



Controlled synthesis of diverse manganese oxide-based catalysts for complete oxidation of toluene and carbon monoxide



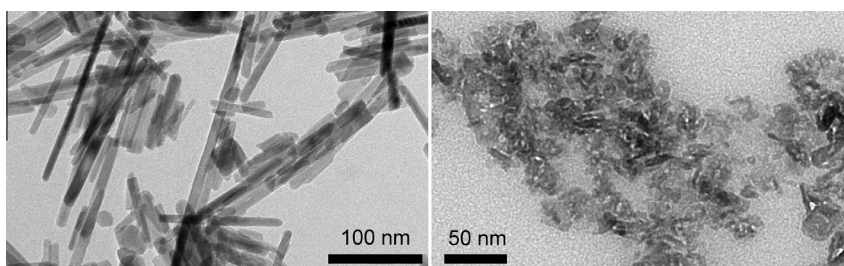
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HIGHLIGHTS

- Reacting fresh manganese hydroxide and acetic acid produces nanosized MnOx.
- The HAC/Mn ratio controls over morphology and crystal phase of produced MnOx.
- Specific surface area of catalyst is crucial in oxidation of carbon monoxide.
- Redox properties of catalyst play dominant roles in oxidation of toluene.

GRAPHICAL ABSTRACT



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ABSTRACT

Manganese oxides with various morphologies and crystal structures for catalytic oxidation of air pollutants were synthesized by reacting fresh manganese hydroxide and acetic acid (HAC) at an HAC/Mn molar ratio of 1, 2 or 3. The characterizations and activity tests indicates that the HAC/Mn ratio has significant influence on the properties and the catalytic activities of the produced manganese oxides. Manganese oxide produced at an HAC/Mn ratio of 2 is composed of nanorods having relatively uniform diameters, and it possesses the most reducible manganese oxide species and the highest content of surface adsorbed oxygen species, which could contribute to its best activity in the catalytic deep oxidation of toluene. Manganese oxide produced at an HAC/Mn ratio of 3 possesses the largest specific surface area and is the most efficient in the catalytic oxidation of carbon monoxide. Palladium was impregnated onto manganese oxide at a loading of 0.3 wt% to investigate their combined effects on catalytic destruction of the pollutants. The incorporation of palladium causes decreased activity in catalytic oxidation of toluene, which might be associated with the reduction in the amount of active surface oxygen species on the catalyst. In contrast, palladium actually promotes the catalytic oxidation of carbon monoxide probably due to the additional adsorption of carbon monoxide on noble metal.

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1. Introduction

Catalytic complete oxidation has been proven to be a cost-effective approach for the removal of combustible air pollutants including carbon monoxide and volatile organic compounds (VOCs), which are crucial precursors of photochemical smog, tropospheric ozone and atmospheric haze. Extensive studies revealed that supported noble metals [1–6], such as palladium and platinum, and

transition metal oxides [7–36], such as the oxides of manganese, copper and cobalt, can be used as catalysts in the complete oxidation of air pollutants. Noble metals are highly active, whereas they are expensive due to rareness. In contrast, transition metal oxides are much cheaper, and their catalytic activities can be optimized by tailoring their crystal structures, morphologies and surface properties during their synthesis [19–27].

Manganese oxides have been considered as one of the most promising transition metal oxide catalysts owing to their strong oxygen storage/release ability and excellent redox properties. The polyvalent property of manganese seems to induce intricate effect

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on the activity. Kim and Shim [27] investigated the catalytic oxidation of toluene and benzene over commercial manganese oxides with various crystal phases, and found that the order of catalytic activity was $\text{Mn}_3\text{O}_4 > \text{Mn}_2\text{O}_3 > \text{MnO}_2$. In another work, Peluso et al. [32] studied the manganese dioxide catalyzed oxidation of ethanol, and suggested that a high concentration of Mn^{3+} could result in weak Mn–O bonds, which might ensure good catalytic activity. On the other hand, morphologies of the manganese oxide can also influence the activity. Wang et al. [25] synthesized manganese oxides having various morphologies and oxidation states of manganese, and demonstrated that both crystal phases and morphologies posed significant influence on the catalytic oxidation of toluene.

Recently, we prepared a well-dispersed manganese oxide from a colloidal dispersion containing nanoparticles of hydrous manganese oxides [30]. In that work, reacting fresh manganese hydroxide and excess acetic acid (HAc) produced a transparent colloidal dispersion, and the subsequent dilution-induced destabilization of the colloid caused precipitation of nanoparticles. In latest work, we found that manganese oxides having diverse properties could be produced by treating manganese hydroxide with acetic acid at HAc/Mn ratios ranging from 1 to 3 although colloidal solutions cannot form without enough amount of acetic acid. The objective of this work is to reveal the influence of HAc/Mn ratio on the properties of the products, including morphologies, crystal phases, redox behaviors and the catalytic activities in destruction of toluene and carbon monoxide. Further, minute quantities of palladium were loaded onto the manganese oxide to investigate the combined effect of noble metal and transition metal oxide on reaction.

2. Experimental

2.1. Chemicals

All chemicals used were of AR grade. An aqueous solution of manganese nitrate (50 wt%), sodium hydroxide, glacial acetic acid (HAc), palladium chloride, nitric acid and toluene were purchased from Sinopharm Chemical Reagent Company Limited. Compressed carbon monoxide was purchased from Shanghai Weichuang Standard Reference Gas Analytical Technology Company Limited.

2.2. Catalyst preparation

In a typical synthesis, 200 mL of 1.5 M NaOH solution was added into 500 mL of 0.2 M $\text{Mn}(\text{NO}_3)_2$ solution with stirring, and the formed manganese hydroxide was separated by centrifugation after statically aging the slurry for 2 h. Then a measured amount of HAc was added to the wet cake (with a HAc/Mn molar ratio of 1, 2 or 3), and the mixture was stirred for 1 h. A black dispersion without visible solids was obtained at a HAc/Mn ratio of 3, while a black slurry containing some insoluble solids was obtained with a HAc/Mn ratio of 1 or 2. 1 L pure water was added to the mixture and stirred for another 1 h, and then centrifugation was taken to collect the solid. After drying in air at 60 °C, the solid was calcined in a muffle furnace at 300 °C or 500 °C for 2 h at a ramping rate of 10 °C/min to obtain manganese oxide catalyst denoted as $\text{MnOx-}n\text{-}T$, where n is the HAc/Mn molar ratio during the synthesis and T is the calcination temperature. The yields of products at HAc/Mn ratio of 1, 2 and 3 were estimated to be ca. 73%, 31% and 15%, respectively. Further increasing HAc/Mn ratio led to significant decrease in yield. Therefore, the cases at higher HAc/Mn ratios were not included in this study.

The manganese oxide-supported palladium catalyst was prepared by incipient wetness impregnation method, and $\text{MnOx-}2\text{-}500$

was selected as the catalyst support. The nominal loading amount of palladium is 0.3% in weight. The impregnation solution was prepared by dissolving 1 g of palladium chloride in 250 mL of 1 M HNO_3 solution, and required volumes of this impregnation solution was taken in catalyst preparation. The impregnated solids were finally calcined at 500 °C in a muffle furnace to obtain the catalyst Pd/MnOx-2-500.

For comparison, iron oxide $\text{Fe}_2\text{O}_3\text{-}500$ was also prepared. In a typical synthesis, 160 mL of 1 M NaOH solution was added into 200 mL of 0.2 M $\text{Fe}(\text{NO}_3)_3$ solution with stirring, and the formed ferric hydroxide was immediately separated by centrifugation, and washed using water, and then dried at 60 °C and calcined at 500 °C for 2 h at a ramping rate of 10 °C/min. Pd/ $\text{Fe}_2\text{O}_3\text{-}500$ with a palladium loading of 0.3 wt% was also prepared by the incipient wetness impregnation method.

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns were recorded on a Panalytical diffractometer using Cu K α radiation at a generator voltage of 40 kV and a tube current of 40 mA.

The transmission electron microscopy (TEM) images were taken on a JEOL-2100 transmission electron microscope at an acceleration voltage of 200 kV. The samples were crushed, dispersed in ethanol, and deposited on a microgrid prior to observation.

The specific surface areas were obtained on an ASAP-2020 gas sorption analyzer, the samples were degassed under vacuum at 250 °C for more than 5 h before measurement, and the Brunauer–Emmett–Teller (BET) specific surface areas were calculated based on the linear part of the BET plot ($P/P_0 = 0.05\text{--}0.25$).

The actual palladium contents of the catalysts were determined by atomic absorption spectroscopy using TAS-990 spectrophotometer (Beijing Purkinje General Instrument Company Limited, China). The calcined catalysts were dissolved in nitrohydrochloric acid before analysis.

The temperature-programmed reduction tests were performed in hydrogen ($\text{H}_2\text{-TPR}$) on a self-built setup and the hydrogen consumption was measured by a thermal conductivity detector. In each test, the sample was firstly treated in 50 mL/min of air flow at 300 °C for 30 min. After cooling down to room temperature, the gas flow was switched to 50 mL/min of 5% hydrogen balanced by nitrogen, and then the temperature was increased to 700 °C with a ramp rate of 10 °C/min controlled by a temperature programmer.

The temperature-programmed desorption of oxygen tests ($\text{O}_2\text{-TPD}$) were performed with the same setup as the $\text{H}_2\text{-TPR}$ tests and the desorbed oxygen was measured by a thermal conductivity detector. Before each test, the sample was treated in 50 mL/min of nitrogen flow at 300 °C for 30 min, and then cooled down to room temperature and treated in 50 mL/min of 10% oxygen balanced with nitrogen for 30 min, followed by purging with 50 mL/min of nitrogen for 30 min. Finally the $\text{O}_2\text{-TPD}$ test was carried out under nitrogen flow from room temperature to 900 °C with a ramp rate of 10 °C/min.

2.4. Activity evaluation

The catalytic oxidations of carbon monoxide and toluene were performed in a continuous-flow fixed-bed reactor (i.d. 4 mm) located in a temperature-controlled tubular electric furnace. In each test run, 0.1 g (approximately 0.1 mL) of catalyst was placed in the reactor, and both ends of the catalyst bed were packed by quartz wool. After reactant gas flow was passed through, the temperature of the catalyst bed was raised step by step. In the catalytic oxidation of carbon monoxide, the concentration of carbon monoxide was 10,000 ppm, balanced by air, and the total flow rate was

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