



Amorphous MnO_x modified Co₃O₄ for formaldehyde oxidation: improved low-temperature catalytic and photothermocatalytic activity



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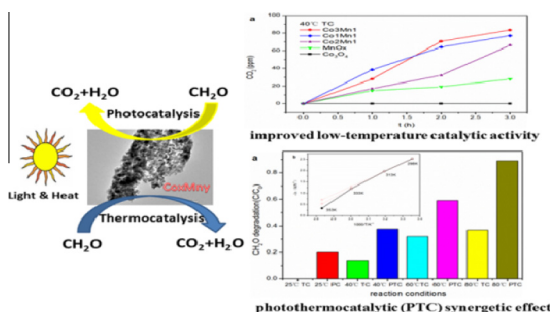
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HIGHLIGHTS

- The introduction of MnO_x improves both the TC activity and PTC activity.
- A synergetic effect between PC and TC oxidation does exist.
- Integration of NIR absorption activity with TC activity of the catalyst realizes.
- This work suggests a new idea of utilizing full solar spectrum light.

GRAPHICAL ABSTRACT

Amorphous MnO_x modified Co₃O₄ (CoxMny) with improved low-temperature catalytic and photothermocatalytic activity for formaldehyde degradation was prepared, and the photothermocatalytic synergetic activity was carefully investigated.



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ABSTRACT

Amorphous MnO_x modified Co₃O₄ (CoxMny) with high BET surface area was prepared by a template-free strategy. The introduction of amorphous MnO_x dramatically improved both the low-temperature thermocatalytic activity and photothermocatalytic (PTC) activity. The results demonstrated the integration of near-infrared absorption activity of Co₃O₄ with the low-temperature thermocatalytic activity of amorphous MnO_x and excellent PTC activity was achieved. The unique property of amorphous MnO_x, the oxygen absorption behavior, and the interaction between amorphous MnO_x and Co₃O₄ are found to be responsible for the enhanced thermocatalytic activity of CoxMny. This work provides the insights into the rational design of high-performance photocatalyst and suggests a new idea of utilizing solar energy from UV, visible to infrared light.

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1. Introduction

Great efforts have been devoted to control the emission of volatile organic compounds (VOCs) for air purification [1,2]. Photocatalysis (PC) and thermocatalysis (TC) are promising

technologies because the pollutants can be oxidized into H₂O and CO₂. However, high temperatures of 200–1200 °C are generally required to activate thermocatalytic oxidation. Photodegradation usually proceed at room temperature and ambient pressure, but the overall reaction rate is undesirably low. Herein, photo/thermo-catalysis is designed to integrate the advantages and overcome the disadvantages of the PC and TC processes.

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Due to the energy restriction, the infrared (IR) part of the solar energy has rarely been utilized in conventional PC. The inspiration for utilizing the infrared radiation heating effect comes from the research of photothermal therapies [3,4], which use electromagnetic radiation for the treatment of various medical conditions. While the IR can supply needed endothermic energy for TC [5], the UV–Vis light of the solar spectrum with higher energy could be used to activate photocatalytic reaction. An integration of PC and TC generates unique synergistic photo/thermo-catalytic (PTC) effect. Compared with sole PC and TC, PTC possesses following advantages: (i) the temperature on the catalyst surface rises quickly due to photothermal effect (especially for black catalyst), resulting in more electron excitation and relaxation and intensified heat emission [6]; (ii) the total oxidation of VOCs is processed without a need of other energy input and device maintaining temperature; and (iii) the rate constant of the PTC process is much higher than a linear combination of TC and PC. In this light, to realize an effective PTC oxidation of VOCs, one should find a material that possesses both photocatalytic property and excellent low-temperature catalytic property. Up to now, such photo/thermo-related research is still rare, and nearly all attempts involved noble metals as cocatalysts [7,8].

Co_3O_4 comes into our view because of its unique catalytic activity and light absorption property. It is emerging as an excellent material for catalytic processes owing to its light harvesting and electron mediating properties. As a catalyst of gas-phase reactions, Co_3O_4 has been applied to low-temperature CO oxidation [9], Fischer–Tropsch synthesis, and oxidation of organic compounds. The high activity of Co_3O_4 is likely to be related to the relatively low ΔH of vaporization of O_2 . Therefore, the Co–O bond strength of Co_3O_4 affects the desorption of lattice oxygen [10,11]. On the other hand, Co_3O_4 is visible light responsive and exhibits absorption at 200–300 nm, 350–450 nm, and 700–800 nm. More recent experimental studies have shown that Co_3O_4 is a promising photocatalyst in photodegradation [12] and photocatalytic hydrogen production [13].

Yet just as our experience, the photocatalytic activity of Co_3O_4 is limited; besides, Co_3O_4 gets used to high temperatures and barely works below 100 °C for the catalytic oxidation of VOCs. To overcome the above barriers, we take notice of manganite, which is known as effective low-temperature catalyst [14,15]. Manganese oxide is an oxygen storage material, in which lattice oxygen and surface oxygen in manganese oxide play a dominant role in the catalytic combustion of VOCs. Amorphous MnO_x is particularly attractive because of their relatively high catalytic activity, low cost, and minimum environmental impact. Lee et al. [16] reported that ketjenblack carbon supported amorphous MnO_x nanowires is highly efficient for the oxygen reduction reaction (ORR) in a Zn air battery. The large surface area of the amorphous MnO_x nanowires, together with other microscopic features (e.g., high density of surface defects), potentially offers more active sites for oxygen adsorption, thus significantly enhancing ORR activity. Several studies found that heterogeneous cobalt catalysts often benefit from Mn-promoting effects, but this interesting phenomenon remains to be fully understood [17].

In this study, amorphous MnO_x modified Co_3O_4 (denoted as CoxMny) was synthesized. With temperature control to simulate the thermal effect of the infrared radiation, the TC process, PC process, and PTC process of formaldehyde oxidation on CoxMny were studied for the first time. The experimental results proved that integrating of amorphous MnO_x with Co_3O_4 dramatically improves both the low-temperature TC activity and PTC activity. Insights are provided to better interpret the unique catalytic activity of CoxMny and the PTC synergy.

2. Experimental

2.1. Catalysts preparation

Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, A. R.), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, A. R.) and oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, A. R.) were purchased from Shanghai Chemical Company. All of the materials were used without further purification.

Co–Mn catalysts were synthesized through a template-free strategy of decomposing self-made bimetal oxalate as previously reported [18]. In a typical process, 0.01 mol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with a fixed Co/Mn molar ratio (3:1, 2:1 or 1:1) was dissolved in 40 mL deionized water under magnetic stirring. 0.01 mol $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 15 mL deionized water at 60 °C. The latter solution was added dropwise to the former under vigorous magnetic stirring, resulting in a precipitation forming. After stirring for another 1 h in an ice bath, the solid residue was separated by filtration, washed copiously with deionized water, and dried in air at 60 °C followed by calcinations in air at 300 °C for 3 h (at 2 °C min^{-1} heating rate). The samples were denoted as CoxMny where x/y stands for the Co/Mn molar ratio. The Co_3O_4 (MnO_x) was prepared by the same method as described above without adding of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

2.2. Characterization

The phase and composition of the as-prepared samples were measured by X-ray diffraction (XRD) using a Rigaku D/MAX 2250 V diffractometer with monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) under 40 kV, 100 mA and with the 2θ ranging from 10° to 80°. The morphologies and microstructures of all of the materials were examined by TEM using a TecnaiG2 F20 S-Twin. Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw 1000NR) with an excitation of 514 nm laser light. Nitrogen adsorption–desorption isotherms at 77 K were measured on a V-sorb 2800P. All the samples were degassed at 120 °C for 3 h under vacuum prior to measurement. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Pore volume and pore size distribution plots were obtained by the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was employed to study the chemical states of the prepared samples. XPS signals were collected on ESCALAB 250, THERMO SCIENTIFIC Ltd. with a 320 mm diameter spot of monochromated Al $K\alpha$ X-rays at 1486.6 eV under ultrahigh-vacuum conditions. Charging effects were corrected by adjusting the binding energy of C 1s to 284.6 eV.

Oxygen temperature-programmed desorption (O_2 -TPD) measurements were performed on a ChemiSorb 2750 instrument. Typically, 50 mg of the sample, placed in a glass tube, was pre-treated by a He gas flow at 300 °C for 2 h, and then cooled down to 50 °C. The adsorption of O_2 was performed in a 4 vol% O_2/He gas flow for 1 h at 50 °C. After purge by He gas, the sample was heated from 50 °C to 900 °C at a rate of 10 °C min^{-1} . The TPD signal was recorded by a thermal conductivity detector. All the gas flow rates were set as 25 mL min^{-1} .

2.3. Catalytic tests

The catalytic activities of the as-prepared samples (100 mg) were evaluated by the gas-phase degradation of formaldehyde (550 ppm). The apparatus used was described in earlier papers [19]. Experiments were conducted in a gas-closed vitreous reactor (capacity 600 mL) with a quartz window and a double-walled

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