Nickle and Cobalt Spinel Catalyzing Wet Air Oxidation of Refractory Pollutants under Mild Condition

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Abstract. Refractory organic pollutants are critical issues in water or wastewater treatment, and catalytic wet air oxidation (CWAO) is a common method. To improve the efficiency and decrease the reaction conditions, a type of NiCo$_2$O$_4$ (NCO) spinel with urchin-like hollow structures was synthesized and used in CWAO of organics at low temperature and atmosphere pressure. Both scanning electron microscopy and X-ray photoelectron spectra were used to characterize NCO. The 3-D hierarchical architectures, solid state redox couple M$^{2+}$/M$^{3+}$ (M represents Ni or Co), and plenty of surface oxygen species were proved. Furthermore, the reaction path of CWAO with NCO as the catalyst was concluded, i.e. consecutive adsorption, surface oxidation, and re-oxidation of reduced NCO by O$_2$. NCO showed excellent catalytic performance in CWAO of refractory organics, such as alkaline lignin and bisphenol A. The removal rates of total organic carbon exceeded 80% within 3 h. These findings promise a convenient and economical way for the treatment of refractory organics in water or wastewater.

1. Introduction

Hazardous and refractory organic pollutants from industrial wastewater, landfill leachate, and ground-to-drinking water can cause serious environmental problems due to its toxicity, unpleasant color and odor production, and recalcitrance to microbial degradation. In order to eliminate its harm to environment of pollutants, satisfy the stringent water quality regulations and the demand for recycling of water in the process, it is particularly urgent to develop appropriate pollutant removal technologies. Flocculation and filtration can only concentrate these organic substances, while advanced oxidation processes (AOPs) can degrade or mineralize them. Catalytic wet air oxidation (CWAO) is a promising technology to remove refractory organic substances with the capability of generating and exploiting free radicals [1]. Moreover, CWAO is one of the most economically, technologically and eco-friendly viable AOPs for wastewater treatment [1], as it uses O$_2$ as oxidant instead of harmful and expensive oxidants like ozone and hydrogen peroxide in other AOPs. Furthermore, as the dosage of catalysts are allowed to be quite high, usually 1–5 g/L in slurry reactors and several orders higher in fixed-bed reactors, it is a suitable process with great potential for the treatment of wastewater containing high concentration of organics at high flow [1]. However, reaction conditions applied in CWAO are generally quite harsh at present, mostly at oxygen partial pressure of 0.1–3.0 MPa and temperature of 100–280°C [1-3], which increase operational cost and complexity. Hence, it is an essential issue to develop compatible catalysts to reduce the severity of reaction conditions and improve the degradation efficiency of organics.
There have been an increasing number of novel catalysts with non-noble metals or carbon materials in recent studies. Catalysts with transition metals of Ni, Co, Mn, Mo, etc. are often studied because of their abundant resources, convenient synthetic methods and strong redox properties derived from the d-electron layer of metal cations being easy to lose or capture electrons. Composite metal oxides, hydrotalcite [4], perovskite [5, 6], and spinels [7] for instance, are such catalysts have been used in CWAO and have been found with good performance, robustness and oxygen storage capacity. Nevertheless, reaction conditions in most of the studies are still quite severe. Morphology and structure of catalysts are important factors affecting their performance. Hierarchical hollow structures are considered with the ability to improve catalytic performance by offering a high specific surface area, short diffusion path for ions or electrons, and efficient channels for mass transport [8]. Hierarchical NiCo2O4 (NCO) with structures of nanorods, nanosheets and microspheres have been verified to have excellent performances of electronic conductivity [8] and catalytic peroxymonosulfate activation [9], and it has been widely applied to lithium-ion batteries, super capacitors, electro catalysts, AOPs, etc [10]. However, the performance of NCO in CWAO has not been investigated before.

The aim of our work is to develop a novel CWAO with mild operational conditions by using NCO as the catalyst. Urchin-like hollow NCO spinel was synthesized at first, and its performance was tested using glucose as model substance under different parameters including pH, temperature, concentration and the existence of O2. Finally, humic substances (HS), alkaline lignin (AL), and bisphenol A (BPA) were chosen as the models of refractory organics, and their decomposition was investigated with the assistance of NCO.

2. Experimental Sections

2.1. Materials
The reagents and solvents used were of analytical reagent grade, and they were not further purified. Commercial HS (sodium humate), AL, and glucose were purchased from Aldrich Chemistry, U.S.A., and BPA was supplied by Anpel Laboratory Technologies Inc. (Shanghai). The chemicals used for NCO synthesis, i.e. Co(NO3)2·6H2O, Ni(NO3)2·6H2O, and urea, and isopropanol (IPA), were also supplied by Aldrich Chemistry, U.S.A..

2.2. Synthesis and Characterization of NCO
The urchin-like NCO hollow microspheres were synthesized by a solvothermal method followed by calcination according to the literature [8]. Co(NO3)2·6H2O, Ni(NO3)2·6H2O, and urea were dissolved in a mixture of isopropanol (IPA) and water, and the mass ratio was 0.58:0.29:3.6:11.78:3 for Co(NO3)2·6H2O: Ni(NO3)2·6H2O: urea: IPA: H2O. The resulting mixture was stirred thoroughly and then transferred into Teflon-lined stainless steel vessels. The vessels were heated at 120°C for a period of 12 h in an electric oven. After that, the vessels were cooled naturally to room temperature, and then the mixture in the vessels was centrifuged to collect the precipitate. The precipitate was washed using deionized water and ethanol several times and then dried at 105°C overnight. All of the synthesized products were calcined at 350°C in air for 2 h at a ramping rate of 1°C/min.

Morphological and chemical composition of the synthesized NCO were studied by scanning electron microscopy (SEM, FEI APREO S, Netherlands). X-ray diffraction (XRD, RINT2000 V/PC, Bruker DS, Germany) was used to obtain crystallographic information and chemical states of the used NCO. X-ray photoelectron spectra (XPS) were measured by using an ESCALAB-MKIi spectrometer (UK) with Al Kα radiation (1486.6 eV), and the raw spectra were curve-fitted by non-linear least squares fittings with a Gauss-Lorentz ratio (80:20) through the XPS PEAK41 software.

2.3. CWAO Procedures
CWAO was carried out in two modes including anaerobic batch mode, aerobic batch mode and aeration mode. Anaerobic batch mode was used to explore the interaction between NCO and organics...
without external oxygen. Experiments were carried out in airproofed bottles. For glucose, 10 mL 1.8 g/L glucose solution and 1.25 g NCO were added into each bottle. The bottles were first blew with nitrogen in advance to get rid of the initial air in head space, and then placed in a water bath for reactions. After 3 h reaction, the bottles were taken out and placed in an ice-water bath to stop the reactions. After cooling, the mixtures in the bottles were centrifuged at 5800 g for 20 min. The supernatant was collected and then filtered with a 0.45 μm aqueous membrane. The filtrate was used for further analysis. The used NCO precipitation in centrifuge tubes was washed using ultrapure water to remove the residual solution; while the filtration residual of NCO was freeze-dried.

The procedure of aerobic batch mode was similar except for the initial step where the bottles were blew with O2 in head space and then sealed tightly. Same operations for HS and AL in anaerobic batch mode and aerobic mode.

Experiments in aeration mode was carried out in a series of 2-L glass reactors, each of them was equipped with a reflux condenser, a magnetic stir-heater, an aeration device and a sampling valve. In a typical run, a group of reactors were used, and 1 L solution and 5 g NCO were added into each reactor. These reactors were heated from room temperature to a certain reaction temperature. After that, magnetic stirring started, and oxygen was immediately bubbled into the solutions continuously at 250 mL/min to ensure excessive oxygen in the reaction. For convenient discussion, this moment was defined as the "zero time" of the run. Solution samples containing used NCO were collected from different reactors at regular intervals. The samples were treated with the same methods as described in anaerobic mode.

Total organic carbon (TOC) was determined by a TOC IR analyzer (TOC-LCSH, Shimadzu, Japan).

3. Results and discussion

3.1. SEM of NCO
Morphology of the synthesized NCO was shown in Figure 1. Figure 1A, 1B and 1C exhibit that NCO particles have hollow microsphere structure with diameters of around 5 μm with a similar shape of hollow urchin shells. Figure 1D shows three dimensional hierarchical architectures of NCO, which is self-assembled from these low-dimensional nanostructured building blocks such as nanorods and nanosheets. The hierarchical architectures can offer more active sites for reaction, high energy adsorption capacity and efficient channels for mass transport [8, 11].

![Figure 1. SEM images of the NCO with the amplification times of 2500 (A), 10000 (B), 20000 (C), 120000 (D)]

3.2. XPS of NCO
Chemical bonding states and composition of the synthesized NCO were characterized by XPS measurement (Figure 2). The typical signals of O1s, Co2p, and Ni2p core levels were obviously observed from the full scan spectra (Figure 2A). The O1s spectra (Figure 2B) exhibit three oxygen contributions. The fitting peak at 529.5 eV (denoted as O-1) is derived from typical metal-oxygen bonds, i.e. lattice
oxygen. The peak located at 531.8 eV denoted as O-2 is attributed to the oxygen in hydroxyl groups and/or oxygen ions in low coordination sites at the surface. The fitting peak at 533 eV denoted as O-3 is attributed to the multiplicity of physi-/chemisorbed water at and within the surface. The Ni$_{2p}$ spectra and Co$_{2p}$ spectra (Figure 2C and 2D) both consist of two spin-orbit doublets and two shakeup satellites (identified as “Sat.”), and the two spin-orbit doublets of these two spectra are ascribed to Ni$^{2+}$ and Ni$^{3+}$ (or Co$^{2+}$ and Co$^{3+}$). These results showed that the surface of NCO had a composition containing Co$^{2+}$, Co$^{3+}$, Ni$^{2+}$, and Ni$^{3+}$ species. O-1 and O-2 are considered as active and essential oxygen species \[12\] for oxygen delivery and activation. Besides, the O-2 species with higher mobility have the ability of reacting with organic substance directly or facilitating electron transfer to produce radicals \[13\].

![Figure 2. XPS profiles of NCO: survey scan (A), O$_{1s}$ core level (B), Ni$_{2p}$ core level (C), and Co$_{2p}$ core level (D)](image)

### 3.3. Catalytic performance of NCO in oxidative degradation of glucose

This section explored the way NCO worked in CWAO of organics by using glucose as the model, and the experiments were divided into three groups. First group (Figure 3A) was in anaerobic batch mode to investigate the interaction between NCO and glucose at different pH or temperature (Figure 3A). The TOC removal rates were basically the same at initial pH 7.0–12.0, but they tended to decrease under stronger alkaline condition, especially at 60°C. In fact, it was found that the inorganic carbon (IC) contents in most samples increased after reactions. For example, the IC at pH 13.2 and 90°C increased by 240.0 mg/L, and that at pH 12.9 and 90°C increased by 111.6 mg/L. These results verified that NCO had the ability to oxidize, degrade, and even mineralize organics. Besides, pH of the solutions after reaction reduced to some degree (Table 1), indicating some acidic products generated to react with OH$^-$.

Furthermore, when the used NCO was eluted by dilute H$_2$SO$_4$, organic carbon was found in the elution, meaning that the interaction between NCO and organics involves consecutive adsorption and surface oxidation. As higher temperatures increased TOC removal, the adsorption of organics by NCO possibly belonged to chemisorption, and neutral pH should be more feasible to chemisorption and activation of organics by NCO.

According to Figure 3B, the actual quantity of organics removed increased as TOC$_0$ (initial TOC) was higher, which followed reaction kinetics. Figure 3C showed that external O$_2$ enhanced the removal efficiency of TOC, which verified catalytic oxidation ability of NCO. Thus, a preliminary judgment can be made that in CWAO of organics by NCO, the organics were chemisorbed on NCO at first, then transferred electrons to NCO, and finally decomposed. External O$_2$ re-oxidized the reduced NCO to make the reactions ongoing. The XRD pattern of the used NCO, which reacted with glucose in aerobic batch mode, was shown in Figure 4. The resultant diffraction peaks identify well with the
standard patterns of cubic spinel NCO (JCPDS No. 20-0781) [8, 14]. This indicated the robust performance of NCO crystal structure.

Figure 3. TOC removal after 3 h anaerobic batch experiments (A: 10 mL 1.8 g/L glucose solution (TOC 727.3 mg/L), 1.25 g NCO, and different temperature or pH; B: pH 11.0, 10 mL glucose solution with different initial concentrations, and different temperature; C: compare aerobic batch mode with anaerobic batch mode at 90°C and pH 11.0)

Table 1. The pH of the solution after 3 h reactions

| Initial pH | 7.0 | 10.0 | 10.7 | 11.0 | 12.0 | 12.3 | 12.6 | 12.9 | 13.2 |
|------------|-----|------|------|------|------|------|------|------|------|
| 90°C       | 7.1 | 7.1  | 7.1  | 7.1  | 7.2  | 7.3  | 7.5  | 8.5  | 11.6 |
| 80°C       | 7.0 | 7.0  | 7.0  | 7.1  | 7.2  | 7.3  | 7.7  | 10.3 | 12.3 |
| 60°C       | 7.1 | 7.5  | 7.5  | 7.5  | 7.6  | 7.6  | 7.8  | 10.8 | 12.4 |

Figure 4. The XRD pattern of used NCO
3.4. Catalytic performance of NCO in CWAO of refractory organics

NCO of 5 g/L was used in CWAO of HS and AL (Figure 5). TOC removal rates kept high level at low concentrations of TOC₀, while the rates decreased at high TOC₀. This should be attributed to the limited external O₂ supply (in the headspace of the vessels). In addition, with the increase of TOC₀, the quantity of organic carbon removed still increased. The possible reason might be that chemisorption was the rate-limiting step, and high concentration of organics enhanced the contact with NCO’s active sites. Further experiments were carried out at atmosphere pressure and continuous oxygen supply (Figure 6). TOC of BPA kept decreasing, while TOC of AL decreased at first 3h and then increased slightly. Such difference might be caused by the properties of AL and BPA, and the mechanism needs further investigation. Even so, these results exhibited the excellent catalytic performance of NCO in CWAO at mild conditions with TOC removal higher than 80% within 3 h.

![Figure 5. TOC removal after 3 h CWAO reaction of HS (A) and AL (B) with different initial concentrations](image)

![Figure 6. Kinetic tests in CWAO of AL and BPA at 90°C and pH 10 using NCO as the catalyst](image)

4. Conclusion

A novel catalyst with hierarchical structures, urchin-like NCO hollow microspheres, was proposed and applied in CWAO of organics. It can mineralize organics, and its crystal structure was stable after redox reaction. With NCO as the catalyst, CWAO of organics involved consecutive adsorption, surface oxidation, and re-oxidation of reduced NCO by O₂. NCO exhibited excellent catalytic performance of degrading refractory and toxic organics under mild conditions, and TOC removal rate exceeded 80% within 3 h. These results promised an easy and cheap method to clean the water or wastewater rich in refractory organic substances.
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