

XPS and TEM study of new carbon material: N-containing catalytic filamentous carbon

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Abstract

N-containing fibrous carbon material prepared by decomposition of CH_4/H_2 /pyridine mixtures over Ni–Cu catalysts has been studied by X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM). The essential effect of the decomposition temperature (in the range of 820–1020 K) and reaction mixture composition on the nitrogen content, its chemical state and the texture of produced carbon filaments was found. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The modification of porous carbon materials by ligand heteroatoms (N, P, S) is a promising way to the synthesis of both functionally active sorbents and catalyst supports. Among them, bulk-modified carbons are of particular interest, in which heteroatoms are constituents of structure-forming associates of carbon atoms. The only way to build in heteroatoms to the bulk carbon structure is certainly to use some N-, P-, S-containing species during the preparation of carbon materials. However, when produced by pyrolysis of various heteroatoms-containing

compounds, bulk modified carbons have a *microporous* structure that limits their potential application areas, particularly, their use for adsorptive catalytic transformations of bulky substrates. Recently, Nakajima and Koh [1] reported the synthesis of carbon–nitrogen (C_xN , $x = 14\text{--}62$) layered fibrous compounds by chemical vapor deposition of pyridine and acetonitrile at 1070–1270 K over Ni and Co catalysts. Even earlier, the profound advances have been achieved in the Boriskov Institute of Catalysis in the catalytic preparation and characterization of carbon filaments (abbreviated CFC for “catalytic filamentous carbon”) [2–6].

On the basis of these results, we developed a quite easy method to produce a new *mesoporous* (5–20 nm) carbon material, bulk modified by nitrogen atoms. This material, called N-CFC (N-containing CFC), was prepared by

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decomposition of gaseous “hydrocarbon/H₂/N-containing species” mixtures over Ni and Ni–Cu catalysts at 820–1020 K [7]. This paper presents the results of X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) study of N-CFC formed using methane as hydrocarbon and pyridine (C₅H₅N, Py) as N-containing compound over Ni–Cu catalysts, with the other conditions having been varied.

2. Experimental

N-CFC samples were synthesized as follows. 0.05–0.1 g catalyst containing (% by weight): Ni 65–76, Cu 4–5, Al₂O₃ — the rest, was placed in a vertical-shaken quartz reactor. Procedure of the catalyst preparation has been described in Ref. [8]. Gaseous CH₄/H₂/Py mixture of composition (mol%): CH₄ 0–90, H₂ 0–90, Py 10 was allowed to flow over catalyst at 820–1020 K. During the reaction, grown fibers stayed in the reacting zone. After cooling the reactor by argon, the granules of carbon material were taken out.

XPS study was carried out with “VG ESCALAB HP” electron spectrometer pre-calibrated against Au4f_{7/2} and Cu2p_{3/2} photoelectron lines. C1s, O1s, N1s spectra were recorded using MgK_α excitation with 20 eV pass energy. The sample granules were pressed to double-side adhesive tape fixed on the standard P8 holder. To correct the measured values of binding energy (BE) for the charging effect, all spectra were calibrated to adjust BE(C1s) to 284.4 eV [9].

3. Results and discussion

The analysis of survey XPS spectra shows the surface of all samples to contain mainly C, N, O and Ni atoms. The presence of oxygen is

most likely explained by its adsorption during the sample transfer to the spectrometer, since its concentration does not correlate with either Ni or N content. Moreover, Ni2p spectra do not reveal the satellite peak peculiar to Ni²⁺. The precise spectra showed that C1s peak has distinct shake-up satellite meaning that N-CFC consists of graphitic carbon (see Fig. 1A). Note that the width of C1s peak varies slightly indicating the surface of sample 3 (H₂/Py mixture) is more uniform as compared with sample 1 (CH₄/Py mixture). The main peculiarity found was the complex shape of the N1s region (see Fig. 1B). Apparently, there are at least two different states of nitrogen at the surface of N-CFC. The one with lower BE (~398.6 eV) could be interpreted as N in pyridine-type structures (N_{py}) [1]. The BE value of another N state (~400.8 eV) is close to that for NH_x moieties in organic species (N_{am}) [1,10]. The higher the decomposition temperature, the higher is N content in N-CFC formed (see Table 1). The most probable reason is that temperature elevation leads to faster pyridine dehydrooligomerization and consecutive catalytic decomposition of oligomers, thus minimizing pyridine losses due to washing out by gas-carrier. The presence of hydrogen in the reaction mixture decreases ni-

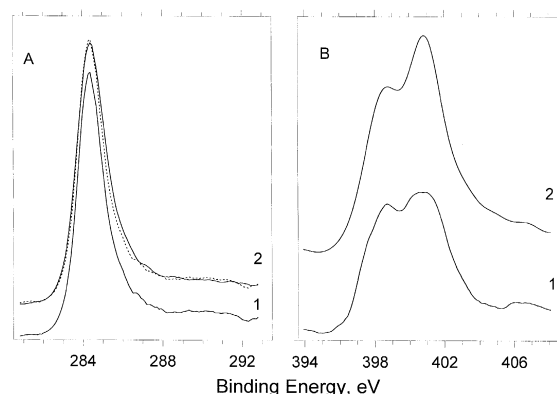


Fig. 1. C1s (A) and N1s (B) spectra of sample 3 (curves 1) and sample 1 (curves 2). The dashed line in section A corresponding to sample 3 demonstrates the slight difference in the peak width.

Table 1

The characteristics of N-CFC samples obtained by CH₄/H₂/Py mixture decomposition on Ni–Cu catalysts
Py concentration is 10 ± 2 mol%.

Sample	Reaction mixture	Run temperature (K)	S _{BET} (m ² g ⁻¹)	Average pore diameter (nm)	Yield (g/g Ni)	Ni content ^a (mass%)	O content ^a (mass%)	N content ^a (mass%)	N _{py} /N _{am} ratio	N content ^b (mass%)	N1s binding energy (eV)
1	CH ₄ /Py	1020	70	18	17	1.03	3.9	6.2	0.79	5.2	398.6 400.8
2	CH ₄ /H ₂ /Py	1020	110	15	62	0.43	4.0	4.3	0.82	4.8	398.6 400.8
3	H ₂ /Py	1020	110	10	49	0.41	3.1	3.1	0.96	3.0	398.4 400.9
4	CH ₄ /H ₂ /Py	920	120	6	50	2.72	4.4	3.1	1.13	3.3	398.6 400.9
5	CH ₄ /Py	820	150	17	9	3.01	4.6	2.9	1.70	3.2	398.7 400.7
6	CH ₄ /H ₂ /Py	820	215	6	24	0.36	4.7	1.8	1.27	2.7	398.6 400.9
7	H ₂ /Py	820	190	7	30	1.06	3.2	1.0	1.13	1.4	398.4 400.7

^aEstimated from XPS data.

^bElemental analysis data.

trogen concentration. We have found pyridine hydrodenitriification (involving the molecule cracking and NH₃ evolution) to run more effec-

tively in these conditions. Indeed, N_{py}/N_{am} ratio drops with temperature elevation (i.e. fastening the rate of hydrodenitriification).

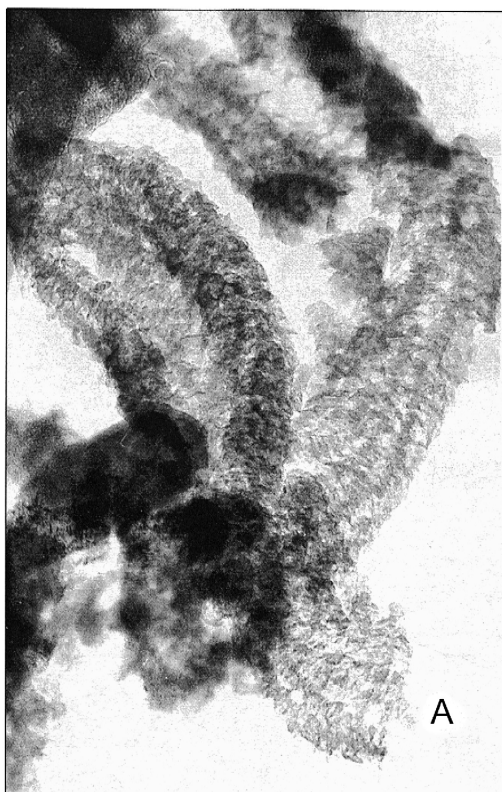


Fig. 2. TEM micrographs of N-CFC samples 3 (A) and 1 (B). Magnification 200,000. The differences in morphology of filaments are clearly seen.

TEM examination found N-CFC granules to consist of chaotically interlaced filaments of a few types. In agreement with XPS data, the sample prepared using H₂/Py mixture looks like a rather uniform material consisting of porous 100–150 nm thick filaments (see Fig. 2A). These filaments have rather peculiar structure looking like “fleecy” ones with periodically loosen (up to 1–2 nm) or omitted graphene layers. In the presence of methane, another filament type is observed as well (see Fig. 2B) that is similar to those described for the usual CFC [3]. Thus, the latter type of filament probably resulted from methane only.

4. Conclusions

Therefore, the variation of the hydrogen/methane ratio affects strictly the structure of N-CFC. Both content and the chemical states of nitrogen depend on the temperature as well as on the composition of the reaction mixture. Thus, we can conclude that the varying of the temperature and reaction mixture is a very powerful tool to control the texture, the functional and adsorption properties of N-modified carbon fibers.

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