Enhanced formaldehyde-removal over modified cryptomelane catalysts

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Abstract. M-OMS-2 materials (M = K⁺, Cu²⁺, Co²⁺) were prepared by an uncomplicated reflux method, and the cryptomelane crystalline structure was confirmed by X-ray diffraction patterns. Element analysis recorded ~56 - ~59 wt.% of Mn in the three synthesized samples and ~2.8 wt.% loadings of dopants over Co-OMS-2 and Cu-OMS-2 materials. A titration method valued the average oxidation states of manganese at 3.60, 3.71 and 3.77 for K-OMS-2, Co-OMS-2 and Cu-OMS-2, respectively. In comparison with K-OMS-2, Co and Cu dopants depicted a significant enhancement catalytic activity in removal of formaldehyde at low (5%) and high (65%) relative humidity (RH). Cu-OMS-2 showed the highest catalyst performance with ~90% of formaldehyde conversion at 150 °C, 65% RH, whereas only ~40% (for Co-OMS-2) and ~26% (for K-OMS-2) of that were observed. The finding results promised a potential Cu-OMS-2 material for designed low-costly catalyst in formaldehyde removal at a wide range of RH.

1. Introduction
Nowadays, along with the evolution of civilizations, more and more attention had been paid to human life quality. Volatile organic compounds (VOCs), which were well-known indoor air pollutants, were negatively impacted human health and the environment [1, 2]. Formaldehyde (HCHO) was one of the most hazardous VOCs, posed critical harms like nausea, skin irritation, and even carcinogenic to humans if they had been exposed to HCHO for the long term [3, 4]. Therefore, many efforts had been performed on removing HCHO, focusing on adsorption, photocatalytic oxidation and catalytic oxidation [5, 6]. Among all of these methods, catalytic oxidation was an effective technique to eliminate the low concentration of HCHO in the indoor environment. For decades, one of the main challenges in HCHO abatement might be the design of economically and effectively catalysts, when the most effective oxidation ones were supported noble metals [7–9], which were costly, lack resources and limited widespread applications.

Transition metal oxides, especially manganese oxides with tunnel structure, had been demonstrated to be more promising to replace supported noble metal catalysts for HCHO oxidation due to their excellent catalytic performances [10, 11]. Manganese oxide octahedral molecular sieve cryptomelane
(K-OMS-2) was a type of manganese oxide with a 1D tunnel structure, formed from 2 x 2 units of octahedral MnO₆ with K⁺ ions in the tunnels played a role in charge balance. Thanks to mixed manganese valence, distinct morphologies, and tunnel structure, it possessed excellent properties as a catalyst with great potential for environmental applications [12, 13]. To promote cryptomelane catalytic performance, various transition metal ions (Fe³⁺, Cr³⁺, Ni²⁺, Zn²⁺, etc.) were introduced into the material structure to create more structural defects and active sites [14–16]. Copper and cobalt had been ordinarily appointed as favorite dopants for cryptomelane modification [17]. However, the impacts of Cu/Co dopants on the natural properties of these modified materials which could affect the HCHO oxidation performance were rarely published. In this work, K-, Co- and Cu-OMS-2 materials were synthesized by a simple reflux method and tested for the HCHO removal under atmospheric pressure, with different temperature and humidity conditions. The influences of dopants on the characteristics and performances of the catalysts were also discussed.

2. Experimental

All reagents in this research were available commercially and used as received without further refinement. Cryptomelane (K-OMS-2) was prepared via a simple reflux method [14]: MnSO₄·H₂O, KMnO₄, HNO₃ and distilled water were mixed to form an acidic medium. The suspension was reflux at a reaction temperature of 100 °C for 24 hours. The resulting slurry was filtrated, washed, and dried at 100 °C in the oven overnight for further experiments. Transition metal-doped cryptomelane materials were prepared by the same method, except a certain amount of M²⁺ precursor was dissolved in the solution to archive M/Mn molar ratios of 0.22 in the final mixture.

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (40 kV, 25 mA). The average oxidation states (AOS) of Mn in M-OMS-2 samples were acquired by a titration method [15]. For elemental composition analysis of manganese, potassium, and other dopant cations, inductively coupled plasma-mass spectrometry (ICP-MS) was performed.

The catalytic activities of M-OMS-2 materials for the HCHO oxidation were conducted in a fixed-bed reactor under atmospheric pressure. Formaldehyde solution (37 wt. %) was purchased from Sigma-Aldrich while N₂ and O₂ were supplied from purified gas cylinders. 0.1 g of catalyst was loaded and placed between two layers of glass wool in a glass U-tube reactor. A pure N₂ flow that was passed through the HCHO container was maintained at 5 °C for evacuation of HCHO saturated-vapor and was named with HCHO/N₂ flow. A 50 mL/min of total flow comprised from pure O₂, pure N₂ and HCHO/N₂ flows with 1:3:1 of volume ratio, respectively was simulated airflow containing 90 ppm HCHO and 5 % of relative humidity (RH). For a 65% RH in the feeding, the pure N₂ flow was introduced in a liquid water container stored at 30 °C before joining to the total flow. The gaseous effluent was directly connected with the GC-FID (VF-1ms capillary column) by an autosampler for analysis of the concentration of HCHO in the by-pass flow ([HCHO]in) and for that in the outlet one ([HCHO]out). The reaction temperature was studied in the range of 80 - 150 °C and the HCHO conversion (H%) was calculated as the following equation:

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H(\%) = \frac{[HCHO]_{in} - [HCHO]_{out}}{[HCHO]_{in}} \times 100 \%
\]

3. Results and discussion

The structure of synthesized materials was confirmed by the XRD patterns (Figure 1), revealed high-intensity diffraction peaks of M-OMS-2 at 2θ of 12.8°, 18.1°, 28.9°, 37.8°, 42.2°, 50.1°, and 60.2°, respectively, agreed with the standard cryptomelane (JCPDS 029-1020) [18].
Figure 1. XRD patterns of M-OMS-2 samples.

Table 1 summarized the elemental composition of as-prepared materials from ICP-MS analysis. K-OMS-2 and Cu-OMS-2 gave a similar wt% of Mn (~59 wt.%) while Co-OMS-2 had a lower manganese content (56.46 wt.%). The molar ratio of manganese and potassium (nMn/nK) was in the range of 8/0.94 - 8/0.78. The presence of Cu significantly reduced the amount of potassium loading in the tunneled manganese oxide. The AOS of Mn (as shown in Table 1) increased in the order of K-, Co-, and Cu-OMS-2 samples. Consequently, there was highly possible that the Mn ions with a lower oxidation state (< 4+) were partially replaced by doped species in the two ways of (i) incorporation into the Mn-O bond, and (ii) placement of the K⁺ positions. The existence of dopants could affect either surface properties or increase oxygen vacancies, which played a crucial role in the enhancement of oxidative catalytic activity [15, 19, 20]. Moreover, the impressively rise of the AOS of Mn regarded a decrease Mn(III)/Mn(IV) ratio under the existence of transition-cation dopants that were reported in our previous work [15].

Table 1. ICP-MS and AOS analysis results of M-OMS-2 samples.

| Sample     | ICP results | Molar ratio nMn/nMn/nK | Mn-AOS | Ref.   |
|------------|-------------|------------------------|--------|--------|
| K-OMS-2    | 59.59       | 0/8/0.86               | 3.60   | [15]   |
| Co-OMS-2   | 56.46       | 0.36/8/0.94            | 3.71   | This work |
| Cu-OMS-2   | 59.51       | 0.32/8/0.78            | 3.77   |        |

The results of HCHO conversion with the reaction temperature at low and high humidity conditions over prepared M-OMS-2 samples were shown in Figure 2. When the RH was about 5 %, the conversion of HCHO on K-, Co- and Cu-OMS-2 samples were ~3%, ~4%, and ~6%, respectively at 80 °C of reaction temperature (Figure 2a). The HCHO conversion clearly increased with the increase of reaction temperature from 80 °C to 150 °C. Co-OMS-2 showed a noticeable HCHO conversion from ~18% to ~40 % at above 120 °C while K-OMS-2 only displayed ~13 % of HCHO conversion at 150 °C. Cu-OMS-2 presented a dramatic increase of HCHO conversion from ~19 to ~80 % under the
increase of reaction temperature from 100 to 150 °C at 5% RH suggesting an impact of dopant elements upon enhancement of HCHO oxidation at low RH.

Figure 2b presented the increase of HCHO conversion over synthesized catalysts with reaction temperature at 65% RH. The higher RH, the more enhancement of HCHO conversion that was obviously observed over K-OMS-2 and Cu-OMS-2 samples. Similarly, Cu-OMS-2 exhibited the most activated one among the three synthesized samples. Figure 2b recorded ~90% of HCHO conversion over Cu-OMS-2 while only ~27 % and ~40 % of that over K-OMS-2 and Co-OMS-2, respectively at 150 °C, 65 % RH. This suggested the wet durability of cryptomelane catalytic performance in HCHO oxidation and reflected the effect of dopants on formaldehyde removal at low temperatures. Generally, a decrease of Mn(III)/Mn(IV) ratio corresponded to an increase of the AOS of Mn attributed to a partial replacement of dopants for the Mn(III) sites [15, 19, 20]. A noticeable increase of the AOS of Mn from 3.60 (for K-OMS-2) to 3.71 (for Co-OMS-2) resulted in a moderate increase of HCHO conversion with reaction temperature; confirming the vital role of exotic cobalt-dopant in the enhancement of HCHO oxidation [15]. Besides an incline of the molar ratios of dopant/potassium from 0.38 to 0.41 under alternating cobalt with copper dopants (Table 1), the AOS of Mn also increased from 3.71 (for Co-OMS-2) to 3.77 (for Cu-OMS-2). This may be assigned the impact of modified-copper to the expansion of Cu-O bond length leading to a notable increase of HCHO conversion from ~40 % to ~90 % at 150 °C and at 65% RH over Co-OMS-2 and Cu-OMS-2, respectively (Figure 2b) [15].

![Figure 2](image_url)  
**Figure 2.** HCHO conversion on M-OMS-2 catalysts with (a) RH = 5%, (b) RH = 65%.

### 4. Conclusion

A facile reflux process was applied to synthesize copper- and cobalt-modified cryptomelane materials. The AOS of manganese increased from 3.6 to 3.7-3.8 after modification of K-OMS-2 with Co and Cu dopants evidencing a partial replacement of the dopants in the crystalline framework. Exotic dopants led to a significant increase of HCHO conversion and copper dopant showed the highest HCHO conversion with ~80% (at 5% RH) and ~90% (at 65 % RH) at 150 °C promising a copper-designed catalyst for HCHO removal in a wide range of relative humidity.

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