Catalytic Oxidation of Thiol Compounds by Novel Fuel Cell-inspired Co-Porphyrin and Co-Imidazole Catalysts

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Abstract. The catalytic performance of pyrolyzed carbon-supported cobalt-nitrogen donor (CoN_4) catalysts for the oxidation of thiol compounds by dioxygen in aqueous solution was studied. This paper continues our previous line of research, which was inspired by the electrocatalytic reduction of oxygen on pyrolyzed carbonsupported cobalt-porphyrins and related tetra-coordinated nitrogen donor-transition metal complexes (MeN₄, where Me stands for a transition metal atom). Both pyrolyzed carbon-supported Co-imidazole and Co-porphyrin exhibited fast catalytic oxidation of the different thiols. The rate of oxidation of different thiols on the pyrolyzed CoN_4 catalysts was compared to the homogeneous rate of oxidation using 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin Co(II) tetrasodium salt as catalyst. Based on the cobalt content, the heterogeneous catalysts always outperformed the homogeneous one, and at times even exhibited 4,100-fold better catalysis. The dependence of the catalytic rate of oxidation on the preparation temperature was investigated, showing an optimal catalysis at ~ 650 °C for the cobalt-imidazole catalyst. The decrease in catalytic performance after heat treatment at elevated temperature was attributed to the formation of cobalt metal acting as a generator of carbon nanotubes.

INTRODUCTION

Metal-porphyrin catalysis is one of the outstanding success stories of biomimetic chemistry. P450 monooxygenases, heme protein–oxygen-binding mimics, and peroxidase and catalase emulations are only a few of the possibilities that were opened with the evolution of porphyrin and phthalocyanine chemistry.^{1–3} One of the earliest and most active scientific activities involved the ability of metaloporphyrins to bind dioxygen and by way of superoxo-metal-porphyrin complexes (Por-Me-OO⁻) to activate the otherwise inactive triplet oxygen. This process can end by formation of either potent short-lived hydroxyl and other oxo radicals, or by less aggressive oxo and peroxo moieties that can function as monooxygenases for epoxidation, hydroxylation, and other fine chemistry catalyses.

From its early inception, the fuel cell industry⁴ realized that the high affinity of oxygen to metaloporphyrins and other metalo-tetrapyrrols can be utilized to promote oxygen electroreduction. Carbon-adsorbed metal-porphyrins reduced the oxygen reduction overpotential by several hundred millivolts compared to blank carbon electrodes. However, the vulnerability of tetrapyrroles to free radical attack-at least relative to the demanding requirements of the energy industry-hindered dissemination of the technology. The situation started to change with the discovery that pyrolyzed carbon powder-supported cobalt-porphyrin maintains the excellent electrocatalytic reduction of dioxygen.^{5,6} This came as a surprise to many in the industry since there was never any doubt that the tetrapyrrole structure was destroyed during the pyrolysis step. Still, electrocatalysis was preserved even after over 900 °C heat treatment, while the catalyst's susceptibility to free radical and hydrogen peroxide attacks was practically eliminated. Jasinsky's electrocatalyst soon found practical applications for *Author to whom correspondence should be addressed. E-mail: ovadia@vms.huji.ac.il

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mobile vehicles and electrical appliances.7 However, despite the favorable oxygen reduction characteristics of the pyrolyzed carbon-supported cobalt-porphyrin electrodes, their penetration into the main stream of the fuel cell industry was slowed down by the prohibitively high costs of porphyrins and phthalocyanines. Several approaches were devised to replace the metal porphyrins by less expensive nitrogen donors. Holoporphyrins and holophthalocyanines and then nitrogen-donor polymers such as polypyrrole and polyacrylonitrile were investigated as electrode donors in place of the costly porphyrins.8-10 Next, it was demonstrated that the performance of the pyrolyzed carbon-supported forms of common, low molecular and inexpensive nitrogen donors were comparable to the performance of the carbon-supported metal-porphyrins.¹¹ Interestingly, even simple and relatively cheap nitrogen donors such as pyrrole, imidazole, and their methylated forms were proven valuable for oxygen electroreduction in acidic media. However, one has to admit that the success of these catalysts is still limited, probably since they tend to electrocatalyze the first 2-electron reduction of oxygen to hydrogen peroxide better than the following step involving the reduction of hydrogen peroxide to water. Thus, a buildup of hydrogen peroxide in the electrolyte and less than 4-electron exploitation of the dioxygen are observed, which limit further progress in this field.

Despite the proven success of the cobalt-porphyrins in the activation of triplet oxygen, this ability was never transferred to the chemical catalysis arena, although conceptually they share the same target-the utilization of the high oxidation potential of the conversion of triplet dioxygen to water. In our first publications on the subject we have demonstrated that pyrolyzed carbonsupported cobalt-porphyrins and their mimics are not limited to electrocatalysis and can indeed exhibit nonelectrochemical (environmental) catalysis as well. We have demonstrated that the catalysts catalyze the oxidation of hydrogen sulfide by dissolved dioxygen in aqueous media. The catalyst outperformed other granular and catalytic activated-carbon powders that are widely used for air and water dehydrosulfurization, and also performed better than dissolved and carbon-adsorbed cobalt-porphyrin that did not undergo the pyrolysis step. We then showed that pyrolysis of carbon powder impregnated with imidazole and cobalt(II) acetate provides a catalyst with equal, and at times superior, catalytic performance for hydrogen sulfide oxidation compared to the pyrolyzed cobalt porphyrin.

It was found that the cobalt-porphyrin and cobaltimidazole catalysts share much in common. Notably, the active sites of the two types of pyrolyzed catalysts are very similar, and optimal catalytic performance of the Co-imidazole catalyst occurs for Co:imidazole ratio = 1:2, corresponding to a 1:4 Co:N ratio, similar to the Co:N ratio of Co-porphyrin. However, there were also some differences between the two types of catalysts, the most significant one being the optimal pyrolysis temperature. The best performance was obtained after 880 °C treatment for the cobalt-porphyrin, while the cobalt-imidazole catalyst started to lose activity already after 760 °C treatment. The primary task of the current study was to expand the scope of catalytic activities of two model MeN₄-based catalysts, cobalt-imidazole and cobalt-porphyrin, and to examine their performance for the oxidation of different mercaptans by dissolved oxygen under aqueous, room-temperature conditions.

The removal of mercaptans and other sulfur compounds is an important environmental reaction due to the abundance of thiols that are inevitably byproducts of virtually all anaerobic wastewater treatments, with their volatility and malodor.^{14,15} The desulfurization of fuels is also continuing to be of major concern in oil refineries.16 Cobalt-phthalocyanines were introduced in the sixties for the oxidation of sulfur-rich fuels, and different variants of the process were commercialized.^{17,18} More recently, several processes for the oxidation of mercaptan compounds on copper(I) complexes were proposed by Bagiyan et al.^{17,19} The homogeneous oxidation of thiols by molecular oxygen without added catalysts (also called self-oxidation) has been amply studied, mostly in connection with protein chemistry and biology.^{20,21}

EXPERIMENTAL

Materials

Diphenyldisulfide (≥95%) was synthesized from benzenethiol according to the solvent-free permanganate oxidation procedure. Sodium sulfide hydrate was purchased from Merck (Darmstadt, Germany). Dibasic ammonium phosphate, N,Ndimethyl-p-phenylenediamine hemioxalate and 3,5-dinitrobenzoic acid (DNBA) were from Sigma (Milwaukee, WI, USA). Imidazole, heptanethiol, dodecanethiol, 2-aminothiophenol (cysteamine), L-cysteine, p-chlorobenzenethiol, 2,2'dithiobis(5-nitropyridine) (DTNP), and tetrabutylammonium hydrogen sulfate (TBAHS) were from Aldrich (Milwaukee, WI, USA). Thiosalicylic acid was from Fluka (Taiwan) and p-thiocresol was from Fluka. Naphthalene and iron (III) chloride anhydrous were from BDH (Poole, England). Sulfuric acid (98%), hydrochloric acid (37%), phosphoric acid (85%), methanol, ethanol, acetonitrile, dichloromethane, and sodium hydrogen phosphate were from J.T. Baker (Deventer, Holland). Sodium dihydrogen phosphate and sodium acetate anhydrous were from Mallinckrodt (Phillipsburg NJ, USA). Benzenethiol and Co(II) acetate tetrahydrate were from AC-ROS. Co(II) mesotetra-4-methoxy-phenylporphyrin (CoMT-MPP) was donated by Frontier Scientific Advanced Discovery Chemicals. 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin Co(II) tetrasodium salt (CoTSPP) was purchased from Porphyrin Systems (Lübeck, Germany).

Acetylene black (AB50%, also named Shawinigan Black) was purchased from Chevron Phillips Chemical Company. All chemicals were of analytical grade and were used as received unless otherwise stated. We used deionized water (conductivity < 0.1 mS/cm) purified by a Seradest SD 2000 system.

Analytical Procedures

Some analytical procedures were described in our previous articles.12,13 Hydrogen sulfide was analyzed according to a Standard Methods protocol using the 4500-S²⁻ D procedure. Nonvolatile thiols (cysteamine, thiosalicylic acid, and L-cysteine) were determined by a method based on Vairavamurthy and Mopper's procedure of derivatization with DTNP, followed by reversed phase HPLC separation. We used a Thermoquest HPLC equipped with uv600lp PDA detector operated at 390 nm for quantification of the thiols and at 250 nm for the determination of the internal standard. The separation was conducted on a C-18 SYNERGI Hydro-RP 80A 250 mm × 4.6 mm, 4 µm column using as eluant a gradient of acetonitrile and aqueous solution containing 7.5 mM TBAHS and 0.05 M sodium acetate at pH 3.5. Volatile thiols (benzenethiol, p-chlorobenzenethiol, p-thiocresol, heptanethiol, dodecanethiol) and diphenyldisulfide were determined by GC/MS using Agilent GC 6890N with MS 5973N, as detailed below.

GC/MS analysis

A 125-mL sample was spiked with 100 μ L of 6.25 mM naphthalene in methanol as internal standard and extracted with 5 + 3 + 3 mL of dichloromethane. A 2- μ L aliquot of the extract was injected to the GC/MS using J&W-DB1, 60 m, i.d. 0.32 mm, 0.25 μ m column. When needed, extracts were stored in brown glass vials for up to a week in a 4 °C refrigerator to prevent further oxidation of the residual thiols. Typically, the following temperature program was used: 10 min at 100 °C, 10 °C/min T gradient, and finally 17 min at 250 °C. Other GC conditions: Inlet, T = 200 °C; solvent delay, 11 min; He flow, 1.5 mL/min.

Electrochemistry and microscopy

Cyclic voltammetry was carried out using a PARC 263 potentiostat/galvanostat (EG&G, Princeton, NJ, USA). We used a conventional three-electrode cell with a 3-mm i.d. carbon paste working electrode, Pt counter, and KCl satd Ag/AgCl reference. All tests were carried out in 0.5 M sulfuric acid solution. The carbon paste electrodes were prepared by mixing 100 mg of catalyst-loaded carbon powder with 30 mg mineral oil (Aldrich) and loading the paste into a 3-mm-diameter glass tube. All potentials are reported versus KCl satd Ag/AgCl reference. Scanning electron microscope imaging was performed by JEOL JXA-8600 Superprobe.

Preparation of cobalt-imidazole modified catalysts

The preparation conditions of the pyrolyzed cobalt-porphyrin catalysts were identical to those used in our previous study.¹³ Briefly, set quantities of cobalt acetate and imidazole were dissolved in 50 mL of ethanol, and then 1 g of carbon was added to obtain a suspension. The suspension was sonicated for 10 min for better homogenization. The suspension was dried by rotary evaporator. The catalysts were heated in vacuumed quartz ampoules for 4 h at $T_1 = 360$ °C and then for an additional 4 h at the specified temperature ($T_2 = 760$ °C unless otherwise specified). The catalysts were immersed in the appropriate buffer for at least 2 h before usage.

Preparation of cobalt-porphyrin modified catalysts

The preparation conditions of the pyrolyzed cobalt-porphyrin catalysts were identical to those used in our previous study.¹² Briefly, 100 mg of CoMTMPP was dissolved in 50 mL of CH_2Cl_2 , and then 1 g of carbon was added to obtain a suspension. The suspension was sonicated for 10 min for better homogenization and then dried by rotary evaporator. The catalysts were heated for 5 h at the specified temperature (880 °C unless otherwise specified) in a flow of 99.999% pure nitrogen. The catalysts were immersed in the appropriate buffer for at least 12 h before usage.

Oxidation of Thiols

Pyrolyzed carbon-supported cobalt-imidazole and cobaltporphyrin catalysts

125 mL of 0.01 mM thiol solutions were prepared in dark bottles from air-saturated distilled water (containing 8.0 mg/L dissolved oxygen). The solutions were kept at pH 7.0 by 0.02 M phosphate buffer, unless otherwise specified. To these solutions we added 12 µg of modified Co-imidazole catalyst or 57 µg of Co-porphyrin catalyst, suspended in buffer. 100 µL of 6.25 mM naphthalene in methanol was added as internal standard. The bottles were stoppered and left to react with magnetic stirring at ambient temperature (usually 23 ± 2 °C). After a set reaction period the solutions were quickly filtered through 0.2-mm glass filters of Whatman GF/B (Maidstone, England) to remove the carbon catalyst, extracted with 5 + 3 + 33 mL of dichloromethane, and analyzed by GC/MS. In order to avoid catalyst loss or hydrogen sulfide evaporation during sampling, each test was conducted using a dedicated bottle, which was used for a single analysis only.

Homogeneous Co-porphyrin catalysis

The oxidation of different thiols by CoTSPP was conducted under similar conditions, in all cases using 73 μ g of cobalt-porphyrin dissolved in buffer.

RESULTS

The first round of tests included kinetic oxidation tests that were conducted for the set of thiol compounds listed in Table 1, in order to determine the dominant substrate-dependent rate law and the relevant rate constants. This initial study was not meant to give a comprehensive account of the reaction rate at a large parametric range; it was merely used to provide a basis for comparison and ranking of the individual rate constants and to allow a comparison to the rate constants of homogeneous cobalt-porphyrin catalysis. All the tests were conducted under identical starting conditions: 0.02 M phosphate buffer, pH 7, 0.01 mM thiol, and 8 mg/L

Table 1

Kinetics of the catalytic conversion of thiol compounds by dioxygen on pyrolyzed carbon-supported cobalt-imidazole, pyrolyzed carbon-supported cobalt-porphyrin (CoTSPP), and homogeneous catalysis by the water-soluble Co-porphyrin (CoTSPP). All rate constants are based on the cobalt content (i.e., normalized to 1 μ g Co/L) of the catalysts and measured in min⁻¹ (μ g Co/L)⁻¹

compound name	molecular formula	k _{Co-imidazole}	k _{CoMTMP}	k _{CoTSPP}	pKa _{sH} *	k _{Co-imidazole}	k _{CoMTMP}
						k _{CoMTMP}	k _{CoTSPP}
hydrogen sulfide	H_2S	0.0016	0.0025	_	7.0	0.6	_
benzenethiol	C_6H_5SH	0.027	0.049	0.0023	6.6	0.6	22
p-chlorobenzenethiol	p-ClC ₆ H ₄ SH	0.026	0.034	0.0062	6.1	0.8	6
<i>p</i> -thiocresol	p-CH ₃ C ₆ H ₄ SH	0.027	0.033	0.0045	6.8	0.8	7
heptanethiol	$C_7H_{15}SH$	0.017	0.014	0.0062	10.8	1.2	2
dodecanethiol	$C_{12}H_{25}SH$	0.013	0.0050	0.0014	10.6	2.5	3
2-aminoethanthiol	HSCH ₂ CH ₂ NH ₂	0.020	0.019	0.00048	10.5	1.0	40
thiosalicylic acid	HSC ₆ H ₄ COOH	0.014	0.031	0.00030	8.9	0.5	103
L-cysteine	HSCH ₂ CHNH ₂ COOH	0.015	0.0064	0.000001	6 11.5	2.4	4100

*pKa_{SH} values correspond to the proton dissociation constants of the thiol groups.



Fig. 1. (a) Time trace of the oxidation of different thiol compounds by dissolved oxygen on pyrolyzed carbon-supported Co-imidazole catalyst. (b) Logarithmic form of the time traces. (0.02 M phosphate buffer, pH 7; initial concentration of dissolved oxygen, 8 mg/L; initial concentration of the different thiols = 0.01 mM; 96 μ g/L catalyst.) Legend: 1—benzenethiol, 2—2-aminoethanethiol (cysteamine), 3—thiosalicylic acid, 4—diphenyldisulfide.

oxygen. Figure 1 demonstrates that, at least for the low concentration range addressed in the current studies, the time trace of the conversion of the different thiols followed a first-order rate law with respect to the different substrates. It is indeed plausible that at higher reactant

concentrations a Dean–Hinshelwood or more complex kinetics may prevail, but this was not searched for in the current phase of this study. In all cases, the oxidation rate constants of the different thiols by dioxygen, in the absence of the catalysts, were negligible compared to the much higher rate of reaction in the presence of either cobalt–porphyrin or pyrolyzed cobalt-imidazole catalysts.

The fact that the kinetics of disappearance of the different thiols followed a first-order rate law allowed direct comparison between the rate constants for the oxidation of the different thiols on the different catalysts. Figure 2 and Table 1 detail the observed reaction kinetics (based on pH 7 and 8 mg/L oxygen) for the homogeneous cobalt-porphyrin and the two heterogeneous MeN₄ catalysts.

Table 1 (right column) demonstrates that in all cases the heterogeneous catalysts outperformed the homogeneous catalysis of thiols. The difference in performance is quite substantial and at times, e.g., for thiosalicylic acid, for the heterogeneous catalysts we observed as much as 100-fold faster heterogeneous catalysis compared to the homogeneous catalysts, and for L-cysteine a 4,100-fold increase was observed. The two types of pyrolyzed MeN₄ behaved somewhat differently and exhibited a different degree of catalysis for different thiols. However, linear correlation of the two catalysts exhibited a significant linear dependence (correlation coefficient, $R^2 = 0.81$) between the *k*-values for the oxidation of the different thiols on the two catalysts.



Fig. 2. (a) Comparison of the catalytic performance of homogeneous cobalt-porphyrin, CoTSPP (blank bars), and pyrolyzed carbon-supported cobalt-porphyrin, CoMTMPP (striped bars) and cobalt-imidazole catalysts (dotted bars). For comparison, the rate constants were normalized by the cobalt content in the different catalysts. (b) A correlation between the relative efficiencies of the Co-imidazole and CoMTMPP catalysts.

Figure 2b shows that when the absolute catalysis was large, then the CoMTMPP exhibited better catalysis, and for the more refractive thiols the Co-imidazole catalyst exhibited better performance. This, in fact, is an encouraging observation, showing that the much cheaper Co-imidazole catalyst exhibits competitive performance, and more so when the catalysis is slow. For simplicity, the abscissa of Fig. 2b delineates the catalytic rate for CoMTMPP, but a very similar curve was obtained when the *x*-coordinate delineated the average of CoMTMPP and Co-imidazole rates.

The most pronounced catalysis was observed for the aryl compounds (benzenethiol, chlorobenzenethiol, and thiocresol), though the internal pecking order amongst the aryls followed neither the electrophilicity of the thiols nor their dissociated fraction. The good chelating agents, aminothiols and thiosalicylic acid, also exhibited rather fast reaction rates, which are ascribed to the bidentate coordination of the active cobalt center. Bagiyan et al.¹⁹ observed a similarly high reaction rate of aminothiols on copper catalysts and attributed the improved catalysis to the bidentate chelating ability of these ligands. The alkylthiols exhibited the poorest im-

provement in catalysis by the pyrolysis step, which is at least partly explained by the very high pKa's of these compounds, which implies that only a negligible fraction of these compounds is present in the active deprotonated form at pH 7.

pH Effects

In order to clarify the influence of the pH on the catalytic conversion rate, we investigated the pH dependence of the rate constant of several thio-compounds. The rate constants of benzenethiol, cysteamine, and thiosalicylic acid are depicted in Fig. 3 as a function of the pH of the solution. The figure demonstrates three different behaviors. Benzenethiol's rate of conversion is almost constant up to $pH \sim 7-8$, and then the rate is gradually increased. The threshold of the kinetic increase coincides with the pKa of the benzenethiol (pH 6.6, see Table 1, column 6). The kinetic coefficient of the thiosalicylic acid was indifferent to the pH level, regardless of the pH "distance" to the pKa values of the thiosalicylic acid. Note that $pKa_{,1}$, corresponding to the deprotonation of the carboxyl group = 3.5, and pKa₂, corresponding to the deprotonation of the thiol = 8.9.

Similar indifference of oxidation kinetics of strong chelating agents to pH change was also noted by Bagiyan et al.¹⁹ The kinetics of the conversion of cysteamine (Fig. 3, curve 2) followed bell-shape dependence, with an optimal rate around pH 8. A similar dependence was noted by Bagiyan et al. for copper complexes and other catalysts.^{19,20} The peak performance coincides with the dissociation constant (pKa 7.9) of the amino group. Presumably the lower affinity of the ammonium moiety compared to the deprotonated amino coordinating group is responsible for lower binding of the thiol to the CoN₄ centers, which reduces the rate constants as the pH is lowered below the pKa of the amino group.

For the weak chelating agents (aromatic and alkyl thiols), the change in catalytic activity is associated with the deprotonation of the thiol and formation of the thiolate anion. Formation of the negatively charged thiolates accelerates the rate of the reaction, probably due to increased association with the CoN4 center. Similar observations were indeed reported for the homogeneous oxidation of alkylthiols on Co-porphyrin²⁵ as well as for the homogeneous and heterogeneous catalytic oxidation of alkylthiols.^{17,20} The bell-shape dependence of the oxidation rate of the aminothiol compounds on the pH was previously reported by Bagiyan et al.,²⁰ and it was attributed to the chelation of transition metal impurities by the different aminothiols. The authors noted that the maximal activity cannot be explained by the pKa's of the aminothiols. Presumably the chelation ability of the thiosalycilic acid is so strong that it does not constitute a rate-determining step, and therefore a pH change does not influence the observed kinetics.

Identification of the Oxidation Products

GC/MS and ESI/MS analyses of the oxidation products of the different thiols on pyrolyzed carbon-supported Co-imidazole catalysts at pH 7 revealed that in all cases the primary oxidation product was the disulfide form, RSSR. Only for the benzenethiol we noticed that at high pH (>8.5) there is a significant deviation from mass balance, and diphenyldisulfide is not the sole product. However, we were unable to identify the missing oxidation product. Comparison of the HPLC chromatogram of the products with the retention time of benzenesulfonic acid reference material precluded the possibility that this is the missing reaction product. Negative mode ESI/MS also precluded the formation of benzenesulfinic acid.

Dependence of the Catalytic Performance on the Pyrolysis Temperature of the Co-Imidazole Catalyst

In our previous publications on the pyrolyzed MeN₄ catalysts^{12,13} we have noted that the catalytic performance is optimal after 880 °C treatment for Co-porphyrin and after 760 °C for the cobalt-imidazole catalysts. It was interesting to compare the catalytic performance with regard to the thiol oxidation with the catalytic rates for conversion of hydrogen sulfide on the same pyrolyzed carbon-supported MeN₄ catalyst. Figure 4 provides such a comparison. The figure shows that there is a good qualitative correlation between the observed rate constants for hydrogen sulfide conversion (curve 3 in the upper frame) and for the conversion of benzenethiol (curve 2, right axis). Consistent with our prior knowledge about the oxidation of hydrogen sulfide, the catalyst exhibited an optimal catalytic performance after heat treatment at intermediate temperatures (~650 °C) for benzenethiol (curve 2) and ~760 °C for hydrogen sulfide (curve 1). Interestingly, the temperature dependence is more pronounced for the benzenethiol conversion compared to the hydrogen sulfide. To complete the comparison we have included in Fig. 4 a curve delineating the electrocatalytic performance, i.e., dependence of the half wave potential for oxygen electroreduction on pyrolyzed carbon-supported cobalt-imidazole carbon paste electrode. In this curve, lower oxidation potential is a manifestation of better catalysis. The bold curve delineating $E_{1/2}$ dependence on the heat treatment tempera-



Fig. 3. First-order kinetic coefficients for the oxidation of 1—benzenethiol, 2—2-aminoethanthiol (cysteamine), and 3—thiosalicylic acid by air oxygen with pyrolyzed carbon-supported cobalt-imidazole catalyst as a function of pH.

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Fig. 4. (a) Catalytic performance of heat-treated cobalt-imidazole (curves 1, 2) and cobalt-porphyrin catalysts (curve 3). The curves depict the observed kinetic coefficient in $[\min^{-1}(\mu g \text{ Co/L})^{-1}]$ calculated based on 8 mg/L oxygen as a function of the heat treatment temperature for hydrogen sulfide (curves 1 and 3) and benzenethiol oxidation (curve 2). (b) Electrocatalytic performance of heat-treated cobalt-imidazole (curve 1) and cobalt-porphyrin (curve 2) catalysts. The curves depict the dependence of the half wave potential, (E1/2 vs. Ag/AgCl, satd reference) for O₂ electroreduction on the heat treatment temperature.

ture goes through a shallow maximum at around 600 °C, similar to the catalytic performance curves, though the electrocatalysis curve is even less steep than for the hydrogen sulfide catalysis. The comparison between the curves indicates that the electrocatalytic and catalytic mechanisms are somewhat different, which came as no surprise. But the overall tendency is maintained. The performance of both electrocatalysts is improved for higher pyrolysis temperature.

SEM Analysis

The temperature dependence of the rate constants for the hydrogen sulfide oxidation as well as for benzenethiol electrooxidation (curves 1 and 2 in Fig. 4) differed from the temperature dependence of the cobalt porphyrin catalysts (curve 3). The optimal temperature for the pyrolysis of the cobalt-porphyrin was much higher compared to the cobalt-imidazole catalysts. A similar tendency was observed for the electrocatalytic behavior.^{12,13} In order to examine the reason for the different behavior of the two different MeN₄ catalysts we examined the surface morphology of the catalysts by electron microscopy. Figure 5a-d depicts the SEM micrographs of Coimidazole catalysts that were prepared at different temperatures. While the morphology of the 360 and 465 °C catalysts is very similar, the morphology of the catalysts changes dramatically above 760 °C. Starting at 760 °C we witness the evolution of carbon nanotubes, and at even higher temperature the carbon nanotubes become more abundant and practically cover the whole catalyst. Close examination of Fig. 5c,d shows that at the base of each carbon nanotube there is a bright spot. We attribute the bright spots to melted cobalt metal dots, which serve as catalyst for the pyrolysis of the organic substrate (imidazole and its degradation products) and nanotube growth from this center. In contrast, Fig. 5e, which depicts the morphology of the cobalt-porphyrin catalyst, does not contain any nanotube, although this catalyst was prepared at 880 °C. Apparently, the Co-imidazole catalyst loses its active Co sites at high temperature,



Fig. 5. SEM micrographs of pyrolyzed carbon-supported cobalt-imidazole catalysts prepared at (a) 360 °C, (b) 465 °C, (c) 760 °C, (d) 1020 °C, and (e) cobalt-porphyrin catalyst prepared at 880 °C. Accelerating voltage = 5.0 keV (b, e) and 15 keV(a, c, d).

some of the cobalt is melted, and it serves as a catalytic site for the conversion of the imidazole to carbon. The cobalt centers in the heat-treated Co-porphyrin are better ligated, which elevates the melting temperature. Additionally, the lower volatility of the tetrapyrrole does not support evaporation and nanotube formation.

Repeatability Studies

We have carried out stability tests in order to elucidate the stability of the catalysts under prolonged usage. The repeatability studies were carried out by repeated introduction of 0.01 mM thiosalicylic acid to a phosphate-buffered solution held at pH 7.0. At the beginning of the test, 0.43 mg/L of pyrolyzed carbon-supported CoMTMPP catalyst was added. Two hours after the introduction of the thiosalicylic acid its concentration was measured, and the oxygen was bubbled for 15 min. Then, another round of thiol oxidation starting with 0.01 mM thiosalicylic acid dosing and its catalytic removal was initiated. We did not notice any degradation of the catalyst performance after 15 repeated tests, which correspond to ~660 thiol–disulfide turnovers (based on Co loading). The repeatability tests are shown in Fig. 6.

Some Mechanistic Aspects

The catalysis of thiol oxidation by transition metals or by metal-porphyrins often proceeds through a complex mechanism involving the generation of active oxo radicals or hydrogen peroxide. Hydrogen peroxide is an (undesirable) byproduct of oxygen electroreduction on pyrolyzed, as well as non-pyrolyzed metal-porphyrinmodified electrodes. In order to explore the possibility that the catalytic oxidation of thiols on pyrolyzed carbon-supported cobalt-imidazole involves a free radical mechanism, we compared the benezenthiol catalytic oxidation rate with and without the additions of 0.1 M KI or 0.1 M NH₃, keeping the constant pH 7 conditions. Iodide was reported to inhibit radical chain reactions, while ammonia accelerates free radical reactions.19 However, the observed rate of reaction remained practically unaltered, within our experimental error, by the presence of these catalytic effectors. Similarly, our attempt to detect traces of hydrogen peroxide during the catalytic oxidation of benzenethiol by the Enhanced ChemoLuminescence (ECL) using the luminol and HRP procedure, detailed in ref 26 was unsuccessful. Other observations that were already detailed above also support the conclusion that the reaction does not involve free radical formation. First, radical chain reactions invariably result in nonlinear concentration dependence, whereas Fig. 1 shows simple linear concentration



Fig. 6. Repeatability test: Time trace of thiosalicylic acid oxidation on Co-imidazole catalyst at pH 7. Catalytic turnovers, calculated based on the number of thiol molecules that were oxidized on each Co atom, are depicted in the upper section of the curve.

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Scheme 1. Dioxygen activation, intraparticle charge transfer, and oxidation of four thiols on supported CoN₄ sites.

dependence. Free radical chain reactions should have yielded a variety of oxygenated sulfur byproducts, while we have observed predominantly the disulfide product. Admittedly, none of these observations alone is conclusive, yet their cumulative weight points against a free radical chain mechanism.

Scheme 1 provides a qualitative postulate for the reaction mechanism. It is based on the following guiding observations: (1) The reaction does not involve free radical formation. (2) Adsorption of the thiols is essential for their catalytic removal, which is manifested in the observed pH dependence and the higher oxidation rate of better chelating agents. (3) Substrate oxygenation is rather scarce. (4) The conductivity of the carbon substrate is essential for efficient catalysis. The second and third observations lead us to the postulate that the oxygen activation site may be remote from the thiol adsorption site, and the reaction may proceed through intraparticle electron transfer between these sites. A similar observation was used to explain photocatalytic oxidations by dioxygen on titania photocatalysts. In a similar manner we postulate that the carbon particle behaves as a miniature electrochemical cell where oxygen bonding and its reduction to H2O occurs on one site and the thiolate adsorption takes place elsewhere on two nearby sites (to allow dimerization of the bound thiolates). Otherwise it would be difficult to conceive how three species (oxygen and two thiolates) adsorb on the same or very close by sites and how oxygen transfer is so scarcely observed.

Scheme 1 depicts a postulated mechanism. For simplicity, each of the six arrows denotes several elementary steps rather than a single one. Arrow 1 marks the first step in a catalytic cycle, with the adsorption of dioxygen on one of the Co (or cobalt- N_4) sites. Then, by intraparticle two-electron transfer steps, two remote cobalt sites are oxidized, while the adsorbed oxygen is converted to hydrogen peroxide (or its deprotonated form or to a bound superoxo species). However, the bound hydrogen peroxide is not released to the solution and does not start chain radical reactions or give oxygenated products. Rather, it is dehydrated, leaving a bound oxo species. Arrow 3 signals the subsequent (and probably consecutive) adsorption of two thiolates on the Co(III) sites (though it is also possible that the adsorption of the thiols precedes and stimulates the intramolecular charge transfer step). Subsequently, the two adsorbed thiolates can undergo charge exchange with the Co(III) sites, stimulating the formation of a disulfide bond by the reaction of the two adsorbed thiol radicals (marked by arrows 4 and 5). The disulfide is then released from the active sites (arrow 6).

Concluding Remarks

Pyrolyzed carbon-supported nitrogen-donor cobalt catalysts are a mature, well-researched class of electrocatalysts and an emerging class of chemical catalysts. The article shows that in addition to the already proven efficient hydrogen sulfide catalysis and the proven electrocatalytic activity of these materials, they are efficient oxidation catalysts for thiol–disulfide conversions. Apparently, the catalysis does not go through free radical formation, which, on the one hand, precludes the application of this catalysis for organic degradation and decontamination of complex mixtures of contaminants, but, on the other hand, may open the door for fine chemistry-targeted catalytic reactions.

It is known that cobalt is the least active transition metal catalyst for thiol oxidation, and the fast, efficient catalysis demonstrated in this study is indeed most encouraging because it may be extended to other metals and other nitrogen donors as well.

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