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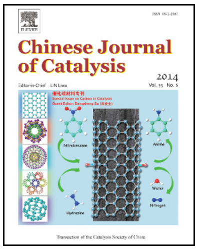

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Catalytic and capacity properties of nanocomposites based on cobalt oxide and nitrogen-doped carbon nanofibers

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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 Co_3O_4 content, such nanocomposites have different morphologies of cobalt oxide nanoparticles, distributions over the bulk, and ratios of Co^{3+}/Co^{2+} cations. The 90%Co_3O_4-N-CNFs nanocomposite showed the best activity because of the increased concentration of defects in N-CNFs. The capacitance of electrodes containing 10%Co_3O_4-N-CNFs was 95 F/g, which is 1.7 times higher than electrodes made from N-CNFs.

1. Introduction

Spinel cobalt oxide (Co_3O_4) 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%Co_3O_4/γ-Al_2O_3 [6] or at negative temperatures in the case of Co_3O_4 nanorods [7,8] or mesoporous Co_3O_4 [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, Co_3O_4-SiO_2 [10], Co_3O_4-CuO [11], or Co_3O_4-CeO_2 [12] nanocomposites demonstrate higher activity and stability in the oxidation of CO than Co_3O_4.

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 Co_3O_4/graphene for Li-O_2 batteries [22] or Co_3O_4-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, Co_3O_4, and Co_3O_4-N-CNFs nanocomposites

N-CNFs (2.7 wt% N) were synthesized by decomposition of a 50%C_2H_4/50%NH_3 mixture over the 65%Ni-25%Cu-10%Al_2O_3 catalyst at 550 °C for 3 h [30]. The resulting N-CNFs were treated with concentrated hydrochloric acid to remove the initial catalyst particles.

Co_3O_4 was synthesized by homogeneous precipitation from a $Co(NO_3)_2$ solution by a NH_4OH 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.

Co_3O_4-N-CNFs nanocomposites were synthesized at room temperature by homogeneous precipitation from the $Co(NO_3)_2$ solution containing dispersed N-CNFs by a NH_4OH 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% H_2-90% Ar 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 H_2-TPR spectra were recorded after pretreatment of the samples in Ar at room temperature or after treatment in a mixture of 20% O_2-80% 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.

Table 1
Characteristics of Co_3O_4-N-CNF nanocomposites.

Sample	A_{BET} (m^2/g)	XRD
Co_3O_4	88	Co_3O_4: a = 8.086 Å
90%Co_3O_4-N-CNFs	100	Co_3O_4: a = 8.069 Å
50%Co_3O_4-N-CNFs	190	C: d/n = 3.408 Å; Co_3O_4: a = 8.081 Å
10%Co_3O_4-N-CNFs	274	C: d/n = 3.425 Å; Co_3O_4: a = 8.083 Å
N-CNFs	275	C: d/n = 3.414 Å

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 ($h\nu$ = 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 Co_3O_4 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 cm^3 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% O_2-0.5 vol% Ne/He was fed at a rate of 1000 cm^3/min (240000 h^{-1}) to the initial catalyst that was cooled to