Journal of Molecular Catalysis A: Chemical 395 (2014) 494–499

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Cobalt(II) phthalocyanine covalently anchored to cellulose as a recoverable and efficient catalyst for the aerobic oxidation of alkyl arenes and alcohols

Ahmad Shaabani*, Sajjad Keshipour, Mona Hamidzad, Shabnam Shaabani

Faculty of Chemistry, Shahid Beheshti University, G.C., P.O. Box 19396-4716, Tehran, Iran

ARTICLE INFO

Article history:
Received 4 April 2014
Received in revised form 6 August 2014
Accepted 4 September 2014
Available online 16 September 2014

Keywords:
Cobalt(II) phthalocyanine
Cellulose
Heterogeneous catalysis
Aerobic oxidation
Alkylarenes

ABSTRACT

Cobalt(II) phthalocyanine covalently immobilized on cellulose as a heterogeneous catalyst was synthesized and characterized. The catalyst showed good catalytic activity for the aerobic oxidation of alkyl arenes and alcohols under relatively mild reaction conditions. The catalyst can readily be recovered from the reaction mixture and reused for several runs without significant decrease in catalytic activity.

1. Introduction

The selective aerobic oxidation of hydrocarbons and alcohols are very important commercial processes for the production of aldehydes and ketones. Conventionally, for effective oxidation of alcohols and alkylarenes, stoichiometric amounts of hazardous and toxic oxidants such as nitric acid, potassium permanganate, potassium dichromate, sodium hypochlorite or organic peroxides are necessary. However, these oxidants generate copious amounts of wastes. In this regard, environmentally benign procedures such as using green oxidants and heterogeneous recoverable catalysts are especially attractive for the synthesis of pharmaceuticals, flavors and fragrances, and agrochemicals. Thus, there is an increasing demand for catalytically oxidation processes with green, economic, and efficient strategies [1–3].

Metal phthalocyanines (MPcs) as macrocyclic complexes are easily accessible, stable and cost effective biomimetic oxidation catalysts which widely used in organic reactions [4–10]. Recently, MPcs were used widely for the oxidation of organic compounds [11]. Immobilization of these catalysts via covalent attachment to the functionalized polymers is an interesting approach to facilitate catalyst recovery, recycling, and to reduce effluent contamination [11]. The main purpose to use a support for MPc is to increase the effective surface area of the catalyst.

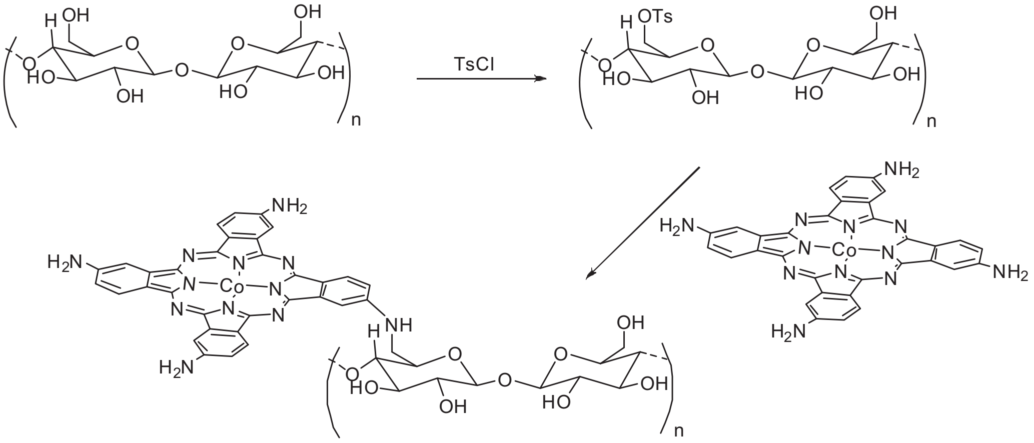
As the most important structural material in plants, cellulose is a highly functionalized and linear stiff-chain homopolymer, formed by the repeated connection of D-glucose building blocks. This polysaccharide has fascinating properties such as hydrophilicity, chirality, biodegradability and broad chemical modifying capacity. Recently, modifying of cellulose with various functionalities for catalytic purposes has attracted more attentions [12–15] and in this regard, Co(II) Pc as a useful catalyst was immobilized on cellulose by the reaction of amine groups on Co(II) tetraamino Pc with the aldehyde groups which were created on cellulose [16,17]. However, the attachment of Pc to cellulose established using imine bonds which such connection is corruptible due to hydrolyzing particularly in aqueous media and acidic conditions [18].

In continuation of our efforts to synthesis of chemically supported heterogeneous cellulose-based catalysts [19,20] and oxidation of organic compounds with phthalocyanines [21,22], herein we wish to introduce a new and efficient strategy for immobilization of Co(II) Pc on cellulose which are useful for environmentally benign aerobic oxidation of alkyl arenes and alcohols. Co(II) 4,9,16,23-tetraamine-phthalocyanine supported on cellulose (CoPc@Cell) was prepared through covalent immobilization of Co(II) 4,9,16,23-tetraamine-phthalocyanine onto chemically modified cellulose (Scheme 1).

---

* Corresponding author. Tel.: +98 2129902800.
E-mail address: a-shaabani@sbu.ac.ir (A. Shaabani).

http://dx.doi.org/10.1016/j.molcata.2014.09.003
1381-1169/



Scheme 1. Preparation of CoPc@Cell.

2. Experimental procedures

2.1. Preparation of CoPc@Cell

In a typical procedure, a mixture of cellulose (2.00 g) and LiCl (0.05 g) in 20 mL of DMF was prepared. After 8 h stirring at room temperature, 8 mmol tosylchloride and 0.10 mL triethylamine were added to the mixture, and stirring continued for 24 h at 8 °C to afford cellulose tosylate (CT) as a white solid powder. Then, the mixture containing CT was treated with 9 mL water and 7.00 mmol Co(II) 4,9,16,23-tetraamine-phthalocyanine. Instantly, temperature was raised to 100 °C and stirring continued. After 24 h, the mixture cooling down to room temperature and it was poured into 60 mL acetone. The polymer was filtrated and washed with acetone (2× 5 mL) and H_2O (3× 10 mL). It was dried under vacuum at 60 °C to afford CoPc@Cell as a gray powder.

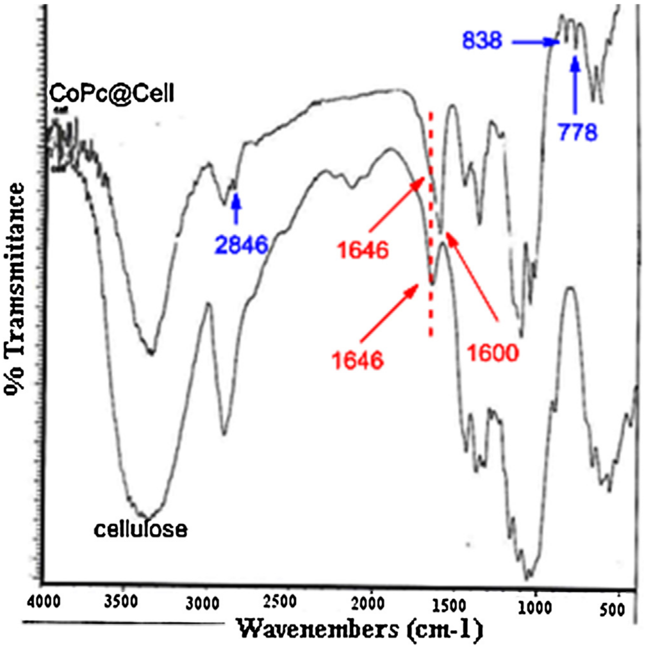


Fig. 1. FT-IR spectra of cellulose and CoPc@Cell.

2.2. Materials and methods for determination of Co(II) on CoPc@Cell using flame atomic absorption spectroscopy (FAAS)

CoPc@Cell (0.05 g) was added to a mixture of $HCl:HNO_3$ (3:1) (10 mL) and sonicated for 3 h. Then, the mixture was filtered and the total volume of the filtrate made up to about 30 mL with distilled water. The final solution was aspirated into the flame of the AAS against the blank prepared with cellulose. The Co(II) concentration was obtained using calibration curve prepared with cobalt solution standards.

2.3. Typical procedure for the oxidation of 1-phenyl-ethanol

1-Phenyl-ethanol (0.14 g, 1.00 mmol) was added to a two-necked flask equipped with a gas bubbling tube containing colloidal of CoPc@Cell (0.05 g) and KOH (0.25 mmol) in *o*-xylene (5 mL) at room temperature. The mixture was stirred at room temperature under O_2 atmosphere provided with a balloon. The progress of the reaction was followed by thin layer chromatography (TLC). Upon completion, CoPc@Cell was separated by filtration and washed with acetone (5 mL). Acetophenone was isolated from the mixture using column chromatography with *n*-hexane in 90% yield.

2.4. Typical procedure for the oxidation of tetraline

N-Hydroxyphthalimide (0.01 g, 0.06 mmol) was added to a two-necked flask equipped with a gas bubbling tube containing colloidal of CoPc@Cell (0.05 g), tetraline (0.13 g, 1.00 mmol) and KOH (0.25 mmol) in *o*-xylene (5 mL). The mixture was stirred under reflux conditions in O_2 atmosphere provided with a balloon. The reaction temperature was raised to refluxing *o*-xylene. The progress of the reaction was followed by TLC. Upon completion, CoPc@Cell was separated by filtration and washed with acetone (5 mL). Tetralone was isolated from the mixture using column chromatography with *n*-hexane:ethyl acetate (10:1) in 88% yield.

3. Results and discussion

Cellulose tosylate was prepared as previously reported method [7] and converted to CoPc@Cell via a nucleophilic substitution reaction of amine groups of 4,9,16,23-tetraamino phthalocyanine with tosylate functionality of cellulose.

The synthesized catalyst was characterized by FT-IR, XRD, FAAS and elemental analysis. Phthalocyanine content on the cellulose was calculated to be 0.06 mmol g^{-1}, according to the nitrogen

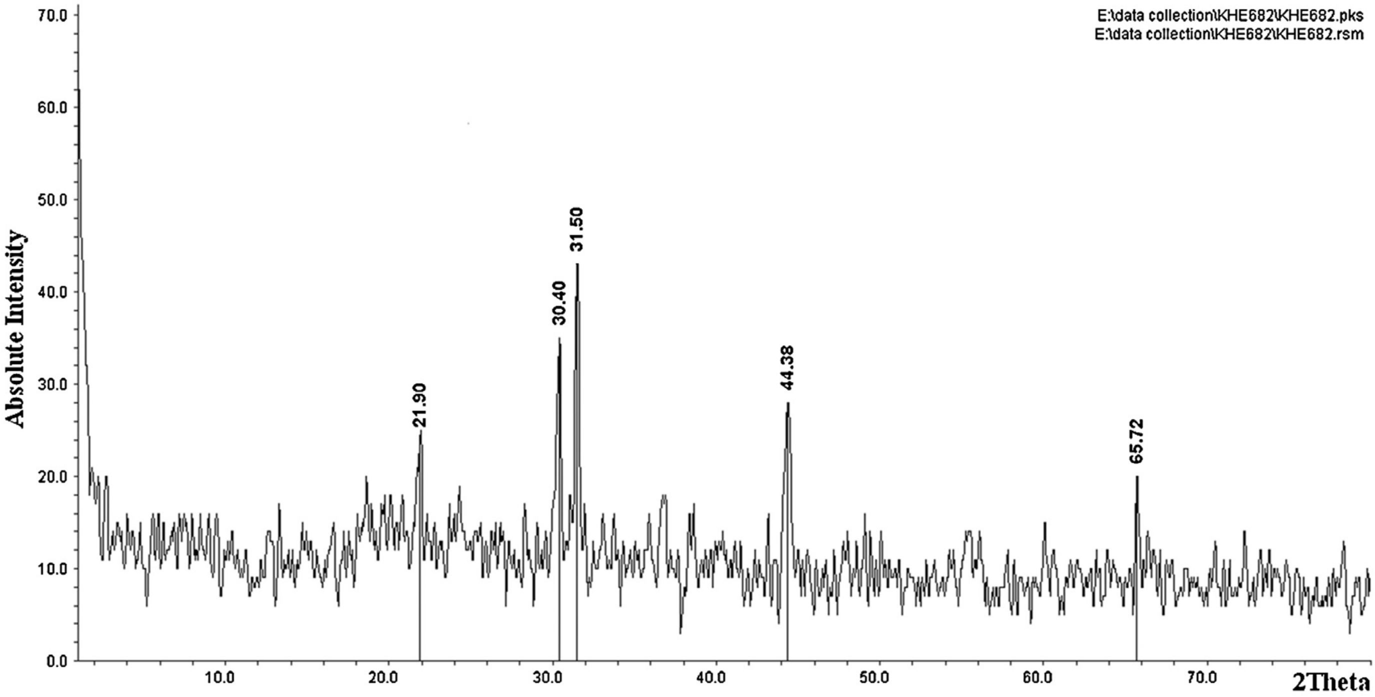


Fig. 2. XRD pattern of CoPc@Cell.

Table 1
Optimization of the reaction conditions for aerobic oxidation of tetraline.[a]

Entry	Co (mol%)	Base (mol%)	Solvent	Time (h)	Yield (%)[b]
1	0.01	KOH (25)	*o*-Xylene	10	79
2	0.02	KOH (25)	*o*-Xylene	10	87
3	0.03	KOH (25)	*o*-Xylene	10	88
4	0.04	KOH (25)	*o*-Xylene	10	88
5	0.02	NaOH(25)	*o*-Xylene	10	56
6	0.02	K_2CO_3(25)	*o*-Xylene	24	0
7	0.02	Et_3N (25)	*o*-Xylene	24	0
8	0.02	KOH (25)	MeCN	18	81
9	0.02	KOH (25)	H_2O	24	0
10	0.02	KOH (25)	EtOH	24	0
11	0.02	KOH (25)	*n*-Hexane	24	0

[a] Reaction conditions: tetraline (1.00 mmol), NHPI (0.06 mmol), solvent (5 mL), under O_2 balloon, reflux.
[b] Isolated yield.

content on the EDACs measured by CHN analysis. The Co loading in CoPc@Cell was determined to be 0.36 wt% based on the FAAS analysis. Immobilization of the Co(II) Pc on cellulose was confirmed by FT-IR spectroscopy. For the catalyst a characteristic strong band for C=N bonds is seen at 1600 cm^{-1} next to cellulose band at 1646 cm^{-1}. In addition, the FT-IR spectrum of CoPc@Cell has some weak bands at 2846, 838 and 778 cm^{-1} which did not observed for cellulose (Fig. 1).

Finally, the structure of CoPc@Cell was determined by powder XRD. Characteristic diffraction peaks at $2\theta = 21.90^\circ$, 30.40°, 31.50° and 44.38° can be clearly observed for the CoPc@Cell (Fig. 2).

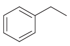
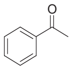
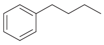
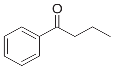
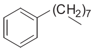
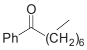
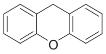
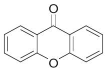
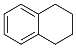
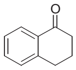
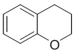
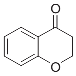
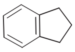
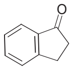
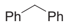
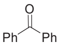
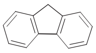
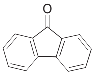
At the onset of the research, we made a conscious effort to develop a heterogeneous catalytic system for the aerobic oxidation of various alkyl arenes to the corresponding aldehydes and ketones. During the preliminary studies with the CoPc@Cell the aerobic oxidation of tetraline to tetralone was investigated as a model substrate in the presence of various amounts of CoPc@Cell using a base and *N*-hydroxyphthalimide under O_2 balloon. At low amounts of CoPc@Cell, the reaction gave low yields even in long duration time. As the Co amount was increased to 0.02 mol%, the reaction carried out more efficiently (Table 1, entries 1–4). The addition of a base increased the reaction yield, with KOH in 25 mol% providing the best result (Table 1, entries 5–7). Moreover, the effect of various solvents was investigated on the reaction yields and the reaction gave high yield in *o*-xylene (Table 1, entries 8–11).

The efficiency of the catalyst was studied for the selective oxidation of a large variety of alkyl arenes to the corresponding aldehydes and ketones using O_2 as an oxidant (Table 2). The results showed that CoPc@Cell was highly active and extremely selective for the oxidation of all substrates, indicating a high versatility of the CoPc@Cell. It is interesting to note, *o*-xylene as an alkyl arene did not oxidize under our reaction conditions and we used it as the solvent.

To extend catalytic applications of CoPc@Cell, selective aerobic oxidation of various benzylic, allylic and aliphatic alcohols to the corresponding aldehydes and ketones was studied. The reaction conditions were optimized for 1-phenyl-ethanol as the model substrate with 0.02 mol% of Co and 25 mol% of KOH in *o*-xylene at room temperature without using *N*-hydroxyphthalimide under O_2 balloon as the best reaction conditions (Table 3, entry 2).

The efficiency of the catalyst was studied for the selective oxidation of a large variety of alcohols to the corresponding aldehydes and ketones in the presence of KOH in *o*-xylene using the optimum 0.02 mol% of Co (Table 4). The results showed that CoPc@Cell was highly active and extremely selective for the oxidation of

Table 2
Aerobic oxidation of various alkyl arenes to the corresponding aldehydes and ketones.[a]

Entry	Alcohol	Product	Time (h)	Yield (%)[b]
1			10	89
2			12	85
3			14	85
4			9	91
5			13	88
6			11	91
7			12	87
8			11	87
9			10	82

[a] Reaction conditions: alkyl arene (1.00 mmol), CoPc@Cell (0.05 g), KOH (0.25 mmol), NHPI (0.06 mmol), *o*-xylene (5 mL), under O_2 balloon, reflux.
[b] Isolated yield.

all substrates. A high versatility of the secondary benzylic alcohols, especially alcohols with two phenyl groups as the substituents, was converted to the corresponding ketones in quantitative yields (Table 4, entries 5–8). 2-Hydroxy-1,2-diphenylethanone was also rapidly oxidized into the corresponding ketone in excellent yield (Table 4, entry 9). A high conversion was achieved for allylic alcohol to the desired aldehyde (Table 4, entry 10).

Despite the low reactivity of aliphatic alcohols, CoPc@Cell was also applicable to the oxidation of various cyclic and acyclic aliphatic alcohols to afford the corresponding aldehydes and ketones in high yields but in relatively long durations at room temperature (Table 4, entries 11–15).

Potential Co leaching into the reaction mixture was also analyzed with FAAS analysis. For this purpose, samples were taken through a syringe filter during the heterogeneous oxidation reaction of tetraline, the solvent was evaporated, and the residue was dissolved in HNO_3. The analysis of these samples with FAAS showed that the Co concentration in the reaction solution was less than the detection limit. The same result was obtained when the complete reaction mixture of the heterogeneous oxidation reaction of 1-phenyl-ethanol was filtered, the solvent was evaporated, and the residue was dissolved in HNO_3. Both findings indicate that virtually no Co leaches from the surface into the solution. Also, did not observe any change in IR spectrum and XRD analysis for the catalyst recovered from the reaction.

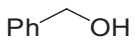
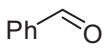
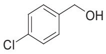
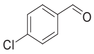
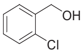
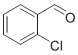
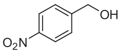
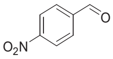
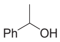
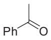
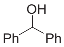
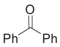
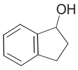
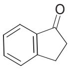
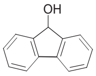
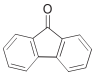
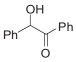
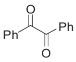
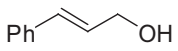
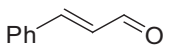
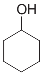
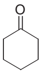
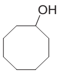
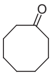
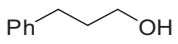
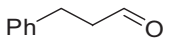
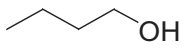
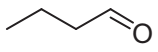
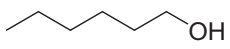
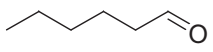
The recyclability of CoPc@Cell was surveyed for aerobic oxidation of tetraline and 1-phenyl-ethanol, separately. After carrying out the oxidation reaction of tetraline and 1-phenyl-ethanol, the

Table 3
Optimization of the reaction conditions for aerobic oxidation of 1-phenyl-ethanol.[a]

Entry	Co (mol%)	Base (mol%)	Solvent	Time (h)	Yield (%)[b]
1	0.01	KOH (25)	*o*-Xylene	5.5	81
2	0.02	KOH (25)	*o*-Xylene	5.5	90
3	0.03	KOH (25)	*o*-Xylene	5.5	91
4	0.04	KOH (25)	*o*-Xylene	5.5	91
5[c]	0.02	KOH (25)	*o*-Xylene	4	92
6	0.02	NaOH(25)	*o*-Xylene	10	65
7	0.02	K_2CO_3(25)	*o*-Xylene	24	0
8	0.02	Et_3N (25)	*o*-Xylene	24	0
9	0.02	KOH (25)	MeCN	18	83
10	0.02	KOH (25)	H_2O	24	0
11	0.02	KOH (25)	EtOH	24	0
12	0.02	KOH (25)	*n*-Hexane	24	0

[a] Reaction conditions: 1-phenyl-ethanol (1.00 mmol), solvent (5 mL), under O_2 balloon, room temperature.
[b] Isolated yield.
[c] Reflux conditions.

Table 4
Aerobic oxidation of various alcohols to the corresponding aldehydes and ketones.[a]

Entry	Alcohol	Product	Time (h)	Yield (%)[b]
1			8.5	83
2			8	83
3			9	78
4			8	79
5			5.5	91
6			3.5	87
7			2.5	90
8			4	93
9			1.5	90
10			3.5	86
11			10.5	85
12			10	90
13			9.5	81
14			12	88
15			12	90

[a] Reaction conditions: alcohol (1.00 mmol), CoPc@Cell (0.05 g), KOH (0.25 mmol), *o*-xylene (5 mL), under O_2 balloon, room temperature.
[b] Isolated yield.

reaction mixtures were filtered off, and CoPc@Cell and KOH separated as a gray solid. CoPc@Cell was washed with acetone (2× 5 mL) and H_2O (3× 5 mL) to remove KOH and organic impurities, and reused. Only minor decreases in the reaction yield was observed after five repetitive cycles (Fig. 3).

We proposed a mechanism for this reaction in the absence of NHPI, previously [22]. In this reaction, NHPI with a radical proton abstraction from alkyl arene **1** produced intermediate **2**. Benzylic radical **2** reacted with a O_2 molecule which activated by PcCo(II) to give intermediate **3**. An intermolecular radical proton transfer of **3** was afforded intermediate **4** which under leaving of a hydroxyl radical gave ketone **5**. For the alcohols, the mechanism proceeded through the removal of a hydrogen atom from the carbon attached to the hydroxyl group of alcohols by phthalocyanine superoxocobalt(III) (**8**). The results of this radical proton abstraction are intermediates **7** and **9**. Finally, compound **9** was reacted with **7** to yield product **5** and H_2O_2 as a by-product (Scheme 2). Also, application of base for improving the reaction yield is necessary [23].

The results of our catalyst are compared with some recent reports for oxidation reaction of alcohols using Co-phthalocyanines

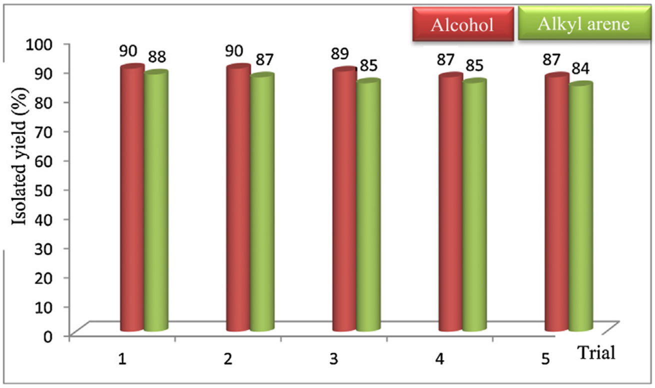
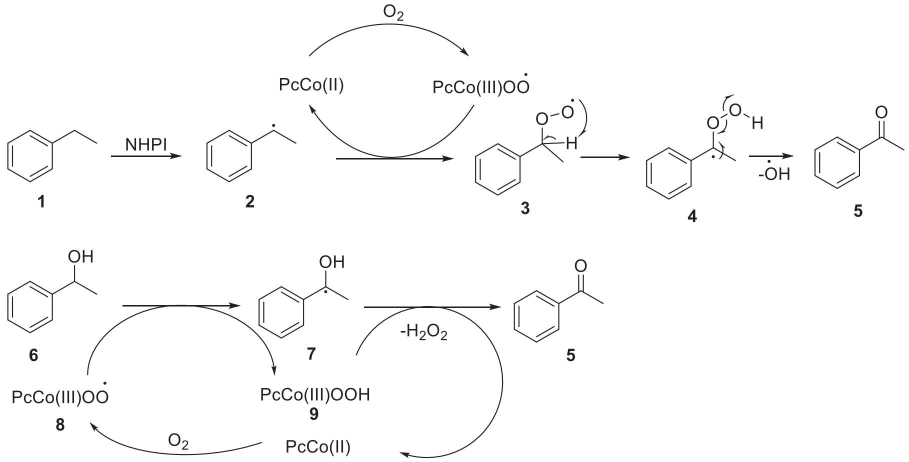


Fig. 3. Successive trials by using recoverable CoPc@Cell for aerobic oxidation of 1-phenyl-ethanol[a] and tetraline[b]. [a] Reaction conditions for alcohol: 1-phenyl-ethanol (1.00 mmol), CoPc@Cell (0.05 g), KOH (0.25 mmol), *o*-xylene (5 mL), under O_2 balloon, room temperature. [b] Reaction conditions for arene: tetraline (1.00 mmol), CoPc@Cell (0.05 g), KOH (0.25 mmol), NHPI (0.06 mmol), *o*-xylene (5 mL), under O_2 balloon, reflux.



Scheme 2. Proposed mechanisms for the aerobic oxidation of alkyl arenes and alcohols.

Table 5
Comparasion of the results for oxidation of alcohols using CoPc@Cell and some other Pcs.

Entry	Catalyst	Substrate	Oxidant	Temp. (°C)	Time (h)	Selectivity (%)	Yield (%)
1	Co(II)-tetrachlorophthalocyanine supported on SiO_2 [24]	1-Phenyl-ethanol	H_2O_2	60	3	88	100
2	Co(II)-tetrachlorophthalocyanine supported on nano-SiO_2 [25]	Benzyl alcohol	H_2O_2	70	5	38.9	92.7
3	Co(II) phthalocyaninenano-shell carbon [26]	1-Phenyl-ethanol	O_2/benzaldehyde	110	16	100	98
5	This work	1-Phenyl-ethanol	Air	Room temp.	5.5	100	90

with respect to their yields, selectivity, the time and temperature required for the reaction and used oxidant. As shown in Table 5, CoPc@Cell has some advantages such as a cheap and green oxidant, high selectivity, relatively short reaction time and progress of the reaction without using co-oxidant such as H_2O_2, initiator such as NHPI and activation (room temperature reaction conditions).

4. Conclusions

Cobalt(II) 4,9,16,23-tetraamino phthalocyanine chemically supported on cellulose was synthesized and used for the selectively aerobic oxidation of alkyl arenes and various aliphatic, aromatic and allylic primary and secondary alcohols to the corresponding aldehydes and ketones. High selectivity, good conversion in low Co loading and easily recovery and recycling of the catalyst from reaction mixture are advantages of this approach. The catalyst showed good catalytic activity in the case of aerial oxidation of the most challenging primary aliphatic alcohols to the corresponding aldehydes.

Acknowledgements

We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University and Catalyst Center of Excellence (CCE).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.09.003.

References

[1] C.N. Satterfield, in: J.E. Backvall (Ed.), Modern Oxidation Methods, Wiley-VCH, Germany, 2004.
[2] R.C. Larock, Comprehensive Organic Transformations, Wiley-VCH, New York, 1999, pp. 1234–1250.
[3] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidation of Organic Compounds, Academic, New York, 1981, pp. 350–382.
[4] C. Perollier, A.B. Sorokin, Chem. Commun. (2002) 1548–1549.
[5] B. Meunier, A. Sorokin, Acc. Chem. Res. 30 (1997) 470–476.
[6] A. Sorokin, S. De Suzzoni-Dezard, D. Poullain, J.P. Noel, B. Meunier, J. Am. Chem. Soc. 118 (1996) 7410–7411.
[7] A. Hadasch, A. Sorokin, A. Rabion, L. Fraisse, B. Meunier, Bull. Soc. Chim. Fr. 134 (1997) 1025–1032.
[8] A. Sorokin, B. Meunier, J. Chem. Soc., Chem. Commun. (1994) 1799–1800.
[9] A. Sorokin, J.L. Seris, B. Meunier, Science 268 (1995) 1163–1166.
[10] K. Kasuga, K. Mori, T. Sugimori, M. Handa, Bull. Chem. Soc. Jpn. 73 (2000) 939–940.
[11] M.J.F. Calvete, M. Silva, M.M. Pereira, H.D. Burrows, RSC Adv. 3 (2013) 22774–22789.
[12] A. Shaabani, A. Maleki, Appl. Catal. A: Gen. 331 (2007) 149–151.
[13] A. Shaabani, A. Maleki, J. Moghimi Rad, E. Soleimani, Chem. Pharm. Bull. 55 (2007) 957–958.
[14] A. Shaabani, A. Rahmati, Z. Badri, Catal. Commun. 9 (2008) 13–16.
[15] A. Shaabani, M. Seyyedhamzeh, A. Maleki, F. Rezazadeh, Appl. Catal. A 358 (2009) 146–149.
[16] S.L. Chen, X.J. Huang, Z.K. Xu, Cellulose 18 (2011) 1295–1303.
[17] S.L. Chen, X.J. Huang, Z.K. Xu, Cellulose 19 (2012) 1351–1359.
[18] P.W.N.M. van Leeuwen, Appl. Catal. A: Gen. 212 (2001) 61–81.
[19] S. Keshipour, S. Shojaei, A. Shaabani, Cellulose 20 (2013) 973–980.
[20] S. Keshipour, A. Shaabani, Appl. Organomet. Chem. 28 (2014) 116–119.
[21] A. Shaabani, A.H. Rezayan, M. Heidary, A. Sarvary, Catal. Commun. 10 (2008) 129–131.
[22] A. Shaabani, E. Farhangi, A. Rahmati, Appl. Catal. A: Gen. 338 (2008) 14–19.
[23] V.B. Sharma, S.L. Jain, B. Sain, Tetrahedron Lett. 44 (2003) 383–386.
[24] R.K. Sharma, S. Gulati, A. Pandey, J. Porous Mater. 20 (2013) 937–949.
[25] F. Adam, W.T. Ooi, Appl. Catal. A: Gen. 445–446 (2012) 252–260.
[26] Y. Kuang, Y. Nabae, T. Hayakawa, M. Kakimoto, Appl. Catal. A: Gen. 423–424 (2012) 52–58.