>4</sub> alkanes, C<sub>2</sub>-C<sub>4</sub> alkenes, aromatics and pyrolytic carbon. Methane pyrolysis is carried out both on a catalytic surface and in a volume and contribution of the surface is determined by pyrolysis temperature. Materials with curved carbon surface show an activity in methane dehydrogenation at lower temperatures, than materials with planar basic structure elements. Materials with a small specific surface area favor methane aromatization at 950-1000°C with formation of mainly benzene, toluene and naphthalene. The primary activation of C-H bond in methane at temperatures of lower than 850°C, as well as the multiple dehydrogenation conversions resulting in the formation of pyrolytic carbon and its precursors (aromatics), are, probably, heterogeneous reactions.

### Introduction

The data on comparative catalytic activity of different carbon materials in the reaction of methane pyrolysis are practically absent. Earlier we have reported methane activation over fullerene black in the temperature range of 600-1000°C [1]. The products of methane conversions over the mixed catalyst (10 % wt. of fullerene black (FB)/quartz) were, in addition to stoichiometric amounts of hydrogen, pyrolytic carbon, alkanes C<sub>3</sub>-C<sub>4</sub> and alkenes C<sub>2</sub>-C<sub>4</sub>.

In the present work we report of methane conversions over wide range of mixed catalysts based on carbon materials in a gas flow reactor under identical experimental conditions, that has allowed to quantitatively compare activities of the catalysts and to make some conclusions on the mechanism of methane pyrolysis.

### Experimental

Mixed catalysts containing 3.3 % wt. of a carbon

\*corresponding authors. E-mail: ksd@icp.ac.ru

material in a mixture with crushed (0.1-0.25 mm particle size) quartz (0.1 g of a carbon material per 2.9 g of quartz) were used. All experiments have been carried out in a isothermal gas flow reactor with a fixed bed catalyst retained from below by a grate and from above - by a basalt thread (catalyst volume is 2.4 cm<sup>3</sup>). Methane fed from below with gas hourly space velocity GHSV=1000 h<sup>-1</sup>. The express experiments have shown that under these conditions the carbon material is not entrained by gas flow. The measurements of catalytic activity of carbon catalysts in temperature range from 500 to 1000°C are carried out over fresh sample of catalyst to avoid the influence of deposited pyrolytic carbon. Temperature was regulated by a thermocouple placed in the catalyst bed. The other features of the experiment are reported in ref. [1].

As an initial carbon component in this work we have used materials of different morphology, structure and specific surface area:

1. Fullerene cocoons representing the not sublimed residue after sublimation of crystalline fullerene (fullerite) C<sub>60</sub> at 630°C [2]. This material has spe-

- cific surface area  $SSA = 495 \text{ m}^2/\text{g}$  measured by BET method on  $\text{N}_2$ .
- Vacuum carbon arc black (VCB) with  $SSA = 440 \text{ m}^2/\text{g}$  obtained by electric arc evaporation of a graphite rod with diameter 6 mm in deep vacuum [3, 4] at arc current intensity  $I = 65 \text{ A}$ .
  - Fullerene black with  $SSA = 185 \text{ m}^2/\text{g}$  was prepared as follows. The condensed soot, obtained by electric arc evaporation of a graphite rod (diameter 6 mm) under He pressure 66.7 kPa and arc current intensity 55 A, was subjected to exhaustive toluene extraction from fullerenes in a Soxhlet apparatus. The solid residue after extraction was dried in vacuum at  $150^\circ\text{C}$  for 12 h.
  - Onion-like carbon (OLC), obtained by thermolysis of ultra-disperse diamond particles having size  $\sim 4\text{-}5 \text{ nm}$ . OLC represents associates of embedded one into another, closed carbon shells. The sample contained particles having on the average 5–7 closed shells [5, 6] and  $SSA = 418 \text{ m}^2/\text{g}$ .
  - A loose central part of cathode deposit obtained by electric arc evaporation of a 6 mm graphite rod (80 kPa He, 80 A) and containing up to 30 % of nanotubes [7], named further as carbon nanotubes (CNT), with  $SSA = 20 \text{ m}^2/\text{g}$ .
  - A solid shell of cathode deposit (40 kPa He, 65 A) with  $SSA = 17 \text{ m}^2/\text{g}$ .
  - Glassy carbon [8] with  $SSA = 1.96 \text{ m}^2/\text{g}$ .
  - Graphite of spectral purity grade with  $SSA = 6.4 \text{ m}^2/\text{g}$ .
  - Carbon fiber with  $SSA = 13.8 \text{ m}^2/\text{g}$  was obtained by polyacrylonitrile pyrolysis [<http://trcs.he.utk.edu/textile/nonwovens/carbon.html>].
  - Carbonaceous mineral shungite [9] with  $SSA = 0.63 \text{ m}^2/\text{g}$ .

All carbon materials have been crushed to 40–50  $\mu\text{m}$  particles. Carbon fiber has been cut to pieces of 1 mm length. Fullerene cocoons have been molded without binder in tablets under the molding pressure 15.2 MPa and crushed to  $\sim 0.1 \text{ mm}$  particles.

Hydrogen, alkanes  $\text{C}_1\text{--}\text{C}_4$ , alkenes  $\text{C}_2\text{--}\text{C}_4$ , benzene and toluene were detected by the GLC on-line. Hydrogen was detected by thermal conductivity detector, molecular sieves 13A, 3mm $\times$ 3m, carrier gas Ar, alkanes and alkenes - by a flame ionization detector, alumina (0.1–0.25 mm), 3mm $\times$ 3m, carrier gas  $\text{N}_2$ , benzene and toluene - on a column Poropak Q (0.1–0.25 mm), 3mm $\times$ 3m, carrier gas  $\text{N}_2$ . Condensed aromatics (CAr) were trapped in an coil cold trap, immersed in ice-water slush. The trap was weighed before and after experiment. CAr were analysed by

the GLC with absolute calibration. The weight of pyrolytic carbon (PC) was determined by difference in the weight of the reactor before and after an experiment. The carbon and hydrogen contents in PC evidenced the approximate formula of PC  $\text{C}_6\text{H}$ .

The conversion degrees and selectivity were controlled by the weight balance at the end of experiment taking into account a weight and composition of formed PC and CAr. Thus the inaccuracy of weight balance in all cases, as a rule, did not exceed 5 %.

## Results and discussion

Both all studied carbonaceous materials and the diluent (quartz) exhibited an activity in methane pyrolysis at different temperatures with formation of hydrogen, hydrocarbons and pyrolytic carbon. Carbonaceous materials are ranged according to the temperature point when methane pyrolysis starts and the conversion degree  $\eta$  reaches 0.1 %, see inset in Fig. 1, Table 1. In this range the curvature of basic structure elements of a carbonaceous material decreases. So, the average radius of curvature of surface of the studied carbonaceous materials increases from about 3.5 Å to infinity in the range: fullerene cocoons < fullerene black < OLC < VCB < CNT, deposit shells  $\ll$  shungite, glassy carbon, carbon fiber, graphite [2–12]. A high dehydrogenating activity of curved carbon surfaces promotes an increase of the selectivity with respect to pyrolytic carbon and a decrease - with respect to aromatics, that especially characterizes the materials in the top of Table 1. These effects are consistent with the data of ref. [13], where fullerene soot was reported to exhibit catalytic activity at lower temperatures, than acetylene black or activated charcoal Norit A.

Both over different catalysts of the composition 3.3 % wt. of carbonaceous material/quartz and quartz alone, the products of methane pyrolysis are hydrogen, pyrolytic carbon and hydrocarbons. In the gas products, in addition to the stoichiometric amounts of hydrogen, there are alkanes and alkenes (given in decreasing order):  $\text{C}_2$  (ethene (prevalent), ethyne (0.01–0.1 of ethene) and ethane traces),  $\text{C}_3$  (propene in the amounts comparable with ethene and propane),  $\text{C}_4$  (butadiene and vinylacetylene (1:3), butanes and butenes); also aromatics (benzene, toluene and condensed aromatics.  $\text{C}_5$  and  $\text{C}_6$  hydrocarbons are detected only in traces. Over different studied catalysts hydrocarbons appear in products at a temperature  $\geq 750^\circ\text{C}$ . Hydrogen and pyrolytic carbons are the main prod-

**Table 1**  
Methane pyrolysis at GHSV=1000 h<sup>-1</sup> over carbon materials (0.1 g per 2.9 g of quartz)

Carbon material	SSA, m <sup>2</sup> /g at		T, °C at $\eta=0.1\%$	$\eta$ , % at 1000°C	Selectivity S <sub>i</sub> , % at 1000°C (average for 3 h) with respect to								
	0	3 h			C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>6</sub> H <sub>6</sub>	MePh	CAr	ΣAr	PC	ΣAr+PC
Fullerene cocoons	16.6	0.16	550	30.2	11.5	12.4	1.1	11.1	9.4	9.9	30.4	44.3	74.7
VCB	14.9	0.13	616	28.7	12.8	13.2	1.3	20.6	9.6	8.9	39.1	33.6	72.7
Fullerene black	5.2	0.26	626	29.9	16.1	12.1	0.4	6.0	3.9	0.6	10.5	60.0	70.5
OLC	14.1	0.17	715	30.0	10.1	8.6	1.2	19.1	12.1	10.9	42.1	32.2	74.3
Solid shell	1.1	0.15	753	28.6	15.2	14.1	0.8	10.7	5.7	9.4	25.8	45.8	71.6
Carbon fibers	1.8	1.6	765	32.2	12.4	13.3	0.6	27.3	14.8	11.3	53.4	19.4	72.8
CNT	1.2	0.06	782	23.2	11.4	10.2	1.0	21.0	11.4	15.1	47.5	29.0	76.5
Shungite	0.6	0.04	814	21.1	11.4	9.7	1.0	29.1	18.1	20.0	67.2	9.7	76.9
Glassy carbon	0.55	0.04	821	25.4	11.7	10.2	0.3	27.3	24.4	23.1	74.8	1.8	76.6
Graphite	0.73	0.06	824	21.2	15.4	11.6	1.3	23.1	16.9	9.3	49.3	21.6	70.9
Quartz	0.55	0.04	867	20.8	15.3	11.5	1.1	22.3	20.7	13.8	56.8	16.5	73.3

SSA – specific surface area;  $\Sigma Ar = S_{benzene} + S_{MePh} + S_{CAr}$ ;  $\Sigma Ar + PC = S_{benzene} + S_{MePh} + S_{CAr} + S_{PC}$

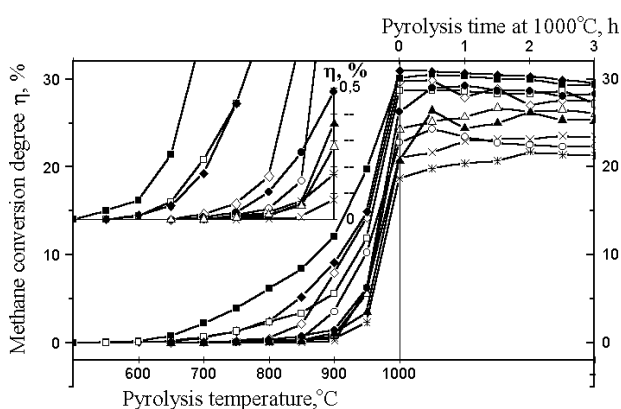


Fig. 1. Dependence of methane conversion degree  $\eta$  from pyrolysis temperature and pyrolysis time at 1000°C over mixed catalysts based on: ■- fullerene cocoons; □- vacuum carbon arc black; ◆- fullerene black; ◇- onion-like carbon; ●- solid shell of the cathodic deposit; ○- a loose central part of the cathodic deposit; ▲- glassy carbon; △- shungite; \*- graphite; ×- quartz.

ucts of methane conversion at temperatures ranging from the temperature when the methane conversion degree is more than 0 to 750°C. The temperature of hydrocarbons C<sub>2+</sub> appearance in reaction products increases top-down in Table 1.

The gaseous composition of pyrolysis product differs from the one observed in ref. [13] in methane catalytic pyrolysis at the temperature 950°C and contact time higher by 4 times. The sum of the values

of selectivity with respect to hydrocarbon products (40-50 %) in ref. [13] differs from 100 %. The difference seems to relate to the formation of pyrolytic carbon that has not been reported in this work. The catalyst specific surface area dependence of the methane conversion degree has not been reported as well [13]. The data of Table 1 evidence about sybarte change in these parameters. In ref. [14] the data on methane pyrolysis over carbon fiber at 950°C and for longer (by 5 times) contact time also showed a formation of respective amounts of ethyne and ethane. These data point to the influence of catalytic surface on methane pyrolysis.

At the same time, the methane conversion degree at 1000°C (Table 1) only slightly differs from the one over diluent-quartz and for homogeneous (without catalyst) pyrolysis, which has been carried out by us under identical condition. These facts evidence insignificant contribution of surface reactions at 1000°C.

The products distribution of methane pyrolysis over the 3.3 % FB/quartz (Fig. 2, Table 1) catalyst differs from the one over the 10 % FB/quartz catalyst [1]. The main difference is the presence of alkane and alkene at a short time of methane pyrolysis and also the presence of aromatics in the products when the catalyst 3.3 % FB/quartz is used. Only aromatics traces and CAr absence were observed over the 10 %

FB/quartz catalyst [1]. Hydrocarbons were absent at the initial moments of pyrolysis (pyrolysis products were hydrogen and pyrolytic carbon). In contrast, over the catalyst 3.3 % FB/quartz hydrocarbons  $C_{2+}$  were detected in reaction products at temperatures  $\geq 750^\circ\text{C}$ . Over fullerene black the maximum selectivity with respect to methane pyrolysis products were observed: with respect to ethene - at  $800^\circ\text{C}$ , with respect to propane - at  $800^\circ\text{C}$ , with respect to propene - at  $950^\circ\text{C}$ , with respect to ethyne - at  $950^\circ\text{C}$ , with respect to benzene - at  $950^\circ\text{C}$ , with respect to toluene - at  $1000^\circ\text{C}$ . Condensed aromatics are formed at  $950\text{--}1000^\circ\text{C}$  (Table 1, Fig. 2). For fullerene cocoons the similar results were obtained (Table 1, Fig. 3). If quartz alone is used as a catalyst, the maxima of selectivity with respect to pyrolysis products were observed: with respect to ethane - at  $900^\circ\text{C}$ , with respect to propane - at  $900\text{--}950^\circ\text{C}$ , with respect to propene - at  $950^\circ\text{C}$ , with respect to ethyne - at  $900\text{--}950^\circ\text{C}$ , with respect to benzene - at  $950^\circ\text{C}$ , with respect to toluene - at  $1000^\circ\text{C}$ . The available maximal values of selectivity with respect to ethene, propane and propene decrease with the temperature increasing and are constant in methane pyrolysis at  $1000^\circ\text{C}$ . The selectivity with respect to benzene, toluene and condensed aromatics is constant in methane pyrolysis at  $1000^\circ\text{C}$  (Fig. 4).

At methane pyrolysis over quartz alone ( $S = 0.75\text{ m}^2$ ) and in a void reactor the methane conversion degree is lower (Fig. 1) than that over carbon materials especially in the top of Table 1. These facts show that at temperatures lower than  $850^\circ\text{C}$  the activation of C–H bond in methane seems to be predominantly

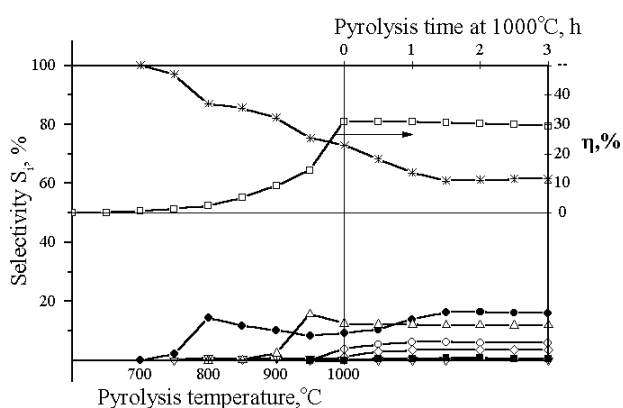


Fig. 2. Dependence of methane conversion degree  $\eta$  and selectivity with respect to products  $S_i$  in methane pyrolysis from temperature pyrolysis and pyrolysis time at  $1000^\circ\text{C}$  over fullerene black:  $\square$  -  $\eta$ , selectivity with respect to:  $\bullet$  - ethene;  $\triangle$  - propene;  $\nabla$  - propane;  $\circ$  - benzene;  $\diamond$  - toluene;  $\blacksquare$  - sum of the condensed aromatics;  $*$  - pyrolytic carbon.

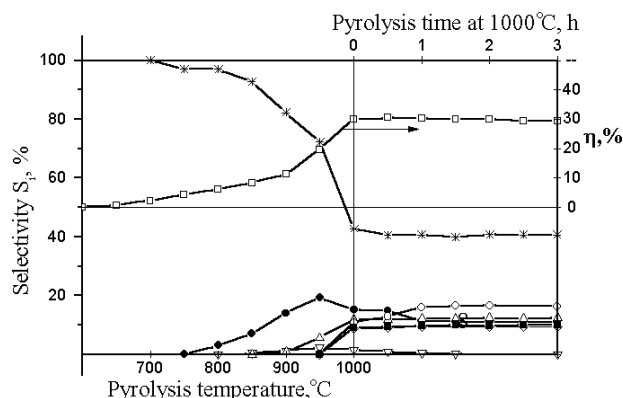


Fig. 3. Dependence of  $\eta$  and  $S_i$  with respect to products in methane pyrolysis from pyrolysis temperature and pyrolysis time at  $1000^\circ\text{C}$  over fullerene cocoons. The designations correspond to Fig. 2.

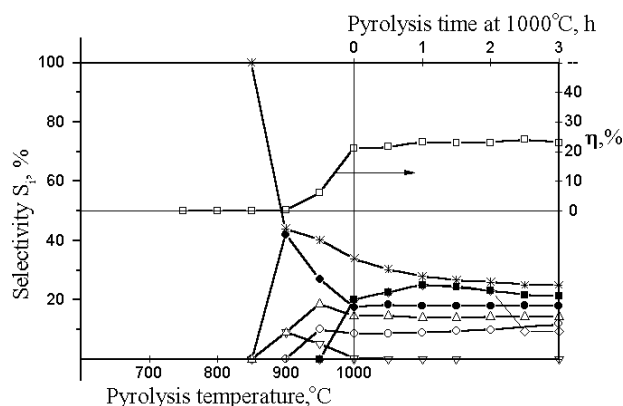


Fig. 4. Dependence  $\eta$  and  $S_i$  with respect to products in methane pyrolysis from pyrolysis temperature and pyrolysis time at  $1000^\circ\text{C}$  over quartz. The designations correspond to Fig. 2.

heterogeneous reaction determined by the catalytic surface area.

The results for fullerene black and fullerene cocoons can be compared with the data of ref. [15], obtained in pyrolysis of 8 % mol. methane/He mixture at  $1050^\circ\text{C}$  over the mixed catalyst composed of fullerene  $C_{60}$  (0.05 g) and quartz (2 g), where the total selectivity with respect to ethane, ethene and ethyne comprises 12.4, with respect to benzene - 9.0, with respect to pyrolytic carbon - 78 % at  $\eta = 50.2\%$  [15]. For quartz alone these data are significantly different: the conversion degree  $\eta$  is raised up to 13.5 %, and according selectivity are equal to 18.3, 12.5 and 62.9 % [15]. This difference of methane conversion degree evidences the effect of fullerene component in methane pyrolysis, but amount of this component in the mixed catalyst is unknown. Fullerene  $C_{60}$  are easily sublimed under reaction conditions and removed by a gas flow. The methane conversion degree in-

creased almost by 4 times after the active component addition to quartz [15], whereas under the conditions of this work the similar additions caused only the increase of the one by 1.5 times (Table 1).

The specific surface area of a carbon material definitely influences process parameters. In particular, aromatics formed at high temperature seem to be poorly adsorbed on undeveloped surface of carbon materials with small curvature radii and therefore easily carried away by a gas flow. As a result the tendency to increase the selectivity with respect to aromatics and to decrease the selectivity with respect to pyrolytic carbon is observed when moving from the top to the bottom through Table 1.

The compositions of condensed aromatics in all cases are close with prevailing products being naphthalene (45–75 %), indene, acenaphthene, phenanthrene, chrisene and pyrene. The analysis of these products has shown that the average composition can be described by the empirical formula  $C_{10}H_8$ .

The high (more than 50 %) total selectivity with respect to aromatics observed for some mixed catalysts (Table 1, Fig. 2, 3) allows to say on methane aromatization as the main process in methane pyrolysis. The selective realization of this process is a more difficult task in comparison with aromatization of other alkanes [16, 17]. Formation of aromatics, especially CAr, is a consequence of multiple high-temperature processes, and it was observed in homogeneous methane pyrolysis (for example, [18]). The observed difference in the selectivity with respect to aromatics for the mixed catalysts and quartz alone evidences the realization of some of these high temperature processes in the heterogeneous reaction, i.e. on the catalyst surface.

The minimal selectivity with respect to pyrolytic carbon (10 %) was achieved for the catalyst based on glassy carbon (Table 1) while the maximal one was achieved in methane pyrolysis over the catalyst based on soot-like graphite oxide [19], having initial SSA = 13.0 m<sup>2</sup>/g. This catalyst has exhibited the highest selectivity with respect to pyrolytic carbon (93 %) at stable conversion 26 % for 3 h at 1000°C.

Thus, although catalytic properties of the carbon containing mixed catalysts are somewhat similar at 1000°C due to an averaging influence of deposited pyrolytic carbon. However, were found both the material having the high (74.8 %) selectivity in methane aromatization (glassy carbon) and the material having the low one but exhibiting the high selectivity with respect to pyrolytic carbon (soot-like graphite oxide).

Deposited pyrolytic carbon has small value of specific surface area. For all carbon materials excepting carbon fiber the specific surface area of mixed catalysts after 3 h of methane pyrolysis at 1000°C does not exceed 0.15 m<sup>2</sup>/g. The data of element analysis of pyrolytic carbon obtained at 1000°C correspond to its empirical formula  $C_6H$ . Such C/H molar ratio is peculiar to pyrolytic carbon produced via the «high-temperature» mechanism, corresponding to the condensation of aromatic rings, and is usually observed in methane pyrolysis [20]. Maximal positions of the C1s peak on x-ray photoelectron spectra for the samples of pyrolytic carbon varied in the range 284.3–284.5 eV with the half width being 0.7–0.9 eV, that is consistent with incomplete graphitization of pyrolytic carbon [16]. These observations give additional evidences that at 950–1000°C aromatics are immediate precursors of pyrolytic carbon, which is thermodynamically the most favourable carbon product under these conditions.

## Conclusion

Methane pyrolysis is carried out both on catalyst surface and in reacting volume at temperatures up to 850°C over carbon catalysts. Thus, the influence of catalyst surface is revealed in lower, than in case of quartz and carbon materials with low curvature of based structure elements, temperature points, at which methane is converted into hydrogen, hydrocarbons and pyrolytic carbon. Homogeneous gas phase thermal reactions of multiple dehydrogenations in volume are prevalent above 850°C and the influence of catalyst surface decreases. It is noteworthy that the total selectivity with respect to multiple dehydrogenation products (the sum of values of the selectivity with respect to aromatics and pyrolytic carbon) is practically constant (Table 1) that evidences pyrolytic carbon formation from aromatics, i.e. aromatics is pyrolytic carbon precursors. The influence of surface catalytic reactions at high (above 900°C) temperatures is demonstrated by the higher, than in the case of gas phase reactions, selectivity with respect to aromatics and differences in the ratios aromatics/pyrolytic carbon.

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