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Catalytic activity of carbons for methane decomposition reaction

Nazim Muradov [*], Franklyn Smith, Ali T-Raissi

Florida Solar Energy Center, University of Central Florida, 1679 Clearlake Road, Cocoa, FL 32922, USA

Abstract

Catalytic decomposition of methane is an environmentally attractive approach to CO_2-free production of hydrogen. The objective of this work is to evaluate catalytic activity of a wide range of carbon materials for methane decomposition reaction and determine major factors governing their activity. It was demonstrated that the catalytic activity of carbon materials for methane decomposition is mostly determined by their structural and surface properties. Kinetics of methane decomposition reaction over disordered (amorphous) carbons such as carbon black and activated carbon were determined. The mechanism of carbon-catalyzed methane decomposition reaction and the nature of active sites on the carbon surface are discussed in this paper.

Keywords: Hydrogen; Carbon; Methane decomposition; Catalyst

1. Introduction

Direct decomposition (or pyrolysis, cracking) of methane has been researched as an environmentally attractive approach to production of hydrogen from natural gas [1–3]. The process produces hydrogen without CO/CO_2 byproducts, which eliminates the need for water gas shift and CO_2 removal stages required by conventional hydrogen production processes (e.g. steam methane reforming, SMR). This significantly simplifies the process and dramatically reduces overall CO_2 emissions. Much research on methane decomposition over transition metal catalysts (e.g. Ni, Fe, Co, Pd, etc.) has been reported in the literature since early 60's (e.g. [4–6]). These studies point to a catalyst deactivation problem associated with the carbon lay down on the catalyst surface, and in most cases carbon was burned off of the catalyst surface (e.g. [4]), or gasified with steam (e.g. [7]) in order to regenerate its original activity. Gasification or combustion of carbon deposits, however, results in production of large amounts of CO_2 byproduct. Recently, there have been reports on simultaneous production of hydrogen and nanostructured carbon (nanotubes) via Ni- and Fe-catalyzed decomposition of methane [8,9].

In our earlier work, we explored the possibility of using various carbons as catalysts for hydrocarbon decomposition reactions [10,11]. The use of carbon-based catalysts offers certain advantages over metal catalysts: (i) high temperature resistance, (ii) tolerance to sulfur and other potentially harmful impurities in the feedstock, (iii) no metal carbides formed (formation of carbides may complicate the regeneration of metal catalysts), (iv) production of a marketable byproduct carbon (that could substantially reduce the net cost of hydrogen production), and (v) effect to mitigate overall CO_2 emissions from the process. We have reported on the catalytic activity and stability of a number of carbon materials of different origin and structure for methane decomposition reaction [11]. Recently, catalytic decomposition of methane over coal-derived activated carbons was reported by other researcher groups [12,13]. The objective of this work is to expand the range of carbon materials examined and gain further understanding of the nature of the catalytic action of carbons during methane decomposition reaction. Of particular interest are the nature of active sites and the correlation between the structural and surface properties of carbon materials and their catalytic activity.

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[*] Corresponding author. Tel.: +1 321 638 1448; fax: +1 321 638 1010.
E-mail address: muradov@fsec.ucf.edu (N. Muradov).

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2. Experimental

Methane (99.99 vol.%) (Air Products and Chemicals Inc.) was used without further purification. Carbon black (CB) samples were obtained from CABOT Corp. The samples of activated carbons (AC) were obtained from NORIT Americas, Barnebey Sutcliff Corp. and Kanzai Coke & Chemicals (MAXSORB carbons). Samples of graphites, glassy carbon, synthetic diamond powder and acetylene black (AB) were purchased from Alfa Aesar. Carbon nanotubes (multi-walled, containing 10–40% of nanotubes with 7–12 nm OD and 0.5–10 micron length), fullerenes $C_{60/70}$ (20% C_{70} and 1% of higher fullerens), and fullerene soot (containing 2–20% of $C_{60/70}$) were obtained from Strem Chemicals and used without further purification. Most of the carbon samples tested were obtained in the form of fine powders (particle size <100 microns), and were used "as received".

Methane decomposition experiments were conducted using a quartz microreactor with a thin bed of carbon material (30–100 mg, on dry basis) to ensure low pressure drop. The reactor was maintained at a constant temperature using a type K thermocouple and a Love Controls PID temperature regulator. All experiments were conducted at atmospheric pressure. Before the experiments, all carbon samples were heated at 500 °C for 0.5 h and 850 °C for another 0.5 h in a stream of 99.999% argon to remove all the surface-adsorbed and pore-entrained oxygen and water from the samples. Testing of all the carbon samples for catalytic activity was conducted at identical experimental conditions (850 °C and a residence time of approximately 0.1 s in the carbon sample bed). Control experiments using an inert contact (silica gel) demonstrated that no appreciable thermal (non-catalytic) decomposition of methane occurs at these conditions. Analysis of methane decomposition products was performed gas chromatographically using SRI-8610A GC (TCD, argon carrier gas, silica gel packed column) and Varian-3400 GC (FID, helium carrier gas, HysepD_B packed column).

3. Results

3.1. *Effect of carbon origin and its surface area on catalytic activity*

In this paper, all references to the catalytic activity of carbon samples relate to the initial rate of methane decomposition per unit mass (IRMD/m) or surface area (IRMD/s) of carbon. The data on IRMD/m and IRMD/s using different carbon materials along with the data on their surface area are summarized in the Table 1. AC had highest initial activity (per unit mass) among all the carbon materials tested. However, the initial activity of AC could not be sustained and the rate of AC-catalyzed methane decomposition gradually dropped to a quasi-steady value (in most cases over a period of 2–3 h). The comparison of the catalytic activities of AC (hardwood) and CB (Black Pearls 2000) with the same surface area points in AC favor. It is noteworthy that AB, although structurally close to CB, had lower catalytic activity than CB with comparable surface area. Glassy carbon, a brittle form of carbon with a randomized structure and no open porosity, delivered relatively high initial catalytic activity followed by very

Table 1
Initial rates of methane decomposition over various carbon materials at 850 °C

Number	Carbon	Surface area (m^2/g)	K_m^o (mmol/min g)	K_s^o (μmol/min m^2)
1	AC, coconut KE	1150	1.76	1.53
2	AC, coconut CL	1650	1.67	1.01
3	AC, coconut GI	1300	1.90	1.46
4	AC, hardwood	1500	2.04	1.36
5	AC, lignite	650	1.77	2.72
6	AC, peat	900	1.63	1.81
7	AC, phenol resin	1980	1.66	0.84
8	AC, phenol resin	2260	1.53	0.68
9	AC, petroleum coke	2570	1.43	0.56
10	AC, petroleum coke	3370	1.29	0.38
11	Glassy carbon	–	0.95	–
12	Acetylene black	80	0.22	2.75
13	CB, black pearls 120	25	0.22	8.80
14	CB, regal 330	94	0.42	4.47
15	CB, vulcan XC72	254	0.48	1.89
16	CB, black pearls 2000	1500	1.15	0.77
17	Graphite, natural	4–6	0.02	–
18	Graphite, polycrystalline	3–10	0.10	–
19	Diamond powder	–	0.16	–
20	Carbon nanotubes	–	0.2	–
21	Fullerene soot	–	1.90	–
22	Fullerenes $C_{60/70}$	–	0.55	–

K_m^o and K_s^o denote the initial rates of methane decomposition per unit mass and surface area, respectively.

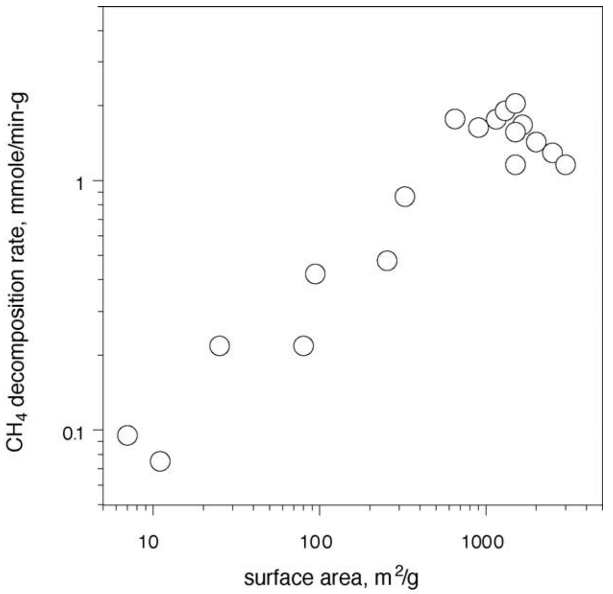

Fig. 1. Initial rate of methane decomposition (per unit mass) as a function of carbon surface area.

rapid deactivation that occurred in less than 10 min. Structurally ordered carbons (i.e. natural and polycrystalline graphites, diamond powder) with very low surface area demonstrated negligible catalytic activity per unit mass (methane conversion was so low that the IRMD/s could potentially be affected by side effects, e.g. impurity-assisted reactions). Nanostructured carbons (e.g. carbon nanotubes and fullerenes) also showed relatively low catalytic activity, whereas, fullerene soot was especially active for methane decomposition. Fig. 1 depicts the IMDR/m as a function of carbon surface area. In general, there is a correlation between IMDR/m and carbon surface area, which points to the heterogeneous nature of the methane decomposition over carbon materials. However, this correlation does not hold for the activated carbons having very high surface area.

It is interesting to compare the catalytic activity of carbons with that of transition metal-based catalysts for methane decomposition reaction. We note that metal-catalyzed decomposition of methane is not a steady state process, and, in most cases, the catalysts rapidly deactivate due to carbon deposition on their surface. The experiments indicated that at comparable experimental conditions (850 °C) alumina-supported Fe (10–30 wt.%) catalysts showed initial methane decomposition rate of 1.7–2.9 mmol/min g (Fe), which is somewhat higher than that of carbon-based catalysts. The reported experimental data [6] on methane decomposition (at 600 °C) over a number of zeolite- and silica-supported Ni (10 wt.%) catalysts also point to higher catalytic activity (per unit mass) of Ni-catalysts compared to carbon catalysts.

3.2. *Effect of impurities and surface groups*

Many of the chemical properties of carbon materials, including their catalytic activity has been shown to be related to the presence of impurities and various surface groups [14]. The amount and type of impurities present depend on the carbon origin and the method of preparation. Graphite and diamond are the purest forms of carbon, whereas, AC and CB contain significant amounts of impurities. Thus, it is important to elucidate the role of impurities in the catalytic action of carbons for methane decomposition. Two types of impurities are of particular interest: transition metals and oxygen.

3.2.1. *Effect of metals*

It is well known that some transition metals (most importantly, Fe, Ni and Co) can efficiently catalyze methane decomposition reaction (e.g. [4,5]). Therefore, we investigated the extent to which trace amounts of metals could affect the catalytic properties of carbons. Atomic absorption spectroscopic (AAS) analysis of a fresh carbon black (Black Pearls 2000) sample showed the presence of trace amounts of nickel (1.5 ppm) and iron (13.2 ppm) (Co and Cu were not detected). Apparently, these metallic impurities originate from the heavy petroleum fractions used as feedstock in the CB manufacturing process. It should be noted that the amount of metallic impurities in the CBs tested (all produced by the Oil Furnace process) are comparable, however, their catalytic activity varied in a wide range (almost two orders of magnitude, see Table 1). This finding does not support the notion that the catalytic action of carbons is determined mainly by the presence of metallic impurities. The amount of Fe in some samples of AC was in the range of 10–200 ppm, however, no particular correlation between Fe content in AC and its catalytic activity could be found. Furthermore, if one assumes that the catalytic activity of carbons for methane decomposition reaction is governed by the presence of transition metals, it would be reasonable to expect that the activation energy of the carbon-catalyzed reaction to be close to that of metal-catalyzed reactions, which is not the case (see Section 3.3 for more discussions on this topic). The control experiments with the inorganic ash produced from the lignite-derived AC showed no particular catalytic activity for methane decomposition. Thus, these observations point to a negligible role that metal impurities play in carbon-catalyzed methane decomposition.

3.2.2. *Effect of surface groups*

It is a well-established fact that CB and, particularly, AC contain significant amounts of oxygen and other elements (H, S, N, Cl, Si, etc.). Two main sources of these impurities are the feedstocks and oxidizing agents (oxygen, steam, CO_2) during the carbon manufacturing process. These elements can form various surface functional groups that can affect the chemical and catalytic properties of carbon materials. The presence of carboxylic, carbonyl, lactonic, phenolic groups on the carbon surface has been well documented [15]. In a number of studies, the authors demonstrated a link between the catalytic properties of carbons and the presence of oxygenated surface groups (e.g. in carbon-catalyzed oxidation of H_2S, NO and SO_2 [14]).

According to the specifications provided by the Kanzai Coke and Chemicals (Japan), the manufacturer of petroleum coke-based AC (similar to ones used in this work), the AC with the surface area of 2700 m^2/g has the following average chemical composition (wt.%): C-89.9, H-0.1, O-9.1, N-0.6, S-0.3 (on dry, ash-free basis); the amounts of carbon–oxygen functional surface groups such as R–COOH, R–OCO, R–OH and R=O are (meq/100 g AC): 30, 30, 52 and 0, respectively [16]. These researchers have shown that as the surface area of the AC increases, so does the amount of oxygenated surface groups. Some of these groups (especially, R–OCO and R–OH) are very difficult to remove from the carbon surface by simple thermal treatment in an inert atmosphere.

Most of CB is currently manufactured by partial combustion of heavy aromatic feedstocks involving flames (Oil Furnace process). The average chemical composition of commercial carbon blacks is as follows (wt.%): C-98.2, H-0.3, O-0.6, S-0.6 and ash-0.3 [17]). X-ray photoelectron spectroscopic (XPS) studies of the carbon black (Black Pearls 2000) conducted in this work indicated the presence of oxygen and small amounts of sulfur and silicone: the surface atomic concentrations of elements are as follows (at.%): carbon-98.6, oxygen-1.0, sulfur-0.2 and silicon-0.1. The comparison of chemical compositions of AC and CB shows that the latter contains much lesser amount of oxygen. This fact correlated with the observation that CB is catalytically less active than AC (with the comparable surface area), may point to the crucial role oxygenated surface groups play in the catalytic activity of carbons. However, several other experimental observations do not support this conclusion. For example, in the family of AC produced by KOH activation of petroleum coke and carbonized phenol resins (manufactured by Kanzai Coke and Chemicals), the increase in the surface area (and the amount of the oxygenated surface groups) did not result in an increase in methane decomposition rate (the effect was in fact opposite).

To elucidate the role of surface oxygenated groups on the methane decomposition reaction, we conducted several experiments where the catalytic activity of original AC (lignite) samples were compared with that of AC (lignite) pre-treated with pure hydrogen at 850 °C (according to [14], high-temperature treatment of carbon with hydrogen removes most of carbon-oxygen groups from the carbon surface). The results are presented in Fig. 2. Decomposition of methane over the original AC resulted in an effluent gas with initial CO concentration of 0.77 vol.%, whereas, the hydrogen-pretreated AC produced gas with initial CO concentration of 0.17 vol.% (i.e. 4.5 times less). Fig. 2 depicts that the removal of oxygenated surface groups dramatically reduces the initial CO concentration, but it slightly affects the initial hydrogen yield. Furthermore, if one assumes that the methane decomposition rate is governed by the concentration of oxygenated surface groups, it would be reasonable to expect H_2 and CO kinetic curves to follow the same pattern, which is apparently not the case ([CO] drops much faster than [H_2]). These observations imply that, although carbon–oxygen surface groups may play a role in methane dissociation, particularly, at the initial stage of the process, the catalytic activity of carbons, in general, could not be solely attributed to the presence of such surface functional groups.

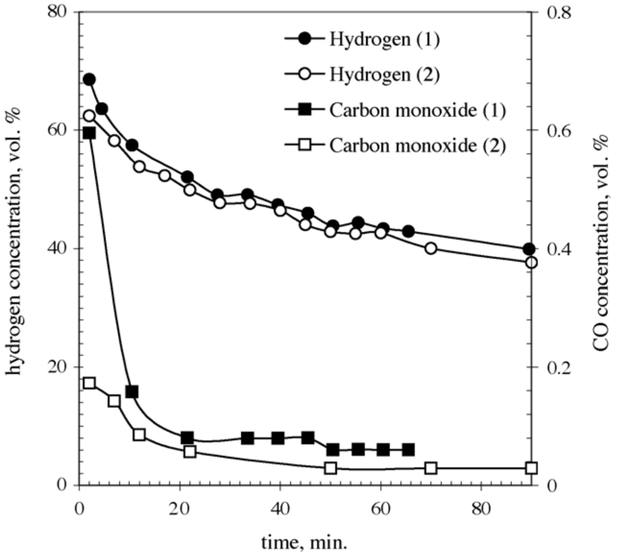

Fig. 2. The effect of removal of oxygenated surface groups on H_2 and CO yields. (1) and (2) relate to the original and hydrogen-treated carbon samples, respectively.

3.3. Kinetics of methane decomposition over carbons and catalyst deactivation

The apparent reaction order of carbon-catalyzed methane decomposition reaction was determined to be 0.6 ± 0.1 for AC (lignite) and 0.5 ± 0.1 for CB (BP2000) catalysts. A half-order reaction has been previously reported for methane decomposition catalyzed by a number of carbon-based catalysts [12,18]. Thus, the rate equation for carbon-catalyzed decomposition of methane can be written as follows:

$$-r_{CH_4} = kP_{CH_4}^{0.5}. \quad (1)$$

The apparent activation energies for carbon-catalyzed methane decomposition varied in a wide range not only within different types of carbon (e.g. AC versus CB), but also within the family of carbons. For example, amongst the AC-based catalysts tested, the apparent activation energies (E_a) varied in a range of 160–201 kJ/mol (at 600–900 °C). These data are in fairly good agreement with the reported activation energies for a number of coal-derived AC (186–198 kJ/mol [12]). For CB-based catalysts, the measured E_a were somewhat higher (205–236 kJ/mol, at the same

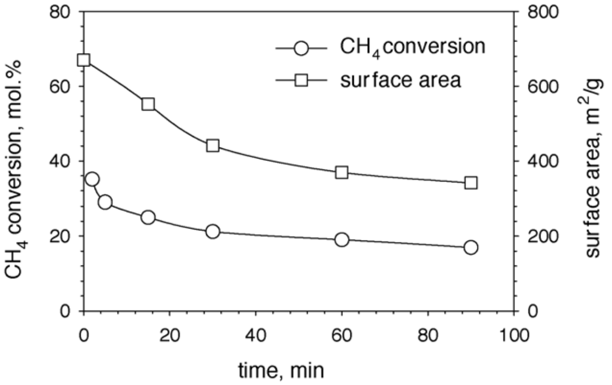

Fig. 3. Correlation between methane conversion yield and carbon surface area.

conditions). It is interesting to note that the values of activation energies for carbon-catalyzed methane decomposition lie between the E_a for non-catalytic and metal-catalyzed reactions. For the reference, the activation energies for non-catalytic methane decomposition were reported in the range of 370–433 kJ/mol (e.g. [19]), whereas, E_a for transition metal-catalyzed reactions were reported 60 kJ/mol and below (e.g. [20]).

Fig. 3 depicts the kinetic curve of methane decomposition over AC (lignite) correlated with the time dependence of carbon surface area. There was an initial drop in the catalytic activity of AC over a period of 0.5 h followed by a relatively mild decline in methane decomposition rate. Fig. 3 depicts that the surface area curve closely follows the methane conversion curve (initial drop followed by shallow decline). These data suggest that carbon catalyst deactivation could be attributed to the loss in the surface area of the carbon. Fig. 4 compares the deactivation kinetics for AC- and CB-catalyzed reactions; in particular, the data shows the time dependence of the carbon surface area for AC (lignite) and CB (BP2000) in log–log coordinates. The empirical decay law for the surface area of AC and CB catalysts are given by the following equations:

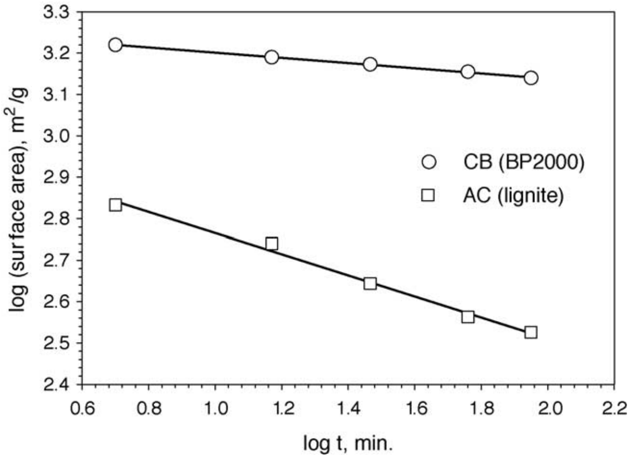

Fig. 4. Carbon surface area reduction during methane decomposition as a function of time.

$$S_{AC} = 10^3 t^{-0.25} \quad (2)$$

$$S_{CB} = 1.8 \times 10^3 t^{-0.057} \quad (3)$$

where S_{AC} and S_{CB} are the surface areas of AC and CB, respectively, and t denotes time.

Trends indicated by Eqs. (2) and (3) show that the surface area of AC diminishes much faster than that of CB. It is interesting to compare the above decay law with the known correlations for catalyst deactivation kinetics, for example, deactivation due to carbon deposition (i.e. catalyst coking). A typical empirical formula for the decay of catalytic activity by coking is given by Voorhies correlation, which relates the amount of coke on the catalyst surface to a power of time on stream [21]:

$$C_c = A(t_c)^n \quad (4)$$

where C_c is the number of moles of carbon on the catalyst surface, t_c is time on stream; both A and n are fouling parameters that are determined experimentally.

It should be noted that the correlation (4) refers to the amount of coke, not the activity factor (AF). Therefore, it is necessary to develop additional correlation in the form AF = $f(C_c)$ to complete the correlation for activity (or surface area). Carbon catalyst deactivation models presented by the Eqs. (2) and (3) are in a fair agreement with the Voorhies correlation (4) (negative values of n point to the inverse proportionality between surface area and the number of moles of carbon deposited), i.e. as the amount of carbon deposited increases, the surface area per unit mass decreases. It is noteworthy that the derived deactivation models (2 and 3) are in less satisfactory agreement with the exponential decay function AF = exp $(-Kt)$, also commonly used to relate catalyst activity to the time during catalyst coking [21].

3.4. Catalytic activity of carbons produced by decomposition of hydrocarbons

Based on the bulk of experimental data available, it is apparent that carbon produced by decomposition of methane possesses insignificant catalytic activity, otherwise the process would become autocatalytic (i.e. carbon produced from methane would further catalyze methane decomposition leading to the reaction acceleration, rather than deceleration). We conducted X-ray diffraction (XRD) studies of CB and AC before and after exposure to hydrocarbons (methane and propane). Fresh CB (Black Pearls 2000) displayed one- and, to a lesser extent, some two-dimensional ordering, whereas, carbon sample produced after the CB exposure to hydrocarbons revealed ordering in a “columnar” or stacking direction. The *d*-spacing (lattice spacing) or spacing between plates is practically uniform, so that the (0 0 3) columnar reflection is clearly present. Thus, the carbon produced by CB-catalyzed decomposition of hydrocarbons revealed a

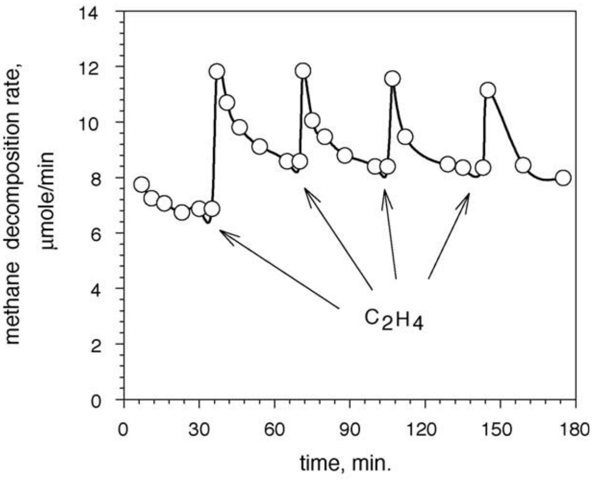

Fig. 5. Effect of ethylene pulses on methane decomposition rate at 850 °C. (Time of purging the reactor with Ar after C_2H_4 pulses is not included in the plot).

graphite-like a-b-c-a type stacking of the carbon ring plates (as opposed to a-b-a-b for pure graphite). The actual *d*-spacing ($d = 3.4948$ Å) of this (0 0 3) peak is larger than that of the standard graphite structure ($d = 3.3480$ Å), which indicates that the plates are slightly further apart in the columnar stacking direction. This type of arrangement has been termed in the literature as a turbostratic structure [17].

It was interesting to compare the catalytic activity of carbons produced by decomposition of different hydrocarbons with that of methane-derived carbon. Of particular interest were unsaturated (UH) and aromatic (AH) hydrocarbons, which are more readily decomposed compared to methane. It was found that carbon produced by thermal decomposition of UH and AH exhibited higher catalytic activity compared to carbon produced from methane. Fig. 5 demonstrates the accelerating effect of the ethylene-derived carbon on methane decomposition rate. Methane was thermally decomposed (850 °C) over the surface of activated alumina over a period of 1 h until a quasi-steady state was established. A pulse of ethylene was introduced into the reactor (at the same temperature), followed by rapid and thorough purging of the reactor with an inert gas (for removing gaseous products of ethylene decomposition). Methane was introduced into the reactor, and a sharp increase (spike) in methane decomposition rate was observed, followed by its gradual decline over a period of about half an hour. This procedure was repeated several times, and the effect was almost the same. This experiment indicates that carbon produced from ethylene is catalytically more active toward methane decomposition reaction than carbon produced from methane. Likewise, even more pronounced effect, was observed when acetylene, or benzene pulses were introduced into the reactor where methane decomposition took place. The relative activity of carbons produced by decomposition of various hydrocarbons toward methane decomposition reaction could be arranged in the following order: $C_{\text{benzene}} > C_{\text{acetylene}} > C_{\text{ethylene}} > C_{\text{propane}} > C_{\text{methane}}$.

4. Discussion

Carbons exist in many diverse morphological forms; they occur naturally (e.g. natural graphite, diamond), or could be produced from carbon-containing materials such as biomass, coal, hydrocarbons, etc. Physical, chemical and catalytic properties of carbons depend on the starting material and the conditions of the manufacturing process. Carbon-catalyzed decomposition of methane is a very complex process: too many factors could potentially affect the catalytic properties of carbons. The origin of the carbon material, its crystallographic structure, surface area, the presence of surface groups and energetic abnormalities are among major factors governing the catalytic activity of carbons. The aim of this paper is to sort out and identify the most important parameters.

As discussed in Section 3.2, presence of trace quantities of transition metals in some carbon materials has a negligible effect on the rate of methane decomposition. Likewise, our experimental results imply that the catalytic activity of carbons could not be solely attributed to the presence of surface carbon–oxygen groups and complexes. The majority of catalytic reactions in a gas–solid interface involve surface defects, dislocations, vacancies, low-coordination sites, etc. Therefore, the possibility of this type of catalytic action in the carbon-catalyzed methane decomposition reaction needs to be closely examined.

Various modifications of carbon could be distinguished in terms of crystallinity or the degree of order, i.e. from highly ordered carbons, such as graphite and diamond, to less ordered (turbostratic and pyrolytic carbons) and, finally, to disordered (or amorphous, microcrystalline) carbons, such as carbon black, charcoal, activated carbon. Amorphous carbons consist of hexagon plates or layers stacked parallel to each other, but without further ordering (crystallites). The various forms of amorphous carbon differ in the size of crystallites (from a few tens to a few hundreds Angstroms) and in their mutual orientation [22]. On the surface of amorphous carbons, the regular array of carbon bonds is disrupted, forming ‘‘free’’ valences, discontinuities (i.e. the edges and corners of crystallites) and other energetic abnormalities that could be generalized as high-energy sites (HES). Evidently, the surface concentration of HES increases with the decrease in carbon crystallite size, and, vice versa, decreases as carbon becomes more ordered (e.g. during graphitization). It is apparent from the Table 1 that amorphous carbons (e.g. AC, CB) are particularly active in methane decomposition reaction, compared to well-ordered carbons such as graphite, diamond, and carbon nanotubes. This may point to the direct correlation between the surface concentration of HES and catalytic activity in methane decomposition reaction. The driving force for the catalytic action of carbon is that carbon atoms in HES tend to react with approaching methane molecules in order to satisfy their valency requirements and energetically stabilize.

It would be worthwhile to give some more consideration to how carbon structure affects its catalytic activity. The carbon-carbon distance within the hexagon layers in amorphous carbons is the same as in graphite (1.420 Å), however, interlayer spacing is considerably larger (about 3.6 Å versus 3.354 Å in graphite) [22]. XRD studies conducted in this work (Section 3.3) demonstrated that in the original carbon black sample (BP2000) the plates are not stacked in a columnar arrangement, but, instead, are randomly oriented with respect to each other. However, after exposure to hydrocarbons the ordering in the "columnar" or stacking (0 0 3) direction has evolved. The distance between layers (*d*-spacing) was found to be $d = 3.4948$ Å, which lies between the *d*-spacing for amorphous carbon and pure graphite. Thus, carbons produced by decomposition of methane and propane feature more ordered structure compared to amorphous carbons, but they are less structurally ordered than graphite (which is characteristic of turbostratic carbon). This clearly correlates with the order of catalytic activity of carbons toward methane decomposition (amorphous > turbostratic > graphite).

Let's now consider the carbons produced by decomposition of unsaturated and aromatic hydrocarbons. What makes them more catalytically active than carbon produced from methane? The XRD analysis of the carbon produced from ethylene indicated the turbostratic structure, however, the crystallite size was smaller than that formed from methane or propane. Fig. 6 depicts the relative catalytic activity of carbons produced from ethylene, acethylene, benzene and methane (normalized against the activity of carbon from methane) as a function of carbon crystallite size (the data on crystallite size are taken from [23]). Apparently, a correlation exists between catalytic activity of carbons for methane decomposition and their crystallite size, i.e. smaller the crystallites, higher the activity. Smaller crystallite size, in all likelihood, translates into higher surface concentration of HES (i.e. more discontinuities and energetic abnormalities per unit of surface area). This explains accelerating effect of carbons produced from ethylene, benzene or acethylene on methane decomposition rate.

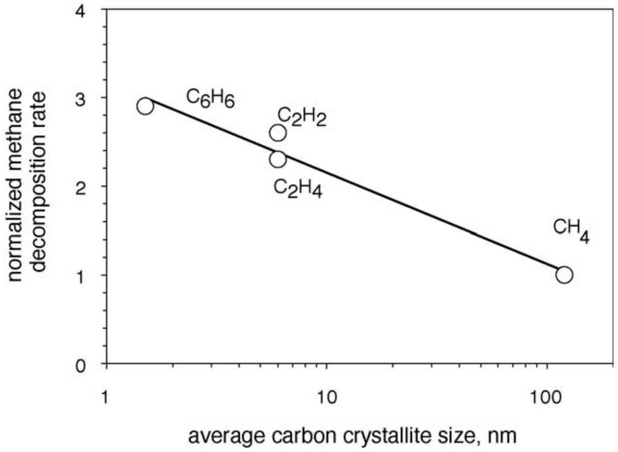

Fig. 6. Relative catalytic activity of carbons produced by decomposition of hydrocarbons as a function of carbon crystallite size. Activity of methane-derived carbon assumed to be 1.

Based on the above considerations, it can be said that HES constitute the predominant fraction of active sites on the surface of carbons. Methane molecules dissociate via interaction with the chemically reactive edges of carbon crystallites (or other energetic abnormalities and/or active surface radicals). During this process, C–H bonds in methane molecule break and new C–C bonds in a hexagon layer of carbon form. The mechanism of the overall process at the molecular level is very complex and yet to be fully understood. For example, it is not clear if carbon atoms formed from methane build upon the existing hexagon layer, or they give rise to a new carbon crystallite. In any event, the growth of carbon crystallites is likely to occur at the periphery of existing crystallites. It is assumed that the process of new carbon phase build-up is a combination of two simultaneous events: carbon nuclei formation and carbon crystallites growth. The rate of carbon nuclei formation is proportional to the concentration of HES or, in general, substrate surface area. Thus, carbons with high surface area tend to have a high initial catalytic activity. The activation energy of the carbon nuclei formation during methane thermal decomposition (316.8 kJ/mol) is much higher than the activation energy of the carbon crystallites growth (227.1 kJ/mol) [23]. This implies that, in general, the rate of carbon crystallites growth tends to be higher than the rate of carbon nuclei generation. The rapid crystallite growth may lead to the formation of a pseudo-ordered (turbostratic) carbon (accompanied with the loss in surface area and the concentration of HES) and, as result, loss in catalytic activity. Relatively high catalytic activity of fullerene soot could be attributed to the presence of carbon species with extremely high surface energy, e.g. precursors or "debris" of fullerenes.

Thus, the difference in catalytic activity between different carbons can be explained by the difference in their crystallinity and surface morphology. Carbon blacks differ in particle size, average aggregate mass, surface area (e.g. the Oil Furnace process produces CB with particle diameters in the range of 10–250 nm, and surface area of 25–1500 m^2/g). Most of CB surface is "open" and relatively easily accessible to methane molecules. CB with high external surface area (e.g. Black Pearls 2000) provide relatively high methane decomposition rate. The process goes on for several hours until most of the surface is covered by carbon crystallites produced from methane. This is followed by a gradual decrease in methane decomposition rate due to rapid growth of carbon crystallite and, hence, the reduction in the catalytic surface. The differences in the catalytic activity of acetylene black (AB) and CB may stem from the nature of the feedstock and specifics of the manufacturing process. In particular, AB is produced by thermal decomposition of acetylene at 800–1000 °C in the absence of air. XRD data indicated that AB is also the most ordered (crystalline) among commercial carbon blacks [17]. As a result, AB is less catalytically active compared to CB with comparable surface area.

In contrast, most of AC surface is ''internal'' (pores, mesopores, micropores) and relatively difficult to reach. Thus, the rapid deactivation of AC catalysts can be explained by blocking of the mouth of AC pores by growing carbon crystallites and, as a result, sharp decrease in the overall surface area. Micropore analysis and pore size distribution measurements of AC (lignite) used in methane decomposition experiments indicated the effective pore diameter in the range of 25–32 Å. This is smaller than the size of crystallites produced from methane (>100 Å). Thus, the deposition and growth of a single crystallite near the mouth of a micropore could block the access to the entire pore structure of the carbon particle. Based on the kinetic curves of methane decomposition over AC catalysts, most rapid deactivation of the catalysts occurs during first 0.5 h, which is followed by relatively slow decline in catalytic activity. It is estimated that the amount of carbon produced from methane during this period roughly corresponds to 20% of the amount of the carbon catalyst present in the reactor.

No definite conclusion has yet been made on the mechanism for carbon-catalyzed methane decomposition. Most likely, the reaction starts with dissociative adsorption of methane molecule on the surface active sites:

$$(\mathrm{CH_4})_\mathrm{g} \rightarrow (\mathrm{CH_3})_\mathrm{a} + (\mathrm{H})_\mathrm{a} \tag{5}$$

This is followed by a series of surface stepwise dissociation reactions leading to elemental carbon and hydrogen (the stepwise mechanism was suggested for Ni-catalyzed methane decomposition in [24,25]):

$$(\mathrm{CH}_{3-x})_\mathrm{a} \rightarrow (\mathrm{CH}_{2-x})_\mathrm{a} + (\mathrm{H})_\mathrm{a} \tag{6}$$

$$(\mathrm{C})_\mathrm{a} \rightarrow \frac{1}{n}(\mathrm{C}_n)_\mathrm{c} \qquad \text{(carbon crystalline growth)} \tag{7}$$

$$2(\mathrm{H})_\mathrm{a} \rightarrow (\mathrm{H_2})_\mathrm{g} \tag{8}$$

where $0 < x < 2$; subscripts (a), (c) and (g) denote adsorbed, crystalline and gaseous species, respectively.

Several of our experimental observations are in accord with the above scheme. For example, as the surface concentration of HES diminishes over time (due to growth of carbon crystallites and loss in carbon surface area) one could expect the formation of C_2H_6 and C_2H_4 via dimerization reactions, for example:

$$2(\mathrm{CH_3})_\mathrm{a} \rightarrow (\mathrm{C_2H_6})_\mathrm{g} \tag{9}$$

Indeed, after approximately 2–3 h through experimental run, the presence of small amounts of C_2H_6 and C_2H_4 in the effluent gas were detected.

5. Conclusions

Carbon-catalyzed decomposition of methane is an environmentally attractive low-emission approach to production of hydrogen. Carbon, as a valuable byproduct of the process, could potentially reduce the net cost of hydrogen production. A variety of high-surface carbon materials, including activated carbons and carbon blacks, are capable of producing hydrogen-rich gases at moderate temperatures. It was found that catalytic properties of carbons for methane decomposition reaction are mostly determined by their structural and surface properties. The surface concentration of high-energy sites (which are presumed to be catalytic active sites) is the most important factor governing the activity of carbons. The activation energy of carbon-catalyzed decomposition of methane lies between the activation energies for thermal (non-catalytic) and transition metal-catalyzed reactions. No definite conclusion has yet been reached on the mechanism of carbon-catalyzed methane decomposition. It is likely that the reaction begins with dissociative adsorption of methane followed by a series of stepwise surface dissociation reactions leading to elemental carbon and hydrogen. The catalytic activity of deactivated carbons can be regenerated via surface gasification reactions using steam and/or carbon dioxide. From practical point of view, thermocatalytic decomposition of methane could be arranged in a continuous process employing a fluidized bed reactor-regenerator system with carbon particles circulating between the apparatuses in a fluidized state (similar to fluid catalytic cracking or fluid coking industrial processes).

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