



Facile, green encapsulation of cobalt tetrasulphophthalocyanine monomers in mesoporous silicas for the degradative hydrogen peroxide oxidation of azo dyes

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ABSTRACT

A facile and green approach that improves the catalytic lifetime of cobalt tetrasulphophthalocyanine (CoTSPc) for the degradation of dyes is presented. Structurally ordered mesoporous silicas (MCM-41, MCM-48 and SBA-15), microporous aluminosilicates (ZSM-5) and macroporous alumina (γ -Al₂O₃) with different pore sizes were selected for the immobilization of CoTSPc, and a wide range of pH conditions (pH values from 4 to 12) were tested with the CoTSPc immobilization procedure. In the catalytic oxidation study, CoTSPc that was immobilized to MCM-41 silica (CoTSPc@MCM-41) prepared at a pH of 12 showed the longest catalytic lifetime. The TOC removal and discoloration of C. I. Acid Red 73 was approximately 60% and 82%, respectively, in the presence of CoTSPc@MCM-41 with H₂O₂ after 3 h. These results indicate that MCM-41, which has a matching size between its mesopores (30 Å) and CoTSPc molecules (25 Å), can prevent CoTSPc molecules from aggregating and improve its catalytic lifetime. In addition, the ability of CoTSPc@MCM-41 to degrade other dyes, and the reuse studies, demonstrated that CoTSPc@MCM-41 could be reused for the degradation of most common dyes.

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1. Introduction

Due to the facile preparation, good thermal stability, high catalytic activity and low toxicity, metallophthalocyanine-based catalysts have attracted considerable attention for their environmental applications [1] especially in the treatment of dye pollutants, which are a serious source of environment contamination in many countries [2]. However, many homogeneous metallophthalocyanine catalysts often have a limited lifetime of activity because of the formation of inactive aggregates and bridged μ -oxo dimers in solution, which block the access of the reagents to the catalytically active sites and diminishes the catalytic efficacy [3–5]. Therefore, the immobilization of metallophthalocyanines to solid supports by wetness impregnation or chemical bonding methods has been developed accordingly, where the macrocycle was isolated, and the catalytic site was protected [6–13]. Through the combination of adsorption processes and catalytic oxidation, the CoTSPc@chitosan–H₂O₂ system achieved an efficient water treatment [12]. However, we recently observed that dimeric CoTSPc was also present on CoTSPc@chitosan by diffuse reflectance UV–vis spectrum analysis. The dimers were likely formed during the preparation of the catalyst because CoTSPc was immobilized

on the surface of the chitosan microsphere by covalent bond anchoring, which cannot protect CoTSPc from the formation of inactive aggregates. In addition, previous systems also led to the aggregation of phthalocyanine even if it was encapsulated within mesoporous silica by chemical bond anchoring [14]. The chemical bond method normally requires a complex preparation process that involves modification of the supports with an alkoxysilane silylation reagent [14], and organic solvents are employed in most immobilization processes, which are often not green mediums. Therefore, it is highly desirable to explore environmentally benign and operationally simple methods for the immobilization of metallophthalocyanines to produce catalysts, which are truly efficient and readily recycled.

Metallophthalocyanines and metalloporphyrins have similar structural and functional models for the ubiquitous monooxygenase or peroxidase heme enzymes. Recently, Eddaoudi et al. developed a zeolite-like metal–organic framework (ZMOF) as a support for metalloporphyrins [15]. The overall ZMOF structure used large cages and isolated catalytic porphyrins, which led to an enhanced catalytic activity. Because ZMOF can only immobilize cationic porphyrins, which is due to its anionic nature, we hypothesized that it may be possible to explore porous materials to immobilize anionic metallophthalocyanines.

Here, we report the preparation of a green, simple and effective catalyst. The catalyst used mesoporous MCM-41 (Mobil Composition of Matter No. 41) that was immobilized to CoTSPc, and it

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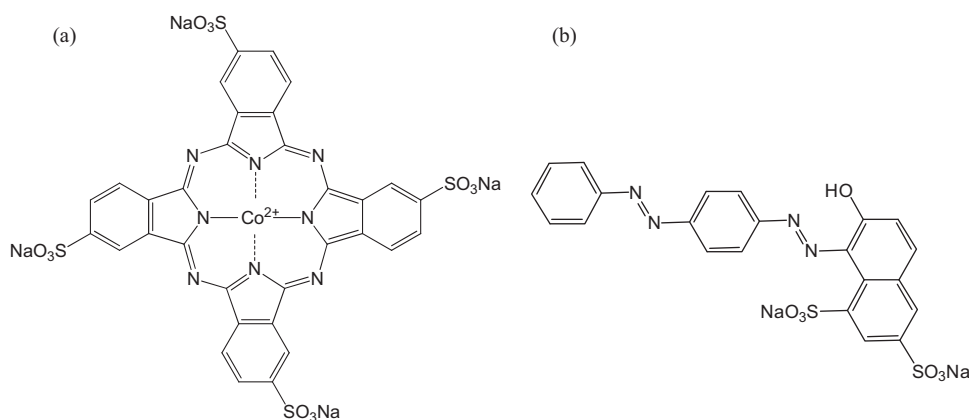


Fig. 1. The chemical structure of cobalt (II) tetrasulfophthalocyanine (a) and C. I. Acid Red 73 (b).

catalyzed the oxidative degradation of dyes in water using H₂O₂. MCM-41 possesses hexagonally ordered mesoporous structures and was selected to entrap CoTSPc because of its two main features: (i) the mesoporous MCM-41 materials with various pore sizes are commercially available, and (ii) the external surface area of MCM-41 amounts to less than 10 m²/g, the internal surface area was approximately 700 m²/g, and the pore sizes ranged from 15 to 100 Å [16,17]. Therefore, separating CoTSPc aggregates into monomers and selecting MCM-41 with an appropriate cavity size, each CoTSPc, a planar electron-rich aromatic macrocyclic molecule with a diameter of approximately 25 Å [18], will be tightly anchored inside the mesopores of MCM-41 and will be isolated from other molecules of CoTSPc. Therefore, aggregation of the catalyst will be avoided, and the diffusion of the reactants and products will be relatively unrestricted.

2. Materials and Methods

2.1. Materials and reagents

Cobalt tetrasulfophthalocyanine (CoTSPc, Fig. 1a) was prepared by modifying previously reported methods [19]. The porous materials MCM-41, MCM-48, SBA-15, ZSM-5 and γ -Al₂O₃, which all contained different pore diameters and structures, were purchased from Shanghai Novel Chemical Technology Co., Ltd. (Shanghai, China). C. I. Acid Red 73 (Fig. 1b) was supplied by Zhejiang Runtu Chemical Co. Ltd., (Zhejiang, China). All other dyes were commercial compounds (molecular structures are shown in Fig. S1 in Supplementary information) and were used without further purification. Double distilled water was used throughout this study. Other chemicals were of laboratory reagent grade and were used as received without further purification.

2.2. Immobilization of CoTSPc into different porous materials

A CoTSPc stock solution was prepared by dissolving 0.0502 g of CoTSPc in 1000 mL of distilled water under stirring to a final concentration of 50 μ M. Phosphate buffers regulated the pH of the CoTSPc solutions. Porous material (0.1 g) was added to 25 mL of the CoTSPc solution, and the solution was stirred at room temperature for 4 h. The immobilized porous materials of CoTSPc were collected by centrifugation and were dried at 80 °C. CoTSPc loading was determined by monitoring the change in the strong absorption band at 667 nm, and the concentrations are listed in Table 1. Because of the hydrophobic properties of silica and alumina supports, CoTSPc molecules that contain a symmetrically planar 18 π -electron aromatic macrocycle could be anchored by their

hydrophobic interactions. Although the hydrophilic sulfo groups that were grafted onto the benzene rings negatively affected the immobilization of the catalyst, the loading of CoTSPc to the various silica supports all achieved a final concentration that was greater than 4.5 μ mol/g.

2.3. Measurement of the degradation of the dyes

The catalytic oxidation of the dyes was performed in a 10 mL tube at room temperature. All reactions were performed in neutral aqueous solutions. The typical reaction mixture contained the dyes (10 mg/L), CoTSPc-immobilized porous materials (0.03 g) and H₂O₂ (100 mM). For the reuse studies, the catalysts were collected by centrifugation and were dried at 80 °C. The samples were analyzed on a UV-vis spectrophotometer at set time intervals.

2.4. Analysis

The concentration of the dyes was determined using a Shimadzu UV-2401 spectrophotometer (Tokyo, Japan) at the maximum wavelength of the dyes studied. The color removal was based on the change of the maximum absorbance. The diffuse reflectance UV-vis spectra were measured on a UV-vis spectrophotometer equipped with a Shimadzu integrating sphere ISR-2200 attachment (Tokyo, Japan). TOC (total organic carbon) analysis was performed using a Shimadzu TOC-V CPH (Tokyo, Japan). The surface area was determined by performing N₂ adsorption-desorption isotherms with a Micrometric ASAP 2010C apparatus (Atlanta, US). GC-MS analysis was performed using a Finnigan Trace DSQ GC-MS instrument equipped with a UA-5 capillary column (30 m \times 0.25 mm \times 0.25 mm) for the analysis of the degradation products. The carrier gas was helium and the temperature of the injection port was 250 °C. The temperature program of the column was set to an initial oven temperature of 50 °C and was increased at a rate of 10 °C/min to 250 °C, and the oven was held at 250 °C for 10 min. The sample for GC-MS analysis was prepared as follows [20]: after reaction of C. I. Acid Red 73 (10 mg/L), the aqueous solution was withdrawn, and the water was removed under drying, which left a pale yellow residue. The residue was dissolved using a sufficient volume of 3 M HCl, and the resulting solution was saturated with NaCl and was extracted with diethyl ether (3 mL \times 10 mL). The combined ether extracts were dried with anhydrous sodium sulfate, and the ether was evaporated under a vacuum. The residue was dissolved in 1 mL methanol, and 0.5 mL of 0.2 M Me₃S⁺OH in methanol was added to the methanol solution before GC-MS analysis.

Table 1
Total surface area, pore size, pore structure and CoTSPc loading to the different porous materials.

Sample	Surface Area (m ² /g)	Pore size (Å)	Pore structures	CoTSPc loading (μmol/g)
MCM-41	837	30	1D, hexagonal	5.19
MCM-48	950	25	3D, cubic	4.89
SBA-15	650	75	1D, hexagonal	5.71
ZSM-5	350	5.5	pentasil chains	4.67
γ-Al ₂ O ₃	200	500	disordered	4.91

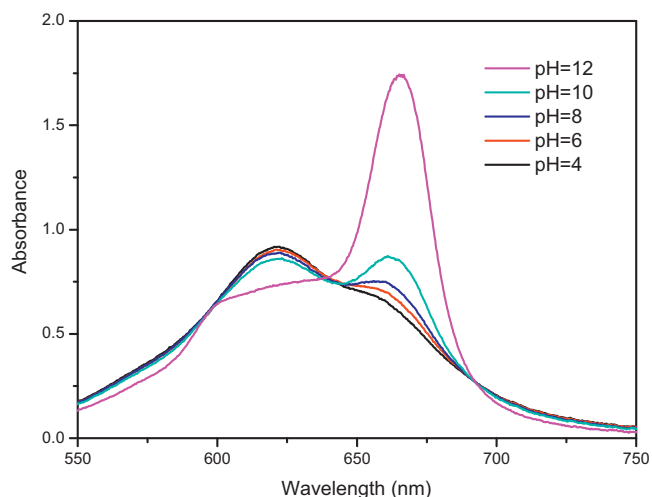


Fig. 2. UV-vis spectrum of CoTSPc aqueous solution (at a concentration of 25 μM) under different pH conditions.

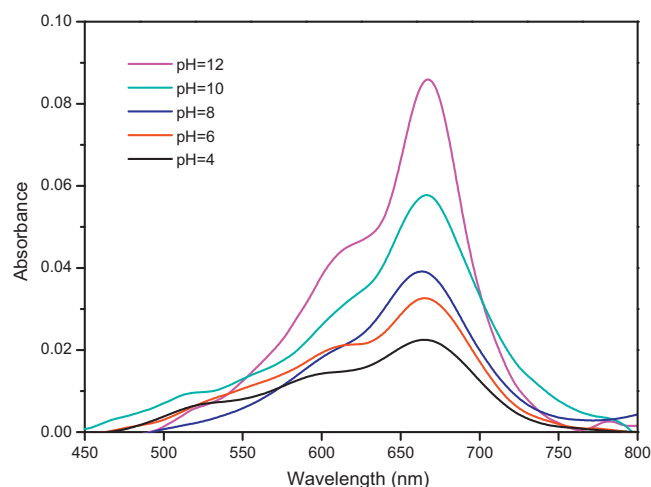


Fig. 3. Diffuse reflectance UV-vis spectrum of CoTSPc@MCM-41, which were prepared under different pH conditions.

3. Results and discussion

3.1. Spectroscopic characterization

CoTSPc occurs as a monomer–dimer equilibrium in aqueous solutions, and its UV-vis spectrum exhibits two peaks in the Q-band region. The lower energy absorption band near 670 nm was associated with the monomeric species, and the high-energy absorption band near 620 nm was assigned to the dimeric species [21]. The Q-band, which is attributed to a π - π^* transition in the macrocycle, strongly depends on the solution environment. In general, aggregation is very common for large hydrophobic π systems, particularly in polar media such as water [22]. Therefore, the effect of the solution pH on aggregation was investigated. Fig. 2 describes the UV-vis spectra of CoTSPc aqueous solutions that were obtained in various pH conditions. From these results, it is clear that a lower pH favored for the formation of inactive aggregates of CoTSPc. However, it was intriguing and useful that the peak of the monomer increased while the peak of dimer decreased with an increase in pH, and a sharp peak around 670 nm appeared when the pH was 12. According to the literature, the enhancement of the monomeric CoTSPc species under alkaline conditions is mainly due to the axial coordination of a hydroxyl ion (OH⁻) in solution to the central cobalt ion in the macrocycle, which impedes the π - π^* interactions between the phthalocyanine molecules [23]. This result suggests that the CoTSPc molecules were not aggregated at a pH of 12, and we were able to obtain abundant CoTSPc monomers in alkaline solution.

To determine the presence of CoTSPc monomers in the porous materials after the immobilization of the catalysts, diffuse reflectance UV-vis spectra of CoTSPc molecules that were immobilized in MCM-41 (CoTSPc@MCM-41) were collected. MCM-41 is one of the most common types of mesoporous silica, and it contains a long-range ordered framework with uniform mesopores (Table 1). As shown in Fig. 3, the absorption maxima that corresponded to the Q bands (in the range of 500–700 nm) observed in

the CoTSPc absorption spectrum (Fig. 2) also appeared in the diffuse reflectance UV-vis spectrum of CoTSPc@MCM-41 (Fig. 3). Similarly, the presence of CoTSPc monomers in MCM-41 can be clearly observed in Fig. 3 under the various preparation conditions. With an increase in the pH, the strength of the monomer peak increased and a sharp peak at approximately 670 nm appeared at a pH of 12. Fig. 3 also shows that the peak that was associated to the CoTSPc dimers (around 620 nm) was clearly decreased when the CoTSPc molecules were immobilized in MCM-41. These results suggest that the uniform nanometer-sized pores (30 Å) of MCM-41 allow it to separate the CoTSPc monomers and dimers by size during the immobilization procedure of the catalysts. The smaller monomers (25 Å) [18] were impregnated into pores while the larger monomers (>30 Å) were excluded from the pores and a portion of the dimers were adsorbed onto the external surface of MCM-41. Moreover, MCM-41 has a pore size that is approximately 30 Å, which is good match for the CoTSPc molecule (25 Å), and the size of the pore may prevent CoTSPc monomers from aggregating.

Four other kinds of porous materials with different pore sizes and structures were selected as potential CoTSPc carriers, and the selected materials were MCM-48, SBA-15, ZSM-5 and γ -Al₂O₃. Table 1 summarizes the surface area, pore size, pore structure and CoTSPc loading of the porous materials used in our experiments. MCM-41, MCM-48, and SBA-15 are all mesoporous silica materials, and the materials have similarly sized mesopores (25–75 Å) and well-defined nanochannel structures. ZSM-5 is a microporous (5.5 Å) aluminosilicate material that belongs to the pentasil family of zeolites, and γ -Al₂O₃ is a macroporous alumina material that has extra-large pores (>500 Å).

As shown in Table 1, it was determined that CoTSPc loading in different porous materials were similar to each other after the same immobilization procedures. However, the diffuse reflectance UV-vis spectra of CoTSPc supported on these porous materials were different (Fig. 4). In comparison with the CoTSPc molecules that were immobilized to MCM-41, the CoTSPc molecules supported

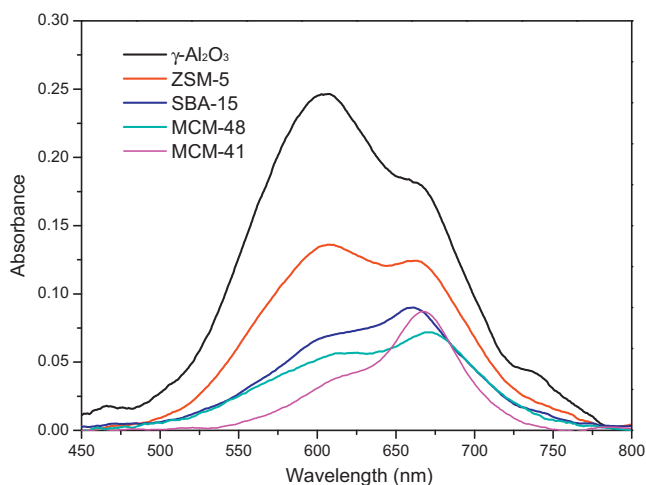


Fig. 4. Diffuse reflectance UV-vis spectra of CoTSPc immobilized in different porous materials.

on the four other porous materials showed an increased tendency to aggregate. CoTSPc molecules were predominately dimers when they were supported on microporous ZSM-5 (CoTSPc@ZSM-5) and macroporous γ -Al₂O₃ (CoTSPc@ γ -Al₂O₃) supports. Because the pore size of ZSM-5 is relatively small, CoTSPc molecules can only attach to its external surface, and the supported CoTSPc monomer would rapidly attract other monomers and form aggregates when the pH was adjusted to a neutral value. Similarly, the extra-large pore size (>500 Å) of γ -Al₂O₃ failed to control the aggregation of CoTSPc because the large pores did not offer a constricting environment that would inhibit CoTSPc molecules from aggregating. However, when the CoTSPc molecules were immobilized in the mesoporous MCM-48 (CoTSPc@MCM-48) and SBA-15 (CoTSPc@SBA-15) supports, the CoTSPc monomers slightly dominated the monomer-dimer equilibrium. Although the pore size and structures of MCM-48 and SBA-15 were similar to MCM-41, minor differences still led a lower efficiency for controlling CoTSPc aggregation.

3.2. The effect of pH in the preparation of the catalysts

C. I. Acid Red 73, a typical acidic azo dye, was selected as the model pollutant for the investigation of oxidative degradation by the catalyst. Degradation of the dye was performed by employing various catalysts in neutral aqueous solutions. Fig. 5 shows the influence of the preparation conditions of catalysts on the degradation of C. I. Acid Red 73. The dye could not be removed by MCM-41 in the presence of H₂O₂. However, when the CoTSPc@MCM-41 catalyst was prepared below a pH of 4, CoTSPc@MCM-41 still failed to catalyze the degradation of dye, which was attributed to the formation of inactive aggregates of CoTSPc. In addition, the reduced degradation of dye was observed in the presence of the catalyst that was generated under a pH of 6 or a pH of 8. However, when the pH of the solution used for the generation of the catalyst was increased to 10 or 12, an increased catalytic degradation (ca. 82% of the dye) was achieved after 180 min. When Fig. 2 and Fig. 3 are compared, we observed that the efficiency of degradation of the dye decreased when the amount of inactive dimer was increased. The greater catalytic activity of CoTSPc could be accomplished by immobilizing catalyst monomers in the mesoporous structures of MCM-41 under elevated pH conditions, which was mainly because we could obtain abundant CoTSPc monomers in alkaline solution (Fig. 2).

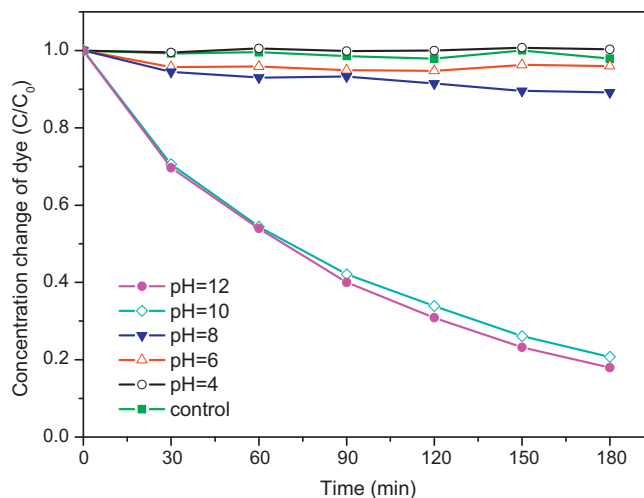


Fig. 5. Degradation by hydrogen peroxide (100 mM) oxidation of C. I. Acid Red 73 (initial concentration (C₀) of 10 mg/L in 10 mL at pH 7) catalyzed by CoTSPc@MCM-41 (0.03 g) prepared under different pH conditions (Control: MCM-41 without CoTSPc).

3.3. The effect of the porous carrier with different pore sizes and structures

To determine the importance of suitable pore sizes and structures of the support matrices, four other kinds of porous materials were used as the support matrices for CoTSPc immobilization. The catalysts CoTSPc@MCM-48, CoTSPc@SBA-15, CoTSPc@ZSM-5, and CoTSPc@ γ -Al₂O₃ were used in the C. I. Acid Red 73 removal procedure, and the results are shown in Fig. 6. When using macroporous γ -Al₂O₃ and microporous ZSM-5 as the catalyst carrier, the extent of the degradation of the dye was inferior to the degradation of the dye that was obtained with CoTSPc@MCM-41. In addition, the mesoporous materials with different framework structures (MCM-48 and SBA-15) also had decreased degradation efficiency when compared to CoTSPc@MCM-41. Based on the diffuse reflection UV-vis spectra of CoTSPc supported on different porous materials, which is shown in Fig. 4, it was determined that selecting a mesoporous material with a matching pore size to immobilize CoTSPc monomers was crucial to improve the catalytic activity of CoTSPc. This was likely because MCM-41 could provide a confined

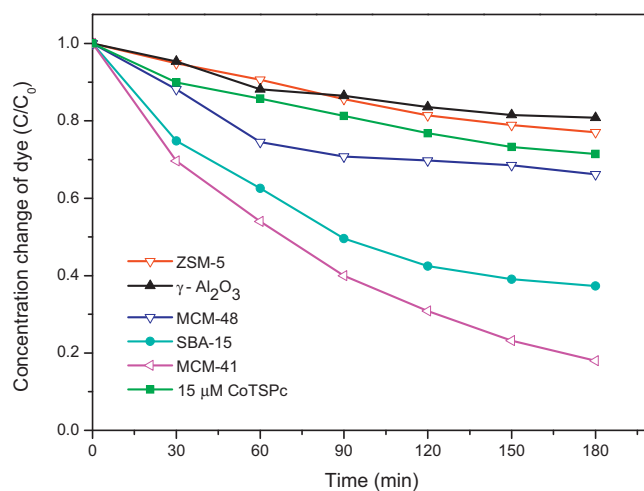


Fig. 6. Degradation by hydrogen peroxide (100 mM) oxidation of C. I. Acid Red 73 (initial concentration (C₀) of 10 mg/L in 10 mL at pH 7) catalyzed by CoTSPc immobilized in different porous materials (0.03 g).

space that could anchor and isolate the catalyst while prohibiting its aggregation, which allowed for an enhancement of catalysis.

The homogeneous catalysis of CoTSPc in the presence of H₂O₂ was performed to compare the catalytic lifetime of CoTSPc in aqueous solutions with CoTSPc immobilized in MCM-41, and the amount of CoTSPc immobilized in MCM-41 was approximately 15 μM. Therefore, 15 μM CoTSPc without a porous carrier was also used to degrade the dyes, and the results are shown in Fig. 6. It was observed that without MCM-41, CoTSPc had low catalytic degradation efficiency. However, during our experimental process, CoTSPc that was immobilized in mesoporous MCM-41 supports exhibited greater activity than the same catalyst in aqueous solution. Although the catalytic activity of CoTSPc@MCM-41 was not so high when the action was carried out under 10 mg/L of dye and 100 mmol/L of H₂O₂ in this study, it has already been improved to a high extent through the immobilization in mesopores of MCM-41, compared with the homogenous CoTSPc in aqueous solution. This result further suggests that choosing a mesoporous silica with a matching pore size and proper structure can improve the catalytic activity of CoTSPc for the removal of dyes.

3.4. Mineralization and reaction products of C. I. Acid Red 73

The extent of mineralization is one of the most important factors to evaluate a new oxidative degradation system. The TOC value indicates a loss of aromaticity and overall degree of compound degradation. As shown in Fig. 7, it was observed that the TOC residue was approximately 40% when the dyes were treated with CoTSPc@MCM-41 for 4 h. This result indicated that C. I. Acid Red 73 was almost completely degraded, and a considerable amount of the dye was mineralized; however, only a fraction of the C. I. Acid Red 73 was converted into lower organic products. Moreover, gas chromatography–mass spectrometry (GC–MS) was used to identify residual organic compounds in the reaction mixture (detailed results are shown in the supporting information). The results revealed that the major product was phthalic acid (6), and the other measurable reaction products were mostly propane-1,2-diol (1), butane-2,3-diol (2), succinic acid (3), glutaric acid (4), and benzoic acid (5) (Fig. 8). These results indicate that the most detectable degradation products were mainly small molecule organic acids, which are known to be biologically degradable.

3.5. The reuse of catalyst

The reuse and stability of catalyst were two major concerns for a catalyst to be used in practical applications. In the durability tests,

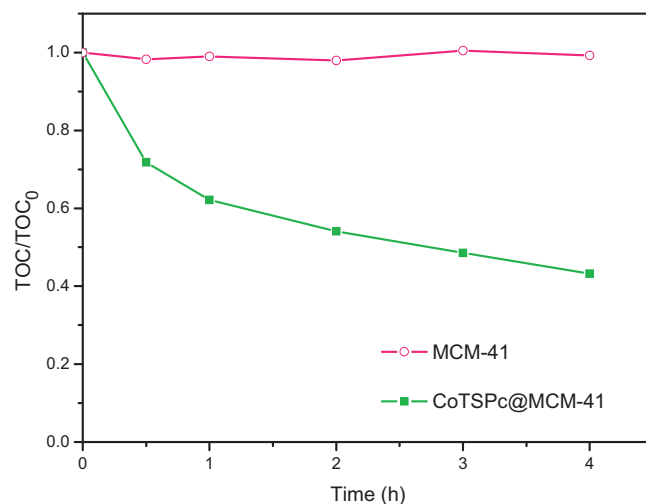


Fig. 7. TOC residue of C. I. Acid Red 73 (initial concentration of 10 mg/L in 10 mL at pH 7) by hydrogen peroxide (100 mM) and CoTSPc@MCM-41 (0.03 g) (TOC₀ is initial TOC concentration).

the same CoTSPc@MCM-41 samples were repeatedly used in the degradation reaction five times. It appeared that there were no obvious differences in the extent of degradation when the catalysts were prepared at either pH 10 or pH 12, which is presented in Fig. 5. However, a definite difference was observed when the catalyst was reused. For example, when the catalyst was prepared in pH 10 buffer, 80% of the dyes were removed after the first use of the catalyst (Fig. 9a), and the corresponding degradation ability was quickly decreased to 52% after the second use (Fig. 9b). The degradation ability was slightly diminished after each recycling (Fig. 9c–e). Finally, only 41% dyes were removed after the fifth use of the catalyst. However, when the catalyst was prepared in pH 12 buffer, the corresponding degradation ability was slightly diminished from 82% to 71% after recycling (Fig. 9a–e). This could be due to the fact that when prepared in the pH 10 buffer, approximately half of the CoTSPc existed in the dimer form (Fig. 3), which would easily lose its activity during the long usage time. Therefore, it is important to control the aggregation of the catalysts during their preparation. In addition, for CoTSPc@MCM-41 prepared at pH 12, the approximately 10% loss in activity was likely due to leaching and/or mechanical losses during the degradation process. Further research would still need to be conducted to generate an enhanced stability for CoTSPc@MCM-41 catalysts.

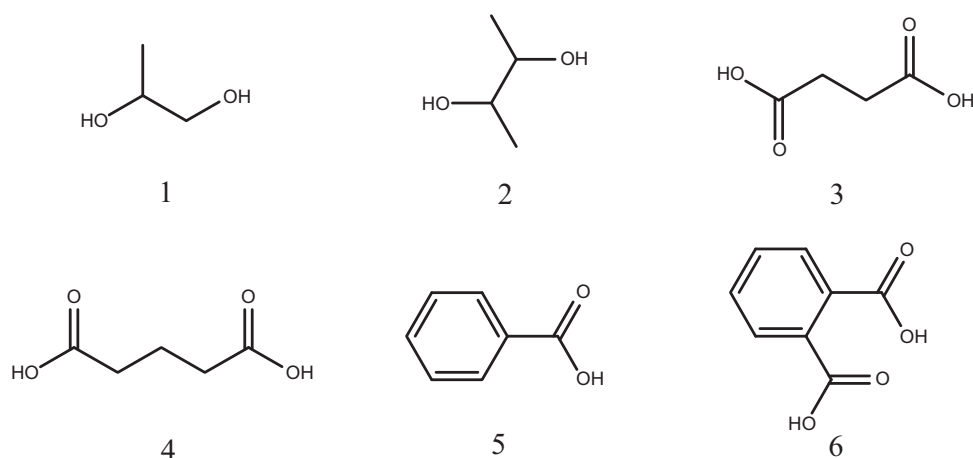


Fig. 8. Products formed after C. I. Acid Red 73 degradation catalyzed by CoTSPc@MCM-41 and hydrogen peroxide oxidation.

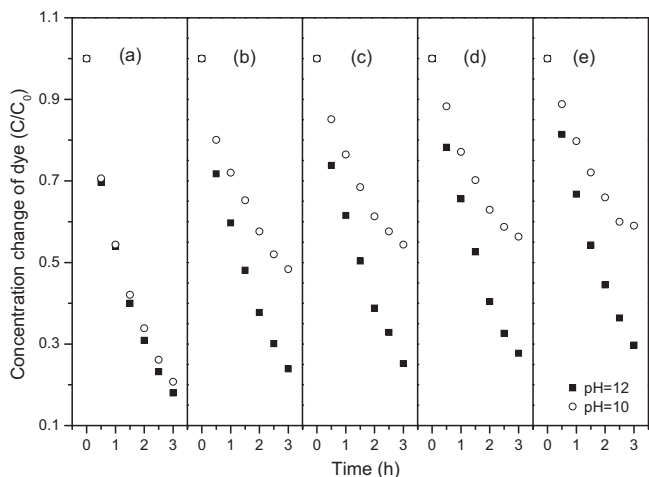


Fig. 9. Reuse of CoTSPc@MCM-41 that was obtained from different preparation conditions (initial dye concentration (C_0): 10 mg/L in 10 mL at pH 7; H_2O_2 : 100 mM; CoTSPc@MCM-41: 0.03 g). (a–e) show the dye residue in five degradation reactions.

3.6. Possible mechanisms and implications

Phthalocyanine compounds have been extensively examined as catalysts for redox reactions with the advantage of facile preparation and non-toxicity. There have been many reports that have suggested the mechanism of the phthalocyanines catalytic process [24–26]. It was proposed that nucleophilic Pc–Metal–OOH and electrophilic Pc–Metal=O were the active species in the homogenous MPC/ H_2O_2 system. By oxo-transfer between phthalocyanines and H_2O_2 , phthalocyanine–metal–oxo (Pc–Metal=O) with high catalytic activation was formed. This intermediate also can be transformed by phthalocyanine–metal–hydroperoxo (Pc–Metal–OOH), which was formed by axial ligand substitution. Nevertheless, the homogeneous metallophthalocyanine catalysts often suffer from a limited lifetime of activity because of the formation of inactive aggregates in solution, which essentially block the active sites of the molecules. To avoid aggregation, we proposed to use MCM-41 as a carrier of CoTSPc, which would separate CoTSPc molecules by its ordered framework and uniform hexagonal mesopores.

A large amount of CoTSPc monomers were obtained by tuning the conditions of CoTSPc aqueous solutions to a pH of 12. Because the diameter of CoTSPc molecules is approximately 25 Å, MCM-41 with a matching pore size (30 Å) provides a confined space that can anchor and isolate catalytically active monomers (Fig. 10). In addition, the external surface area of MCM-41 amounts to less than 10 m²/g while the internal surface area was approximately 700 m²/g [6]. The majority of immobilized CoTSPc monomers were located in the internal pores of MCM-41; therefore, they were separately anchored inside the structural cage of MCM-41. The

Table 2

Degradation by hydrogen peroxide oxidation of various dyes with CoTSPc@MCM-41.^a

Entry	Dye	TOC removal (%)
1 ^b	C. I. Acid Blue 193	65.67
2 ^b	C. I. Acid Blue 113	78.82
3 ^b	C. I. Reactive Blue 194	79.32
4 ^b	C. I. Reactive Red 24	13.63
5 ^b	C. I. Reactive Red 11	76.65
6 ^b	C. I. Reactive Yellow 18	86.14
7 ^b	C. I. Reactive Yellow 2	92.40
8 ^c	C. I. Reactive Blue 74	38.48
9 ^c	C. I. Acid Blue 25	79.33
10 ^c	C. I. Acid Blue 62	69.36
11 ^c	C. I. Acid Blue 40	52.48

^a The initial concentration of the dyes was 10 mg/L in 10 mL of buffer at a pH of 7, and the amount of CoTSPc@MCM-41 added was 0.03 g

^b Azo dyes.

^c Anthraquinone dyes.

matching size between CoTSPc and MCM-41 further provided the confined spaces that prevented CoTSPc monomers from aggregating. By BET analysis, we observed that the surface area of MCM-41 was significantly decreased from 837.34 to 403.35 m²/g after the immobilization of CoTSPc. The reduction in surface area was a result of the tight localized packing of CoTSPc in the pores. Moreover, the confined pores of mesopores were able to impose specific conformations that were able to magnify their catalytic activity [27]. Thus, due to the pH tuning in the CoTSPc immobilization procedure, the pore sizes and structures of the carrier had a dramatic effect on the outcome of the catalytic efficiency. MCM-41, with CoTSPc monomers immobilized in its pores, displayed an increased catalytic lifetime and stability in comparison with catalysts in aqueous solution.

During the degradation process, dye molecules which contain the aromatic macrocycle could be anchored by the hydrophobic silica supports, although that hydrophilic sulfo groups grafted on benzene rings would bring the negative effects on dyes adsorption. The diameter of C. I. Acid Red 73 molecules is 17.63 Å, which was calculated by VMD, thus the MCM-41 with a pore size of 30 Å could provide an enough space to anchor the dye molecules in pore channels. It can be observed in Fig. 5 that 3% of dyes were adsorbed on CoTSPc@MCM-41 in 180 min. When the dyes were degraded to small organic acids, the hydrophilic products would diffuse back in the solution for further reaction.

3.7. Degradation of other dyes

The substrate scope is one of the critical factors for the evaluation of a new oxidative degradation system. One key requisite for ideal catalysts that degrade organic dye pollutants is that the catalyst is able to degrade a variety of dye pollutants. The optimized degradation conditions were later applied for the degradation of a

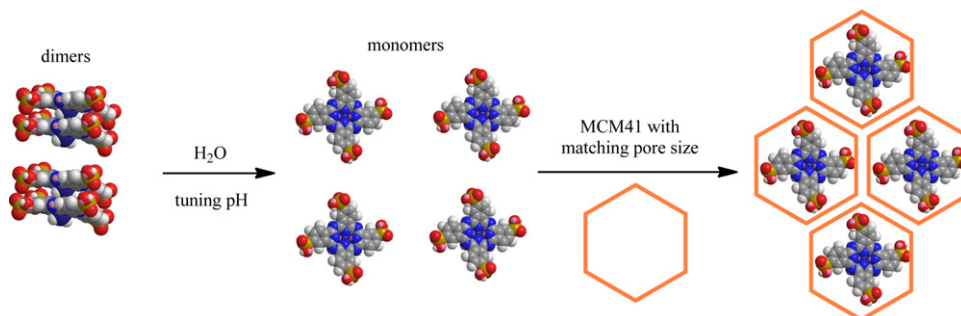


Fig. 10. The possible mechanism for the improvement of the catalytic lifetime of activity using cobalt tetrasulphophthalocyanine.

variety of prototypical dye pollutants. The scope of the catalyst is evident (Table 2) by the wide range of both azo and anthraquinone dyes that it is able to degrade. Except for C. I. Reactive Blue 74 (removal 38.48%) and C. I. Reactive Red 24 (removal 13.68%), high mineralization of the other dyes in Table 1 were observed through catalytic degradation.

4. Conclusions

Our study showed that CoTSPc immobilization through reasonable methods was able to improve its catalytic lifetime of activity by preventing CoTSPc molecules from aggregating in neutral aqueous solutions. We determined that an efficient and facile approach for CoTSPc immobilization should meet the following two factors: (a) an adequate concentration of CoTSPc monomers, which could be obtained by tuning the pH conditions in the immobilization procedure, and (b) a proper pore size and structure of the porous carrier that should match the size of the CoTSPc monomers; therefore, individual confined spaces could stabilize and prevent the monomers from aggregating. In addition, the removal of other dyes and the reuse studies demonstrated that the CoTSPc@MCM-41 catalyst could be recovered and effectively reused for the degradation of most common dyes. The immobilization of CoTSPc in MCM-41 was a facile, green approach that improved the catalytic activity of CoTSPc for the degradation of dye pollutants. Follow-up studies in our laboratory are aimed at exploring further potential uses for the present system in other catalytic transformations, and we are attempting to anchor cationic metallophthalocyanines and porphyrins with MCM-41 in an attempt to determine other advantages of this catalytic strategy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.07.046.

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