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Microporous cobaltporphyrin covalent polymer mediated Co₃O₄@PNC nanocomposites for efficient catalytic C-H bond activation



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A R T I C L E I N F O	A B S T R A C T			
Keywords: Co3O4@PNC C-H activation Pyrolysis process Oxidation Metalloporphyrin polymer	A Cobalt porphyrin conjugated porous polymer (Co/PCP) was obtained by hybrid polymerization of a mixture of Co(II)(5,10,15,20-tetrakis(4-bromophenyl)-21H,23H-porphyrin) (CoTBPP) and 5,10,15,20-tetrakis(4-bromophenyl)-21H,23H-porphyrin (TBPP) (3:7 M ratio) with the coupling reagent of p-phenyldiboric acid. This Co/PCP was carbonized at 400 °C and the obtained catalyst (denoted as Co_3O_4 @PNC-400) was composed of Co_3O_4 nanoclusters wrapped in the nitrogen-carbon materials. This catalyst has an extremely high catalytic activity for the aerobic oxidation of C–H bonds. It can efficiently catalyze the oxidation of the C–H bonds in toluene and cyclohexane with high conversion and high selectivity of (alcohol + aldehyde), (alcohol + ketone) compounds, respectively. When heat-treated at 400 °C, the porous framework structure of the porphyrin polymer was partially retained, and the highly active Co_3O_4 nanoclusters were generated in situ. The reaction of C—N to C—N and connection with the Co_3O_4 and nitrogen-carbon framework during the catalytic reaction. The defective structure caused by the migration of cobalt also greatly improved the catalytic activity. Co/PCPs with different cobalt contents were also synthesized and heat treated at different temperature. These catalysts were a new type of efficient C–H oxidation catalysts with excellent potential application value.			

1. Introduction

The selective oxidation of C–H bonds is an important reaction in catalytic chemistry [1], and it is of great significance to the drug synthesis process, fine chemical industry and petrochemical industry [2]. For example, cheaper toluene can be oxidized to benzaldehyde and has a higher value. However, due to the high bond energy, the stable C–H bond oxidation is a relatively difficult process [3]. The simple method of directly oxidizing the C–H bond is attractive, but the degree of oxidation is difficult to control and usually resulting in poor selectivity to the target product [4]. Using molecular oxygen such as air or oxygen as an oxidant makes it more difficult to oxidize C–H bonds, and there are many kinds of oxidation products with poor selectivity.

Transition metals and their oxides are effective catalysts for C–H bond functionalization [5]. At present, the catalysts used to activate C–H bonds are mainly concentrated in relatively inexpensive transition metals [6]. Due to the low bond energy of the Co-O bond, cobalt oxide catalysts are generally used as an electrocatalyst to catalyze electrode materials such as CO oxidation, water oxidation, or fuel cells [7–19].

Due to the different preparation methods, the performance of the obtained cobalt oxide catalyst is also different [20–24]. In this paper, a highly active Co_3O_4 @PNC catalyst supported on porous nitrogen-carbon materials was prepared in situ by using cobalt porphyrin conjugated porous polymer as a raw material. It exhibited excellent oxidation performance of C–H bonds in alkanes with surprisingly high catalytic activity and selectivity.

Our previous research shows that the conjugated porous metal porphyrin polymer itself has good catalytic oxidation activity [25,26], and the porphyrin conjugated organic polymer has uniform, rich pores and rich nitrogen content. However, its stability and thermal stability in the solution phase are insufficient [27,28]. So, the further improvement of the catalytic activity of metal porphyrin polymer is a subject worthy of further research. To the best of our knowledge, use the conjugated porous metal porphyrin polymers as templates to synthesize supported transition metal catalyst have not been reported.

In this study, we used a mixture of monomers tetraphenyl cobalt porphyrin and uncomplexed metal porphyrin in different proportions as raw materials. Through the coupling effect of the coupling agent (p-

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Scheme 1. Co/PCP synthesis from CoTBPP and TBPP, and Co/PCP heated treatment to prepare Co₃O₄@PNC-400 catalyst.

phenyldiboric acid), a hybrid porphyrin conjugated polymer (PCP) with low content and high dispersion of cobalt was obtained. So the porous composite catalyst Co_3O_4 @PNC was prepared by heat treatment of this polymer. The catalytic performance of the catalyst was tested by oxidizing different kinds of C–H bonds including toluene and cyclohexane, and the catalytic performance of the catalyst was compared with the corresponding monomeric cobalt porphyrin and the original polymer in detail.

2. Experimental

2.1. Experimental instruments and reagents

CoCl₂·6H₂O was purchased from Shanghai Titan Scientific Co. Ltd.. The commercial Co₃O₄ for comparison experiment was purchased from Shanghai Macklin Reagent Co. Ltd..It was 99.5% metals basis with average diameter of 30 nm. Pyrrole, p-phenyldiboric acid and 1,4 -dioxane were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. and other chemicals were purchased from commercial suppliers. All chemicals were analytical reagents and without further purification before use.

Powder X-ray diffraction data was collected on a Bruker D8 Advance X-ray diffractometer (Bruker, Germany). The radiation source was Cu-K α ray, and the scan angle was selected from 10° to 80°. FT-IR spectra were obtained on a WQF-410 FT-IR spectrometer (Ruili, China) ranging from 400–4000 cm⁻¹. The UV–vis diffuse reflectance spectroscopies of Co₃O₄/PCP and Co/PCP (Cobalt porphyrin conjugated porous polymer) were obtained over a UV–vis spectrophotometer (Cary 100) using BaSO₄ as reference. Scanning electron microscope (SEM) images were collected on a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). Transmission electron microscope (TEM) was acquired from Tecnai G2 F20 S-TWIN. The specific surface area and pore size distribution were obtained on tri-star 3020. The thermogravimetric analysis (TGA) was recorded using a DTG-60 thermogravimetric analyzer. X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB Xi spectrometer. A Raman spectrometer was obtained at in Via-Reflex from

 $400-3200 \text{ cm}^{-1}$, England (532 nm excitation wavelength). EPR spectra were obtain on a JES-FA200 EPR Spectrometer. As for the parameter, center field intensity, sweep time, sweep width, mod width and amplitude were 335 Mt, 30 s, 1×10 mT, 0.2×1 mT, 4.00×100 Mt, respectively. Elemental Analyzer(C,H,N) were performed on a Vario MACRO cube. The Co and Br contents were measured by inductively coupled plasma mass spectrometer Agilent 7900.

2.2. Synthesis of catalyst

2.2.1. Synthesis of monometallic cobalt porphyrin

5,10,15,20-tetrakis(4-bromophenyl)-21H,23H-porphyrin (TBPP) was synthesized firstly. The typical procedure: 18.5 g (0.1 mol) of pbromobenzaldehyde dissolved in 120 mL of propionic acid and heated to reflux, within 30 min dropwise addition of 30 mL of propionic acid solution dissolved in 6.7 g (0.1 mol) of pyrrole. After refluxing for 0.5 h, it was cooled to room temperature and filtered with suction to obtain a solid, which was washed three times with 50 mL of methanol. Recrystallized three times with chloroform: methanol (15 mL:60 mL) and dried to obtain 5,101,520-tetrakis(4-bromophenyl)-21H,23H-porphyrin (TBPP) purple crystals. The product was characterized by ¹HMR, UV–vis and FT-IR, and proved to be TBPP.

Then 0.93 g (1 mmol) and 2.85 g CoCl₂ 2 6H₂O (12 mmol) of the obtained TBPP placed in a round bottom flask, add 100 mL of DMF, and heat to reflux for 12 h. After cooling to room temperature, the precipitate was precipitated by adding water and suction filtered. After washing with water and methanol several times, it was vacuum dried at 70 °C for 8 h to obtain a red-brown cobalt porphyrin complex Co(II) (5,10,15,20-tetrakis(4-bromophenyl)-21H,23H-porphyrin) (CoTBPP).

2.2.2. Synthesis of cobalt porphyrin conjugated polymer (Co/PCP)

Cobalt porphyrin conjugated polymer was synthesized by using the Suzuki-Coupling reaction. The typical procedure is as follows: CoTBPP and TBPP with different proportions were mixed as reactants to synthesize hybrid porphyrin conjugated polymer Co/PCP with different cobalt contents. For example, the typical steps for synthesis a polymer



Fig. 1. a) XRD of Co₃O₄@PNC-400; b, d)FT-IR spectrum of porphyrin conjugated polymer (Co/PCP) and Co₃O₄@PNC-400; c) ultraviolet spectrum of different samples.

with a raw material ratio of CoTBPP: TBPP = 3.7 (molar ratio) are as follows: p-phenylenediboronic acid (280.4 mg, 2 mmol), CoTBPP (289.5 mg, 0.3 mmol) and TBPP (634.5 mg, 0.7 mmol) were added to a three-necked flask, and 80 mL of 1,4-dioxane was added. After three cycles of freeze-evacuation-nitrogen protection thaw, 20 mL of deionized aqueous solution in which 1.105 g of potassium carbonate (8 mmol) (0.1 mmol) was dissolved and 0.116 g of red-brown tetrakis (triphenyl)phosphine palladium were added. Freeze-evacuate-thaw cycle three times under the protection of argon, then reflux for 24 h under argon atmosphere, cool to room temperature and add a large amount of deionized water to precipitate the product. It was filtered under reduced pressure and washed with deionized water, methanol and acetone, respectively. Finally the solid was extracted with Soxhlet with THF, methanol and acetone for 24 h, respectively. The solid was dried under vacuum at 70 °C for 12 h to obtain 770 mg of reddish brown polymer product.

2.2.3. Preparation of Co₃O₄@PNC catalyst

The above-prepared polymer was heated to a set temperature at a heating rate of 5 °C/min in argon atmosphere, and maintained at the temperature for 1 h to obtain a corresponding heat-treated catalyst. The catalyst after heat treatment at 400 °C is marked as Co_3O_4 @PNC-400, and the polymer after heat treatment at 300 °C, 500 °C and 600 °C is

marked as Co/PCP-300, Co/PCP-500 and Co/PCP-600, respectively.

2.2.4. Catalytic oxidation reaction and experimental procedures

Toluene and cyclohexane containing different C–H bonds are used as substrates, and oxygen used as oxidant. The oxidation reaction is carried out in a miniature autoclave. The steps are as follows: 3 mmol of toluene or cyclohexane, 1.0% mol of substrate as catalyst amount (based on the content of cobalt), 5 mL of acetonitrile, was placed in a 25 mL miniature autoclave. 1.0 MPa oxygen was introduced into the reactor, and the oxygen pressure was maintained at 1.0 MPa by connecting to an oxygen cylinder during the reaction. The reaction was stirred for 6 h at 110 °C. The gas chromatography was used to detect the yield and conversion rate (Scheme 1)[1–9].

3. Results and discussion

3.1. Characterization analysis of catalysts

3.1.1. XRD, FT-IR and UV spectrum analysis

The x-ray diffraction pattern of the sample after 400 °C heat treatment (Fig. 1a) shows a distinct diffraction peak corresponding to Co_3O_4 , which can correspond well to the card [Co_3O_4 PDF#43-1003]. Comparing with precursor of Co/PCP (Fig. S4), the catalyst keep



Fig. 2. a) Raman spectrum of Co_3O_4 @PNC-400; c,d) N₂ adsorption-desorption isotherm and pore size distribution of Co_3O_4 @PNC-400; b) Thermogravimetric analysis of Co/PCP in Argon; e,f) N₂ adsorption-desorption isotherm and pore size distribution of Co/PCP.

basically original structure. The peaks at 20 of 19°, 31.3°, 36.9°, 38.5°, 44.8°, 55.6°, 59.3°, and 65.3° correspond to (111), (220), (311), (222), (400), (422), (511), (440) crystal planes in the Co_3O_4 crystal structure, respectively [29]. Because the precursor of the catalyst, Co/PCP, is a highly microporous material, its pores adsorb much air and cannot be

discharged completely. Although pyrolysis is carried out in an inert atmosphere, the limited amount of oxygen adsorbed in the pores can still oxidize Co atoms into Co_3O_4 with high catalytic activity, and is closely bound to the nitrogen-carbon structure.

The UV-vis spectra of Co₃O₄@PNC-400 and Co/PCP (Fig. 1c) clearly



Fig. 3. SEM of Co/PCP (a,b) and Co₃O₄@PNC-400 (c,d).

show that the Soret and Q bands of both have not changed significantly [30]. Compared with Co/PCP, the FT-IR spectrum of Co₃O₄@PNC-400 (Fig. 1d) shows a decrease in the peak intensity at 1660 cm^{-1} , which may be due to the weak π -bonded electron cloud in C=N loses its overlap and breaks to form C-N. And the present of the peak at 554 cm^{-1} indicates that cobalt oxide formed [31]. This indicates that during the inert atmosphere pyrolysis at 400 °C, the porphyrin polymer skeleton mainly undergoes the reaction of C=N bond to C-N, and the Co transform to Cobalt tetroxide. Therefore, conbining with previous XRD analysis results, we believe that the structural characteristics of the organic framework of Co3O4@PNC-400 are basically the same as Co/PCP, but the oxidation, migration and fusion of cobalt atoms occurred during the pyrolysis process, forming active Co₃O₄ clusters. During this process, the conversion of C=N into C-N single bond and connection with Co₃O₄ nanoclusters also occurred, thus forming a highly active, well-developed, porous nitrogen-carbon-coated Co₃O₄ catalyst.

3.1.2. Raman spectroscopy, thermogravimetry, nitrogen adsorption and desorption, and pore size distribution analysis

From the Raman spectra (Fig. 2a), the Co_3O_4 @PNC-400 curve does not show a clear G band, but it shows obvious characteristic peaks of some functional groups like FT-IR spectra. This indicates that there was no graphitization occurred when the sample heat-treated under 400 °C. However, the Co/PCP-500 clearly shows the G band, indicating that the sample heat treated at 500 degrees has a certain degree of graphitization. The Raman spectra of Co/PCP and Co₃O₄@PNC-400 overlap well, which also confirms that the framework structure of the porphyrin polymer basically remains integrality. The stability of Co/PCP was tested by thermogravimetric analysis (TGA). When the temperature rises to 100 °C, the mass loss is about 7.6% (Fig. 2b), which results from absorbed water molecules before TGA. From 160–430 °C, the sample quality remains relatively stable, with a mass loss of approximately 8.6%. When the temperature rises to 490 °C, the mass loss is only 10%, which indicates that Co/PCP has high stability. Fig. 2c-f are the specific surface area and pore size distribution of Co_3O_4 /PNC-400 and Co/PCP. The N₂ adsorption-desorption isotherm shows that the specific surface area of Co_3O_4 /PNC-400 and Co/PCP are 384.6 and 380.0 m2/g, respectively; The pore size distribution charts show that the pore size of the two catalysts is mainly distributed between 1-2 nm, which is mainly a microporous structure. It is obvious that before or after Co/PCP pyrolysis, the specific surface area is almost the same, and the pore size distribution is also almost consistent, although there are slight variations in specific surface area and pore size. So it is inferred that the two are very similar in structure.

3.1.3. SEM/TEM analysis

The morphology of Co₃O₄@PNC-400 was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). It can be seen from the SEM pictures of the sample that there are no obvious changes seen on the surface (Fig. 3) after pyrolyzed. However, the high-resolution TEM image of Co₃O₄@PNC-400 shows that Co₃O₄ nanoclusters are generated after pyrolysis. Fig. 4a shows Co₃O₄ nanoparticles encapsulated in a carbon structure. Fig. 4d shows the 0.289 nm lattice spacing, which can be assigned to the (220) plane of Co₃O₄. The lattice spacing of 0.244 nm is consistent with the Co₃O₄ (311) plane. Fig. 4c shows the obvious interplanar spacing (0.23 nm), which corresponds to the (222) plane of Co₃O₄ [32]. Fig. 4d shows that the obvious cobalt oxide nanoparticles are embedded in the N-C structure formed by the porphyrin polymer framework, and the size of Co₃O₄ particles is about 2-5 nm. The raw material ratio of CoTBPP: TBPP = 3:7 can reduce the distribution density of cobalt ions in the polymer and ensure the production of uniform and fine Co₃O₄ nanoparticles after pyrolysis, thus obtaining the highly active catalysts.



Fig. 4. a-d) HRTEM images of Co₃O₄@PNC-400; e)HAADF-DTEM and f-i) corresponding element mapping images in STEM mode of Co₃O₄@PNC-400.

3.1.4. X-ray photoelectron spectroscopy

The element valence state of the catalyst surface was studied by Xray photoelectron spectroscopy. Fig. 5a and b are the energy spectrum of the original catalyst Co_3O_4 @PNC-400 and the catalyst after five catalytic cycles (toluene oxidation). Two main peaks and two satellite peaks can be observed in the spectra. The peaks of 780.3 eV and 795.9 eV are assigned to Co 2p3/2 and Co 2p1/2, respectively. The main peak can be divided into three sub-peaks, corresponding to Co^{3+} , Co^{2+} , and Co-N. The peaks at 779.9 eV and 795.4 eV can be assigned to Co^{3+} , and the peaks at 780.7 eV and 796.2 eV can be attributed to Co^{2+} . The content of Co^{3+} changed from 56.49% before the reaction to 56.4% after the reaction. It can be seen that the content of Co^{3+} remained basically unchanged before and after the catalytic reaction. The high-resolution spectrum of N1 s in Fig. 5c shows that it can be fitted to five peaks, including pyridine N (397.9 eV), Co-N_x (398.8 eV), pyrrolic nitrogen (399.9 eV), graphitic nitrogen (400.7 eV) and oxidized Nitrogen (403 eV) [33]. Among them, the content of Co-N_x is relatively high, which is consistent with the previously speculated structural characteristic of the catalyst. The three peaks at 531.9, 533.5, and 535.0 eV in Fig. 5d can be assigned to lattice oxygen (O1), adsorbed oxygen (O2), and hydroxyl oxygen (O3) [34]. The presence of adsorbed oxygen may be the result of the catalyst being preserved in the air. The high lattice oxygen content indicates that cobalt oxide crystals do exist in the catalyst. Fig. 5f shows that the atomic content of C, N, O, Co is approximately 87.54, 8.81, 3.16, 0.49% respectively, which is basically consistent with the results of the elemental analysis (SI).

3.1.5. Catalytic Oxidation of C-H bonds

Toluene and cyclohexane were selected as substrates for oxidation. First of all, catalysts with different cobalt content were obtained by 400 $^{\circ}$ C heat treatment for the polymers prepared from different raw material ratios, and the catalysts were used in the catalytic oxidation



Fig. 5. XPS high resolution spectrum of Co 2p before (a) and after (b) reaction, N 1s (c), O 1s (d) and C 1s (e), of Co₃O₄@PNC-400 and survey spectrum (f).

Table 1

Catalytic performance	for	selective	oxidation	of	toluene
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Cotolyat	Selectivity (%)						
Catalyst	Conv.%	alcohols	aldehydes	others			
no catalyst	0.8	7.5	92.5	0			
Co/PCP-400 (1:0) ^a	17.1	9.5	83.8	6.7			
Co/PCP-400 (1:1) ^b	19.3	15.2	73.0	17.8			
Co ₃ O ₄ @PNC-400	22.0	7.2	85.9	6.9			
PCP-400 (0:1) ^c	1.4	10.4	86.2	3.4			
Co/PCP	9.0	29.3	64.6	6.1			
(Co ₃ O ₄ +PCP)-400 ^d	10.3	5.0	86.1	8.9			
Co/PCP-300	9.7	0	86.2	13.8			
Co/PCP-500	15.1	10.2	80.5	9.3			
CoTBPP	8.6	22.3	61.7	16.0			
Co(acac) ₂	14.3	4.6	83.7	11.7			

Reaction conditions: 3 mmol of substrate, 1.0% mol of substrate as catalyst amount (based on the content of cobalt), 5 mL of acetonitrile, 1.0 MPa O₂, 110 °C. 6 h.

^a Prepared from 400 °C heat treatment of porphyrin polymer(a raw material ratio of CoTBPP: TBPP = 1:0 (molar ratio)).

^b Prepared from 400 °C heat treatment of porphyrin polymer (a raw material ratio of CoTBPP: TBPP = 1:1 (molar ratio)).

^c Prepared from 400 °C heat treatment of porphyrin polymer without cobalt in the structure (a raw material ratio of CoTBPP: TBPP = 0.1 (molar ratio)), catalyst weight equals to Co3O4@PNC-400.

^d A mixture of commercial Co₃O₄ and PCP-400, the Co content and PCP-400 content equals to Co3O4@PNC-400.

reaction of toluene (Table 1). It can be seen from Table 1 that the catalyst obtained by CoTBPP: TBPP = 3:7, namely Co₃O₄@PNC-400, had the best catalytic performance. So the polymer with this ratio was selected to continue heat treatment at different temperatures (300–500 $^\circ\text{C})$ to investigate the effect of heat treatment temperature on the performance of the catalyst. As can be seen from Table 1, heat treatment at 400 °C produced the best catalytic effect (Scheme 2).

The catalytic performance of Co₃O₄@PNC-400 for C-H bond oxidation was further tested and compared with Co/PCP and CoTBPP. As can be seen from Tables 1 and 2, Co₃O₄@PNC-400 has excellent catalytic oxidation activity of C-H bond. Compared with the polymer before heat treatment (Co/PCP), Co₃O₄@PNC-400 not only improves the conversion rate of each substrate several times (such as 5.5 times for toluene and 1.5 times for cyclohexane), but also improve the selectivity of target products. For example, the selectivity of benzaldehyde increased from 64.6%-85.9%. We know that the metalloporphyrin conjugated polymer itself is an excellent catalyst [18-21], and in this study, CO /PCP did have a good catalytic oxidation effect on toluene and cyclohexane (Tables 1 and 2). After heat treatment, its catalytic performance has been greatly improved. This is mainly due to the in situ generated Co₃O₄ which has a lower Co-O bond energy and a higher Co₃O₄ oxygen bonding rate, so that molecular oxygen can be activated by Co_3O_4 and transferred to the substrate [19]. Compared with

cyclohexane, the conversion rate of toluene is lower, and the selectivity of oxidation products is different. This is mainly because that the C-H bonds of methyl have stronger bond energy than methylene, and are more difficult to oxidize.

As shown in Table 1, toluene cannot be oxidized under a catalyst-free oxygen atmosphere. The heat treatment product of the porphyrin conjugated polymer without metal cobalt, PCP-400 (0:1), exhibits a very low conversion rate for toluene oxidation. A mixture of commercial Co₃O₄ and PCP-400 has a much worse catalytic effect on toluene oxidation than Co₃O₄@PNC-400. From these experimental results, we can infer that the high activity of Co3O4@PNC-400 is caused by the synergistic effect of the in-situ generated Co3O4 and the heat-treated porous porphyrin polymer framework. In Table 1, it can be found that the catalyst has better selectivity for toluene C-H activation to benzaldehyde comparing with other cobalt catalysts.

Co₃O₄@PNC-400 has better performance in the selective oxidation of C-H bonds under oxygen conditions, and the comparation results with other literatures were listed in Table 3 and Table S1. It can be seen that the selectivity of benzaldehyde is better than that of most catalysts when the conversion is similar. It also has good reuse performance (Fig. S3). After five cycles, the performance of the catalyst almost did not decrease. Its high conversion rate and selectivity are mainly attributed to the redox characteristics of Co^{2+}/Co^{3+} cobalt tetroxide embedded in the porphyrin-based nitrogen-carbon framework (PNC). [47] The electron spin resonance test (EPR) found that the intensity of the spin resonance signal (g = 2.0032) of Co₃O₄@PNC-400 is about twice that of Co/PCP (Fig. 6). This shows that part of the trivalent cobalt was converted into high-spin bivalent cobalt, thus Co₃O₄ is generated [48,49]. Bivalent cobalt has higher intensity of spin signals than trivalent Cobalt, which actually proves to be equivalent to XPS test results. The EPR signal of the catalyst before and after oxidation of toluene and cyclohexane hardly changed, indicating that the total amount of magnetic field sensitive substances in the catalyst remained basically constant.

Table 2			
Catalytic performance for	selective	oxidation	of cvclohexane

Catalyst	Substrate	Come 0/	Selectivity (%)			
		COIIV.90	ketones	alcohols	others	
Co ₃ O ₄ @PNC-400 Co/PCP CoTBPP Co(acac) ₂	cyclohexane cyclohexane cyclohexane cyclohexane	16.5 11.2 6.8 6.4	50.4 41.7 39.3 33.6	40.1 42.3 45.0 48.2	9.5 16.0 15.7 18.2	

Reaction conditions: 3 mmol of substrate, 1.0% mol of substrate as catalyst amount (based on the content of cobalt), 5 mL of acetonitrile, 1.0 MPa O2, 110 °C, 6 h.



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Scheme 2. Catalytic oxidation equation.

Table 3

A comparison of toluene oxidation activity of the Co₃O₄@PNC-400 catalyst with other reported catalysts.

Catalyst	T/P	t(h)	Solvent	Conv.%	Selectivity (%)/aldehydes	References
Co ₃ O ₄ @PNC-400 ^a	110°C /1MPa	6	CH ₃ CN	22	85.9	This work
Co(acac)2 ^a	100°C /10atm	5	CH ₃ CN	11	92	[35]
sub-Au/LC-CeO2 ^a	160°C /1.2MPa	10	\	6.5	81.2	[36]
MnTPPCl ^a	160°C /1.5MPa	4	CH ₃ CN	12	38.9	[37]
8-CN-600 ^a	160°C /1MPa	16	Acetone	2	99	[38]
MnCo-MOF-74 ^a	80°C /1atm	6	CH ₃ CN	17.6	98.3	[39]
CeO ₂ nanocube ^a	90°C /1atm	12	H ₂ O	44.19	100	[40]
MnWO ₄ NFs ^b	80°C /1atm	18	CH ₃ CN	59.5	90	[41]
CNB _{0.15} ^b	150°C /-	2	CH ₃ CN	12.4	99	[42]
Cu-CNB ^b	70°C/-	16	CH ₃ CN	6.3	99	[43]
Fe ₂ O ₃ /HZSM-5 ^b	90°C /-	4	\	17.3	51.4	[44]
FeCl ₁₆ Pc-Na-X ^b	120°C /-	8	\	62.7	39	[45]
MPAV2/Nb2O5*	25°C /1atm	8	λ	22	76	[46]

^a Oxidant was O₂.

^b Oxidant was H₂O₂ (30%).

* Oxidant was TBHP.



Fig. 6. EPR measurement of various samples.

4. Consideration on the reaction pathways

In order to confirm whether the mechanism of Co_3O_4 @PNC-400 catalytic oxidation of toluene C–H bond is a free radical process, we conducted a free radical suppression test. In the catalytic reaction system, 0.2% of free radical inhibitor TEMPO (2, 2, 6, 6-tetramethylpiperidinyloxy) was added, and the reaction conditions was the same as Table 1. No oxidation product was detected. This shows that Co_3O_4 @PNC-400 catalytic oxidation of toluene C–H bond is a free radical reaction. According to the aforementioned experimental research results and related reports in the comprehensive literatures [50–55], the process of this catalytic reaction can be described as follows (Fig. 7).

The initiation of this reaction is the trivalent cobalt metal cluster to extract an H on the methyl group of toluene to produce a benzyl radical [56]. At the same time, the nitrogen-carbon framework based on polymerized cobalt porphyrin can activate oxygen and transfer it to benzyl radicals to form benzyl peroxy radicals [25,57,58]. It then reduced to the product benzaldehyde by the defect site containing nitrogen and the divalent cobalt metal cluster. As the reaction proceeds, benzaldehyde will be further oxidized to benzoic acid.

The raw material ratio of CoTBPP: TBPP = 3:7 can reduce the distribution density of cobalt ions in the polymer and ensure to generate ultra fine Co_3O_4 nanoclusters after pyrolysis. Cobalt diffusion and

migration in the pyrolysis process under 400 °C produced active Co_3O_4 nanoparticles, and the cobalt migration from the porphyrin ring caused defect site. This low temperature process made the defect not been completely repaired during the pyrolysis and partly retained. The retained defective structure were alkaline site containing nitrogen, which played an important catalytic role in the hydrogen peroxide intermediate decomposition to form benzaldehyde and phenylcarbinol.

Pyrolysis under 400 °C can not only trigger the migration and diffusion of cobalt ions and fusion to produce highly active Co_3O_4 nanoparticles, but also preserve part of the defective structure and generate part of the nitrogen-carbon structure. 400 °C is a proper pyrolysis temperature, which is an important reason for the high catalytic performance of CO_3O_4 @PNC-400.

5. Conclusions

For the first time, a metal porphyrin conjugated porous polymer was used as a template and a cobalt source to form in-situ Co_3O_4 nanoclusters coated with porphyrin-based nitrogen-carbon porous materials by low-temperature heat treatment. The experimental results show that the composite material Co_3O_4 @PNC-400, which obtained by heat-treatment the polymer polymerized from CoTBPP: TBPP = 3:7 at 400 °C, had the best catalytic performance on alkane oxidation. It was found that when pyrolysis the cobalt porphyrin conjugated porous



Fig. 7. Possible pathways for catalytic toluene oxidation.

polymer at 400 °C, fine and highly active Co_3O_4 nanoclusters can be generated in situ, while the porphyrin polymer still retains the main characteristics of the porphyrin framework structure. The porous composite catalytic material obtained in this way has ultra-high catalytic activity in the selective catalytic reaction of oxygen to oxidize C–H bonds in alkane such as toluene and cyclohexane. Its performance is significantly better than the unpyrolyzed polymer Co/PCP and monomer metalloporphyrin CoTBPP at other ratios and other heat treatment temperatures. It is also superior to the results reported in many literatures. Co_3O_4 @PNC-400 has obvious synergistic catalytic effect between Co_3O_4 and nitrogen-carbon framework during the catalytic reaction. The defective structure caused by the migration of cobalt also greatly improved the catalytic activity. So Co_3O_4 @PNC-400 is a new type of C–H oxidation catalyst with good potential application value.

CRediT authorship contribution statement

Mingyang Tan: Writing - original draft, Investigation. Liang Zhu: Writing - review & editing. Hao Liu: Data curation. Yajun Fu: Investigation, Validation. Shuang-Feng Yin: Methodology, Project administration. Weijun Yang: Conceptualization, Supervision.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118035.

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