Catalytic oxidation of formaldehyde on nano-Co$_3$O$_4$, 2D-Co$_3$O$_4$, and 3D-Co$_3$O$_4$ catalysts

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Introduction
Formaldehyde (HCHO) emitted from the widely used building and decorative materials is becoming a major indoor pollutant in airight 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$_3$O$_4$ is widely used in catalytic field [3], however, the Co$_3$O$_4$ with the different structures and the same components for HCHO oxidation is seldom reported. In this work, nano-Co$_3$O$_4$, 2D-Co$_3$O$_4$, and 3D-Co$_3$O$_4$ 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$_3$O$_4$ was prepared by the precipitation method [5]. In a typical synthesis of 2D-Co$_3$O$_4$ or 3D-Co$_3$O$_4$, 3.0 g of SBA-15 or KIT-6 molecular sieve was added to a Co(NO$_3$)$_2$·6H$_2$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 centrifugal separation were used to eliminate sodium silicate, and the samples were dried at 100 °C. The obtained powders were 2D-Co$_3$O$_4$, or 3D-Co$_3$O$_4$.

Results and Discussion

Figure 1 displays that the wide-angle and low-angle XRD patterns of the Co$_3$O$_4$ catalysts. The 3D-Co$_3$O$_4$ catalyst showed diffraction peaks at 1°, 1.14° and 1.85° (2θ), which correspond to the (211), (220), and (332) planes. It indicates that 3D-Co$_3$O$_4$ is a mesoporous material with a three-dimensional porous structure (ia3d) of the KIT-6. The 2D-Co$_3$O$_4$ had peaks at 1° (2θ) corresponding to the (100) crystal plane and demonstrating that 2D-Co$_3$O$_4$ has the structural characteristics (p6mm) of SBA-15 mesoporous material [4]. The nano-Co$_3$O$_4$ 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$_3$O$_4$ has the (111) crystal plane and the (220) crystal plane with lattice spacing of 0.286 nm. The top left corner displays 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$_3$O$_4$ is highly conducive to formaldehyde oxidation. Figure 2B shows HCHO catalytic activity of normalized by BET surface areas. It is observed that normalized activity of the 3D-Co$_3$O$_4$ 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$_3$O$_4$ (85.9 m$^2$/g), than for the nano-Co$_3$O$_4$ (28.1 m$^2$/g) synthesized by the precipitation method.

Figure 3 shows HCHO catalytic conversion (A) and conversion normalized by BET surface area (B) of the different Co$_3$O$_4$ catalysts under the following conditions: HCHO concentration = 400 ppm, 20 vol% O$_2$, N$_2$ as balance gas, GHSV = 30000 mL/(g.h).

Significance
The 3D-Co$_3$O$_4$ had the best performance of HCHO catalytic oxidation due to the three-dimensional porous channel structure, larger specific surface area and active Co$^{3+}$ cationic species on the exposed (220) crystal face. It might be a non-noble catalyst for catalytic removal of formaldehyde in practical application.

References