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Catalytic and capacity properties of nanocomposites based on cobalt oxide and nitrogen-doped carbon nanofibers

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ABSTRACT

The nanocomposites based on cobalt oxide and nitrogen-doped carbon nanofibers (N-CNFs) with cobalt oxide contents of 10–90 wt% were examined as catalysts in the CO oxidation and supercapacity electrodes. Depending on Co₃O₄ content, such nanocomposites have different morphologies of cobalt oxide nanoparticles, distributions over the bulk, and ratios of Co³⁺/Co²⁺ cations. The 90%Co₃O₄-N-CNFs nanocomposite showed the best activity because of the increased concentration of defects in N-CNFs. The capacitance of electrodes containing 10%Co₃O₄-N-CNFs was 95 F/g, which is 1.7 times higher than electrodes made from N-CNFs.

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1. Introduction

Spinel cobalt oxide (Co₃O₄) is one of the most well-known magnetic p-type semiconductors and has been successfully used in many fields, including heterogeneous catalysis, gas sensing, electrochemical devices, and lithium ion batteries [1–4]. Cobalt oxide is highly active in the low-temperature oxidation of carbon monoxide, which has been thoroughly studied for several decades because of the practical importance of this reaction for indoor air cleaning, purification of exhaust gases from motor vehicles, and gas sensing of CO levels. In addition, the low-temperature oxidation of CO is used as a model reaction to estimate the low-temperature activity of new catalysts and reveal the mechanisms of catalytic reactions [5]. Depending on the preparation method, cobalt oxide can be active in the

oxidation of CO at different temperatures: at 20–50 °C in the case of 20%Co₃O₄/γ-Al₂O₃ [6] or at negative temperatures in the case of Co₃O₄ nanorods [7,8] or mesoporous Co₃O₄ [9].

A new approach to applying known systems for the development of advanced nanotechnologies is the design of nanocomposites composed of two or more nanomaterials that substantially differ in their chemical properties and morphologies. For example, Co₃O₄-SiO₂ [10], Co₃O₄-CuO [11], or Co₃O₄-CeO₂ [12] nanocomposites demonstrate higher activity and stability in the oxidation of CO than Co₃O₄.

Nanocomposites based on carbon nanomaterials and metals composed of Me-C or Me-O-C, where Me = Pt, Pd, Au, Fe, Co, Mn, V, Ti, etc., are being studied now in various catalytic reactions. In the field of catalysis, a standard approach [13,14] is employed for Me-C or Me-O-C nanocomposites: carbon is consid-

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ered as a support and Me or Me-O are the supported catalytic components. Such nanocomposites have demonstrated high activity in environmentally friendly energy-generating processes [15–17], hydrogenation of cinnamaldehyde [18], decomposition of ammonia [19], Fischer-Tropsch reactions [20,21], and other processes.

Some recent studies have been devoted to nanocomposites based on cobalt oxide and carbon nanomaterials, including Co₃O₄/graphene for Li-O₂ batteries [22] or Co₃O₄-carbon nanotubes (CNTs) for supercapacitors with electric double layers and pseudocapacitances [23].

Here, we investigate the catalytic and capacity properties of nanocomposites containing cobalt oxide and nitrogen-doped carbon nanofibers (N-CNFs). The introduction of nitrogen into the carbon structure is known to alter the physical and chemical properties of CNFs by increasing their conductivity and basicity. In addition, the presence of nitrogen-containing sites on the CNF surface facilitates stabilization of supported nano-sized metal particles [24–29].

2. Experimental

2.1. Synthesis of N-CNFs, Co₃O₄, and Co₃O₄-N-CNFs nanocomposites

N-CNFs (2.7 wt% N) were synthesized by decomposition of a 50%C₂H₄/50%NH₃ mixture over the 65%Ni-25%Cu-10%Al₂O₃ catalyst at 550 °C for 3 h [30]. The resulting N-CNFs were treated with concentrated hydrochloric acid to remove the initial catalyst particles.

Co₃O₄ was synthesized by homogeneous precipitation from a Co(NO₃)₂ solution by a NH₄OH solution at room temperature. The precipitate was filtered, carefully washed with distilled water, dried at room temperature, and calcined at 250 °C for 6 h.

Co₃O₄-N-CNFs nanocomposites were synthesized at room temperature by homogeneous precipitation from the Co(NO₃)₂ solution containing dispersed N-CNFs by a NH₄OH solution. The precipitate was filtered, carefully washed with distilled water, dried at room temperature, and calcined in air at 250 °C for 6 h. The content of cobalt oxide in the resulting nanocomposites varied from 10 to 90 wt% (see Table 1).

2.2. Physicochemical characterization

X-Ray diffraction (XRD) patterns were taken on an HZG-4 diffractometer with monochromatic Co *K*_α radiation (λ_{av} = 1.79021 Å).

Textural properties of the synthesized nanocomposites were studied using low-temperature nitrogen adsorption at –196 °C on a Micromeritics ASAP-2400 instrument. The specific surface area was calculated by the BET method.

Differential thermal analysis (DTA) was carried out on a Shimadzu DTG-60H analyzer. Samples (10 mg) were heated to 1000 °C at a rate of 10 °C/min.

Thermoprogrammed reduction (TPR) experiments were carried out using the gas mixture containing 10% H₂-90% Ar

Table 1

Characteristics of Co₃O₄-N-CNF nanocomposites.

Sample	<i>A</i> _{BET} (m ² /g)	XRD
Co ₃ O ₄	88	Co ₃ O ₄ : <i>a</i> = 8.086 Å
90%Co ₃ O ₄ -N-CNFs	100	Co ₃ O ₄ : <i>a</i> = 8.069 Å
50%Co ₃ O ₄ -N-CNFs	190	C: <i>d</i> / <i>n</i> = 3.408 Å; Co ₃ O ₄ : <i>a</i> = 8.081 Å
10%Co ₃ O ₄ -N-CNFs	274	C: <i>d</i> / <i>n</i> = 3.425 Å; Co ₃ O ₄ : <i>a</i> = 8.083 Å
N-CNFs	275	C: <i>d</i> / <i>n</i> = 3.414 Å

with a 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 rate of 10 °C/min. The H₂-TPR spectra were recorded after pretreatment of the samples in Ar at room temperature or after treatment in a mixture of 20% O₂-80% Ar at 200 °C for 1 h. After pretreatment, the samples were cooled to room temperature and flushed with an Ar flow. The mass of the samples was 20 mg and their particle size was 0.25–0.5 mm. The water produced during the TPR experiment was removed using a cold trap.

Transmission electron microscopy (TEM) was performed with transmission electron microscopes JEOL JEM-2010 and JEM-2200FS with an accelerating voltage of 200 kV and a spatial lattice resolution of 1.4 and 1 Å, respectively. The samples were deposited on copper grids 3 mm in diameter, which were covered with a carbon film with a set of holes. Alcohol suspensions of the samples were dispersed by ultrasound and deposited onto the substrates.

X-Ray photoelectron spectroscopy (XPS) measurements were made on an ES-300 (KRATOS Analytical) photoelectron spectrometer with Al *K*_α line (*hν* = 1486.6 eV). The energy scale of the spectrometer was calibrated against the binding energies of the Au 4f_{7/2} line at 84.0 eV and the Cu 2p_{3/2} line at 932.7 eV. Spectral calibration for the Co₃O₄ sample was performed using *E*_b(C 1s) = 284.8 eV. Other samples were not characterized by the charging effect. Control of the surface chemical composition was attained using survey spectra in the range of 0–1100 eV. We acquired narrow scans using a pass energy of 25 eV and a 0.1-eV step to analyze the composition and chemical state of the elements. The quantitative analysis of the composition was made on the basis of calculating the integral intensity of the corresponding narrow lines in the XPS spectra, taking into account the atomic sensitivity of each element. We performed decomposition of the spectra into components, smoothing, normalization, and other spectral treatment procedures with the aid of the original XPS Calc package, which was successfully applied to various systems including N-CNFs materials [28–30].

2.3. Catalytic testing

The catalytic properties of the samples were tested using the temperature-programmed reaction (light-off) in an automated setup with a stainless steel flow reactor and mass spectrometric analysis of the gas mixture. A sample 0.25 cm³ in volume with particle sizes ranging from 0.25 to 0.5 mm was placed into the reactor. The reaction mixture containing 0.2 vol% CO-1.0 vol% O₂-0.5 vol% Ne/He was fed at a rate of 1000 cm³/min (240000 h^{–1}) to the initial catalyst that was cooled to

–15 °C. We used cyclical heating and cooling in the reaction mixture. The catalyst was heated from –15 to 250 °C at a rate of 10 °C/min with subsequent cooling and repeated heating, after which the catalyst was cooled in He. The concentrations of CO, O₂, and CO₂ were monitored over the course of the reaction. The concentrations were measured in each point at a frequency of 0.34 Hz.

2.4. Capacity testing

The electrochemical properties of the nanocomposites were studied using the cyclic voltammetry method. First, a cell was examined by means of a comparison with the readings of the same electrodes obtained for the known cell [31]. A symmetric two-electrode cell was used for the measurements of the N-CNFs samples, whereas an asymmetric two-electrode cell was used in the case of Co₃O₄-N-CNFs nanocomposites. In the asymmetric cell, we used an electrode made of microporous carbon nanomaterial Kemerit-5 with a known capacity of 348 F/g at 10 mV/s. Aqueous solutions of potassium hydroxide (6 mol/L) served as the electrolyte. The electrodes of the supercapacitors were prepared from a mixture of 80% N-CNFs or Co₃O₄-N-CNFs and 20 wt% acetylene black.

3. Results and discussion

3.1. Nitrogen adsorption, XRD, and DTA results

A decrease in the cobalt oxide content in the nanocomposite from 90% to 10% was accompanied by a monotonic increase in its specific surface area from 100 to 275 m²/g. The XRD data indicated the formation of Co₃O₄ phase in all nanocomposites (see Table 1).

The DTA curve of Co₃O₄ (Fig. 1) showed a single endothermic peak at 919 °C, which can be attributed to Co₃O₄ decomposition into CoO and O according to the literature [32,33].

The combustion resistance of N-CNFs is described by Fig. 1 (curve 2); it has a single exothermic peak at 508 °C, which agrees with the DTA data for carbon nanomaterials reported in the literature [34,35]. The absence of additional exothermic

Fig. 1. DTA curves of (1) Co₃O₄, (2) N-CNFs, (3) 10%Co₃O₄-N-CNFs, and (4) 90%Co₃O₄-N-CNFs.

peaks indicates the homogeneity of N-CNFs. Curves (3) and (4), which correspond to nanocomposites, exhibit a weak exothermic peak at ~200 °C, whereas the main peak, corresponding to combustion of N-CNFs, shifted toward low temperatures by ~100 °C in the case of 10%Co₃O₄-N-CNFs and by ~150 °C in the case of 90%Co₃O₄-N-CNFs.

3.2. TEM results

The Co₃O₄ sample was composed of spherical nanoparticles 3–20 nm in diameter and nanoparticles with flattened or nanorod-like shapes with widths of 3–7 nm and lengths of 15–40 nm (Fig. 2(a)). A typical selected area electron diffraction pattern for an aggregate of particles is ring-shaped (see the insert in Fig. 2(a)); the measured interplanar spacings ($d_{111} = 4.67$ Å, $d_{220} = 2.86$ Å, $d_{311} = 2.44$ Å, and $d_{400} = 2.02$ Å) correspond to the Co₃O₄ phase with a spinel-like structure (CC = 150805 in Inorganic Crystal Structure Database, 2011, Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany)).

Co₃O₄-N-CNFs nanocomposites comprise CNFs (100–200 nm in length and approximately 50 nm in width) with platelet and herringbone structures, which are covered with Co₃O₄ nanoparticles. The morphology of such nanocomposites strongly depends on the cobalt oxide content. In the case of 90%Co₃O₄-N-CNFs (Fig. 2(b)), the surface of N-CNFs is covered with cobalt oxide nanoparticles; in addition, regions of agglomerated cobalt oxide particles are observed here, as was the case for the Co₃O₄ sample. The size and shape of the Co₃O₄ nanoparticles in 90%Co₃O₄-N-CNFs did not change in comparison with

Fig. 2. TEM images of (a) Co₃O₄ and (b–d) Co₃O₄-N-CNFs nanocomposites containing 90%, 50%, and 10% Co₃O₄, respectively; (e–f) HRTEM images of flattened and spherical Co₃O₄ nanoparticles on the N-CNF surface in 90%Co₃O₄-N-CNFs, respectively; (g) HRTEM image of monolithic Co₃O₄ nanoparticle in 10%Co₃O₄-N-CNFs.

the Co_3O_4 sample (Fig. 2(b), (e), and (f)). A decrease in the cobalt oxide content to 50–10 wt% produced a uniform distribution in the bulk of the nanocomposites and prevented agglomeration of Co_3O_4 nanoparticles (Fig. 2(c) and (d)). These results indicate that interaction between Co_3O_4 and N-CNFs is stronger than that between Co_3O_4 particles [36]. Furthermore, a decrease in the cobalt oxide content in the nanocomposites resulted in the formation of extended Co_3O_4 particles with lengths up to 100 nm and widths close to 10 nm. The largest number of such particles was observed for the 10% Co_3O_4 -N-CNFs sample (Fig. 2(d)). One can see from the HRTEM images (Fig. 2(g)) that the extended particles are monolithic and are formed because of intergrowth of Co_3O_4 nanoparticles on the N-CNF surface.

3.3. XPS results

Figure 3 shows the Co 2p XPS spectra after the spectroscopic treatment, including background subtraction and deconvolution into components. The initial spectra (not shown here) demonstrated that all of the studied samples had similar states of cobalt; the line shape of the Co 2p spectrum, the $E_b(\text{Co } 2p_{3/2}) \approx 780$ eV, and the presence of indistinct satellite structure in the region of 786–790 eV indicated the formation of Co_3O_4

[37–40]. Co^{2+} and Co^{3+} are known to have similar binding energy [37,38], so the decomposition of the spectrum into individual components was hindered. Decomposition of the Co 2p spectrum into components with a binding energy of 779.8 eV for Co^{3+} and 782.1 eV for Co^{2+} has been reported in the literature [41]. We used these data for the decomposition of the full Co 2p line, which allowed us to extract doublets that can be attributed to cobalt in the oxidation states +3 and +2 and also two doublets of the satellite structures. As seen in Fig. 3, the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio in the initial Co_3O_4 sample corresponds to the spinel structure, and the intensity ratio of the main peaks with $E_b(\text{Co } 2p_{3/2}) \approx 780$ and 782 eV, relating to Co^{3+} and Co^{2+} , respectively, is about 2. The introduction of N-CNFs into the nanocomposites decreased the intensity of the components relating to Co^{3+} virtually by a factor of 2; a minimum amount of Co^{3+} was observed for the 10% Co_3O_4 -N-CNFs sample. The data in the Table 2 testify that the chemical interaction occurred between Co_3O_4 nanoparticles and N-CNFs.

The C 1s spectra shown in Fig. 4 completely confirm the above conclusions related to the interaction of N-CNFs with cobalt oxide nanoparticles in nanocomposites. One can see from the C 1s spectrum of N-CNFs a maximum at 284.5 eV, which is typical of the carbon sp^2 structures [28–30].

Fig. 3. Decomposition of Co 2p XPS spectra into individual components for (a) Co_3O_4 and (b–d) Co_3O_4 -N-CNFs nanocomposites containing 90%, 50%, and 10% Co_3O_4 , respectively. Spectral characteristics of the Co 2p line for Co^{3+} ions are shown in red dot lines, and peaks characterizing the state of Co^{2+} ions are shown in blue dash lines.

Table 2

The ratio of different cobalt, carbon, and nitrogen species in the samples according to XPS.

Sample	Co ⁿ⁺ amount (%)			Carbon species amount (%)			N (at%)	N species ratio ^c $N_{\text{Py}} : N_{\text{Pyr}} : N_{\text{Q}} : N_{\text{ox}}$
	Co^{3+}	Co^{2+}	$\text{Co}^{3+}/\text{Co}^{2+}$	sp^2 (284.5 eV) ^a	sp^3 (285.5 eV)	CO_x (287–289 eV)		
Co_3O_4	70.53	29.47	2.39	0.00	88.39 ^b	11.61	0.4	—
90% Co_3O_4 -N-CNFs	66.14	33.86	1.95	56.91	31.90	11.19	0.6	0.64 : 0.24 : 0.12 : 0.00
50% Co_3O_4 -N-CNFs	60.53	39.47	1.53	73.75	14.45	11.80	2.2	0.36 : 0.17 : 0.20 : 0.27
10% Co_3O_4 -N-CNFs	42.37	57.63	0.74	92.05	0.86	7.09	1.8	0.40 : 0.24 : 0.30 : 0.06
N-CNFs	—	—	—	92.76	0.00	7.24	2.3	0.44 : 0.06 : 0.41 : 0.09

^a The main peak and shake-up satellite were summed to calculate the amount of sp^2 carbon.

^b In the case of Co_3O_4 , sp^3 carbon is represented by amorphous surface carbon deposits with $E_b(\text{C } 1s) = 284.8$ eV.

^c Atomic ratio of N states. N_{Py} —pyridine N; N_{Pyr} —pyrrole N; N_{Q} —graphite-like N; N_{ox} —oxidized state N.

Fig. 4. Decomposition of C 1s XPS spectra into individual components for (a) Co_3O_4 , (b–d) Co_3O_4 -N-CNFs nanocomposites containing 90%, 50%, and 10% Co_3O_4 , respectively, and (e) N-CNFs.

Low-intensity peaks with $E_b(\text{C } 1s) > 287 \text{ eV}$ correspond to the surface oxygen-containing groups. When going to nanocomposites (Fig. 4(b)–(d)), the C 1s spectrum shows not only the carbon sp^2 structures but also a component with $E_b(\text{C } 1s) = 285.4 \text{ eV}$, which can reliably be attributed to carbon in the sp^3 hybridized state. Thus, three different states of carbon were detected in Co_3O_4 -N-CNFs nanocomposites: carbon with sp^2 or sp^3 hybridization and carbon as a component of the oxygen-containing groups. As seen from Table 2, the amount of sp^2 carbon decreased when the cobalt oxide content in the nanocomposite was increased and the amount of carbon with sp^3 hybridization and carbon in the oxygen-containing groups increased. For 90% Co_3O_4 -N-CNFs, the contribution of sp^3 carbon is maximized compared with other nanocomposites, which indicates a pronounced inhomogeneity and an increased concentration of defects in N-CNFs in this case. This finding suggests that the interaction of Co_3O_4 nanoparticles with N-CNFs proceeds via sp^3 carbon because a direct correlation is observed between the cobalt oxide amount in nanocomposite and the amount of carbon in the sp^3 hybridized state.

The O 1s spectra also demonstrated that nanocomposites have a complicated line shape. A broad line with $E_b \approx 530 \text{ eV}$ appeared; it has two maxima corresponding to the lattice O with $E_b = 529.7\text{--}530 \text{ eV}$ and O with $E_b = 531 \text{ eV}$, which can be a component of OH groups, chemisorbed water [38], or O²⁻ oxygen ions with low coordination on the surface of samples [39,42]. A more detailed analysis of O 1s spectra is beyond the scope of this paper; the decomposition of the O 1s line into

components is not attempted in this work.

An interesting behavior of the states of elements was observed in the N 1s spectra of the samples shown in Fig. 5. As was shown in our earlier studies [28–30], N in N-CNFs can be in pyridine, pyrrole, graphite-like, and oxidized states; the pyridine and graphite-like states are the most predominant. In Co_3O_4 -N-CNFs nanocomposites, all states of N are retained, but their ratio changes: the amount of graphite-like N decreases and that of pyrrole N increases (Table 2). A decrease in the $N_0/(N_{\text{py}}+N_{\text{pyr}})$ ratio indicates a lower ordering of N-CNFs in nanocomposites and, accordingly, a higher concentration of defects.

3.4. H_2 -TPR results

Figure 6 shows the H_2 -TPR curves for the samples after treatment in Ar and in the O-containing medium. An intense absorption of H occurs in the temperature range of 250–400 °C and shows as two poorly resolved peaks with maxima at 285–300 and 355–360 °C. The data obtained agree well with the available literature data [43,44] and correspond to the two-step reduction of $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ [41,45,46]. The oxidative pretreatment of Co_3O_4 increases the surface area and shifts the maximum of the low-temperature peak from 305 to 285 °C in the H_2 -TPR spectrum. An additional low-intensity peak also appears at 190 °C, which can be attributed to the weakly bound surface oxygen. In the case of Co_3O_4 -N-CNFs nanocomposites, the overall shape of the H_2 -TPR curves is retained after the

Fig. 5. N 1s XPS spectra of (a–c) Co_3O_4 -N-CNFs nanocomposites containing 90%, 50%, and 10% Co_3O_4 , respectively, and (d) N-CNFs.

Fig. 6. H_2 -TPR curves for Co_3O_4 (a) and Co_3O_4 -N-CNFs nanocomposites (b) after treatment in Ar at 25 °C (1) or O_2 +Ar (1:4) at 200 °C ((2) Co_3O_4 , (3) 90% Co_3O_4 -N-CNFs, (4) 50% Co_3O_4 -N-CNFs, (5) 10% Co_3O_4 -N-CNFs, and (6) N-CNFs).

oxidative treatment. However, there are some distinctions from bulk Co_3O_4 . First, all three maxima are shifted to the low-temperature region, and second, a new extended low-intensity peak with the maximum at 575–595 °C appears in the spectrum. The new adsorption peak is most likely caused by the reduction of Cu(II) and Ni(II) impurity cations, which are components of the N-CNF growth catalyst.

The amount of absorbed H depends on the pretreatment and composition of the sample. From Table 3, a maximum amount was observed for Co_3O_4 after the oxidative treatment ($\text{H}_2/\text{Co} = 1.45$), while a minimum amount was observed in the case of 10% Co_3O_4 -N-CNFs ($\text{H}_2/\text{Co} = 0.78$). A theoretical H_2/Co ratio for Co_3O_4 is equal to 1.33. These data indicate that the

$\text{Co}^{3+}/\text{Co}^{2+}$ stoichiometry changed substantially when going from Co_3O_4 to Co_3O_4 -N-CNFs nanocomposites, which completely agrees with the XPS data.

3.5. Catalytic properties of Co_3O_4 -N-CNFs in CO oxidation

A comparison of catalytic properties of the samples in the CO oxidation was made using the temperature at which 50% CO conversion was reached (T_{50}). From Fig. 7(a), one can see that the activity of the samples during the first heating was not strongly different; there is a small decrease of activity in the following series: Co_3O_4 ($T_{50} = 135$ °C) > 90% Co_3O_4 -N-CNFs ($T_{50} = 142$ °C) ~ 50% Co_3O_4 -N-CNFs ($T_{50} = 146$ °C) > 10% Co_3O_4 -

Table 3H₂-TPR data of the samples.

Sample	Treatment	H ₂ /Co molar ratio at 100–430 °C	Temperature of reduction steps (°C)
Co ₃ O ₄	Ar	1.18	—/305/360/—
	O ₂ +Ar	1.45	190/285/355/—
90%Co ₃ O ₄ -N-CNFs	O ₂ +Ar	1.33	175/260/350/595
50%Co ₃ O ₄ -N-CNFs	O ₂ +Ar	1.00	175/260/310/575
10%Co ₃ O ₄ -N-CNFs	O ₂ +Ar	0.78	175/260/300/595
N-CNFs	O ₂ +Ar	—	—

CNFs ($T_{50} = 162$ °C). N-CNFs did not show activity in the CO oxidation over the studied temperature range. The samples were activated during the first heating cycle; their activity increased considerably and a maximum activity was observed for the 90%Co₃O₄-N-CNFs nanocomposite (Fig. 7(b)). The samples with high content of cobalt oxide yielded the unusual, U-shaped temperature dependence of CO conversion. The temperature curve of CO conversion can be divided into three phases: (1) starting from -15 °C, activity increases and attains a maximum at ~ 20 °C; (2) starting from 20 °C, CO conversion decreases to a minimum value at 80 – 90 °C; (3) at temperatures above 80 – 90 °C, CO conversion increases to 100% . This dependence was

Fig. 7. Temperature dependences of CO conversion during the first (a) and second (b) heating cycles at 240000 h^{-1} over Co₃O₄ (1), 90%Co₃O₄-N-CNFs (2), 50%Co₃O₄-N-CNFs (3), and 10%Co₃O₄-N-CNFs (4) and at 12000 h^{-1} over 10%Co₃O₄-N-CNFs (5).

Table 4

Activity of the samples after the first heating cycle in the CO oxidation.

Sample	CO conversion (%)		$T_{100}/^{\circ}\text{C}$
	At 30°C	At 80°C	
Co ₃ O ₄	60	64	165
90%Co ₃ O ₄ -CNFs	80	74	145
50%Co ₃ O ₄ -CNFs	34	10	145
10%Co ₃ O ₄ -CNFs	0.5	3	165

also observed in the next heating cycles (Table 4). Note that all samples were also activated and demonstrated similar catalytic behavior after pretreatment with $20\%\text{O}_2/\text{Ar}$ mixture at 200 °C.

3.6. Capacity properties of Co₃O₄-N-CNFs

The volt-ampere curves obtained at different scan rates for a cell with N-CNFs electrode are close to the classical squared shape, which corresponds to carbon nanomaterials (Fig. 8 [47,48]). At a scan rate of 10 mV/s , the capacitance is equal to 57 F/g . Among the studied nanocomposites, only 10%Co₃O₄-N-CNFs showed the electrochemical activity. Its capacitance was 1.7 times higher than that of the electrode based on N-CNFs and reached 95 F/g . In this case, volt-ampere curves deviated from the squared shape and were closer to the curves that are typical of electrodes with pseudocapacitance [23] although no distinct peaks were observed in the studied region of potentials, both for direct and inverse scanning.

3.7. Discussion

In this work, the same precipitation method was employed for the synthesis of nanocomposites containing cobalt oxide and N-CNFs; the Co₃O₄ content varied from 10 to 90 wt%. The phase composition of the synthesized nanocomposites was constant and was represented by cobalt oxide phases with lattice parameters of 8.06 – 8.08 Å , which is typical of Co₃O₄ spinel, and by the carbon phase. The morphologies of the nanocomposites, state of the surface, and redox ability depend on the composition and determine catalytic and capacity properties. In 90%Co₃O₄-N-CNFs, cobalt oxide nanoparticles do not differ in shape from bulk cobalt oxide particles, whereas in the case of 10%Co₃O₄-N-CNFs, the extended monolithic Co₃O₄ particles in close contact with N-CNFs are formed in nanocomposite (Fig. 2(g)). As the cobalt oxide content in nanocomposite decreases, its surface becomes more reduced because the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio decreases about three-fold compared with Co₃O₄. This conclusion is supported by TPR data, which showed that the 10%Co₃O₄-N-CNFs nanocomposite has the lowest H₂/Co ratio (Table 3). A new carbon species with sp^3 hybridization was detected in nanocomposites, which differed from sp^2 carbon in N-CNFs. This new carbon species is formed during the synthesis, which is accompanied most likely by partial burning of N-CNFs due to formation of close contacts between cobalt oxide particles and N-CNFs. The partial burning of N-CNFs is supported by DTA data, which showed the appearance of a new low-temperature exothermic peak in nanocomposites at 200 °C and explained changes in the ratio of N species with different

Fig. 8. Cyclic voltammograms of N-CNFs (a) and 10%Co₃O₄-N-CNFs (b) at different voltage sweep rates.

electronic states (Table 2).

The activity of nanocomposites was studied in the CO oxidation. The first heating cycle in the reaction resulted in activation of the samples, which is typical of the oxidation catalysts and is related to the removal of surface deposits. Indeed, maxima of the hydrogen absorption peaks on the TPR curve of activated Co₃O₄ shifted toward low temperatures compared with the initial Co₃O₄; an additional low-temperature peak, which can be attributed to the reduction of weakly bound oxygen, appeared at 190 °C (Fig. 6). It is known that activity of Co₃O₄ in the CO oxidation is determined by the amount and stability of Co³⁺ cations [8]. In reality, the activation of Co₃O₄ increased the H₂/Co ratio from 1.18 to 1.45, indicating an increase in the amount of Co³⁺; hence, activity of the activated sample was substantially enhanced.

A nonlinear dependence of activity of the activated nanocomposites on the cobalt oxide content was revealed: 10% Co₃O₄ < 50% Co₃O₄ < 100% Co₃O₄ < 90% Co₃O₄. In the 10%Co₃O₄-N-CNFs nanocomposite, the amount of Co²⁺ exceeds that of Co³⁺, and the H₂/Co ratio is below the stoichiometric value. Accordingly, this nanocomposite has the lowest activity among all the samples; its activity becomes comparable with other nanocomposites only after decreasing the space velocity of the reaction flow from 240000 to 12000 h⁻¹ (Fig. 7(b)). In the 90%Co₃O₄-N-CNFs nanocomposite, the Co³⁺ amount is two times higher than that of Co²⁺ and H₂/Co = 1.33, which is close to the ratio typical of Co₃O₄. Therewith, the CO conversion over 90%Co₃O₄-N-CNFs at 30 °C exceeds the CO conversion over Co₃O₄ by 20% (Table 4). In the study of Co₃O₄ supported on CNTs [41], it was suggested that the defect structure of CNTs affects the formation of weakly bound surface oxygen on the Co₃O₄ particles and facilitates the oxidation/reduction of cobalt oxide, thus increasing the catalyst activity in the oxidation of toluene. N-CNFs also have a high concentration of defects, which was demonstrated by Raman spectroscopy data; *I*_b/*I*_g being equal to 3.3 [28]. In this work, an additional increase in the concentration of defects in N-CNFs of nanocomposites was revealed by XPS, which showed a decreased amount of graphite-like N and an increased amount of pyrrole N compared with initial N-CNFs. A minimum ratio of N_Q/(N_{py}+N_{pyr}) was observed

exactly in the case of 90%Co₃O₄-N-CNFs. In addition, N-CNFs are the conductive materials; their conductivity reached 15 S/cm [28]. These properties of N-CNFs may facilitate the reduction of cobalt oxide and increase the activity of the nanocomposite. Indeed, in comparison with Co₃O₄, the doped 90%Co₃O₄-N-CNFs nanocomposite showed a decrease in the temperature of Co₃O₄ reduction to CoO and an additional low-temperature peak corresponding to the reduction of weakly bound oxygen; hence, the activity of 90%Co₃O₄-N-CNFs increased.

It should be noted that the temperature curve of CO conversion over the activated samples during the second heating has an unusual U-shape. Such a shape has been reported in the literature [9,10,49,50]. A decrease in CO conversion with an increase in reaction temperature on a certain part of the curve indicates that at such temperatures the apparent activation energy has a negative value. The literature does not provide a reliable explanation for such a decrease in the CO conversion with increasing temperature. Two main reasons are discussed now: (1) the rapid deactivation of highly active low-temperature sites due to their reduction and (2) accumulation of the surface carbonate or hydroxyl groups. The results obtained cannot explain the shape of the curve; we accordingly plan to perform additional studies using in situ XPS.

It is known that an increase in capacitance of carbon electrodes with an electric double layer after the introduction of transition metal oxides is caused by Faraday electrode processes that are based on redox reactions [23,51]. For example, the use of 95%Co₃O₄-CNTs electrodes allowed to increase its capacitance by 150% compared with Co₃O₄. Among the samples examined in this work, only the 10%Co₃O₄-N-CNFs nanocomposite showed electrochemical activity as a capacitor electrode; its capacitance reached 95 F/g, which is 1.7 times higher than that of N-CNFs. According to TEM results, in this sample cobalt oxide is distributed homogeneously and the cobalt oxide particles formed interesting extended structures, which strongly contacted with N-CNFs and differed from cobalt oxide particles in other nanocomposites. Evidently, in this case, the electrochemical activity of the nanocomposite is determined primarily by its morphology.

4. Conclusions

Co_3O_4 -N-CNFs nanocomposites were synthesized by the precipitation method. Depending on Co_3O_4 content, such nanocomposites had different morphologies in terms of cobalt oxide nanoparticles, their distribution over the bulk, and the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio. We found that Co_3O_4 doping using 10% of N-CNFs increases the activity of bulk cobalt oxide by 20%. We propose that N-CNFs enhance the ability of Co_3O_4 to conduct redox processes because of the substantial increase in the concentration of N-CNF defects in the nanocomposite. In turn, 10% Co_3O_4 -N-CNFs nanocomposites with specific morphology of cobalt oxide nanoparticles demonstrated electrochemical activity as a supercapacitor electrode.

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Graphical Abstract

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Catalytic and capacity properties of nanocomposites based on cobalt oxide and nitrogen-doped carbon nanofibers

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The paper describes the properties of Co_3O_4 -N-CNFs nanocomposites: doping of Co_3O_4 by 10 wt% of N-CNFs improves the low-temperature activity of Co_3O_4 in CO oxidation reaction.

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