



Three-dimensional ordered mesoporous cobalt oxides: Highly active catalysts for the oxidation of toluene and methanol

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ABSTRACT

Three-dimensional (3D) ordered mesoporous cubic Co_3O_4 (denoted as Co-KIT6 and Co-SBA16) were fabricated adopting the KIT-6- and SBA-16-templating strategies, respectively. It is shown that Co-KIT6 and Co-SBA16 possessed large surface areas (118–121 m^2/g), high oxygen adspecies concentrations, and good low-temperature reducibility. Over Co-KIT6 at space velocity = 20,000 $\text{mL}/(\text{g h})$, 90% toluene and methanol conversions were achieved at 180 and 139 $^\circ\text{C}$, respectively. The excellent catalytic performance of Co-KIT6 and Co-SBA16 was associated with their larger surface areas, higher oxygen adspecies concentrations, better low-temperature reducibility, and 3D ordered mesoporous structure.

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1. Introduction

Volatile organic compounds (VOCs), such as toluene and methanol, are harmful to the environment. Catalytic oxidation is an effective pathway for the removal of VOCs [1]. Although supported precious metals (e.g., Pt and Pd) can catalyze the oxidation of different VOCs at lower temperatures [2], the high cost and limited availability restrict their wide applications. Therefore, it is highly desired to develop efficient and cheap catalytic materials.

Mesoporous transition metal oxides possess unique physicochemical properties, such as high surface areas and porous structures. A higher surface area can provide more active sites, whereas a porous structure facilitates the adsorption and diffusion of reactant molecules. Both factors favor the enhancement in catalytic performance. It is reported that nonporous transition metal oxides (i.e., MnO_x [3] and Co_3O_4 [4]) showed good catalytic activities in the oxidation of propane, ethanol and toluene [3,4]. Such transition metal oxides would be able to catalyze better if they were made to the three-dimensional (3D) ordered mesoporous materials with high surface areas. For example, mesoporous chromium oxide (surface area = 78 m^2/g) prepared with triblock copolymer Pluronic F127 as template showed good catalytic activity for the oxidation of toluene (toluene conversion = 65% at 85 $^\circ\text{C}$) [5]; mesoporous Co_3O_4 could oxidize propane effectively at 250 $^\circ\text{C}$ [6]. In the past several years, mesoporous cobalt oxides with surface areas of 122–151 m^2/g have

been synthesized using FDU-12-, KIT-6-, SBA-16-, and vinyl-functionalized silica-templating approaches [7,8]. The key issue of such a hard-templating process is the complete filling of the mesopores within the hard templates by the precursor solution.

Previously, our group investigated the fabrication and catalytic properties of mesoporous chromia via a novel KIT-6-templating solvent-free route, and observed excellent performance for the oxidation of toluene and ethyl acetate [9]. As an extension work, we have recently generated a series of mesoporous transition metal oxides using KIT-6 and SBA-16 as hard template. We envision that under the assistance of vacuum, the air encapsulated in the mesopores of the hard templates can be minimized and the cobalt precursor solution readily infiltrates into the mesopores of the hard templates, as a result a maximization of mesopore filling would be achieved. Here, we report the vacuum-aided hard-templating fabrication and catalytic activities of high-surface-area cobalt oxides with 3D ordered mesoporous structures for the complete oxidation of toluene and methanol.

2. Experimental

2.1. Catalyst preparation

The 3D mesoporous silicas, KIT-6 and SBA-16, were synthesized adopting the procedures described elsewhere [10,11]. In a typical synthesis of 3D ordered mesoporous Co_3O_4 catalysts, 0.75 g of the as-synthesized KIT-6 or SBA-16 powders was put in a glass tube, in which a branched open end was connected to the vacuum (70 kPa) and another open end was sealed by a funnel containing 1.00 g of Co

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(NO₃)₂·6H₂O and 5 mL of ethanol. After evacuation under vacuum for 1 h, the cobalt precursor solution was added dropwise to the KIT-6 or SBA-16 powders. After being dried at room temperature (RT) under vacuum, the obtained mixture was calcined in air at a ramp of 1 °C/min from RT to 400 °C and kept at this temperature for 3 h. The resulting powders were treated with 14 mL of 10 wt% HF aqueous solution (for the removal of KIT-6 or SBA-16), followed by filtering, washing with deionized water and absolute ethanol 3 times, and drying in air at 60 °C overnight. The as-obtained mesoporous Co₃O₄ catalysts were denoted as Co-KIT6 and Co-SBA16, respectively. It is worth pointing out that cobalt nitrate usually decomposes at 110 °C and can be totally converted to Co₃O₄ below 300 °C [12]. In order to maintain a higher surface area and satisfactory crystal structure, we prepared the Co-KIT6 and Co-SBA16 catalysts at a calcination temperature of 400 °C. For comparison purposes, a bulk Co₃O₄ (denoted as *bulk-Co*) catalyst was also prepared by calcining cobalt nitrate in air at 400 °C for 3 h.

All of the chemicals were of analytical grade (Beijing Chem. Co.) and used without further purification.

2.2. Catalyst characterization

The as-obtained materials were characterized by means of the XRD, HRTEM/SAED, BET, TPR, and XPS techniques. The detailed procedures were described in the [Supplementary data](#).

2.3. Catalytic evaluation

Catalytic activity evaluation was carried out in a quartz fixed-bed micro-reactor (i.d. = 4 mm). The reactant gas mixture was composed of 1000 ppm VOC (toluene or methanol), oxygen, and nitrogen (balance), and the VOC/O₂ molar ratio was 1:20. About 0.1 g of the catalyst (40–60 mesh) was diluted with 0.5 g of quartz sands (40–60 mesh) to avoid the occurrence of hotspots, and the space velocity (SV) was 20,000 mL/(g h). The product gas mixture was analyzed on-line by a gas chromatograph (Shimadzu GC-14C) equipped with a TCD using a Chromosorb 101 column for VOC separation and a Carboxen 1000 column for permanent gas separation. The balance of carbon in each run was estimated to be around 99.5%.

3. Results and discussion

3.1. Crystal and pore structure

By comparing the XRD pattern of the standard cobalt oxide sample (JCPDS PDF# 74-1657), one can realize that the Co-KIT6 and Co-SBA16 catalysts were cubic Co₃O₄ in crystal structure. All of the Bragg diffraction peaks can be well indexed, as indicated in [Fig. S1A\(b\)](#) (see [Supplementary data](#)). The appearance of a weak signal at $2\theta = \text{ca. } 1^\circ$ for Co-KIT6 or Co-SBA16 in the small-angle XRD patterns ([Fig. S1B](#)) indicates the formation of ordered mesoporous structure. Similar results were also reported by other researchers [7,8].

The KIT-6 and SBA-16 templates possessed 3D ordered mesoporous structures and narrow pore size distributions ([Fig. S2 of the Supplementary data](#)). [Fig. 1](#) shows the N₂ adsorption–desorption isotherms and pore size distributions of the Co-KIT6 and Co-SBA16 catalysts. It is observed that there was a H2 type hysteresis loop in the p/p_0 range of 0.45–0.95 for the Co-KIT6 catalyst and in the p/p_0 range of 0.50–0.90 for the Co-SBA16 catalyst. The IV-typed isotherms suggest the presence of mesopores in the two Co₃O₄ catalysts. Such a deduction was confirmed by the results of pore size distribution measurements (inset of [Fig. 1](#)). There were two peaks centered at pore size = 2.7 and 9.3 nm for the Co-KIT6 catalyst and those centered at pore size = 3.1 and 12.6 nm for the Co-SBA16 catalyst, respectively. This result indicates the formation of dual mesopores. A similar isotherm has also been observed for mesoporous Co₃O₄ [13]. The

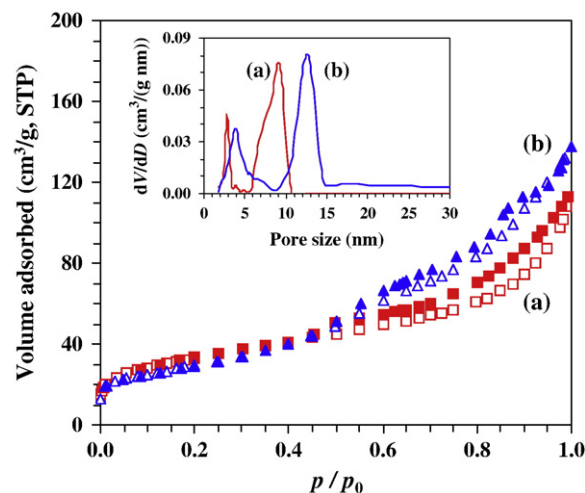


Fig. 1. N₂ adsorption–desorption isotherms and pore size distributions (inset) of (a) Co-KIT6, and (b) Co-SBA16.

textural parameters of the as-prepared catalysts are summarized in [Table 1](#). It is observed that Co-KIT6 and Co-SBA16 possessed similar surface areas (118–121 m²/g), average pore sizes (6.2–6.5 nm), and pore volumes (0.17–0.19 cm³/g). The surface areas of our mesoporous Co₃O₄ were much higher than those of *bulk-Co* (10 m²/g) and Co₃O₄ (98 m²/g) obtained after calcination at 500 °C [13]. It is known that a higher calcination temperature results in a lower surface area of a material. It should be noted that the use of vacuum treatment was beneficial for the improvement in surface area because such a treatment might favor the full filling of the mesopores in KIT-6 by cobalt nitrate, so that a better ordered mesoporous architecture could be obtained.

[Fig. 2](#) shows the HRTEM images of Co-KIT6 and Co-SBA16. It is clearly observed that there were a number of cobalt oxide entities with 3D ordered mesopores, and the pore size was in the range of 4–10 nm for Co-KIT6 ([Fig. 2a](#)) and 3–15 nm for Co-SBA16 ([Fig. 2b](#)). The 3D ordered mesopores and their walls of Co₃O₄ were formed due to the removal of silica in the walls of KIT-6 (or SBA-16) and the decomposition of cobalt nitrate filled in the mesopores of KIT-6 (or SBA-16) during calcination, respectively. Similar nanocasting methods have also been utilized to fabricate mesoporous chromia [5]. From the additional HRTEM images as well as the SAED patterns of Co-KIT6 and Co-SBA16 shown in [Fig. S3](#) ([Supplementary data](#)), one can realize that the mesopore walls of Co-KIT6 and Co-SBA16 were polycrystalline Co₃O₄.

3.2. Surface composition and reducibility

XPS is an effective technique to investigate the surface element compositions and surface species of a solid catalyst. [Fig. 3a'–c'](#) shows the Co 2p_{3/2} XPS spectra of the as-fabricated samples. The asymmetrical Co 2p_{3/2} signal of each catalyst could be decomposed to two components at binding energy (BE) = 779.8 and 782.1 eV, ascribable to Co³⁺ and Co²⁺ [14], respectively. The recording of a weak signal at BE = 789.8 eV indicates the presence of Co²⁺ ([Fig. S4 of the Supplementary data](#)). Quantitative analyses of the Co 2p_{3/2} XPS

Table 1
Textural parameters of the as-fabricated cobalt oxide catalysts.

Catalyst	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
Co-KIT6	121	6.2	0.19
Co-SBA16	118	6.5	0.17
<i>bulk-Co</i>	10	–	–

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