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Influence of the nitrogen-doped carbon nanofibers on the catalytic properties of supported metal and oxide nanoparticles

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ABSTRACT

Catalysts containing platinum (1 and 10 wt.%) or cobalt oxide (10, 50 and 90 wt.%) and nitrogen doped carbon nanofibers (N-CNFs) were synthesized. X-ray photoelectron spectroscopy, CO chemisorption and temperature-programmed reduction methods were used to reveal that pyridine-like nitrogen of N-CNFs is involved in the anchoring of metal or oxide particles on the carbon surface and determines their size, electronic state and redox ability, thus changing the catalytic performance of the catalysts in the oxidation of carbon monoxide. Various models of particle stabilization on the surface of N-CNFs were proposed: (1) stabilization of nanoparticles with the retention of their metallic state by the pyridine-like site; (2) stabilization of electron deficient nanoparticles by a pair of pyridine-like nitrogen sites and (3) stabilization of electron deficient nanoparticles by the pyridine-like site near the carbon vacancy.

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1. Introduction

There is a constant interest in the study of nitrogen-doped carbon nanomaterials (N-CNMs) for the application as catalysts or catalyst supports [1–8]. It is assumed that change of the catalytic properties of the nanoparticles supported on N-CNMs is caused by: (1) decreasing the particle size due to increasing the energy of its binding to carbon; (2) changing the electronic state of the particles due to their interaction with nitrogen sites of N-CNMs; (3) accelerating electron transfer in the system, and (4) forming new adsorption sites on the carbon surface. Indeed, the authors of [5,9–12] observed that a decrease in the size of metal particles supported on N-CNMs affected their catalytic behavior in different reactions. According to the literature, electronic density of the particles supported on N-CNMs can increase or decrease. For example, in [13], the contribution of metallic state of ruthenium supported on the nitrogen-doped carbon nanofibers (N-CNFs) increased due to the interaction with pyridine-like sites of N-CNFs. On the other hand, in some works it was proved that the electron deficient Pt^{δ+}, Pd^{δ+} and Ru^{δ+} nanoparticles are formed via

their interaction with pyridine-like sites of structurally different N-CNMs [14–18]. DFT calculations made it possible to propose the models of such sites represented by a pair of pyridinic nitrogen atoms at the edge of graphene sheets [16,17] or by a single pyridine-like site [18]. In [19], stabilization of Pd^{δ+} particles on the surface of nitrogen-doped carbon nanotubes (N-CNTs) was attributed to the interaction of palladium particles with pyrrolic nitrogen sites. The role of pyrrolic nitrogen in changing the properties of Co/SiO₂-N-C in the Fischer-Tropsch reaction was investigated by the authors of [20] who concluded that pyrrolic nitrogen atoms can act as a nonmetallic and electrical promoter for the catalyst. Changes of the carbon surface properties due to the presence of nitrogen sites, which facilitate the adsorption of reactants, enhance the activity of supported metal catalysts, for example, in the liquid-phase aerobic oxidation of hydrocarbons and alcohols [21] or hydrogenation of nitrobenzene [22].

Carbon nanofibers doped with nitrogen and having the coaxial-conical or stacked packing of graphite layers are interesting representatives of a broad spectrum of different N-CNMs (N-CNTs, N-CNFs, N-graphene, N-mesoporous carbon, N-microporous carbon, etc.). In N-CNFs, multiple edges of graphite sheets come to the external surface of the fiber, thus increasing the degree of interaction between the surface and supported components and making N-CNFs attractive for use as catalyst supports [3,23].

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Methods and approaches based on the direct formation of material from a nitrogen-containing carbon precursor or on the thermal treatment of undoped CNMs in a nitrogen-containing atmosphere are being developed now for the synthesis of N-CNMs. Among them are low-temperature (catalytic) and high-temperature (physical) methods of synthesis [1]. The catalytic synthesis of N-CNMs on iron subgroup metals (Fe, Co, Ni) is a direct method. It is performed at moderate temperatures and results in the selective formation of the target product; so, this method is most attractive in comparison with physical methods such as laser ablation, electric arc synthesis or magnetron sputtering. For example, when N-CNFs are synthesized by decomposition of simple compounds like ethylene and ammonia, structurally uniform N-CNFs are formed on the Ni-Cu catalyst, and the yield of material can reach 70 g C/g catalyst depending on the nitrogen content [24].

In this work, the effect of N-CNFs on physicochemical and catalytic properties of the supported Pt and Co_3O_4 nanoparticles was investigated. The oxidation of CO was chosen as the test reaction. This reaction has been studied for several decades owing to its practical importance related to air purification in enclosed spaces or determination of CO level by gas sensors. On the other hand, low-temperature oxidation of CO is used as a model reaction to estimate the low-temperature activity of advanced catalysts and describe the mechanisms of catalytic reactions [25]. Studies of N-CNMs as supports for CO oxidation catalysts are quite scarce [12,18,26], although some theoretical works predict high catalytic activity of the platinum nanoparticles supported on N-doped graphene [27,28]. In this connection, it is of theoretical and practical interest to investigate in CO oxidation the catalytic properties of metal and oxide nanoparticles supported on N-CNFs with different total nitrogen content and content of nitrogen in different electronic states.

2. Experimental

2.1. Synthesis of the catalysts

N-CNFs (0, 1, 3 and 7.5 wt.% N) were synthesized by decomposition of a $\text{C}_2\text{H}_4/\text{NH}_3$ mixture ($\text{C}_{\text{NH}_3} = 0, 25, 50$ and 75 wt.%) over the 65%Ni-25%Cu-10% Al_2O_3 (wt.%) catalyst at 550 °C [24]. To remove the catalyst from the N-CNFs, they were treated with concentrated HCl several times for several weeks at room temperature and then boiled in 2 M HCl for 12 h. After this, the materials were washed with distilled water until no chloride ions were detected in the rinsing liquid. This severe treatment reduced the content of initial catalyst to 2–3 wt.%, while the remaining catalyst particles were encapsulated in the carbon framework.

Platinum (1 or 10 wt.%) was supported on N-CNFs via homogeneous precipitation from a H_2PtCl_6 solution by NaOH at 70 °C. The alkali was taken in a stoichiometric ratio to the metal precursor ($\text{NaOH}/\text{H}_2\text{PtCl}_6 = 6 \text{ mol/mol}$; final pH ~ 7), which assures complete deposition of Pt and maximum dispersion of supported particles [29]. After platinum deposition, the samples were filtered, carefully washed with distilled water to remove Cl^- anions, dried in air at room temperature, and reduced in a flow of 70%Ar/30% H_2 at 250 °C for 1 h.

Co_3O_4 -N-CNFs catalysts were synthesized at room temperature by homogeneous precipitation from the $\text{Co}(\text{NO}_3)_2$ solution containing dispersed N-CNFs using NH_4OH . The precipitate was filtered, carefully washed with distilled water, dried in air at room temperature, and calcined in air at 250 °C for 6 h. The content of cobalt oxide in the resulting catalysts varied from 10 to 90 wt.%. For comparison purposes, bulk cobalt oxide was synthesized by a similar method.

2.2. Physicochemical methods

2.2.1. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded on a ES-300 photoelectron spectrometer (KRATOS Analytical) with a AlK_α (1486.6 eV) X-ray source. The spectrometer was calibrated by setting the binding energies of the $\text{Au}4f_{7/2}$ and $\text{Cu}2p_{3/2}$ core-level values to 84.0 eV and 932.7 eV, respectively. Spectra processing was performed after Shirley background subtraction using an original XPS-Calc program tested on various catalytic systems in our recent studies [12,14,15,30]. The Doniach–Sunjic type line was used to describe the Pt4f spectra [31]. For N1s and Co2p spectra, curve fitting was carried out with a combination of Gaussian and Lorentzian functions. To shed light on a localization of nitrogen species within N-CNF materials, a depth analysis with a variation of the incident photon energy ($h\nu$) was applied. The experiments were performed at the BESSY II RGL station at Helmholtz-Zentrum (Berlin). The N1s spectra were collected with $h\nu = 500$ eV and $h\nu = 850$ eV that corresponded to the kinetic energy (KE) of photoelectrons ~ 100 eV and 450 eV, respectively. Such a change of the KE should result in ca. two-fold increase in the analysis depth [32].

2.2.2. Transmission electron microscopy

The electron microscopy images were obtained using a JEM-2010 (JEOL Ltd.) microscope with accelerating voltage 200 kV and resolution 1.4 Å. For TEM studies, the samples were supported on a holey carbon film mounted on a copper grid.

2.2.3. Chemisorption of CO

Chemisorption measurements were performed on an AutoChem II 2920 (Micromeritics) in pulse mode [29] using CO as the adsorbing gas and He as the carrier gas. The catalyst samples were reduced during the preparation and re-reduced before CO chemisorptions under mild conditions. About 100 mg of sample were loaded into the quartz tube for the measurements, the tube was purged with He, and the sample was then heated in flowing H_2 to 100 °C and kept under H_2 for 10 min. After cooling, purging of the sample tube with He, and stabilizing the temperature at $20^\circ\text{C} \pm 1^\circ\text{C}$, the sample was dosed with CO by 70 μL STP pulses, in 2-min intervals, until apparent saturation (constancy in the peak area) occurred.

2.2.4. Temperature-programmed reduction (TPR)

The H_2 -TPR experiments were carried out using the gas mixture containing 10% H_2 in Ar with the flow rate of 30 mL/min in a laboratory instrument equipped with a thermal conductivity detector. The temperature was raised from 25 to 800 °C at a 10 °C/min rate. The H_2 -TPR curves were recorded after pretreatment of the samples in 1:4 mixture of oxygen and argon at 200 °C for 1 h. After pretreatment, the samples were cooled to room temperature and flushed with an Ar flow. The weight of the samples was 20 mg and the particle size was 250–500 μm . Water produced during the TPR experiment was removed using a cold trap.

2.3. Catalytic activity measurements

The catalytic activity toward carbon monoxide oxidation was measured using the temperature-programmed reaction in an automated unit with flow reactor and mass-spectrometric analysis of a gas mixture. The original powder-like samples were tableted to the pellets of 0.25–0.5 mm in size and 0.25 cm^3 of the sample was loaded into a stainless steel reactor. A mixture containing 0.2 vol.% CO, 1.0 vol.% O_2 and 0.5 vol.% Ne (helium the balance) was fed to the initial catalyst cooled to -10°C ; the feed flow rate was 1000 cm^3/min . Space velocity was equal to 240,000 h^{-1} . In the reaction mixture, the catalyst was heated from -10 to 250 °C at a ramp rate 10 °C/min with subsequent cooling in the reaction mixture.

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