The optimization of preparation mode of metal-carbon catalysts for oxidative desulfurization of diesel fractions

E V Matus, O S Efimova, A N Popova, A P Nikitin, S A Sozinov and Z R Ismagilov
Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Science, 18 Sovetskiy Ave., 650000, Kemerovo, Russia
E-mail: matus@catalysis.ru

Abstract. To create new nanosized catalysts for oxidative transformations of sulfur compounds of thiophene series, monometallic catalysts based on carbon nanotubes M/CNTs (M = Ce, Cu, Mo) were prepared with a variation of the synthesis method. The incipient wetness impregnation method, adsorption, and precipitation methods were applied for active component introduction onto CNTs. The effect of preparation mode on textural and structural characteristics of M/CNTs was investigated using a set of physicochemical methods (optical emission spectrometry with inductively coupled plasma, low-temperature nitrogen adsorption, X-ray phase analysis, Raman spectroscopy, and scanning electron microscopy). It was shown that precipitation and impregnation methods provide appropriate metal content in catalyst composition while adsorption is suitable for synthesizing samples with a low active component concentration. The kinds of active component species are similar (CeO₂, Cu₂O/Cu or MoO₃/MoO₂) but their distribution behavior and dispersion are controlled by the preparation mode. The using precipitation method for M/CNTs synthesis provides uniform distribution of the nanosized metal-containing particles on the carbon matrix surface.

1. Introduction
Oxidative desulfurization (ODS) is considered as a promising method for the non-hydrogen deep purification of diesel fuel oil from sulfur compounds [1–7]. ODS takes place under mild conditions in the presence of a suitable oxidizing agent with/without a catalyst. In this method, sulfur compounds are oxidized to sulfoxides and sulfones, which are then separated from the hydrocarbon component of the fuel by adsorption or extraction. Cheap reagents (air oxygen, hydrogen peroxide, or organic peroxides) serve as an oxidizing agent, of which H₂O₂ is the most frequently used. It was found [5] that the activity of metals supported on aluminum oxide in the oxidation reaction of thiophene (200 ppmw), dibenzothiophene (200 ppmw), and 4,6-dimethyl dibenzothiophene (200 ppmw) by tert-butyl hydroperoxide increases in the following order: Zn < Co ~ Fe < Sn < Mn < Mo, which is associated with low oxidation potentials and high Lewis acidity of Mo in the highest oxidation state. Among the systems studied (Co-Mo/Al₂O₃ < manganese oxides < Cr₂O₃ < Pd), a high activity of the Pd catalyst in the oxidation of organosulfur compounds with hydrogen peroxide was noted [6]. It was shown [7] that carbon materials can act as promising supports for the ODS catalyst. However, today carbon-containing materials (activated carbon Filtrasorb 400 [8], coconut shell-based Nantong [9]) have found application mainly in the method of adsorption desulfurization. It has been shown that their modification with transition metal oxides (Fe [8], ZrO₂ [9], Ce-Fe [10], Co [11]) makes it possible to increase the sorption capacity of the samples by increasing the concentration of Lewis acid sites and,
accordingly, to improve the process parameters. Fragmentary information is available on testing carbon [12–14] and metal-carbon [7, 15] materials in the process of oxidative desulfurization.

The aim of this work was to optimize the procedure for the synthesis of metal-carbon catalysts for oxidative desulfurization of diesel fractions. The introduction of an active component onto the support matrix was carried out by precipitation (p), incipient wetness impregnation (i), or adsorption (a). This can provide different strength of the metal-support interaction, which will affect the forms of stabilization of M and, therefore, the functional properties of M/support in the ODS.

2. Experimental

2.1. Catalyst preparation

The carbon nanotubes (CNTs) «Taunit» (NanoTech-Center Ltd., Tambov, Russia) were used in this work as supports. Their physicochemical properties were given and discussed in [16, 17].

The M/CNTs (M = Ce, Cu, Mo) were prepared by precipitation, incipient wetness impregnation, or adsorption methods. Metal nitrates Ce(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O and ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O were used as metal precursors. The main stages of the preparation procedure are shown in Figure 1.

![Figure 1. Stages of M/CNT catalysts preparation](image_url)

For precipitation, the appropriate aqueous solutions of active metal precursors were prepared and mixed with CNTs. The pre-fixed portion of a precipitator was added dropwise to the suspension at vigorous stirring. For cerium and copper-containing samples, a solution of sodium hydroxide was used as a precipitant, and in the case of molybdenum-containing samples, a solution of nitric acid. After adjusting the pH of Ce, Cu, and Mo-containing suspension to 10, 9, and 3, respectively, the slurry was stirred at 80°C for 2 h. Then slurry was cooled to room temperature, filtered and washed with water till neutrality. After that, the sample was dried at 80°C for 6 h in the air followed by the calcination at 600°C for 2 h in Ar.
In the case of the incipient wetness impregnation method, a CNTs support was impregnated by an aqueous solution of an active metal precursor with a given concentration. After the active component introduction, the formed moist paste was dried at 80°C for 6 h in the air followed by the calcination at 600°C for 2 h in Ar.

For adsorption, appropriate aqueous solutions of active metal precursors were prepared. The CNTs were added to the solution. The liquid to solid ratio was equal to 10. The suspension was stirred continuously for 24 h, then the solid phase was collected by filtering to obtain M/CNTs. The sample was washed with water till neutrality and then dried at 80°C for 6 h in the air followed by the calcination at 600°C for 2 h in Ar.

2.2. Catalyst characterization
The elemental composition of the samples was determined by inductively coupled plasma optical emission spectrometry on an atomic emission spectrometer iCAP 6500 Duo LA (ThermoFisher-Scientific, USA).

Textural characteristics of the materials (specific surface area $S_{BET}$, pore volume $V_p$ and average pore diameter $D_p$) were examined on an automated volumetric setup ASAP 2400 (Micromeritics, USA) by measuring and processing the low-temperature nitrogen adsorption isotherms taken at 77 K.

The X-ray diffraction (XRD) analysis of the catalysts was accomplished in a powder X-ray diffractometer Bruker D8 ADVANCE A25 (Bruker, Germany) in monochromatic CuK$\alpha$ radiation, $\lambda = (1.5406 \ \text{Å})$. The scanning region of the angles $2\theta = 10^\circ$–$90^\circ$ with a step of 0.02 degrees and an accumulation time of 2 seconds were applied. The crystallite size (the coherent scattering regions, CSR) was calculated from the Debye–Scherrer formula. ICDD and PDF2 databases were used for phase identification from diffraction peaks.

Raman spectra were recorded in the spectral shift range of 100–4000 cm$^-1$ on a Raman spectrometer Renishaw Invia (Renishaw plc., UK) with excitation by an argon laser with the wavelength 514.5 nm, diffraction lattice 1800 l/mm and L50× objective. Laser power on a sample did not exceed 0.175 mW, and the accumulation time of the useful signal was 120 s.

Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6390 LA (JEOL, Japan) electron microscope with an X-ray energy dispersive detector JED 2300.

3. Results and discussions
The CNTs were multi-walled nanotubes with an inner diameter 10–20 nm and an $S_{BET} = 180 \text{ m}^2/\text{g}$, $V_p = 0.33 \text{ m}^3/\text{g}$, and $D_p = 7.5 \text{ nm}$. The phases of the CNT support are the graphitic carbon phase and the phase of metallic nickel and mixed nickel-magnesium oxide. The average lattice parameter $c$ of graphitic carbon phase is equal to $\sim 6.81 \text{ Å}$, and the size along the direction perpendicular to graphite layers, $\sim 6 \text{ nm}$. The presence of metal-containing phases in CNTs is caused by their synthesis procedure [16].

The chemical composition, textural and structural characteristics of M/CNTs samples prepared by different methods are shown in Table 1 and Figures 2–7.
Table 1. Chemical composition, textural and structural properties of M/CNTs

| Sample  | Content of M, mass % | Sample | Content of M, mass % |
|---------|----------------------|--------|----------------------|
| Ce/CNT-p | 7.4±0.1              | Ce/CNT-i | 10.0±0.2            |
| Cu/CNT-p | 6.7±0.1              | Cu/CNT-i | 9.5±0.2             |
| Mo/CNT-p | 9.5±0.1              | Mo/CNT-i | 10.9±0.3            |

| Sample  | Content of M, mass % | Sample | Content of M, mass % |
|---------|----------------------|--------|----------------------|
| Ce/CNT-a | 1.2±0.1              | Ce/CNT-a | 0.9±0.1             |
| Cu/CNT-a | 0.9±0.1              | Mo/CNT-a | 1.2±0.1             |

| Sample  | Content of M, mass % | Sample | Content of M, mass % |
|---------|----------------------|--------|----------------------|
| Ce/CNT-p | 7.4±0.1              | Ce/CNT-i | 10.0±0.2            |
| Cu/CNT-p | 6.7±0.1              | Cu/CNT-i | 9.5±0.2             |
| Mo/CNT-p | 9.5±0.1              | Mo/CNT-i | 10.9±0.3            |

| Sample  | Content of M, mass % | Sample | Content of M, mass % |
|---------|----------------------|--------|----------------------|
| Ce/CNT-a | 1.2±0.1              | Ce/CNT-a | 0.9±0.1             |
| Cu/CNT-a | 0.9±0.1              | Mo/CNT-a | 1.2±0.1             |

3.1. Precipitation

According to the chemical analysis of M/CNT-p catalysts, the contents of cerium and copper are slightly lower than the calculated one, while the content of molybденum satisfactorily corresponds to the calculated value. This indicates an incomplete course of the deposition process for Ce/CNT-p and Cu/CNT-p samples and requires improvement of the synthesis procedure.

The specific surface of the samples depends on the type of metal. It is higher for Ce/CNT-p and Cu/CNT-p (117 m²/g), but significantly lower for Mo/CNT-p (76 m²/g). The pore volume of the samples is close to each other and amounts to 0.24 cm³/g. The average pore diameter varies in the narrow range of 8.0–11.5 nm. A decrease in the S_{BET} and V_p and an increase in the D_p can be associated with the blocking of thin pores of support by the active component particles.

In all of the XRD patterns (Figure 2), there was a characteristic peak of the CNTs at 2Θ: 26°, 42°, and 54° indexed with (002), (101), and (004) diffraction planes of hexagonal graphite (JCPDS no. 41-1487). The major diffraction for nickel Ni and mixed nickel-magnesium oxide NiO-MgO are observed. The reflections at 2Θ: 44.4°, 51.8°, and 76.3° correspond to the (111), (200), and (220) planes of face centered cubic lattice of Ni (JCPDS no. 04-0850) and reflections at 2Θ: 37.1°, 43.2° and 62.6° correspond to the (111), (200), and (200) planes of a face-centered cubic lattice of NiO-MgO. These phases are similar to those which observed in the CNT support. It indicates that the support has not been destroyed after the loading of M species. The other diffraction peaks can be attributed to M-containing phases.
For Ce/CNT-p sample the reflections at 2θ: 28.5°, 33°, 47.5°, and 58.9° correspond to (110), (200), (220), and (311) planes of the cubic lattice of cerium oxide CeO₂ (JCPDS No. 34-0394). For Cu/CNT-p sample the reflections at 2θ: 36.2°, 42.1° correspond to (111) and (200) planes and the reflections at 2θ: 43.2°, 50.3°, 73.9° correspond to (111), (200) and (200) planes of the cubic lattice of copper (I) oxide Cu₂O (JCPDS No. 34-1352) and Cu (JCPDS No. 04-0836), respectively (Figure 1). For Mo/CNT-p sample the reflections at 2θ: 37.1°, 54.2° correspond to (211) and (311) planes of the tetragonal lattice of molybdenum (IV) oxide MoO₂ (JCPDS No. 073-1249). In addition, traces of the monoclinic lattice of molybdenum (VI) oxide MoO₃ (JCPDS No. 21-0569) are observed. The presence of Cu⁰ and MoO₂ phases indicates the process of reduction of metal cations during the deposition of metal precursors and subsequent heat treatment of M/CNT samples in an inert atmosphere.

![Figure 2. X-ray diffraction patterns of CNT, Ce/CNT-p, Cu/CNT-p and Mo/CNT-p](image)

The change in the defectiveness of the structure of the carbon structure after the active component introduction was estimated by the value I_D/I_G (Table 1). For unmodified CNTs this parameter is equal to 1.93 [18]. The deposition of Cu and Mo by precipitation doesn’t affect the CNTs structure. The decrease in I_D/I_G for Ce/CNT-p in comparison with unmodified CNTs may testify to both a decrease in the fraction of amorphous component of the carbon framework and a decrease in the number of defects [19].

According to the SEM study, the morphology of the samples weakly depends on the type of metal and is determined by the properties of the initial support (Figure 3). The aggregation of the metal-
containing phase is less pronounced for the Mo/CNTs. From EDX analysis follows that the molar ratio O/M increases from 1.7 to 6.4 and 7.2 in the next row of metal Cu < Mo < Ce.

3.2. Impregnation

The content of metals in samples obtained by impregnation is fully consistent with the specified values (Table 1). The behavior of the change in the texture properties is similar to that observed for samples obtained by the precipitation method. In the case of Ce/CNTs, the active component is represented by the cerium dioxide phase with an average crystallite of ~8 nm in size. For Cu/CNT-i, the formation of the copper (I) oxide phase and metallic Cu^0 particles is observed. For Mo/CNT-i samples, the active component is stabilized as oxides of molybdenum VI and IV, the CSR size of which can hardly be measured because their diffraction maxima cannot be resolved (Figure 4). For all samples of i-series the ratio I_D/I_G is reduced, compared to that for the unmodified support. It is seen (Figure 5) that the high uniformity of metal distribution on the surface of the support is observed for Ce/CNT-i sample. For the Cu/CNT-i sample Cu-contained phase has a tendency to aggregation. From EDX analysis follows that the molar ratio O/M increases from 2.7 to 9.2 and 12.5 in the next row of metal Cu < Mo < Ce.

![Figure 4. X-ray diffraction patterns of CNT, Ce/CNT-i, Cu/CNT-i and Mo/CNT-i](image)

![Figure 5. SEM images of samples Ce/CNT-i (a, d), Cu/CNT-i (b, e) and Mo/CNT-i (c, f), obtained in the registration mode of reflected electrons (a, b, c) and characteristic x-ray radiation O (blue), M (red), Ni (green) images d, e, f – with superposition of all signals](image)

3.3. Adsorption
The samples of a-series contain small content of active component (Table 1) that indicates the low ability of CNTs to adsorption of metal cations due to the specific composition of the surface [16]. As a consequence, a decrease in the specific surface area is observed to a lesser extent. According to XRD data (Figure 6), Ce/CNT-a exhibits reflections characteristic of the cerium oxide phase (2θ angle range: ≈ 28.4 °; 33 °; 47.4 °; 53.7 °; 56.3 °). X-ray diffraction patterns Cu/CNT-a contains weak reflections characteristic of the phases of copper (2θ: ≈ 43.2°) and copper (I) oxide of the cubic modification (2θ: ≈ 36.3 °). Mo/CNT-a exhibits weak reflections characteristic of the monoclinic molybdenum (IV) oxide phase (2θ angle range: ≈ 26 °; 37.2 °).

The I_D/I_G ratio is 1.5–1.7, which is lower compared to the support, which indicates that the contact of CNTs with a solution of a metal precursor affects the carbon structure. For all samples, a uniform distribution of the active component on the surface of the support is observed (Figure 7). EDX analysis shows a high value of molar ratio O/M: 12 for Cu/CNT-a and ~40 for Ce and Mo-containing samples.

**Figure 6.** X-ray diffraction patterns of CNT, Ce/CNT-a, Cu/CNT-a and Mo/CNT-a (2)

**Figure 7.** SEM images of samples Ce/CNT-a (a, d), Cu/CNT-a (b, e) and Mo/CNT-a (c, f), obtained in the registration mode of reflected electrons (a, b, c) and characteristic x-ray radiation O (red), M (green) images d, e, f – with superposition of all signals

### 4. Conclusion

The M/CNTs catalysts (M = Ce, Cu, Mo) were prepared by incipient wetness impregnation method (i), adsorption (a), and precipitation (p) methods. Using physicochemical methods (optical emission spectrometry with inductively coupled plasma, low-temperature nitrogen adsorption, X-ray phase analysis, Raman spectroscopy, and scanning electron microscopy) the effects of preparation mode on structural properties, texture, and morphology of samples were elucidated. The specific surface area of M/CNTs increases in the following row of methods i < p < a and metal types Mo < Ce ≈ Cu. The
preparation mode influences the distribution and dispersion of the active component but does not affect the phase composition of catalysts. The precipitation method is selected as the optimal approach for the introduction high content of nanosized M-containing particles with uniform distribution onto the surface of CNT support.

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