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Selective oxidation of benzyl alcohol to benzaldehyde over Co-metalloporphyrin supported on silica nanoparticles

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ABSTRACT

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Keywords: Rice husk ash Metalloporphyrin Sol-gel technique Nano particle Oxidation Benzyl alcohol Heterogenation of the metalloporhyrin ligand, [tetrakis(o-chlorophenyl)porphyrinato]Co(II) was effected by immobilizing the complex onto inorganic silica support to form spherical nanoparticles of RHAC-CoPor. This insoluble mesoporous hybrid showed a high specific surface area of $114 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of 0.177 cm³ g⁻¹. The prepared catalyst possessed a narrow pore size distribution centered at around 4.17 nm. The ¹³C MAS NMR showed that RHAC-CoPor had three chemical shifts at 12.60, 26.60 and 45.18 ppm consistent with the three carbon atoms of the propyl group and a series of chemical shifts in the range of $\delta = 108-167$ ppm consistent with the presence of the metalloporphyrin complex. Elemental analysis showed the successful immobilization of metalloporphyrin complex onto functionalized RHA silica support. RHAC-CoPor appeared to be an active catalyst in the oxidation of benzyl alcohol, producing 97.1% conversion and 97.7% selectivity for benzaldehyde under an ambient temperature of 70 °C. RHAC-CoPor could be regenerated and reused several times by washing with water, followed by drying at 100 °C.

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1. Introduction

Rice husk (RH) is a major agricultural biomass residue in nearly all developing countries in the world including Malaysia [1]. The rice milling industry is always facing problems of RH disposal. In order to solve this problem, RH can be transformed into ash. Rice husk on burning gives rice husk ash (RHA) containing high silica content [2]. Many researchers have utilized this as a renewable silica source. This insoluble RHA silica can be used as a support to functionalize various organic groups and by different immobilization techniques in order to generate novel materials with interesting new properties [3]. For instance, RHA silica functionalized with organohalotrialkoxysilane can facilitate the immobilization of a wide variety of organic ligands. The use of this inorganic silica support plays a very important role in the preparation of hybrid materials [4–6].

Over the past few decades, metalloporphyrin have become well known for their catalytic activity. It has been used in a range of reactions including oxidation, epoxidation as well as hydroxylation [7–12]. Metalloporphyrins used as a catalyst in homogeneous catalytic systems have a number of disadvantages such as decomposition of the catalyst during reaction and difficulty of recovery at the end of the reaction for reuse [13–15]. Hence, in order to enhance the stability of the metalloporphyrin catalyst and to utilize some of the remarkable properties of porphyrin, it is important to immobilize them on suitable insoluble solid supports, which include alumina, silica, zeolite, clays and resins.

Oxidation of benzyl alcohol to benzaldehyde is of an important chemical reaction as benzaldehyde is one of the most industrially useful compounds. For instance, it is widely used as a precursor for certain dyes and other organic compounds, ranging from pharmaceuticals to plastic additives [16-18]. Besides, benzaldehyde is also used in perfumery, cosmetic as well as food industries as it is commonly used to confer flavor and odor [19,20]. Literature review shows that gold and palladium supported materials have been used for the oxidation of benzyl alcohol but with a relatively low selectivity toward benzaldehyde [17.21-26]. Only a few cobalt or cobalt supported catalyst have been reported for the partial oxidation of benzyl alcohol. Xavier et al. [27] have reported the liquid phase partial oxidation of benzyl alcohol by zeolite-encapsulated cobalt(II) complex, resulting in a very low percentage of conversion and extremely low selectivity toward benzaldehyde. Similar results were obtained when using various alkali metals added to impregnated cobalt with inorganic oxides including NaY, SiO₂ and NaUSY (ultra-stable Y) zeolites in gas phase oxidation [28,29].

Herein we present the synthesis of organic-inorganic hybrid material as an effective catalyst by immobilizing metalloporphyrin complex onto the silica support in a simple co-condensation system. Functionalization of RHA silica with 3-aminopropyltriethoxysilane was carried out by a fast sol-gel technique at room

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temperature and pressure. While the heterogenation of metalloporphyrin complex, [tetrakis(o-chlorophenyl)porphyrinato]Co(II) onto RHA–APTES was carried out under reflux condition in toluene. To the best of our knowledge, the oxidation of benzyl alcohol has not been carried out using catalyst synthesized from immobilized [tetrakis(o-chlorophenyl)porphyrinato]Co(II). The search for green chemistry prefers the use of H₂O₂ compared to other oxidants as it is inexpensive and it will not produce any hazardous waste since water is its only by-product formed during the reaction [20,30,31]. Therefore, in this work we report the catalytic activity of RHAC-CoPor in liquid phase oxidation of benzyl alcohol using hydrogen peroxide as a green oxidant to form benzaldehyde. All the preparation methods used are simple, cost-effective, less time-consuming and eco-friendly.

2. Experimental procedures

2.1. Materials

The RH was obtained from a local rice mill in Penang. Nitric acid (65%) and sodium hydroxide (99%) were obtained from QReC. Propionic acid was purchased from HmbG Chemicals. Pyrrole and dichloromethane (DCM) (99%) were purchased from Merck. 3-Aminopropyltriethoxy silane (APTES) (98%) was purchased from Sigma–Aldrich. Toluene and acetonitrile were purchased from J.T. Baker (99.8%). Benzyl alcohol was obtained from Unilab. All chemicals are of AR grade and used as obtained without further purification.

2.2. Sources of silica

Rice husk ash (RHA) was chosen as the source of amorphous silica from which the silica was extracted according to a previously reported method [32].

2.3. Functionalization of RHA with APTES

RHA silica was functionalized with APTES via a sol-gel reaction according to the method reported elsewhere [33] with some modification. About 3.0 g of RHA was stirred in 300 mL of 1.0 M NaOH at room temperature overnight. The sodium silicate formed was filtered to remove undissolved particles. APTES (6.0 mL, 0.026 mol) was then added to this sodium silicate solution and the solution was titrated slowly with 3.0 M nitric acid until pH 3 with constant stirring. A white gel started to form when the pH decreased to less than 10. The gel formed was aged for 24 h at room temperature. The gel was separated by centrifuge at 4000 rpm for 15 min (Rotina 38, Hittich Zentrifugn) and washing 5 times with distilled water. Final washing was done with hot water. The sample was then dried in an oven overnight. Finally, it was ground to produce a fine powder. A 3.45 g of RHAC-NH₂ was collected from this method and it was then used as the support to anchor the [tetrakis(o-chlorophenyl)porphyrinato] cobalt(II) complex.

2.4. Synthesis of [tetrakis(o-chlorophenyl)porphyrinato] cobalt(II)

Tetrakis(o-chlorophenyl)porphyrin was synthesized first by following the reported Alder–Longo method [34] with some modification. 2-Chlorobenzaldehyde (20.3 mL, 0.18 mol) and pyrrole (12.5 mL, 0.18 mol) were added simultaneously to the refluxing propionic acid (300 mL). The mixture was then refluxed for 30 min and was allowed to cool to room temperature. The precipitate formed was filtered and washed with an appropriate amount of cold methanol and hot water to give a violet solid of tetrakis(o-chlorophenyl)porphyrin. The synthesized tetrakis(ochlorophenyl)porphyrin was refluxed with cobalt(II) chloride in dimethylformamide for 1 h and stirred in an ice bath before pouring cold distilled water into the mixture. An immediate precipitate of the complex [tetrakis(o-chlorophenyl)porphyrinato]Co(II) was formed and it was recrystallized in a 4:1 chloroform–methanol mixture. The product yield was 75.8%.

2.5. Preparation of RHAC-CoPor catalyst

Preparation of the catalyst was carried out by a modified technique reported elsewhere [35]. The ligand, [tetrakis(*o*-chlorophenyl)porphyrinato]Co(II) (12.0 mmol) was added to a suspension of RHAC-NH₂ (3.0 g) in dry toluene (50 mL) and triethylamine (1.67 mL, 12.0 mmol). The reaction mixture was allowed to reflux at 110 °C in an oil bath for 24 h. Then, the solid phase was filtered and washed with toluene, DCM, and distilled water. The solid sample was then dried in an oven. Finally, it was ground to a fine powder and the sample was labeled as RHAC-CoPor.

2.6. Characterization of RHAC-CoPor

RHAC-CoPor was characterized by several spectroscopic and physical methods. These includes FTIR spectroscopy (Perkin Elmer System 2000), N₂ adsorption–desorption analysis (Micromeritics Instrument Corporation model ASAP 2000, Norcross), solid state ²⁹Si and ¹³C nuclear magnetic resonance, elemental analysis (CHN, EDX) transmission electron microscopy (TEM, Phillips CM12), scanning electron microscopy (SEM) and image analyzer.

2.7. Catalytic activity

The catalytic liquid phase oxidation of benzyl alcohol was carried out in a 50 mL round-bottom flask that was equipped with a reflux condenser. In a typical run, benzyl alcohol (1.08 g, 10 mmol) and an amount of catalyst (0.08 g) was placed into the flask containing 10 mL of acetonitrile and the reaction mixture was heated in an oil bath with continuous stirring at 70°C. H₂O₂ (15 mmol, 30%) was then added drop wise slowly into the reaction flask within 5 min and the reaction was allowed to continue for 5 h. During the reaction, 0.5 mL of the sample was withdrawn periodically from the mixture and filtered to remove the catalyst so as to determine the percentage conversion by analyzing it with gas chromatography (Perkin Elmer Clarus 500) equipped with Elite Wax $(30 \text{ m} \times 0.2 \text{ mm ID})$ using 20 µL of cyclohexanone as an internal standard. The products formed were further confirmed by GC-MS (Perkin Elmer, Clarus 600) analysis. After the reaction, the catalyst was filtered and washed thoroughly with water in order to separate it from the reaction mixture. The separated catalyst was dried, and then reused again for three times to test the reusability of the catalvst.

3. Results and discussion

3.1. Characterization of porphyrin and metalloporphyrin complex

The ¹H NMR spectrum of the ligand, tetrakis(*o*-chlorophenyl)porphyrin (Fig. 1a) displayed a singlet highly shielded peak at around -2.60 ppm. This was attributed to the rapidly exchanging N–H proton at the center of the porphyrin ligand in the core of the macrocycle. Whereas, the aromatic protons in the porphyrin ring resonated at 8.22 ppm, 7.88 ppm, 7.77 ppm and 7.68 ppm. Multiplet at δ = 8.22 ppm and 7.68 ppm were assigned to the proton at the *meso*-position of the phenyl rings. The proton of the *m*-phenyl which is located just beside the substituted electronegative atom, chlorine was deshielded



Fig. 1. The ¹H NMR spectra of (a) tetrakis(o-chlorophenyl)porphyrin and (b) [tetrakis(o-chlorophenyl)porphyrinato]Co(II).

downfield compared to the one located further away from the substituted chloro group. The multiplicity of the peak is due to the proton coupling and long range coupling between neighboring protons. While a triplet at δ = 7.77 ppm and a doublet at δ = 7.88 ppm was assigned to protons of the phenyl rings at the para- and *ortho*-position, respectively. The β -protons on the periphery of the macrocycle were strongly deshielded by the diamagnetic ring current. Hence the singlet peak resonated at δ = 8.75 ppm was attributed to the eight proton of β -pyrrole in the basic skeleton of porphyrins. The disappearance of the inner NH peak at high field for [tetrakis(o-chlorophenyl)porphyrinato]Co(II) can be observed in Fig. 1b. This is good evidence that the metallation of porphyrin ligand was successful as the cobalt had been incorporated in the core of the macrocycle. The metallation caused shielding of the β -pyrrole which appeared at δ = 8.21 ppm and the deshielding of all protons in the substituted phenyl ring shifted them to a more downfield resonance.

Fig. 2 shows the IR spectra of tetrakis(o-chlorophenyl)porphyrin and [tetrakis(o-chlorophenyl)porphyrinato]Co(II). From the spectra, tetrakis(o-chlorophenyl)porphyrin showed the presence of N–H stretching vibration of pyrrole at 3404 cm $^{-1}$ as well as $\nu_{\text{N-H}}$ (in planarity) and ν_{N-H} (out of planarity) transmission bands of porphyrin at 968 cm⁻¹ and 800 cm⁻¹, respectively. The N–H peak disappeared after the metallation of porphyrin. This is because the secondary amines (=N-H) lost the H atom when coordinated to the cobalt ion as shown in the respective structures in Fig. 1. The N-H stretching vibration is thus not observed in the FTIR spectrum of the cobalt coordinated complex. The transmission bands at 3325 cm⁻¹, 3061 cm^{-1} are due to the C–H (sp²) stretching of macrocyclic and the C–H (sp²) stretching of the phenyl groups, respectively. Another two bands at 1636 cm⁻¹ and 1469 cm⁻¹ were due to the C=C stretching of the phenyl groups which showed the presence of an aromatic ring. For [tetrakis(o-chlorophenyl)porphyrinato]Co(II), these two bands appeared at 1628 cm⁻¹ and 1443 cm⁻¹. The C–N



Fig. 2. The FT-IR spectra of (a) tetrakis(*o*-chlorophenyl)porphyrin and (b) [tetrakis(*o*-chlorophenyl)porphyrinato]Co(II).

stretching vibration of the porphyrin ring is seen at 1205 cm^{-1} (Fig. 2a) and 1243 cm^{-1} (Fig. 2b).

3.2. Characterization of catalyst

The IR spectra of RHA, RHAC-NH₂, and RHAC-CoPor (before and after reaction) are shown in Fig. 3. Typically, a broad band with high intensity in the range of 3500–3400 cm⁻¹ corresponded to the O–H vibration of SiO–H groups and HO–H of adsorbed water [36]. The bending vibration of the trapped water molecules in the silica matrix was detected as an intense peak at 1648 cm⁻¹. The vibration



Fig. 3. The FT-IR spectra of (1) RHA, (2) RHAC-NH₂, (3) RHAC-CoPor before the reaction and (4) RHAC-CoPor after the catalytic reaction.

peak at 1098 cm⁻¹ was assigned to the asymmetric vibration of the siloxane bond, Si-O-Si associated with the condensed silica network in the silica. C-H stretching vibration can be observed in both RHAC-NH₂ and RHAC-CoPor at 2981 cm⁻¹ and 2962 cm⁻¹, respectively. Another strong band at 1378 cm⁻¹ which can be only observed in both RHAC-NH2 and RHAC-CoPor was assigned to the C-N stretching of the primary amides. However, the intensity of this band decreased once the metalloporphyrin complex was immobilized onto the silica support. Apart from that, RHAC-CoPor showed additional peaks at 1638 cm⁻¹, 1486 cm⁻¹ and 1352 cm⁻¹ which were ascribed to the C=C and C=N bonds of benzene and porphyrin ring as well as peaks at 793 cm⁻¹ and 702 cm⁻¹ which corresponds to the skeletal vibration of porphyrin ring. These differences proved that the metalloporphyrin complex was successfully incorporated onto the silica support, RHAC-NH₂. Since there is no difference in FT-IR spectra of RHAC-CoPor before and after the reaction, hence it was possible to conclude that the structure of catalyst did not collapse after the catalytic reaction.

Stronger evidence for the successful incorporation of tetrakis(ochlorophenyl)porphyrinato Cobalt(II) on silica comes from ²⁹Si and ¹³C MAS NMR studies. Both ²⁹Si and ¹³C MAS NMR spectra of RHAC-CoPor are shown in Fig. 4. The solid state ²⁹Si NMR spectrum of RHAC-NH₂ (Fig. 4a) shows the presence of Q⁴ (Si(OSi)₄) and Q³ (Si(OSi)₃OH) silicon centers at $\delta = -110.15$ ppm and -101.28 ppm, respectively. These values had shifted to $\delta = -99.23 \text{ ppm}$ and -88.60 ppm in RHAC-CoPor (Fig. 4b). A chemical shift at $\delta = -66.93$ ppm for RHAC-NH₂ indicates the formation of Si-O-Si linkages via three siloxane bonds, i.e. (SiO₂)(-O-)₃Si-CH₂CH₂CH₂-Por (T³) and a chemical shift at $\delta = -59.04$ ppm was attributed to the formation of two siloxane linkages, i.e. $(SiO_2)(-O_2)Si(OH)CH_2CH_2CH_2-Por(T^2)$, to the silica. While for RHAC-CoPor, T² and T³ peaks appeared at $\delta = -48.71$ ppm and -57.18 ppm, respectively. The slight shift in the ²⁹Si NMR spectrum of RHAC-CoPor with respect to RHAC-NH₂ proves the formation of the new C–N bond that immobilized the [tetrakis(ochlorophenyl)porphyrinato[Co(II) onto the silica.

While in the analysis of the ¹³C MAS NMR spectrum, the incorporated propyl group (C₁, C₂ and C₃) in RHAC-NH₂ (Fig. 5a) appeared at δ = 12.57 ppm, 24.17 ppm and 44.71 ppm, respectively. These values were shifted to δ = 12.60, 26.60 and 45.18 ppm. Similar shifts were observed by other researchers [2,37]. Several unresolved peaks at chemical shifts in the range of δ = 100–168 ppm were ascribed to the carbons of the metalloporphyrin complex as shown in Fig. 5b. Hence, it can be concluded that [tetrakis(*o*-chlorophenyl)porphyrinato]Co(II) was successfully immobilized onto the silica via the formation of new C–N bond. To the best of our knowledge, the ¹³C MAS NMR study has not been reported in the literature before with respect to the supported metalloporphyrin complexes.

The N₂ adsorption-desorption isotherm of RHAC-NH₂ and RHAC-CoPor are shown in Fig. 6. Both RHAC-NH₂ and RHAC-CoPor showed type IV isotherm and H2 hysteresis loop according to IUPAC classification, indicating the existence of mesopores. The H2 hysteresis loop was observed at $P/P_0 = 0.3-0.9$ and it is a characteristic of mesoporous material consisting of agglomerates or particles having a narrow neck and wide body pore such as an "ink bottle" [38,39]. The BET analysis (Table 1) showed that the specific surface area of RHAC-NH₂ and RHAC-CoPor was $253 \text{ m}^2 \text{ g}^{-1}$ and $114 \text{ m}^2 \text{ g}^{-1}$, respectively. The decrease in the surface area of RHAC-CoPor could be due to the immobilization of the porphyrin ligand network of the metalloporphyrin complex, [tetrakis(o-chlorophenyl)porphyrinato]Co(II) which resulted in the reduction of surface area. RHAC-CoPor showed slight reduction in pore size compared to RHAC-NH₂ which may also be due to the 'blockage' by the metalloporphyrin complex moiety.



Fig. 4. ²⁹Si MAS NMR of (a) RHAC-NH₂ and (b) RHAC-CoPor.

Table 1

The result of BET analysis for RHACNH2 and RHAC-CoPor.

Sample	Specific surface	Average pore	Average pore
	area (m ² g ⁻¹)	volume (cm ³ g ⁻¹)	diameter (nm)
RHAC-NH ₂	253	0.343	5.92
RHAC-CoPor	114	0.177	4.17

The TEM micrographs of RHAC-NH₂ and RHAC-CoPor are shown in Fig. 7. From the micrographs, it can be seen that RHAC-NH₂ appear as spherical nano particles with a diameter range of about 20–40 nm. Immobilization of the metalloporphyrin complex onto RHA silica caused the agglomeration of the particles and expansion of the particle size to 35–75 nm. SEM analysis of RHAC-CoPor showed the existence of porous surface which had resulted in a high surface area. The elemental composition of RHAC-CoPor was determined by CHN and EDX analysis as represented in Table 2, which further confirmed the presence of carbon, oxygen, silicon, nitrogen and cobalt. The EDX analysis showed that nitrogen was only present in RHAC-NH₂ and RHAC-CoPor as expected with the percentage of 5.61% and 6.60%, respectively. RHAC-CoPor also showed the presence of cobalt with 0.52% in EDX analysis while AAS analysis showed a cobalt content of 0.79%. Besides, there was no chlorine atom present in RHAC-CoPor which showed that all the chlorine had been eliminated after the immobilization. Once again, this shows that the metalloporphyrin complex was successfully incorporated on the RHA silica support. The percentage of C and H in RHAC-CoPor was significantly higher than that in RHA and RHAC-NH₂ as expected.

X-ray diffraction measurement was performed to investigate the influence of the metalloporphyrin complex on the structure of RHAC-NH₂. Fig. 8 shows the XRD patterns of RHAC-NH₂ and RHAC-CoPor. It can be seen that RHAC-NH₂ showed a broad diffraction peak at 2θ angle 22.5°. While a slight shift of the peak to 2θ angle 23.3° can be seen in the X-ray diffraction pattern of RHAC-CoPor. The broad diffraction bands show the amorphous nature of the samples. The immobilization of tetrakis(*o*-chlorophenyl)porphyrinato cobalt(II) did not change the basic amorphous structure of silica as in RHA silica [40].

Table 2

Percentages of C, H and N obtained by elemental analysis, EDX and AAS analysis for RHA, RHAC-NH₂ and RHAC-CoPor.

Sample	Elemental analysis (%)	Elemental analysis (%)				
	С	Н	Ν	Si	Со	Cl
RHA	(0.27) ^a	(1.10) ^a	-	36.66	_	-
RHAC-NH ₂	13.15 (6.17) ^a	$(2.44)^{a}$	5.61 (2.36) ^a	24.66	-	-
RHAC-CoPor	17.88 (17.34) ^a	(2.68) ^a	6.60 (5.07) ^a	30.06	0.52 [0.79] ^b [0.67] ^c	-

^a Values in bracket were obtained by CHN analysis.

^b Cobalt content obtained by AAS analysis for fresh catalyst.

^c Cobalt content obtained by AAS analysis after 3rd reused analysis.



Fig. 5. ¹³C MAS NMR of (a) RHAC-NH₂ and (b) RHAC-CoPor.

3.3. The oxidation benzyl alcohol

The effectiveness of the prepared organic-inorganic hybrid material (RHAC-CoPor) as a catalyst was tested in the liquid phase oxidation of benzyl alcohol. The influence of various parameters on the percentage conversion and selectivity



Fig. 6. The N_2 adsorption–desorption isotherms and narrow pore size distribution graphs (inset) of (a) RHAC-NH₂ and (b) RHAC-CoPor.

of products were studied (Tables 3–7). The major product detected from GC and GC–MS was benzaldehyde while benzoic acid and benzyl benzoate were detected as byproducts.

3.3.1. Influence of reaction temperature

The effect of reaction temperature on the conversion of benzyl alcohol and the selectivity of the products was demonstrated by considering 6 different temperatures in the range of 303–373 K. Conversion of benzyl alcohol increased from 44.9% to 91.9% (343 K) as the temperature increased as shown in Table 3. There was no remarkable difference in the percentage conversion when the temperature was increased up to 373 K. Therefore, 343 K was taken to be an optimum temperature in this study to achieve highest conversion.

Selectivity toward benzaldehyde decreased slightly as the temperature increased. This observation showed that the temperature has only a very small impact on the selectivity of the product but it has a strong influence on the progress of benzyl alcohol oxidation. In previous studies, lower conversion was obtained when the reaction was carried out in the temperature range 343–363 K. In order to get a high conversion (>95%), high temperature (>500 K) was used [18–20,41]. However, in this study, ~98% conversion was achieved at 343 K over a short contact time of 5 h.



Fig. 7. TEM images of (a) RHAC-NH₂ and (b) RHAC-CoPor catalyst showing the distribution of particle size.

Tab



Fig. 8. The X-ray diffraction pattern for (a) RHAC-NH₂ and (b) RHAC-CoPor.

3.4. Effect of mass of catalyst

Table 4 shows the changes in the conversion of benzyl alcohol by varying the mass of catalyst from 30 mg to 150 mg at 343 K. The results indicate that the conversion of benzyl alcohol increased with an increasing amount of catalyst until the maximum conversion of 97.1% was achieved when 80 mg of catalyst was used. Lower conversion of benzyl alcohol with lower mass of catalyst was due to the fewer catalytic sites. Whereas, increasing catalyst mass beyond 80 mg, decreased the selectivity of benzaldehyde. This is due to the excess catalyst resulted in further oxidation of benzaldehyde to benzoic acid [42]. This study showed that only 80 mg of the catalyst was needed for the reaction to reach an optimum conversion of

Table 3

Effect of temperature on the oxidation of benzyl alcohol using RHAC-CoPor as the catalyst.

Temperature	(K) Benzyl alcohol conversion (%)	Selectivity (%)		TOF^a (h^{-1})
		Benzalde	hyde Benzoic ac	id
303	44.9	98.8	1.2	132.4
323	70.8	98.1	1.9	207.3
333	82.8	97.1	2.9	239.9
343	91.9	96.3	3.7	264.1
353	91.3	96.1	3.9	261.8
373	90.8	94.2	5.8	255.2

Reaction condition: 50 mg RHAC-CoPor, molar ratio of substrate: H_2O_2 = 1:1.5, 10 mL CH₃CN solvent, 5 h.

 $^{\rm a}$ Turn over frequency (TOF): moles of substrate converted per mol of Co in the catalyst $\rm h^{-1}.$

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Influence of amount of catalyst used on the oxidation of benzyl alco	ohol.
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Catalyst mass (mg)	Benzyl alcohol conversion (%)	Selectivity (%)		TOF ^a (h ⁻¹⁾
		Benzaldehyde	Benzoic acid	
30	84.6	96.5	3.5	406.0
50	91.9	96.3	3.7	264.1
80	97.1	97.7	2.2	176.9
100	96.2	96.4	3.6	138.4
150	94.1	93.1	6.9	87.1

Reaction condition: 343 K, molar ratio of substrate: H_2O_2 = 1:1.5, 10 mL of CH₃CN solvent, 5 h reaction time.

 $^{\rm a}$ Turn over frequency (TOF): moles of substrate converted per mol of Co in the catalyst/h.

ca. 97% compared to the works reported in literature. For instance, Cristina et al. [43] reported the usage of large amount of bimetallic gold–copper catalysts (about 0.2 g) in order to get similarly high conversion (98%) and selectivity (>99%) toward benzaldehyde.

3.4.1. The effect of mole ratio of reactant (benzyl alcohol: H_2O_2)

Concentration of H_2O_2 used in the reaction is another vital factor influencing the progress of benzyl alcohol oxidation. Thus, several benzyl alcohol: H_2O_2 molar ratios were investigated in this study and the results are shown in Table 5. With 1:0.5 molar ratio of benzyl alcohol to H_2O_2 , low conversion of benzyl alcohol was observed (85.6%) as compared to the percentage conversion obtained at 1:1.5. The conversion was found to increase to 97.1% with a TOF value of 176.9 h⁻¹ when the molar ratio was increased to 1:1.5. Since oxygen produced on decomposition of H_2O_2 oxidizes benzyl alcohol, hence the conversion of benzyl alcohol was increased progressively when the molar ratio of benzyl alcohol to H_2O_2 was increased due to increased amount of available oxygen [41]. The selectivity of products did not show significant variation as the molar ratio of benzyl alcohol to H_2O_2 was varied. Therefore, 1:1.5 molar ratio of benzyl

Table 5

The effect of different benzyl alcohol: H_2O_2 molar ratio on the oxidation of benzyl alcohol using RHAC-CoPor as the catalyst.

Benzyl alcohol:H ₂ C molar ratio	Benzyl alcohol:H2O2 Benzyl alcohol Selectiv molar ratio conversion (%)		ry (%)	TOF ^a (h ⁻¹
		Benzalde	hyde Benzoic acid	
1:0.5	85.6	96.5	3.5	154.1
1:1	92.2	97.1	2.9	167.0
1:1.5	97.1	97.7	2.3	176.9
1:2	95.8	94.4	5.6	168.7

Reaction condition: 343 K, 80 mg RHAC-CoPor, 10 mL CH₃CN solvent, 5 h.

 $^{\rm a}$ Turn over frequency (TOF): moles of substrate converted per mol of Co in the catalyst $h^{-1}.$

Table	6
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Influence of the types of solvents used on the oxidation of benzyl alcohol using RHAC-CoPor as the catalyst.

Types of solvent used	Benzyl alcohol conversion (%)	Selectivity (%)			TOF^a (h^{-1})
		Benzaldehyde	Benzoic acid	Benzyl benzoate	
Solventless	92.7	38.9	34.7	18.1	67.3
Cyclohexane	17.2	99	1	_	31.8
Dichloromethane	49.2	99	1	_	90.8
Acetonitrile	97.1	97.7	2.3	-	176.9

Reaction condition: 343 K, 80 mg RHAC-CoPor, molar ratio of substrate: $H_2O_2 = 1:1.5, 5$ h.

^a Turn over frequency (TOF): moles of substrate converted per mol of Co in the catalyst h⁻¹.

Table 7

The result of leaching test on RHAC-CoPor during its use as the catalyst in the oxidation of benzyl alcohol.

Time (h)	Conversion (%)	Selectivity (%)	
		Benzaldehyde	Benzoic acid
1	48.8	99.9	0.1
3 ^a	49.9	99.2	0.8
5 ^a	50.1	98.9	1.1

Reaction condition: 343 K, 80 mg RHAC-CoPor, molar ratio of substrate: H_2O_2 = 1:1.5, acetonitrile (10 mL), 5 h reaction time.

^a After removing the catalyst.

alcohol to H_2O_2 was the optimum in terms of percentage conversion. In the past, Yu and co-workers [16] were able to obtain a very high conversion (100%) and high selectivity (100%) toward benzaldehyde. However, the reaction was carried out at higher ratio of H_2O_2 to alcohol (4.5:1) with the help of a large amount of catalyst (0.2 g) over a longer reaction time (6 h) compared with the optimum conditions in this study.

3.4.2. Effect of solvents on oxidation of benzyl alcohol

In order to determine the effects of solvents on the oxidation of benzyl alcohol, the reaction was carried out separately by using three different types of solvents (neat - no solvent, cyclohexane, dichloromethane and acetonitrile) keeping all other parameters fixed: namely mass of catalyst (80 mg), temperature (70 °C), reaction time (5 h) and benzyl alcohol to H_2O_2 molar ratio (1:1.5). The results are summarized in Table 6. It shows that a significantly lower conversion and TOF values were obtained in non-polar solvent, i.e. cyclohexane and a maximum conversion was obtained in acetonitrile (TOF = $176.9 h^{-1}$). In addition, the selectivity of benzaldehyde decreased with increasing polarity of the solvent which indicates that the polar solvent may favor the formation of acid since benzoic acid is a more polar molecule compared with benzaldehyde [44]. Whereas the selectivity of benzaldehyde was quite low and an additional by-product of benzyl benzoate was formed when the reaction was run without using any solvent.

3.4.3. Leaching and reusability of RHAC-CoPor

Table 7 presents the data obtained for the leaching test for RHAC-CoPor. During the catalytic activity, the catalyst was removed after 1 h and the reaction was allowed to continue. A slight increase in benzyl alcohol conversion was observed after the removal of

Table 8

The reusability of RHAC-CoPor in the oxidation of benzyl alcohol using $\rm H_2O_2$ as the oxidant.

RHAC-CoPor	Conversion (%)
1st recycle	96.5
2nd recycle	95.1
3rd recycle	93.3

Reaction condition: 343 K, 80 mg RHAC-CoPor, molar ratio of substrate: H_2O_2 = 1:1.5, acetonitrile (10 mL), 5 h.

catalyst, from 48.8% (1 h) to 49.9% (3 h). However, there was no further increase in conversion at 5 h. Since significant increase in the conversion of benzyl alcohol was not observed, hence it can be said that leaching of cobalt metal during the reaction can be considered as negligible. RHAC-CoPor was subjected for AAS analysis after the reaction to further confirm the heterogeneity of the catalyst. It was found that the cobalt content after the 3rd cycle of oxidation reaction was 0.67% compared to the fresh catalyst which is 0.79% as shown in Table 2. It can thus be concluded that the catalytic oxidation of benzyl alcohol by RHAC-CoPor proceeds via a heterogeneous process.

In order to further evaluate the performance of the catalyst, RHAC-CoPor was used repeatedly for 3 cycles under the same conditions to test its catalytic reusability as illustrated in Table 8. The used catalyst was filtered and regenerated by washing it with distilled water and drying at 110 °C for 24 h before using it in the subsequent runs. From Table 8, it can be seen that only 3.8% decrease in conversion was observed after three cycles. This shows that the activity of catalyst was not affected even after three cycles. Therefore, it can be concluded that the prepared catalyst can be easily recovered and recycled which is potentially useful for industrial application.

4. Conclusions

All the spectroscopic evidence obtained in this study showed that an organic-inorganic hybrid material labeled as RHAC-CoPor was successfully synthesized by immobilizing the metallopor-phyrin complex onto the silica support prepared from RHA. The procedure used in this study was simple, time-saving and environmental friendly. RHAC-CoPor showed excellent catalytic performance in the oxidation of benzyl alcohol with good conversion of almost 97% and very high benzaldehyde selectivity by using H_2O_2 as an oxidant. In addition, the catalyst can be reused several times without significant loss in the conversion and selectivity.

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