



# Cobalt-aluminum mixed oxides prepared from layered double hydroxides for the total oxidation of benzene

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## ABSTRACT

A series of Co-Al mixed oxides were prepared by co-precipitation method via Co-Al layered double hydroxides (LDHs) as precursors. The influence of chemical compositions of Co-Al LDHs on the structural and physicochemical properties of Co-Al mixed oxides as well as their catalytic performance for benzene total oxidation was investigated. The samples were characterized by using ICP, N<sub>2</sub> physical adsorption, XRD, TG-DTA, SEM, TEM, Raman, H<sub>2</sub>-TPR, and XPS techniques. The characterization results showed that calcination of Co-Al LDHs gave rise to Co(Co, Al)<sub>2</sub>O<sub>4</sub> spinel-like mixed oxide as the main phase. The crystallite size of Co(Co, Al)<sub>2</sub>O<sub>4</sub> spinel (6~19 nm) decreased with decreasing the Co/Al molar ratio, suggesting the inhibition of crystal growth by the incorporation of Al<sup>3+</sup> ions in the spinel phase. A drastic change in the state of Co-Al mixed oxide occurred at Co/Al=6, as indicated by H<sub>2</sub>-TPR and XPS. In benzene total oxidation, the activity of Co-Al mixed oxide increased with increasing the Co/Al molar ratio, with the highest activity at Co/Al=5; further increase in the Co/Al molar ratio to 6 led to significant decrease in the activity, properly caused by the change of surface state of mixed oxide. The 50 h long-term stability test revealed that the optimized Co-Al mixed oxide was stable for the total oxidation of benzene.

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## 1. Introduction

Volatile organic compounds (VOCs) are recognized as the major components responsible for the increase in global air pollution due to their contribution to ozone and photochemical smog [1]. Among the various methods employed for VOCs removal, catalytic oxidation is considered as one of the most efficient methods, which can destroy pollutants totally to carbon dioxide and water at relatively low temperatures (e.g. <423 K). So far, many kinds of catalysts including supported noble metals such as Au, Pt, and Pd, transition metal oxides (AB<sub>2</sub>O<sub>4</sub>), and perovskite-type oxides (ABO<sub>3</sub>), have been investigated for the combustion of VOCs [2,3]. Supported Pt and Pd catalysts are currently the most active for the VOCs combustion. However, high cost and low availability of noble metals limit their wide applications. Among transition metal oxides, cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) and its mixed oxides appear as one of the most efficient catalysts for the VOCs combustion [4–11]. Recently, Co<sub>3</sub>O<sub>4</sub> has also received great interest for the applications in catalytic oxidation of CO [12] and CH<sub>4</sub> [13] due to its high activity at low tem-

peratures, e.g., 100% conversion at –196 K for CO oxidation, and 50% conversion at 586 K for CH<sub>4</sub> combustion.

Generally, Co<sub>3</sub>O<sub>4</sub> was prepared by thermal decomposition of cobalt precursors such as Co(NO<sub>3</sub>)<sub>2</sub> [14], Co(OH)<sub>2</sub> [13], Co(CO<sub>3</sub>)<sub>0.5</sub>(OH)·0.11H<sub>2</sub>O [12,13], CoC<sub>2</sub>O<sub>4</sub> [15], and CoO(OH) [16], and Co<sub>3</sub>O<sub>4</sub> with different morphologies or structures such as nanoparticles, nanorods, nanocubes, nanotubes, and mesoporous structures has been reported to show different activities. On the other hand, layered double hydroxides (LDHs) have attracted much attention as an effective precursor of mixed metal oxides due to their versatility and unique structural properties. LDHs, also known as hydrotalcite-like compounds (HTLcs), is anionic clay that consists of positively charged two-dimensional brucite-like sheets in which a fraction of the divalent cations are isomorphously substituted by trivalent cations, together with charge-compensating anions and water in the interlayer [17]. The formula of LDHs can be expressed as [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup><sub>x/n</sub>)·mH<sub>2</sub>O, where M<sup>2+</sup> = Mg<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, M<sup>3+</sup> = Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, and A<sup>n-</sup> = CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, etc. Upon calcination, LDHs form mixed oxides that show several interesting properties such as high dispersion, good thermal stability, large surface area, and basic character, which make them to be promising catalysts or supports [17]. Many reports have contributed to the synthesis, characterization, and catalytic applications of Co-containing LDHs. For example, Co-Al LDHs-derived

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cobalt-aluminum mixed oxides are reported to be active for CO oxidation [18], N<sub>2</sub>O decomposition [19,20], removal of NO<sub>x</sub> and soot particles [21], as well as aldol condensation of furfural with acetone and self-condensation of acetone [22]. However, the structural properties of the LDHs-derived Co-Al mixed oxides are not well studied and as far as we know, their application in VOCs total oxidation has not yet been reported.

In the present work, we report details on the preparation of cobalt-aluminum mixed oxides using Co-Al LDHs as precursors and their potential application in VOCs total oxidation. Particularly, the influence of chemical composition of Co-Al LDHs on the structure and catalytic performance of Co-Al mixed oxides were investigated. The as-synthesized precursors and the resulting Co-Al mixed oxides were characterized by various techniques including ICP, N<sub>2</sub> physical adsorption, TG-DTA, XRD, SEM, TEM, Raman, H<sub>2</sub>-TPR, and XPS, and tested for the total oxidation of benzene as a model compound of VOCs.

## 2. Experimental

### 2.1. Catalyst preparation

Co-Al LDHs were prepared by co-precipitation method [23]. Typically, an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was dropwise added into a beaker containing an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> under stirring at room temperature and a constant pH of 10 ± 0.5. The pH of the solution was adjusted with an aqueous solution of NaOH (2 M). The resulting suspension was kept at room temperature for 24 h. The resulting precipitate was filtered, washed several times with de-ionized water, and dried at 373 K for 12 h. The precipitate was ground to fine powders and then calcined at 773 K for 5 h in a static air atmosphere. The obtained material was pressed to a disk, then crushed and sieved to particles with 30–60 mesh size (0.3–0.6 mm diameter). The as-synthesized precursors and their calcined products are denoted as CoxAl-LDHs and CoxAl, respectively, where *x* is the Co/Al molar ratio (*x* = 1 ~ 6).

### 2.2. Catalyst characterizations

The metal contents in each precursor were determined by inductively coupled plasma (ICP) after the sample was completely dissolved using nitro-hydrochloric acid. The ICP measurements were carried out using OPTIMA 8000 (PerkinElmer).

N<sub>2</sub> physical adsorption was conducted at 77 K on a Micromeritics ASAP 2020 instrument. The sample was pretreated at 453 K for 4 h in vacuum before N<sub>2</sub> adsorption. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore diameter distribution was evaluated by the Barret–Joiner–Halenda (BJH) method.

Thermogravimetric and differential thermal analysis (TG-DTA) profiles were recorded with PerkinElmer TG and DTA analyzers (TG-7, DTA-7) over ~5 mg of sample under an air flow (30 mL min<sup>-1</sup>) and from ambient temperature to 1073 K at a heating rate of 10 K min<sup>-1</sup>.

Powder X-ray diffraction (XRD) patterns were measured with a PANalytical X'PertPro diffractometer using Co Kα radiation (λ = 0.179 nm) generated at 40 kV and 40 mA. The diffraction pattern was identified by comparison with those included in the Joint Committee of Powder Diffraction Standards (JCPDS) data base. The particle size of spinel was calculated from the Scherrer equation:  $d = K\lambda/\beta\cos\theta$ , where β is the full width at half maximum, *K* = 0.94, and λ = 0.179 nm.

Field emission scanning electron microscopy (FE-SEM) measurements were conducted using Hitachi-S4800 equipment

operated at 5.0 kV. Transmission electron microscopy (TEM) measurement was performed on a FEI-Tecnai G2F20 field emission transmission electron microscope operated at 200 kV.

Temperature-programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) was performed on a Micromeritics AutoChem2910 instrument equipped with a thermal conductivity detector (TCD). Typically, 50 mg of the sample was first pre-treated in a quartz reactor at 573 K for 0.5 h with an Ar gas flow (30 mL min<sup>-1</sup>). After the sample was cooled to room temperature, a 5.0% H<sub>2</sub>-Ar mixture (30 mL min<sup>-1</sup>) was introduced into the reactor, and the temperature was raised to 1173 K at a rate of 10 K min<sup>-1</sup>.

Laser Raman spectra were recorded by using a Renishaw inVia Reflex Raman spectrometer from 1000 to 100 cm<sup>-1</sup> at room temperature. The excitation source was the 514.5 nm line of Ar ion laser.

X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 spectrometer (Thermo Scientific) using Al Kα radiation (1486.8 eV) generated at 120 W. All binding energies (BE) were calibrated with respect to the C1s peak (BE = 284.6 eV) arising from adventitious carbon.

### 2.3. Catalytic reaction

Benzene total oxidation was conducted on a continuous-flow fixed-bed reactor in a gas mixture of 516 ppm C<sub>6</sub>H<sub>6</sub>/21%O<sub>2</sub>/N<sub>2</sub>(balance). A U-shaped quartz tube reactor (8 mm inner diameter) was used and 100 mg of catalyst was loaded. The flow rate of the reactant gas was controlled with an electronic flow meter and kept at 60 mL min<sup>-1</sup>, which corresponded to a space velocity of 36,000 mL g<sup>-1</sup> h<sup>-1</sup>. The operation temperature was controlled with a thermocouple placed in the heating oven, and the reaction temperature was measured with a second thermocouple located in the catalyst bed. For a light-off test, the operation temperature was increased from room temperature to 773 K at a heating rate of 3 K min<sup>-1</sup>. The concentration of benzene in the effluent gas was analyzed with an online FID-gas chromatography. The conversion of benzene was calculated by the equation: benzene conversion (%) =  $([C_6H_6]_{in} - [C_6H_6]_{out})/[C_6H_6]_{in} \times 100\%$ , where [C<sub>6</sub>H<sub>6</sub>]<sub>in</sub> and [C<sub>6</sub>H<sub>6</sub>]<sub>out</sub> are the concentrations of benzene in the feed and effluent gas, respectively. The experimental error in conversion data was estimated to be ±1%. To investigate the catalyst stability, a long-time test was carried out at 573 K and 773 K for 50 h.

## 3. Results and discussion

### 3.1. Characterization of the as-synthesized Co-Al LDHs

#### 3.1.1. Morphology and chemical composition analysis

The SEM images of the as-synthesized precursors showed a tiny plate-like shape characteristic of LDHs (Supporting information, Fig. S1). The thickness of LDHs plates was estimated to be 10 ~ 20 nm. The metal compositions of the as-synthesized precursors measured by ICP analysis are listed in Table 1. The measured Co/Al molar ratios are similar to the nominal values of the starting materials within experimental errors, suggesting that both Co and Al cations were approximately completely precipitated under the present precipitation conditions.

#### 3.1.2. XRD measurement

Fig. 1A shows the XRD patterns of the as-synthesized Co-Al LDHs. The characteristic diffraction peaks of LDHs with a rhombohedral symmetry (3R) were observed in all precursors. The diffraction peaks at 2θ = 13.7°, 27.4°, 40.7°, 46.5°, 55.4°, 71.9°, and 73.6° could be indexed to (003), (006), (012), (015), (018), (110), and (113), respectively. No other diffraction peaks of impurities

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