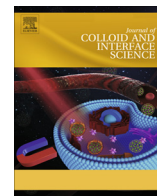




Contents lists available at ScienceDirect

## Journal of Colloid and Interface Science

journal homepage: [www.elsevier.com/locate/jcis](http://www.elsevier.com/locate/jcis)

## Regular Article

## Facile synthesis of ultrafine cobalt oxides embedded into N-doped carbon with superior activity in hydrogenation of 4-nitrophenol



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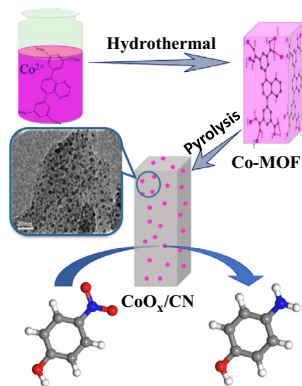
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## GRAPHICAL ABSTRACT

Ultrafine cobalt oxides embedded into N-doped carbon (CoO<sub>x</sub>/CN), synthesized via a MOF pyrolysis route, exhibit high catalytic activity and stability in hydrogenation of 4-nitrophenol at ambient conditions.



## ARTICLE INFO

## Article history:

Received 4 August 2017

Revised 1 November 2017

Accepted 2 November 2017

## Keywords:

Cobalt oxides

Metal-organic frameworks

N-doped carbon

Hydrogenation reaction

## ABSTRACT

Design and synthesis of low-cost catalysts with high activity and stability for hydrogenation reactions is an important research area of applied catalysis. In this work, we present a kind of ultrafine cobalt oxides encapsulated by N-doped carbon (denoted as CoO<sub>x</sub>/CN) as efficient catalysts for hydrogenation of 4-nitrophenol (4-NP) process. The CoO<sub>x</sub>/CN was fabricated through a pyrolysis strategy using an N-containing metal-organic framework (Co-MOF) as precursor followed by a fine thermal-treatment. With an optimized pyrolysis temperature of 500 °C, the CoO<sub>x</sub> species present as ultrafine particles highly dispersed in the obtained catalyst (CoO<sub>x</sub>/CN-500). CoO<sub>x</sub>/CN-500 exhibits excellent activity and stability in hydrogenation of 4-NP at ambient conditions. The activity is much higher than that of not only bulk cobalt oxides, but also carbon supported CoO<sub>x</sub> catalysts. It could be used for more than 8 times without obvious fading in activity. In addition, the concrete role of Co-MOF precursor and pyrolysis condition in the catalyst design was investigated in detail. The interaction between organic ligands and Co ions and the confinement of the crystalline structure of Co-MOF could restrain the aggregation of Co ions during

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pyrolysis and lead to high dispersion of ultrafine  $\text{CoO}_x$  species. Meanwhile, the N-containing ligands could be transformed into doped N species (pyridinic and pyrrolic N), endowing the  $\text{CoO}_x$  species with high electron density and promoting the formation of active sites for the hydrogenation reaction.

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## 1. Introduction

Metal oxide nanoparticles with unique optical and electrical properties have received intensive attention in electrochemistry and biomedicine, and have attracted considerable and increasing interest in the field of catalysis [1–4]. Over the past two decades, noble metal-based catalysts such as Au, Pt, and Pd, have demonstrated outstanding catalytic performance for numerous important chemical reactions [5–7]. However, the high price and limited availability of these noble metals, made it desirable to search for new alternatives with more earth-abundant metals, such as Fe, Co or Ni [8–11]. So far, even though several non-noble metal-based catalysts have been successfully applied in certain transformations of selective oxidation, exhaust gas purification, or Fischer-Tropsch process [12–15], the relatively low catalytic activity under mild conditions remains as a major issue that needs to be solved. It is believed that high catalytic activity and stability could be achieved from fabricating nanostructured catalysts.

Controlling the size and morphology is regarded as an efficient strategy to tune the catalytic performance of metal oxides. As the catalytic reactions take place mainly on the surface of the catalysts, slight changes in the structure, size, or compositions, therefore, may bring fundamental influence on their catalytic performance [16–19]. Recent research demonstrated that nanoparticles with ultrafine size (<5 nm) exhibited unique redox properties compared with corresponding bulk oxides [20–22]. Reducing particle size could lead to a significant increase of surface area and the number of atoms located at either edges or corners, which will greatly improve the catalytic performance of metal oxides. However, the decrease of particle size is always accompanied by the increase of surface energy, which lowers the stability of nanostructured particles and results in aggregations in the synthesis and reaction processes [23,24]. A variety of stabilizers, including polymers, dendrimers and different types of ligands, have been used as capping agents to stabilize the nanosized particles during the synthesis process [25–27]. However, the necessary removal of the capping agents afterward by thermal treatment always imposes difficulties in controlling aggregation in this process.

Metal-organic frameworks (MOFs), a new class of porous crystalline materials, have attracted enormous attention in many fields such as gas storage/separation [28–30], catalysis [31–33], sensing and biomedical field [34–36]. Recently, MOFs with different structure and composition were widely used as both templates and/or precursors for the fabrication of porous carbon or metal-carbon composites [37–39]. MOFs derived porous materials, with high surface area and excellent stability, have been successfully applied in the field of advanced adsorption, electrochemistry and F-T synthesis [40–42]. For example, Wang and co-workers reported a new type of robust Co/C electrocatalyst through a MOF pyrolysis route. The obtained composites have high surface area and show outstanding electrochemical performance for Zn-air batteries [40]. In Zou's work, Co/CN catalysts derived from ZIF-67, with Co particles confined in carbon matrix, exhibits excellent stability and selectivity toward short-chain hydrocarbons ( $\text{C}_2$ – $\text{C}_4$ ) during Fischer-Tropsch processes [41]. Traditionally, either used as templates or precursors, these MOFs were usually thermal treated at high temperature (800 °C, for example) to increase the surface area and graphite degree of the resulting nanocomposites. Meanwhile,

aggregation of the metal particles is likely to occur via the decomposition of MOFs during high temperature pyrolysis, leading to the decrease of catalytic performance. Therefore, further efforts are still needed toward developing metal catalysts with both high activity and high stability.

In the present work, ultrafine  $\text{CoO}_x$  nanoparticles embedded into N-doped carbon ( $\text{CoO}_x/\text{CN}$ ) were synthesised using an N-containing metal-organic framework (Co-MOF) as precursor followed by a fine thermal-treatment. The  $\text{CoO}_x$  particles with an average diameter of 3 nm were homogeneously dispersed in the carbon matrix. The obtained catalyst exhibits excellent activity and stability in 4-nitrophenol (4-NP) reduction at ambient conditions. It is worth noting that the size and morphology of  $\text{CoO}_x$  particles could be maintained during the reaction process, and the catalyst could be used for more than eight times without obvious fading in activity, demonstrating a relatively high stability.

## 2. Experimental section

### 2.1. Materials and catalyst preparation

All chemical reagents of analytical grade were commercially available, and used without further purification.

The Co-MOF precursor was synthesized via a hydrothermal method. A mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2 mmol), 5,5-(quinoxaline-5,8-diyl)diisophthalate ( $\text{H}_4\text{L1}$ , 0.1 mmol), N,N-dimethyl formamide (DMF) (4 mL), ethanol (EtOH) (2 mL),  $\text{H}_2\text{O}$  (5d) and  $\text{HBF}_4$  (2d) was mixed in a 20 mL vial and heated at 65 °C for 72 h. The vial was then cooled to room temperature and the crystalline precipitate of violet prisms were collected by filtration. Crystals were washed with DMF (yield: 57.3% based on  $\text{H}_4\text{L1}$ ).  $\text{CoO}_x/\text{CN}$  catalyst was prepared by the fine-thermal treatment of the obtained Co-MOFs under mild conditions. Typically, 30 mg of precursor was loaded into a small ceramic boat and placed into a muffle furnace. Under nitrogen flow, the crystalline precursor was annealed at different temperatures for 4 h with a heating rate of 1 °C/min. The final product was obtained after the boat was cooled to room temperature.

For the sake of comparison, two other carbon materials (commercial activated carbon and ordered mesoporous carbon) were chosen as supports for the synthesis of supported cobalt oxide catalysts. The activated carbon (surface area  $372 \text{ m}^2 \text{ g}^{-1}$ ) was used without further purification. Ordered mesoporous carbon was synthesized following our group's previously reported procedure [14]. To remove residual metal species, the carbon supports were immersed in 6 M  $\text{HNO}_3$  solution and heated at 80 °C for 6 h. Carbon-supported cobalt oxide catalyst was then prepared by the wet-impregnation method. Typically, a moderate amount of carbon support was added to aqueous  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and the mixture was stirred for 3 h at room temperature. Afterward, the water was evaporated at 80 °C and the resultant solid was calcined at 500 °C for 4 h under a nitrogen atmosphere. The obtained catalysts were designated as  $\text{CoO}_x/\text{AC}$  and  $\text{CoO}_x/\text{C}$ , respectively. The loading of cobalt oxide was same to that of  $\text{CoO}_x/\text{CN}$  (calculated with Co).

### 2.2. Catalyst characterization

Transmission electron microscopy (TEM) images were taken with a FEI Tecnai F20EM with an accelerating voltage of 200 kV.

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