



## Performance of a biomimetic oxidation catalyst immobilized on silica particles

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### ABSTRACT

A biomimetic oxidation catalyst, cobalt porphyrin with thiol linkers, was chemically conjugated to silica particles and utilized in the oxidation of hydroquinone to benzoquinone. The cobalt porphyrin/silica particle catalyst was characterized with Inductively Coupled Plasma (ICP) and X-ray Photoelectron Spectroscopy (XPS). The catalytic performance of the cobalt porphyrin molecules was compared to previous results for the same catalyst grafted to a gold surface and on silicon wafers. The measured catalytic activity, after background correction, was 100 times higher than that of its homogeneous counterpart, 10 times higher than that on a silicon wafer, and almost the same as that on a gold surface. The turnover frequency rates after 400 h are still comparable with initial rates reported for homogeneous porphyrins and salophens, whereas the use of particles as support increases the active surface area, which removes the limitations for scale-up associated with the previously used silicon wafers and gold surfaces.

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### 1. Introduction

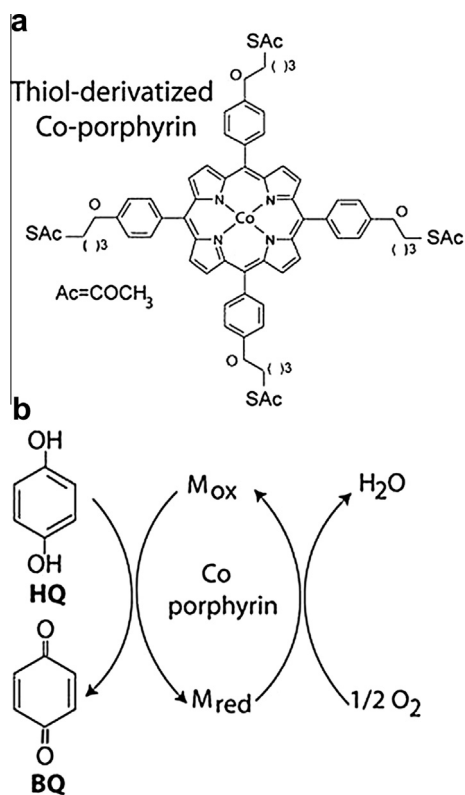
The knowledge of the human impact on the environment has stimulated the development of green chemistry into a research area of large interest. Green chemistry is defined as the design of chemistry, so that reactions can proceed more energy efficient, atom economic, without waste, in a selective way, and without harmful reactants, clearly evidencing that catalysis is one fundamental pillar [1–6]. One common example of green chemistry is the use of metal catalysts that activate molecular oxygen as the oxidant in oxidation reactions [7–13]. Other examples of oxygen-activating catalysts are found among the metal porphyrin catalysts, which have been used in various types of oxidations, both homogeneous [14–17] and heterogeneous on supports such as zeolites [18], chitosans [19,20], silicas [21], and magnetic nanospheres [22]. Even an increased activity upon immobilization, due to prohibition of catalyst dimerizations and conformational changes, has been observed for manganese(III) porphyrin monolayers on zirconium phosphate Langmuir–Blodgett films [23] and for iron(III) porphyrins immobilized on chitosans [24]. In previous studies, Bäckvall et al. investigated the catalytic performance of a biomimetic oxidation catalyst, cobalt porphyrins, in solution [16,17].

When the cobalt porphyrins were modified with thiol linkers [25] and chemically grafted to gold surfaces (prepared by thermal evaporation of a 150 nm gold layer on a silicon wafer) [26] or to silicon wafers [27], it was found that their catalytic activity on gold and on silicon was 100 and 10 times higher, respectively, than their homogeneous congener. Also, the lifetime of the catalyst increased dramatically upon immobilization since no deactivation of the catalyst was observed during the reaction. The reason why two-dimensional surfaces were chosen as supports was that it allowed us to use surface-characterizing techniques such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) in order to investigate the orientation of individual catalyst molecules on the surface. The lower activity found on silicon wafers compared to that on gold surfaces was suggested to be due to catalyst cluster formation as observed by AFM. On the gold surfaces, on the other hand, the catalyst formed a complete homogeneous single layer. Extending from two-dimensional surfaces to three-dimensional supports such as particles increases the active surface area dramatically, as required for process scale-up to practical catalysis.

In the present study, we have used silica particles as support for the heterogenization of a thiol-derivatized cobalt porphyrin molecule (CoTPP-L) shown in Fig. 1a. The thiol groups are acetylated to prevent disulfide formation between molecules, causing polymerization and inactivation of the catalytic activity. CoTPP catalyzes the biomimetic oxidation of hydroquinone (HQ) to benzoquinone (BQ) with molecular oxygen (Fig. 1b), where cobalt activates molecular oxygen by formation of a cobalt–oxygen complex. As

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**Fig. 1.** (a) Structure of thiol-derivatized cobalt porphyrin (CoTPP) and (b) the oxidation of hydroquinone (HQ) to benzoquinone (BQ) with molecular oxygen, catalyzed by a CoTPP molecule.

hydroquinone is oxidized to benzoquinone, the cobalt–oxygen complex is reduced. Formation of water from molecular oxygen regenerates the cobalt porphyrin complex. At present, very little information concerning the mechanism of the  $O_2$ –cobalt–quinone couple is available, and other oxygenated complexes such as superoxo compounds may be involved [28]. The stepwise electron transfer leads to low energy barriers, via this biomimetic approach [25].

The catalytic activity of immobilized CoTPP on silica particles was measured by following the production of BQ using ultraviolet–visible (UV/Vis) spectroscopy and compared to our previous findings of activity on silicon wafers [27] and gold surfaces [26]. The CoTPP/silica particle catalyst was characterized with Inductively Coupled Plasma (ICP) and X-ray Photoelectron Spectroscopy (XPS). After background correction, the catalytic activity of CoTPP on silica particles was almost the same as that on gold, 10 times higher than that on silicon wafers and 100 times higher than its homogeneous counterpart. As for CoTPP attached to gold and silicon surfaces, no deactivation was observed during 400 h reaction, while homogeneous CoTPP showed deactivation already after 40 h. Furthermore, we detected a high background oxidation reaction of hydroquinone with the magnetic silica particles, which was almost negligible with non-magnetic silica particles. This is proposed to be due to active iron species present on the magnetic particles.

## 2. Experimental section

### 2.1. Catalyst preparation

The synthesis of cobalt porphyrins with thiol linkers (CoTPP-L) has been described elsewhere [25]. Magnetic silica particles with

amine functional groups, Sicastar<sup>®</sup> M-NH<sub>2</sub>, with a diameter of 1.5 μm, purchased from Micromod Partikeltechnologie GmbH, were used as a support for heterogenization of the CoTPP molecules. An overview of the various reaction steps to covalently attach the CoTPP onto the silica particles is illustrated in Fig. 2. In Fig. 2a, the aminogroups on the particle surface are reacted with *N*-Succinimidyl-3-(2-pyridyldithio)-propionate (SPDP) introducing thiol-reactive disulfide linkers onto the particle surface. In Fig. 2b, free thiols on the CoTPP molecule are formed during base (NaOH) deprotection of the thioacetate linkers (reaction step not shown in the figure). The thiols are then reacted with the disulfides on the particles; thus, CoTPP is covalently attached to the silica particles through a disulfide bond. The catalyst was also immobilized on 1.5-μm-sized non-magnetic silica particles with amino functional groups (Sicastar<sup>®</sup> -NH<sub>2</sub>, micromod).

#### 2.1.1. Silica particles

Commercially available magnetic silica particles (Sicastar<sup>®</sup> -M) are produced by hydrolysis of orthosilicates in the presence of magnetite and have a hydrophilic surface with terminal Si-OH-bonds. They have monomodal size distributions with a mean diameter of 1.5 μm and are designed with amino functionalities (Sicastar<sup>®</sup> M-NH<sub>2</sub>). The silica particles are extremely stable in organic solvents, at high temperatures and are dispersed in water with a concentration of 50 mg particles per ml solution. According to the manufacturer, there are  $2.8 \times 10^8$  particles per mg and 5 nmol NH<sub>2</sub> per mg particles.

#### 2.1.2. Conjugation of SPDP to silica particles

100 mg Sicastar<sup>®</sup> M-NH<sub>2</sub> (Micromod GmbH, 50 mg/mL in distilled water) was washed three times with 2 mL PBS (10 mM phosphate, 150 mM NaCl, pH 7.4) and finally re-suspended in 2 mL PBS. The particles were washed by collecting the particles to the wall of the tube with an external permanent magnet while changing the solution and then re-suspended in the absence of the magnet. 500 μL *N*-Succinimidyl-3-(2-pyridyldithio)-propionate (SPDP) (20 mM in DMSO) in 1.2 mL PBS was added to 2 mL Sicastar<sup>®</sup> M-NH<sub>2</sub> (50 mg/mL in PBS). The reaction was allowed to proceed for 2 h at room temperature. Sicastar<sup>®</sup> M-N-SS-Pyridyl was washed three times with 2 mL DMF and re-suspended in 2 mL DMF.

#### 2.1.3. Immobilization of CoTPP on silica particles

Prior to the immobilization, the thioacetate protecting groups were removed by addition of base [29]. CoTPP-L, CoTPP with thioacetate linkers (0.675 mg in 2 mL DMF), was added in a darkened lab at room temperature to 450 μL 0.8 M NaOH in methanol for 60 s, thus forming free thiols on CoTPP's. The CoTPP solution from the previous step was added to 2 mL Sicastar<sup>®</sup> M-N-SS-Pyridyl (50 mg/mL in DMF). The reaction proceeded in a darkened lab on vortex at room temperature for about 12 h. Sicastar<sup>®</sup> M-N-CoTPP was washed five times with 10 mL DMF and re-suspended in 10 mL DMF and kept at +4 °C.

### 2.2. Heterogeneous catalysis

100 mg of silica particles grafted with CoTPP as described above was added to a 10 mL-solution containing 25 mg/mL of hydroquinone (HQ) in acetic acid (HOAc) in a loosely packed Teflon reaction chamber. A gentle flow of oxygen above the surface of the reaction solution kept the oxygen partial pressure at one atmosphere. The whole setup was held at room temperature with gentle mixing. At sampling time, 1 mL of reaction mixture was taken and centrifuged to remove the catalyst–particle complex for UV/Vis measurements to determine the oxidation rate of hydroquinone (HQ) to benzoquinone (BQ) and afterward returned to the reaction solution

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