



# Immobilization of cobalt porphyrin on CeO<sub>2</sub>@SiO<sub>2</sub> core–shell nanoparticles as a novel catalyst for selective oxidation of diphenylmethane

Xiang Guo, Yuan-Yuan Li, Dan-Hua Shen, Yuan-Yuan Song, Xiao Wang, Zhi-Gang Liu\*

School of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, PR China

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## ABSTRACT

In this study, CeO<sub>2</sub>@SiO<sub>2</sub> core–shell nanoparticles have been synthesized and used as supports to graft cobalt porphyrin via an amide bond. The catalyst was characterized using techniques such as FT-IR, UV–vis, SEM, TEM and BET. The results show that the catalyst was composed of regular nanoparticles (around 50 nm) with a core–shell structure. In addition, the catalyst exhibits an excellent activity, selectivity and stability for solvent-free selective oxidation of diphenylmethane with atmospheric pressure of oxygen. The conversion of diphenylmethane was as high as 41.6% with selectivity to diphenyl ketone of 96.3%. Even after reused up to 6 times, the catalyst maintained stable working ability.

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## 1. Introduction

Supported metalloporphyrin catalysts have been used as effective catalysts for a wide range of selective oxidations of hydrocarbons, for the micro-environment of the support can bring higher selectivity and prevent catalyst self-oxidation [1,2]. Therefore, there has been a wide-spread interest in the synthesis of metalloporphyrin catalysts supported on inorganic, organic, or hybrid materials, especially those with a core–shell structure [3–6].

Because of the advantages of core–shell structured nanocomposites resulting in non-aggregated nanoparticles with a controlled surface and/or coating properties [7–10], the prospect of materials with core–shell structure used as catalyst carriers has attracted more attention. Huang et al. [11,12] employed magnetic polymer nanospheres (with Fe<sub>3</sub>O<sub>4</sub> core and polystyrene shell) as a support of metalloporphyrin. It was found that these nanospheres have good magnetic responsiveness and thus can be recycled by employing an external magnetic field. Liu et al. [13] adopted silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a carrier and synthesized a series of supported metalloporphyrin catalysts with different saturation magnetization. The influence of the saturation magnetization of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the catalytic abilities of supported metalloporphyrin was also investigated. Unfortunately, the effect of Fe<sub>3</sub>O<sub>4</sub> embedded in the nanospheres on catalysis of the nanospheres was

reported to be negligible and cannot be used as promoter of catalysts [12].

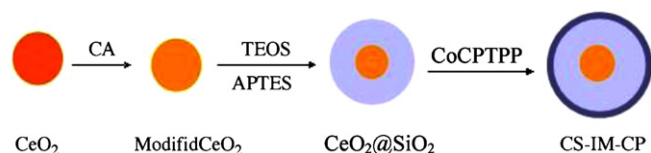
CeO<sub>2</sub> is a well-known promoter additive because of its oxygen storage and releasing capacity [14,15]. Herein, CeO<sub>2</sub> was expected to be used as the core in the core–shell materials since CeO<sub>2</sub> possesses catalytic activity and cooperates with metalloporphyrin in redox reactions.

However, the surface precipitation of ceria on silica is inadequate when precipitant such as ammonium solution is used [16], because the pH of the precipitate is 10, surface of silica is negatively charged, and the pH of ceria is above 8. As a result, silica could not coat the ceria as core due to the expected electrostatic repulsion between both particles. To induce the attraction interaction between the silica and ceria, Grasset et al. [17] moved the pH of the silica–ceria suspension to pH 4, where the silica and ceria were oppositely charged with respect to each other.

However, it could not look forward to lower the pH with the addition of acid when ammonium solution was used as precipitant during the synthesis of CeO<sub>2</sub>@SiO<sub>2</sub>. To achieve the electrostatic attraction between the silica–ceria, the surface of the silica particles was modified with amine group via the hydrolysis of 3-aminopropyl-trieth-oxysilane [18].

As illustrated in Scheme 1, we used citrate sodium to modify the surface properties of ceria and synthesized the CeO<sub>2</sub>@SiO<sub>2</sub> core–shell structured support. Cobalt porphyrin was then immobilized on these synthesized CeO<sub>2</sub>@SiO<sub>2</sub> structures for the first time. The catalysts were characterized using FT-IR, UV–vis, SEM, TEM, XRD and BET, and the catalytic performance for solvent-free oxidation of diphenylmethane to diphenyl ketone was measured. The

\* Corresponding author. Tel.: +86 731 88821314; fax: +86 731 88821667.  
E-mail addresses: [liuzhigang@hnu.edu.cn](mailto:liuzhigang@hnu.edu.cn), [cerialiu@gmail.com](mailto:cerialiu@gmail.com) (Z.-G. Liu).



**Scheme 1.** Illustration of the major steps for preparation of CoCPTPP grafted on  $\text{CeO}_2/\text{SiO}_2$  nanoparticles.

results show that the catalysts exhibit excellent catalytic activity, selectivity and stability.

## 2. Experimental

### 2.1. Materials

5-(4-Carboxyphenyl)-10,15,20-triphenyl porphyrin (CPTPP) was synthesized and purified in our laboratory. The metal oxides used in this work were prepared with coprecipitation method from corresponding metal nitrates. Water used in all experiments was deionized and doubly distilled prior to use. 4-Carboxy benzaldehyde, benzaldehyde and pyrrole were redistilled before use. All other reagents were obtained commercially and used without further purification.

### 2.2. Characterization of catalysts

UV–vis patterns were recorded on a Shimadzu UV-2450 spectrophotometer using  $\text{BaSO}_4$  as reference with a range of 200–800 nm and a scan step of 0.5 nm. FT-IR spectra were measured on an Agilent Perkin-Elmer 783 infrared spectrometer in KBr disc. The specific surface areas of samples were determined by analyzing the results of  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  in a Micromeritics ASAP 2020 apparatus and applying the Brunauer–Emmett–Teller (BET) method to the experimental values. All samples were dehydrated at  $150^\circ\text{C}$  for 24 h prior to  $\text{N}_2$  adsorption. SEM (JSM 6700F) was used to observe the particle sizes and shapes of samples. Prior to the measurements, the samples were mounted on a carrier made from glassy carbon and coated with a film of gold. TEM (Hitachi 800, operated at 175 kV) images were obtained by dispersing samples in ethanol using an ultrasonication bath and then depositing a drop of liquid containing the particles onto a copper grid.

### 2.3. Synthesis of catalysts

#### 2.3.1. Synthesis of cobalt(II)

##### 5-(4-carboxyphenyl)-10,15,20-triphenyl porphyrin

According to literature [19], 200 mL of propanoic acid, 0.0525 mol of benzaldehyde and 0.0175 mol of 4-carboxy benzaldehyde were loaded into a three-neck flask and heated to reflux under stirring, then 0.07 mol of pyrrole was slowly dropped through a funnel within 20 min. Under refluxing condition, the mixture was stirred for 30 min. After cooling the reaction solution in a refrigerator overnight the mixture was then filtered and purified by column chromatography and 5-(4-carboxyphenyl)-10,15,20-triphenyl porphyrin was obtained. 0.50 g of obtained porphyrin was dissolved in 100 mL of N,N-dimethylformamide (DMF), and 2.54 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was added under stirring, and then heated to reflux until porphyrin detected by TLC was exhausted. After cooling overnight, this mixture was filtered and washed repeatedly with hot water, cobalt(II) 5-(4-carboxyphenyl)-10,15,20-triphenyl porphyrin (CoCPTPP) was achieved.

#### 2.3.2. Synthesis of surface modified $\text{CeO}_2$

Surface modified  $\text{CeO}_2$  was synthesized according to literature methods [20,21]. 5.996 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was added into volumetric flask and prepared for 250 mL of solution with deionized water. Under mechanical stirring, 250 mL 0.36 M of NaOH solution was slowly dropped into  $\text{Ce}(\text{NO}_3)_3$  solution until the solution pH was 13. After stirring for 30 min, the precipitate was filtered and washed with deionized water twice and then dispersed in 200 mL 0.3 M of citrate sodium solution. After stirring at  $90^\circ\text{C}$  for 6 h, the product was filtered, washed with ethanol and water, respectively, and dried. The modified  $\text{CeO}_2$  was achieved.

#### 2.3.3. Synthesis of $\text{CeO}_2/\text{SiO}_2$ with core-shell structure

$\text{CeO}_2/\text{SiO}_2$  nanoparticles were prepared as described in the literature [22,23]. Namely, 0.30 g of  $\text{CeO}_2$  was well dispersed in the mixture of ethanol (160 mL), deionized water (40 mL) and concentrated ammonia aqueous solution (5.0 mL, 28 wt.%), followed by addition of tetraethyl orthosilicate (TEOS, 1 mL) and 3-aminopropyltriethoxysilane (APTES, 0.2 mL). After stirring for 6 h at room temperature, the product was filtered and washed with ethanol and water. The obtained  $\text{CeO}_2/\text{SiO}_2$  core-shell nanoparticles were denoted as CS, with the specific surface area  $50.8\text{ m}^2/\text{g}$ . Nanoparticles without coating  $\text{CeO}_2$  were synthesized by the similar method and denoted as NCS.

#### 2.3.4. Synthesis of CoCPTPP anchored on $\text{CeO}_2/\text{SiO}_2$

According to literature [24], 0.05 g of CoCPTPP, 3.50 g of CS and 150 mL N,N-dimethylformamide (DMF) were loaded into a three-neck flask, then heated to reflux for 12 h. After cooling, washing with deionized water and filtering, dichloromethane was used to extract the sample in a Soxhlet extractor till the extracted solution was turned to clarify. The product was designated as CS-IM-CP. The specific surface area of CS-IM-CP was  $25.9\text{ m}^2/\text{g}$  and CoCPTPP loading in CS-IM-CP was  $7.9\text{ mg/g-cat}$ . Following the similar procedure, CoCPTPP was immobilized on NCS, and the product was denoted as CS-IM-CP with CoCPTPP loading of  $8.2\text{ mg/g}$ . The CoCPTPP loading in CS-IM-CP was determined by UV–vis quantitative analysis method.

### 2.4. Measurement of catalytic performance

The catalytic performance of catalysts for solvent-free oxidation of diphenylmethane was measured in a 100 mL four-neck flask with a magnetic stirrer. In a typical experiment, 30 mL of diphenylmethane and 100 mg of catalyst were loaded into the glass reactor. The reactor was sealed and bubbled with oxygen at atmospheric pressure. The reactor was then heated to desired reaction temperature in an oil bath under stirring. Every hour, 0.5 mL of samples were withdrawn with a syringe and analyzed by gas chromatography with internal standard method using chlorobenzene as reference substance. After the reaction, the reactor was cooled to room temperature and the product was filtered through a millipore filter. Then, the catalyst was recovered and dried at  $80^\circ\text{C}$  for 12 h. The regenerated catalyst was used for cycling studies.

## 3. Results and discussion

### 3.1. Characterization of catalysts

Solid-state diffuse-reflectance UV–vis spectroscopy was typically used to analyze metalloporphyrin species because metalloporphyrin species have characteristic peaks, called as Soret band and Q-band, respectively [25]. In Fig. 1, the characteristic bands of CS-IM-CP in the UV–vis spectra can be found at 428 nm and 541 nm. The support CS was measured by UV–vis spectra without characteristic peaks. As for CS-IM-CP, the characteristic peaks of

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