Ruthenium nanoparticles supported on nitrogen-doped carbon nanofibers for the catalytic wet air oxidation of phenol

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ABSTRACT

The effect of nitrogen content in N-doped carbon nanofibers (N-CNFs) on the catalytic activity of Ru/N-CNFs in the wet air oxidation of phenol has been studied. The N-CNFs, irrespective of nitrogen content and Sibunit, are shown to be low active. In the case of Ru-containing catalysts, nitrogen in N-CNFs was found to be responsible for both the increased activity and stability of the catalysts toward deactivation. The XPS showed the formation of carbon-oxygen structures with hydroxyl (carbonyl) end groups blocking ruthenium on the surface of the catalysts without nitrogen. For the catalysts with nitrogen, the ruthenium nanoparticles were not blocked in the course of the reaction and mainly the carboxyl (carbonate) surface groups were formed. The nature of this effect is discussed.

1. Introduction

Wet air oxidation (WAO) is an attractive method for the treatment of concentrated wastewater streams compared with biological treatment techniques, which are ineffective when toxic effluents such as phenols are present [1–3]. However, conventional WAO usually requires high pressures (5–200 bar) and temperatures (150–325 °C), which result in a high capital investment and high energy consumption for operation. Oxidation efficiency can be improved (and reaction temperature can be reduced) by using homogeneous or heterogeneous catalysts [4–7].

Homogeneous catalytic systems composed of transition metal ions, in spite of their efficiency in the oxidation of various organics, have well-known drawbacks, e.g., the production of metal-containing waste sludge which is difficult to dispose, and the catalyst deactivation by some metal complexing agent. The promising heterogeneous catalysts for catalytic wet air oxidation (CWAO) are noble metal catalysts (Ru, Pt, Pd) supported on carbon materials, which are very effective and resistant to active component leaching [7]. The literature data on the activity of noble metals in CWAO of different organic pollutants are contradictory:

some authors consider Pt as the most active metal, whereas in other works Ru shows the highest activity [6,7]. However, taking into account the lowest cost of ruthenium among the mentioned metals, Ru-containing catalysts appeared to be the most promising for treatment of wastewaters.

Recently, some interest has been displayed in using carbon nanomaterials doped with nitrogen as metal catalyst supports [8]. Nitrogen introduction into the carbon structure opens up a good possibility to regulate the surface and electronic properties of carbon nanotubes, carbon nanofibers (CNFs) or graphene [9–13]. By now, a sufficient experimental material has been accumulated, making it possible to conclude that the use of nitrogen-doped carbon nanomaterials as metal catalyst supports increases the catalytic activity in electrochemical oxidation of methanol or hydrogen in fuel cells [14–18], selective hydrogenation of cinnamaldehyde [19,20], ammonia decomposition [21], isotope exchange [22], and CO oxidation [23]. The increase in catalytic activity is associated with several basic factors: (1) introducing a heteroatom into carbon material makes it possible to control the size of the supported metal particles and to obtain a narrower particle size distribution; (2) using a support of higher conductivity leads to enhanced chemical reactivity for electron transfer processes in a catalytic system; (3) there occur changes in the acid-base properties of the support surface.

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In the literature, there are virtually no data on the application of nitrogen-doped carbon nanomaterials as catalysts or catalyst supports in the CWAO processes. Only in a recent work [24], aminated active carbon (AC) was studied as a catalyst in the CWAO of coking wastewater at 140–160 °C and 0.2–1 MPa of oxygen partial pressure. The ACs aminated at 450–650 °C showed a little higher activity than the parent untreated AC. Based on a higher surface content of nitrogen and a lower surface area of the aminated ACs compared to the parent one, the increase in the catalytic activity was attributed to the nitrogen-containing functional groups. However, it is presently unclear how nitrogen in the carbon structure can affect the performances of the graphite-like carbon nanomaterials and noble metals supported on carbon nanomaterials in the CWAO.

In this regard, the present work is focused on the study of the effect of nitrogen in nitrogen-doped carbon nanofibers (N-CNFs) on the catalytic activity of pure CNFs and Ru/N-CNFs in the CWAO of phenol, which is a typical wastewater contaminant.

2. Experimental

2.1. Catalyst preparation

Two types of graphite-like carbon supports were used: N-CNFs and commercial mesoporous carbon Sibunit® [25].

N-CNFs differing in nitrogen content (0, 2, 6.8 wt.%) were synthesized by decomposing C_2H_4, $50\%C_2H_4/50\%NH_3$ or $25\%C_2H_4/75\%NH_3$ gas mixtures, respectively over a 65Ni-25Cu-10Al$_2$O$_3$ (wt.%) catalyst at 550 °C for 1 or 3 h. The methodology is described in detail in [11]. The synthesized supports were treated with concentrated hydrochloric acid to remove the exposed catalyst particles and after that washed by distilled water until the absence of chloride in rinsing water. For comparison, the graphite-like carbon material Sibunit® was used in this work [25]. Before using, it was washed several times in boiling water and oxidized by a wet gas mixture ($O_2/N = 1/5$) [26]. The characteristics of carbon supports are presented in Table 1.

The supported Ru catalysts (1 and 3 wt.%) were prepared by deposition of Ru from aqueous solutions of Ru(NO)(NO$_3$)$_3$ on N-CNFs and Sibunit® using the incipient wetness impregnation technique described in detail in [27,28]. After impregnation, the samples were dried and reduced in flowing H$_2$ at 300 °C for 2 h.

2.2. Physicochemical methods

The conductivity of N-CNFs and Sibunit® was measured via the standard four-contact method [12], the nitrogen content in the N-CNFs was determined by elemental analysis, and the electronic state of atoms was studied by XPS. The XPS spectra were recorded on a photoelectron spectrometer ES-300 (KRATOS Analytical). The spectra were recorded using nonmonochromatic AlKα radiation (photon energy 1486.6 eV). Gold Au 4f$_{7/2}$ and copper Cu 2p$_{3/2}$ lines (binding energies of 84.0 and 932.7 eV, respectively) were used as a calibration standard for the spectrometer. The qualitative control of the surface chemical composition was carried out via survey spectra in the range of 0–1100 eV, with an energy resolution corresponding to the maximum sensitivity (analyzer transmission energy 50 eV and energy step 1 eV).

To analyze the quantitative composition and chemical state of the elements, narrow regions were recorded with the analyzer transmission energy 25 eV and energy step 0.1 eV. The quantitative analysis of the composition was made by calculating the integrated intensities of the corresponding narrow lines in the XPS spectra taking into account atomic sensitivity factors (ASF) for each element [29].

The electron microscopy images were obtained using a JEM-2010 (JEOL) instrument with accelerating voltage 200 kV and resolution 1.4 Å. For TEM studies, the samples were supported on a holey carbon film placed on a copper grid. The size distribution of ruthenium particles and their average size were determined from statistical analysis of the TEM images using 300–500 particles. The average size was calculated by the formula

$$d_l = \sum \frac{d_i}{N},$$

where d_i is the measured diameter of a metal particle, and N is the total number of the particles.

The textural properties of carbon supports and catalysts were studied by low-temperature N$_2$ adsorption at −196 °C using an ASAP-2400 instrument (Micromeritics, USA). The specific surface area (S_{BET}) was calculated according to the BET model.

2.3. Catalytic activity measurements

The catalytic activity was investigated in a 150-mL autoclave made of Hastelloy C276 (Autoclave Engineers) at a constant temperature and with intensive stirring (at 1200 rpm). As shown in [30], the stirring at that speed makes it possible to conduct CWAO processes in the kinetic regime. 75 mL of an aqueous solution of phenol with a required concentration and a catalyst (125 mg) were placed into an autoclave reactor. The reactor was purged with argon five times by the alternate raising of the gas pressure up to 10 atm and depressurization. Then the temperature was raised to a desired value. After the temperature was forced into the regime (ca. 0.5 h), the first sample of the reaction solution was taken and analyzed in order to determine the amount of phenol adsorbed on the surface of the catalysts. The determined concentration of phenol, which was never less than 97% of desired initial concentration, was considered as initial for CWAO. After that the gas mixture ($O_2/N_2 = 1/5$) pressure was set at 50 bar and the reaction was started. In the course of the reaction, samples of the reaction solution (1 mL) were taken every 30 min to obtain information on the reaction kinetics. The samples were filtered through the syringe nozzle with a cellulose acetate membrane (a pore diameter of 0.2 μm), and phenol concentration was analyzed by the high pressure liquid chromatography (HPLC) method using a Shimadzu Prominence LC-20 system equipped with a SPD-M20A diode-array detector (detection wavelength λ = 210 nm) and a Phenomenex Synergi Hydro-RP column (250 mm × 3.0 mm) thermostated at 30 °C. The eluent (65 vol.% H$_2$O + 35 vol.% acetonitrile) was supplied at the 0.7 mL min^{-1} flow rate. The content of the total organic carbon (TOC) was determined after experiment in filtered aliquots of the reaction mixture with a Total Organic Carbon Analyzer (TOC-VCSH, Shimadzu, Japan). The solutions after reaction were analyzed for the presence of ruthenium by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Optima 4300DV instrument (PerkinElmer, USA).

The entire experiment was repeated three times to check the reproducibility of results.

The conversion of phenol (X_{PhOH}) and that of total organic carbon (X_{TOC}) were calculated by the following formulae:

$$X_{PhOH}(\%) = \frac{C_{PhOH}^0 - C_{PhOH}}{C_{PhOH}^0} \times 100,$$

$$X_{TOC}(\%) = \frac{C_{TOC}^0 - C_{TOC}}{C_{TOC}^0} \times 100,$$

where C^0 is the initial concentration of the substrate in the solution, and C is its current concentration.

To compare the catalytic properties of the samples, the catalytic activity (A, mmol L^{-1} min^{-1} g$_{cat}$$^{-1}$) was calculated as the