

# Catalytic oxidation of formaldehyde on nano-Co<sub>3</sub>O<sub>4</sub>, 2D-Co<sub>3</sub>O<sub>4</sub>, and 3D-Co<sub>3</sub>O<sub>4</sub> catalysts

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## Introduction

Formaldehyde (HCHO) emitted from the widely used building and decorative materials is becoming a major indoor pollutant in airtight buildings, and it could cause serious and hazardous effects on human health. Thus it is essential for human health to remove indoor formaldehyde [1]. Currently, the catalytic materials used in HCHO catalytic oxidation are mainly oxide-supported precious metals [2]. Noble metal catalysts are superior, but the high cost is prohibitive. Metal oxide catalysts are cheap, exhibit sufficient activity and are more practical. Co<sub>3</sub>O<sub>4</sub> is widely used in catalytic field [3], however, the Co<sub>3</sub>O<sub>4</sub> with the different structures and the same components for HCHO oxidation is seldom reported. In this work, nano-Co<sub>3</sub>O<sub>4</sub>, 2D-Co<sub>3</sub>O<sub>4</sub>, and 3D-Co<sub>3</sub>O<sub>4</sub> are prepared, and their HCHO catalytic activities are evaluated.

## Materials and Methods

SBA-15 (p6mm) and KIT-6 (ia3d) mesoporous silica were synthesized under acidic conditions using tetraethoxysilane as the silica source and Pluronic P123 as the structure-directing agent [4]. Nano-Co<sub>3</sub>O<sub>4</sub> was prepared by the precipitation method [5]. In a typical synthesis of 2D-Co<sub>3</sub>O<sub>4</sub> or 3D-Co<sub>3</sub>O<sub>4</sub>, 3.0 g of SBA-15 or KIT-6 molecular sieve was added to a Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O ethanol solution (0.84 mol/L, 30 ml). The samples were evaporated to dryness at 80 °C. The products were calcined at 200 °C for 6 h. The above steps about casting and evaporating were repeated. Finally, the materials were calcined at 450 °C for 6 h. The SBA-15 and KIT-6 hard templates were removed using a 2 mol/L NaOH solution. Centrifugal separation was used to eliminate sodium silicate, and the samples were dried at 100 °C. The obtained powder was 2D-Co<sub>3</sub>O<sub>4</sub> or 3D-Co<sub>3</sub>O<sub>4</sub>.

## Results and Discussion

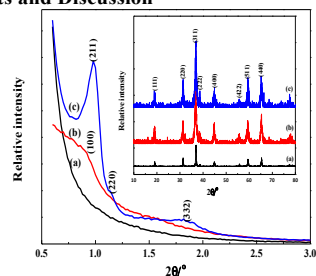


Figure 1. XRD patterns.

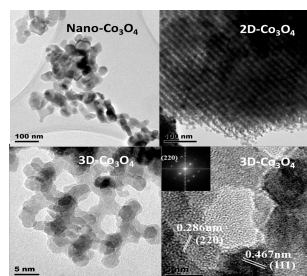


Figure 2. TEM images

Figure 1 displays that the wide-angle and low-angle XRD patterns of the Co<sub>3</sub>O<sub>4</sub> catalysts. The 3D-Co<sub>3</sub>O<sub>4</sub> catalyst showed diffraction peaks at 1°, 1.14° and 1.85° (2θ), which correspond to

the (111), (220), and (332) planes. It indicates that 3D-Co<sub>3</sub>O<sub>4</sub> is a mesoporous material with a three-dimensional porous structure (ia3d) of the KIT-6. The 2D-Co<sub>3</sub>O<sub>4</sub> had peaks at 1° (2θ) corresponding to the (100) crystal plane and demonstrating that 2D-Co<sub>3</sub>O<sub>4</sub> has the structural characteristics (p6mm) of SBA-15 mesoporous material [4]. The nano-Co<sub>3</sub>O<sub>4</sub> showed no diffraction peak because it is a non-perforated material. From the wide-angle XRD image, all catalysts possess the crystalline cobalt oxide of spinel type structure.

Figure 2 shows that the 3D-Co<sub>3</sub>O<sub>4</sub> has the (111) crystal plane and the (220) crystal plane with lattice spacing of 0.286 nm. The top left corner shows FFT of with [220] direction.

Figure 3 shows that the HCHO catalytic oxidation activities of the different Co<sub>3</sub>O<sub>4</sub> catalysts. For conversion (Figure 3A), with an increase in temperature, the nano-Co<sub>3</sub>O<sub>4</sub> catalyst displays the worst catalytic activity, completely converting HCHO at 230 °C, the 2D-Co<sub>3</sub>O<sub>4</sub> catalyst has better oxidation activity, entirely converting HCHO at 150 °C, and the 3D-Co<sub>3</sub>O<sub>4</sub> sample shows the best catalytic oxidation, entirely converting HCHO at 130 °C. The results indicate that the mesoporous materials have an advantage because of their structure. The three dimensional porous channels and the large surface area of the 3D-Co<sub>3</sub>O<sub>4</sub> is highly conducive to formaldehyde oxidation. Figure 3B shows HCHO catalytic activity of normalized by BET surface areas. It is observed that normalized activity of the 3D-Co<sub>3</sub>O<sub>4</sub> is much better than the other catalysts after deducting surface areas. The BET surface areas of the mesoporous catalysts prepared by the hard template method are much larger, especially for 3D-Co<sub>3</sub>O<sub>4</sub> (85.9 m<sup>2</sup>/g), than for the nano-Co<sub>3</sub>O<sub>4</sub> (28.1 m<sup>2</sup>/g) synthesized by the precipitation method.

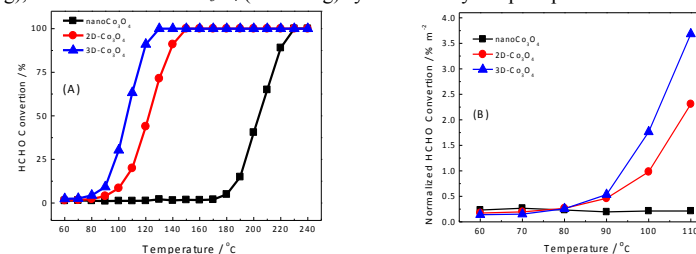


Figure 3 HCHO catalytic conversion (A) and conversion normalized by BET surface area (B) of the different Co<sub>3</sub>O<sub>4</sub> catalysts under the following conditions: HCHO concentration = 400 ppm, 20 vol % O<sub>2</sub>, N<sub>2</sub> as balance gas, GSHV = 30000 mL/(g.h).

## Significance

The 3D-Co<sub>3</sub>O<sub>4</sub> had the best performance of HCHO catalytic oxidation due to the three-dimensional porous channel structure, larger specific surface area and active Co<sup>3+</sup> cationic species on the exposed (220) crystal face. It might be a non-noble catalyst for catalytic removal of formaldehyde in practical application.

## References

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