



An efficient catalyst of manganese supported on diatomite for toluene oxidation: Manganese species, catalytic performance, and structure-activity relationship



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ABSTRACT

The work reports the preparation of diatomite-supported manganese catalysts by deposition-precipitation method, and their application for toluene oxidation. Microstructure and morphology of catalysts were investigated by Powder X-ray diffraction pattern (PXRD), thermogravimetric (TG), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen (N₂) adsorption-desorption isotherms. Temperature-programmed reduction (TPR) and temperature-programmed surface reaction (TPSR) were used to analyze the reducibility of Mn species and the reactivity of surface oxygen species, respectively. The characterization results reveal that the manganese species were mainly in the phase of amorphous MnO₂ and Mn₂O₃ on the diatomite, and the manganese species were successfully loaded on diatomite surface and filled in pores. With the increase of Mn content, the catalytic activity enhanced, due to the increase of surface oxygen species as adsorption-reaction sites. The Mn⁴⁺ played an important role in the superior catalytic activity towards toluene. The catalyst also displays high stability and superior activity towards toluene oxidation, which presents an applied interest. The effect of Mn content on the catalytic activity of catalysts was discussed in view of reaction mechanism and variations of physicochemistry properties.

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1. Introduction

Toluene is an important organic solvent in the manufacture of dye, coating, rubber, and resin. Due to its low boiling point (111 °C), toluene can easily volatilize into air and become one of typical volatile organic compounds (VOCs). Toluene is hazardous to human health and environment. Long-term exposure to low concentration of toluene may result in serious chronic diseases, e.g., reproductive and teratology diseases [1], while inhaling high-level toluene in a short time would cause light-headedness, unconsciousness and even death [2]. Toluene in the atmosphere would transform into the precursor of photochemical ozone (O₃) and secondary organic

aerosol, which are associated with photochemical smog and haze [3]. Thus, toluene in industrial waste gas must be effectively abated before its emission into atmosphere. Various techniques have been developed for the removal of gaseous toluene, e.g., adsorption, catalytic combustion, photocatalytic oxidation, plasma processing, and biological treatment [4]. Among them, catalytic combustion is regarded as an “end-of-pipe” technique, where toluene is destructed into CO₂ and H₂O over the catalysts at relatively low operation temperature (350–500 °C) [5], displaying a bright application prospect.

To achieve high efficiency for toluene removal and high selectivity of target products (CO₂ and H₂O, but no NO_x), the development of effective and efficient catalysts is particularly necessary. Currently, catalysts used for toluene oxidation are classified into two groups, namely, bulk or supported transition metal oxides [6], and supported noble metals [7]. Compared to supported noble

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metal catalysts, transition metal oxide catalysts are more applicable, for their merits of low cost, high resistance to poisons, and thermal stability, though they are slightly less active in most cases [8].

Manganese oxides (MnO_x) including Mn_3O_4 , Mn_2O_3 , and MnO_2 are among the most active oxide catalysts for VOCs oxidation [9]. Manganese with electronic structure $3d^54s^2$ has variable oxidation states from -3 to $+7$. The presence of $\text{Mn}^{2+}/\text{Mn}^{3+}$ or $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couples and the active participation of lattice or surface oxygen in the manganese oxides facilitate the oxidation process through the Mars-Van Krevelen (MVK) mechanism [10]. In last decade, great efforts have been devoted to improving the catalytic activity of MnO_x by focusing on several fundamental constraint factors, e.g., valence, structure, morphology, and dispersion. For example, Ramesh et al. [11] reported that the reactivity shows an order of $\text{MnO} \leq \text{Mn}_2\text{O}_3 < \text{MnO}_2$ in the CO oxidation. MnO_x have various structures and morphology. Pyrolusite ($\beta\text{-MnO}_2$) with rutile-like structure is the most stable polymorph of MnO_2 , while $\gamma\text{-MnO}_2$ has a highly disordered structure and is described as an intergrowth of elements of pyrolusite and ramsdellite. But $\gamma\text{-MnO}_2$ is more suitable than $\beta\text{-MnO}_2$ for VOCs oxidation [12]. Si et al. prepared a high-efficiency $\gamma\text{-MnO}_2$ catalyst processing good catalytic performance in toluene oxidation [13]. The coupling of MnO_x with other metal oxides, e.g., Co_2O_3 [14], CuO [15], Fe_2O_3 [16], CeO_2 [17], is usually favorable for the catalytic performance. CeO_2 increases the oxygen storage capacity, while transition metal oxides improve the reducibility of composite. As large surface area assists in increasing the activity, microporous and mesoporous materials with large surface area, e.g., Al_2O_3 [18], anatase [19], zeolites [20], clays, and pillared clays [21,22], are used as excellent supports to make MnO_x nanoparticles well-dispersed. Materials with large surface area, abundant porosity, strong surface acidity, and high thermal stability, are proper supports for active species of VOCs oxidation [23]. However, the aforementioned catalysts have some disadvantages in practice, such as complicated preparation procedures or costly synthetic ingredients. A cheap and facile method for designing effective and efficient catalysts is still a desirable technical goal.

Diatomite, known as diatomaceous earth or kieselgur, is fine-grained and low-density biogenic sediment [24]. Diatomite frustules are mainly composed of amorphous hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), which is categorized as non-crystalline opal-A according to the mineralogical classification [25]. Diatomite is inexpensive and readily available, because diatomaceous silica is an abundant form of silica on earth and there are many diatomite reserves worldwide. With several unique physical and chemical characteristics, e.g., highly developed mesoporosity and/or macroporosity, strong acid resistance, thermal stability, and high mechanical strength, diatomite has a variety of applications, including as adsorbents, filters, fillers, catalysts supports, and adsorbents. Especially, the bimodal mesoporosity/macroporosity characteristic makes some diatomite exactly appropriate as adsorbent and support, because mesopores enhance specific surface area (SSA) and macropores increase the efficiency of the mass-transport and diffusion processes. From previous studies, naturally occurring and modified diatomite possessing good adsorptive properties has been successfully used for the adsorption of organic pollutants, e.g., benzene [24], toluene [26], dyes [27], and heavy metals, e.g., Cu(II) [25], Pb(II) [28], and Cr(VI) [29]. Based on above merits, diatomite was used as support for manganese oxides and applied in catalyst preparation for thermally oxidation of toluene in this study.

Herein, through the application of diatomite-supported manganese oxide as catalysts for thermally toluene oxidation, three aspects were focused on: (i) the valence, microstructure, and distribution of MnO_x on diatomite (ii) effect of supported MnO_x

content on catalytic performance; (iii) the reaction mechanism, structure-activity relationship, and application prospect of the prepared catalyst. The fundamental information derived from this study is important for the application of diatomite as catalyst support and the development of novel catalysts for toluene abatement.

2. Materials and methods

2.1. Catalyst preparation

All the chemicals and reagents used in this study are of analytical grade. Raw diatomite sample from Changbai, Jilin Province, China, was purified using sedimentation method and denoted as Dt. The major elemental composition (wt%) determined by X-ray fluorescence analysis (XRF) is expressed as their corresponding oxides is SiO_2 , 89.84%; Al_2O_3 , 3.73%; K_2O , 0.77%; Fe_2O_3 , 0.48%; Na_2O , 0.27%; TiO_2 , 0.21%; MgO , 0.18%; CaO , 0.16%; MnO , 0.01%; P_2O_5 , 0.01%; and ignition loss, 4.34%.

The diatomite-supported manganese species catalyst was prepared by the deposition-precipitation method. $\text{Mn(NO}_3)_2$ and $\text{CO(NH}_2)_2$ were added into 500 mL distilled water with mole ratio of 1:10, and then mixed with 10 g of Dt. The predetermined loading contents of Mn on Dt were 2.0%, 5.0%, 10.0%, and 20.0%. The solution was under stirring at 90 °C for 10 h. Then the particles were separated and washed until Mn^{2+} was completely removed in the supernatant. The obtained solid was dried at 80 °C overnight, pressed, crushed, and sieved to obtain particles with size of 0.25–0.50 mm. The particles were calcined at 400 °C in air for 2 h, predetermined calcination temperature to obtain catalyst with the best activity (Fig. A.1). To compare with the supported catalysts, the unsupported sample of MnCO_3 was prepared by above procedure except the addition of diatomite and calcination. The supported catalysts are labeled as Mnx-T , where x and T denote the determined Mn content and calcination temperature, respectively, while their precursors are labeled as Mnx .

2.2. Catalyst characterization

The Mn content on diatomite was determined by PerkinElmer AAnalyst 400 Flame Atomic Absorption Spectrometry. The carbon content was analyzed on a Vario EL III Elemental Analyzer with TCD detector. Powder X-ray diffraction (PXRD) patterns were recorded between 2° and 70° (2θ) at a step of 2° min^{-1} using a Bruker D8 advance diffractometer with $\text{Cu K}\alpha$ radiation (40 kV and 40 mA). Thermogravimetric (TG) analyses were performed on a Netzsch STA 409 PC instrument under air atmosphere. The temperature increased from 30 to 400 °C at a rate of 10 °C min^{-1} , and kept at 400 °C for 2 h, and then increased from 400 °C to 1000 °C at a rate of 10 °C min^{-1} . Specific surface area (SSA) and porosity analysis were analyzed on the basis of N_2 adsorption-desorption isotherms at -196 °C with an ASAP 2020 instrument. All the samples were degassed at 150 °C for 12 h before test. Scanning electron microscopy (SEM) images were obtained using a ZEISS Supra 55 field emission scanning electron microscope in the high vacuum mode and with voltage of 30 kV. The samples were coated with a thin Au film to avoid charge accumulation on sample surface and improve image contrast. The linear scan of EDS was performed at voltage of 15 kV and operational height of 15 mm on EDAX TEAM affiliated to aforementioned SEM. Transmission electron microscopy (TEM) images were acquired using FEI Talos F200S instrument at an acceleration voltage of 200 kV. All particles were dispersed in ethanol on a carbon coated copper grid. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo Scientific K-Alpha instrument equipped with an Al $\text{K}\alpha$ source (10 mA, 14 kV) and

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