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 NOx), 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
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$_2$) including Mn$_3$O$_4$, Mn$_2$O$_3$, 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 Mn$^{2+}$/Mn$^{3+}$ or Mn$^{3+}$/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$_2$ 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 MnO $\leq$ MnO$_2$ $\leq$ Mn$_3$O$_4$ in the CO oxidation. MnO$_2$ has various structures and morphology. Pyrolysis (β-MnO$_2$) with rutile-like structure is the most stable polymorph of MnO$_2$, while γ-MnO$_2$ has a highly disordered structure and is described as an intergrowth of elements of pyrolysis and bimetallic. But γ-MnO$_2$ is more suitable than β-MnO$_2$ for VOCs oxidation [12]. Si et al. prepared a high-efficiency γ-MnO$_2$ catalyst processing good catalytic performance in toluene oxidation [13]. The coupling of MnO$_2$ with other metal oxides, e.g., CeO$_2$ [14], CuO [15], Fe$_2$O$_3$ [16], and 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$_2$O$_3$ [18], anatase [19], zeolites [20], clays, and pillared clays [21,22], are used as excellent supports to make MnO$_2$ 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 kieselguhr, is fine-grained and low-density biogenic sediment [24]. Diatomite frustules are mainly composed of amorphous hydrated silica (SiO$_2$·nH$_2$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$_2$O$_3$, 3.73%; K$_2$O, 0.77%; Fe$_2$O$_3$, 0.48%; Na$_2$O, 0.27%; TiO$_2$, 0.21%; MgO, 0.18%; CaO, 0.16%; MnO, 0.01%; P$_2$O$_5$, 0.01%; and ignition loss, 4.34%.

The diatomite-supported manganese species catalyst was prepared by the deposition–precipitation method. Mn(NO$_3$)$_2$ and 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.
operated at 1486.8 eV, and all binding energies were referenced to C 1s line at 284.8 eV. Temperature-programmed reduction (TPR) was carried out on Builder PCA-1200 equipped with TCD detector. The temperature was set in the range of 30–900 °C at a rate of 10 °C min⁻¹.

2.3. Toluene oxidation

The catalytic combustion of toluene was performed in a conventional fixed-bed reactor in the temperature range of 100–350 °C under atmospheric pressure. 200.0 mg of catalyst was loaded in a quartz tube reactor (i.d. = 6 mm) supported by a porous quartz plate. Gaseous toluene was generated by flowing N₂ into liquid toluene at 0 °C. The inlet gas composes of 1000 ppm toluene and 20 vol% oxygen balanced by N₂. The total flow rate was 100 mL min⁻¹, corresponding to gas hourly space velocity (GHSV) of 30 000 cm³ g⁻¹ h⁻¹. The concentration of toluene and CO₂ in effluent were analyzed on-line by a gas chromatograph (Agilent 7820A) equipped with FID detector, and a non-dispersive infrared CO₂ analyzer (Beijing Huayun GXH-3010E), respectively. No other peaks of other hydrocarbons were detected in effluent chromatographic peak but that of toluene was detected in effluent. The temperature-programmed surface reactions (TPSR) experiments were also conducted. Toluene in N₂ was adsorbed in saturation on 200.0 mg of catalyst at 25 °C, followed by the introduction of N₂ (50 mL min⁻¹) to remove the residual toluene in apparatus for 1 h. Then the temperature was increased from 25 to 600 °C at 10 °C min⁻¹. The produced CO₂ was monitored online. Each experiment was repeated three times, and the error bar was set to standard deviation.

3. Results and discussion

3.1. Catalyst characterization

Chemical analysis results show that the Mn content on the prepared catalysts is 1.6%, 2.9%, 7.6%, and 14.1%, a bit lower than the theoretical content, 2.0%, 5.0%, 10.0%, and 20.0%, respectively, suggesting the incomplete precipitation of Mn cations on diatomite. Thus, the prepared catalysts are labeled as Mn1.6-400, Mn2.9-400, Mn7.6-400, and Mn14.1-400. As the Mn content is 2.9%, a little carbon is found in the catalyst of Mn2.9-400. The carbon content gradually increases with the increment of Mn content, indicating the incomplete decomposition of precursors.

In the PXRD patterns of purified diatomite (Fig. 1a), a broad low-intensity reflection centered at 21.6° appears in the range of 13–35°, which is characteristic of amorphous diatomaceous silica, accompanied with reflections at 20.8° and 26.6° related to quartz impurity (JCPDS No. 46-1045) [30]. With the increase of Mn content in the precursors, the intensity of reflections for MnCO₃ (JCPDS No. 86-0172) gradually increases. This indicates the main phase of MnCO₃ on the catalyst precursors, formed by the precipitation of Mn²⁺ and CO(NH₂)₂. After calcination at 400 °C, the reflections of MnCO₃ disappear except for Mn14.1–400 (Fig. 1b), illustrating the decomposition of MnCO₃ during calcination. For Mn14.1–400, besides the reflections of residual MnCO₃ and diatomite support, two weak reflections are found at 32.7° and 55.0°, ascribed to MnO₂ (JCPDS No. 76-0150). But for most of diatomite-support Mn catalysts, no reflection related to Mn species exists. To verify the presence of Mn oxides on all the calcined samples, Mn7.6–400 was further calcined at 500, 600, 700, and 800 °C for 2 h. The reflections of MnO₂ gradually increase in intensity with calcination temperature increase (Fig. A.2). This suggests the decomposition of most supported MnCO₃ to amorphous Mn oxides during calcination at 400 °C. However, the precursor of unsupported MnCO₃ after 400 °C calcination includes mainly MnCO₃ and a very small amount of MnO₂ (Fig. 1b), in which the content ratio of MnCO₃/MnO₂ is 18.2, obtained by K value method. It indicates that the decomposition temperature of MnCO₃ is higher than 400 °C. Thus, ascribed to dispersion of MnCO₃ by diatomite, the supported MnCO₃ has a lower decomposition temperature than that of unsupported MnCO₃.

To confirm the presence of amorphous Mn oxides on the catalysts, the calcination of precursors were investigated by TG. For MnCO₃ (Fig. A.3), the slow mass loss (about 2%) in TG curve at approximate 30–400 °C results from dehydration and dehydroxyl-ation of MnCO₃ [31]. In the temperature range of 400–650 °C, a sharper mass loss with DTG peak appears approximately at 582 °C, corresponding to the multi-step decomposition of MnCO₃→MnO₂→Mn₂O₃. The mass loss about 31.7% during this decomposition matches well with the theoretical value (31.3%). Another mass loss of 1.3%, corresponding to a DTG peak at 885 °C, is ascribed to the transformation of Mn₂O₃ to Mn₃O₄ [32]. For the precursors (Fig. 2), besides the mass loss by dehydration and dehydroxylat-ion in 30–400 °C, a proportion of mass loss is occurred during the heating at 400 °C for 2 h. This indicates that most MnCO₃ was decomposed during the calcination, consisting with the PXRD results. In Mn7.6 and Mn14.1, a mass loss less than 4% appears in 400–650 °C, increasing with the Mn content, ascribed to the decomposition of residual MnCO₃.

From the PXRD and TG analyses, MnCO₃, MnO₂, and Mn₂O₃ probably exist in the samples. Thus, XPS was carried out to study the composition of Mn species (Fig. 3). The binding energy of Mn 2p3/2 for as-prepared MnCO₃ is 641.7 eV, close to that of Mn²⁺ [33], but different from that of Mn⁴⁺ in range of 642.2–643.2 eV. Thus, the Mn 2p3/2 spectra can be deconvoluted into three components: i) Mn²⁺ of MnCO₃ and Mn³⁺ of Mn₂O₃ at 641.6–641.7 eV; ii) Mn⁴⁺ of amorphous MnO₂ at 643.2–643.5 eV; iii) shake-up satellite of Mn at 645.7–646.5 eV. Through the calculation of peak area, the
surface atomic ratio of Mn$^{4+}/$($\text{Mn}^{3+}+\text{Mn}^{2+}$) is about 0.5. Based on the PXRD, TG, and XPS analyses, the main valence of Mn in the catalysts was $+3$ and $+4$. Moreover, the surface Mn/Si atomic ratio gradually increases from 0.082 (Mn1.6-400) to 0.101 (Mn7.6-400), but then decreases to 0.069 (Mn14.1$^{e}$400). This is probably ascribed to the aggregation of Mn oxides on Mn14.1$^{e}$400, suggesting the worse dispersion in the sample with high Mn content.

Due to the multivalence of Mn on the catalysts, TPR characterization was carried out to analyse the reducibility of prepared catalysts (Fig. 4). Since TCD detector was used to analyse the consumed H$_2$, the dehydration of catalyst in the temperature range of 30–150 °C was also sensitive, but did not overlap the reduction peaks of Mn species. For diatomite support and Mn1.6-400, the reduction by H$_2$ is quite subtle. With the increase of Mn content, the reduction peaks become obvious. Their TPR curves consist of two broad peaks, which are divided to four components. The first two components A and B with high intensity, at approximate 290 and 312 °C, are associated with the reduction of amorphous MnO$_2$→Mn$_2$O$_3$→Mn$_3$O$_4$, respectively [34,35]. The third component C at approximate 370 °C is probably related to the reduction of crystalline Mn$_2$O$_3$ to Mn$_3$O$_4$, whose reduction temperature is higher than that of amorphous Mn$_2$O$_3$. The last component at approximate 416 °C is attributed to the reduction of crystalline and amorphous Mn$_3$O$_4$ to MnO. Among the catalysts, the temperature of relevant reduction is identical, implying the similar lattice oxygen mobility. But the reduction peak area varies with the Mn contents (Table 1).

The morphology of diatomite and the supported Mn species was observed by SEM (Fig. 5). The calcined diatomite is in disc shape,
with rich but irregular submicron pores. In the diatomite-supported Mn catalyst, Mn14.1\textsuperscript{e}400, the diatomite surface becomes rough, indicating the successful loading of Mn species on diatomite. Most pores of the Mn-diatomite composite are still identifiable, which is beneficial for the transfer of reactants. However, the liner scan of EDS (Fig. A.4) shows that in Mn14.1\textsuperscript{e}400, the Mn content of local position is significantly higher than those in adjacent area, ascribed to the existence of large Mn-containing particle. This phenomenon was not found in Mn7.6-400. It suggests that the dispersion of manganese species for Mn14.1–400 was not good as Mn7.6-400, in agreement with the Mn/Si in XPS analysis. The pore morphology was further examined by TEM (Fig. 6). For Mn2.9–400 and Mn7.6–400, most pores are occupied with aggregated particles but not completely blocking. The Mn oxide particles are well-dispersed in the pores, by forming some mesopores. However, some pores of Mn14.1–400 are completely filled by Mn oxide particles. This indicates that the dispersion of Mn species becomes less uniform in Mn14.1–400.

The nitrogen adsorption and desorption isotherms in all catalysts display typical characters of type II with H3 hysteresis loop (Fig. 7a), according to IUPAC-classification [36]. The sharp increase in nitrogen-adsorbed quantity near the relative pressure of 1.0 is ascribed to the presence of macropores in diatomite, in agreement with the SEM and TEM results. But the nitrogen-adsorbed quantity is quite low at relatively low pressure (p/p0 < 0.1), indicating the quite low micropores quantity [37]. According to the pore size distribution (PSD) curves (Fig. 7b), a broad peak related to mesopores is centered at 12 nm for calcined diatomite support, which becomes sharper and shifts approximately to 4 nm for the supported Mn catalysts. These mesopores originate from not only the mesopores on diatomite, but also the spaces between adjacent Mn oxide particles, since Mn oxides on the bulk surface of diatomite shell is non-porous, as observed from TEM. Moreover, the primary mesopores formed by manganese species on diatomite are smaller than that of MnCO\textsubscript{3} calcined at 400 °C, while the isotherms of diatomite-supported Mn catalysts are similar to that of calcined diatomite. Therefore, the Mn oxides are well-dispersed on diatomite. This fact is also evidenced by the results of SSA and porous volume (Table 2), which increase approximately 1.5 times after the loading of Mn oxides. Slight decrease of SSA and porous volume are seen in Mn14.1–400, ascribed to the aggregation of Mn oxide particles on diatomite.

3.2. Catalytic performance for toluene oxidation

The activity of diatomite-supported Mn catalysts for toluene oxidation is shown by the light-off curves as a function of temperature, 200–350 °C (Fig. 8a). To check if toluene was decomposed in thermal combustion, blank test was carried out on non-coated mesh in the reactor, where low toluene oxidation (<5%) was observed below 600 °C (not shown). The temperatures of 10% (T10), 50% (T50), and 90% (T90) toluene conversion are summarized in Table 3. The calcined diatomite support exhibits almost no catalytic activity for toluene oxidation. The catalytic activity gradually enhances as Mn content increases, with remarkable improvement from Mn1.6-400 to Mn7.6-400. But when the Mn content increases from 7.6% up to 14.1%, the increase of catalytic activity is less significant. This phenomenon is evidenced...
by the decrease of T90 in toluene conversion: Mn1.6-400 (higher than detection range) > Mn2.9-400 (314 °C) > Mn7.6-400 (274 °C) > Mn14.1-400 (267 °C).

To examine the catalytic selectivity for CO2, the CO2 generation during toluene oxidation was also traced (Fig. 8b). With the increase of Mn loading, the CO2 generation curves distinctly shift to low temperature, indicating the enhancement of catalytic activity. The decrease of T10, T50, and T90 for CO2 generation with the increase of Mn content is identical to those of toluene conversion. But CO2 generation temperature is lower than that of toluene conversion. This indicates that toluene is not completely oxidized to CO2 and H2O. From previous studies [38,39], the byproducts in toluene oxidation include benzaldehyde, benzoic acid, and other oxygenated aromatic compounds. In 250–300 °C, the CO2 generation rate is a bit lower than toluene conversion rate. For example, the CO2 generation rate at 275 °C by Mn2.9-400, Mn7.6-400, and Mn14.1-400 are 10.1%, 53.0%, and 88.2%, respectively, slightly lower than their toluene conversion rates (22.1%, 94.9%, and 99.8%). But in 300–350 °C, the CO2 generation rate by Mn7.6-400 and Mn14.1-400 is almost the same as toluene conversion rate, indicating the high selectivity to CO2 of studied catalysts.

To investigate the effect of interaction between diatomite and manganese species on the catalytic activity of prepared catalysts, the reference samples were prepared by physically mixing...
diatomite and calcined MnCO$_3$ at 400°C, and used as catalysts for toluene oxidation (Fig. A.5). The catalytic activities of reference samples were worse than that of the supported catalysts with same Mn content, e.g., Mn7.6-400 and Mn14.1 e400. This indicates the important role of well-dispersion of Mn species on diatomite on the catalytic activity.

To evaluate the activity of diatomite-supported Mn catalysts, it is compared to the catalysts with Mn oxides loaded on other supports in toluene oxidation, reported by other groups (Table 4). The T90 by most listed catalysts vary in the temperature range of 200–450°C, ascribed to various preparation methods, loading amount, support species, and reaction conditions. The T90 of Mn14.1–400 is lower or close to that of most reported catalysts. Moreover, diatomite is a kind of natural resource with low price, illustrating the promising application of diatomite as support for Mn oxide catalyst in toluene oxidation.

From previous studies, the catalytic oxidation of toluene over transition metal oxides follows the Mars-Van Krevelen (MVK) mechanism [40,41]. The reaction process includes the oxidation between toluene molecules and surface oxygen species, the reduction of oxidized catalyst by toluene, and the oxidation of catalyst by oxygen to form surface oxygen species. Temperature-programmed surface reaction (TPSR) experiment was performed without dioxygen to determine the nature of active sites, where absorbed toluene was reacted with surface oxygen under continuously increasing temperature (Fig. 9) [42]. The detection of CO$_2$ confirms that surface oxygen participates in toluene oxidation, and MVKs mechanism dominates in the reaction process. Few CO$_2$ was generated over calcined diatomite support and Mn1.6-400, due to the toluene desorption and their low catalytic activity. On Mn2.9-400, Mn7.6-400, and Mn14.1–400, three peaks appear. The first
two peaks in 200–370 °C are related to the adsorption-oxidation sites, i.e., surface lattice oxygen (O$_{2}^-$) and adsorbed oxygen (HO–). The CO$_2$ amount produced in toluene oxidation is related to the availability of surface oxygen. On the catalyst containing more Mn, more CO$_2$ was generated, and CO$_2$ generation peaks shifted to low temperature. This indicates the toluene oxidation on diatomite-supported Mn catalysts followed the MVKs mechanism, improved with the increase of Mn content. For Mn$_{2.9}$-400, Mn$_{7.6}$-400, and Mn$_{14.1}$-400, the total CO$_2$ produced amount for these two peaks was 16.3, 20.5, and 30.0 μmol g$^{-1}$ cat. The last peak in 420–600 °C was ascribed to the decomposition of MnCO$_3$, in agreement with the results of PXRD and TG that the intensity increases with Mn content.

3.3. Structure-reactivity relationship

Based on the MVKs mechanism, the activity of diatomite-supported Mn catalysts for toluene oxidation is probably related to several factors, i.e., specific surface area, surface oxygen species, and the reducibility of Mn oxides. In this study, surface oxygen species was positively related to the intensity of CO$_2$ peak in TPSR reaction, where CO$_2$ was generated in the toluene oxidation by surface oxygen on the catalysts. Mn reduction intensity is related to the intensity of peak area of TPR curves. More bulk oxygen can be reduced, resulting in more lattice oxygen involved in the oxidation. The reduction temperatures of Mn$^{4+}$ and Mn$^{3+}$ center at approximate 290 and 312 °C, which are in the reaction temperature range of 250–350 °C. But the intensity of reduction peak of Mn$^{4+}$ is much larger than that of Mn$^{3+}$. Higher oxidation state of Mn species is preferable for oxidation reactions over the manganese-containing catalysts. Thus, the reducibility of studied catalysts during the reaction mainly depends on the Mn$^{4+}$ reducibility.

From the catalytic oxidation of toluene, the catalytic activity gradually enhances with the Mn content increase, but the enhancement is less significant at high Mn content. The reduction temperature of Mn$^{4+}$ for Mn$_{2.9}$-400, Mn$_{7.6}$-400, and Mn$_{14.1}$-400 is similar, indicating the reduction temperature is not the constraint factor. The decrease of enhancement can be related to the decrease of relative intensity of amorphous MnO$_2$, as shown in Table 2. For diatomite and Mn$_{1.6}$-400, although their SSA value is large (Table 1), the reduction signal of Mn oxides (Fig. 9) and CO$_2$ amount generated in TPSR reaction are quite low, indicating their low Mn content and surface site intensity. The TPR curve of Mn$_{1.6}$-400 also shows low reduction intensity of bulk oxygen. These well explain their worse catalytic activity. For the catalysts with relatively high Mn content, i.e., Mn$_{2.9}$-400, Mn$_{7.6}$-400, and Mn$_{14.1}$-400, they display enhanced reactivity for toluene oxidation, with the increase of Mn content. This is probably ascribed to the increase of surface oxygen and reduction intensity of Mn oxides, which supplies more oxygen and facilitates the redox cycle in catalytic reaction, respectively [43]. But from N$_2$ adsorption-desorption, SEM, and TEM characterizations, the increase of Mn content results in the particle aggregation and the decrease of SSA and pore volume. Moreover, the relative content of residual MnCO$_3$ also gradually increases. These two variations probably lead to the insignificant improvement of catalytic activity over Mn$_{14.1}$-400.

3.4. Catalytic stability and moisture effect

Catalytic stability is critical for the application of catalysts. In this study, a lifetime test was carried out over Mn$_{14.1}$-400 at 325 °C for a week (Fig. 10). In the initial three days, the catalytic activity achieved complete CO$_2$ generation steadily. However, sharp increase of CO$_2$ over 100% appeared in the last four days, and became more frequently as the reaction continued. After lifetime test, the catalyst was recycled for toluene oxidation, and it showed slightly worse catalytic activity than the fresh catalyst. The PXRD pattern of the recycled Mn$_{14.1}$-400 shows the disappearance of MnO$_2$ and the increase of Mn$_2$O$_3$ (Fig. A.6). Thus, the sharp increase of CO$_2$ is derived from the decomposition of residual MnO$_2$. The deactivation of catalyst is attributed to formation of more Mn$_2$O$_3$. But the catalytic activity of the recycled Mn$_{14.1}$-400 is still superior above 300 °C (Fig. A.7).

Besides catalytic stability, the resistance to water is also important for application of catalysts in VOCs oxidation. The effect of water on the catalytic oxidation of toluene over Mn$_{14.1}$-400 was...
In this work, the catalytic oxidation of toluene over manganese-supported diatomite catalysts was studied. The following findings can be derived from the present investigation, which might be beneficial for the application of natural diatomite and the development of catalysts for VOC elimination.

4. Conclusions

In this work, the catalytic oxidation of toluene over manganese-supported diatomite catalysts was studied. The following findings can be derived from the present investigation, which might be beneficial for the application of natural diatomite and the development of catalysts for VOC elimination.

(i) The manganese species are mainly in the phase of amorphous MnO2 and Mn2O3 on the diatomite, accompanied with low content of MnCO3. The Mn oxides gradually aggregate on diatomite as the increase of Mn content.

(ii) The manganese-supported on diatomite catalysts show excellent activity and high selectivity to CO2 for toluene oxidation. With the increase of Mn content, the catalytic activity becomes better. The catalysts also show high activity toward toluene oxidation even after a week of test, indicating strong stability.

(iii) The reaction mechanism in this study follows the Mars-Van Krevelen (MVK) mechanism. With higher adsorption-reaction sites associated with surface oxygen, the catalytic activity of manganese-supported on diatomite catalysts improves. Moreover, the superior catalytic activity is ascribed to the excellent reducibility of Mn4+.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2016.09.053.

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