Insights into the high performance of Mn-Co oxides derived from metal-organic frameworks for total toluene oxidation
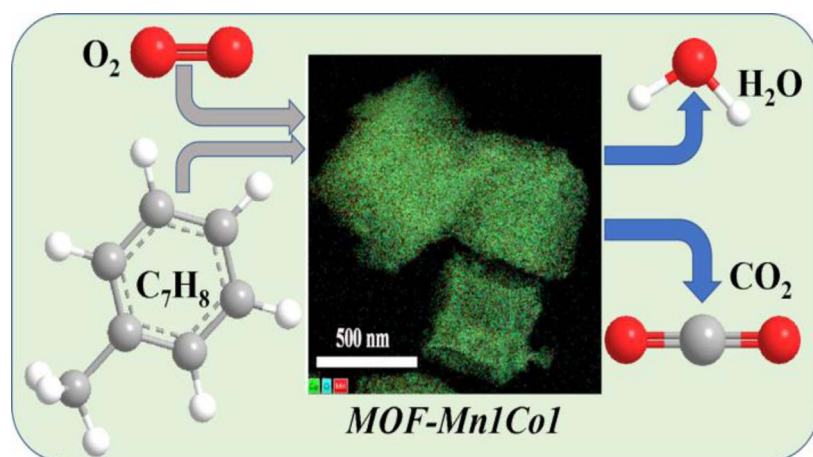
Yongjin Luo[a], Yingbin Zheng[a], Jiachang Zuo[a], Xiaoshan Feng[a], Xiuyun Wang[b,*], Tianhua Zhang[b], Kai Zhang[b], Lilong Jiang[b,*]

[a] Fujian Key Laboratory of Pollution Control & Resource Reuse, Fujian Normal University, Fuzhou 350007, PR China
[b] National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou, PR China

GRAPHICAL ABSTRACT

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ABSTRACT

Mn-Co mixed metal oxide is considered as efficient catalyst for the total oxidation of volatile organic compounds. In this study, nanocube-like metal-organic frameworks ($Mn_3[Co(CN)_6]_2 \cdot nH_2O$) are adopted as the precursor to generate Mn-Co oxides with different Mn/Co molar ratios, which affect little on phase structure and textural properties. The obtained MOF-Mn1Co1 with uniform metal dispersion is rich in high valence of surface Mn^{4+} and Co^{3+} species, leading to high low-temperature catalytic activity of total toluene oxidation. The results of toluene-TPD followed by TPO and toluene-TPSR match well with the catalytic performances of MOF-Mn1Co1, MOF-Mn1Co2, and MOF-Mn2Co1, and in situ FITR proves that the benzoate route exists over MOF-Mn1Co1. It is found that a moderate ratio of Mn/Co (1:1) favors good low-temperature reducibility and high O_{ads}/O_{latt}, resulting in superior oxidation performance. However, the stability in the existence of water for MOF-Mn1Co1 is not satisfied, which should be overcome in the future.

* Corresponding authors.
  E-mail addresses: xywang2017@fzu.edu.cn (X. Wang), jll@fzu.edu.cn (L. Jiang).

1. Introduction

Volatile organic compounds (VOCs) discharged into atmosphere from industrial processes and transport vehicles become a notable problem and cause harm to the human health because of their toxic, mutagenic and carcinogenic properties. Meanwhile, it also raises concerns for its environmental damages because the suspended particulate matter and photochemical smog are also caused by the VOCs precursors. Their elimination has been a serious challenge with increasingly stringent environmental regulations. To address the concern, efficient techniques are needed to eliminate VOCs, among which low temperature catalytic oxidation has attracted considerable attention [1]. Supported Pt and Pd catalysts are the most active for the low temperature VOCs combustion [2]. However, some inevitable drawbacks of this class of catalysts are still present, such as the high cost, low availability of noble metals and especially the potential to aggregate. It is hence desirable to replace noble metals with considerable activity of transition metal oxides comprising low cost and high thermal stability [3].

Manganese oxides, assembled from the basic structure of $[MnO_6]$ units, are known to exhibit high activity in the catalytic combustion of VOCs duo to superior physical and chemical properties. Sang et al. [4] compared the performance of benzene and toluene oxidation over Mn_3O_4, Mn_2O_3, MnO_2 and alkaline metal and alkaline earth metal modified manganese oxides. It is shown that high valence of Mn is favorable for the total oxidation, and alkaline metal and alkaline earth metal addition further enhances the performance. Santos et al. [5] demonstrates that there is a close correlation between the redox properties (mobility and reactivity of the oxygen species) and the catalytic performance of the manganese oxides. Moreover, the redox potential of manganese oxides can be further promoted by the composition of other transition metal oxides, like CoO_x. According to the literature [6], the superior VOC oxidation activity over Co-Mn catalysts is associated to the generation of amorphous phases and redox cycles as a consequence of the cooperative effect among the metals. Previous studies have also reported that the coupling of Mn and Co species has dramatically enhanced the redox properties of $Mn_xCo_{3-x}O_4$, which exhibits much better catalytic activity for the removal of formaldehyde [6,7].

To be noted, apart from the catalyst composition, morphologies reflect the dispersion of active sites to some extent, which in turn determine different catalytic performances [8]. Extensive effort has been dedicated to adjust the synthetic conditions to obtain manganese oxides with desirable morphologies, and crystal structures to improve the catalytic performance. Dai et al. [9] have synthesized rod-, wire-, tube-, and flower-Like morphologies of manganese oxides, which were evaluated for toluene oxidation. They concluded that the excellent catalytic performance of α-MnO_2 nanorods might be associated with the high oxygen adspecies concentration and good low-temperature reducibility. Lou et al. [10] found that hierarchical $Co_xMn_{3-x}O_4$ array micro-/nanostructures with tunable morphology and composition are promising integrated binder-free electrodes for microscale lithium-ion batteries. Metal-organic frameworks (MOFs), made of metal centers and functional organic ligands linked by coordination chemistry, have been used as precursors and templates for the preparation of metal nanoparticles encapsulated in porous carbons with controlled morphologies, high surface area, and uniform porosity. A multilevel core-shell structure of Au nanoparticle@zinc–iron-embedded porous carbons derived from MOFs was prepared and used as a bifunctional electrocatalyst for both oxygen reduction reaction and hydrogen evolution reaction [11]. Zhang et al. [12] rationally designed and synthesized a high performance $DeNO_x$ catalysts based on $Mn_xCo_{3-x}O_4$ nanocages derived from MOFs via an easy air annealing treatment. Recently, controllable morphologies of metal oxides (CeO_2, CuO/Cu_2O, α-Fe_2O_3, Mn_2O_3) synthesized using MOFs precursor [13–17] were applied in efficient catalytic oxidation of CO. Driven by the search for an efficient Mn-Co composite oxides with enhanced low-temperature oxidation activity for

toluene oxidation (a model reaction), the present study adopts "MOFs precursor" strategy to synthesize hierarchical Mn-Co-O_x nanocubes for better redox properties and more exposed surface active sites. The effect of chemical composition and morphologies was investigated to disclose the correlation between physicochemical characteristics and reactivity of Mn-Co oxides. Our goal in this work is to provide guidelines for the rational design of transition metal based catalysts derived from MOFs for effective catalytic oxidation.

2. Experimental

2.1. Preparation

The Mn-Co oxides were prepared according to a similar reported method. Specifically, a mixture of 1.5 g polyvinylpyrrolidone (PVP, K-30), 0.22 g $Mn(CH_3COO)_2 \cdot 4H_2O$, 30 mL deionized water and 60 mL ethanol was under magnetic stirring to form a transparent solution. Subsequently, 60 mL of an aqueous solution of $K_3Co(CN)_6$ (the molar ratio of Mn:Co at 1:1, 1:2 and 2:1 respectively) was added dropwise into the above solution under magnetic stirring. After the mixed solution was maintained under ambient conditions for aging 24 h, the precipitation was collected by filtration, washed by deionized water and absolute ethanol repeatedly. The obtained sample was firstly dried at -46 °C for 12 h in a freeze drier and then transferred to an oven at 60 °C for 6 h. Finally, the as-synthesized precursors were calcined in pipe furnace (OTF-1200X) under a air flow (50 mL/min) at 450 °C for 2 h with a slow heating rate of 1 °C/min. For simplicity, the as-prepared samples were referred to as MOF-MnxCoy, where x and y represent the initial molar ratio of Mn to Co. The actual molar ratios of Mn/Co determined by inductively coupled plasma (ICP) are 1:0.92, 1:1.9 and 2:0.95 in MOF-Mn1Co1, MOF-Mn1Co2 and MOF-Mn2Co1, respectively, which are close to the theory values.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker AXS D8 Avance X-ary diffractometer with Cu-K$_\alpha$ radiation in the 10–80° range with a step size of 0.02°. The used operating source power was 40 kV × 40 mA. N_2 physisorption measurement was performed at 77 K on a BELSORP-mini II instrument; each sample was degassed in vacuo at 200 °C for 3h. The specific surface area was obtained based on the Brunauer-Emmett-Teller (BET) equation. The morphology of samples was characterized by scanning electron microscopy (SEM, Hitachi S-4800) operated at 5 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and elemental mapping were collected by a FEI Technai G2 F20 microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on Physical Electronics Quantum 2000, equipped with a monochromatic Al-K$_\alpha$ source (K$_\alpha$ = 1,486.6 eV) and a charge neutralizer. The peak positions were corrected by using the containment carbon (C 1s peak = 284.6 eV).

Hydrogen temperature-programmed reduction (H_2-TPR) was carried out using a micromeritics AutoChem 2920 apparatus with a thermal conductivity detector (TCD). In each procedure, 0.05 g of the sample was first pretreated with He (30 mL/min) at 300 °C for 0.5 h, and then cooled down to room temperature. Subsequently, the temperature was raised to 900 °C at a constant rate of 10 °C /min under a gas flow of 10 vol% H_2/Ar stream (30 mL/min). O_2 temperature-programmed desorption (O_2-TPD) was performed by using the same apparatus. The sample (0.08 g) was first treated under He at 300 °C for 0.5 h. After cooled down to room temperature, the sample was exposed to a flow of 3 vol% O_2/He for 1 h, followed by He purging (40 mL/min) for 2 h to remove physically adsorbed O_2. Then the sample was heated from 50 to 900 °C under He. The signal of desorbed oxygen was monitored by a quadrupolar mass spectrometer (Cirrus).

Temperature-programmed toluene desorption (TPD) followed by