

Highly selective catalytic preparation of bis(4-oxo-benzo-2-cyclohexen-1-yl) amine from 1-naphthylamine oxidation over metalloporphyrin catalysts by molecular oxygen under air pressure and by hydrogen peroxide

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Abstract

In the presence of molecular oxygen or hydrogen peroxide, 1-naphthylamine (1-NA) was catalytically converted into bis(4-oxo-benzo-2-cyclohexen-1-yl) amine (BOBCHA) over metalloporphyrin catalysts through an oxidative-coupling way. UV–vis, IR, NMR, MS, mp determinations and elemental analysis were employed for product characterization. A possible catalytic mechanism based on in situ UV–vis and EPR determinations was proposed. A spectrophotometric method was established for quantitative analysis of the product according to its characteristic absorption at $\lambda_{\max} = 465$ nm. The influences of reaction conditions, such as solvents, temperature, reaction time, medium alkalinity, as well as species and amount of the catalysts were discussed in detail.

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1. Introduction

Metalloporphyrin researches were focused on mimic model compounds of biological enzymes based on their extremely high selectivity in catalytic conversions of hydrocarbons. Recently, water-soluble ferrous porphyrin, with similar structure as heme, was investigated of thermal and photoinduced properties to unambiguously prove its sitting-atop structure [1]. In another report, iron porphyrin complex catalyzed efficiently alcohol oxidations to the corresponding carbonyl compounds via a high-valent iron-oxo porphyrin intermediate [2]. For getting higher anti-oxidative endurance of the catalysts, some metalloporphyrins with halogen substituted were prepared as the third generation catalysts and applied to catalyze the epoxidation and hydroxylation of hydrocarbons using different strong

oxidant [3–6]. But traditional synthetic metalloporphyrins also exhibited higher catalytic activities and strong endurance in the oxidative preparation of 2-hydroxy-1,4-naphthoquinone from 1- or 2-naphthol, as we reported before [7,8]. Metalloporphyrin catalysts also exhibited high activities in NO disproportionation [9], photosensitized degradation of 4-chlorophenol [10] and unique direct oxidative conversion of *N*-acyl-L-proline to *N*-Acyl-L-glutamate [11]. Our primary research indicated that, under the similar catalytic conditions as literature [8] stated bis(4-oxo-benzo-2-cyclohexen-1-yl) amine (BOBCHA) was prepared when the reactants, 1- or 2-naphthol was replaced by 1-naphthylamine (1-NA) [12]. But, no catalytic mechanistic evidences were provided due to the difficulty in observing catalytic intermediates between iron porphyrin catalyst and O₂ during the reaction.

We presents here, in a methanolic alkaline medium, 1-naphthylamine is converted into bis(4-oxo-benzo-2-cyclohexen-1-yl) amine over 5,10,15,20-tetraphenyl porphyrinato manganese chloride (MnTPPCI) catalyst by O₂ with conversion of

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78.5% and selectivity at 100%, and over 5,10,15,20-tetraphenyl porphyrinato iron chloride (FeTPPCL) catalyst by H_2O_2 with conversion of 79.6% and with the same selectivity. Based on in situ determinations of FeTPPCL with H_2O_2 , a possible catalytic mechanism was proposed and the various factors influencing the catalysis were also discussed. With resembling molecular structure, BOBCHA should have the similar properties to naphthoquinone. It would be used as a receptor to modulate ryanodine in sarcoplasmic reticulum [13] and as the intermediate of fine chemicals preparation. For instance, by electrochemical method, BOBCHA could be polymerized into an oligomer film with excellent optical characteristics [14–16] to provide itself a potential application future.

2. Experimental

2.1. Reagents and instrument

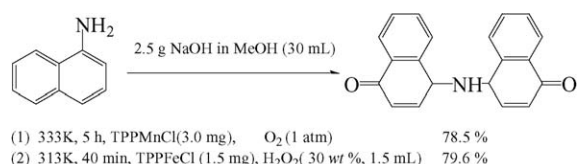
Metalloporphyrin catalysts were prepared by the methods of Adler et al. [17] and Lindsey et al. [18]. Molecular oxygen with purity of 99.99%, methanol, and 1-naphthylamine were purchased with purity higher than 99.99%. An aqueous solution of hydrogen peroxide (30 wt%) and all other reagents with purities higher than 99.9% were directly used without further purification.

The experiments were monitored by a Shimadzu UV-240 spectrophotometer (operating conditions: 40 nm/cm, 0.0–1.5 A; wavelength range: 200–800 nm; sample concentration: 0.0001–0.1 mol/dm³), a Nicolet FTIR 5-PC spectrometer (operating conditions: slow scanning speed; resolution power: 4 cm⁻¹; wave number range: 400–4000 cm⁻¹, KBr), a VG-Quattro series connection mass spectrometer (operating conditions: laser source; 200 °C; ionization voltage: 70 eV; analytic current: 500 μA ; sample feed: Desorption Electro-Impact (DEI), range: 0–300 m/z), a UNTY-400 NMR spectrometer (operating conditions: 300 MHz, standard substance is CDCl_3), a Bruker ER 200D EPR spectrometer (operating conditions: at room temperature; microwave frequency: 9.67 GHz; microwave power: 2 mW; midfield: 348.62 mT; scan range: 600.0 mT; scan time: 200 s; modulation frequency: 100 kHz; field modulation: 0.125 mT) and a X₄ microscope melting point apparatus.

2.2. Catalytic reactions

For preparing BOBCHA, 0.40 g of 1-NA, 2.50 g of NaOH, and 1.50 mg (2.13×10^{-3} mmol) of MnTPPCL were dissolved in 20 ml of MeOH at 333 K, followed by bubbling of molecular oxygen with pressure at 1 atm (101.325 kPa). Color of the reaction mixture was changed from straw yellow to red gradually (see Scheme 1). After 5 h of reaction under continuous stirring, the addition of water into the mixture produced red precipitates. The red product was purified by chromatography (using SiO_2 gel column with toluene as eluant). Finally, 0.63 g of a red powder was obtained in 78.5% yield.

In another catalytic system with H_2O_2 as an oxygen source, the above MnTPPCL catalyst was replaced by 3.0 mg (4.25×10^{-3} mmol) of TPPFeCl and at 313 K while other con-



Scheme 1. A novel compound of bis(4-oxo-benzo-2-cyclohexen-1-yl) amine (BOBCHA), is catalytic prepared coupling-oxidation over metalloporphyrin catalysts.

ditions kept constant. After 40 min of reaction, the red powder was obtained in yield of 79.6%.

2.3. Product characterization

The product was quantitatively analyzed by HPLC and UV–vis techniques. It was also characterized by means of melting point measurement, element analysis, GC-MS, IR and ¹H NMR determination.

Bis(4-oxo-benzo-2-cyclohexen-1-yl)amine: (Melting point: 232–233 °C); (Found: C, 79.46; H 5.08; N 4.52. Calc. for C₂₀H₁₅NO₂: C, 79.73; H, 4.98; N, 4.65%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3444(N–H); 1691(C=O) [19]; $\delta_{\text{H}} = 7.25, 7.42, 7.26, 7.69(\text{H-naph.})$; 6.88, 6.86(H–C=C); 2.0(H–N) [20]; mass spectrum $m/z = 301$ (molecular ion).

The UV–vis spectrum of BOBCHA in CH_2Cl_2 showed 3 absorptions at 289 nm ($\epsilon = 8.2 \times 10^4$), 345 nm ($\epsilon = 4.6 \times 10^4$), and 490 nm ($\epsilon = 2.0 \times 10^4$), and that in CH_3OH showed two absorptions at 277 nm ($\epsilon = 3.9 \times 10^4$) and 465 nm ($\epsilon = 2.3 \times 10^4$), respectively. Meanwhile, other substances in the catalytic system, such as NaOH, O₂, H₂O₂ and 1-NA, with no absorption appeared around 350–800 nm. Therefore, the absorption of BOBCHA at 465 nm can be directly used as the characteristic peak to analyze BOBCHA quantitatively. The linear regressive equation of standard curve for BOBCHA analysis is as $A = 0.02526 + 0.3612 \times 10^{-6} C_{\text{BOBCHA}}$ (linear correlative coefficient, $r = 0.9994$). In the concentration range of $(0.142\text{--}4.656) \times 10^{-6}$ mol/dm³, the standard curve displays a well linear correlation.

3. Result and discussion

3.1. Catalytic mechanism

FeTPPCL reacted with H_2O_2 to form a high valence metalloporphyrin complex, an active catalytic intermediate for the oxidation from 1- and 2-naphthol to 2-hydroxy-1,4-naphthoquinone [7]. The catalytic intermediate is the same one in the oxidative-coupling of 1-NA to form BOBCHA. UV–vis spectrum of FeTPPCL shows an absorption peak at 415 nm (Soret band). By adding H_2O_2 into this solution, an in situ determination reveals a new absorption peak at 461 nm [the absorption of O=Fe(V)TPPOH, Soret band], meanwhile the Soret band of FeTPPOH weakens gradually with an isobestic point emerging at 436 nm (Fig. 1a). Followed by adding 1-NA into the reaction system, the absorption at 461 nm assigned to the new species of metalloporphyrin disappears gradually, possibly owing to the consumption of

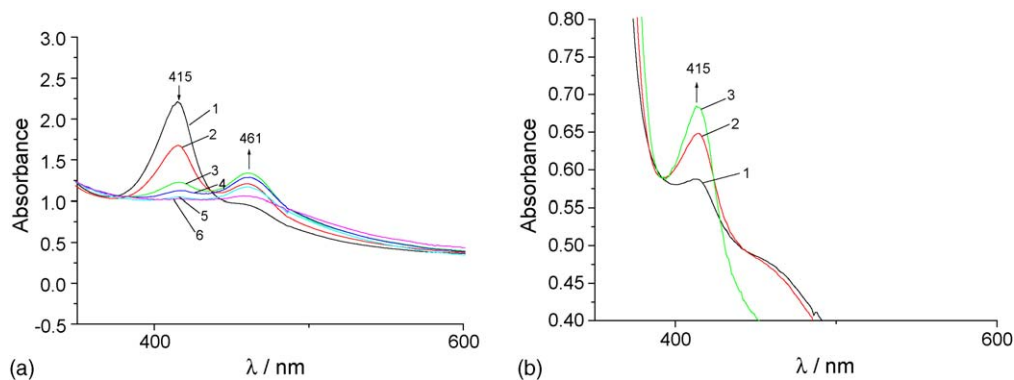


Fig. 1. In situ UV-vis spectrum varying, (a) FeTPPCL + H₂O₂; (b) 1-naphthylamine + (a)-6, after (1) 5 min; (2) 10 min; (3) 15 min.

the intermediate during the formation of BOBCHA (Fig. 1b). These evidences indicate that the active catalytic intermediate must be a new species of metalloporphyrin, [O=Fe(V)TPPOH]. The formation of O=Fe(V)TPPOH is just similar to the high-valent iron-oxo entities of cytochrome P-450 with H₂O₂ as oxygen donating [21,22]. EPR spectra of the catalytic oxidation have confirmed the suggestion. Fig. 2 shows the in situ EPR determination spectra of FeTPPCL reacting with H₂O₂ and 1-naphthylamine. Fe(III)TPPCL (presenting in Fe(III)TPPOH form in the methanolic alkaline medium) itself displays a strong EPR signal at $g = 2.225$ (Fig. 2a). By adding H₂O₂ into the solution, this signal becomes much weaker than before, and disappears completely after 45-min reaction (Fig. 2b–e). The

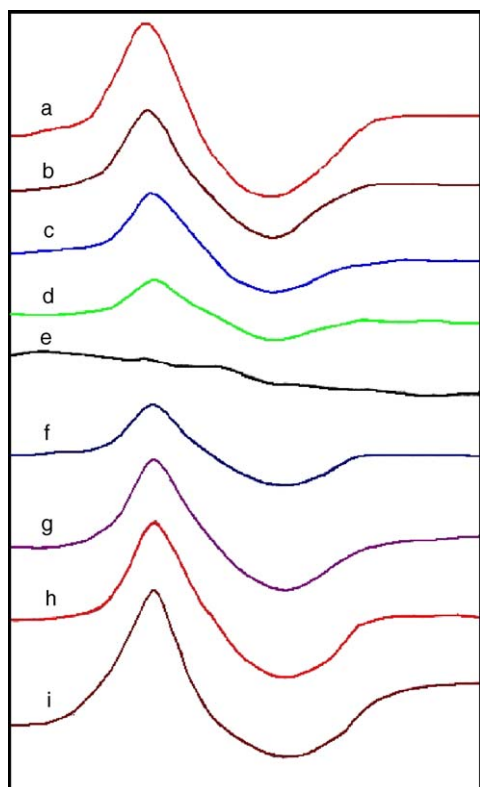


Fig. 2. The in situ EPR spectra of the catalytic system. (a) TPPFeCl + NaOH in MeOH solution. (b)–(e) H₂O₂ + (a), 10 min, 20 min, 35 min, and 45 min. (f)–(i) 1-Naphthylamine + (a), 5 min, 15 min, 25 min, and 30 min.

EPR signal disappearance means the formation of high valence of O=Fe(V)TPPOH. The high valence species is paramagnetic, but is “EPR-inert” one giving a broad spectrum, and hence, is difficult to be detected (see Fig. 2e) [26]. When 1-NA is added to the methanol solution with O=Fe(V)TPPOH, the paramagnetic signal appears again, possibly due to the reaction of O=Fe(V)TPPOH with 1-NA to produce the product, BOBCHA and the original catalyst, Fe(III)TPPOH (see Fig. 2f–i).

Therefore, a possible catalytic mechanism for oxidative-coupling of 1-NA by H₂O₂ is proposed as in Scheme 2.

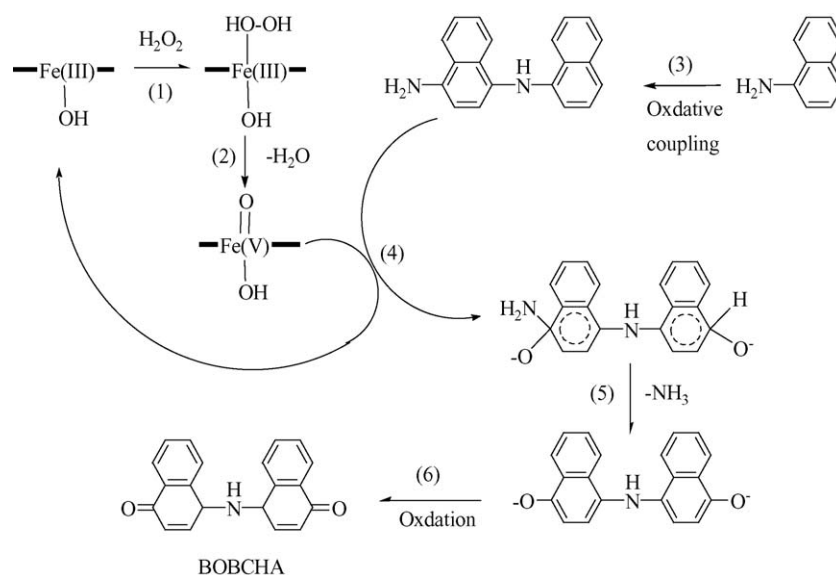
In the alkaline methanol media, the balance chloric anion in Fe(III)TPPCL is replayed by hydroxyl anion to form Fe(III)TPPOH, and Fe(III)TPPOH is coordinated further at the opposite axial trend by H₂O₂ to produce (HOOH)Fe(III)TPPOH (step 1). This unstable (HOOH)Fe(III)TPPOH rapidly dissociates into a high valence form of O=Fe(V)TPPOH, the catalytic intermediate; by the synergism of dehydration and oxidation (step 2) [21–25]. Meanwhile, 1-NA can be polymerized into an oligmer (step 3) in oxidative ambience [27], and the oligmer is oxidized by O=Fe(V)TPPOH (step 4) to form BOBCHA after deamination (step 5) and oxidation (step 6).

In the molecular oxygen system, the catalytic intermediate is in accordance with the model of cytochrome P-450 in hydroxylation of hydrocarbons [21,22]. Therefore, the catalytic intermediates in both H₂O₂ and O₂ oxidative-coupling of 1-NA are considered as an O=M(V) porphyrin form.

3.2. Catalytic condition optimization

3.2.1. Activities of different MTPP catalysts and their amount selection

Influences of the kind and the amount of metalloporphyrin catalysts on the oxidative-coupling of 1-NA were examined. The different effects of metalloporphyrin catalysts are list in Table 1 (the reacting conditions were given under the table). Notably, among metalloporphyrin catalysts with same center metal, M-TPP displays the highest activity in all system of O₂ oxygen donor and H₂O₂ oxygen donor, excepting Co-T(4-NO₂)PP catalyst in H₂O₂ system. These indicate the substituent groups at phenyl rings in metalloporphyrin including both the electron donating –OCH₃, –OH, and the electron attracting –F, –NO₂, are all unfavorable for getting high catalytic activities in



Scheme 2. A possible catalytic mechanism for producing BOBCHA with H_2O_2 as oxygen donor over FeTPPCL catalyst.

the oxidative-coupling. The special demand to form BOBCHA may be account for the amounts and stabilities of high valence metalloporphyrin intermediates in the oxidative-coupling of 1-NA. In fact, the absorbance peaks of $\text{O}=\text{Fe}(\text{V})\text{T}(p\text{-F})\text{PPOH}$, $\text{O}=\text{Fe}(\text{V})\text{TPPOH}$ and $\text{Fe}(\text{V})\text{T}(p\text{-OCH}_3)\text{PPOH}$ appear at $\lambda_{\text{max}} = 462 \text{ nm}$ ($\varepsilon = 1.38 \times 10^4$), $\lambda_{\text{max}} = 465 \text{ nm}$ ($\varepsilon = 2.25 \times 10^4$) and $\lambda_{\text{max}} = 468 \text{ nm}$ ($\varepsilon = 2.60 \times 10^4$), respectively. During the formation of the catalytic intermediates, the electron donating groups ($-\text{OCH}_3$) around porphyrin rings make redox potential descend while the electron attracting groups ($-\text{F}$) make that arise. The redox potential arising reduces the catalytic intermediate amount, and as a result, less BOBCHA is produced. Contrarily, the redox potential descending increases

the catalytic intermediate amount and meanwhile makes the catalytic intermediate too stable in kinetics to react with 1-NA. Therefore, less BOBCHA is produced too. Obviously, both amount and stabilities of the intermediate come from metalloporphyrin without any electron donating or accepting groups, such as MTPPCL, are more suitable in the catalytic preparation of BOBCHA. The intermediate spectra change along with time after adding 1-NA also indicates kinetic stability of the intermediate. Within 15 min, the intermediate spectrum of $\text{O}=\text{Fe}(\text{V})\text{TPPOH}$ is almost changed into its original spectrum of FeTPPOH catalyst (see Fig. 1b), while the intermediate spectrum of $\text{O}=\text{Fe}(\text{V})\text{T}(p\text{-OCH}_3)\text{PPOH}$ becoming into that of $\text{Fe}(\text{III})\text{T}(p\text{-OCH}_3)\text{PPOH}$ almost takes 40 min. The rate to consume $\text{O}=\text{Fe}(\text{V})\text{TPPOH}$ is rather faster than that to consume $\text{O}=\text{Fe}(\text{V})\text{T}(p\text{-OCH}_3)\text{PPOH}$ based on $\text{Fe}(\text{III})\text{T}(p\text{-OCH}_3)\text{PPOH}$, with 4 methoxyls, the strong electron donating substituents.

Table 1
Activity compare of different metalloporphyrin catalysts^a

Metalloporphyrin catalyst	Yield of BOBCHA/%	
	O_2 as oxidant	H_2O_2 as oxidant
Fe-T(4-OCH ₃)PPCL	46.88	19.71
Fe-T(4-OH)PPCL	38.43	24.63
Fe-TPPCL	52.31	51.64
Fe-T(4-F)PPCL	51.91	27.03
Fe-T(4-NO ₂)PPCL	32.74	5.34
Mn-T(4-OCH ₃)PPCL	29.62	0.84
Mn-TPPCL	65.32	19.07
Mn-T(4-F)PPCL	47.28	10.94
Mn-T(4-NO ₂)PPCL	56.41	0.63
Mn-T(3-NO ₂)PPCL	40.94	1.62
Co-T(4-OCH ₃)PP	17.94	3.70
Co-TPP	32.21	2.21
Co-T(4-NO ₂)PP	29.97	14.86
Co-T(4-F)PP	8.16	0.18

^a All catalysts are based on the structure of 5,10,15,20-tetraphenylporphyrin-metal complex (M-TPP), and the substituent at the phenyl ring is labeled in the brackets. Reaction conditions: $V_{\text{MeOH}} = 30 \text{ ml}$, $m_{\text{NaOH}} = 2.5 \text{ g}$, $m_{1\text{-NA}} = 0.4 \text{ g}$. For H_2O_2 system: $T = 313 \text{ K}$, $t = 1 \text{ h}$, $m_{\text{Catalyst}} = 0.5 \text{ mg}$, $V_{\text{H}_2\text{O}_2} = 1.5 \text{ ml}$. For O_2 system: $T = 333 \text{ K}$, $t = 3 \text{ h}$, $m_{\text{Catalyst}} = 1.5 \text{ mg}$, $P_{\text{O}_2} = 1 \text{ atm}$.

The experimental data in Table 1 also indicate that FeTPPCL and MnTPPCL are with relative higher activities than other ones in O_2 and H_2O_2 systems, respectively. After metalloporphyrin catalyst selections, the amount of FeTPPCL and MnTPPCL catalysts for the two catalytic systems were examined (see Fig. 3). When 1.5 mg of MnTPPCL (for O_2 system) or 3.0 mg of FeTPPCL (H_2O_2 system) are added, the highest conversions from 1-NA into BOBCHA reach at 65.3% and 79.6%, respectively under the relative reacting conditions. Less or more catalysts than the best amounts will descend the yield of BOBCHA. The polymer formation of 1-NA may account for the conversion falling [27]. Meanwhile, high concentration of metalloporphyrin catalyst may accelerate the formation of an inactive species of μ -oxygen dimer, [Por-M-O-M-Por], to descend concentration of the active intermediate of $\text{O}=\text{M}(\text{V})\text{TPP}$. As a result, the yield of BOBCHA would be reduced consequentially [28,29].

3.2.2. Influence of the amount of sodium hydroxide

Fig. 4 presents the influence of sodium hydroxide amount in the methanol solution. Alkali reacting medium is beneficial for

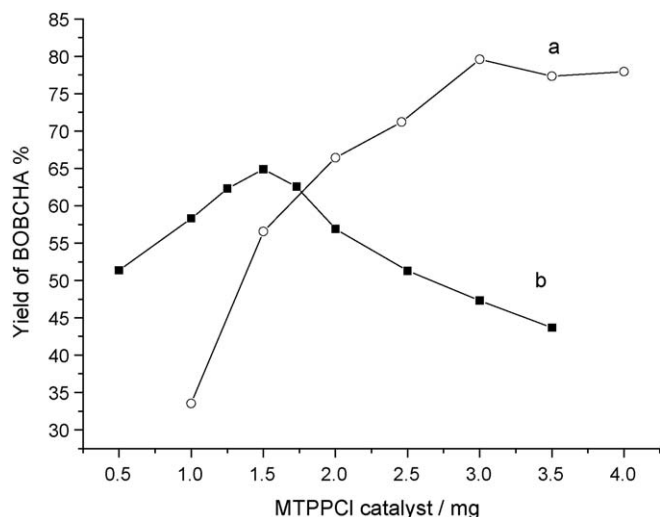


Fig. 3. M-TPPCL catalyst amount selection, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{\text{NaOH}} = 2.5 \text{ g}$, $m_{1-\text{NA}} = 0.4 \text{ g}$. Change the amount of M-TPPCL catalysts, (a) H_2O_2 system: FeTPPCL as catalyst, $t = 40 \text{ min}$, $T = 313 \text{ K}$, (b) O_2 system: MnTPPCL as catalyst, $t = 3 \text{ h}$, $T = 333 \text{ K}$.

both decreasing the redox potential and promoting the organic reaction rate. In the catalytic oxidation of 1-NA, sodium hydroxide displays a very important role. Without sodium hydroxide, no BOBCHA can be detected. Therefore, the conversion of 1-NA to BOBCHA also increases with the amount of NaOH in the reaction solution before its amount reaches 2.5 g for both systems. The MeOH solution as reaction mediate becomes much sticky to barrier the collision between the reactants when the added amount of NaOH is beyond 2.5 g. Under definite reaction conditions, the highest conversions of 1-NA are at 66.18% and 53.20% for O_2 and H_2O_2 systems, respectively.

3.2.3. Reacting time selections

The oxidants of O_2 and H_2O_2 are with different oxidative abilities. So the reaction rates between two catalysis systems

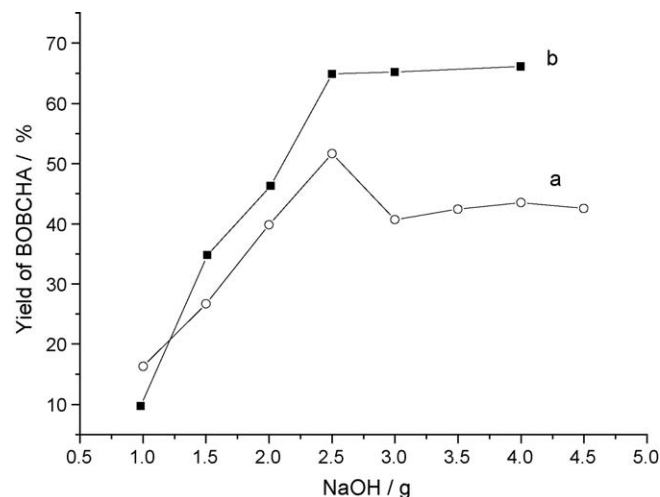


Fig. 4. NaOH dosage selection, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{1-\text{NA}} = 0.4 \text{ g}$. Change the amount of NaOH. (a) H_2O_2 system: $m_{\text{FeTPPCL}} = 0.5 \text{ mg}$, $V_{\text{H}_2\text{O}_2} = 1.5 \text{ mL}$, $t = 60 \text{ min}$, $T = 313 \text{ K}$. (b) O_2 system: $m_{\text{MnTPPCL}} = 1.5 \text{ mg}$, $P_{\text{O}_2} = 1 \text{ atm}$, $t = 3 \text{ h}$, $T = 333 \text{ K}$.

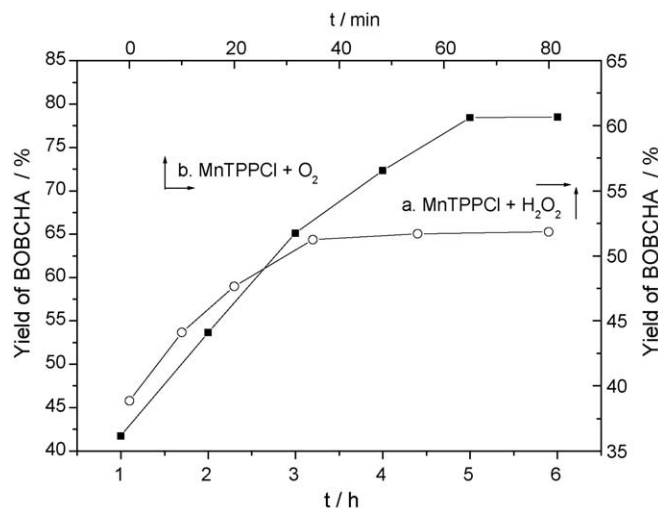


Fig. 5. Reaction time selection, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{1-\text{NA}} = 0.4 \text{ g}$, $m_{\text{NaOH}} = 2.5 \text{ g}$. (a) H_2O_2 system: $m_{\text{FeTPPCL}} = 0.5 \text{ mg}$, $V_{\text{H}_2\text{O}_2} = 1.5 \text{ mL}$, $T = 313 \text{ K}$. (b) O_2 system: $m_{\text{MnTPPCL}} = 1.5 \text{ mg}$, $P_{\text{O}_2} = 1 \text{ atm}$, $T = 333 \text{ K}$.

are different too. Fig. 5 shows the best reacting times are 35–40 min for ($\text{FeTPPCL} + \text{H}_2\text{O}_2$) system and 5 h for ($\text{MnTPPCL} + \text{O}_2$) system. Obviously, the strong oxidant H_2O_2 needs much shorter time than the weak oxidant O_2 does to make the catalytic oxidative-coupling of 1-NA get equilibrium. Remarkably, after long time reaction (especially for the system with suitable amount of H_2O_2 as much stronger oxidant), the yields of BOBCHA do not descend any longer. Then BOBCHA can be considered as a very stable product under the catalytic conditions.

3.2.4. Temperature impacting

Temperature is an important factor to accelerate chemical rate, to shorten the equilibrium time and even to change the reaction direction or to vary the products. For getting its influences on both H_2O_2 and O_2 systems, the oxidative-couplings were carried out at different temperatures. Fig. 6a shows the temperature influencing on ($\text{H}_2\text{O}_2 + \text{FeTPPCL}$) system, and the best temperature range is from 35°C to 40°C (308–313 K). The yields of BOBCHA are lower when the reaction temperature selected is out of the best range. Below 35°C or above 40°C , the reaction rate is small or the BOBCHA may be further oxidized by H_2O_2 , and as results to reduce the yield of BOBCHA. But for ($\text{O}_2 + \text{MnTPPCL}$) system (Fig. 6b), the yield of BOBCHA ascends along with the reaction temperature rising, until reaching the reflux temperature of MeOH solution. So BOBCHA could not be oxidized by the weaker oxidant of O_2 at the reflux temperature.

3.2.5. Influences of oxidant amount and reacting media for ($\text{H}_2\text{O}_2 + \text{FeTPPCL}$) system

In the ($\text{H}_2\text{O}_2 + \text{FeTPPCL}$) system, the oxidant amount influence to the catalysis was investigated. Fig. 7 shows the best amount of H_2O_2 (30 wt% aqueous solution) in preparing of BOBCHA is 1.5 mL at adding rate of 1 drop/6 s. Under

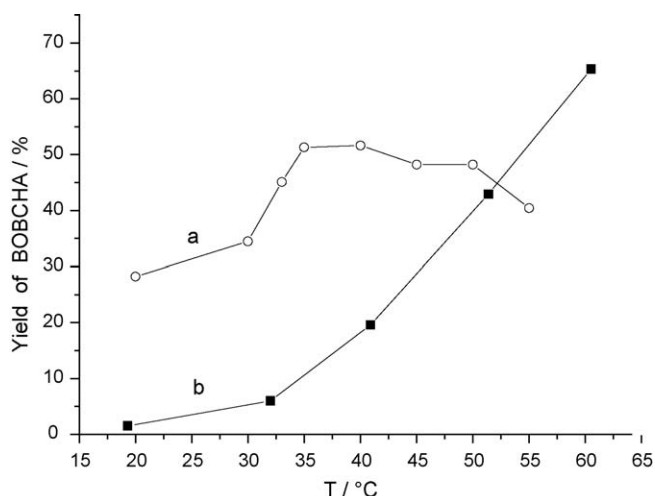


Fig. 6. Affirmance of reaction temperature, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{1\text{-NA}} = 0.4 \text{ g}$, $m_{\text{NaOH}} = 2.5 \text{ g}$. (a) H_2O_2 system: $m_{\text{FeTPPCL}} = 0.5 \text{ mg}$, $V_{\text{H}_2\text{O}_2} = 1.5 \text{ mL}$, $t = 1 \text{ h}$. (b) O_2 system: $m_{\text{MnTPPCL}} = 1.5 \text{ mg}$, $P_{\text{O}_2} = 1 \text{ atm}$, $t = 3 \text{ h}$.

the definite conditions, excess amount of H_2O_2 will oxidize BOBCHA to descend its yield.

Furthermore, different solvents were employed for selection of reacting media in catalytic preparation of BOBCHA. Experimental results indicate that both MeOH and EtOH are much better solvents with suitable polarizing properties. Relatively, water-soluble solvents, including acetonitrile, acetone and even water itself, and other water-insoluble solvents, including ether, dichloromethane, chloroform, benzene and toluene, are all unsuitable media for the catalytic oxidative-coupling of 1-NA. Except methanol and ethanol, although sodium hydroxide is with enough solubility in the other water-soluble solvents, they can supply unsuitable polarities for the catalysis. Otherwise, sodium hydroxide is undissolvable in the water-insoluble solvents for supplying the necessary alkaline to the catalysis. Therefore, both the polarity and the alkaline of the reacting

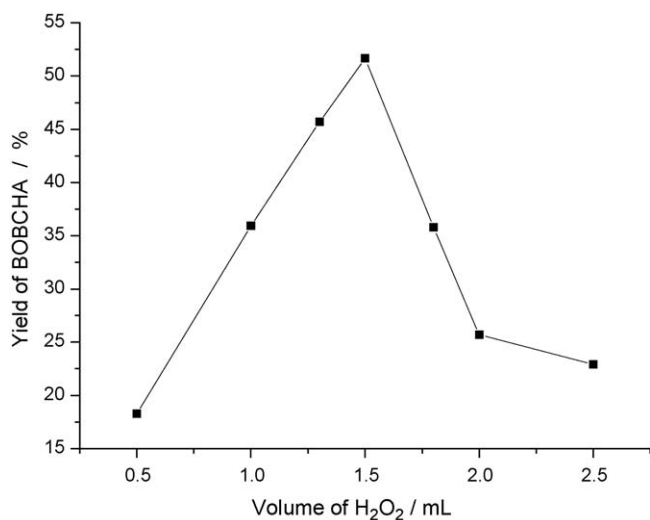


Fig. 7. Selection of H_2O_2 amount for system using MnTPPCL as the catalyst, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{\text{FeTPPCL}} = 0.5 \text{ mg}$, $m_{1\text{-NA}} = 0.4 \text{ g}$, $m_{\text{NaOH}} = 2.5 \text{ g}$, $T = 40^\circ\text{C}$, $t = 1 \text{ h}$, H_2O_2 (30% aq.) as oxygen source.

medium should be strictly controlled for getting high conversion from 1-NA to BOBCHA.

Summarizing all above, the optimizing catalytic conditions to prepare BOBCHA are (1) for ($\text{O}_2 + \text{MnTPPCL}$) system: $m_{\text{MnTPPCL}} = 1.5 \text{ mg}$, $m_{1\text{-NA}} = 0.4 \text{ g}$, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{\text{NaOH}} = 2.5 \text{ g}$, $t = 5 \text{ h}$, $T = 333 \text{ K}$ (60°C), $P_{\text{O}_2} = 1 \text{ atm}$, yield $\text{BOBCHA} = 78.51\%$; and (2) for ($\text{H}_2\text{O}_2 + \text{FeTPPCL}$) system: $m_{\text{FeTPPCL}} = 3.0 \text{ mg}$, $m_{1\text{-NA}} = 0.4 \text{ g}$, $V_{\text{MeOH}} = 30 \text{ mL}$, $m_{\text{NaOH}} = 2.5 \text{ g}$, $t = 40 \text{ min}$, $T = 308\text{--}313 \text{ K}$ ($35^\circ\text{C}\text{--}40^\circ\text{C}$), $V_{\text{H}_2\text{O}_2} = 1.5 \text{ mL}$, yield $\text{BOBCHA} = 79.62\%$.

4. Conclusions

1-Naphthylamine (1-NA) can be converted into the novel oxidative-coupling product of bis(4-oxo-benzo-2-cyclohexen-1-yl) amine (BOBCHA) over metalloporphyrin catalysts by both molecular oxygen and hydrogen peroxide aqueous solution (30 wt%), respectively. The molecular structure of BOBCHA is much different from that of 1,1'-bi-2-naphthol with 2-naphthol as reactant [30], and from that of the cross-coupling product with 2-naphthol and 2-naphthylamine as reactant [31,32], the traditional oxidative-coupling products. These oxidative-coupling reactions exhibit characters as below: (1) relative low temperature is needed in preparing BOBCHA with high selectivity and conversion; (2) both strictly polarity and strong alkali of the reacting medium is demanded, and more suitable reacting media are methanol and ethanol; (3) low solubility of BOBCHA makes it easy to separate from the reacting medium; (4) metalloporphyrin catalysts are stable enough to anti-oxidize and can be reused after separation; and (5) with a special molecular structure and color change property in different media, BOBCHA would be found as a potential useful function material.

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