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PII:	S1010-6030(19)31742-3
DOI:	https://doi.org/10.1016/j.jphotochem.2020.112412
Reference:	JPC 112412
To appear in:	*Journal of Photochemistry & Photobiology, A: Chemistry*
Received Date:	11 October 2019
Revised Date:	22 January 2020
Accepted Date:	25 January 2020

Please cite this article as: Asghari S, Farahmand S, Razavizadeh JS, Ghiaci M, One-step photocatalytic benzene hydroxylation over iron (II) phthalocyanine: a new application for an old catalyst, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2020), doi: https://doi.org/10.1016/j.jphotochem.2020.112412

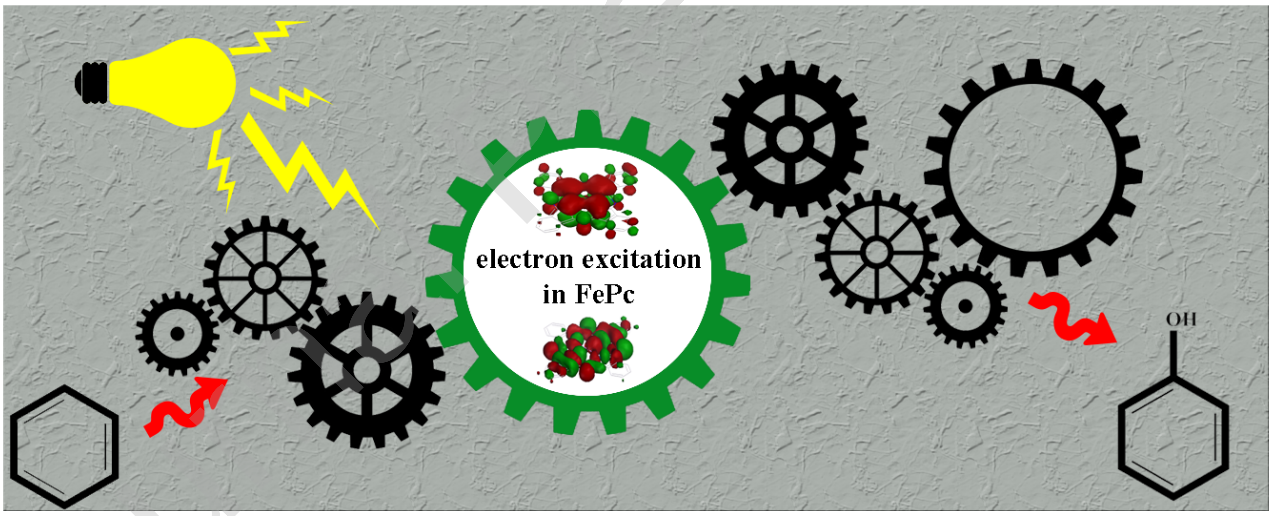
One-step photocatalytic benzene hydroxylation over iron (II) phthalocyanine: a new application for an old catalyst

Saeid Asghari[a], Shohreh Farahmand[a], Jalal. S. Razavizadeh[a], Mehran Ghiaci[a*]

[a] Department of Chemistry, Isfahan University of Technology, Isfahan 8415683111, Iran

*Corresponding author. Tel.; +98-31 3391 3254; FAX: +98-31 3391 2350.
E-mail address: *mghiaci@cc.iut.ac.ir* (M. Ghiaci).

Graphical Abstract



Highlights:

- Visible-light accelerate the hydroxylation of benzene to phenol.
- Phenol was achieved as the only product with high yield and practical TON and TOF.

- High thermal and chemical stability of FePc led to its high reusability.

Abstract

In the present study, iron (II) phthalocyanine was introduced as an effective and recyclable photocatalyst for direct hydroxylation of benzene to phenol as a model reaction under photocatalytic conditions at ambient temperature. The effect of different parameters such as solvent, concentration of the oxidant, irradiation time, and amount of the catalyst was investigated. Acetonitrile was selected as the optimum solvent, where hydrogen peroxide plays the role of the oxidant which is considered as an eco-friendly process. The results not only showed a 15.2% yield of phenol at a selectivity of higher than 99% under optimized condition but also exhibited a highly stable and reusable behavior. The catalyst was thoroughly characterized by UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR), field emission electron microscopy (FE-SEM), high-resolution transmittance electron microscopy (HR-TEM), X-ray diffraction (XRD), nitrogen adsorption-desorption isotherm (BET), and X-ray photoelectron spectroscopy (XPS). Density-Functional Tight-Binding (DFTB+) calculation was used to study the catalyst transition energy on the Materials Studio software.

Keywords: Benzene, Iron phthalocyanine, Photocatalytic hydroxylation, Phenol, Materials studio 8.0

1. Introduction

Phenol is regarded as one of the most important raw materials in the chemical industries due to the key role in the synthesis of various useful compounds such as bisphenol A, epoxy resins, polycarbonates, dyes and pigments, pharmaceuticals, and agrochemicals [1–5].

Therefore, demand for phenol production is rising dramatically [6]. Although the Fenton reagent (Fe^{2+}-H_2O_2) traditionally used for benzene hydroxylation, highly acidic conditions and producing a great quantity of corrosive wastes has limited its application. In spite of the fact that the well-known cumene process is extensively used to produce phenol [7–9], it suffers from notable drawbacks such as high energy consumption, low yield and selectivity of phenol (~5-6%) [10], harsh reaction conditions, and formation of the considerable amount of acetone as a by-product [11]. To meet the elimination of crucial bottlenecks of the cumene process and to consider environmental issues, many attempts have been developed to find an appropriate alternative method for synthesis of phenol. Recently, one-step hydroxylation of benzene to phenol as an appealing route has received considerable attention. In this regard, direct hydroxylation of benzene has been widely studied using several kinds of oxidizing agents such as H_2O_2 [12,13], N_2O [14,15], and O_2 [16,17]. Molecular oxygen can be considered as one of the best choices due to its natural abundance, low cost, and environmentally friendly properties [18,19], however, harsh reaction conditions [20,21] and the need for reducing agents (hydrogen gas, ascorbic acid, nicotinamide adenine dinucleotide (NADH), etc.) has restricted its practicality [16]. Consequently, one-step hydroxylation of benzene using hydrogen peroxide has attracted extensive attention due to the prominent properties such as being an eco-friendly and affordable oxidant, cleaner reaction conditions and producing water as the only by-product. [22]. However, many reported catalysts suffer from the low yield or poor selectivity of the desired product because of the poor reactivity of the aromatic C-H bond [23]. Thus, the effort to design and synthesis of effective catalysts is still a never-ending challenge.

Photocatalytic hydroxylation of benzene to phenol have brought into focus in recent studies. Against this background, employing inexpensive visible light seems to be more efficient and promising. In contrast to conventional methods, photocatalytic reactions carried out under mild conditions. As the aromatic C-H bond activation has been becoming a holy grail particularly in oxidation reactions, driving the hydroxylation of benzene in the presence of visible light as a green source of energy can be considered as a prosperous route. Up to now, several homogeneous systems [24] are introduced such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) [25] for photocatalytic hydroxylation, however, their utilization is restricted due to the problem of catalyst separation [24,25].

Transition metal complexes are regarded as the high-performance catalysts in the oxidation of different organic substrates. Recently, the increasing application of iron complexes predicts a renaissance in the non-noble metal catalysis [26]. Metallophthalocyanines (MPCs) are a class of metal complexes with remarkable features such as high chemical and thermal stability and facile preparation using cheap raw materials. Moreover, they were used as effective oxidation catalysts for a wide range of organic substrates such as toluene [27], benzyl alcohol [28], olefins [29], and mercaptans [30]. MPCs with the extended π-conjugated structures are regarded as versatile photocatalysts capable of the production of highly reactive intermediates via radical routes [31]. These macrocycles are naturally found in most active sites of oxygenase enzymes [32,33] and can activate a variety of inactive bonds even C-H bond in methane [34,35]. Presumably, like other Fe(II) containing materials, Iron (II) phthalocyanine (FePc) can turn hydrogen peroxide into the hydroxyl radicals via the Fenton-like route, which provides a successful pathway to hydroxylation of benzene under the photocatalytic conditions [36]. It is worth noting that, MPCs are normally insoluble in common organic solvents such as acetonitrile which endows them the possibility of recovery. The highlight features above promote the motivation of utilization of MPCs as the heterogeneous photocatalysts in the various oxidation reactions [37,38].

Herein, FePc was successfully synthesized using microwave irradiation known as a green approach, and its photocatalytic behavior was assessed in the liquid-phase hydroxylation of benzene as a model reaction. A proper yield of phenol was achieved by controlling reaction parameters, selecting an appropriate solvent, and optimizing the amount of oxidant and catalyst. By controlling the reaction conditions, the maximum yield of phenol and TON reached 15.2% and 84.7, respectively, which rival those of noble-metal catalysts. Also, the reusability of the catalyst investigated, and the catalytic reactivity maintained during four successive runs.

2. Experimental

2.1. Materials

Ammonium heptamolybdate tetrahydrate and dimethylformamide (DMF) were prepared from Sigma-Aldrich Co. Phthalic anhydride, urea, iron (II) sulfate tetrahydrate, benzene, ethanol, and hydrogen peroxide (30 wt%) were purchased from Merck Chemical Co. All the chemicals were used without any further purification.

2.2. Characterization techniques

The catalyst was fully characterized using ICP-OES, UV-Vis, FT-IR, DRS, XPS, XRD, FE-SEM, HR-TEM, BET, GC, and GC-MS techniques which are described in the supporting information.

2.3. Preparation of FePc

The procedure for the synthesis of FePc is described in detail in the supporting information. The structure of FePc confirmed by FT-IR, NMR, XRD, FE-SEM, HR-TEM, and N_2 sorption-desorption studies (Fig. S1-S6).

2.4. General procedure for photocatalytic hydroxylation

Photocatalytic reactivity of the synthesized catalyst was studied for benzene hydroxylation as a benchmark for the oxidation reaction. In this regard, a suspension containing FePc (5.25×10^{-2} mmol, 30 mg), benzene (11.25 mmol, 1 mL), hydrogen peroxide (32.65 mmol, 3 mL), and acetonitrile (5 mL) was prepared. The resulting mixture was then transferred into the sealed reaction tubes and allowed to stirrer under light irradiation using a 100 W mercury lamp at room temperature conditions. The reaction tube was placed in a 15 cm distance to the lamp (light intensity =383.68 (W/m^2)). After sufficient time, the catalyst was separated using centrifuging (10 min, 6000 rpm). The mixture of reaction was analyzed by GC-MS techniques using acetophenone as the internal standard. Finally, the yield and selectivity of the phenol were calculated by using the following equations:

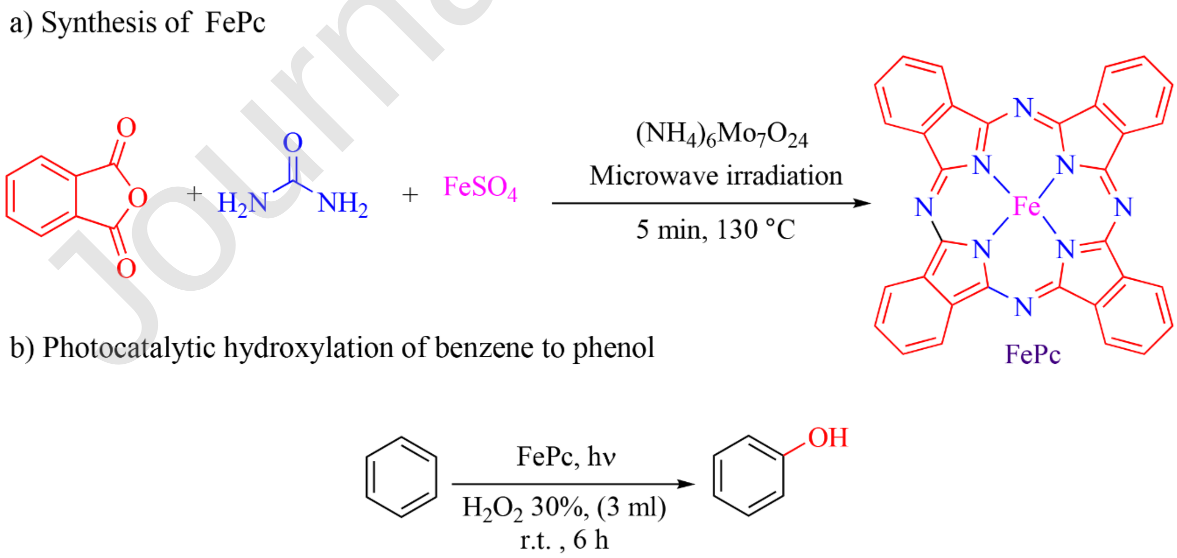
$$Phenol\ yield = \frac{mmol\ of\ phenol}{mmol\ of\ initial\ benzene} \times 100 \qquad (1)$$

$$Phenol\ selectivity = \frac{mmol\ of\ phenol}{mmol\ of\ total\ products} \times 100 \qquad (2)$$

3. Results and discussion

3.1 synthesis of FePc and photocatalytic test

The synthesis of FePc was illustrated in Scheme 1a, where phthalic anhydride has involved in a cyclotetramerization by urea in the presence of iron (II) sulfate tetrahydrate under microwave irradiation. FePc was purified as described in the experimental section and its structure was characterized by FE-SEM, HR-TEM, XPS, XRD, UV-Vis, DRS, and IR. Furthermore, photocatalytic benzene hydroxylation reaction was performed at room temperature using hydrogen peroxide as the oxidant (Scheme 1b). To achieve the highest yield and selectivity of the phenol, several experiments were carried out to optimize conditions.



Scheme 1. Preparation of FePc (a) and benzene hydroxylation over FePc (b)

3.2. UV-Vis studies

Fig. 1 shows the UV-Vis spectrum of FePc in DMF with a considerable extinction coefficient (approximately 10^5 L. $mol^{-1}.cm^{-1}$) due to the 18 π-electron conjugated system [39]. The electron transition of $a_{1u}\rightarrow e_g$ leads to the Q-band at 662 nm [40]. Fig. 2a shows the DRS of FePc which is measured and transformed into the Kubelka-Munk (Fig. 2b) function to calculate the experimental transition energy (E_{Tr}) of FePc and the obtained result is 2.25 eV which is in a good agreement with theoretical data (Table 6).

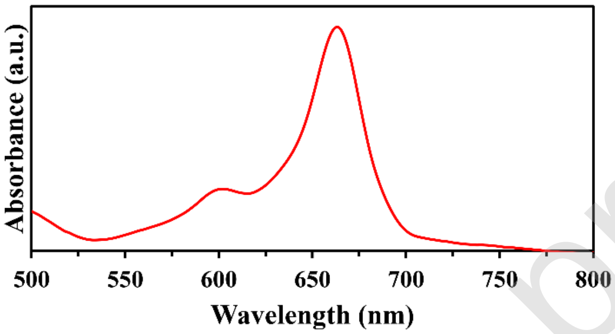


Fig. 1. UV-Vis spectrum of FePc

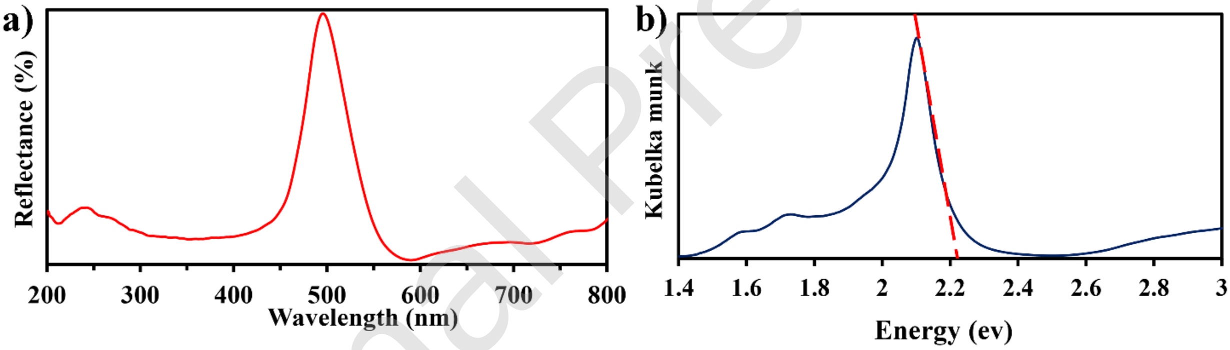


Fig. 2. Diffuse reflectance of FePc (a) and Kubelka-Munk fitted spectrum (b)

3.6. XPS analysis

The XPS spectrum of FePc is shown in Fig.3(a-d). XPS results at the region of Fe 2p (Fig. 3d) displays two main peaks at 712.1 eV and 721.7 eV which are correlated to $2p_{3/2}$ and $2p_{1/2}$, respectively [41]. Splitting of these peaks (Fe $2p_{1/2}$ –Fe $2p_{3/2}$) is about 9.2 eV which indicates a normal state of paramagnetic high spin Fe (II) in FePc [41,42]. Deconvoluted N 1s spectrum (Fig. 3b) consists mainly of four peaks which are related to pyridinic-N of the FePc rings (398.8 eV), pyrrolic-N and imine bonds in the FePc structure (400.4 eV), and shake-up electron transitions of pyrrole rings (402.3 eV and 404.8 eV), respectively [43]. It is worth noting that the nitrogen atoms are mainly coordinated to Fe through the pyridinic-N atoms (85.3 %), whereas the other peaks represent about 6.2%, 4.2%, and 4.2%, respectively [44]. Deconvoluted C 1s spectrum (Fig. 3c) also consists of four peaks. Two main peaks which are found at 284.8 eV and 285.9 eV are related to 24 carbon atoms in the benzene rings and 8 carbon atoms in the pyrrole rings, respectively. Also, the peaks which are observable at 287.5 eV and 289.0 eV are related to shake-up satellites of pyrrole carbon atoms in the FePc structure [45]. The peak at 200.19 eV is attributed to Cl 2p as a result of the residual amount of chlorine from the purification step.

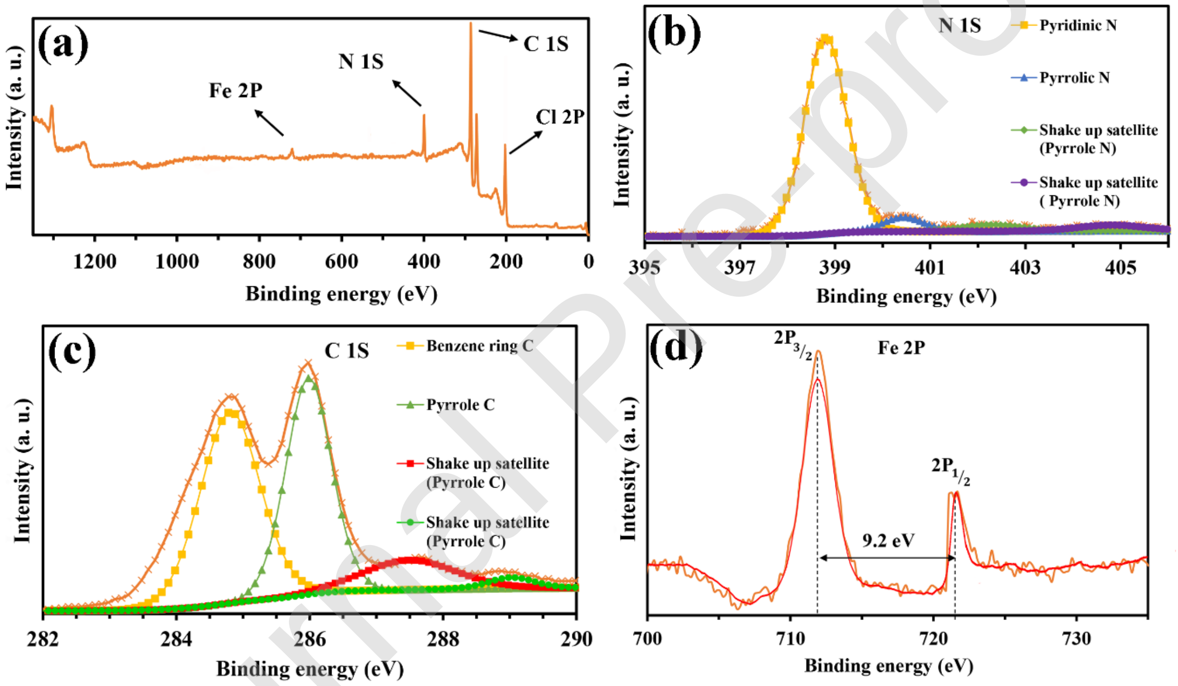


Fig. 3. Full survey XPS spectra (a), at the region of N 1S (b), C 1s (c), Fe 2p (d)

3.8. Photocatalytic reactions

The photocatalytic reactivity of FePc was studied in the hydroxylation of benzene to phenol using hydrogen peroxide as an eco-friendly oxidant. Various parameters such as the effect of the solvent, time, concentration of the oxidant, and amount of the catalyst were investigated and all results are collected in Tables 1-5.

3.8.1 Effect of solvent on the yield of phenol

Various organic solvents tested for the hydroxylation of benzene using hydrogen peroxide (Table 1). The reaction was not performed in solvent-free conditions as well as in non-polar solvents such as hexane, carbon tetrachloride, and chloroform due to insoluble raw material and oxidant. Also, a mixture of H_2O:butanol did not provide the desired medium for this reaction, might be due to the oxidation capability of the solvent. The moderate yield of phenol was achieved using acetone while acetonitrile shows the highest yield of the desired product. Acetonitrile as an aprotic polar solvent leads to the considerable miscibility of the organic and aqueous reactants as two distinct phases [46,47]. Moreover, one of the intriguing features of nitrile solvents is the ability of formation of peroxycarboximidic acid in the presence of hydrogen peroxide, which can act as a co-catalyst to facilitate the hydroxylation of benzene [48].

Table 1. Effect of the solvent on the phenol yield

Entry	Solvent	Yield (%)[a] ±SD	Selectivity (%)
1	Solvent-Free	1.3 ± 0.1	>99
2	H_2O:Butanol (2:1)	1.8 ± 0.1	>99
3	Acetonitrile	15.2 ± 0.1	>99
4	Acetone	7.4 ± 0.1	>99
5	Hexane	<1	>99
6	Carbon tetrachloride	<1	>99
7	Chloroform	1.2 ± 0.1	>99

Reaction conditions: Benzene (11.25 mmol), H_2O_2 (32.65 mmol), FePc (30 mg), solvent (5 mL), r.t., 6 h.
[a] Phenol yield = mmol phenol/mmol initial benzene

3.8.2 Effect of time on the yield of phenol

The reaction did not progress in the first hour, but phenol was formed as time increased. (Table 2). After 2 h, the phenol efficiency did not improve, and therefore the 6 h time was chosen as the optimum time.

Table 2. Effect of time on the phenol yield

Entry	Time (h)	Phenol yield (%)	Selectivity (%)
1	2	2.4 ± 0.1	>99
2	4	8.4 ± 0.1	>99
3	6	15.2 ± 0.1	>99
4	10	15.8 ± 0.1	>99

Reaction conditions: Benzene (11.25 mmol), H_2O_2 (32.65 mmol), FePc (30 mg), Solvent (5 mL), r.t.

The kinetics of the reaction was studied by plotting the ln (C_t/C_0) versus time (Fig. 4). C_0 and C_t are due to the initial benzene concentration and benzene concentration at time t, respectively. Thus, the rate constant of the reaction calculated to be 0.025 h^{-1} ($4.15\ {}^{\times}10^{-4}\ S^{-1}$).

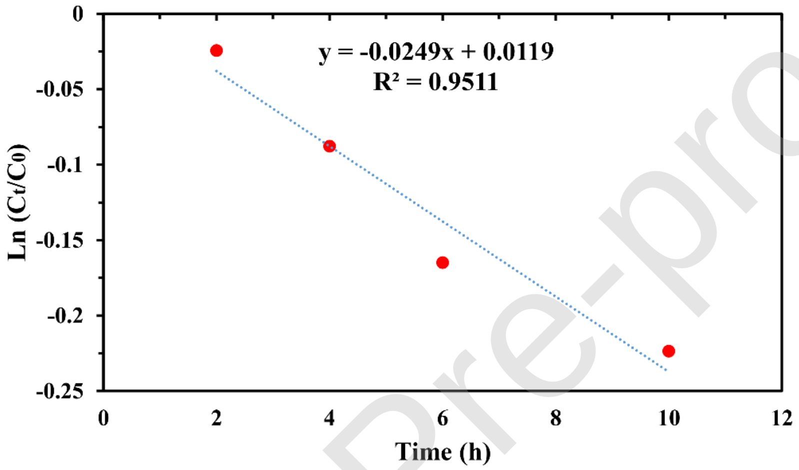


Fig. 4. Kinetics studies for the benzene hydroxylation reaction.

3.8.3 Effect of the oxidant/benzene ratio on the yield of phenol

The effect of the concentration of hydrogen peroxide on the yield of phenol investigated using different molar ratios of oxidant to benzene, and all results collected in Table 3. The yield of phenol reached the maximum when the oxidant/benzene ratio increased from 1 to 3. More increase in this ratio led to over-oxidation products such as hydroquinone. Consumption of the hydrogen peroxide in the oxidation reaction and its self-decomposition made the lower effectiveness of this oxidant. Therefore, the molar ratio of the oxidant to benzene should be more than stoichiometric ratios. Based on the previous studies, the amount of oxidant in the present work is more affordable [13,22].

Table 3. Effect of oxidant to benzene ratio on the phenol yield

Entry	Oxidant/benzene	Phenol yield (%)	Selectivity (%)
1	1	0.7 ± 0.1	>99
2	2	4.0 ± 0.1	>99
3	3	15.2 ± 0.1	>99
4	4	15.5 ± 0.1	>99
5	5	5.4 ± 0.1	62[a]

Reaction conditions: Benzene (11.25 mmol), FePc (30 mg), acetonitrile (5 mL), r.t., 6 h. [a] Hydroquinone identified as the by-product of the reaction.

3.8.4 Effect of the amount of the catalyst on the yield of phenol

For investigating the effect of the amount of catalyst, the amount of FePc was varied from 10 to 40 mg. while the other parameters were kept constant. The results summarized in Table 4, showing the conversion of reaction increased rapidly from 2% for 10 mg of the catalyst to 7.6% for 20 mg of the catalyst, and the maximum conversion achieved using 30 mg of the catalyst. Further increase in the amount of the catalyst had no noticeable effect on the yield of the phenol. Moreover, the catalyst is not active enough in the absence of light, and the yield of phenol was miserable (Table 4, entry 5).

Table 4. Effect of the amount of catalyst on the phenol yield

Entry	Amount of Cat. (mg)	Phenol yield (%)	Selectivity (%)
1	Catalyst-free	Trace	Trace
2	10	2.0 ± 0.1	>99
3	20	7.6 ± 0.1	>99
4	30	15.2 ± 0.1	>99
5	30[a]	1.8 ± 0.1	>99
6	40	15.8 ± 0.1	>99

Reaction conditions: Benzene (11.25 mmol), H_2O_2 (32.65 mmol), acetonitrile (5 mL), r.t., 6 h. [a] In the absence of light.

3.9 Catalyst recovery

The recycle-ability of FePc investigated using a reaction under the optimized conditions. By completion of the reaction, the catalyst separated using centrifugation (10 min, 6000 rpm), washed with acetonitrile and ethanol several times, and then dried at 60 ˚C. The catalyst was subjected to further photocatalytic reactions under optimized conditions. The results depicted in Fig. 5 showed that the synthesized catalyst had no diminution in the reactivity after four cycles that clarifying the catalyst has notable stability in the structure. Also, ICP results showed the iron content of the catalyst is nearly constant during the four runs of reaction (Table. 5).

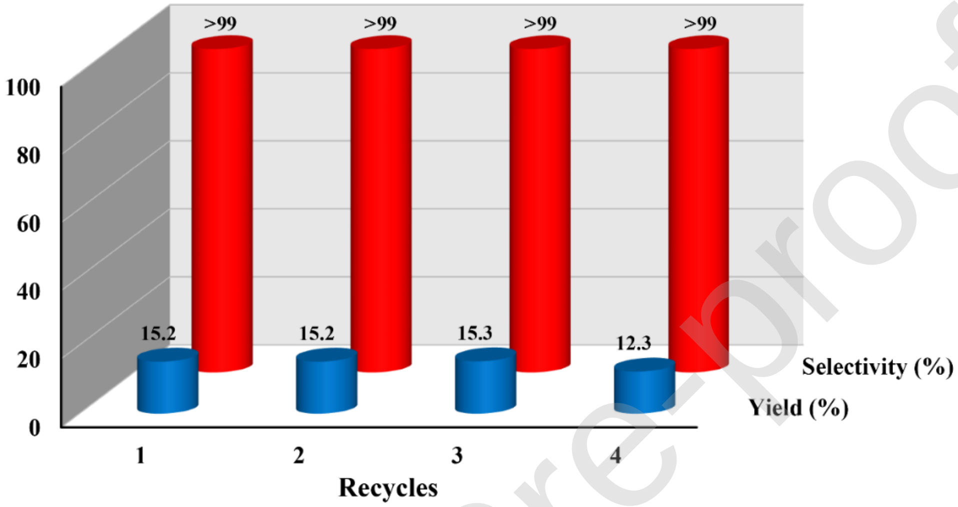


Fig. 5 Reusability of FePc

Table. 5. The results of ICP for Iron content in the FePc during four runs of reactions

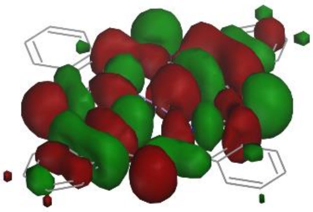
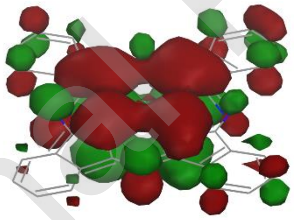
Entry	Run [a]	Iron Content in the catalyst (% wt.) [b]
1	1st	0.3756
2	2nd	0.3586
3	3rd	0.3402
4	4th	0.3422

[a] Reaction conditions: Benzene (11.25 mmol), H_2O_2 (32.65 mmol), FePc (30 mg), acetonitrile (5 mL), r.t., 6 h. [b] Iron content of the FePc in 50 mg catalyst which was measured using ICP-OES

3.10. Molecular Simulation Calculation

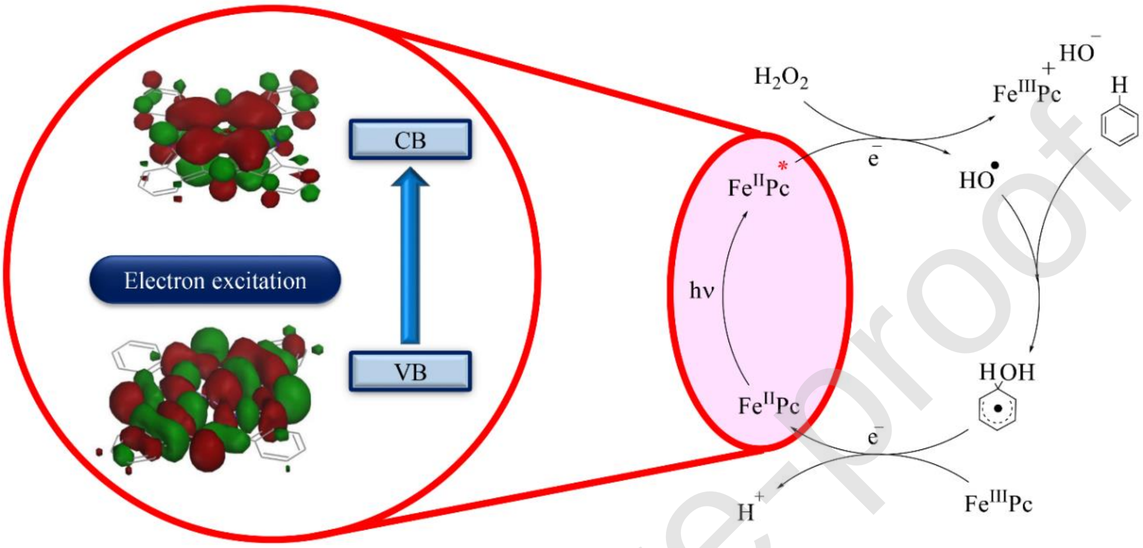
Molecular simulation calculation was applied to explore the Capability of FePc as a photocatalyst. Accordingly, the Dmol^3 module of materials studio 8.0 was used to optimize the FePc structure with density mixing (charge 0.2, spin 0.5) by the PWC local density approximation (LDA) in conjunction with double numerical basis set [49,50]. The optimized structure used to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of FePc by density-functional tight-binding (DFTB+). The theoretical E_{Tr} of FePc is consistent with the experimental E_{Tr} obtained from the Kubelka-Munk function described earlier. The results have summarized in Table 6.

Table 6. Orbital distribution structures and energies for FePc

Structure	Orbital distribution structure	Energy (eV)	E_{Tr} (eV)
HOMO		3.76	2.42
LUMO		6.18	

3.11. A proposed mechanism

Concerning the results attained in this study and reported literature [36], the mechanism of photocatalytic hydroxylation of benzene during a Fenton-like process is shown in Scheme 2. It is clear that the catalytic reactivity of MPCs is strongly dependent on their metal centers [51]. The first step of the photocatalytic hydroxylation of benzene begins with a single electron transition from the valance band to the conduction band. Arguably, the excited state of the FePc (FePc*) can activate the hydrogen peroxide by a single electron transfer process to produce hydroxyl radicals. In the next step, the hydroxyl radical addition to the benzene moiety creates a cyclohexadienyl radical as an intermediate of benzene hydroxylation. Furthermore, a hydrogen abstraction from the intermediate produces phenol and regenerate the catalyst [52].



Scheme 2. A proposed mechanism for photocatalytic hydroxylation of benzene using FePc.

3.12 Comparison of FePc with other reported catalysts

In Table 7 the results obtained from previously reported catalysts for direct hydroxylation of benzene to phenol using hydrogen peroxide are compared to the present study. Composites of iron (II) based on zeolites and mesoporous silica (entries 1-3), graphene, other carbon-based catalysts (entries 4-6), and metal-organic frameworks (entry 7) are examples of catalysts which have been used in liquid-phase hydroxylation of benzene to phenol. In the present study iron (II) phthalocyanine was successfully synthesized using a more beneficial microwave method which represented the desired photocatalytic reactivity.

Table 7. Photocatalytic activity of FePc and some previously reported catalysts for benzene hydroxylation.

Entry	Catalyst	hν	Time (h)	Temp. (˚C)	Phenol yield (%) [a]	Phenol sel. (%)	TON [b]	TOF(h^{-1}) [c]	reference
1	Fe-CN/TS-1	+	4	60	10	96	10.04	2.51	[53]
2	Fe-*g*-C_3N_4/SBA-15	+	4	60	12	94.3	59.4	14.84	[54]

3	VO_x/SBA-16	-	4	60	13.8	97.5	32.4	8.1	[55]
4	CNT7000	-	6	60	5.8	91.5	-	-	[12]
5	FG7-10	-	6	60	1.4	89.1	-	-	[12]
6	CCG	-	8	60	17.5	97	-	-	[56]
7	MIL-100(Fe)	+	8	r. t.	20	98	0.083	0.010	[22]
8	FePc [d]	+	6	r. t.	15.2	100	508.17	84.7	this work

[a] Phenol yield = mmol phenol / mmol initial benzene. [b] Turnover number (TON)= (mmol phenol / mmol Fe). [c] Turnover frequency (TOF)= (TON / time)

[d] Reaction conditions: Benzene (11.25 mmol), H_2O_2 (32.65 mmol), FePc (30 mg), Solvent (5 mL), r.t., 6 h.

5. Conclusion

In summary, FePc was prepared by microwave irradiation during a cyclotetramerization of phthalic anhydride, in the presence of iron (II) sulfate and urea. The uniform spherical structure with a narrow size distribution of catalyst was demonstrated by electron microscopy images. The theoretical and experimental results obtained from DFTB+ calculation and Kubelka-Munk function confirmed the capability of the synthesized structure as a visible-light photocatalyst. In this regard, the FePc* promotes the formation of hydroxyl radicals via a SET mechanism to initiate the one-step hydroxylation of phenol. Controlling the reaction parameters and selection of a proper solvent allowed us to achieve 15.2% yield of phenol. Therefore, this investigation expressed FePc as a stable and reusable photocatalyst which effectively produces phenol from benzene. Moreover, it can compete for the well-known cumene process which involves time- and energy-consuming processes.

Author Statement

The present work is funded by the Isfahan University of Technology, and I as the advisor of the project have submitted the manuscript for publication in the Journal of Photochemistry and Photobiology A: Chemistry.

Conflict of Interest

The authors declare no competing financial interest.

Acknowledgments

This work was partially supported by the research council of the Isfahan University of Technology (IUT), Iran.

References

[1] C. Díaz Blanco, M.D. González, J.M.D. Monmany, T. Tzanov, Dyeing properties, synthesis, isolation and characterization of an in situ generated phenolic pigment, covalently bound to cotton, Enzyme Microb. Technol. 44 (2009) 380–385. doi:10.1016/j.enzmictec.2009.02.003.

[2] C. Sarangapani, G. O'Toole, P.J. Cullen, P. Bourke, Atmospheric cold plasma dissipation efficiency of agrochemicals on blueberries, Innov. Food Sci. Emerg. Technol. 44 (2017) 235–241. doi:10.1016/j.ifset.2017.02.012.

[3] S. Oksana, B. Marian, R. Mahendra, S.H. Bo, Sytar Oksana, Plant phenolic compounds for food, pharmaceutical and cosmetics production, J. Med. Plants Res. 6 (2012) 2526–2539. doi:10.5897/JMPR11.1695.

[4] S. Benyahya, C. Aouf, S. Caillol, B. Boutevin, J.P. Pascault, H. Fulcrand, Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins, Ind. Crops Prod. 53 (2014) 296–307. doi:10.1016/j.indcrop.2013.12.045.

[5] I. McDowell, S. Taylor, C. Gay, The phenolic pigment composition of black tea liquors—part I: Predicting quality, J. Sci. Food Agric. 69 (1995) 467–474. doi:10.1002/jsfa.2740690411.

[6] S.M. Hosseini, M. Ghiaci, S.A. Kulinich, W. Wunderlich, H. Farrokhpour, M. Saraji, A. Shahvar, Au-Pd@g-C3N4 as an Efficient Photocatalyst for Visible-Light Oxidation of Benzene to Phenol: Experimental and Mechanistic Study, J. Phys. Chem. C. 122 (2018) 27477–27485. doi:10.1021/acs.jpcc.8b08788.

[7] H. Hock, S. Lang, Autoxydation von Kohlenwasserstoffen, IX. Mitteil.: Über Peroxyde von Benzol-Derivaten, Berichte Der Dtsch. Chem. Gesellschaft (A B Ser. 77 (1944) 257–264. doi:10.1002/cber.19440770321.

[8] Y. Aratani, K. Oyama, T. Suenobu, Y. Yamada, S. Fukuzumi, Photocatalytic hydroxylation of benzene by dioxygen to phenol with a cyano-bridged complex containing FeIIand RuIIincorporated in mesoporous silica-alumina, Inorg. Chem. 55 (2016) 5780–5786. doi:10.1021/acs.inorgchem.5b02909.

[9] C.A. Antonyraj, K. Srinivasan, One-Step Hydroxylation of Benzene to Phenol Over Layered Double Hydroxides and their Derived Forms, Catal. Surv. from Asia. 17 (2013) 47–70. doi:10.1007/s10563-013-9153-8.

[10] Z. Long, Y. Zhou, G. Chen, W. Ge, J. Wang, C3N4-H5 PMo10V 2O40: A dual-catalysis system for reductant-free aerobic oxidation of benzene to phenol, Sci. Rep. 4 (2014) 1–5. doi:10.1038/srep03651.

[11] W.L. Luyben, Design and control of the cumene process, Ind. Eng. Chem. Res. 49 (2010) 719–734. doi:10.1021/ie9011535.

[12] G. Wen, S. Wu, B. Li, C. Dai, D.S. Su, Active sites and mechanisms for direct oxidation of benzene to phenol over carbon catalysts, Angew. Chemie - Int. Ed. 54 (2015) 4105–4109. doi:10.1002/anie.201410093.

[13] L. Wu, W. Zhong, B. Xu, Z. Wei, X. Liu, Synthesis and characterization of copper(ii) complexes with multidentate ligands as catalysts for the direct hydroxylation of benzene to phenol, Dalt. Trans. 44 (2015) 8013–8020. doi:10.1039/c5dt00575b.

[14] R. Navarro, S. Lopez-Pedrajas, D. Luna, J.M. Marinas, F.M. Bautista, Direct hydroxylation of benzene to phenol by nitrous oxide on amorphous aluminium-iron binary phosphates, Appl. Catal. A Gen. 474 (2014) 272–279. doi:10.1016/j.apcata.2013.08.043.

[15] A.J.J. Koekkoek, W. Kim, V. Degirmenci, H. Xin, R. Ryoo, E.J.M. Hensen, Catalytic performance of sheet-like Fe/ZSM-5 zeolites for the selective oxidation of benzene with nitrous oxide, J. Catal. 299 (2013) 81–89. doi:10.1016/j.jcat.2012.12.002.

[16] S. Shang, B. Chen, L. Wang, W. Dai, Y. Zhang, S. Gao, High-performance recyclable V-N-C catalysts for the direct hydroxylation of benzene to phenol using molecular oxygen, RSC Adv. 5 (2015) 31965–31971. doi:10.1039/c5ra04836b.

[17] S. Fukuzumi, K. Ohkubo, Organic synthetic transformations using organic dyes as photoredox catalysts, Org. Biomol. Chem. 12 (2014) 6059–6071. doi:10.1039/c4ob00843j.

[18] A. Okemoto, Y.H. Tsukano, A. Utsunomiya, K. Taniya, Y. Ichihashi, S. Nishiyama, Selective catalytic oxidation of benzene over Cu/Ti/HZSM-5 under low oxygen pressure for one step synthesis of phenol, J. Mol. Catal. A Chem. 411 (2016) 372–376. doi:10.1016/j.molcata.2015.11.007.

[19] B.B. Sarma, R. Carmieli, A. Collauto, I. Efremenko, J.M.L. Martin, R. Neumann, Electron Transfer Oxidation of Benzene and Aerobic Oxidation to Phenol, ACS Catal. 6 (2016) 6403–6407. doi:10.1021/acscatal.6b02083.

[20] T.D. Bui, A. Kimura, S. Ikeda, M. Matsumura, Determination of Oxygen Sources for Oxidation of Benzene on TiO 2 Photocatalysts in Aqueous Solutions Containing Molecular Oxygen, J. Am. Chem. Soc. 132 (2010) 8453–8458. doi:10.1021/ja102305e.

[21] T. Jintoku, H. Taniguchi, Y. Fujiwara, Palladium catalyzed hydroxylation of benzene with O2 or H2O via the C-H aromatic bond activation. Preparation of phenol., Chem. Lett. (1987) 1865–1868. doi:10.1246/cl.1987.1865.

[22] D. Wang, M. Wang, Z. Li, Fe-Based Metal-Organic Frameworks for Highly Selective Photocatalytic Benzene Hydroxylation to Phenol, ACS Catal. 5 (2015) 6852–6857. doi:10.1021/acscatal.5b01949.

[23] N.A. Harry, S. Saranya, S.M. Ujwaldev, G. Anilkumar, Recent advances and prospects in nickel-catalyzed C-H activation, Catal. Sci. Technol. 9 (2019) 1726–1743. doi:10.1039/c9cy00009g.

[24] K. Ohkubo, T. Kobayashi, S. Fukuzumi, Direct oxygenation of benzene to phenol using quinolinium ions as homogeneous photocatalysts, Angew. Chemie - Int. Ed. 50 (2011) 8652–8655. doi:10.1002/anie.201102931.

[25] K. Ohkubo, A. Fujimoto, S. Fukuzumi, Visible-light-induced oxygenation of benzene by the triplet excited state of 2,3-dichloro-5,6-dicyano-p-benzoquinone, J. Am. Chem. Soc. 135 (2013) 5368–5371. doi:10.1021/ja402303k.

[26] W. Wang, D. Liu, S. Hao, F. Qu, Y. Ma, G. Du, A.M. Asiri, Y. Yao, X. Sun, High-Efficiency and Durable Water Oxidation under Mild pH Conditions: An Iron Phosphate-Borate Nanosheet Array as a Non-Noble-Metal Catalyst Electrode, Inorg. Chem. 56 (2017) 3131–3135. doi:10.1021/acs.inorgchem.6b03171.

[27] C. Huang, R. Liu, W. Yang, C. Zhang, H. Zhu, Iron(II) phthalocyanine immobilized SBA-15 catalysts: Preparation, characterization and application for toluene selective aerobic oxidation, Inorganica Chim. Acta. 467 (2017) 307–315. doi:10.1016/j.ica.2017.08.026.

[28] A. Aktaş, I. Acar, E.T. Saka, Z. Biyiklioglu, Synthesis of polyfluoro substituted Co(II), Fe(II) phthalocyanines and their usage as catalysts for aerobic oxidation of benzyl alcohol, J. Organomet. Chem. 815–816 (2016) 1–7. doi:10.1016/j.jorganchem.2016.04.025.

[29] Ü. Işci, C. Caner, Y. Zorlu, A.G. Gürek, F. Dumoulin, V. Ahsen, Sulfonamide-substituted iron phthalocyanine: Design, solubility range, stability and oxidation of olefins, Dalt. Trans. 43 (2014) 17916–17919. doi:10.1039/c4dt02412e.

[30] D.W. Scott, D.L. Myers, H. Hill, O. Omadoko, Sodium cobalt(II) tetrasulfophthalocyanine and catalytic oxidation of ethanethiol, Fuel. 242 (2019) 573–579. doi:10.1016/j.fuel.2019.01.055.

[31] L.E. Hofmann, L. Mach, M.R. Heinrich, Nitrogen Oxides and Nitric Acid Enable the Sustainable Hydroxylation and Nitrohydroxylation of Benzenes under Visible Light Irradiation, J. Org. Chem. 83 (2018) 431–436. doi:10.1021/acs.joc.7b02333.

[32] C.M. Krest, E.L. Onderko, T.H. Yosca, J.C. Calixto, R.F. Karp, J. Livada, J. Rittle, M.T. Green, Reactive intermediates in cytochrome P450 catalysis, J. Biol. Chem. 288 (2013) 17074–17081. doi:10.1074/jbc.R113.473108.

[33] S. Friedle, E. Reisner, S.J. Lippard, Current challenges of modeling diiron enzyme active sites for dioxygen activation by biomimetic synthetic complexes, Chem. Soc. Rev. 39 (2010) 2768–2779. doi:10.1039/c003079c.

[34] M.M. Forde, B.C. Grazia, R. Armstrong, R.L. Jenkins, M.H.A. Rahim, A.F. Carley, N. Dimitratos, J.A. Lopez-Sanchez, S.H. Taylor, N.B. McKeown, G.J. Hutchings, Methane oxidation using silica-supported N-bridged di-iron phthalocyanine catalyst, J. Catal. 290 (2012) 177–185. doi:10.1016/j.jcat.2012.03.013.

[35] P. Bata, Comparative Study of Immobilized Phthalocyanines in Oxidative Degradation, Open Catal. J. 5 (2012) 50–55. doi:10.2174/1876214X01205010050.

[36] Z. Zhu, Y. Chen, Y. Gu, F. Wu, W. Lu, T. Xu, W. Chen, Catalytic degradation of recalcitrant pollutants by Fenton-like process using polyacrylonitrile-supported iron (II)

phthalocyanine nanofibers: Intermediates and pathway, Water Res. 93 (2016) 296–305. doi:10.1016/j.watres.2016.02.035.

[37] T. Xu, D. Wang, L. Dong, H. Shen, W. Lu, W. Chen, Graphitic carbon nitride co-modified by zinc phthalocyanine and graphene quantum dots for the efficient photocatalytic degradation of refractory contaminants, Appl. Catal. B Environ. 244 (2019) 96–106. doi:10.1016/j.apcatb.2018.11.049.

[38] S. Yin, Y. Chen, Q. Hu, M. Li, Y. Ding, Y. Shao, J. Di, J. Xia, H. Li, In-situ preparation of iron(II) phthalocyanine modified bismuth oxybromide with enhanced visible-light photocatalytic activity and mechanism insight, Colloids Surfaces A Physicochem. Eng. Asp. 575 (2019) 336–345. doi:10.1016/j.colsurfa.2019.05.028.

[39] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, vols. 1–4VCH publishers, New York. (1989).

[40] B.D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanines, New York-Toronto . (1981) 281. http://elibrary.ru/item.asp?id=18869201.

[41] O. Chamlek, S. Pratontep, T. Kerdcharoen, T. Osotchan, Spectroscopys Studies of Iron Phthalocyanine Thin Films, Adv. Mater. Res. 55–57 (2008) 301–304. doi:10.4028/www.scientific.net/AMR.55-57.301.

[42] R.L. Arechederra, K. Artyushkova, P. Atanassov, S.D. Minteer, Growth of phthalocyanine doped and undoped nanotubes using mild synthesis conditions for development of novel oxygen reduction catalysts, ACS Appl. Mater. Interfaces. 2 (2010) 3295–3302. doi:10.1021/am100724v.

[43] R. Burkitt, T.R. Whiffen, E.H. Yu, Iron phthalocyanine and MnOx composite catalysts for microbial fuel cell applications, Appl. Catal. B Environ. 181 (2016) 279–288. doi:10.1016/j.apcatb.2015.07.010.

[44] Y. Liu, Y.Y. Wu, G.J. Lv, T. Pu, X.Q. He, L.L. Cui, Iron(II) phthalocyanine covalently functionalized graphene as a highly efficient non-precious-metal catalyst for the oxygen reduction reaction in alkaline media, Electrochim. Acta. 112 (2013) 269–278. doi:10.1016/j.electacta.2013.08.174.

[45] G. Yuan, G. Zhang, Y. Zhou, F. Yang, Synergetic adsorption and catalytic oxidation performance originated from leafy graphite nanosheets anchored iron (II) phthalocyanine nanorods for efficient organic dye degradation, RSC Adv. 5 (2015) 1–9.

[46] Y. Morimoto, S. Bunno, N. Fujieda, H. Sugimoto, S. Itoh, Direct hydroxylation of benzene to phenol using hydrogen peroxide catalyzed by nickel complexes supported by pyridylalkylamine ligands, J. Am. Chem. Soc. 137 (2015) 5867–5870.

[47] G.C. Silva, N.M.F. Carvalho, A. Horn Jr, E.R. Lachter, O.A.C. Antunes, Oxidation of aromatic compounds by hydrogen peroxide catalyzed by mononuclear iron (III) complexes, J. Mol. Catal. A Chem. 426 (2017) 564–571.

[48] S. Ueno, K. Yoshida, K. Ebitani, K. Kaneda, Hydrotalcite catalysis: heterogeneous epoxidation of olefins using hydrogen peroxide in the presence of nitriles, Chem. Commun. (1998) 295–296.

[49] B. Delley, From molecules to solids with the DMol3 approach, J. Chem. Phys. 113 (2000) 7756–7764. doi:10.1063/1.1316015.

[50] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, J. Chem. Phys. 92 (1990) 508–517. doi:10.1063/1.458452.

[51] A.B. Sorokin, Phthalocyanine metal complexes in catalysis, Chem. Rev. 113 (2013) 8152–8191. doi:10.1021/cr4000072.

[52] X. Ye, Y. Cui, X. Wang, Ferrocene-modified carbon nitride for direct oxidation of benzene to phenol with visible light, ChemSusChem. 7 (2014) 738–742. doi:10.1002/cssc.201301128.

[53] X. Ye, Y. Cui, X. Qiu, X. Wang, Selective oxidation of benzene to phenol by Fe-CN/TS-1 catalysts under visible light irradiation, Appl. Catal. B Environ. 152–153 (2014) 383–389. doi:10.1016/j.apcatb.2014.01.050.

[54] X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, Fe-g-C3N4-catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light, J. Am. Chem. Soc. 131 (2009) 11658–11659. doi:10.1021/ja903923s.

[55] Y. Zhu, Y. Dong, L. Zhao, F. Yuan, Preparation and characterization of Mesopoous VOx/SBA-16 and their application for the direct catalytic hydroxylation of benzene to phenol, J. Mol. Catal. A Chem. 315 (2010) 205–212. doi:10.1016/j.molcata.2009.09.013.

[56] J.-H. Yang, G. Sun, Y. Gao, H. Zhao, P. Tang, J. Tan, A.-H. Lu, D. Ma, Direct catalytic oxidation of benzene to phenol over metal-free graphene-based catalyst, Energy Environ. Sci. 6 (2013) 793. doi:10.1039/c3ee23623d.