Physico-chemical properties and catalytic activity of the Ni-Co-CB material

O Andrienko1,2, N Kobotaeva1,3, T Skorokhodova1,3, E Marakina1 and V Sachkov1

1Laboratory of chemical technologies, National Research Tomsk State University, 36 Lenina Avenue, 634050 Tomsk Russian Federation
2Quantum Electronics Laboratory, Zuev Institute of Atmospheric Optics of the Siberian Branch of the RAS, 1 Zuev Square, 634021 Tomsk Russian Federation
3Laboratory of catalytic processing of light hydrocarbons, Institute of Petroleum Chemistry of the Siberian Branch of the RAS, 4 Akademichesky Avenue, 634055 Tomsk Russian Federation

1E-mail: vioes@mail.ru

Abstract. Carbon materials are widely used in catalysis as a support for active catalyst components due to their chemical inertness and developed surface. The most common carbon carriers are represented by activated carbons, carbon black and various carbon-carbon composites. In petrochemistry, carbon materials are also employed as catalysts to oxidize sulfur compounds contained in heavy fractions of oil being refined. In this regard, the present paper discusses the issues of metal-carbon composite material manufacturing. Technical carbon, or carbon black (CB), was used as a carbon support, the surface of which was modified with nickel and cobalt. The resulting composite material, Ni-Co-CB, has a high specific surface area comparable to that of the pristine carbon material, thereby favoring its catalytic activity. The high catalytic activity of the composite material developed was observed during oxidative desulfurization of heavy oil feedstock. Hence, the degree of sulfur removal for fuel oil was found to be 82.7 %, whereas for oil it reached 70.7 %.

1. Introduction

Currently, carbon materials (activated carbon, carbon black, graphite, carbon nanotubes, fullerenes, etc.) and their products are increasingly used in catalytic, adsorption, electrochemical processes, medicine, hydrometallurgy, etc. The advantages of carbon materials are their resistance and stability in aggressive environments at elevated temperatures, large specific surface area, the ability to adjust the parameters of the porous structure and physical and mechanical properties in a wide range [1].

In the works [2-3] it was found that the structural characteristics of carbon materials (specific surface area, pore size, porosity) affect the catalytic activity of carbon catalysts. In the study of the catalytic wet air oxidation of acetic acid, the graphite-supported Ru catalyst showed much more activity than those based on activated carbon [2].

Catalytic properties of catalysts on carbon carriers are often superior to those on oxide carriers. Thus, in the catalytic wet air oxidation of phenol, Ru and Pt catalysts deposited on the carbon black are more selective than catalysts based on the Si-Ti ones in this process [4].
In addition, carbon materials are used as catalysts in the absence of any metals. Carbon materials have shown good catalytic properties in the processes of methane decomposition, p-toluidine oxidation, aniline conversion, and catalytic ozonation of organic compounds [5-6].

The production of catalysts is of great importance for the development of the oil refining, petrochemical and chemical industries. In petrochemistry, catalysts based on rare and noble metals (platinum, palladium, rhodium, rhenium, etc.) and metal compounds (cobalt, nickel, molybdenum, etc.) are used. At the same time, for more efficient use of the active component (metal, metal compound), it is applied to carriers – materials with high specific surface area and mechanical strength. The most widespread are oxide (aluminum oxide, silicon oxide and zeolites, etc.) and carbon carriers.

In particular, carbon materials and their composites are used as catalysts for oxidation of sulfur compounds contained in various oil fractions [7-8].

Considering the aforementioned, the aim of the present research was to study the physical-chemical properties and catalytic activity of a material composed of carbon black and metal (Ni, Co) nanoparticles.

2. Experimental part
Carbon black (CB) of grade P 354, obtained at the Institute for Hydrocarbon Processing of the Siberian Branch of the Russian Academy of Sciences (Omsk, Russia) and containing C (96.4 %), O (2.5 %), S (0.5 %), N (0.3 %), and H (0.3 %) [1], was used herein as a carbon support for preparing a composite material.

In this starting material, the functional groups are formed already at the stage of its production, i.e. during thermal oxidative pyrolysis of hydrocarbons followed by oxidation of the mixture using a 20-% hydrogen peroxide solution at 100 °C. Being the CB component, oxygen is found in hydroxyl, carbonyl, ether and carboxyl groups [9]. The size and shape of CB particles were examined on a JEM-2100 transmission electron microscope (JEOL, Tokyo, Japan). The CB units dispersed are represented by globule aggregates, as shown in figure 1. The texture characteristics of the CB are given in table 1.

![Figure 1. An image of CB particles (P354) as globule aggregates obtained using transmission electron microscopy.](image-url)
To prepare a metal-carbon composite material (Ni-Co-CB), transition metal (nickel combined with cobalt) nanoparticles were deposited over the CB surface. For this purpose, the method of chemical reduction of metals from solutions of their salts with sodium hypophosphite was used. This technique is widely employed in electroplating to deposit nickel (chemical nickel plating) on compact items (metals and alloys) [9]. Its advantages include obtaining a dispersion coating and the uniformity of metal deposition on a substrate.

The physical-chemical properties of the composite material and CB were studied through powder X-ray diffraction and infrared spectroscopy. The powder X-ray diffraction was measured using a XRD 7000 diffractometer (Shimadzu, Kyoto, Japan). Diffraction patterns were obtained using CuKα radiation in the Bragg–Brentano configuration with steps of 0.03, exposures of 6 s, and angles in the range of 10-80°. Calculations of the amorphous phase fraction were performed using the standard software supplied with the corresponding instrument. IR-spectra were recorded using a Nicolet 5700 Fourier transform infrared spectrometer (Thermo Scientific, Waltham, MA, USA), in a KBr matrix in the frequency range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. Infrared spectra of attenuated total reflectance (ATR) were registered using the same spectrometer equipped with a Smart Performer ATR device (Thermo Scientific). The spectra were captured on a ZnSe crystal in the range of 4000–650 cm⁻¹ with a resolution of 4 cm⁻¹; 640 scans were collected for each spectrum.

The specific surface area of the CB and the Ni-Co-CB was determined using the method of thermal nitrogen desorption using a Sorbtometer M unit (Katakon, Novosibirsk, Russia), and calculation were performed through the multipoint BET method in an automatic mode in accordance with Russian National Standard (GOST) No. 23401-90. The method allows to estimate the volume of gas (nitrogen) first pre-adsorbed on the surface of the analyzed material at a temperature of liquid nitrogen, and then desorbed from the material at increasing temperature. An isotherm of the adsorption of molecular nitrogen at 77.4 K was obtained using anASAP 2020 surface and porosity analyzer (Micromeritics, Norcross, GA, USA).

The catalytic activity of the Ni-Co-CB composite material was studied in the course of oxidative desulfurization of heavy oil feedstock (heavy oil residue or fuel oil and heavy crude oil). This process included the following stages: oxidation of sulfur-containing compounds of the oil feedstock, and extraction of oxidized sulfur-containing compounds from the oil feedstock. To carry out the oxidation, a 500-mL reaction container equipped with a stirrer and a thermometer was loaded with a portion of the oil stock and heated with stirring to the reaction temperature (50 °C). When the desired temperature was reached, the catalyst was thoroughly admixed, and then a 15-wt.% hydrogen peroxide solution was added. The molar ratio of the sulfur contained in the oil feedstock and the S/H₂O₂ oxidizing agent was equal to 1:4. The reaction time was 90 min. Then, the oxidized sulfur-containing compounds were extracted with a polar solvent and water (content 10 v.%) at 35-40 °C. Dimethylformamide was used as an extractant. The solvent:oil feedstock ratio was 2:1. The reaction mass was kept under a layer of the extractant for 60 min at a given temperature. Finally, the extract-oxidized sulfur-containing compounds and the raffinate-desulfurized oil stock phases were separated.

For the extraction, high-grade dimethylformamide (EKROS-1, Moscow, Russia), manufactured according to Russian National Standard (GOST) No. 20289-74, was used.

The feedstock used represented the residue of West Siberian oil from CJSC ‘Chernigov Refinery’ (Novaya Balakhonka, Kemerovo Region, Russia) at 370-560 °C, with a total sulfur content of 1.04 wt.%, and oil from the Usinsk Deposit of CJSC “Chernigov Refinery”, with a total sulfur content 1.64 wt.%.

| Sample       | Preparation method | Average aggregate size, nm | Aggregate surface zeta potential, mV |
|--------------|--------------------|----------------------------|-------------------------------------|
| CB (P354)    | Furnace            | 154±70                     | -6.37                               |
The sulfur content in the feedstock and desulfurized petroleum stock was determined by burning in a lamp in the presence of oxygen. The principle of the lamp method consists in burning a feedstock sample in a platinum holder (basket) of the cork of a Sheniger flask with an oxygenated absorption solution. Upon burning, the absorption solution was titrated with a barium nitrate solution in the presence of an indicator until a stable color appeared. By analogy, a ‘blank’ experiment was conducted (without a weighed feedstock sample) under the same conditions, and the total sulfur content in the analytical sample of feedstock was calculated.

The feedstock degree of desulfurization (sulfur removal) \( X \) (%) was calculated according to equation (1):

\[
X = \left( \frac{\omega_0 - \omega_k}{\omega_0} \right) \cdot 100\% ,
\]

where \( \omega_0 \) is the initial sulfur content, wt.%; \( \omega_k \) is the sulfur content in the feedstock after the desulfurization (residual content), wt.%

3. Results and discussion

The availability of the Ni and Co nanoparticles in the composite material samples was confirmed by IR-spectroscopy, XRD, and HRTEM. Figure 2 demonstrates the IR spectra of the CB activated by the above mentioned nanoparticles.

Figure 2. IR spectra of the CB activated by the Ni and Co nanoparticles.

The bands attributed to vibrations of the \( \text{–C–C–} \) bonds at a frequency of 1057 cm\(^{-1}\) and the bands at frequencies 563 and 580 cm\(^{-1}\) (vibrations of the \( \text{–M–C} \) bond) were observed.

The Raman spectra of a Ni-CNTs composite material were considered in [10], where it was shown that in addition to the structured carbon bands at frequencies 1595 and 1282 cm\(^{-1}\) (G and C bands, respectively), an additional broad band was observed within the range of 600-500 cm\(^{-1}\). The quantum-
chemical calculation of the NiC₂ model compound using the B3LYP/DGDZVP method yielded Ni-C stretching vibrations in the range of 480–500 cm⁻¹ and bending vibrations at 580 cm⁻¹.

Thus, on the basis of the available IR spectrum (figure 2), as well as the calculated and published data, it can be stated that there is a metal-carbon bond (M-C) in the resulting Ni-Co-CB composite material.

The X-ray pattern of the Ni-Co-CB composite material (figure 3) shows broadened and fuzzy peaks of the Ni (at 2θ = 38.42; 44.555; 58.462; 71.074) and the cobalt (at 2θ = 43.838, 51.731).

![Figure 3. X-ray diffraction patterns of: 1 – the crystalline Ni; and 2 – the Ni-Co-CB composite material.](image)

These obviously broadened peaks suggest the amorphous nature of the coating obtained. Such broadening was observed earlier when Ni and Co were deposited on CNTs via chemical reduction from a solution using sodium hypophosphite [10]. This is due to the fact that when using sodium hypophosphite [11], during reduction, the phosphorus precipitates simultaneously with the nickel according to the following reaction: \(2H_2PO_2 \rightarrow H_2PO_2^- + P + H_2O\). The phosphorus penetrates into the nickel crystal lattice, and a so-called nickel-phosphorus coating (Ni-P), with a phosphorus content of about 7–10 %, is formed.

The resulting composite material possesses a developed surface, the parameters of which are comparable with those of the surface of the pristine carbon material (table 2).  

| Sample    | Specific surface area, m²/g | Pore diameter, nm | Pore volume, cm³/g |
|-----------|------------------------------|-------------------|--------------------|
| CB        | 110.0                        | 1.9               | 0.034              |
| Ni-Co-CB  | 107.4                        | 1.8               | 0.031              |

Table 3 presents the results on the oxidation of the heavy oil residue (fuel oil) and heavy oil using the hydrogen peroxide in the presence of the Ni-Co-CB material as catalyst.
Table 3. Oxidation of the fuel oil using 15-wt.% hydrogen peroxide in the presence of the Ni-Co-CB catalyst.

| Oil feedstock | Ni-Co-CB concentration wt.% | \( V_{H_2O_2} \) cm\(^3\) | Reaction temperature, °C | Reaction time, min | Initial sulfur content in oil feedstock wt.% | Residual content of sulfur in the oil stock, wt.% | Degree of sulfur removal (X), % |
|---------------|----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fuel oil      | 1.0                       | 6               | 35              | 90              | 1.04            | 0.20            | 80.8            |
|               | 1.0                       | 6               | 35              | 120             | 1.04            | 0.22            | 78.8            |
|               | 1.0                       | 6               | 50              | 60              | 1.04            | 0.28            | 73.1            |
|               | 1.0                       | 6               | 50              | 90              | 1.04            | 0.18            | 82.7            |
|               | 1.0                       | 6               | 50              | 120             | 1.04            | 0.20            | 80.8            |
|               | 1.0                       | 6               | 95              | 90              | 1.04            | 0.30            | 71.7            |
|               | 1.0                       | 6               | 95              | 120             | 1.04            | 0.32            | 69.2            |
|               | 1.3                       | 6               | 35              | 90              | 1.64            | 0.52            | 68.2            |
|               | 1.3                       | 6               | 35              | 120             | 1.64            | 0.5             | 69.5            |
|               | 1.3                       | 6               | 50              | 60              | 1.64            | 0.6             | 63.4            |
|               | 1.3                       | 6               | 50              | 90              | 1.64            | 0.48            | 70.7            |
|               | 1.3                       | 6               | 50              | 120             | 1.64            | 0.55            | 66.5            |
|               | 1.3                       | 6               | 95              | 90              | 1.64            | 0.72            | 56.1            |
|               | 1.3                       | 6               | 95              | 120             | 1.64            | 0.7             | 57.3            |

As can be seen from this table, under the conditions considered, the high degree of sulfur removal was achieved for the fuel oil and oil – 82.7 and 70.7 % – when using the Ni-Co-CB catalyst at 1.0 and 1.3 wt.%, respectively. This is probably due to the fact that this metal-modified material has a developed surface, as mentioned above.

4. Conclusion

In the present work, a metal-carbon composite material was developed by depositing metal nanoparticles (Ni and Co) over the CB surface via chemical reduction of metals from solutions of their salts.

In the IR spectra of the metal-CB composite material, not only bands related to vibrations of the \(-C-C-\) bonds at the frequency of 1057 cm\(^{-1}\) but also bands at the frequencies of 563 and 580 cm\(^{-1}\) (vibrations of the \(-M-C\) bond) were observed. This can be adequately explained by intermolecular interactions in the system of conjugated graphene bonds.

The XRD method revealed that the nickel-phosphorus coating formed on the CB surface has an amorphous character, thereby suggesting that the particles deposited on the CB surface are nanosized.

The resulting composite material has a high specific surface area comparable to that of the pristine CB, which favors its catalytic activity.

The Ni-Co-CB composite material exhibited a high catalytic activity in the course of oxidative desulfurization. The degree of sulfur removal was found to be 82.7 and 70.7 % for the fuel oil and oil, respectively.

5. Acknowledgments

The work was performed under the financial support of the Ministry of Science and Higher Education (formerly, the Ministry of Education and Science) of the Russian Federation in the framework of Grant Agreement No. RFMEFI57817X0225.
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