



Short communication

Preparation of cobalt-copper-aluminum spinel mixed oxides from layered double hydroxides for total oxidation of benzene



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ABSTRACT

Mixed metal oxides $\text{Co}_{5-x}\text{Cu}_x\text{Al}$ ($x = 0-0.5$) were prepared from Co-Cu-Al layered double hydroxides (LDHs) and tested for benzene total oxidation. By calcination, Co-Cu-Al LDHs were mainly transformed to $(\text{Co}, \text{Cu})(\text{Co}, \text{Al})_2\text{O}_4$ spinels, where both Cu^{2+} and Al^{3+} cations were incorporated into the spinel structure. The incorporation of Cu significantly improved the Co oxide reducibility and remarkably enhanced the light-off activity as well as the total conversion activity, indicative a strong interaction between Cu^{2+} and Co^{3+} active sites. The optimum $\text{Co}_{4.75}\text{Cu}_{0.25}\text{Al}$ spinel mixed oxide was comparable with a 0.3%Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, highlighting the promoting effect of structural modification with Cu.

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1. Introduction

Volatile organic compounds (VOCs) are recognized as the major components in air pollutants because of their toxicity to human health and their contribution to the formation of ozone and photochemical smog. Catalytic combustion is one of the most effective and economically feasible techniques for VOCs removal and great efforts have been made on the development of efficient catalysts [1,2]. Generally, noble metals such as Pt and Pd show good low-temperature activity for the total oxidation of VOCs, but their industrial application is greatly limited due to the high cost and low availability of noble metals. Thus, non-precious transition metal oxide catalysts have attracted much attention. Among the transition metal oxides, Co_3O_4 spinel has been shown to be an efficient catalyst for the total oxidation of VOCs [3–8]. However, in most cases, the activity of transition metal oxides is lower than that of noble metal catalysts. Therefore, the development of transition metal oxide catalyst with improved activity is highly desired.

Using layered double hydroxides (LDHs) as precursor has been proved to be an effective way for the preparation of mixed metal oxides [9–13]. LDHs, also known as hydrotalcite-like compounds (HTLcs), are a class of two-dimensional anionic clays consisting of positively charged brucite-like layers and charge-compensating interlayer anions, which can be expressed by the formula $[\text{M}^{2+}_1 - x\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. One attractive feature of LDHs is that upon calcination they are converted to mixed metal oxides (MMOs), which exhibit several interesting properties such as high surface area, small crystal size, good thermal

stability, and basic character. Another attractive feature of LDHs is their versatility in chemical composition, which enables the preparation of various mixed metal oxides with tunable composition and structure. In a previous study [13], we prepared a series of Co-Al mixed oxides from Co-Al LDHs and found that Al^{3+} cations could be incorporated into the Co_3O_4 structure, which significantly modified the physico-chemical property and the catalytic performance for the total oxidation of benzene. Herein, we report the preparation of Cu substituted Co-Al spinel mixed oxides from Co-Cu-Al LDHs. It was found that the incorporation of Cu^{2+} cations into the Co-Al spinel effectively enhanced the Co oxide reducibility and the catalytic activity for the total oxidation of benzene.

2. Experimental

2.1. Catalyst preparation

Co-Cu-Al LDHs were synthesized by co-precipitation method [13]. Typically, an 100 mL aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (molar ratio of Co: Cu: Al was 5:0:1–4.5:0.5:1) was dropwise added into a beaker containing an 100 mL aqueous solution of Na_2CO_3 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 precipitates were filtered, washed with 1 L de-ionized water to remove Na^+ ions, and dried at 373 K for 12 h. The precipitate was calcined at 773 K for 5 h in a static air atmosphere, then crushed and sieved to particles with 30–60 mesh size (0.3–0.6 mm diameter). The prepared samples are denoted as $\text{Co}_{5-x}\text{Cu}_x\text{Al}$, where x is the relative molar ratio of Cu to Co and Al

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($x = 0-0.5$). For comparison, a Pd/ γ -Al₂O₃ catalyst was prepared by impregnation method using Pd(NO₃)₂ precursor, followed by calcination at 773 K for 3 h. γ -Al₂O₃ was obtained by precipitation of Al(NO₃)₃·9H₂O solution with 25% NH₃·H₂O precipitant, followed by calcination at 873 K for 3 h. The Pd loading measured by ICP was approximately 3 wt%.

2.2. Catalyst characterizations

Inductively coupled plasma (ICP) was conducted on OPTIMA 8000 (PerkinElmer) after the sample was completely dissolved using nitrohydrochloric acid. Powder X-ray diffraction (XRD) patterns were measured with a PANalytical X'PertPro diffractometer using Co K α radiation ($\lambda = 0.179$ nm) generated at 40 kV and 40 mA. N₂ physical adsorption was conducted at 77 K on a Micromeritics ASAP 2020 instrument after the sample was pretreated at 453 K for 4 h in vacuum. H₂ temperature-programmed reduction (H₂-TPR) was performed on a Micromeritics AutoChem2910 instrument equipped with a thermal conductivity detector. Typically, 50 mg of sample was used and the H₂-TPR profile was recorded in a 5.0% H₂/Ar gas flow (30 mL min⁻¹) from ambient temperature to 1173 K at a heating rate of 10 K min⁻¹.

2.3. Catalytic reaction

Benzene total oxidation was conducted on a continuous-flow fixed-bed reactor. A U-shaped quartz tube reactor (8 mm inner diameter) was used and 100 mg of catalyst was loaded. All catalysts including 0.3%Pd/ γ -Al₂O₃ were used in the calcined state without any further pretreatment. The composition of reactant gas was 516 ppm C₆H₆/21%O₂/N₂ and the flow rate was 60 mL min⁻¹, corresponding to a space velocity of 36,000 mL g⁻¹ h⁻¹. For the activity test, the reaction temperature was increased from room temperature to 773 K at a heating rate of 3 K min⁻¹. The concentration of benzene in the effluent gas was analyzed by a GC9560 gas chromatography (Shanghai Huaai Chromatography Analysis Co., Ltd.) equipped with a flame ionic detector (FID) and a polydimethylsiloxane (SE-30) capillary column.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized precursors and the actual molar ratio of Co:Cu:Al determined by ICP analysis is listed in Table 1. It is shown that the actual metal composition was similar to the nominal value, indicating that Co²⁺, Cu²⁺, and Al³⁺ cations were almost completely precipitated. By the way, only a small amount of Na⁺ (<0.1 wt%) was detected in the precursors. As can be seen

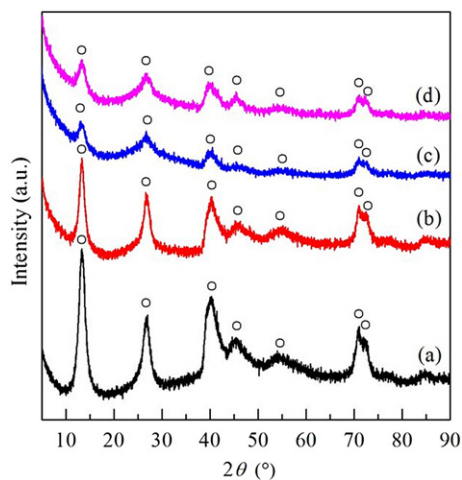


Fig. 1. XRD patterns of Co-Cu-Al LDHs precursors: (a) Co₅Al LDH, (b) Co_{4.9}Cu_{0.1}Al LDH, (c) Co_{4.75}Cu_{0.25}Al LDH, and (d) Co_{4.5}Cu_{0.5}Al LDH. Crystalline phase: (○) LDH.

Table 1
Property of the catalysts.

Catalyst	Molar ratio ^a			BET surface area (m ² ·g ⁻¹)	Crystallite size of spinel (nm) ^b	Reaction temperature (K) ^c		
	Co	Cu	Al			T ₅₀	T ₉₀	T ₉₉
Co ₅ Al	4.9	–	1	63.0	19.3	514	591	766
Co _{4.9} Cu _{0.1} Al	4.8	0.11	1	54.1	16.4	490	533	600
Co _{4.75} Cu _{0.25} Al	4.7	0.24	1	66.1	13.5	477	519	579
Co _{4.5} Cu _{0.5} Al	4.4	0.51	1	63.1	11.9	498	535	579
0.3%Pd/ γ -Al ₂ O ₃	–	–	–	169.8	–	499	537	562

^a Calculated from the result of ICP analysis on the as-synthesized precursors.

^b Calculated from the full width at half maximum of the diffraction peak at $2\theta = 43.1^\circ$ in the XRD (Fig. 2) by the Scherrer equation.

^c The temperatures at which 50%, 90%, and 99% conversions of benzene were achieved (Fig. 5).

from the XRD patterns, all precursors exhibited the characteristic diffraction peaks of LDHs structure, and no other diffraction peaks of impurities such as Al(OH)₃, Co(OH)₂, or Cu(OH)₂ were observed, suggesting the formation of a pure LDH phase. By replacing a part of Co²⁺ with Cu²⁺, the intensity of diffraction peaks of LDHs decreased remarkably, indicating a decreased crystallinity of LDHs. This was probably due to the structural disorder caused by the Jahn-Teller effect of Cu²⁺ [9]. Owing to the Jahn-Teller effect, Cu²⁺ forms LDHs only when a second bivalent metal cation M(II) is presented and the Cu²⁺/M(II) ratio must be equal or lower than one [9]. Considering the lower amount of Cu²⁺ than Co²⁺, it is reasonable to consider that Cu²⁺ cations were incorporated into the LDH structure to form Co-Cu-Al LDHs.

Fig. 2 shows the XRD patterns of Co-Cu-Al mixed oxides obtained by calcination of the Co-Cu-Al LDHs at 773 K. Upon calcination, the LDHs diffraction peaks completely disappeared, and the diffraction peaks of spinel appeared. For the Co₅Al sample, the spinel could be assigned to Co²⁺(Co³⁺, Al³⁺)₂O₄ formed by the dissolution of Al³⁺ cations into the Co₃O₄ spinel structure [13]. It is worth noting that at low Cu contents ($x \leq 0.25$) no diffraction peaks associated with Cu-containing phase were observed, suggesting that Cu²⁺ cations were highly dispersed. A detailed comparison of the strongest peak at $2\theta = 43.1^\circ$ showed that the diffraction peak became broader and slightly shifted to lower angles by the presence of Cu. It was thus considered that Cu²⁺ cations were incorporated into the spinel structure to form a (Co²⁺, Cu²⁺)(Co³⁺, Al³⁺)₂O₄-like spinel. This consideration was in part supported by the significant change in Co oxide reducibility as revealed by H₂-TPR (*vide infra*). Actually, the formation of CuCo₂O₄ spinel was reported [14]. However, at high Cu content ($x = 0.5$), additional

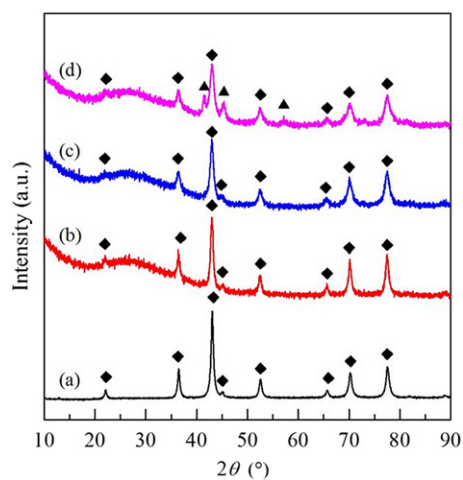


Fig. 2. XRD patterns of Co-Cu-Al mixed oxides: (a) Co₅Al, (b) Co_{4.9}Cu_{0.1}Al, (c) Co_{4.75}Cu_{0.25}Al, and (d) Co_{4.5}Cu_{0.5}Al. Crystalline phase: (◆) spinel, (▲) CuO.

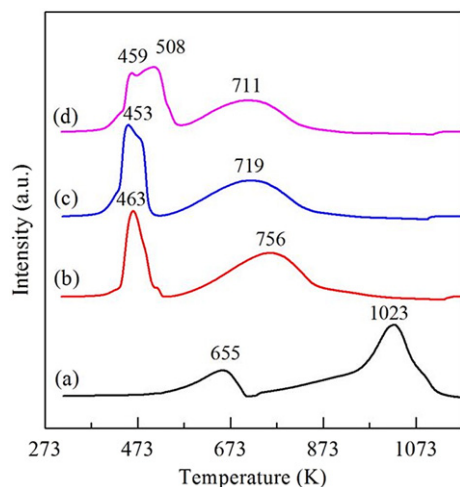


Fig. 3. H_2 -TPR profiles of Co-Cu-Al mixed oxides: (a) Co_5Al , (b) $Co_{4.9}Cu_{0.1}Al$, (c) $Co_{4.75}Cu_{0.25}Al$, and (d) $Co_{4.5}Cu_{0.5}Al$.

peaks due to CuO (JCPDS 48-1548) were observed. This result might suggest that there existed an upper limit of Cu content which could be incorporated inside the spinel framework. The crystallite size of spinel calculated by the Scherrer equation is listed in Table 1. There was a tendency that the spinel crystallite size decreased with increasing the Cu content, and this was probably caused by the incorporation of Cu^{2+} cations into the spinel structure, similar to the effect of Al^{3+} incorporation into Co_3O_4 [13]. The BET surface areas of the samples are listed in Table 1, which were similar in the absence and presence of Cu, suggesting no significant effect of Cu addition on the textural property.

Fig. 3 shows the H_2 -TPR profiles of Co-Cu-Al mixed oxides. It is found that the H_2 -TPR behavior of the Co-Cu-Al mixed oxides was changed remarkably by the presence of Cu^{2+} . The Co_5Al sample showed two H_2 consumption peaks at 655 K and 1023 K, while the reduction peaks were significantly shifted to lower temperatures for the Co-Cu-Al samples. By the addition of a small amount of Cu ($x = 0.1$), the reduction peaks were shifted to 463 K and 756 K, which were 192 K and 267 K lower than those of Co_5Al . The reduction peaks continued to move to 453 K and 719 K with the increase of Cu content ($x = 0.25$) and changed slightly at higher Cu content ($x = 0.5$). It is noted that there appeared another reduction peak at 508 K at $x = 0.5$. To identify the nature of these reduction peaks, the samples were reduced with H_2 at 513–

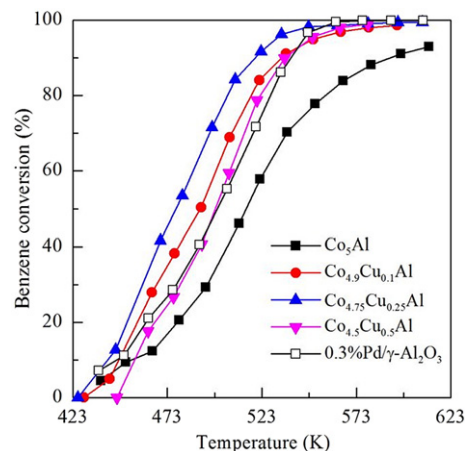


Fig. 5. Catalytic activities of Co-Cu-Al mixed oxides for benzene total oxidation.

773 K for 0.5 h, followed by XRD measurement to monitor the change of crystalline structure (Fig. 4A). The reduction temperature was chosen based on the end temperature of the low-temperature reduction peak as indicated in Fig. 4A. For reference, the XRD patterns of the Co-Cu-Al mixed oxides after H_2 -TPR were also measured (Fig. 4B). After the reduction treatment, the spinel phase completely disappeared, and alternatively a CoO-like phase was detected together with a fraction of metallic Co and/or Cu. After H_2 -TPR, the CoO-like phase was mostly converted to metallic Co. Based on these results, the low-temperature and high-temperature peaks for Co_5Al could be mainly assigned to the reduction of Co^{3+} in $Co(Co, Al)_2O_4$ spinel to form $Co(Al)O$ solid solution and the reduction of $Co(Al)O$ solid solution to metallic Co, respectively [13]. In the case of Co-Cu-Al samples, the presence of CoO-like phase and metallic Cu after the reduction treatment suggested that the low temperature peak might be due to the co-reduction of Co^{3+} and Cu^{2+} in $(Co, Cu)(Co, Al)_2O_4$ spinel to $Co(Al)O$ and metallic Cu. On the other hand, the peak at 508 K could be assigned to the reduction of bulk CuO. From the H_2 -TPR result, it was clear that the presence of Cu significantly improved the Co oxide reducibility, indicating a strong interaction between Co^{3+}/Co^{2+} and Cu^{2+} species. This property was expected to affect the catalytic performance.

Fig. 5 shows the catalytic activities of Co-Cu-Al MMOs for the total oxidation of benzene. The temperatures for 50%, 90% and 99% benzene conversions (T_{50} , T_{90} , T_{99}) are listed in Table 1. It was found that the

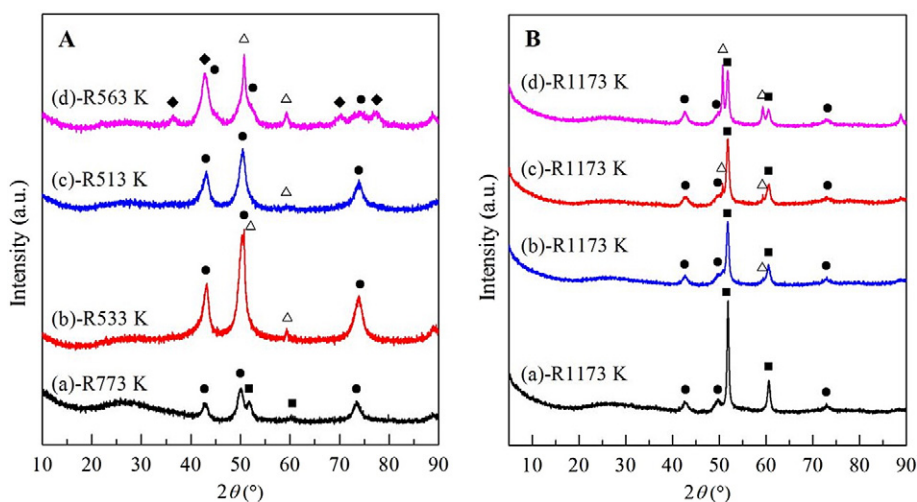


Fig. 4. XRD patterns of samples reduced at low temperature (A) and after H_2 -TPR (B): (a) Co_5Al , (b) $Co_{4.9}Cu_{0.1}Al$, (c) $Co_{4.75}Cu_{0.25}Al$, and (d) $Co_{4.5}Cu_{0.5}Al$. Crystalline phases: (●) $Co(Al)O$, (■) metallic Co, (Δ) metallic Cu, and (◆) spinel. Low-temperature reduction treatment: H_2 30 mL min^{-1} , from ambient temperature to 513–773 K by 10 K min^{-1} and kept for 0.5 h at the final reduction temperature (marked in Fig. 4A).

activity of Co-Cu-Al MMOs increased with increasing the Cu content from $x = 0$ to 0.25 and then decreased with further increasing the Cu content; the highest activity was achieved on $\text{Co}_{4.75}\text{Cu}_{0.25}\text{Al}$. As shown in Table 1, the light-off temperature (T_{50}) for $\text{Co}_{4.75}\text{Cu}_{0.25}\text{Al}$ was approximately 37 K lower than that for Co_5Al . The temperature difference was more significant in the high-conversion region. The difference of T_{90} between the two catalysts was increased to 72 K, and the difference of T_{99} even reached as high as 187 K, indicating a good enhancement in the total conversion activity by the presence of Cu. For comparison, the catalytic activity of 0.3%Pd/ γ - Al_2O_3 was also tested, which showed the T_{50} , T_{90} , and T_{99} at 499 K, 537 K, and 562 K, respectively. The light-off activity of $\text{Co}_{4.75}\text{Cu}_{0.25}\text{Al}$ was slightly higher than that of 0.3%Pd/ γ - Al_2O_3 , and their total conversion activities were comparable, highlighting the promoting effect of structural modification with Cu. It is widely believed that Co^{3+} species in Co_3O_4 are the active sites for the catalytic total oxidation of CO, CH_4 , and VOCs, and the reducibility of Co^{3+} species is an important factor for determining the catalytic activity via $\text{Co}^{3+} \leftrightarrow \text{Co}^{2+}$ redox cycle [6,7,15,16]. In this work, Cu^{2+} cations were incorporated into the Co-Al spinel and effectively improved the Co^{3+} reducibility, which was expected to accelerate the $\text{Co}^{3+} \leftrightarrow \text{Co}^{2+}$ redox cycle and enhance the catalytic activity. Nevertheless, the excess addition of Cu led to the separation of a quite large part of Cu from the spinel to form bulk CuO, which would reduce the number of Co^{3+} active sites (since more Co^{2+} would be required to form a spinel structure) and weaken the interaction between Co^{3+} and Cu^{2+} , resulting in decreased activity.

4. Conclusions

The structural and catalytic properties of $\text{Co}_{5-x}\text{Cu}_x\text{Al}$ mixed oxides changed significantly with Cu content. At low Cu content ($x \leq 0.25$), both Cu^{2+} and Al^{3+} cations were incorporated into the Co_3O_4 structure to form (Co, Cu)(Co, Al) $_2\text{O}_4$ spinel. At higher Cu content, excess Cu separated from the spinel to form bulk CuO. The Co oxide reducibility was significantly improved by the presence of Cu, suggesting a strong interaction between $\text{Co}^{3+}/\text{Co}^{2+}$ and Cu^{2+} species. The catalytic activity of Co-Al spinel was enhanced by the presence of a small amount of Cu ($x \leq 0.25$), while excess Cu addition decreased the catalytic activity. The enhanced activity might be related to the improved reducibility of Co^{3+} active species.

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