Impact of Cu/Mn ratio for CuMnOx prepared by oxalate coprecipitation : the essential point for total oxidation of model pollutants issued from biomass combustion

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Significance and Relevance

This study highlights the importance of Cu/Mn ratio on mixed oxides for the total oxidation of air pollutants application. The influence of this ratio was explored through various physicochemical characterization methods, notably revealing the presence of spinel phase ($Cu_{1.5}Mn_{1.5}O_4$) confirmed and a reducibility at lower temperature in presence of low content of Mn. Relations between catalytic activity and physicochemical properties were established, demonstrating that an optimal ratio enhances CO, toluene and black carbon oxidation at low temperatures, probably due to a synergistic effect between Mn_3O_4 and spinel phases.

Topics: Air cleaning and combustion or Automotive and stationary emission control and Presentation preferred: *Oral only*

Introduction and Motivations

The global shift towards renewable energy sources is reshaping the landscape of energy production, with biomass playing a pivotal role in this transition [1]. As a renewable and versatile fuel, biomass is increasingly favored; however, its combustion releases various pollutants, including carbon monoxide (CO), Volatile Organic Compounds (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs), and soot particles [2]. These emissions pose significant environmental and health risks, underscoring the urgent need for effective remediation strategies.

Transition metal oxides present a cost-effective and efficient alternative to noble metal catalysts traditionally used for oxidation processes. Copper and manganese oxides are particularly promising due to their high activity for CO and VOCs total oxidation at relatively low temperatures [3-5]. Among the synthesis methods, oxalate co-precipitation offers a robust approach to producing mixed-metal oxide. This method not only enables co-precipitation of multiple metals into a single oxalate matrix but also results into small crystallite sizes for the mixed oxide phases, excellent reproducibility and low synthesis duration [6]. These characteristics are essential for developing catalysts that achieve high oxidation efficiency with structural and performance stability. In this study, the main objectives are the development of CuMn mixed oxides catalysts for an application in model oxidation reactions representatives to emission of biomass combustion. The impact of Cu/Mn ratios into mixed oxides will be discussed on the presentation and relations between catalytic activity and physicochemical properties will also be highlighting.

Materials and Methods

Copper-manganese oxalate precursors were synthesized as follows: copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) and manganese nitrate ($Mn(NO_3)_2{\cdot}4H_2O$) were dissolved in 200 mL of pure acetone. Separately, oxalic acid was also dissolved in 200 mL of acetone under identical stirring conditions. The nitrate solution was then added directly to the oxalic acid solution under vigorous stirring, allowing for rapid oxalate precipitation. The resulting mixture was stirred for an additional 30 minutes before filtering, washing with acetone, and drying at 60°C for 48 hours. The dried oxalate precursor was then calcined at 500°C for 4 hours with a 1°C/min heating rate under an air flow of 3 L/h. The calcined samples were named based on their Cu:Mn ratios: $Cu_1Mn_4O_x$ (1:4), $Cu_1Mn_1O_x$ (1:1),

$Cu_4Mn_1O_x$ (4:1), alongside pure copper oxide (CuO_x) and manganese oxide (MnO_x) reference samples synthesized under identical conditions.

These materials were characterized by several physicochemical methods: XRD, H_2-TPR, XPS, N_2 sorption, SEM, Raman, IR, and UV-visible spectroscopy. Carbon black oxidation tests, N330 Degussa was mechanically mixed with the catalyst (10% carbon black, 90% catalyst). This mixture was analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), coupled with mass spectrometer to quantify carbon black oxidation into CO_2. For CO and toluene oxidation tests, 100 mg of each catalyst was pre-treated by heating under an air flow at 150°C. The gas mixture for CO oxidation was prepared to obtain 1000 ppm of toluene or CO in air flow 100 mL/min. Outflow gases were analyzed using Agilent 490 Micro gas chromatography and ADEV 4400 IR CO-CO_2 analyzer.

Results and Discussion

The oxalate precipitation method proved advantageous for the preparation of copper-manganese oxides, revealing significant textural and physicochemical differences. XRD analysis of mixed oxides show the presence of spinel phase ($Cu_{1.5}Mn_{1.5}O_4$) formation suggesting an interesting distribution of copper and manganese species, confirmed by microscopy analysis. The presence of mixed oxides allows to reduce the material at low temperature compared to the single oxide issued from oxalate precursors.

For CO total oxidation tests (Figure 1), the catalysts demonstrated improved performance with higher manganese content. The copresence of Mn_3O_4 and spinel phases enhances the catalytic oxidation at low temperature suggesting a synergetic effect between these two phases for total oxidation of CO. Moreover, the presence of Cu and Mn species is necessary in order to enhance the performance compared to CuO_x and MnO_x samples. Similar conclusions were observed for toluene oxidation, suggesting strong catalytic potential in VOC total oxidation.

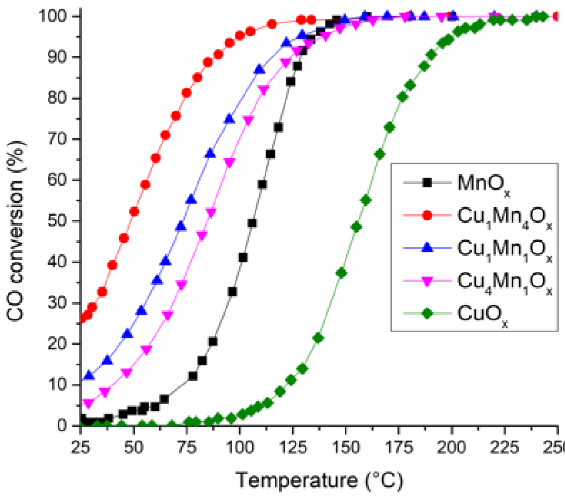

Figure 1. CO Conversion vs. temperature of $CuMnO_x$ mixed oxides

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