

## Oxidation of phenol catalyzed by immobilized phthalocyanine complexes

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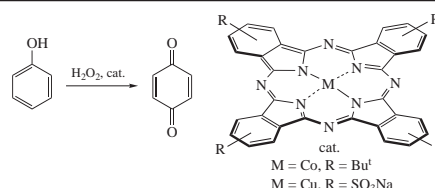
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**Immobilized phthalocyanine complexes of Co<sup>II</sup> and Cu<sup>II</sup> manifest higher catalytic activity in the oxidation of phenol with hydrogen peroxide than individual complexes.**

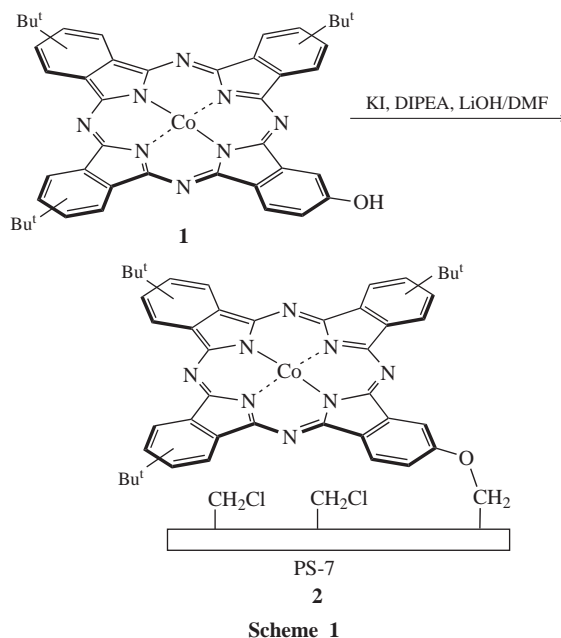


Selective oxidation of phenols to quinones is a key stage in the synthesis of vitamins and valuable synthetic precursors.<sup>1,2</sup> Quinones are important intermediates in organic synthesis and components of natural biologically active compounds.<sup>3–5</sup> Among the oxidants in question,<sup>6–13</sup> the most popular are air oxygen, hydrogen peroxide, and *tert*-butyl hydroperoxide. Hydrogen peroxide being a 'green' oxidant (although currently more expensive than molecular oxygen) can oxidize phenols under mild conditions in the presence of a broad range of catalysts.<sup>6,14,15</sup> Phthalocyanine complexes of transition metals tested recently, especially under photocatalytic oxidation conditions,<sup>16–21</sup> were mainly used as homogeneous catalysts. Such procedures have a number of drawbacks, in particular, isolation and purification of products are complicated.

In this study, we aimed at creating a heterogeneous catalyst for the model oxidation of phenol using immobilized phthalocyanine complexes on polymer supports with highly developed surfaces. Several types of supports on which phthalocyanine complexes were immobilized by adsorption from saturated solutions and by covalent immobilization were investigated. Melamine sponge, Nafen nanofibers and modified super cross-linked polystyrene PS-3 were selected as the supports. According to the low-temperature nitrogen adsorption method (in BET approximation), their specific surface areas were 800, 155 and 1100 m<sup>2</sup> g<sup>-1</sup>, respectively. Furthermore, we performed covalent immobilization of cobalt(II) 2-hydroxy-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine **1** on styrene–divinylbenzene copolymer PS-7 activated by incorporation of chloromethyl groups and thus obtained catalyst **2** (Scheme 1).<sup>†</sup>

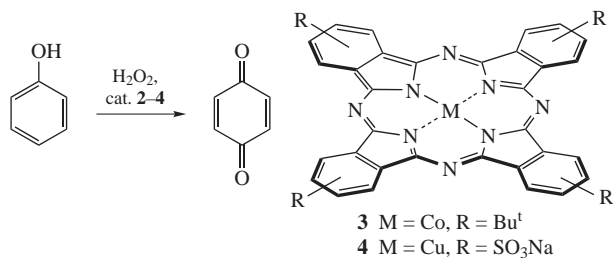
Phthalocyanine complexes **2–4** were used as the catalysts to oxidize phenol with hydrogen peroxide in aqueous medium (Scheme 2).<sup>‡</sup> The reaction progress was controlled by TLC. The catalyst stability was monitored by absorption in the visible region.

When *tert*-butyl substituted cobalt phthalocyanine **1** was used, hydrogen peroxide caused irreversible catalyst oxidation resulting in its gradual destruction under homogeneous catalysis



<sup>†</sup> *Phthalocyanine immobilization procedure.* A 0.5% solution of complex **1** in DMF (0.3 ml), KI (10 mg), diisopropylethylamine (0.65 ml) and LiOH·H<sub>2</sub>O (20 mg) were added to a mixture of PS-7 (a chloromethylated styrene–divinylbenzene copolymer) (300 mg) in DMF (3 ml). The mixture was kept at 110°C for 10 h. After that, the granules were filtered off and sequentially washed with H<sub>2</sub>O, EtOH, acetone and toluene and then dried in air.

<sup>‡</sup> *Phenol oxidation procedure.* The catalytic experiment was carried out at room temperature in a static reactor equipped with a magnetic stirrer and an air-cooled condenser. Phenol (1 g) in H<sub>2</sub>O (10 ml), a phthalocyanine catalyst (0.5 mol%) and a 37% aqueous H<sub>2</sub>O<sub>2</sub> solution (1.5 ml) were used in the reaction that was performed for 2 h. The reaction progress was monitored by TLC. Upon reaction completion, the degree of conversion and the yield of the target product were calculated.



Scheme 2

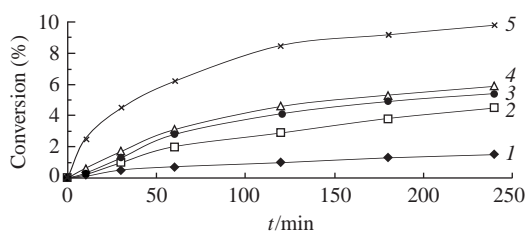
conditions. To improve stability and activity of the catalyst, it was immobilized, which caused increase in phenol conversion (Figure 1).

We found that catalyst oxidation also occurred under heterogeneous catalysis conditions, however, it was much more slow. According to Figure 1, immobilized phthalocyanines manifested noticeably higher activity than individual complexes, though phenol conversion was insufficient. In the case of covalently immobilized on polystyrene catalyst **2**, phenol conversion was higher than in the case of the catalysts physically adsorbed on various supports. Even traces of **1** were not detected in the reaction media (UV-VIS control). Consequently, in the cases of both the covalent immobilization on styrene–divinylbenzene copolymer PS-7 and the application on the surface (melamine sponge, Nafen nanofibers and modified super cross-linked polystyrene PS-3) by adsorption, the catalyst leaching did not occur.

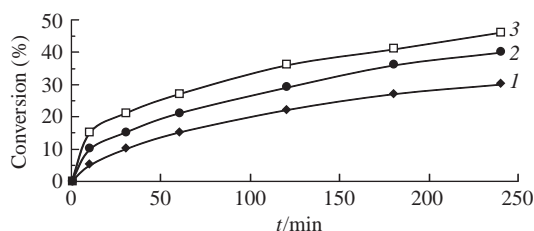
To solve the problem of low catalyst stability under oxidizing conditions, we tested H<sub>2</sub>O<sub>2</sub>-resistant sulfo-substituted copper phthalocyanine **4**. As phenol conversion was low in the presence of this complex, we decided to place it on a heterogeneous support. It appeared that adsorption on hydrophobic PS-3 polystyrene was insufficient, since complex **4** was easily washed off with water or other polar solvents. In the cases of melamine sponge or Nafen fibers, the copper complex was perfectly adsorbed on the support surface and was not washed off during the reaction. With these catalysts, the phenol conversion considerably increased in comparison with that in the presence of non-adsorbed complex **4** (Figure 2).

Catalyst recycling was demonstrated for the melamine sponge or Nafen fiber supported complexes. The catalysts were separated, washed with water and reused. After 5 cycles, their efficiency remained practically unchanged (Figure 3).

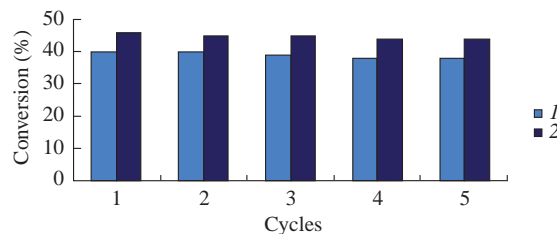
It is of note that supported catalyst **4** provides higher phenol conversion as compared with immobilized catalyst **3** (see Figures



**Figure 1** Conversion of phenol at 25°C with various catalysts: (1) cat. **3**, (2) cat. **3**/melamine sponge, (3) cat. **3**/Nafen, (4) cat. **3**/PS-3, (5) cat. **2**.



**Figure 2** Conversion of phenol at 25°C with sulfonated catalysts: (1) cat. **4**, (2) cat. **4**/melamine sponge, (3) cat. **4**/Nafen.



**Figure 3** Phenol conversion on catalysts: (1) cat. **4**/melamine sponge, (2) cat. **4**/Nafen.

1 and 2). UV-VIS spectroscopic data showed that complex **4** manifested high resistance to both the oxidant used in this process and desorption from substrates. The enhanced resistance of catalyst **4** to oxidation may be due to the presence of electron-withdrawing substituents in the ligand, in contrast to **3** containing *tert*-butyl electron-donating groups. Based on our previous results,<sup>6</sup> it can be stated that immobilized complex **4** is a more stable catalyst than immobilized iron(III) analogue of complex **3**. This allowed us to increase the yield of 1,4-benzoquinone and to reduce the catalyst consumption.

In summary, solid supported sulfonated phthalocyanine complexes seem promising catalysts for hydrogen peroxide oxidation of phenol into benzoquinone. The studies of other phthalocyanine complexes with ligands containing electron-withdrawing substituents for this catalytic oxidation are currently in progress.

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