# Simple and effective approach for catalytic reductive dechlorination of aromatic compounds

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Abstract: An efficient process for the preparation of 2(3),9(10),16(17),23(24)-octa(*n*-hexyl)cobalt(II)phthalocyanine, [(*n*-hexyl)<sub>8</sub>CoPc] (2) was described. The novel cobalt(II)phthalocyanine was characterized by spectroscopic methods. It was employed as a catalyst for the room temperature reductive dechlorination of chlorinated aromatic compounds (CACs). The results were showed that the CACs were completely dechlorinated within (110-120) min.

Key words: Cobalt phthalocyanine, dechlorination, catalyst, chlorinated aromatic compounds.

# Introduction

Chlorinated aromatic compounds (CACs) are resulted as byproducts of several industrial processes. They can be released into water, soil and air from household or industrial facilities. They have accumulated in the food chains. <sup>1,2</sup>

Removal of environmental pollution caused by CACs has been focused, they are considered recalcitrant due to presence of chloride atom at benzene ring. To the best of our knowledge, few chemical methods described the elimination of Chloride atom from CACs, through photochemical dechlorination <sup>3</sup> or electrolytic reduction <sup>4</sup> or sodium, potassium and calcium-based reduction, <sup>5</sup> also sodium borohydride used at elevated temperatures <sup>6</sup> or hydrolytic reductive and oxygen dependent dehalogenation. <sup>7</sup>

The problems associated with CACs incineration have prompted extensive research in developing new disposal methods, such as reductive dechlorination. The reductive dechlorination with sodium alkoxyborohydride by using of transition metal also have been described. <sup>8,9</sup> Additionally, the catalytic hydrodechlorination by using Pd/C–Et<sub>3</sub>N as catalyst has become of interest. <sup>10,11</sup>

Few researchers have performed systematic studies of catalytic hydrodechlorination as an alternate method of treating or recycling chlorinated waste streams. Although many different hydrodechlorination catalysts and many model compounds have been used. <sup>12</sup> It is usually mediated by a transition-metal catalyst, <sup>13</sup> molecular hydrogen (H<sub>2</sub>) in the metal-catalyzed reductive dechlorination, <sup>14</sup> or using the other hydrogen sources such as hydrazine, formic acid and its salts, *etc.* <sup>15</sup> Recently, the hydrodechlorination of polychlorinated biphenyls (PCBs) in water–isopropanol systems and in the presences of catalysts have also been studied. <sup>16</sup>

Metallophthalocyanines (Pcs) have been used as a catalyst for a variety of transforming harmful environmental pollutants into less harmful through eco-friendly reactions, <sup>17</sup> they prepared by conventional methods, <sup>18</sup> especially cobalt(II)phthalocyanines are the most interesting classes of highly effective catalyst because of their easy preparation from cheap precursors in a large scale and their thermal and chemical stability. <sup>19</sup> They exhibit excellent activity, stability and recyclability. <sup>20</sup>

In this work, we present the results from studying the reductive dechlorination of CACs on a cobalt(II)phthalocyanines catalyst. The results of this study could be useful for the degradation of halogenated environmental pollutants.

#### **Experimental**

#### Materials

The starting precursor 4,5-di-*n*-hexylphthalonitrile (1) required for the synthesis of CoPc catalyst was synthesized as reported in our previous work. <sup>18</sup> All the mono chlorinated aromatic compounds (CACs) used in this work: 1-Chloro-4-methylbenzene (98%), 1-Chloro-4-ethylbenzene (97%), 1-Chloro-4-propylbenzene (97%), 4- Chlorobiphenyl (95%), 1-Chloronaphthalene (85%) and 1-Chloroanthracene (95%) were purchased from Acros and Aldrich and used as received. The other reagents, such as organic solvents and bases were analytical grade.

# Preparation of the catalyst

Preparation of 2(3),9(10),16(17),23(24)-octa(*n*-hexyl)cobalt(II)phthalocyanine, [(*n*-hexyl)\_8CoPc] (**2**).

Under a nitrogen atmosphere, a standard Schlenk tube was charged with a mixture of 4,5*n*-dihexyl phthalonitrile 1 (0.6 g, 1.84 mmol), anhydrous cobalt chloride hexahydrate, 6H<sub>2</sub>O (0.14 CoCl<sub>2</sub>. g, 0.77 mmol), deoxygenated DMAE (5 ml) and diazabicyclo[5.4.0]undec-7-ene (DBU) (0.44 g, 3 mmol). It was irradiated with well stirring in a microwave reactor at 370W for 10 min. Then cooled to room temperature. A blue solution was formed, and then poured into MeOH/H<sub>2</sub>O (3:1). The suspended solution was centrifuged. The resulted precipitated was filtered off. It washed with a methanol/water mixture (1/1, v/v) and then dried under vacuum. The crude product (0.98 g) was subjected to column chromatography (50 g of on aluminium oxide using CHCl<sub>3</sub>:CH<sub>3</sub>OH (9:1) as eluent) to yield 0.66 g (67%) of compound 2 as blue violet powder.

IR (KBr, cm<sup>-1</sup>): 3053 mArH; 1650 m(C-C); 1473 (C–CH); 1436 mPh; 1082 (C–CH); 740 (C–C). UV–Vis (DMF),  $\lambda_{max}$  (nm): 668, 602, 346. MS (FD): m/z 1244.74 (M<sup>+</sup>).

Elemental analysis: C<sub>80</sub> H<sub>112</sub>N<sub>8</sub> Co, found C 76.68, H 8.73, N 8.42 (Calcd. C 77.29,H 9.06, N 9.01).

#### Instruments and characterization methods

Microwave oven utilized for heating: Discover Lab Mate single mode microwave cavity from CEM Corporation. The reactions were conducted in a 25 ml Schlenk tube, with a maximum operating temperature of 180 °C and a maximum operating pressure of 8 bar. FT-IR spectra were recorded on a Bruker IFS 48 spectrometer using KBr pellets. The Ultraviolet-Visible Spectroscopy (UV-Vis) spectra of the fresh prepared and produced CoPc were taken in N,N-dimethylformamide (DMF) using a Shimadzu UV-1800 spectrophotometer. FD mass spectra measurements were carried out with a Varian MAT 711 a spectrometer and reported as mass/charge (m/z). Elementary analyses were performed on a Carlo Erba Elemental Analyzer 1104, 1106. BET surface area and pore size distribution measurements were determined from nitrogen adsorption at 200 °C. using the A Nova 2200e instrument (Quantachrome Instrument USA) along with a NOVAWin2 (Quantachrome Instrument) data analysis software [NOVAWin2, V.2.2, operation manual, NoVA series Windows based Operating and Data Analysis Software, Quantachrome Instruments, FL. USA. 2006.]; Surface area was determined from the application of the BET equation. XRD was performed on an INEL CPS 180 powder diffractometer EQUINOX 1000 system (filtered Cu Kal radiation, 30KV 30mA, spinning sample holder). The powder pattern analysis was processed by using Match software for phase identification with both COD and ICDD database, IMAD-INEL data processing software for graphical illustrations, MAUD software for Rietveld analysis method, and Fityk software for FWHM estimations.

Scanning electronic microscope (SEM) was used for investigating the surface morphology of the fresh and produced CoPc. The catalyst was examined with a scanning electron microscope (JSM-6360LA, JEOL, Tokyo, Japan).

# **Experimental-Setup**

A modified commercial stirred glass reactor was used for carrying all the reductive dechloroniation reactions (c.f. Fig. 1). It consists of a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flow meter, three-way valve and a

Helium cylinder, with a magnetic stirrer. At room temperature. Under atmospheric pressure, 100 ml Ethanolic solution of CACs (5.0 mmol chlorine atoms) and 50 mg CoPc were added into the flask. Under mild conditions, CACs were treated with hydrogen gas over CoPc in aqueous solutions with constant H<sub>2</sub> flow rate (250 cm<sup>3</sup> min<sup>-1</sup>). A NaOH trap was added into the reaction system to absorb the poison of HCl gas. A liquid sampling was taken system via a controlled syringe. The product was collected and analyzed by a gas chromatography equipped with a flame ionization detector (FID) at the end of the experiment. All products were identified by Micromass GCTTM GC-mass spectroscopy. The catalyst used after each run was recovered and washed by stirring in water for 24 hrs, before starting on a new reductive dechlorination run.

**Fig. 1.** Schematic diagram of the stirred glass reactor system, showing: (1) He cylinder; (2) hydrogen cylinder; (3) needle valve; (4) mass-flow controller; (5) gas sparge tubing; (6) NaOH trap; (7) HCl gas regulator; (8) thermocouple probe adjusted at 25°C; (9) stirring motor; (10) cooling tower; (11) CACs; (12) jacketed reaction vessel; (13) outlet of dechlorinated aromatic compounds (DACs); (14) GC sampling tubing; (15) GC; (16) data acquisition.

# **Analytical procedure**

Under atmospheric pressure and at room temperature, the reductive dechlorination reaction was performed. In a typical experiment, about 50 mg of catalyst was suspended in a modified commercial stirred glass reactor and CACs were reduced in a flow of hydrogen (30 mL/min) for 2.5 hrs prior to the reaction as shown in Fig. 1. The H<sub>2</sub> flow was kept constant during all experiments. The gas chromatography with a flame ionization detector used for analyzing the products with a VF-Ims capillary 30 M column. by using a deuterated chlorobenzene (C<sub>6</sub>D<sub>5</sub>Cl) as internal standard .

The gas chromatograph Varian, equipped with an FID detector and a VF-Ims capillary column (dimeter: 0:25 mm, length: 30 m, film thickness: 0:25 micro m). Injection was made in splitless mode using helium (He) as the carrier gas and the temperature was set at 200 °C. The products were quantified from peak areas obtained through automated interrogation and by comparison of standards. The concentration of All the mono chlorinated aromatic compounds (CACs) used in this work: (1-Chloro-4-methylbenzene,

1-Chloro-4-ethylbenzene, 1-Chloro-4-propylbenzene, 4- Chlorobiphenyl, 1-Chloronaphthalene and 1-Chloroanthracene) in Ethanol was determined from the total mass in the reaction mixture. The relative peak area% was converted into mol% using regression equations. The amount of HCl produced and hydrogen consumption during the reaction (mol dm<sup>-3</sup>) was calculated from a molar balance based on the GC analysis of organic content. The conversion and yield (as a percentage) were calculated using Eqs. 1 and 2 with respect to dechlorinated aromatic compounds (DACs) in the HDC of CACs is defined as:

$$Conversion_{CACs} = \frac{Feed CACs(mol)_{-} Unreacted CACs(mol)}{FeedCACs(mol)} \times 100(\%)$$
(1)

**Yield** <sub>DACs</sub> =  $\frac{\text{DACs Produced (mol)}}{\text{Feed CACs(mol)} - \text{Unreacted CACs(mol)}} x \ 100(\%)$  (2)

#### **Results and discussion**

#### Characterization of the catalyst

The physical properties CoPc catalyst are given in Table 1 and Fig. 2. BET surface area and pore size distribution measurements were measured using an A Nova 2200e micrometrics instrument.

**Fig. 2.** The linear regression of BET data (top) and pore size distribution (bottom) measurements.

The synthetic route to novel peripherally octa-substituted cobalt(II) phthalocyanine **2** is shown in Scheme 1. The phthalonitrile derivative **1** was synthesized as reported in our previous work.<sup>18</sup>

The phthalonitrile derivative 1 was irradiated in a microwave reactor at 370W for 10 min, in the presence of  $CoCl_2$  to form the desired complex 2. The new cobalt phthalocyanine 2 was purified by column chromatography with aluminum oxide as an adsorbent. It was obtained in a yield of 67% and was characterized previously by spectral data (IR, UV– Visible spectroscopy, mass spectral data and elemental analysis) [18].

The characterization data of the new compound were consistent with the assigned formula. No aggregation behavior in the purified CoPc **2** spectrum.

Scheme 1. Preparation of peripherally octa-substituted cobalt(II)phthalocyanine 2.

Its main characteristics such as pore size, pore volume, BET surface area was presented in Table 1.

#### Table 1. Catalyst physical properties.

The <sup>1</sup>H NMR spectrum of CoPc **2** could not be taken due to the paramagnetic cobalt(II) centers. In the mass spectrum of **2**, the presence of molecular ion peaks at m/z 1244.74 ( $M^+$ ), confirmed the proposed structures. The results of elemental analysis also confirmed the structure of complex **2**. The electronic absorption spectrum of cobalt phthalocyanine **2** in DMF at room temperature. The split **Q** bands appeared at 669 and 602 nm, while the split **B** band remained at 346 nm c.f. Fig. 3.

Fig. 3. UV–Visible spectrum in DMF of CoPc before and after reductive dechlorination.

The XRD patterns of the fresh CoPc catalyst (a) and after six runs of reductive dechlorination experiments (b) are shown in Fig. 4. The catalyst was showed the peaks at  $2\theta$  values of 10, 20, 30 and 45, respectively, related to phthalocyanine moiety.

Fig. 4. XRD patterns of CoPc before and after reductive dechlorination .

Scanning electronic microscope was used for the investigation of the surface morphology. Figures (5a&b) were showed the surface morphology of the CoPc catalyst, the results were showed that the image (a) is a mirror image of the image (b) after six runs.

**Fig. 5.** SEM images of CoPc catalyst fresh (a) and after used six runs (b), respectively. **Reductive dechlorination of CACs under different experimental conditions** 

Firstly, a series of blank experiments were examined without catalyst with the CACs preliminary concentration of 100 mg and hydrogen flow rate (250 cm<sup>3</sup> min<sup>-1</sup>). It was found that, no reductive dechlorination of CACs occurred in the absence of catalyst.

The reductive dechlorination of CACs with molecular hydrogen over CoPc catalyst in water were carried out at room temperature and atmospheric pressure Scheme 2.

A modified commercial stirred glass reactor used for all the reductive dechlorination reactions as shown in Fig. 1. The main results obtained can be summarized in Table 2. Chlorinated aromatic compounds (CACs) were mainly transformed to dechlorinated aromatic compounds (DACs), and at the same time HCl was formed, but quickly directed

to the NaOH trap in the reactor system to prevent accumulation of HCl at the surface of the catalysts. Therefore, the presence of NaOH trap effectively prevents the poisoning of the CoPc catalyst.

**Table 2.** The reductive dechlorination dynamic data.

Scheme 2. The reductive dechloroniation of CACs over CoPc catalyst at room temperature.

The catalytic reductive dechloroniation of 1-Chloro-4-methylbenzene, 1-Chloro-4ethylbenzene, 1-Chloro-4-propylbenzene, 4- Chlorobiphenyl, 1-Chloronaphthalene and 1-Chloroanthracene in Ethanol as solvent over CoPc catalyst have been investigated. It can be seen from Figs. 6(c-f), a complete dechlorination was occurred with 100% selective through the system within (110-120) min, respectively.

**Fig. 6(a-f).** Reductive dechlorination of 1-Chloro-4-methylbenzene, 1-Chloro-4ethylbenzene, 1-Chloro-4-propylbenzene, 4- Chlorobiphenyl, 1-Chloronaphthalene and 1-Chloroanthracene over CoPc catalyst, respectively.

Analysis of the data plotted in Figs. 6(a-f) shows the kinetic measurements of the decrease in the concentration of the CACs (red curves) as well as the increase in the concentration of the dechlorinated products DACs (violet curves).

The catalytic reductive dechlorination results by using CoPc catalyst with hydrogen gas could be proposed as a process for the detoxification of CACs, where the CACs transformed into lower toxic products, i.e. toluene, ethylbenzene, propylbenzene, biphenyl, naphthalene and anthracene were formed. Therefore, we believe that the CoPc-catalyzed dechlorination could develop an economic technology for removal of chlorinated aromatic compounds in water (Scheme 2).

## The Lifespan of CoPc Catalyst

The Lifespan of CoPC catalyst was tested through the reductive dechloroniation of 1-Chloro-4-methylbenzene into toluene. After each run, the CoPc catalyst was collected. It can reused in the next run by using a fresh solvent. The result of a lifespan test of CoPC catalyst was described through four reductive dechloroniation runs with the same catalyst as shown in Fig. 7.

Fig. 7. Conversion of CoPc catalyst used in repeated reductive dechlorination runs.

The activity of the fresh CoPc catalyst in the four runs approximately the same and the conversion of 1-Chloro-4-methylbenzene was 99.66%. For the first run or after the fourth runs of the catalyst, the conversion of 1-Chloro-4-methylbenzene was at 99.27%. This means, no activity of the catalyst was lost.

# Conclusions

In this study microwave-assisted synthesis of new peripherally octa-substituted Co(II) phthalocyanine **2** have been demonstrated as an efficient and green method. The target symmetrical Co(II)phthalocyanine **2** used as catalyst in the reductive dechloroniation of CACs and the complete dechlorination achieved after 120 min with first order reaction kinetic. The CoPc catalyst has exhibit high activity and stability for the room temperature reductive dechloroniation of CACs. This reductive dechloroniation strategy has excellent yield, more high recovery of catalyst, simple experimental working up as well as isolation procedures.

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# Table 1. Catalyst physical properties.

Property (units)	Value	
BET surface area $(m^2/g)$	139.637 m <sup>2</sup> /g	
Pore volume $(cm^3/g)$	$0.395 \text{ cm}^3/\text{g}$	
Average pore diameter (nm)	7.452 nm	

# Table 2. The reductive dechlorination dynamic data

<sup>a</sup> Time required for C-Cl bond cleavage. <sup>b</sup> Yield and recovery values of substrate and product were determined by GC-MS.

CACs Substrate	Time(min) <sup>a</sup>	DACs Product	Yield <sup>b</sup> (%)	Recovery <sup>b</sup> (%)
1-Chloro-4-methylbenzene	110	Toluene	85	>98
1-Chloro-4-ethylbenzene	110	Ethylbenzene	88	>97
1-Chloro-4-propylbenzene	115	Propylbenzene	80	>99
4- Chlorobiphenyl	115	Biphenyl	82	>98
1-Chloronaphthalene	120	Naphthalene	85	>97
1-Chloroanthracene	120	Anthracene	88	>97



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