

## Regular Article

# Metallic cobalt nanoparticles imbedded into ordered mesoporous carbon: A non-precious metal catalyst with excellent hydrogenation performance

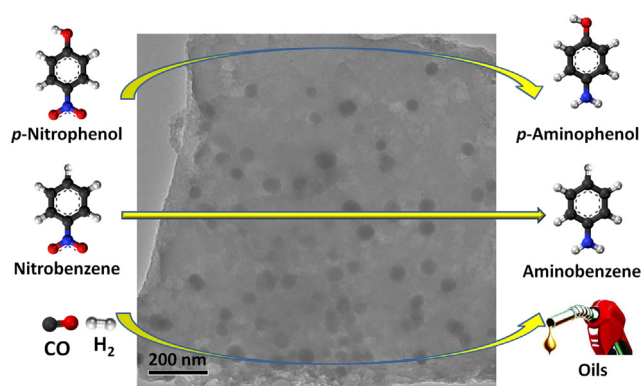


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Ordered mesoporous carbon (OMC)-metal composites have attracted great attention owing to their combination of high surface area, controlled pore size distribution and physicochemical properties of metals. Herein, we report the cobalt nanoparticles/ordered mesoporous carbon (CoNPs@OMC) composite prepared by a one-step carbonization/reduction process assisted by a hydrothermal pre-reaction. The CoNPs@OMC composite presents a high specific surface area of 544 m<sup>2</sup> g<sup>-1</sup>, and the CoNPs are uniformly imbedded or confined in the ordered mesoporous carbon matrix. When used as a non-precious metal-containing catalyst for hydrogenation reduction of *p*-nitrophenol and nitrobenzene, it demonstrates high efficiency and good cycling stability. Furthermore, the CoNPs@OMC composite can be directly used to catalyze the Fischer-Tropsch synthesis for the high-pressure CO hydrogenation, and presents a good catalytic selectivity for C<sub>5</sub><sup>+</sup> hydrocarbons. The excellent catalytic performance of the CoNPs@OMC composite can be ascribed to synergistic effect between the high specific surface area, mesoporous structure and well-imbedded CoNPs in the carbon matrix.

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## 1. Introduction

Ordered mesoporous carbons (OMCs), with uniform pores, tunable pore size, large surface area and chemical inertness, have

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aroused great attention owing to their wide applications in catalysis, adsorption, energy conversion and storage, etc. [1–7]. One of the most traditional ways for the synthesis of OMCs is the “hard-template” method, which involves the utilization of ordered mesoporous silicas as hard templates and sacrificial scaffolds [8–10]. However, the tedious procedure and high cost impede the large scale application of this hard-template strategy. Recently, a flexible and effective method known as the “soft-template” method has been developed for the synthesis of OMCs, which generally involves the self-assembly of amphiphilic triblock copolymers as soft templates and carbon precursors followed by the carbonization [11–15].

For the purpose of catalysis application, OMCs have been functionalized by heteroatoms doping or incorporation with metal components [15–18]. The conventional way for the preparation of metals/OMCs catalysts is the impregnation method with metals supported on OMCs by the typical procedures of impregnation, drying and calcination [2,17,19–21]. Although the impregnation techniques have great practical simplicity, the metals always distribute uncontrollably and randomly on the surface or within the channels of OMCs accompanying the presence of pore blockage. For the obtainment of confined reaction environment, we have recently developed a new-type cobalt imbedded zeolite catalyst with conventional Co/SiO<sub>2</sub> as the precursor [22–24]. However, in these catalysts, the metallic cobalt particles can only be obtained through the high-temperature and time-consuming hydrogen reduction process.

In this study, we report a simple one-pot synthesis of metallic cobalt nanoparticles/ordered mesoporous carbon (CoNPs@OMC) composite by combination of hydrothermal and carbonization reactions. The as-synthesized CoNPs@OMC composite is utilized as a bifunctional catalyst for the hydrogenation reduction of nitroaromatic compounds (*p*-nitrophenol and nitrobenzene) and the high-pressure CO hydrogenation process (Fischer-Tropsch synthesis, FTS). The CoNPs@OMC composite exhibits high catalytic activities and cycling stabilities in both applications.

## 2. Experimental

### 2.1. Materials preparation

Pluronic F127 (poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>) with an average molecular weight of 12,600 was used as the structure-directing agent. In a typical procedure, 2.5 g F127 was dissolved in 10 mL of deionized water and 10 mL of ethanol under continuous stirring for 1 h. Then 1.65 g of resorcinol was added into the solution and stirred for 30 min. Afterwards, 0.4 g of hydrochloric acid (HCl, 37 wt%) was added and stirred continuously for 1 h, followed by the addition of 1.11 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with stirring for another 1 h. Thereafter, 1.41 mL of formaldehyde (HCHO, 37 wt%) was added dropwise, and the mixture was further vigorously stirred for 1.5 h before the hydrothermal process was performed at 100 °C for 10 h. The polymeric monolith was obtained by filtration and washed thoroughly with deionized water and ethanol, followed by curing at 50 °C for 4 h and 80 °C for 15 h. Carbonization was conducted in a tubular furnace under Ar atmosphere at 600 °C for 3 h with a ramping rate of 3 °C min<sup>-1</sup>. For comparison, the pure OMC was prepared under similar conditions without Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

### 2.2. Physical characterization

The small-angle X-ray diffraction patterns (SA-XRD) were performed on a Rigaku D/max-2500VB2+/PC diffractometer (40 kV,

50 mA) using Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm) within the 2 $\theta$  range of 0.5–10°, while the wide-angle XRD (WA-XRD) measurements were scanned at 40 kV and 200 mA between the 2 $\theta$  range of 5–90°. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449C thermogravimetric analyzer. The morphology was investigated with a field-emission scanning electron microscope (SEM) (JEOL JSM-7800F). The Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-3010 microscope. N<sub>2</sub> isothermal adsorption-desorption measurement at 77 K was performed with a Micromeritics ASAP 2010 system. Prior to the test, the samples were outgassed at 473 K for 5 h. The surface area of the samples was determined by the Brunauer–Emmett–Teller (BET) method, while the pore volume was calculated at a relative pressure ( $P/P_0$ ) of about 0.99, where  $P$  and  $P_0$  are the measured and equilibrium pressures, respectively. The pore size distribution curves were obtained with the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms. The XPS data were collected on a Thermo, Fisher Scientific ESCALAB 250 spectrometer in the constant analyzer energy (CAE) mode, with an Al K $\alpha$  monochromatized X-ray source (1486.6 eV). The survey spectra were measured at 30 eV pass energy.

### 2.3. Catalytic reactions

The CoNPs@OMC composite was employed for the hydrogenation reduction of *p*-NP (*p*-nitrophenol) or NB (nitrobenzene). Typically, 5 mL of NaBH<sub>4</sub> aqueous solution (0.04 M) was added to 20 mL of *p*-NP or NB aqueous solution (0.1 mM). Then the reaction was initiated by adding 0.5 mL of CoNPs@OMC catalyst suspension (1.0 g/L) into the mixed solution. The hydrogenation reduction process was monitored by measuring the absorption spectra via a UV–vis spectrophotometer.

For the FTS reaction, the CoNPs@OMC catalyst was directly employed in a continuous-flow-type fixed-bed reactor without the conventional hydrogen reduction process. The reaction temperature and pressure of the FTS reaction were 523 K and 2.0 MPa, respectively. The molar ratio of H<sub>2</sub>/CO was 2.0, and the  $W_{\text{catalyst}}/F_{\text{syngas}}$  was 10 g h mol<sup>-1</sup>. The product was analyzed by online and offline gas chromatography [22–24]. All the analysis results were summed up to obtain the CO conversion and the hydrocarbon selectivity (in terms of carbon mol percentage, c-mol %).

## 3. Results and discussion

### 3.1. Structure and morphology characterization

The ordered mesoporous structure of the OMC was examined by the SA-XRD analysis. The intense single diffraction peak indexed to the (100) plane of carbon in the SA-XRD profile of OMC (Fig. 1a) suggests a highly ordered mesoporous structure [16]. The weaker peak intensity for CoNPs@OMC indicates a decrease in the structure regularity possibly owing to the introduction of cobalt salts in the precursor solution. The WA-XRD patterns (Fig. 1b) show that both OMC and CoNPs@OMC have two broad peaks centered at 22 and 43°, indicating the amorphous state of the carbon framework [25]. Three other peaks in the XRD pattern of CoNPs@OMC locating at 44.3, 51.6 and 75.8° correspond to the (111), (200) and (220) crystal planes of face-centered Co (JCPDS 15-0806), respectively. This suggests that Co<sup>2+</sup> has been reduced to metallic cobalt (Co<sup>0</sup>) during the carbonization process [26,27]. Obviously, no diffraction peaks of cobalt oxide or cobalt carbide was detected by XRD measurement. The grain size of CoNPs was calculated using Scherrer

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