Synthetic Metals 197 (2014) 233–239

Contents lists available at ScienceDirect

Synthetic Metals

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

Highly selective oxidation of benzyl alcohol catalyzed by new peripherally tetra-substituted Fe(II) and Co(II) phthalocyanines

Volkan Çakır, Ece Tuğba Saka*, Zekeriya Bıyıklıoğlu, Halit Kantekin

Department of Chemistry, Faculty of Science, Karadeniz Technical University, 61080 Trabzon, Turkey

ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form 24 July 2014
Accepted 11 September 2014

Keywords:
Phthalocyanine
Iron
Cobalt
Benzyl alcohol
Oxidation
TBHP

ABSTRACT

In this study, new iron and cobalt phthalocyanines bearing (2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy) groups at peripheral positions have been synthesized and characterized by the spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, UV–vis, mass spectroscopies and elemental analysis). Catalytic activity of Fe(II) and Co(II) phthalocyanines have been investigated in the presence of an oxidant such as TBHP (*tert*-buthylhydroperoxide), m-CPBA (*m*-chloroperoxybenzoic acid) and H_2O_2 (hydrogen peroxide). Fe(II) and Co(II) phthalocyanines exhibit excellent activity and high conversion under mild conditions. Substrate ratio, oxidant ratio, temperature and oxidant type have also been investigated in 3 h and found the best optimum reaction conditions in this catalytic system.

1. Introduction

The selective oxidation of benzyl alcohol is essentially vital in life science and extremely useful in industry for preparing many drugs, vitamins and fragrance [1,2]. The oxidation products of benzyl alcohol are benzaldehyde, benzoic acid and benzoquinone. In terms of industrial use, benzaldehyde has an important role among the oxidation products of benzyl alcohol. Benzaldehyde is commonly used as a precursor for dyes and other organic compounds, ranging from pharmaceuticals to plastic additives (for instance; the aniline dye malachite green is prepared from benzaldehyde and dimethylaniline) [3–5]. Additionally, benzaldehyde is also used in perfumery, cosmetic, food industries to confer flavor and odor [6,7].

Due to metalloprophyrin complexes have been used in the oxidation reactions, they have become well known for their catalytic activity during the past few decades [8–11]. They could be used as intermediate of oxygen carriers for biological systems, as model catalysts of cyctochrome P-450. Metalloporphyrin complexes are widely used as homogeneous catalysts with TBHP, m-CPBA, H_2O_2, PhIO (iodosyl benzene) as oxidant in oxidation catalysis [12–15]. But the several problems (such as easily decomposition and difficulty in recovery process) have croped up during their use in homogeneous catalysis systems [16–18]. Metallophthalocyanine complexes have similar structure of the metalloporphyrins, but the former are more stable. Metallophthalocyanine complexes have macro aromatic ring that contain delocalized 18-π electron system and their derivatives have been studied since 19th century. However, researchers are still interested in this class of compounds [19]. Thanks to their attractive properties, Pc-based materials find many applications such as in nonlinear optics [20], optical data storage [21], photodynamic cancer therapy [22], sensor [23], catalysis [24], and solar energy conversion [25].

In the literature, gold and palladium catalysts have been used for oxidation of benzyl alcohol [26–32] but only a few cobalt and iron catalysts have been reported. Bekaroglu et al. have reported catalytic activity of perfluoroalkyl group substituted Co(II) and Pd(II) phthalocyanines in fluorous biphasic system on benzyl alcohol oxidation. In another report, Co(II) and Pd(II) phthalocyanines have been found active catalysts with high benzaldehyde selectivity [33]. Iron and cobalt phthalocyanine complexes can transfer oxygen from various oxygen donors to aromatic compounds, phenols, alcohols [34–41]. Iron(II) phthalocyanine complexes can react with oxygen to form μ-oxo diiron phthalocyanine complexes ($PcFe^{III}$—O—$Fe^{III}Pc$) via intermediate formation of μ-peroxo dimer. But this dimer molecule can not be formed for sterical reason. Then, homolytical cleavage of O—O bond produces $PcFe^{IV}$=O complex. Cobalt(II) phthalocyanine complexes can also react with oxygen to achieve O—O bond formation. Because of this, iron and cobalt phthalocyanine complexes have been known as oxidation catalysts [42].

* Corresponding author. Tel.: +90 462 377 3666; fax: +90 462 325 3196.
E-mail address: ece_t_saka@hotmail.com (E.T. Saka).

http://dx.doi.org/10.1016/j.synthmet.2014.09.022
0379-6779/

Herein, we have reported the synthesis and characterization of new iron(II) (**4**) and cobalt(II) **5** phthalocyanine substituted with four (2-{2-[3-(diethylamino)phenoxy]ethoxy} ethoxy) groups. We choosed especially (2-{2-[3-(diethylamino) phenoxy]ethoxy}ethoxy) group due to the high solubility of polyoxyethylene groups. In this report, iron(II) (**4**) and cobalt(II) **5** phthalocyanine complexes have been found excellent activity on benzyl alcohol oxidation. Moreover, different factors effecting benzyl alcohol oxidation, such as substrate, oxidant amount, temperature and oxidant type, have been investigated.

2. Experimental

The used materials, equipments and the general procedure for the oxidation of benzyl alcohol were supplied as supplementary information.

2.1. Synthesis

2.1.1. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato iron(II) (4)

A mixture of 4-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}-ethoxy)phthalonitrile **3** (0.35 g, 0.99 mmol), $Fe(CH_3COO)_2$ (85 mg, 0.49 mmol), 4 drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in n-pentanol (4 ml) was refluxed with stirring for 12 h under N_2. After cooling to room temperature, 50 ml ethanol was added to precipitate the product. The precipitate was filtered and dried in vacuo. Lastly, purification was achieved using column chromatography with basic alumina as column material and $CHCl_3$ as eluent. Yield: 206 mg (57%). IR (KBr tablet) ν_{max}/cm^{-1}: 3072 (Ar-H), 2921–2871 (Aliph. C—H), 1606, 1572, 1481, 1446, 1406, 1341, 1278, 1231, 1119, 1091, 997, 958, 820, 746, 685. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 8.71–8.43 (m, 8H, Ar-H), 7.15–7.12 (m, 8H, Ar-H), 6.38–6.31 (m, 12H, Ar-H), 4.23–4.07 (m, 32H, -CH_2-O), 2.88 (s, 24H, -CH_3). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 163.64, 151.93, 148.62, 142.19 135.81, 134.20, 129.72, 122.99, 120.86, 112.63, 110.70, 105.91, 101.08, 99.92, 70.64, 66.07, 40.50. UV–vis (DMF): λ_{max}, nm (log ε): 360 (5.08), 607 (4.63), 705 (5.02). Elemental analysis calcd (%) for $C_{80}H_{84}N_{12}O_{12}Fe$: C 65.75, H 5.79, N 11.50%; found: C 65.97, H 6.10, N 11.23. MALDI-TOF-MS *m*/*z*: 1461 $[M]^+$.

2.1.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato cobalt(II) (5)

Synthesized similarly to **4** from **3**. Yield: 94 mg (30%). IR (KBr tablet) ν_{max}/cm^{-1}: 3077 (Ar-H), 2921–2872 (Aliph. C—H), 1607, 1573, 1500, 1480, 1446, 1409, 1349, 1279, 1230, 1120, 1093, 1060, 997, 961, 820, 751, 685. UV–vis (DMF): λ_{max}, nm (log ε): 329 (5.14), 605 (4.63), 667 (5.05). Elemental analysis calcd (%) for $C_{80}H_{84}N_{12}O_{12}Co$: C 65.61, H 5.78, N 11.48%; found: C 65.90, H 6.06, N 11.20. MALDI-TOF-MS *m*/*z*: 1464 $[M]^+$.

3. Results and discussion

3.1. Synthesis and characterization

Cyclotetramerization of the phthalonitrile derivative **3** to the peripherally tetra-substituted iron(II) and cobalt(II) phthalocyanines **4** and **5** was achieved in the presence of anhydrous $Fe(CH_3COO)_2$, $CoCl_2$ in n-pentanol and DBU (Fig. 1). IR, ^{1}H NMR, ^{13}C NMR, MS, UV–vis and elemental analyses confirmed the proposed structures of the compounds.

The synthesis of the iron(II) and cobalt(II) phthalocyanines **4** and **5** were accomplished by cyclotetramerization of dinitrile compound **3**. Conversion of dinitrile derivative **3** into the iron and cobalt phthalocyanines, the sharp peak for the C≡N vibration disappeared in the IR spectra. The ^{1}H NMR spectrum of iron(II) phthalocyanine **4** was as expected. The ^{1}H NMR spectrum of **4** showed aromatic protons as multiplets at 8.71–8.43, 7.15–7.12, 6.38–6.31 and aliphatic protons as multiplet at 4.23–4.07, singlet at 2.88 ppm. ^{13}C NMR spectrum of **4** showed typical chemical shifts for aliphatic carbon signals at 70.64, 66.07, 40.50 ppm and aromatic carbon signals between 163.64 and 99.92 ppm. On the other hand, NMR spectrum of cobalt phthalocyanine **5** could not be taken because of the paramagnetic cobalt(II) centers [43]. The MALDI-TOF mass spectrum showed the molecular ion peaks at 1461 for complex **4**, 1464 for complex **5**, respectively.

The UV/vis spectra of iron(II) and cobalt(II) phthalocyanines **4** and **5** in DMF at room tempereture is shown in Fig. 2. In UV–vis spectra of the iron and cobalt phthalocyanines Q-bands were observed at around 705 nm for **4**, 667 nm for **5** with the shoulders at around 607 nm for **4**, 605 nm for **5** and the B bands were observed between 360 and 329 nm.

3.2. Catalytic studies

3.2.1. Oxidation of benzyl alcohol with 4 and 5

Schlenk tube was charged with benzyl alcohol (0.71×10^{-3} mol), catalyst (3.41×10^{-6} mol) and TBHP (1.70×10^{-3} mol) in acetonitrile (0.01 l) and refluxed at 70 °C with 900 rpm stirring in a pattern catalytic reaction. Slowly progressive reactions in the absence of complexes **4** and **5** under these conditions demonstrate that catalyst have a worthy role in this oxidation process. In Tables 1–4, comparative studies of the catalytic activity of **4** and **5** for oxidation of benzyl alcohol confirmed that both complexes are active catalysts in acetonitrile. The benzyl alcohol oxidation reactions gave benzaldehyde as the main product and benzoquinone and benzoic acid in small yields by using gas chromatography by both spiking and comparison with standards (Fig. 3). Based on the activity work we have done before [44,45], we chosed this group as a substituent and investigated activity of iron(II) and cobalt(II) phthalocyanines. The influence of various parameters on the percentage conversion and selectivity of products were studied (Tables 1–4).

Fig. 4a and b shows that the changing of product yield with reaction time on benzyl alcohol oxidation with TBHP as an oxidant. Higher yield was obtained for benzaldehyde than benzoic acid and benzoquinone by using catalysts **4** and **5**. Conversion of the three products increased with time, but after 3 h these conversions are level off. This situation is most probably owing to the degradation of the FePc and CoPc catalyst by oxidant, with time.

As depicted clearly in Table 1, the reaction rate and conversion enhance with increasing the substrate catalyst molar ratio. For both catalysts **4** and **5**, same main product (benzaldehyde) was obtained with selectivity of 72% and 70% respectively. In order to control the experiments, same reaction was carried out with the iron and cobalt salts ($FeCl_2$ and $CoCl_2$) as catalysts, it is seen that the oxidation process was not triggered. Also only trace amount of benzyl alcohol could be converted to benzaldehyde (<8%).

Table 2 shows the changes in the conversion of benzyl alcohol by varying the oxidant-to-catalyst ratio from 300/1 to 900/1 at 70 °C. The results indicate that the conversion of benzyl alcohol increased with an increasing oxidant ratio until the maximum conversion of 94% for complex **4** and 89% for complex **5** when 500/1 oxidant/catalyst ratio was used. Whereas, increasing oxidant ratio beyond 500/1, decreased the selectivity of benzaldehyde. The excess oxidant effects coordination around the iron and cobalt ion and leads to the generation of inactive intermediate species. [46–51]. This study showed that only 500/1 ratio of oxidant/catalyst was needed for the reaction to get an optimum conversion of benzyl alcohol to reduced products.

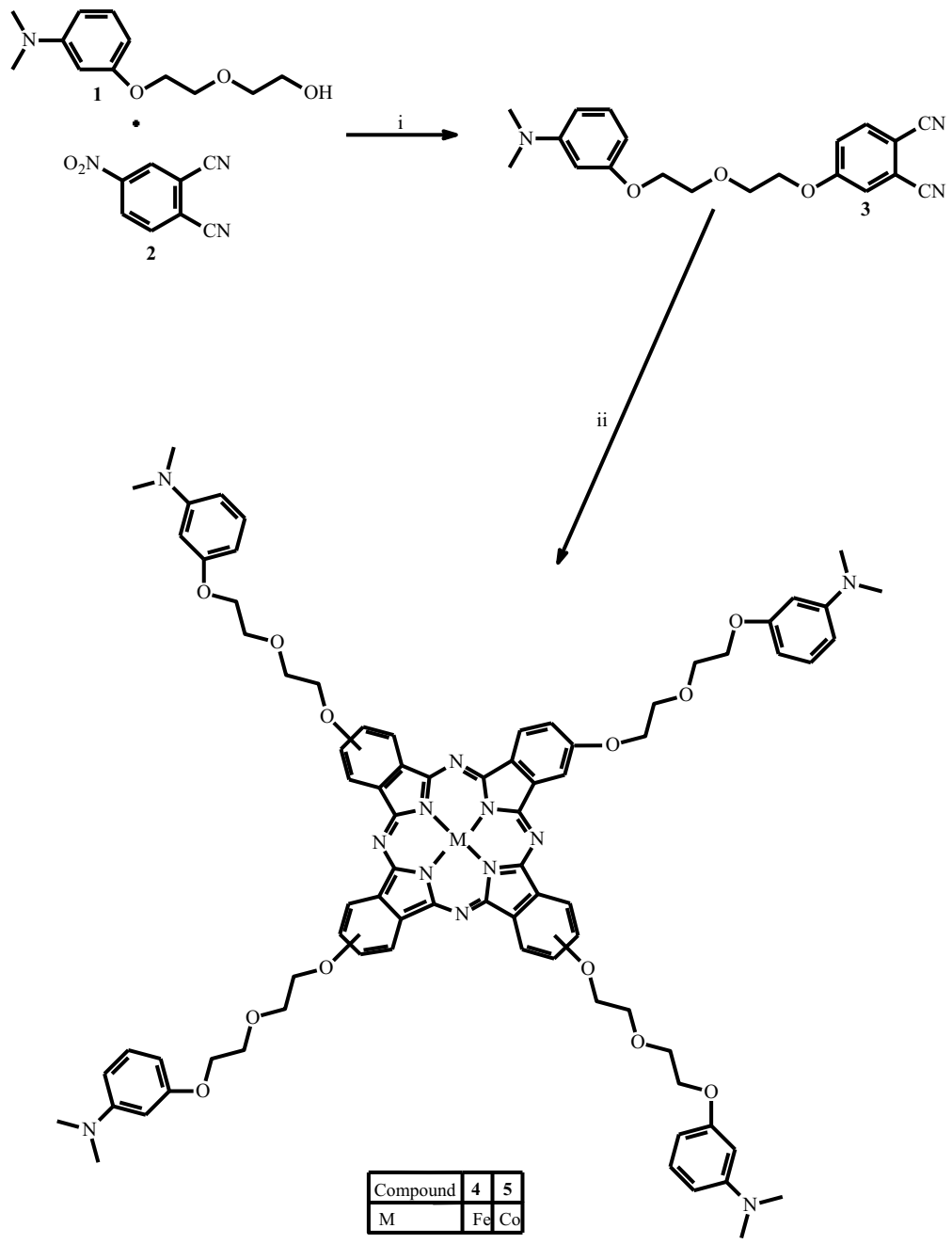

Fig. 1. The synthesis of iron and cobalt phthalocyanines. Reagents and conditions: (i) dry DMF, K_2CO_3, 60 °C; (ii) n-pentanol, DBU, 160 °C, $CoCl_2$, $Fe(CH_3COO)_2$.

Table 3 reflects all results about the effect of the reaction temperature on the oxidation of benzyl alcohol with **4** and **5**. All experiments were done five different temperatures in the range of 25–70 °C. Total conversion of benzyl alcohol increased from 22% to 94% for complex **4** and 18% to 89% for complex **5**. There was no exceptional conversion when the temperature was increased beyond 70 °C. Thus, 70 °C was taken to be an optimum temperature in our study to succeed the highest conversion with TON (280 for complex **4** and 266 for complex **5**) and TOF (93 for complex **4** and 88 for complex **5**).

Table 4 summarizes the effect of oxygen source on the reaction rate of benzyl alcohol oxidation. TBHP, H_2O_2, m-CPBA, air oxygen and were used as an oxidant on these experiments. According to the results on Table 4, complexes **4** and **5** were showed remarkable activity with TBHP than m-CPBA, air oxygen and H_2O_2. No conversion was observed with air oxygen for both catalysts on benzyl

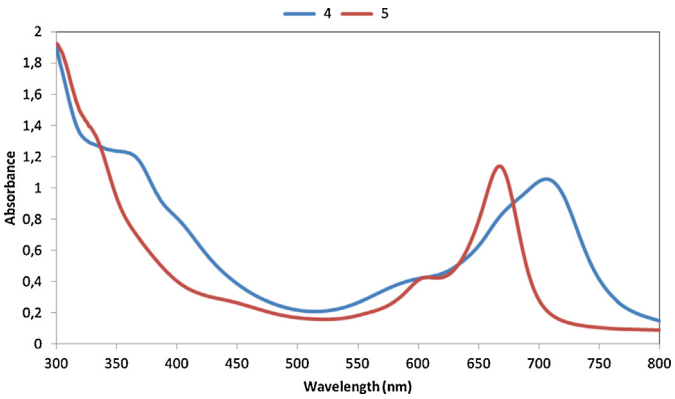

Fig. 2. UV–vis spectrum in DMF for complexes **4** and **5**.

Table 1
Amount of substrate effect of benzyl alcohol oxidation with complexes **4** and **5**.

Catalyst	Subs./cat.	Aldehyde[a]	Quinone[b]	Acid[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
4	300/1	72	12	10	94	280	93
5		70	10	9	89	266	88
4	600/1	69	10	8	87	523	174
5		62	10	9	81	487	162
4	900/1	64	9	7	80	720	240
5		59	8	6	73	657	219
4	1200/1	57	7	5	69	828	276
5		51	5	3	59	708	236
4	1500/1	48	4	3	55	825	275
5		42	3	1	46	687	229
4	1800/1	39	2	2	43	774	258
5		29	2	1	32	480	160

[a] Yield of benzaldehyde.
[b] Yield of benzoquinone.
[c] Yield of benzoic acid.
[d] TON: mole of product/mole of catalyst.
[e] TOF: mole of product/mole of catalyst × time.
Conversion was determined by GC.

Table 2
Amount of oxidant effect of benzyl alcohol oxidation with complexes **4** and **5**.

Catalyst	Oxidant/catayst	Aldehyde[a]	Quinone[b]	Acid[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})
4	300/1	38	10	4	52	156	52
5		31	11	6	48	144	48
4	400/1	49	12	8	69	207	69
5		38	10	7	55	165	55
4	500/1	72	12	10	94	280	93
5		70	10	9	89	266	88
4	600/1	33	10	6	49	147	49
5		30	10	6	46	138	46
4	900/1	24	6	3	33	99	33
5		21	5	1	27	81	27

[a] Yield of benzaldehyde.
[b] Yield of benzoquinone.
[c] Yield of benzoic acid.
[d] TON: mole of product/mole of catalyst.
[e] TOF: mole of product/mole of catalyst × time.
Conversion was determined by GC.

Table 3
Temperature effect of benzyl alcohol oxidation with complexes **4** and **5**.

Catalyst	*T* (°C)	Aldehyde[a]	Quinone[b]	Acid[c]	Tot. conv. (%)	Reaction conversion (%)	TON[d]	TOF[e] (h^{-1})
4	25	12	7	3	22	–	65	22
5		12	5	1	18	–	53	18
4	40	28	7	3	38	16	113	37
5		34	6	2	42	24	125	42
4	50	33	11	5	48	26	134	45
5		31	9	7	47	29	140	46
4	60	47	12	10	69	47	172	57
5		51	10	9	70	42	155	52
4	70	72	12	10	94	72	280	93
5		70	10	9	89	71	266	88

[a] Yield of benzaldehyde.
[b] Yield of benzoquinone.
[c] Yield of benzoic acid.
[d] TON: mole of product/mole of catalyst.
[e] TOF: mole of product/mole of catalyst × time.
Conversion was determined by GC.

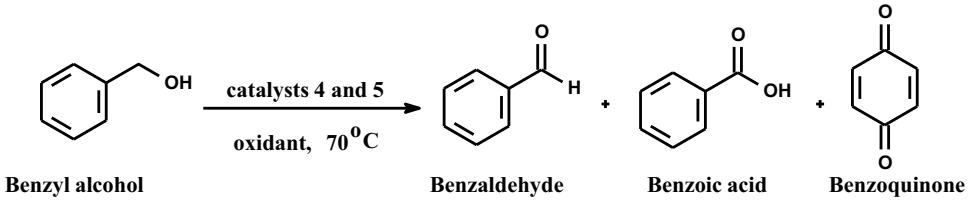

Fig. 3. Product formed through benzyl alcohol oxidation by an oxidant in the presence of catalysts **4** and **5**.

Table 4
Different oxidant effect of benzyl alcohol oxidation with complexes **4** and **5**.

Catalyst	Oxidant	Aldehyde[a]	Quinone[b]	Acid[c]	Tot. conv. (%)	TON[d]	TOF[e] (h^{-1})	Selectivity (%aldehyde)
4	TBHP	72	12	10	94	280	93	76
5		70	10	9	89	266	88	78
4	H_2O_2	33	17	15	65	193	64	50
5		31	14	10	55	164	54	56
4	m-CPBA	14	10	8	32	95	31	43
5		5	15	10	30	89	29	16
4	Air oxygen	–	–	–	–	–	–	–
5		–	–	–	–	–	–	–

[a] Yield of benzaldehyde.
[b] Yield of benzoquinone.
[c] Yield of benzoic acid.
[d] TON: mole of product/mole of catalyst.
[e] TOF: mole of product/mole of catalyst × time.
Conversion was determined by GC.

alcohol oxidation. All results are given in Table 4 and Fig. 5. It is concluded that TBHP is the best oxidant on benzyl alcohol oxidation with high selectivity of aldehyde in our works. Rapid degradation of the Fe(II) and Co(II) phthalocyanines were observed when m-CPBA was employed as an oxidant. During the oxidation reaction, the color of reaction mixture turned from blue to brown and then to yellow and finally pale yellow by the addition of TBHP. On the other hand, when m-CPBA was used as an oxidant, the reaction color suddenly changed from blue-green to colorless. This situation is a proof that m-CPBA is not suitable oxidant on benzyl alcohol oxidation and cause to decomposition of complexes **4** and **5**. Table 4 shows TON, TOF and selectivity values by the use of different oxidants ranging.

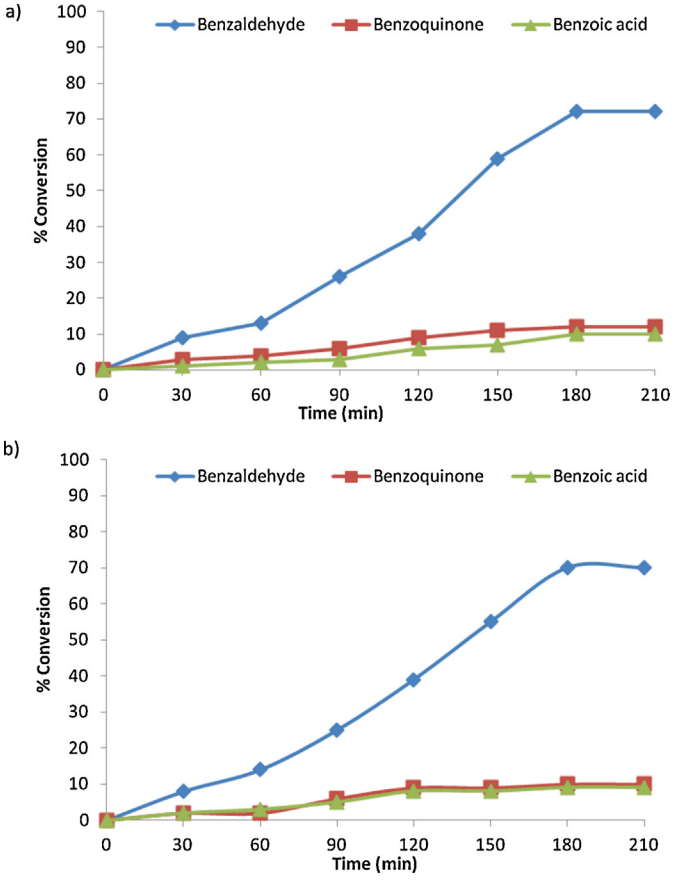

Fig. 4. Time-dependent conversion of benzyl alcohol oxidation (a) for catalyst 4, (b) for catalyst 5. [Reaction conditions: benzyl alcohol (1.02×10^{-3} mol), complex 4 (3.42×10^{-6} mol), complexes 5 (3.41×10^{-6} mol), TBHP (1.70×10^{-3} mol), acetonitrile (0.01 L), 3 h and 70 °C.]

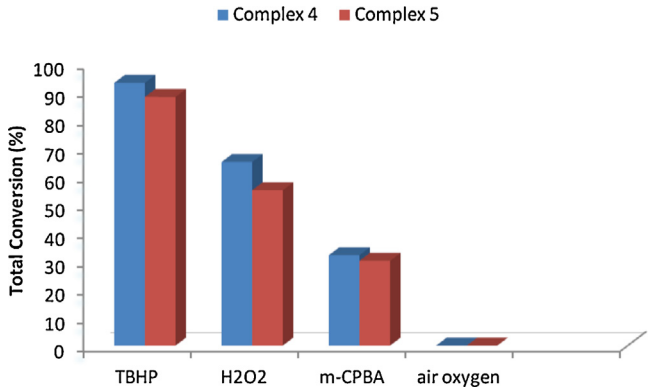

Fig. 5. The oxidant effect on benzyl alcohol oxidation. [Reaction conditions: benzyl alcohol (1.02×10^{-3} mol), complex 4 (3.42×10^{-6} mol), complexes 5 (3.41×10^{-6} mol), TBHP (1.70×10^{-3} mol), acetonitrile (0.01 L), 3 h and 70 °C.]

In addition these parameters, changing of the catalysts was monitored by UV–vis spectrophotometer during the oxidation reaction. Decompositon of Fe(II) and Co(II) phthalocyanines is a frequent situation in oxidation process with the addition of an oxidant [47–51]. It is seen that Fe(II) phthalocyanine has broad vibronic Q band as non oxidized complex in Fig. 6f. Co(II) phthalocyanine in acetonitrile has distinctive sharp vibronic Q band due to the monomeric species in the absence of oxygen source [52]. Before adding oxidant, characteristic sharp Q band of Co(II) phthalocyanine is seen at 668 nm (Fig. 7f). With the oxidation reaction

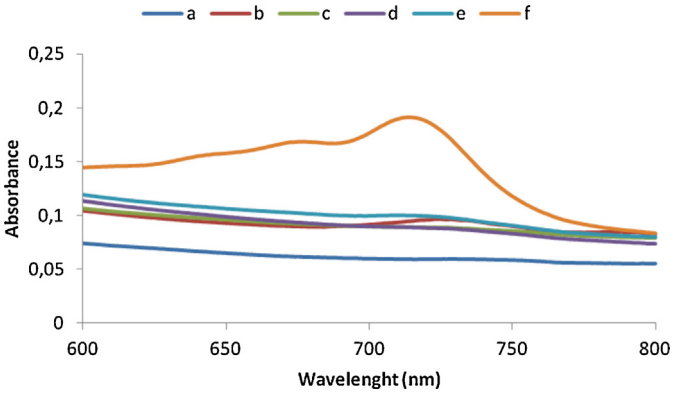

Fig. 6. Time-dependent changes in the visible spectrumof the oxidized complex **5** observed on addition of TBHP (1.70×10^{-3}mol) to a reactio mixture containing 1.02×10^{-3} mol benzyl alcohol and 3.42×10^{-6} mol complex **4** catalyst in 10 ml: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min; (a) 180 min after addition of m-CPBA. All spectra for the oxidized complex **4** were taken after sixfold dilution with acetonitrile. (f) Visible spectrum of (non-oxidized) complex **4**.

Table 5
Catalytic activities toward the homogeneous oxidation of benzyl alcohol of some previously reported catalyst.

Catalyst	Rxn time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
CuPc[b]	30 min	70	TBAOX	25	[54]
CoPc[a]	5.5	70	TBHP	26.6	[33]
PdPc[a]	24	50	m-CPBA	31.3	
Ru(TPP)Cl[c]	30 min	60	O_2	43	[55]
Co(TPP)Cl[c]				42	
Mn(TPP)Cl[c]				45	
Fe(TPP)Cl[c]				32	
MnTEPyP[d]	4	60	TBHP	47	[56]
			$NaIO_3$	16	
			$NaIO_4$	84	
CuTPP[e]	nr[f]	60	O_2	40 (in toluene) 35 (in benzene) Trace (in acetonitrile)	[57]

[a] Pc: perfluoroalkylphthalocyanine.
[b] Pc: un-substituted phthalocyanine.
[c] (TPP)Cl: *meso*-tetraphenylporphyrinchloride.
[d] TEPyP: water soluble metalloporphyrins.
[e] TPP: copper meso tetraphenylporphyrin.
[f] rt: room temperature.

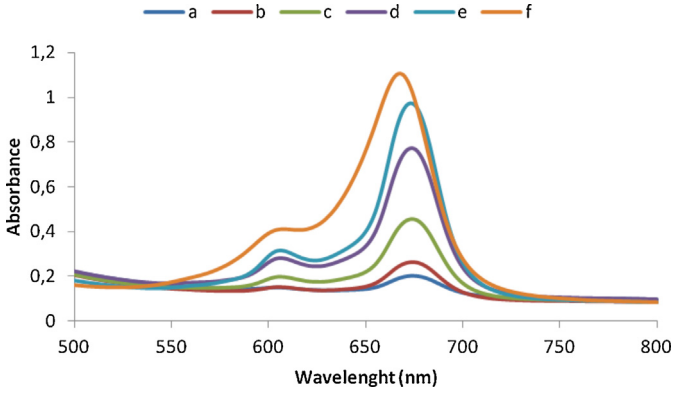

Fig. 7. Time-dependent changes in the visible spectrumof the oxidized complex **5** observed on addition of TBHP (1.70×10^{-3} mol) to a reactio mixture containing 1.02×10^{-3} mol benzyl alcohol and 3.41×10^{-6} mol complex **5** catalyst in 10 ml: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min; (a) 180 min after addition of m-CPBA. All spectra for the oxidized complex **5** were taken after sixfold dilution with acetonitrile. (f) Visible spectrum of (non-oxidized) complex **5**.

proceeds, this Q band shifts to 673 nm, broads and disappears at the end of the reaction. Shifting from 668 to 673 nm attested that metal oxidation of Co(II)-Pc to Co(III)-Pc [44–51]. After 3 h, this oxidized intermediate decomposed. Besides, there was no further conversion of any products. Similar statement can be formed for Fig. 6. As the reaction time progresses, widenning and disappearing of Q band are interpreted as in Co(II) phthalocyanine [44–51].

F. Adam and W.T. Ooi have synthesized organic–inorganic hybrid material as an effective catalyst by immobilizing metalloporphyrin complex onto the silica support in a simple co-condensation system. They reported that the catalytic activity of RHAC-CoPor (rice husk ash cobalt porphyrine) in liquid phase oxidation of benzyl alcohol using hydrogen peroxide as a green oxidant to form benzaldehyde. RHAC-CoPor employed good catalyst at 70 °C with high benzyl alcohol conversion (91.9%) [53]. Rezaeifard et al. [54] have investigated catalytic activity of Co and Mn porphyins in neat water. 93% product conversion was obtained using Fe(TPP)Cl as catalyst with TBAOX as an oxidant. M. Özer and co-workers reported that the synthesis and characterization of some novel substituted novel CoPc derivatives and cataliytic behavior of these complexes in the oxidation of benzyl alcohol. After 5.5 h, they were obtained 26.6% total conversion at 70 °C [55]. As shown in Table 5 the performance of the Fe-Pc and Co-Pc catalysts **4** and **5** toward the benzyl alcohol oxidation is more successful comparison to the other phthalocyanines and porphyrins as catalyst. Lastly, we achieved the most accomplish results in terms of % conversion, TON and TOF in literature for homogeneous benzyl alcohol oxidation with TBHP in the presence of complexes **4** and **5**. When they were compared with each other, FePc was also found the best catalyst on this work.

4. Conclusion

In this study, all spectroscopic data of Fe(II) and Co(II) phthalocyanines proved to successfully synthesized. Then, catalytic activities of Fe(II) and Co(II) phthalocyanines were investigated by examining the effects of certain parameters. Fe(II) and Co(II) phthalocyanines showed excellent catalytic performance in benzyl alcohol oxidation with benzaldehyde conversion by using TBHP as an oxidant. In particular, it is undoubtly proof that Fe(II) phthalocyanine would be an excellent biomimetic catalysts in a reaction time as short as 3 h to give 94% yield conversion. In conlusion, we done this catalytic works as feasible, time-saving in terms of procedure and determined the best oxidation conditions for catalysts **4** and **5** with high TON and TOF values.

Acknowledgement

This study was supported by The Scientific & Technological Research Council of Turkey (TÜBİTAK, project no: 111T963).

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.synthmet.2014.09.022.

References

[1] B.A. Jazdzewski, W.B. Tolman, Coordin. Chem. Rev. 200–202 (2000) 633–685.
[2] J.-E. Backvall, Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004.
[3] U.M. Lindstrom, F. Andersson, Angew. Chem. Int. Ed. 45 (2006) 548–551.
[4] M.C. Pirrung, Chem.-A Eur. J. 12 (2006) 1312–1317.
[5] B.M. Trost, R. Braslau, J. Org. Chem. 53 (1988) 532–537.
[6] B.R. Travis, B.P. Ciaramitaro, B. Borhan, Eur. J. Org. Chem. 20 (2002) 3429–3434.
[7] D. Mohajer, N. Iranpoor, A. Rezaeifard, Tetrahedron Lett. 45 (2004) 631–634.
[8] P.T. Anastas, M.M. Kirchhoff, Accounts Chem. Res. 35 (2002) 686–694.
[9] B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, VCH, New York, 1996.
[10] C.J. Li, T.K. Chan, Organic Reactions in Aqueous Media, John Wiley & Son, New York, 1997.

[11] P.A. Grieco, Organic Synthesis in Water, Blackie Academic and Professional, London, 1998.
[12] (a) B. Meunier, Biomimetic, in: Oxidations Mediated by Metal Complexes, Imperial College Press, London, 2000;
(b) X.T. Zhou, H.B. Ji, L.X. Pei, Y.B. She, J.C. Xu, L.F. Wang, Chinese J. Org. Chem. 27 (2007) 1039–1041.
[13] (a) W. Adam, S. Prikhodovski, K.J. Roschmann, C.R. Saha-Moller, Tetrahedron-Asymmetry 12 (2001) 2677–2681;
(b) E. Baciocchi, S. Belvedere, Tetrahedron Lett. 39 (1998) 4711–4714.
[14] P.E.F. Neys, I.F.J. Vankelecom, R.F. Parton, W. Dehaen, G. Labbe, P.A.J. Jacobs, J. Mol. Catal. A: Chem. 126 (1997) L9–L12.
[15] J.H. Han, S.K. Yoo, J.S. Seo, S.J. Hong, S.K. Kim, C. Kim, Dalton Trans. 2 (2005) 402–406.
[16] R. Breslow, Accounts Chem. Res. 24 (1991) 159–164.
[17] S. Otto, J.B.F.N. Engberts, Org. Biomol. Chem. 1 (2003) 2809–2820.
[18] C.-J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68–82.
[19] C.C. Leznoff, A.B.P. Lever Mc Keown, Phthalocyanines: properties and applications, VCH, New York, 1989.
[20] G. De La Torre, P. Vazquez, F. Lopez-Agullo, T. Torres, J. Mater. Chem. 8 (1998) 1671–1683.
[21] M. Emmelius, G. Pawlowski, H.W. Vollmann, Angew. Chem.: Int. Ed. (English) 28 (1989) 1445–1471.
[22] I. Rosenthal, Photochem. Photobiol. 53 (1991) 859–870.
[23] G. Guillaud, J. Simon, J.P. Germain, Coordin. Chem. Rev. 178 (1998) 1433–1484.
[24] B. Meunier, A. Sorokin, Accounts Chem. Res. 30 (1997) 470–476.
[25] M.K. Nazeeruddin, R. Humphry-Baker, M. Gratzel, B.A. Murrer, Chem. Commun. 6 (1998) 719–720.
[26] V.R. Choudhary, D.K. Dumbre, Ind. Eng. Chem. Res. 48 (2009) 9471–9478.
[27] P.J. Miedziak, Q. He, J.K. Edwards, S.H. Taylor, D.W. Knight, T. Brian, C.J. Kiely, G.H. Hutchings, Catal. Today 163 (2011) 47–54.
[28] N. Dimitratos, J.A. Lopez-Sanchez, D. Morgan, A. Carley, L. Prati, G.J. Hutchings, Catal. Today 122 (2007) 317–324.
[29] C.Y. Ma, B.J. Dou, J.J. Li, J. Cheng, Q. Hu, Z.P. Hao, S.Z. Qiao, Appl. Catal. B: Environ. 92 (2009) 202–208.
[30] J. Pritchard, L. Kesavan, M. Piccinini, Q. He, R. Tiruvalam, N. Dimitratos, J.A. Lopez-Sanchez, A.F. Carley, J.K. Edwards, C.J. Kiely, G.J. Hutchings, Langmuir 26 (2010) 16568–16577.
[31] V.R. Choudhary, D.K. Dumbre, Catal. Commun. 10 (2009) 1738–1742.
[32] L.A. Parreira, N. Bogdanchikova, A. Pestryakov, T.A. Zepeda, I. Tuzovskaya, M.H. Farias, E.V. Gusevskaya, Appl. Catal. A: Gen. 397 (2011) 145–152.
[33] M. Özer, F. Yılmaz, H. Erer, I. Kani, O. Bekaroğlu, Appl. Organomet. Chem. 23 (2009) 55–61.
[34] N. Sehlotho, T. Nyokong, J. Mol. Catal. A: Chem. 219 (2004) 201–207.
[35] B. Basu, S. Satapathy, A.K. Bhatnagar, Catal. Rev.: Sci. Eng. 35 (1993) 571–609.
[36] M. Chibwe, L. Ukrainczyk, S.A. Boyd, T.J. Pinnavaia, J. Mol. Catal. A: Chem. 113 (1996) 249–256.
[37] S.M.S. Chauhan, B. Kalra, P.P. Mohapatra, J. Mol. Catal. A: Chem. 137 (1999) 85–92.
[38] V.M. Kothari, J.J. Tazuma, J. Catal. 41 (1976) 180–189.
[39] T. Ichinohe, H. Miyasaka, A. Isoda, M. Kimura, K. Hanabusa, H. Shirai, React. Funct. Polym. 43 (2000) 63–70.
[40] T.V. Rao, K.N. Rao, S.L. Jain, B. Sain, Synthetic Commun. 32 (2002) 1151–1157.
[41] H. Turk, Y. Cimen, J. Mol. Catal. A: Chem. 234 (2005) 19–24.
[42] A.B. Sorokin, Bioinorg. React. Mech. 8 (2012) 59–84.
[43] Z. Bıyıklıoğlu, I. Acar, Synthetic Met. 162 (2012) 1156–1163.
[44] E.T. Saka, D. Çakır, Z. Bıyıklıoğlu, H. Kantekin, Dyes Pigments 98 (2013) 255–262.
[45] Z. Bıyıklıoğlu, E.T. Saka, S. Gökçe, H. Kantekin, J. Mol. Catal. A: Chem. 378 (2013) 156–163.
[46] E.T. Saka, Z. Bıyıklıoğlu, H. Kantekin, I. Kani, Appl. Organomet. Chem. 27 (2013) 59–67.
[47] I. Acar, R. Bayrak, E.T. Saka, Z. Bıyıklıoğlu, H. Kantekin, Polyhedron 50 (2013) 345–353.
[48] E.T. Saka, I. Acar, Z. Biyiklioğlu, H. Kantekin, I. Kani, Synthetic Met. 169 (2013) 12–17.
[49] S. Gökçe, E.T. Saka, Z. Bıyıklıoğlu, H. Kantekin, Synthetic Met. 176 (2013) 108–115.
[50] A. Aktaş, E.T. Saka, Z. Bıyıklıoğlu, I. Acar, H. Kantekin, J. Organomet. Chem. 745–746 (2013) 18–24.
[51] E.T. Saka, Z. Biyiklioğlu, J. Organomet. Chem. 745–746 (2013) 50–56.
[52] V.N. Nemykin, V. Ya Chernii, S.V. Volkov, N.I. Bundina, O.L. Kaliya, V.D. Li, E.A. Lukyanets, J. Porphyr. Phthalocya. 3 (1999) 87–98.
[53] F. Adam, W.T. Ooi, Appl. Catal. A: Gen. 445–446 (2012) 252–260.
[54] A. Rezaeifard, M. Jafarpour, A. Naemi, Catal. Commun. 16 (2011) 240–244.
[55] H.B. Ji, Q.L. Yuan, X.T. Zhou, L.X. Pei, L.F. Wang, Bioorg. Med. Chem. Lett. 17 (2007) 6364–6368.
[56] Q.G. Ren, S.Y. Chen, X.T. Zhou, H.B. Ji, Bioorg. Med. Chem. 18 (2010) 8144–8149.
[57] R. Rahimi, E. Gholamrezapor, M.R. Naimi-jamal, Inorg. Chem. Commun. 14 (2011) 1561–1568.