Preparation and Deodorizing Performance of a Novel Air-Purifying Material

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ABSTRACT: Two kinds of water-soluble metallophthalocyanine derivatives, binuclear phthalocyaninecobalt(II) (Co_2Pc_2) and binuclear phthalocyanineiron(III) (Fe_2Pc_2), were supported on cationic wool fibers (CWF) to obtain a novel air-purifying material, binuclear metallophthalocyanine fibers (Mt_2Pc_2CWF), and the optimal supporting conditions were pH 5, 100°C, and 60 min. Mt_2Pc_2CWF could eliminate efficiently the malodors of methanthiol and hydrogen sulfide at room temperature by catalytic oxidation reaction used oxygen in atmosphere as oxidant. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4378–4382, 2006

Key words: catalysts; fibers; modification; recycling; malodors

INTRODUCTION

Indoor air quality has received a great deal of attention since the early 1990s. This is because studies showed that the level of pollutants in indoor environment was actually higher than that in outdoor environment.[1–3] In addition, people generally spend more than 80% of their time in indoors, which contributes a higher risk from inhalation of pollutants than outdoors. Indoor air contains different types of air pollutants, including volatile organic compounds (VOC) emitted from various sources, e.g., building materials, paints, and other consumable products.[4] These pernicious gases have resulted in various diseases in humans, such as headache, nausea, eye irritation, and sore throats.[5] Hence, a large amount of effort has been directed towards the development of efficient deodorizing methods, such as sensory, physical, chemical, and biological techniques.[6,7] Sensory techniques cannot provide an ultimate solution for the elimination of bad-smelling compounds, which only change our perception of the smell by using different smelling compounds. Physical deodorization eliminates smelling compounds through physical adsorption. Therefore, deodorizing capacity is rather limited and also adsorbed smelling compounds can be desorbed depending on the conditions. Chemical and biological methods can make smelling compounds converted into odorless substances. Various materials have been used as deodorants in those methods. Among them, metallophthalocyanine derivatives have been given special attention.[8]

Metallophthalocyanine complexes are a class of synthetic compounds, which consist of *N*-Donor macrocyclic structure and resemble that of metalloporphyrin complexes, widely used by nature in the active sites of cytochrome p-450. Catalytic activities of metallophthalocyanines derived from similarity to metalloporphyrin complexes have been widely studied because of their rather cheap and facile preparation in a large scale, and their chemical and thermal stability.[9] However, one drawback of metallophthalocyanine derivatives is that they are limited to be used in some fields because they are generally available only as powder or in solution form. If they are fixed to a suitable support material, the drawback mentioned earlier can be overcome. For such a material, several types of supports have been used for this purpose, such as charcoal, organic polymers, zeolites, etc.[10–12] Comparing to these materials, fibers may be the preferable candidate because not only is it easy to handle, it can also be manipulated structurally by well-established chemical and physical methods. In addition, wool is a very ordinary fiber material, so there is a large quantity of wool that can be exploited. To our knowledge, wool fibers (WF) have not been studied as air-purifying materials.

In this paper, two kinds of water-soluble binuclear metallophthanine derivatives (Mt_2Pc_2), binuclear pht halocyanineiron(III) (Fe_2Pc_2) and binuclear phthalocyaninecobalt(II) (Co_2Pc_2), were supported on cationic

wool fibers (CWF) to obtain a novel air-purifying material, binuclear metallophthalocyanine fibers (Mt_2Pc_2CWF). This materials showed high performance in eliminating CH_3SH and H_2S at room temperature by catalytic oxidation reaction used oxygen in atmosphere as oxidant. In comparison with the biological technologies, physical absorption, and chemical treatment nowdays,[13–15] Mt_2Pc_2CWF excellently combines the advantages of wool fibers and metallphthalocyanine, so that it could absorb a great deal of odorous gas and eliminate them in Mt_2Pc_2CWF at room temperature. Furthermore, the air purifying material is easy to handle and can be weaved in all kinds of shape according to the practical requirement, so there is a great potential for this air purifying material to be applied in home textile.

EXPERIMENTAL

Reagents

Pyromellitic anhydride and ammonium molybdenum were purchased from Shanghai Pharmaceutical Co., Ltd. (Shanghai, China). WF, marseilles soap, cationic trimethyl epoxybutane ammonium SM, (Fig. 2) and levelling agent Peregalo were donated by Dying and Finishing Lab in Zhejiang Sci-Tech University. Methanthiol (20%, w/w) was obtained from the Shanghai Research Institute of Flavour and Fragrance Industry. Hydrogen sulfide was prepared by reaction of sodium sulfide solution (20%, w/w) with phosphoric acid (10%, w/w). All the other solvents and reagents were of analytical grade and used without further purification.

Synthesis of binuclear metallophthalocyanine derivatives

According to the literatures,[16,17] two kinds of planar binuclear metallophthalocyanines were synthesized by phenylanhydride-urea route, and their structures were shown in Figure 1. The products were purified to obtain Co_2Pc_2 and Fe_2Pc_2,[18] and their final yields were
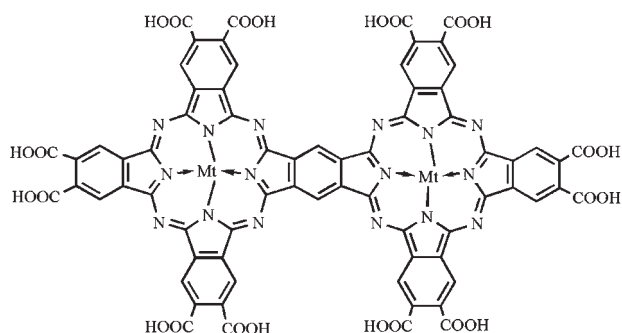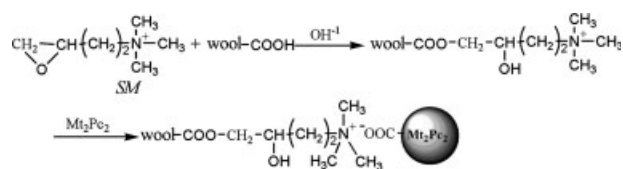

Figure 2 Supporting Mt_2Pc_2 on WF treated by SM.

24.59 and 19.12%, respectively. The results of the purified Co_2Pc_2 and Fe_2Pc_2 for elemental analysis by Carlo Erba 1106 were given as follows: Calc. for Co_2Pc_2, $C_{70}H_{26}O_{24}N_{16}Co_2 \cdot 4H_2O$: C 50.49%; H 2.06%; N 13.46%. Found: C 50.12%; H 2.10%; N 13.49%. Calc. for Fe_2Pc_2, $C_{70}H_{26}O_{24}N_{16}Fe_2 \cdot 4H_2O$: C 50.68%; H 2.07%; N 13.51%. Found: C 50.32%; H 2.11%; N 13.56%.

Preparation for binuclear metallophthalocyanine fibers

2 g WF was treated with SM solution (1 g/L) at a liquor ratio of 1 : 50 for 30 min at 90°C using a thermostatic vibrator. Sodium carbonate solution (5%, w/w) was used to adjust pH 9 and the treatment continued for a further 30 min. The products were washed with hot water, acetic acid solution (2 g/L) and cold water, respectively, to obtain cationic wool fibers. WF or CWF was added in the solution of Co_2Pc_2, sodium sulfate, and levelling agent Peregalo, supported 0.8% (w/w) Co_2Pc_2 on CWF by controlling reaction conditions, washed with hot distilled water and then dried in oven at 50°C to obtain Co_2Pc_2WF and Co_2Pc_2CWF. Fe_2Pc_2WF and Fe_2Pc_2CWF were prepared similarly using Fe_2Pc_2 in place of Co_2Pc_2.

The uptake of catalyst (Mt_2Pc_2) was calculated by the following equation:

$$\text{Catalyst uptake} (\%) = (A_0 - A)/A_0 \times 100$$

where, A_0 refers to the absorbance at 618 nm (Co_2Pc_2), 614 nm (Fe_2Pc_2) of the initial solution, and A refers to the absorbance of the solution after immobilization.
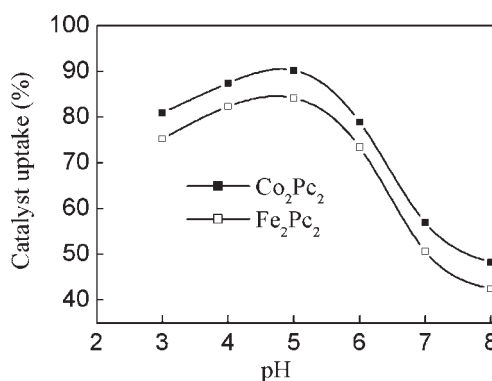

Figure 1 The structure of binuclear metallophthalocyanine (Mt = Co, Fe).

Figure 3 Effect of pH on catalyst uptake of Co_2Pc_2 and Fe_2Pc_2 ($T = 100$°C, 60 min).
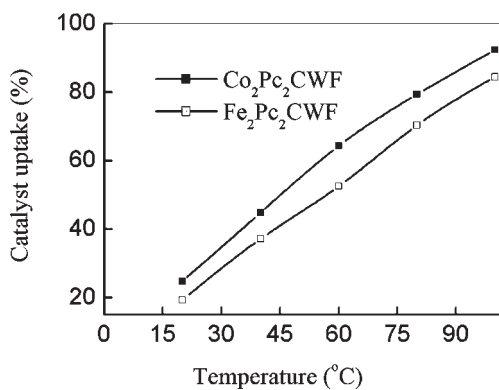
Figure 4 Effect of temperature on catalyst uptake of Co_2Pc_2 and Fe_2Pc_2 (pH = 5, 60 min).

Figure 5 Rate of catalyst uptake of Co_2Pc_2 and Fe_2Pc_2 (pH = 5, T = 100°C).

Sample measurements

The soap fastness for Mt_2Pc_2WF and Mt_2Pc_2CWF was tested in terms of standard GB/T 3921.1-1997 (China).

The deodoring speed of Co_2Pc_2CWF and Fe_2Pc_2CWF was tested as follows: 2 g Mt_2Pc_2CWF was suspended in a 5-L airtight flask, in which quantitative malodors (100 ppm) were injected, and then the initial and subsequent gas concentrations of malodors were measured by corresponding Japanese precision gas detector tubes. The deodoring ability of Mt_2Pc_2CWF on malodors was determined by the concentration of the residual malodors.

RESULTS AND DISCUSSION

Uptake of catalyst

A little catalyst can only be supported on WF if the WF was untreated with SM, and the uptake of catalyst was 12.3% (Co_2Pc_2) or 9.8% (Fe_2Pc_2), while the uptake of catalyst was up to 92.3% (Co_2Pc_2) or 87.1% (Fe_2Pc_2) after treatment with SM, so the SM treatment was propitious to improve the uptake of catalyst. The carboxyl, hydroxyl, and amino, etc. on WF could react with SM. Taking carboxyl for example, the reaction process was illustrated in Figure 2. WF was initially treated with SM to provide a bridge group for the Mt_2Pc_2. SM on CWF had a strong electrostatic attraction to the dissociated carboxyl groups on Mt_2Pc_2 molecule. Thus, Mt_2Pc_2 can become bound to CWF to provide the deodorant package. The whole process of treatment and supporting catalyst on WF was given in Figure 2.

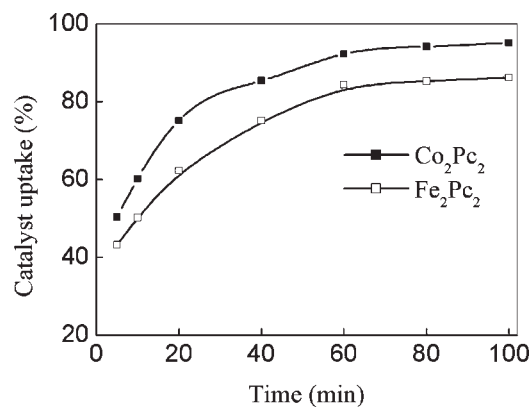pH, temperature, and time were very important factors determining the uptake of catalyst. The effect of pH on the uptake of catalyst was shown in Figure 3. It was clear that the catalyst uptake increased as the pH from 3 to 5 and then rapidly decreased. The ionized carboxyl anions of Mt_2Pc_2 became more and more as the pH increased below pH 5, which were much easier to be bond to CWF because of the electrostatic attraction between the ionized carboxyl anions of Mt_2Pc_2 and CWF. However, WF would become electronegative above pH 5, and the negative wool fibers were repulsive from the ionized carboxyl anions of Mt_2Pc_2, so the catalyst uptake decreased. The effect of temperature on the uptake of catalyst was shown in Figure 4. It was obvious that the uptake increased with the temperature increasing, and the best exhaustion was achieved at 100°C. This was because the activity of chains in amorphous region of WF increased and the high temperature can provide enough energy to move around at higher speed for the molecule of Mt_2Pc_2 so that the Mt_2Pc_2 could not be aggregated together. In this way, Mt_2Pc_2 was convenient to enter into the cationic wool fibers. Figure 5 showed the catalyst uptake after different periods. The uptake increased with the increasing time, but the uptake increased slowly after the time reached 60 min, so the optimum time is 60 min. The conclusion overall was that the optimum supporting parameters were pH 5, 100°C, and 60 min.

Soap fastness of binuclear metallphthalocyanine fibers

According to the optimal technics described earlier, Mt_2Pc_2WF and Mt_2Pc_2CWF had been prepared, and their soap fastness were shown in Table I. The results

TABLE I
The Soap Fastness of Mt_2Pc_2WF and Mt_2Pc_2CWF

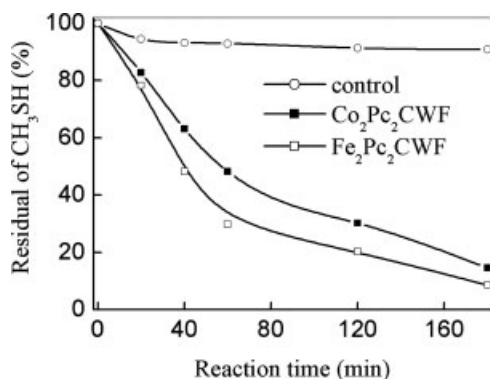| Types of fibers	Co_2Pc_2WF	Co_2Pc_2CWF	Fe_2Pc_2WF	Fe_2Pc_2CWF
Stained color for wool fabric	4 grade	5 grade	4 grade	5 grade
Stained color for cotton fabric	4 grade	5 grade	4 grade	5 grade
Fading for original sample	2 grade	2–3 grade	2 grade	2–3 grade

Figure 6 Rate of oxidation of methanethiol by Co_2Pc_2 and Fe_2Pc_2 ($[CH_3SH]_0 = 100$ ppm, $T = 25°C$).

Figure 8 The reactive process of RSH by binuclear metallophthalocyanine fibers.

revealed that the soap fastness of the latter was better than that of the former. After WF was modified, the electrovalent bond produced between WF and Mt_2Pc_2, so the soap fastness for Mt_2Pc_2CWF was improved.

Deodoring performance of Mt_2Pc_2CWF

Co_2Pc_2 and Fe_2Pc_2 showed high catalytic activity in the oxidation of 2-mercaptoethanol in aqueous solution.[19] After supporting them on WF, these catalysts may equally be expected to assist the elimination of methanethol and hydrogen sulfide. Compared with WF without supporting Mt_2Pc_2 (control), both Co_2Pc_2CWF and Fe_2Pc_2CWF demonstrated excellent deodorizing activity, as shown in Figures 6 and 7. The results showed that Fe_2Pc_2CWF was more effective than Co_2Pc_2CWF on both CH_3SH and H_2S.

The reactive process of CH_3SH and H_2S by binuclear metallophthalocyanine fibers was shown in Figure 8, and RSH was used to replace CH_3SH and H_2S. Figure 8 indicated that the whole reaction consisted of two steps, (1) absorption equilibrium, (2) reaction between RSH and binuclear metallophthalocyanine fibers. Binuclear metallophthalocyanine fibers provided large contacting surface, a great deal of RSH was enriched
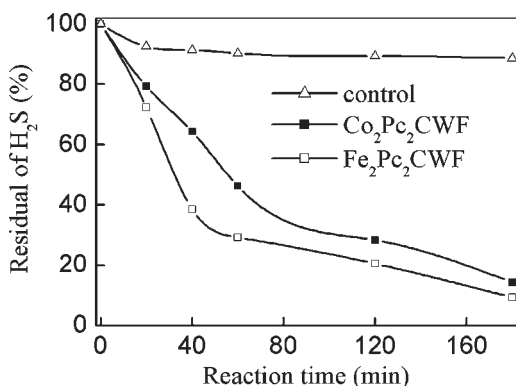
continuously to reach absorption equilibrium, and RSH reacted simultaneously with O_2 catalyzed by binuclear metallophthalocyanine fibers at room temperature. Therefore, most of absorbed RSH was removed and binuclear metallophthalocyanine fibers started to absorb RSH once again, so the absorption and catalytic reaction occured repeatedly. The catalytic mechanism of metallphthalocyanine on RSH was illustrated in Figure 9.[20] The central metal in phthalocyanine coordinates with RS^- given by RSH, which then RS^- combines with O_2 molecule to form ternary complex, and the single-electron transfer from RS^- to O_2 through a central metal in phthalocyanine ring, forming the radicals RS and O_2^-. The single-electron transfer process is the rate-determining step in the oxidation reaction.[21] Following the rate-determining step, the succeeding
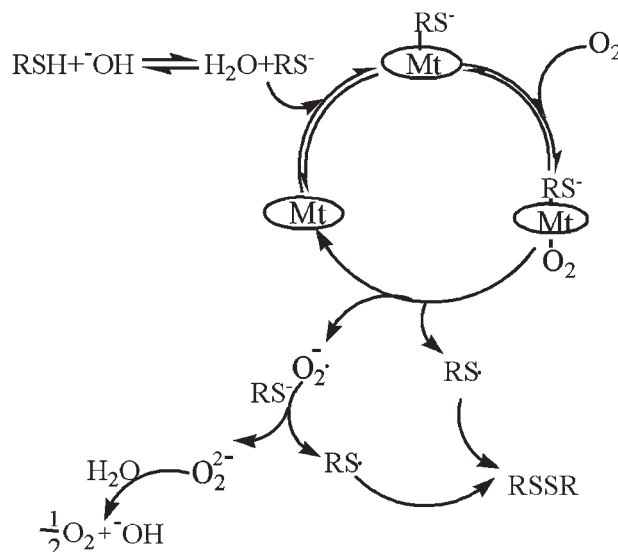

Figure 7 Speed of removing hydrogen sulfide by Co_2Pc_2 and Fe_2Pc_2 ($[H_2S]_0 = 100$ ppm, $T = 25°C$).

Figure 9 Mechanism of catalytic oxidation of RSH by metallophthalocyanine.

TABLE II
Deodorizing Ratios for Methanethiol by
Co$_2$Pc$_2$CWF and Fe$_2$Pc$_2$CWF

Run no.	Deodorizing ratio (%)	
	Co$_2$Pc$_2$CWF	Fe$_2$Pc$_2$CWF
1	85.4	91.4
2	86.3	90.3
3	83.2	92.4
4	84.5	91.3
5	82.4	89.5

Reaction temperature: 25°C; the initial concentration of CH$_3$SH : 100 ppm.

steps are rapid: O$_2^-$ reacts with the other RS$^-$, forming RSSR and O$_2^{2-}$. O$_2^{2-}$ reacts with H$_2$O, giving O$_2$.

Finally, the persistence of the catalytic effect of Co$_2$Pc$_2$ and Fe$_2$Pc$_2$ on WF was verified by repeating the oxidation of methanethiol five times under the same condition. Co$_2$Pc$_2$CWF and Fe$_2$Pc$_2$CWF were selected to test the deodoring ability on CH$_3$SH. 2 g Co$_2$Pc$_2$CWF or Fe$_2$Pc$_2$CWF was suspended in a 5-L flask, and quantitative methanthiol (100 ppm) was injected into the flask. Most of CH$_3$SH was removed after about 180 min, so the supplement of methanthiol was added to keep the initial concentration of 100 ppm. The initial and subsequent concentrations of CH$_3$SH were measured by a gas detector tube. The same procedure was repeated five times, and their results were shown in Table II. The results showed the deodoring activity of Co$_2$Pc$_2$ and Fe$_2$Pc$_2$ on CH$_3$SH was not impaired by five repetitive experiments. Therefore, it was obvious that Mt$_2$Pc$_2$CWF can be used repeatedly and its deodorizing capacity is not limited.

CONCLUSIONS

The uptake of catalyst on WF was obviously improved after the treatment with SM. Fe$_2$Pc$_2$ and Co$_2$Pc$_2$ were supported on cationic wool fibers to obtain Fe$_2$Pc$_2$CWF and Co$_2$Pc$_2$CWF. The optimal supporting process was

as follow: pH = 5, T = 100°C, t = 60 min. At room temperature, Mt$_2$Pc$_2$CWF had perfect deodoring ability on CH$_3$SH and H$_2$S, and the deodoring ability of Fe$_2$Pc$_2$CWF was better than that of Co$_2$Pc$_2$CWF. Comparing to the traditional air-purifying material such as activated carbon, zeolites etc, Mt$_2$Pc$_2$CWF can absorb the odorous gas and simultaneously catalyze them in Mt$_2$Pc$_2$CWF at room temperature, so it can be used repeatedly and its deodorizing capacity is not limited.

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