



Synthesis, structure and adsorption properties of nonstoichiometric carbon nitride in comparison with nitrogen-containing carbons



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ABSTRACT

The samples of nonstoichiometric carbon nitride characterized by spatial ordering, large pore volume (up to 0.8 cm³/g) and specific surface area (up to 585 m²/g) were obtained via matrix carbonization of ethylenediamine in the presence of carbon tetrachloride in mesoporous molecular sieves KIT-6 and MCF as exotemplates. In contrast to nitrogen-containing carbons (obtained by modification of carbon samples with nitrogen in the result of compatible thermal treatment of the initial porous carbon with melamine) nonstoichiometric carbon nitride contains much more nitrogen (up to 13.7 wt.% (C/N = 6), compared with preceding 0.6 wt.%) and increased the quantity of basic nitrogen-containing groups (in particular, amino groups)—up to 0.68 mmol/g (vs. 0.46 mmol/g). The increase of adsorption capacity towards hydrogen and carbon dioxide: adsorption potential, differential heat of CO₂ adsorption, specific adsorption on the pore surface—from 5.4 to 7.3 μmol H₂/m² and from 2.2 to 5.4 μmol CO₂/m² for carbon and synthesized samples of nonstoichiometric carbon nitride, respectively, due to the incorporation of nitrogen atoms into the carbon framework was noticed.

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Introduction

Materials based on carbon nitride attracted close attention of scientists due to their unique properties—such as high strength, low friction coefficient, chemical inertness, stable autoelectronic emission, transparency in a wide range of optical frequencies and high water resistance. Because of their properties such materials are promising for technological and biological applications, such as biocompatible coatings for medical implants, electrodes in power sources, protective coatings against corrosion, sensors for determination of moisture and composition of gas mixtures [1–6].

Substitution of carbon atoms with nitrogen in the graphite structure preserving its regularity can occur in several ways, leading to existence of a family of related in structure compounds of carbon nitride with different stoichiometry such as C₃N₄, C₃N₂, C₃N, C₅N, C₁₀N₃ etc. [7]. Accordingly various strategies were proposed for obtaining such nitrogen-rich carbon materials [8].

Preferably synthesis of carbon nitrides foresees pyrolysis of nitrogen-containing organic precursors at which condensation of C–N bonds occurs. Under their heating a series of intermediate products is formed consistently including melamine with cyclic structure of the molecule, which can also be used as an initial material in the synthesis. Melamine during heating turns into melem – heptazine cycle with a planar triangular structure which due to free aminogroups polymerizes in melon. The last one forms plane nanolayers which under further heating are transformed in carbon nitride [9,10].

Porosity significantly expands the range of applications of carbon nitride based materials due to a possibility of using them for selective adsorption and gases storage at high pressure, in particular hydrogen, adsorption of biomolecules, and base catalysis [11]. In addition, a significant increase in the specific surface area due to porosity enhances their photocatalytic activity [12–15]. Several new approaches were proposed for synthesis of porous modifications of carbon nitride. Template methods using soft or hard templates are the most important among them. For example, amorphous carbon nitride with an almost stoichiometric composition C₃N₄ and broad reflexes in diffractograms similar in position

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to the graphite reflections was obtained during decomposition of melamine derivative at temperatures of 400–500 °C [16]. The method of obtaining carbon nitride via solvothermal condensation of melamine with cyanuric chloride, which can be used for large-scale production was also described [17]. This work was restored by the authors [18] who synthesized carbon nitride by condensation of cyanuric chloride with calcium cyanamide and established temperature limits (500–600 °C) for the formation of the ordered product with the composition close to stoichiometric. The authors [19] used 2-amino-4,6-dichlorotriazine as the precursor and obtained at high temperature and pressure graphite-like carbon nitride with high degree of crystallinity as a product. Crystalline carbon nitride was also obtained via solvothermal synthesis from cyanuric chloride and sodium amide in benzene under heating above 200 °C for 8–12 h [20].

Carbon nitride in particular nonstoichiometric one (with a lower nitrogen content than in C_3N_4) attracts attention as base catalyst in a number of acid–base processes (Knoevenagel condensation, transesterification of ethylene carbonate and ethyl acetoacetate to dimethyl carbonate, Friedel–Crafts acylation, oxidation of cyclic olefins to epoxides, dehydrogenation) [1,21–25]. Nonstoichiometric carbon nitride due to a large concentration of basic nitrogen-containing groups and developed porosity is also a promising carbon dioxide adsorbent [8,26], component of the enzyme-based biosensors [27], sensor for acidic/basic molecules [28].

Nonstoichiometric porous carbon nitride causes therefore a large interest in particular for base catalysis and adsorption of carbon dioxide due to the presence of basic groups. Comparison of such materials with nitrogen-containing carbon nanostructures obtained as a result of porous carbons modifications in the process of their heat treatment with nitrogen-containing compounds can be also interesting.

The aim of this paper is to determine the conditions of nonstoichiometric porous carbon nitride synthesis via matrix carbonization of ethylenediamine in the presence of carbon tetrachloride as well as clarification of the features of its structure, composition and sorption properties towards hydrogen and carbon dioxide, in comparison with nitrogen-containing carbons.

In the current work a comparison is provided for the composition and sorption properties of different N-doped carbons prepared using various initial organic precursors thus resulting in carbons with different nitrogen content. According to our knowledge such comparative studies are absent in the literature.

Experimental

Preparation

Carbon nitride samples with different porous structure were obtained via matrix synthesis using silica mesoporous molecular sieves (MMS) such as KIT-6 and MCF as exotemplates [8]. For this purpose a weighted amount of the initial KIT-6 0.5 g (MCF weight was 0.3 g) was added to a mixture of 2 ml of ethylenediamine and 1.5 ml of carbon tetrachloride and heated to 90 °C for 6 h under reflux. The resulting dark brown mass was dried at 60 °C for 12 h and mixed with a mixture of 2 ml of ethylenediamine and 1.5 ml of carbon tetrachloride. The mixture was re-heated to 90 °C for 6 h under reflux and dried. The obtained light brown powder was heated in an inert atmosphere to 600 °C with a rate 3 °C/min and kept at this temperature for 5 h. Silica matrix was removed by treatment in HF solution (HF:H₂O = 1:3), the obtained products were washed with distilled water and ethanol several times, then dried at 100 °C. Carbon nitride samples obtained in MMS KIT-6 were marked as CN–KIT-6, samples obtained in MMS MCF were marked as CN–MCF.

A carbon replica of the matrix KIT-6 (CMK-8) was prepared via carbonization of sucrose according to the method [29].

For synthesis of mesoporous N-containing carbon in the KIT-6 matrix (N–CMK-8) carbon–silica composites prepared via matrix carbonization of sucrose in silica MMS KIT-6 were used. Functionalization of these composites with nitrogen was done in accordance with [30] using melamine.

Characterization

The phase composition of the samples was analyzed using X-ray diffractometer Bruker D8 Advance with monochromated $CuK\alpha$ -radiation.

Scanning electron images (SEM) were recorded using the MIRA3 TESCAN microscope at an accelerating voltage of 5–20 kV.

IR-specters were recorded using Perkin Elmer Spectrum One spectrometer in 400–4000 cm^{-1} frequency range. Samples were pelleted by pressing 2 mg of highly dispersed powder with 30 mg of KBr.

A Perkin-Elmer PHI 5400 spectrometer with a Mg $K\alpha$ X-ray source operated at 14 kV and 200 W was used in the XPS-analysis of the samples. The pass energy of the analyzer was 17.9 eV and the energy step 0.025 eV.

Peak fitting was performed with the program XPS Peak 4.1. The background was corrected with the Shirley function. The sensitivity factors used in the quantitative analysis for C 1s, N 1s, and O 1s were 0.296, 0.477 and 0.711, respectively.

Elemental composition of the obtained materials was determined using CHN-analyzer Carlo Erba 1106. The analysis method is based on the complete and instantaneous oxidation of the sample by “flash combustion” on the catalyst in an oxygen atmosphere. The resulting combustion gases passed through a reduction furnace, swept on the chromatographic column and thereafter detected by the thermal conductivity detector.

Adsorption isotherms of nitrogen and hydrogen with a purity of 99.999% were measured by a volumetric method at 77 K up to ambient pressure (up to 1 atm) on Sorptomatic 1990. Micropore size was calculated by Horvath–Kavazoe equation [31]. For micro-mesoporous materials (S-like isotherms) adsorption parameters were determined by a comparative *t*-plot method [32] using standard isotherms for non-porous compounds (micropore and mesopore volume V_{micro} , V_{meso} , mesopore surface area S_{meso}). External surface area S_{ext} was calculated according to [33]. The total specific surface area S_{BET} was estimated by the BET equation [32]. Mesopore size was determined by the BJH method [34]. For isotherms in which ad(de)sorption hysteresis ends at relative pressure 0.45–0.50 and corresponds to the ultimate strength of the liquid meniscus to break, the mesopore size distribution was determined from the adsorption branches of isotherms. Additionally, the initial adsorption potential $|\Delta\mu_0|$ was determined. It was calculated by the method of excess surface work for determination of the specific surface area [35]. The CO₂-adsorption isotherms were measured using a Sorptomatic 1990 at 253 and 273 K.

Boehm titration. Samples of obtained N-containing carbons with the mass of about 0.05 g were placed in 20 ml of 0.05 N hydrochloric acid solution. To establish equilibrium, suspensions were stirred for 24 h at room temperature. After this, 5 ml of each filtrate was pipetted and the excess of acid was titrated with NaOH. Concentration of basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon sample (namely, total concentration of basic sites was obtained). Total concentration of basic sites was calculated for 1 g of N-containing carbon and expressed in mmol/g.

Thermogravimetric studies were performed using serial derivatograph Q-1000 in the range of the temperatures from ambient (20 °C) to 1000 °C. The heating rate of the sample and the standard

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