



# Environmentally friendly and efficient catalysis of cyclohexane oxidation by iron meso-tetrakis(pentafluorophenyl)porphyrin immobilized on zinc oxide



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## ABSTRACT

The use of zinc oxide-promoted catalysis of tetrakis(pentafluorophenyl)porphyrin iron chloride for cyclohexane oxidation was studied. Tetrakis(pentafluorophenyl)porphyrin iron chloride was immobilized onto zinc oxide, generating zinc oxide-supported tetrakis(pentafluorophenyl)porphyrin iron chloride, which was characterized by a variety of spectroscopic techniques and was employed to provide a stable catalyst for the oxidation of cyclohexane in the absence of any solvents or co-reductants. The small amount of tetrakis(pentafluorophenyl)porphyrin iron (1.0  $\mu\text{mol}$ ) in the supported catalyst could be reused 10 times for the oxidation optimized at 150 °C and 0.7 MPa. This stable catalyst provided higher turnover numbers and yields of ketone and alcohol than those obtained using the boehmite-supported tetrakis(pentafluorophenyl)porphyrin iron chloride. These results were attributed to the following factors: (1) stronger coordination of ZnO to the iron porphyrin improved its catalysis of the oxidation. (2) Improved dispersal of the iron porphyrin by ZnO enhanced the effective catalytic center. (3) Faster decomposition of peroxide into the main products.

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## 1. Introduction

Metal porphyrin acting as a biomimetic catalyst model for the cytochrome P450 enzyme in the hydroxylation of hydrocarbons has been used for over 30 years [1,2]. Currently, at least two models of reaction conditions mimicking the hydroxylation of the substrate by P450 in vivo exist. In the first model, the reaction system contains only substrate (hydrocarbon) and catalyst. This reaction proceeds under conditions with higher than normal air pressure and above room temperatures [3–11]. These conditions are similar to those used by the Lyons catalysis system, which does not require the addition of co-reductants or stoichiometric oxidants and the use of photochemical or electrochemical techniques [12]. In the second model, the reaction system contains solvents, co-reductants and/or other additives. It proceeds at normal air pressure (i.e., 0.1 MPa) and at room temperature [13–16]. The first method is preferred in the chemical industry. However, although the second-generation metal meso-tetrakis(pentafluorophenyl)porphyrins are recognized as some of the most efficient catalysts for biomimetic oxidation reactions, they are expensive, poisonous to the

environment and prone to rapid deactivation when not immobilized on a support [17]. For both the first catalytic system and the use of the supported metal polyhalogenated porphyrin catalysts, there are enormous potential industrial applications, with significant economic and environmentally friendly outcomes.

Cobalt tetraphenylporphyrin has been successfully used as a biomimetic catalyst for the aerobic oxidation of cyclohexane to cyclohexanone and cyclohexanol. It gives a catalyst turnover number (TON) of  $1.1 \times 10^4$  and yields of 7–9% (KA oil), and the reaction has been industrialized in China in recent years [18]. However, there is no doubt that second-generation metal meso-tetrakis(pentafluorophenyl)porphyrins and, in particular, the corresponding supported catalysts would be more beneficial for the oxygenation of hydrocarbons [6,17,19,20]. In the present study, iron tetrakis(pentafluorophenyl)porphyrin [Fe (TPFP)] supported on zinc oxide (ZnO) was used as a catalyst for the oxidation of cyclohexane to cyclohexanone and cyclohexanol, without the use of solvents or sacrificial co-reductants, extending the previous work by this group [10,11,19,21–23] that utilized a supported catalyst affording a catalyst TON of only  $(0.7–2.5) \times 10^5$  and yields of 4.1–13.5% (KA oil). Nanoparticles of ZnO form 2-dimensional (2-D) sheet-like structures with a positive surface charge. This helps to immobilize the anionic charge on the porphyrin and promotes the catalytic oxidation of hydrocarbons [24,25]. The effect is greater

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than that for titanium and aluminum oxides [26,27], and ZnO is biosafe and biocompatible [28]. The aim of the present study was to understand the mechanism for the efficient and high yielding catalytic oxidation of cyclohexane to KA oil in the absence of any solvents, co-reductants or additives by this new ZnO-supported Fe (TPFPF) catalyst [Fe (TPFPF)/ZnO].

## 2. Experimental

### 2.1. Reagents

All reagents and solvents were of analytical grade and were obtained commercially. Fe (TPFPF) was purchased from Sigma–Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). Cyclohexane was examined with gas chromatography prior to use to ensure it was free from oxidation products.

### 2.2. Preparation of ZnO-immobilized Fe (TPFPF)

With stirring, 70.64 g of zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) was dissolved in distilled water, and sodium hydroxide was added as the precipitation agent until pH=8. The white zinc hydroxide precipitate that formed was filtered and washed with distilled water until no  $\text{SO}_4^{2-}$  ions could be detected. The precipitate was added to 100 ml of ethanol in a three-necked flask with stirring at high speed for 0.5 h. Subsequently, 20 mg of Fe (TPFPF), dissolved in 20 ml of absolute ethanol, was slowly added to the suspension. The mixture was heated to 60 °C with rapid stirring for 6 h. The gray suspension was filtered and washed with bulk-distilled water, and the gray cake was dried at 0.08 MPa and 160 °C for 5 h to give 20.5 g of the gray supported catalyst, Fe (TPFPF)/ZnO. The amount of immobilized metalloporphyrin in the Fe (TPFPF)/ZnO catalyst was determined using atomic emission spectroscopy with inductively coupled plasma (ICP-AES, Spectroflame model FVM03). The samples were digested using a traditional acid method ( $\text{HNO}_3$  and HCl), diluted adequately and analyzed for iron. The amount of immobilized Fe (TPFPF) per gram of the supported catalyst was 0.98 mg (0.92  $\mu\text{mol}$ ), a value consistent with that determined using ultraviolet–visible (UV–vis) spectrophotometry [29].

### 2.3. Characterization of the Fe (TPFPF)/ZnO catalyst

The UV–vis spectra of the immobilized catalyst in a toluene suspension and the unsupported catalyst in a toluene solution were recorded using a PerkinElmer L-17 spectrometer.

The Fourier transform infrared (FTIR) spectra of the Fe (TPFPF)/ZnO catalyst were recorded on a PerkinElmer (model 783) IR spectrophotometer in the range 4000–400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  using potassium bromide (KBr) pellets.

The X-ray diffraction (XRD) patterns for the powder samples of ZnO and Fe (TPFPF)/ZnO were collected on a Rigaku D/MAX RINT 2500 X-ray diffractometer with copper (Cu)  $\text{K}\alpha$  radiation. Scans were performed from ( $2\theta$ ) 10° to 70° at a rate of 5°  $\text{min}^{-1}$ .

The particle sizes of the Fe (TPFPF) and Fe (TPFPF)/ZnO catalysts and support were measured on a Tecnai G2F20 S-TWIN transmission electron microscope with a 100 kV accelerating voltage and using a Holland Philips Ltd. Sirion 200 Field Emission Gun Scanning Electron Microscope System with a 10 or 15 kV accelerating voltage. The specific surface area (SSA) of the catalyst material samples was examined with a Build SSA-3600 porosimetry analyzer.

Thermogravimetric (TG) curves for the Fe (TPFPF)/ZnO samples were recorded using a NETZSCH STA 409 PC thermoanalyser. The measurements were conducted using 64.7 mg samples in air over a temperature range of 0–1000 °C and with a heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.4. Use of the immobilized catalyst for cyclohexane oxidation

The catalyst material obtained by the immobilization of Fe (TPFPF) on nano-sized ZnO was used for the oxidation of cyclohexane. The oxidation was conducted in a KCF-10 500-ml autoclave reactor equipped with a magnetic stirrer and a frozen ethanol recondenser at –20 °C [22]. The mixture, which was a measured amount of the catalyst (containing  $1.0 \times 10^{-6}$  mol of Fe (TPFPF)) and 200 ml of cyclohexane, was stirred and heated to 150 °C. Afterward, air was continuously pumped into the reaction system and the pressure was maintained at 0.7 MPa. The set reaction conditions were optimized by experimental exploration, as described by Guo et al. [4]. The airflow was measured with a rotameter and the oxygen concentration of the tail gas was determined with a CYS-1 digital oxygen detector. Samples of the reaction mixture were identified using gas chromatography–mass spectrometry (GC–MS) and were quantified with a Shimadzu GC-16A chromatograph equipped with a 30 m  $\times$  0.32 mm  $\times$  0.5  $\mu\text{m}$  FFAP capillary column and a flame ionization detector using chlorobenzene as the internal standard [23]. After the oxidation was terminated—that is, when the oxygen content in the tail gases stopped falling—the supported catalyst was recovered by simple filtration from the reaction mixture, washed with ethanol and air-dried to extract any reaction product retained in the catalyst. This supported catalyst was then used in the subsequent cyclohexane oxidation reactions.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

#### 3.1.1. UV–vis spectra of Fe (TPFPF)/ZnO

The presence of immobilized Fe (TPFPF) in the Fe (TPFPF)/ZnO material was demonstrated using UV–vis spectroscopy (Fig. 1A). The UV–vis spectra of Fe (TPFPF) and Fe (TPFPF)/ZnO shown in Fig. 1A(a) and (b), respectively, demonstrate the characteristic Soret peaks of immobilized iron porphyrin. When Fe (TPFPF) was immobilized on the ZnO support, its characteristic Soret peak was blue-shifted from 416 nm to 405 nm. The blue-shift phenomenon is opposite to the red-shifts reported elsewhere [30–35]. This means that the original saddle Fe (TPFPF) molecules were set on the surface of the ZnO crystals in a co-planar configuration. This suggests that when the original saddle (not planar) Fe (TPFPF) was immobilized on the surface of the ZnO crystal the interaction between the negative fluorine (F) atoms on the phenyl rings of the iron porphyrin and the positive zinc ion on the surface of the ZnO crystal resulted in Fe (TPFPF) becoming more planar, as previously reported [28,36]. Thus, ZnO imposed a steric pushing action on the immobilized iron porphyrin. The immobilization process increased the planarity of the porphyrin ring so that the porphyrin  $a_{2u}$  orbital (the highest occupied molecular orbital) was shifted up with respect to the  $e_g$  orbital (the lowest unoccupied molecular orbital), which then resulted in a blue-shifted Soret band. The evidence for this being the original saddle for Fe (TPFPF) was obtained in a comparison experiment: the Soret peak for TPP Fe appeared at 420 nm, whereas the Soret peak for Fe (TPFPF) appeared at 416 nm under the same conditions.

Based on the above results, the interaction between the iron porphyrin and the surface of the ZnO crystal can be described in the following two ways. The most obvious is the coordination of O atoms from ZnO into the empty orbital of the Fe ion. This interaction is accompanied by the coordination of  $\pi$  electrons from the porphyrin ring containing F atoms into the empty orbital of the Zn cation, as shown in Fig. 2(left), in a face-to-face/parallel orientation. Another less favorable possibility is a face-to-edge/orthogonal orientation, as shown in Fig. 2(right).

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