



## Short communication

Synthesis of highly efficient  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts for CO oxidation derived from MIL-100(Fe)Lifeng Cui<sup>a</sup>, Di Zhao<sup>a</sup>, Yang Yang<sup>a</sup>, Yuxin Wang<sup>b</sup>, Xiaodong Zhang<sup>a,\*</sup><sup>a</sup> Environment and Low-Carbon Research Center, School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, China<sup>b</sup> Institute of Applied Biotechnology, Taizhou Vocation & Technical College, Taizhou, Zhejiang 318000, China

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## ABSTRACT

Mesoporous hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks were synthesized via a hydrothermal method to create a precursor MIL-100(Fe) and a subsequent calcination process was applied to prepare the Fe<sub>2</sub>O<sub>3</sub> phase. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results showed the morphology of hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks which inherited from the MIL-100(Fe) template. The catalytic activities of hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks for CO oxidation are studied in this work. Due to better low temperature reduction behavior, mesoporous hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks obtained at calcination temperature of 430 °C displayed high catalytic activity and excellent stability with a complete CO conversion temperature (T<sub>100</sub>) of 255 °C.

## 1. Introduction

The catalytic CO oxidation is one of the most studied chemical reactions in the fields of environmental science and energy source, such as air purification devices, proton exchange membrane fuel cells et al. [1–4]. Recent developments and trends in catalytic CO oxidation towards the synthesis of nanocatalysts which mainly aiming at good economic benefit [5]. Among the cheap transition metal oxides, hematite is an extremely attractive candidate for potential applications duo to the most thermodynamically stable phase of iron oxide with an environment-friendly nontoxic n-type semiconductor under ambient conditions [6].

Recently, Fe<sub>2</sub>O<sub>3</sub> nanocatalysts with various structures were synthesized for CO oxidation by many researchers [6–9]. To date there are a large number of synthetic strategies such as hydrothermal [10], sol-gel and precipitation [11] has been reported for the preparation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. However, most of the preparation methods of Fe<sub>2</sub>O<sub>3</sub> nanocatalysts that reported involved complicated procedure and poor controllability [12,13]. Previous studies show that a template method is a relatively straightforward and simple approach to synthesize nanocatalyst with unique particle size and controlled morphology. Recently, metal organic frameworks (MOFs), displaying high surface area, tunable porosity, well-defined structure and good catalytic selectivity, can be used as templates in the synthesis of metal oxides nanoparticles [14–18]. Compared with other templates, MOFs templates can prepare higher quality metal oxides catalysts with uniform particle size [19]. In

addition, metal oxides catalysts retain the original morphology and porosity of MOFs templates [20]. In this work, an iron-based metal-organic framework MIL-100(Fe) has been used as template in the synthesis of Fe<sub>2</sub>O<sub>3</sub> nanocatalysts. To the best of our knowledge, there has been no report on using MOFs as the template to synthesize Fe<sub>2</sub>O<sub>3</sub> crystals as the catalyst for CO oxidation.

## 2. Experimental

## 2.1. Catalyst preparation

The MIL-100(Fe) was synthesized under hydrothermal conditions according to the procedure reported by Ferey [21]. Typically, 1, 3, 5-benzenetricarboxylic acid (1.76 g), iron powder (0.654 g), hydrofluoric acid (1.02 mL) and concentrated nitric acid (0.48 mL) were mixed in a Teflon-lined steel bomb with 56.9 mL pure water. Then the reactant mixtures were loaded in a Teflon autoclave and kept at 150 °C for 12 h and followed by a final cooling to room temperature. The light-orange solid product was recovered by filtration, washed with deionized water and dried at 70 °C to obtain the final product. The produced MIL-100(Fe) was taken in a ceramic boat and calcined in a muffle furnace at different temperatures (400–500 °C) for 2 h. The obtained sample was defined as Fe<sub>2</sub>O<sub>3</sub>-x, where the x is thermal treatment temperature. In addition, the commercial Prussian blue (PB) was purchased from Shanghai Chemical Reagent Ltd. Co. of China and used as a contrasting MOF material and calcined with the same method of MIL-100(Fe) at a

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final temperature of 430 °C. The obtained sample was defined as PB-430.

## 2.2. Catalysts characterization

X-ray powder diffraction (XRD) experiments were characterized by a Bruker D8 Advance X-ray diffractometer with monochromatic detector. Copper K $\alpha$  radiation was used, with accelerating voltage of 40 kV and emission current 40 mA, and a scan rate of 5°/min, the sample was scanned in the range between 10° and 80°. Scanning electron microscopy (SEM) images of as-synthesized materials were taken by a TESCAN (VEGA-3-SBH) scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) images were obtained by using a JEM 2100 instrument. Temperature programmed reduction (TPR) experiments were carried out using a ChemBET TPR/TPD under 10 vol% H<sub>2</sub> flow diluted with Ar gas. The samples (50 mg) were reduced in a flow of H<sub>2</sub>/Ar mixture. The temperature was increased from room temperature to 850 °C at a heating rate of 10 °C min<sup>-1</sup>. Brunauer–Emmett–Teller (BET) surface areas were gotten on a Quantachrome autosorb-iQ-2MP. The pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) analysis using the desorption branch of the isotherms. Uncalcined MIL-100(Fe) was analyzed by a simultaneous thermal analyzer (PerkinElmer, STA8000). The temperature was increased from 50 to 750 °C applying a heating rate of 10 °C/min.

## 2.3. Catalytic activity measurements

CO oxidation activity measurements were carried out in a fixed-bed flow reactor (6 mm outer diameter) at the atmospheric pressure and with 0.1 g of catalyst (20–40 mesh). The reactants were fed with a volume ratio of He/CO/O<sub>2</sub>=79/1/20 (a total flow rate of 30 mL/min) controlled by independent thermal mass flow controllers. The CO conversion was analyzed after 30 min of the reaction by using on-line gas chromatograph (GC 2060) with a thermal conductivity detector (TCD) equipped with 5 Å molecular sieve column (length: 3 m, inner diameter: 3 mm).

## 3. Results and discussion

### 3.1. Preparation and characterization of hollow $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks

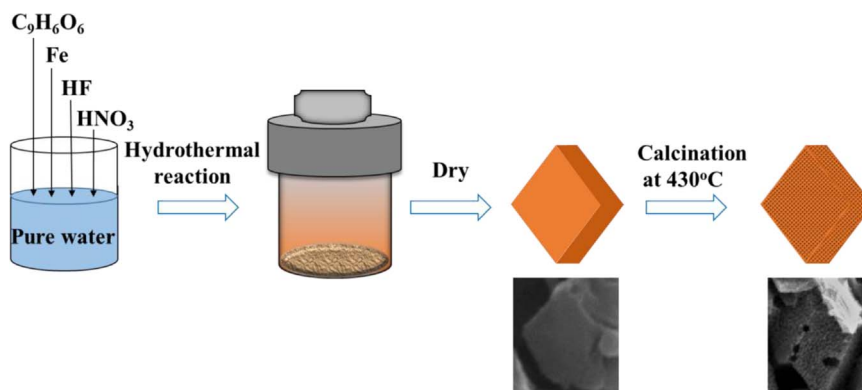
Scheme 1 illustrates the procedure for generating hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks. Firstly, the turbid precursor of metal-organic complex was prepared by hydrothermal treatment of the water solution of 1, 3, 5-benzenetricarboxylic acid, iron powder, hydrofluoric acid and nitric acid. Fig. 1(a) shows typical SEM image of the prepared MIL-100(Fe) precursor. It can be seen that the precursor is brick-like with lengths of 2–3  $\mu$ m and widths of 2–3  $\mu$ m. The morphology of MIL-100(Fe)

precursor is further analyzed by TEM (Fig. S1). These MIL-100(Fe) bricks display dense solid texture without discernible porosity. The BET surface area and total pore volume of MIL-100(Fe) precursor is 2330 m<sup>2</sup>g<sup>-1</sup> and 0.747 cm<sup>3</sup>g<sup>-1</sup>, respectively. In addition, the crystalline structure of MIL-100(Fe) bricks is characterized by XRD, with the results shown in Fig. S2. It is found that the MIL-100(Fe) precursor shows the characteristic peaks at 2 $\theta$ =6.3°, 10.2°, 11.0°, and 20.0° consistent with those reported in the literature [22]. MIL-100(Fe) bricks are insecure and can be easily decomposed into iron oxides at elevated temperatures. During the heat treatment, MIL-100(Fe) will be oxidized to iron oxides. In addition, the organic components are removed by calcination. In order to study the decomposition behavior of MIL-100(Fe), TGA analysis in air flow is performed (Fig. S3). Firstly, a weight loss of about 19.8 wt% below 300 °C corresponds to the departure of the water inside the pore and the water coordinated to the iron trimers. Secondly, the significant weight loss between 300 °C and 430 °C is attributed to decomposition of the trimesic acid [23]. Therefore, the transformation of MIL-100(Fe) into iron oxides is carried out at 430 °C, during which the simultaneous oxidative decomposition of MIL-100(Fe) is expected to take place completely.

Secondly, mesoporous hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks were prepared by calcining the precursor at 430 °C in air. From the XRD pattern of the calcined product in Fig. 2, it is clearly shown that the diffraction peaks for the precursor disappear and all the peaks are in good agreement with the standard spectrum of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS Card No. 33-0664), which means that the precursor was transformed into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructure. Furthermore, the morphology is successfully maintained during the process of calcination, and Fe<sub>2</sub>O<sub>3</sub>-430 also has a brick-like morphology, as shown in Fig. 1(b) and (c). Compared with the precursor, a large number of well-ordered pores can be clearly observed on Fe<sub>2</sub>O<sub>3</sub>-430 sample. Further TEM results also prove that Fe<sub>2</sub>O<sub>3</sub>-430 sample has many well-ordered pores (Fig. 1(d)). The fringes in Fig. 1(e) give a d-spacing of 0.251 nm, corresponding the (110) atomic plane of rhombohedral Fe<sub>2</sub>O<sub>3</sub> lattices. Combined with the result of TGA (Fig. S3), CO<sub>2</sub>, H<sub>2</sub>O and other gases coming from the decomposition of organic framework could escape to the surface of the catalyst, consequently resulting in the formation of a large number of well-ordered pores.

### 3.2. Catalytic performance

The CO catalytic oxidation reaction is tested to evaluate catalytic activity of various  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples. Fig. 3 displays catalytic activity over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples synthesized through controlling the calcination temperature. It is obviously found that the activity of CO firstly increases and then decreases with the increase of calcination temperature. At 430 °C, Fe<sub>2</sub>O<sub>3</sub>-430 reveals good catalytic performance for CO oxidation in comparison with other samples. The complete conversion temperature is 255 °C. Moreover, compared with previously reported



Scheme 1. Synthetic route of mesoporous hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> bricks.

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