Enhancing Catalytic Activity through Manganese Addition in Co or Cu Mixed Oxides for catalytic treatment of wood combustion emissions

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Significance and Relevance

This study demonstrates that the combination of manganese with cobalt or copper in mixed oxide catalysts significantly enhances catalytic performance in both CO and toluene oxidation reactions. The synergistic effects between Mn and the transition metals (Co and Cu) lead to improved redox properties, higher surface area, and more efficient oxidation processes. These materials show promise for real-world applications where oxidation reactions need to be conducted at moderate temperatures, such as in environmental pollution control.

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

Introduction and Motivations

The biomass sector, and more specifically domestic wood heating, appears today to be a particularly promising alternative. In France, wood and biomass account for around 65% of renewable energy consumption for heat production. Thus, wood heating represents real challenges: energy issues for the environment and for public health. Nevertheless, wood energy is an integral part of the environmental issue. Emissions from wood combustion, both gaseous compounds and fine particles, are undeniably controversial. Among the pollutants produced by wood heating, several families can be distinguished: unburnt gases such as carbon monoxide (CO), Volatile Organic Compounds (VOCs), which include BTEX (Benzene, Toluene, Ethylbenzene and Xylene), and unburnt solid carbonaceous compounds [1].

Reducing these polluting emissions is crucial and requires the implementation of filtration and treatment technologies. Catalytic oxidation is known as one of the best solutions for reducing CO and VOCs. Total oxidation of CO at low temperature by transition metal oxides is a widely studied subject in heterogeneous catalysis [2,3]. Specifically, manganese oxides are interesting for toluene oxidation due to its availability and reactivity of surface oxygen species [3]. Transition metal oxides are also being studied as part of the total oxidation of VOCs and are very promising [3,4]. The use of LDH route for the synthesis of mixed oxides allows to develop some interesting properties for pollutants oxidation at low temperature, like high specific surface area and reducibility at low temperature.

To get as close as possible to the real conditions of wood combustion, this work is carried out on the simultaneous elimination of pollutants. Catalytic oxidation is one of the most effective methods for eliminating separately CO and VOCs, this is why it has also been chosen for treating mixtures of pollutants. The simultaneous catalytic oxidation of toluene and CO compounds in mixture has begun to be studied over the last decade, but the number of studies remains fairly limited [4]. In this work, we chose to study the activity of mixed oxides issued from LDH route. The main objective is to evaluate the influence for the association of Mn to Co or Cu-based catalysts for oxidation reactions of pollutants issued from the wood combustion (e.g. CO and toluene).

Materials and Methods

The synthesis method chosen to prepare LDH materials is classical co-precipitation with metal ratio M^{2+}/M^{3+} equal to 6/2. First, metal nitrates (Al, Mn, Co and/or Cu) are dispersed in 200 mL of distilled water. The solution is then added dropwise to a sodium carbonate solution (Na_2CO3). The pH is controlled throughout the addition, at around 9.5, by a sodium hydroxide solution (NaOH). Stirring is maintained at room temperature for 24 hours. Then, the solution is filtered and washed with hot demineralized water (60 °C), then dried in an oven at 60 °C for 24 hours. Finally, the powder obtained was thermal treated, up to 500 C for 4 hours under an air flow. For the trimetallic materials (MnCuAl and MnCoAl), the metal ratio for Co (or Cu) /Mn is equal to 3/3. The catalysts prepared will hereafter be referred to as MnAl, CoAl, CuAl, MnCoAl and MnCuAl, it will be specified whether they are calcined or not.

The materials are characterized by XRD, XPS, N_2 sorption, H_2-TPR.

The toluene and CO mixture oxidation reactions were conducted at atmospheric pressure in a micro reactor containing 100 mg of catalyst. Catalytic tests were made using a gas mixture containing of 1000 ppm C_7H_8 and/or 1000ppm CO and 20% O_2 in He. The feed gases were analyzed by an Agilent 490 Micro gas chromatography and ADEV 4400 IR CO- CO_2 analyzer

Results and Discussion

Five different LDH materials were synthesized: CoAl, MnCoAl, MnAl, MnCuAl, and CuAl. These materials were first analyzed by X-ray diffraction (XRD) to confirm the presence of the LDH precursor phase. The characteristic diffraction peak of the LDH phase appeared at 2θ = 12°, confirming the presence of the layered structure in all precursor materials. Upon calcination at 500°C, the LDH phase fully decomposed, and the resulting mixed oxide phases were identified by XRD. Notably, the MnAl sample contained Mn_2O_3, Mn_3O_4, and the spinel phase $MnAl_2O_4$, while the CoAl sample showed Co_3O_4 and $CoAl_2O_4$. MnCuAl primarily showed the $MnAl_2O_4$ spinel phase, and CuAl exhibited only the CuO phase.

The catalytic performance of the mixed oxides was tested for CO oxidation. CoAl showed the highest activity, with 80% CO conversion at ambient temperature. However, when manganese was added to either Co or Cu (as in MnCoAl and MnCuAl), a significant improvement in catalytic performance was observed due to a synergistic effect.

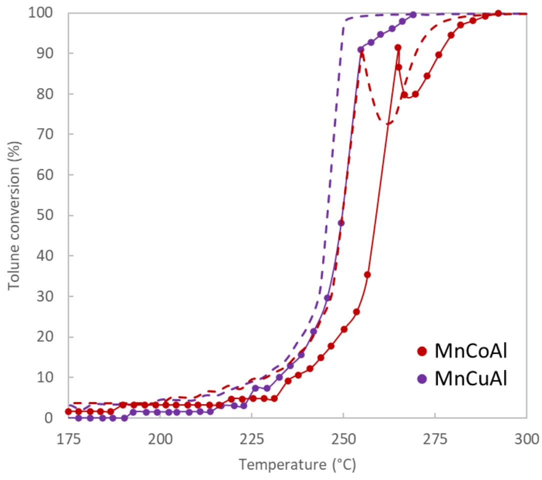

Figure 1 Conversion vs. temperature of toluene in presence or absence of CO

For toluene oxidation, MnCuAl and MnCoAl exhibited significantly better activity than the individual components. The temperature for 50% toluene conversion (T_{50}) for MnCuAl and MnCoAl was below 260°C, whereas for CoAl, MnAl, and CuAl, the T_{50} values were higher, indicating lower catalytic activity. This synergy likely arises from the redox couples of Mn^{4+}/Mn^{3+} with Cu^{2+}/Cu^{+} (for MnCuAl) and Mn^{4+}/Mn^{3+} with Co^{3+}/Co^{2+} (for MnCoAl), which optimize the catalytic sites and enhance overall performance. A further experiment tested the effect of CO in a toluene/air gas mixture to simulate real-world catalytic conditions. The results showed that the presence of CO positively influenced the catalytic performance of both MnCuAl and MnCoAl, leading to better toluene conversion at lower temperatures. This improvement is likely due to the exothermic oxidation of CO, which generates localized heating on the catalyst surface, thus promoting the oxidation of toluene (Figure 1). The trimetallic samples (MnCuAl and MnCoAl) exhibited superior performance compared to the bimetallic samples due to this additional thermal effect. These materials show promise for real-world applications where oxidation reactions need to be conducted at moderate temperatures, such as in environmental pollution control.

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