

Ozone-assisted Catalytic Oxidation (OzCO) of Methane: Impact of the Cu/Mn Ratio in Bimetallic Hydroxyapatite-supported Catalysts

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Highlights

- Mn/HAP possessed smaller (0.5 X) crystallites compared to Cu/HAP.
- Lower Cu/Mn ratio yielded smaller CuO crystallites and higher surface O_{ads} species.
- Formation of CuMnO_x spinel phase in bimetallic catalysts enhanced reducibility.

1. Introduction

In recent decades, the rise in volatile organic compounds (VOCs) emissions has posed significant environmental and health challenges. The present work focuses on CH₄, a highly stable alkane VOC and the second most abundant anthropogenic greenhouse gas after CO₂. Ozone-assisted Catalytic Oxidation (OzCO) is recognized as a promising method for VOC elimination, particularly effective at lower temperatures. Generally, MnO_x materials have exhibited high activity in OzCO, attributed to its pronounced reducibility, multiple oxidation states and superior performance in O₃ decomposition. The addition of a second transition metal has been explored to enhance the MnO_x performance. Cu-Mn bimetallic oxides stand out as a favorable option in this respect, offering both low cost and high activity [1]. However, the impact of Cu addition on the ultimate properties of Cu-Mn bimetallic catalysts, such as redox and O₂ desorption characteristics, and how these factors affect the catalytic performance, require further exploration to fully understand and optimize their efficiency in VOC elimination.

2. Methods

A hydroxyapatite (HAP) support was prepared via co-precipitation using Ca(NO₃)₂·4H₂O and NH₄H₂PO₄ precursors. Two monometallic catalysts (Cu/HAP and Mn/HAP) each containing 10 wt% metal were synthesized via wetness impregnation. Additionally, three bimetallic catalysts denoted as Cu_{0.5}Mn/HAP, CuMn/HAP, and Cu₂Mn/HAP (Cu/Mn molar ratio: 0.5; 1; 2) were also synthesized via wetness impregnation, with a total metal loading of 10 wt%. These six materials were characterized using XRD, H₂-TPR, and O₂-TPD techniques.

The catalytic performance of the materials is being assessed in a novel, custom-built setup denoted as Low-Pressure Ozone-assisted Oxidation (LoPOx), specifically designed for intrinsic VOC catalytic ozonation experiments at precisely-controlled, near-ambient total pressures. LoPOx is equipped to handle both gaseous and liquid VOCs, employing highly precise Mass Flow Controllers (MFCs) to maintain VOC concentrations within a realistic range of 100 – 5000 ppmv, typical of indoor/outdoor environments. The setup includes an O₃ generator for producing O₃ from O₂, and several MFCs for co-feeding reactants and products such as H₂O and CO₂. The LoPOx setup includes a 500 mm fixed-bed reactor (ID=9.0 mm) and a thermocouple (OD=3.2 mm), placed inside the reactor for precisely monitoring the catalyst bed temperature. This reactor can operate at low temperatures (50 – 150 °C), where O₃ thermal decomposition is negligible, and can go as high as 600 °C for conventional catalytic oxidation (without O₃) experiments. A unique feature of LoPOx is its capability to precisely regulate the total reactor pressure at (near-)atmospheric levels, a rarely seen functionality in OzCO setups. The analytical capabilities of LoPOx are robust, featuring an O₃ analyzer, GC, and MS for online transient and non-transient measurement of components concentration ranging from ppm to percentage levels.

3. Results and discussion

XRD analysis (Figure 1a) revealed larger ($>2 \times$) CuO crystallites (d_{CuO}) in the Cu/HAP catalyst compared to MnO₂ in Mn/HAP. In bimetallic catalysts, increasing the Cu/Mn ratio led to larger d_{CuO} , likely due to CuO agglomeration. The smallest d_{CuO} (13 nm) were observed in Cu_{0.5}Mn/HAP catalyst.

The H₂-TPR profile (Figure 1b) of the bimetallic catalysts revealed a noticeable decrease in reduction temperatures. Specifically, the reduction temperature for Cu²⁺ (1st peak of Cu/HAP) decreased by approximately 20 °C, and for Mn⁴⁺ to Mn³⁺ (1st peak of Mn/HAP) by around 40 °C, when compared with their monometallic counterparts. This decrease is attributed to a CuMnO_x spinel phase formation [2], which led to reduced Cu-Cu and Mn-Mn interactions, resulting in smaller particle sizes (as indicated by XRD results) and enhanced reducibility compared to the monometallic catalysts.

O₂-TPD profiles (Figure 1c) indicated that the amount of surface adsorbed oxygen (O_{ads}) species of Mn/HAP was four times higher than that of Cu/HAP. The Cu_{0.5}Mn/HAP catalyst exhibited the lowest O₂ desorption temperature at 135 °C (compared to 190 °C for Mn/HAP) and also displayed the highest amount of O_{ads}, being 20% greater than Mn/HAP. These O_{ads} species are highly reactive and play a crucial role in VOC OzCO by attacking adjacent VOC molecules and breaking stable C-H bonds [3].

Kinetic experiments for conventional catalytic oxidation over the Cu/HAP catalysts have been completed as a benchmark (Figure 1d), yielding a 40% CH₄ conversion at 450 °C and a space time of 535 kg_{cat} s mol_{CH₄,0}⁻¹. These results highlight the high temperature requirement of this method, aligning with initial expectations. Currently, kinetics performance testing of CH₄ OzCO is being carried out over all these materials in the LoPOx setup, aiming to investigate the impact of Cu/Mn ratio on the performance of bimetallic catalysts.

The spinel phase formation leads to multiple oxidation states in Cu (Cu⁺¹ and Cu²⁺) and Mn (Mn²⁺, Mn³⁺, and Mn⁴⁺), potentially altering the proportion of each oxidation state, especially Mn³⁺/Mn⁴⁺, which is vital for the catalyst's O₃ decomposition capability [2]. XPS analysis is ongoing to quantify Mn³⁺/Mn⁴⁺ on the surface for deeper insights into the O₃ decomposition capability of these catalysts.

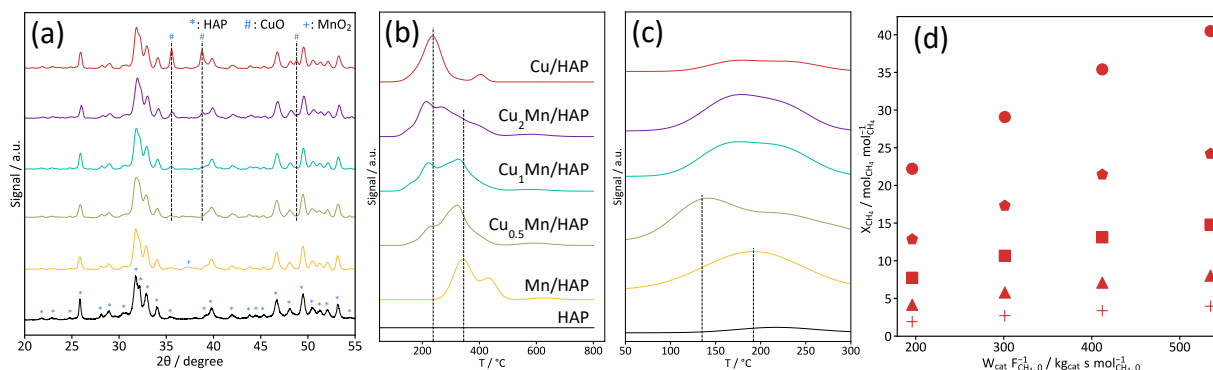


Figure 1. (a) XRD pattern, (b) H₂-TPR, (c) O₂-TPD profiles, and (d) CH₄ conversion (X_{CH_4}) vs. $W_{\text{cat}} F_{\text{CH}_4,0}^{-1}$ over Cu/HAP catalyst in conventional catalytic oxidation at T=350 (+), 375 (▲), 400 (■), 425 (◆), and 450 °C (●).

4. Conclusions

The formation of a spinel phase in bimetallic catalysts led to smaller particle sizes and improved reducibility. The Cu_{0.5}Mn/HAP catalyst, with the lowest Cu/Mn ratio, exhibited smaller crystallites and a higher quantity of surface O_{ads} species, both advantageous for the OzCO reaction.

References

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Keywords

Volatile Organic Compounds; Catalytic Ozonation; Cu-Mn catalyst