AMORPHOUS CARBONS AND CNFS GROWN ON TRANSITION METALS AND URANIUM CATALYSTS FOR METHANE AND HYDROGEN STORAGE

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Introduction

Hydrogen is an important modern source of energy. Use of hydrogen in fuel cells for automobile engines solves the problem of toxic pollutant emissions. There are several ways to obtain pure hydrogen, e.g., process of methane reforming or its catalytic decomposition. The increase of demand for hydrogen and methane causes the problem of storage and transportation of these gases. Traditional storage of gases in the compressed form at pressures of 200 atm and higher requires using multi-stage compressors and special process safety measures. This is the reason why the study of the possibility to store these gases in the adsorbed form at moderate – up to 60 – 80 atm pressures is very urgent.

To solve this problem we propose to use new carbon materials: carbon nanofibers (CNFs) different by structure: with carbon layers arranged perpendicular to the filament axis (deck of cards morphology), at an angle of 45° to the axis (herringbone morphology) or parallel to the axis, forming multi-wall nanotubes, and amorphous microporous carbons (AMC), in which the free space between graphite layers and micropores can serve as containers for the adsorbed gases.

CNFs have been prepared by decomposition of methane and ethylene on 3d-metal (Ni, Co, Fe, Cu) and uranium (U) catalysts. The growth rate and properties of CNFs depend on the type of the catalyst, reaction temperature, chemical composition of hydrocarbon etc. AMC are produced from oil coke or other organic initial materials and their textural characteristics are strongly affected by the type of a carbon precursor.

Experimental

Using aqueous solutions of salts $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $UO_2(NO_3)_2{\cdot}6H_2O$ and NaOH or NH_4OH as a precipitate, we prepared the catalysts by a procedure described in detail elsewhere (Kruissink, 1981). The samples were carefully washed with distilled water, dried at 110°C, and calcined in a flow of N_2 at 350°C for 3 h. The catalysts were reduced in a flow of pure hydrogen at 550°C for 3 h. To minimize pyrophoric behavior of the reduced catalysts, the samples were in situ passivated in ethanol and dried at room temperature. This procedure did not influence the properties of the catalysts. Catalytic activity of the reduced samples (100 mg) was measured in a vibrating flow quartz reactor 30 cm^3 in volume. Methane or ethylene was supplied at a rate of 3 to 12 l/h.

Concentration of hydrocarbons was measured by gas chromatography and their conversion was calculated. To determine the total amount of CNFs formed, the sample was weighted after the reaction, which was performed to the complete catalyst deactivation.

AMC was prepared by mixing the oil coke with alkali and carbonization at temperatures of 700 – 800°C in the reducing or inert medium. Such conditions lead to the formation of nanostructured carbon materials possessing high specific surface area and microporosity. Oil coke consists of extremely complex mixture of aromatic hydrocarbons of different composition. Some of these components in the pure form also have been used as precursors for the production of AMC by the method described.

Textural characteristics of the obtained samples of carbon materials were determined from isotherms of N_2 adsorption at 77 K taken with an ASAP-2400 Micrometrics instrument. The characteristics such as BET surface area $\mathbf{S_{BET}}$, the micropore volume $\mathbf{V_\mu}$, total area of meso- and macropores $\mathbf{S_\alpha}$ remaining after filling of micropores, total volume $\mathbf{V_\Sigma}$ of pores with characteristic sizes up to ~100 nm were determined.

The samples were studied also by methods of high resolution electron microscopy (HRTEM JEOL 2010, magnification up to 3116000×) and X-ray diffraction (HZG-4 with CuK_α radiation). Hydrogen and methane adsorption was studied at a specially mounted high-pressure volumetric setup.

Results and discussion

Upon variation of the synthesis conditions, CNFs with different properties have been obtained. It is shown that the chemical nature of a catalyst, ratio of the elements in bimetallic catalysts, size of the nanoparticles of catalytically active metal and nature of the hydrocarbon reactant impose significant influence on the amount of carbon material produced and on the microstructural properties of CNFs obtained (Avdeeva, 2002; Reshetenko, 2003, 2004).

For example, upon decomposition of methane on Ni-Al_2O_3 catalysts, formation of the fibers with diameter 20 – 50 nm occurs, consisting of graphite planes which are stacked into each other in the shape of cones. The angle formed between graphite layers and fiber axis constitutes 45°. It should be noted that from one catalyst particle grows one carbon fiber.

Decomposition of methane using Co-Al_2O_3 and Co-U-Al_2O_3 catalysts also leads to the formation of carbon fibers with herringbone structure. The angle formed between fiber axis and graphite layers is 15° (Fig. 1a). On HRTEM images of CNFs prepared using the mixed Co-U-Al_2O_3 catalyst, the elements Al, U and Co have been found at the base of carbon fibers (Fig. 1b), and according to EDX analysis the atomic ratio of these elements is 7:8:85 (Fig. 1c) (in the parent catalyst the ratio was 28:4:68). Inside the internal space of carbon fiber only Co has been found. In the beginning of growth of carbon fibers the detachment of active components Co and UO_2 from the surface of Al_2O_3 possibly takes place, so at the base of carbon fibers the content of these elements is higher than in the parent catalyst, and then separation of the particles occurs. Further growth of CNFs takes place on the metallic particle of Co, while UO_2 remains outside the fiber. However, the promotional effect of UO_2 on the CNF formation process is observed. Decomposition of methane on Co-U-Al_2O_3 catalyst proceeds with higher conversion (χ_{CH4}) and higher rate of CNF formation (V) compared to Co-Al_2O_3 catalyst (χ_{CH4} = 20 and 15 %, V = 7 and 5.5 g(CNFs)/g(Co)·h, respectively).

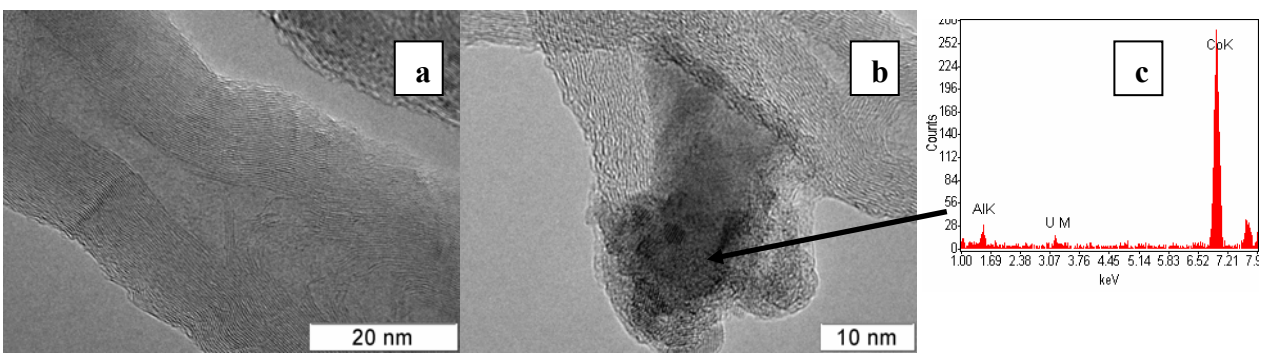

Figure 1. Data of HRTEM for CNF Sample Obtained by Decomposition of Methane on 60Co-15U-Al_2O_3 Catalyst: (a) Orientation of Graphite Planes inside Carbon Fiber, (b) Catalyst at the Base of Carbon Fiber, (c) EDX Analysis of Catalyst at the Base of Carbon Fiber.

Decomposition of methane on Ni-Cu-Al_2O_3 catalysts leads to the formation of so called octopus-type carbon, when growing of several carbon fibers from one catalytic particle is observed, and diameter of them can reach 100 – 200 nm. Graphite layers are located perpendicular to the fiber axis. Upon decomposition of ethylene on Ni-Cu-Al_2O_3 catalyst, formation of spiral shaped carbon nanofibers takes place. Diameter of fibers constitutes 70 – 100 nm. Internal structure of CNFs is represented by cone-shaped graphite layers located at the angle of 45° to the fiber axis, with gradual decrease of this angle to 0° at larger distances from the axis.

Multiwall nanotubes with fiber diameter 10 – 30 nm and internal channel diameter 5 – 10 nm are obtained upon decomposition of methane or ethylene on Fe-Co-Al_2O_3 and Fe-Ni-Al_2O_3 catalysts. Nanotubes consist of 7 – 15 graphite-like cylindrical layers, folded into each other.

Textural characteristics of some types of CNFs are presented in Table 1. The CNFs obtained by decomposition of ethylene are characterized by higher values of specific surface area and micropore volume.

The AMC prepared from oil coke and different model aromatic components of oil coke via thermocatalytic synthesis possess BET surface area up to 3000 – 4000 m^2/g and micropore volume 1.1 – 1.8 cm^3/g. The data obtained reveal that the textural characteristics of synthesized AMC are strongly affected by the type of carbon precursor (see Table 2). The largest surface area and microporosity are observed with the samples produced from oil

coke. The HRTEM data show that the AMC from oil coke contains fragments with fully disordered cellular structure which are built up by graphite-like layers of monoatomic thickness (ca. 0.3 nm). There are cells of subnanometer characteristic size corresponding to micropores between the bent graphene layers. These are partly oriented graphene packages with the distance from one another also corresponding to nanosized pores. Microdiffraction studies also support the conclusion about amorphous structure of these carbon materials. Electron diffraction gives ring reflections of hexagonal carbon in graphenes.

Table 1. The Main Textural Characteristics of the Typical CNFs and H_2 Adsorption Values at 60 atm.

Preparation condition of CNFs				Textural characteristics			H_2 adsorption at 60 atm, mg/g		
#	Catalyst	Precursor	T,°C	S_{BET}, m^2/g	V_{Σ}, cm^3/g	V_{μ}, cm^3/g	vac.	H_2	He
1	$65Ni25Cu/Al_2O_3$	CH_4+25%H_2	675	176.2	0.30	0.007	2.5	1.8	-
2	$65Ni25Cu/Al_2O_3$	CH_4+25%H_2	675	175.3	0.37	0.012		1.6	
3	$65Ni25Cu/Al_2O_3$	CH_4+25%H_2	675	130.9	0.28	0.008		1.4	2.5
4	$65Ni25Cu/Al_2O_3$	CH_4+25%H_2	700	165.1	0.34	0.005	2.3	1.6	-
5	$65Ni25Cu/Al_2O_3$	CH_4+50%H_2	675	115.4	0.29	0.007	-	1.0	-
6	$65Ni25Cu/Al_2O_3$	CH_4+50%H_2	700	103.8	0.31	0.008	-	3.3.	-
7	$65Ni25Cu/Al_2O_3$	CH_4	675	210.4	0.43	0.005	1.0	1.2	2.4
8	$57Ni23Cu/20Al_2O_3$	C_2H_4	650	178.5	0.33	0.014	6		-
9	90Ni/MgO	CH_4	550	92.1	0.22	0.002	1.2	-	-
10	$85Fe5Co/Al_2O_3$	CH_4	625	103.1	0.44	0.005	4.4	4.8	-
11	$70Ni30Cu/Al_2O_3$	C_2H_4	650	243.6	0.19	0.041	5.9	-	-
12	$75Co/Al_2O_3$	Isobutane	500	116.4	0.21	0.007	-	5.8	4.4

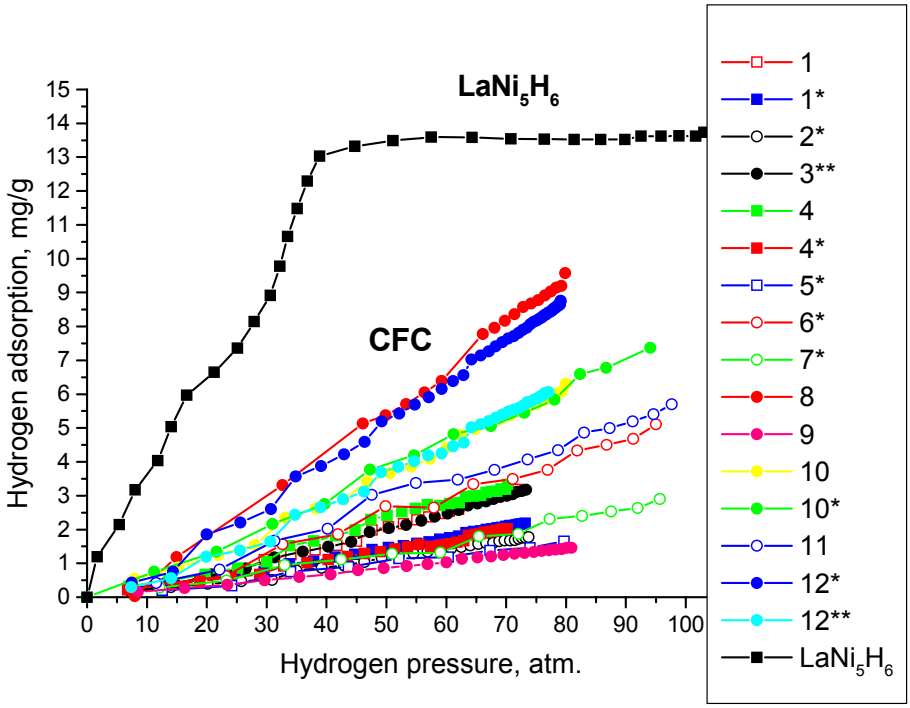

Figure 2. Typical Hydrogen Adsorption Isotherms on Different CNFs. H_2 adsorption isotherm on $LaNi_5H_6$ is given for comparison (CNF samples are numbered as in Table 1; not labeled samples were treated in vacuum, samples treated with flowing H_2 are labeled by one asterisk, the ones treated with flowing helium by two asterisks).

Table 2. Textural and adsorption characteristics of AMC.

#	Precursor	S_{BET}, m^2/g	S_α, m^2/g	V_Σ, cm^3/g	V_μ, cm^3/g	A, adsorption, mg/g; pressure 60 atm.	
						Methane	Hydrogen
1	Phenol	2240.1	369.0	1.53	0.98	167	5.2
2	Oxyquinoline	2548.2	313.3	1.59	1.21	167	5.7
3	Hydroquinone	2453.2	111.3	1.36	1.22	175	5.6
4	Oil coke	3331.0	182.0	1.84	1.56	196	12.8
5	o-nitroaniline K^+	1673.7	55.9	0.87	0.79	118	4.6
6	o-nitroaniline K^+	1691.8	30.7	0.85	0.80	122	6.3
7	o-nitroaniline Na^+	1920.6	242	1.34	1.05	145	6.4
8	o-nitroaniline Na^+	2559.0	392.3	1.74	1.25	189	6.2
9	o-nitroaniline Na^+	2508.0	156.7	1.51	1.31	179	7.5
10	Hydroquinone K^+	2697.4	104.6	1.50	1.38	218	9.1
11	Hydroquinone K^+	2835.0	171.9	1.70	1.50	230	12
12	Hydroquinone K^+	2764.8	172.0	1.64	1.43	201	9
13	2,4 dinitrophenol	632.4	55.8	0.36	0.26	96	-
14	2,4 dinitroaniline	1148.3	24.8	0.57	0.52	108	-
15	Barbituric acidNa^+	500	81	0.38	0.19	60.1	9.8
16	Barbituric acid K^+	1400	610	1.47	0.41	155	11.2
17	n-hydroquinon n-hydroquinone 1:2	2470.0	304.0	1.64	1.27	193.0	-
18	n-hydroquinon n-hydroquinone 1:2	2620.0	824.0	2.14	1.07	188.2	-
19	n-hydroquinon n-hydroquinone 1:2	2770.0	499.0	1.92	1.29	177.3	-
20	Quinolic ether	2360.0	95.0	1.25	1.10	250.3	-

We studied hydrogen and methane adsorption at room temperature and pressure up to 80 – 100 atm over CNF and AMC materials.

Typical isotherms of hydrogen adsorption on CNF samples are shown on Figure 2, experimental data on hydrogen adsorption are listed in Table 1. For comparison, Figure 2 shows measured additionally under the same conditions hydrogen adsorption isotherm on $LaNi_5$ alloy, which forms metal hydride $LaNi_5H_6$.

Table 2 shows structural and adsorption characteristics of a number of model cokes produced from different precursors and presents amounts of hydrogen and methane adsorbed at 60 atm and room temperature. Isotherms of methane adsorption on AMC samples under study are plotted in Figure 3.

The textural and adsorption characteristics of developed samples of amorphous microporous carbon are comparable with the best known carbon sorbents: Maxsorb-A, AX-21 Amoco or AX-31 Anderson Development Co, which have surface area 3100 m^2/g, micropore volume 1.38 cm^3/g. and adsorbed about 0.2 g CH_4/g at room temperature and pressure 40 atm (Lozano-Castello, 2002). The samples of AMC with maximal capacity are synthesized from oil coke. The capacities of this sample at 60 atm and ambient temperature with respect to hydrogen and methane storage are correspondingly 12.8 mg/g and 196 mg/g.

It was established that methane and hydrogen are adsorbed in the amounts proportional to the micropore volume. That is seen from plots in Figure 4 showing adsorbed amounts (60 atm) normalized to micropore volume. Amounts of adsorbed methane deviate from the mean value of 146 ± 20 mg CH_4/cm^3 micropores, the same value for hydrogen is 6.2 ± 1.5 mg H_2/cm^3 micropores.

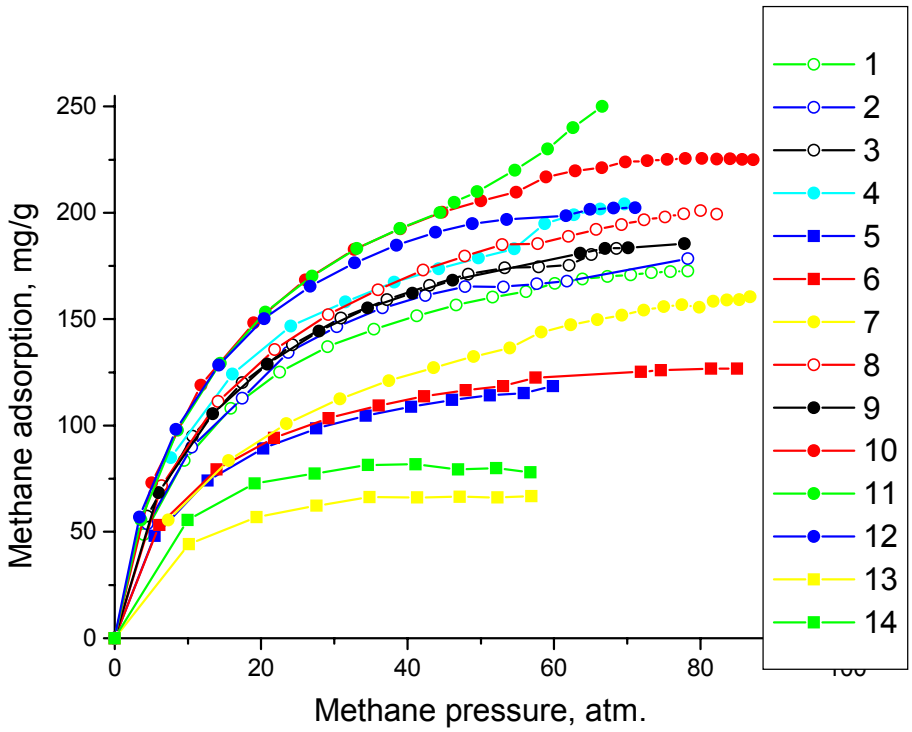

Figure 3. Methane Adsorption Isotherms on Different Nanostructured Carbons (numbers for AMC correspond to the numbers given in Table 2).

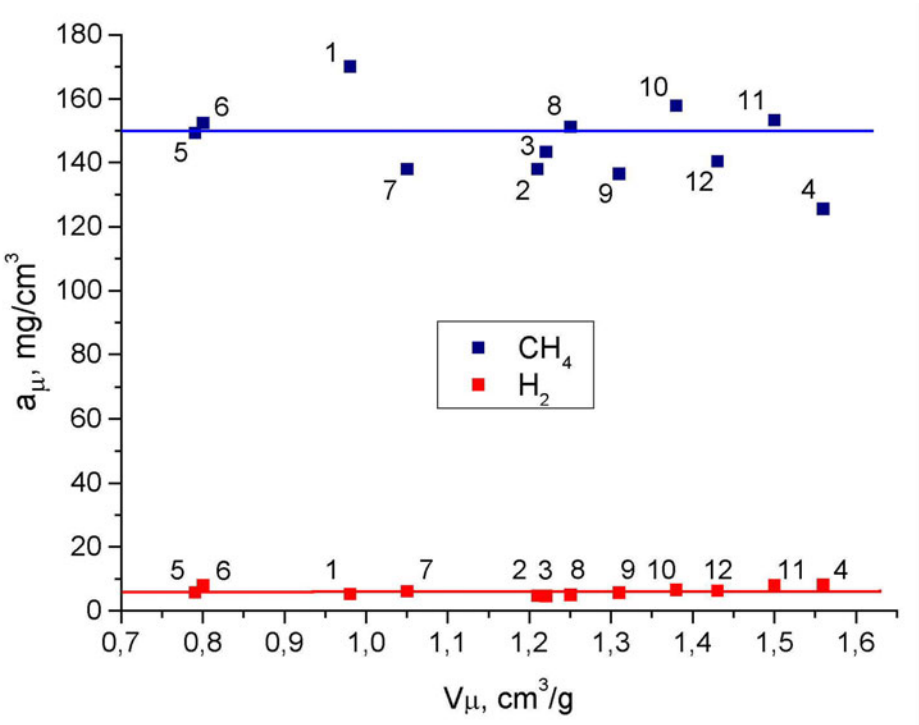

Figure 4. Dependence of Specific Adsorption of H_2 and CH_4 on Micropore Volume (V_μ).

Conclusions

Carbon nanofibers (CNFs) have been prepared by decomposition of methane and ethylene on 3d-metal (Ni,Co,Fe, Cu) and uranium catalysts. The growth rate and properties of CNFs depend on the type of the catalyst, reaction temperature, chemical composition of hydrocarbon etc. New catalysts have been prepared for synthesis of three types of CNFs different by structure: with carbon layers arranged perpendicular to the filament axis (deck of cards morphology), at an angle of 45º to the axis (herringbone morphology) or parallel to the axis, forming multi-wall nanotubes. Amorphous microporous carbons (AMC) are produced from oil coke or other organic initial materials and their textural characteristics are strongly affected by the type of carbon precursor. The largest surface area (ca. 3300 m^2/g) and microporosity (ca. 1.8 cm^3/g) were found for samples produced from oil coke. Capabilities of both CNFs and AMC as prospective accumulators for storage of methane and hydrogen under low pressure have been studied. The capacities of these new carbon materials at 60 atm and ambient temperature with respect to hydrogen and methane storage are correspondingly 12.8 mg/g and 196 mg/g.

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