

Enhancement of Nitrite Oxidation by Heat-Treated Cobalt Phthalocyanine Supported on High Area Carbon

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Our ongoing effort is to develop efficient electrocatalysts and sensors for nitrite detection. Nitrite is one of the major components of wastewater from nuclear power production¹ and involved in the corrosion² and bacterial process known as the nitrogen cycle. It also plays important physiological roles in the form of NO, for example, as an intra- and intercellular messenger, a neurotransmitter, and an immune system mediator.³⁻⁵ The detection of nitrite, therefore, is important from an environmental and biological point of view.⁶ We have been utilizing transition-metal (particularly Fe and Co) phthalocyanines and porphyrins for this purpose as they often display catalytic activities toward many important electrochemical reactions such as oxygen reduction and CO oxidation.⁷ We found that iron phthalocyanine (FePc) is a very effective catalyst for nitrite reduction, undergoing structural changes on the surface as a function of the redox state.⁸⁻¹⁰

Since the discovery by Jahnke *et al.*¹¹ that the heat treatment of metal-N₄ systems under an inert atmosphere can ensure both catalytic activity and stability, much effort has been poured to elucidate the nature of catalysis. Now there seems to be a consensus that different catalyst structures result depending on the heat-treatment temperature, thus leading to different catalytic activities.¹²⁻¹⁶ For low and medium pyrolysis temperatures, the metal-N₄ moiety or its fragment of the macrocycles is responsible for the activity. With treatment at higher temperature, metal-N bonds are no longer found but rather metallic clusters surrounded by a graphite envelope are observed.

In this paper, we have extended our previous research on nitrite reduction with FePc and its μ -oxo dimer, (FePc)₂O to cover nitrite oxidation with CoPc this time. The changes in catalytic activity induced by heat-treatment at high temperatures (500-1000 °C) have been correlated with structural aspects monitored by XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure).

Experimental Section

Cobalt phthalocyanine was purchased from Aldrich and used without further purification. The adsorption of CoPc

was effected by adding 50 mg of carbon black (KB, EC600JD, 1360 m²·g⁻¹, Akzo Chemie, Japan) dispersed in 100 mL of methanol to the solution containing 20 mg of CoPc dispersed in 100 mL of methanol. The mixture was ultrasonicated for 5 min followed by 1 h of vigorous agitation. The carbon particles were filtered through Whatman No. 2 paper and washed with methanol until the filtered solution was colorless to ensure there was no non-adsorbed CoPc. The thus prepared CoPc/KB was dried under vacuum at 100 °C for 2 h.

Heat-treatment was done in a home-made tubular furnace under an N₂ flow in the range of 500 to 1000 °C with an interval of 100 °C. The temperature was raised at 10 °C·min⁻¹ from 200 °C to a set value and maintained there for 2 h. Then samples were left to cool down to room temperature under the N₂ stream.

A conventional electrochemical setup with a potentiostat (PGSTAT 30, Autolab, The Netherlands) and a three-electrode system (Ag|AgCl|KCl_(sat), reference and Pt counter electrodes) was used for electrochemical measurements. A small amount of heat-treated or untreated CoPc/KB powder was applied to the graphite rod whose surface was slightly recessed and this served as a working electrode. Unless otherwise stated, all the chemicals were of reagent grade and used without further purification. The nitrite oxidation was performed for 5 mM NaNO₂ solution prepared in 0.5 M sulfuric acid at room temperature.

XAFS data were collected at beam line 3C1 at PLS (Pohang Light Source), operating at 2.5 GeV with *ca.* 100-140 mA of stored current. A pair of Si(111) crystals was used as a monochromator. All the measurements were carried out in a transmission mode with ion chamber detectors filled with Ar and N₂.¹⁷ The higher harmonics contained in the incident beam were minimized by detuning the crystals by 20% of the maximum intensity, *I*₀. The near-edge region was scanned at equal energy steps of 0.30 eV per point to resolve fine structures. The EXAFS spectra were obtained at a constant wave vector *k*, of 0.05 Å⁻¹. The spectrum of an cobalt foil of three-absorption length was simultaneously measured with the sample spectra for energy calibration. 7709.0 eV was used as the energy reference, *E*₀. The primary XAFS data, Ln(*I*₀/*I*_i), were analyzed by WinXAS software.¹⁸

Results and Discussion

Panel in Figure 1 shows a series of voltammograms of CoPc/KB and corresponding nitrite oxidation at different heat-treatment temperatures. When not heat-treated, CoPc/KB showed a reversible redox peak at 0.8 V. This is ascribed to the one-electron process involving cobalt metal ion, $[\text{Co(III)Pc(-2)}]^- + e^- \rightleftharpoons \text{Co(II)Pc(-2)}$. A large cathodic peak at 0.25 V is not due to the CoPc reduction, but rather to the functional groups present at the high area carbon surface. Upon heat-treatment, these peaks disappeared, suggesting structural alteration has been occurred. It seemed that the phthalocyanine structure was lost determined from the voltammogram even at 500 °C. However, XAFS revealed the Pc structure was maintained at even higher temperatures (see below).

Panel B shows the nitrite oxidation by heat-treated CoPc. Since nitrite undergoes disproportionation reaction in acidic conditions, it is NO that actually is oxidized: $3\text{HONO} \rightleftharpoons \text{NO}_3^- + 2\text{NO} + \text{H}_2\text{O} - \text{H}^+$. From the voltammogram a, $[\text{Co(III)Pc(-2)}]^-$ catalyzes the NO oxidation, which proceeds irreversibly. Heat-treatment temperature greatly affects the NO oxidation. For a quantitative comparison, we expressed the catalytic activity in terms of a current ratio, I_F/I_C with heat-treatment temperature, where I_F is the faradaic current due to the nitrite oxidation and I_C the charging current. Since the amount of catalyst was different for each measurement, this current ratio was again normalized against that of untreated catalyst, $(I_F/I_C)_T/(I_F/I_C)_{\text{untreated}}$ (Table 1). Figure 2 is the plot of the normalized catalyst activity expressed in this

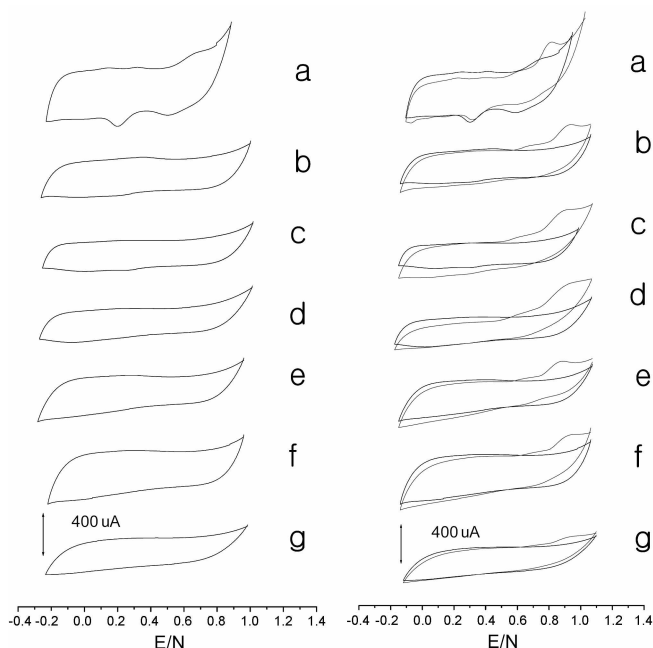


Figure 1. Cyclic voltammograms of CoPc/KB (panel A) and corresponding NO oxidation (panel B) in 0.5 M H_2SO_4 at different temperatures: (a) unheat-treated, (b) to (g) are heat-treated at 500 °C to 1000 °C with 100 °C interval, respectively. Scan rate = 10 $\text{mV}\cdot\text{s}^{-1}$; $[\text{NO}_2^-] = 5 \text{ mM}$.

Table 1. Normalized catalytic activities expressed by current ration with respect to that of unheat-treated CoPc/KB

T (°C)	$(I_F/I_C)_T^a$	$(I_F/I_C)_T/(I_F/I_C)_{\text{untreated}}$
Untreated	0.85	1.0
500	0.94	1.1
600	1.5	1.7
700	1.6	1.9
800	0.72	0.85
900	0.58	0.68
1000	0.43	0.51

^aThe ratio of faradaic current (I_F) due to the NO oxidation and charging current (I_C) at different temperatures obtained from panel A in Figure 1.

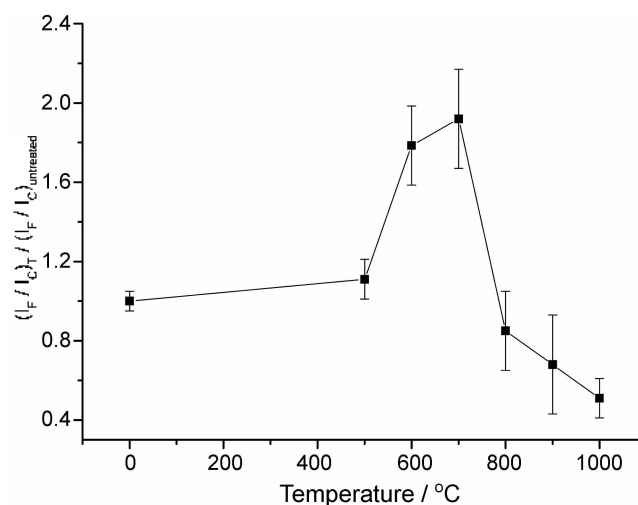


Figure 2. Normalized activity for the NO oxidation by heat-treated CoPc/KB with respect to that of unheat-treated CoPc as a function of heat-treatment temperature. 0 °C means unheat-treatment. I_F , I_C are faradaic current due to nitrite oxidation and charging current, respectively.

way vs heat-treatment temperature. The catalyst activity gradually increased with temperature reaching the maximum value at 700 °C and then rapidly decreased beyond this temperature. The activity at 1000 °C is only half that of untreated sample. It should be noted here that heat-treated CoPc only catalyzes nitrite oxidation, not nitrite reduction. This result is quite opposite to the FePc and $(\text{FePc})_2\text{O}$ cases in which nitrite reduction is catalyzed by heat-treated FePc and $(\text{FePc})_2\text{O}$.¹⁹

Detailed knowledge can be obtained by analyzing the local structure around a cobalt atom by XANES and EXAFS measurements (Figs. 3 and 4). XANES of untreated CoPc (Fig. 3a) shows several fine structures. A distinctive shoulder peak at 7715.4 eV is characteristic of phthalocyanine ring structure and known to be due to the dipole-allowed $1s \rightarrow 4p_z$ transition. A small pre-edge peak at 7709.4 eV is $1s \rightarrow 3d$ transition, known as a dipole-forbidden but quadrupole-allowed transition the orbital mixing. This feature was maintained until heat-treatment up to 700 °C though intensity became smaller, indicating that Co- N_p (N_p is the pyrrole nitrogen) structure is not completely destroyed.

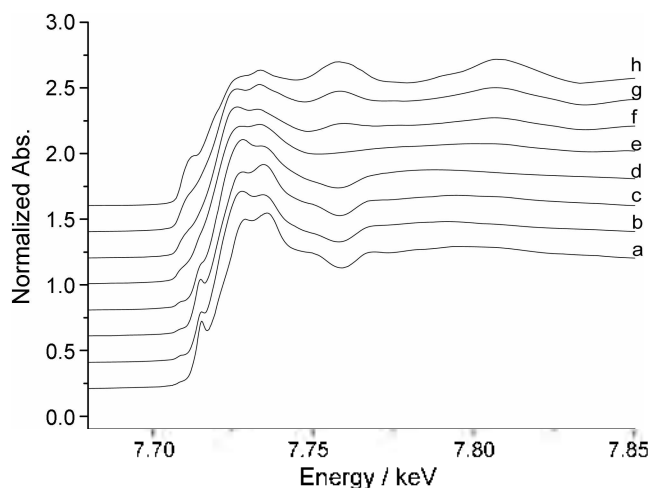


Figure 3. Normalized XANES spectra for unheat-treated CoPc/KB (a) and heat-treated at 500 (b), 600 (c), 700 (d), 800 (e), 900 (f), and 1000 °C (g). (h) is XANES of cobalt foil.

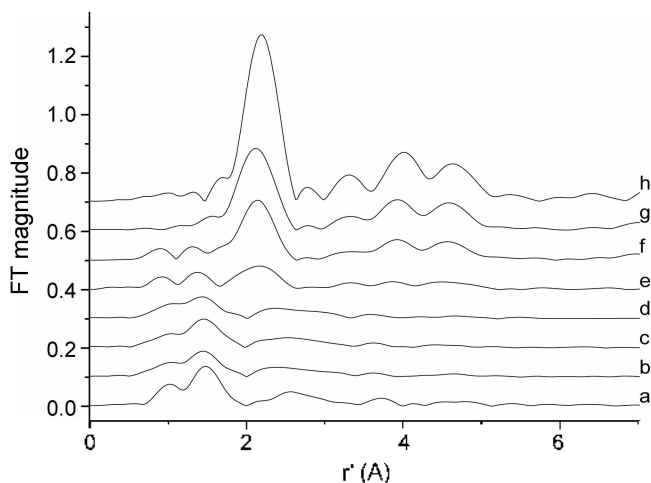


Figure 4. Fourier transformed spectra for unheat-treated CoPc/KB (a) and heat-treated at 500 (b), 600 (c), 700 (d), 800 (e), 900 (f), and 1000 °C (g). (h) is FT of cobalt foil.

Above approximately 800 °C, this Pc structure disappears and new fine structures belonging to metallic cobalt begin to emerge. XANES at 1000 °C (curve g) quite resembles that of metallic Co (curve h). This indicates that heat-treatment at high temperature causes the decomposition of Co-N₄ to metallic Co. The similar phenomenon was observed in cobalt porphyrin and iron phthalocyanine.^{20,21}

Detailed structural information can be obtained from Fourier transformed spectra of EXAFS (Figure 4). Well-defined Co-N_p and Co-C_α (C_α is carbon bonded to N_p) shells at 1.46 and 2.56 Å respectively (before phase-shift correction) were observed for the untreated CoPc (curve a), indicating adsorption itself did not induce structural alteration. Upon heat-treatment, a peak due to Co-C_α scattering rapidly disappeared since this is the second shell in the Pc ring and thus quite vulnerable to change. Although Co-N_p structure was pretty much maintained up to 700 °C, intensity

was weakened implying that the coordination number is less than 4. This means that the Co-N₄ structure is not an absolute requisite for the catalytic activity. While only Co-N₄ structure is responsible for the untreated sample, both Co-N_x and other effect play roles in exhibiting high catalytic activities. From 800 °C, a new peak began to grow at *ca.* 2.19 Å at the expense of the magnitude of Co-N₄ shell. With reference to Co foil, this new peak was assigned to the Co-Co shell. As heat-treatment temperature goes higher, this peak becomes more prominent and the catalytic activity rapidly decreased accordingly even below that of untreated CoPc. This can be attributed to the formation of larger cobalt metal clusters. It is well known that the sintering effect of heat-treatment at higher temperatures leads to the larger metallic particles. According to Tourillon *et al.*,²⁰ larger metallic clusters lose catalytic activities for the oxygen reduction. The same argument may apply to the nitrite case. Although it is not possible to estimate the exact size of the clusters, the coordination numbers could be estimated from the relative FT magnitude of the first Co-Co shell by comparing it with that of cobalt foil. The coordination number increased from 2.0 at 800 °C to 6.0 at 1000 °C, indicating that more metallic character appeared when treated at higher temperature.

In this paper, we have shown that the higher catalytic activity of heat-treated CoPc toward the nitrite oxidation comes from both Co-N_x structure and highly dispersed cobalt metal ion characteristics. This result can be compared with FePc case in which the Fe-N_x structure existed even after heat-treatment at 1000 °C. However, almost entire CoPc molecules were converted to metallic Co. Therefore, the best electrocatalyst could be prepared by any means to give Co-N_x characteristics and high degree of dispersion of Co metal atoms.

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