Structure-Activity Relationship of Manganese Oxide Catalysts for the Catalytic Oxidation of (chloro)-VOCs

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Abstract: Manganese oxide catalysts, including $\gamma$-MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$, were synthesized by a precipitation method using different precipitants and calcination temperatures. The catalytic oxidations of benzene and 1,2-dichloroethane (1,2-DCE) were then carried out. The effects of the calcination temperature on the catalyst morphology and activity were investigated. It was found that the specific surface area and reducibility of the catalysts decreased with the increase in the calcination temperature, and both the $\gamma$-MnO$_2$ and Mn$_3$O$_4$ were converted to Mn$_2$O$_3$. These catalysts showed good activity and selectivity for the benzene and 1,2-DCE oxidation. The $\gamma$-MnO$_2$ exhibited the highest activity, followed by the Mn$_2$O$_3$ and Mn$_3$O$_4$. The high activity could be associated with the large specific surface area, abundant surface oxygen species and excellent low-temperature reducibility. Additionally, the catalysts were inevitably chlorinated during the 1,2-DCE oxidation, and a decrease in the catalytic activity was observed. It suggested that a higher reaction temperature could facilitate the removal of the chlorine species. However, the reduction of the catalytic reaction interface was irreversible.

Keywords: benzene; 1,2-Dichloroethane; catalytic oxidation; manganese oxide catalysts

1. Introduction

Volatile organic compounds (VOCs) are not only toxic to the human body [1] but also act as the precursors of the PM$_{2.5}$ and near-surface ozone [2–4], causing severe environmental problems. In recent years, many countries have enacted laws and regulations to limit the emissions of VOCs. Generally, catalytic oxidation methods can achieve a complete decomposition of the VOCs at low temperatures (i.e., 250–500 °C) [5,6], which is suitable for the abatement of the VOCs that have no recycling value, such as waste gases from printing or spraying industries, which mainly consist of the BTX (benzene, toluene and xylene) and oxygenated VOCs (OVOCs), as well as partially chlorinated VOCs (CVOCs) [7,8].

Noble metal catalysts have been successfully utilized for the abatement of the VOCs [9,10]. However, the cost of these catalysts is very high. Recent investigations have shown that the transition metal oxide catalysts (Mn, Co and Cu, etc.) show an activity that is comparable with the noble metal catalysts [11–25]. In particular, these catalysts often show better resistance to the chlorine poisoning [26]. Among these catalysts, the manganese oxide catalysts are highly active [16–25] and have an ability to
resist the chlorine poisoning in the catalytic oxidation of the CVOCs [27]. Additionally, these catalysts are considered to be environmentally friendly.

Manganese has many valence states, including Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, Mn$^{6+}$ and Mn$^{7+}$, allowing the electron transfer to readily occur [28]; thus, the manganese materials are widely used as catalysts [29–31]. Manganese oxides (Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$, etc.) are known to exhibit a good activity in the catalytic oxidation of the VOCs [18–22,24,25]. The morphology of the manganese oxide catalysts can vary with different precursors and preparation conditions [23], which clearly affects their catalytic behaviors. It is generally agreed that the specific surface area, the valence states of the surface manganese species, the active oxygen species and the surface defects of the catalyst are the most important factors for the catalytic activity [20,22,25,32]. The reduction of the calcination temperature of the catalyst seems beneficial as well [23]. According to previous reports [16–25,32], most studies focus on approaches to increase the catalytic activity of the manganese oxide catalysts. However, in real applications, controlling a stable reaction temperature may not be very practical because the concentration of the VOCs is continually changing, and the catalytic oxidation process is an exothermic reaction. Therefore, the effects of the thermal stability and crystal structure change on the catalytic activity warrant an in-depth study. Manganese oxide catalysts undergo a catalyst deactivation during the catalytic oxidation of the CVOCs [27,33]. It is thus necessary to evaluate the chlorine resistance of the catalysts, since the CVOCs are prevalent in the practical waste gases [7,8]. Notably, previous studies often studied only a few catalyst samples, so the results of the structure-activity relationship were not comprehensive enough [21,24], and the results of different studies are often inconsistent. In addition, only a few reports include the simultaneous study of the CVOCs. Consequently, lack of a clear understanding regarding these issues has obviously hindered further improvements in the manganese oxide catalysts and their applications.

In this study, we synthesized a series of manganese oxide catalysts by the traditional precipitation method, and typical manganese oxide structures, such as MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$, were obtained by changing the precipitants and calcination temperatures. In addition to benzene, 1,2-dichloroethane (1,2-DCE) was also used as a model reactant to investigate the chlorine resistance were obtained by changing the precipitants and calcination temperatures. In addition to benzene, were not comprehensive enough [21,24], and the results of the di

2. Results and Discussion

Figure 1 shows the XRD patterns of the manganese oxide catalysts (Figure 1a–c), and the standard XRD patterns including the $\gamma$-MnO$_2$ (JCPDS PDF 30-0820), Mn$_2$O$_3$ (JCPDS PDF 78-0390), Mn$_3$O$_4$ (JCPDS PDF 24-0734), MnCO$_3$ (JCPDS PDF 44-1472) and MnC$_2$O$_4$ (JCPDS PDF 01-0160) (Figure 1d). As shown in Figure 1a, the MnCO$_3$ precipitate retains its original crystal structure after drying at 100 $^\circ$C. With the increase in the calcination temperature, MnCO$_3$ is first converted to the $\gamma$-MnO$_2$ and then converted to a pure Mn$_2$O$_3$. As shown in Figure 1b, the crystal structure of the MnC$_2$O$_4$ precipitate also remains unchanged after drying. With the increase in the calcination temperature, MnC$_2$O$_4$ is first converted into a mixture of the Mn$_3$O$_4$ and Mn$_2$O$_3$ (mainly Mn$_2$O$_3$), and then Mn$_2$O$_3$ becomes the sole crystal phase. As shown in Figure 1c, the Mn(OH)$_2$ precipitate has already been converted into Mn$_3$O$_4$ through the dehydration process. With the increase in the calcination temperature, Mn$_3$O$_4$ is also converted into Mn$_2$O$_3$. These results show that, although the structures of the manganese oxide catalysts are quite different as a result of different precipitated precursors at low calcination temperatures, both the $\gamma$-MnO$_2$ and Mn$_3$O$_4$ are converted into Mn$_2$O$_3$ with the increase in the calcination temperature, suggesting that Mn$_2$O$_3$ has the best thermal stability. However, a peak for
MnCO₃ is observed in the XRD patterns of the MnCO₃-350 and MnCO₃-425 catalysts, indicating that the catalysts contain the MnCO₃ species.

![XRD patterns of manganese oxide catalysts.](image)

**Figure 1.** XRD patterns of (a) MnCO₃, (b) MnC₂O₄, (c) Mn(OH)₂, and (d) standard XRD patterns of γ-MnO₂, Mn₂O₃, Mn₃O₄, and MnCO₃.

The catalytic evaluation of the manganese oxide catalysts for the benzene oxidation were performed, and the results are shown in Figure 2. In addition, the 50% conversion temperature (T₉₀) and 90% conversion temperature (T₉₀) of these catalysts for benzene are summarized in Table 1.

| Catalyst   | Benzene | T₉₀ (°C) | T₉₀ (°C) |
|------------|---------|----------|----------|
| MnCO₃-350  |         | 182      | 202      |
| MnCO₃-425  |         | 191      | 218      |
| MnCO₃-500  |         | 205      | 230      |
| MnCO₃-575  |         | 213      | 241      |
| MnC₂O₄-350 |         | 195      | 223      |
| MnC₂O₄-425 |         | 202      | 229      |
| MnC₂O₄-500 |         | 213      | 240      |
| MnC₂O₄-575 |         | 223      | 252      |
| Mn(OH)₂-350|         | 225      | 252      |
| Mn(OH)₂-425|         | 225      | 252      |
| Mn(OH)₂-500|         | 223      | 250      |
| Mn(OH)₂-575|         | 227      | 255      |
with the crystal structure of Mn\(_2\)O\(_3\) phenomenon, suggesting that the manganese oxide crystalline grains aggregate during the calcination \(2019\). The pore sizes of these two catalysts are 6.5 nm and 17.5 nm, respectively. This is a typical sintering surface areas of the Mn\(_2\)O\(_3\) calcination temperature, and the pore size of the catalyst changes inversely. For instance, the specific CO\(_2\) Mn\(_2\)O\(_3\) completely converted at 200 \(^\circ\)C. Overall, the activity of the manganese oxide catalysts for the benzene oxidation is very high, and benzene can not only be completely converted at 200 \(^\circ\)C by the \(\gamma\)-MnO\(_2\) catalyst but also can be completely oxidized below 275 \(^\circ\)C by the Mn\(_3\)O\(_4\) catalyst. Figure 2 shows the benzene conversion and CO\(_2\) selectivity of the Mn\(_2\)O\(_3\)-350, Mn\(_2\)O\(_3\)-500 and Mn\(_2\)O\(_3\)-425 catalysts as a function of the temperature. (1000 ppm benzene/20 vol.% O\(_2\)/N\(_2\); 200 mg catalyst; WHSV 30,000 mL·g\(^{-1}\)·h\(^{-1}\)).

As shown in Figure 2a–b, the T\(_{50}\) and T\(_{90}\) for the Mn\(_2\)O\(_3\)-350 (182 \(^\circ\)C and 202 \(^\circ\)C) and Mn\(_2\)O\(_3\)-425 (191 \(^\circ\)C and 218 \(^\circ\)C) are lower than that for the Mn\(_2\)O\(_4\)-425 (202 \(^\circ\)C and 229 \(^\circ\)C), which shows the best activity among the manganese oxide catalysts with the crystal structure of the Mn\(_2\)O\(_3\) (the Mn\(_2\)O\(_4\)-350 catalyst is a mixture of the Mn\(_2\)O\(_4\) and Mn\(_2\)O\(_3\)). Therefore, it is clear that the \(\gamma\)-MnO\(_2\) is more active than the Mn\(_2\)O\(_3\) in benzene oxidation. As shown in Figure 2c, the activity of the Mn\(_2\)O\(_4\)-500 catalyst with the crystal structure of Mn\(_2\)O\(_3\) is better than that of the Mn\(_2\)O\(_4\)-425 catalyst with the crystal structure of Mn\(_3\)O\(_4\), suggesting that the transformation of the Mn\(_3\)O\(_4\) to the Mn\(_2\)O\(_3\) is beneficial to the catalytic activity. Thus, the \(\gamma\)-MnO\(_2\) has the best activity in the benzene oxidation, followed by the Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\). Furthermore, the activity of the manganese oxide catalysts with the same crystal structures decrease significantly with the increase in the calcination temperature. Overall, the activity of the manganese oxide catalysts for the benzene oxidation is very high, and benzene can not only be completely converted at 200 \(^\circ\)C by the \(\gamma\)-MnO\(_2\) catalyst but also can be completely oxidized below 275 \(^\circ\)C by the Mn\(_3\)O\(_4\) catalyst. Figure 2d shows the benzene conversion and the CO\(_2\) selectivity of the Mn\(_2\)O\(_3\)-425, Mn\(_2\)O\(_3\)-500 and Mn\(_2\)O\(_3\)-425 catalysts as a function of the temperature. As shown, CO\(_2\) is the only oxidation product.

The porous structures of the manganese oxide catalysts are shown in Table 2. Overall, it was found that both the specific area and the pore volume of the catalysts decrease with the increase in the calcination temperature, and the pore size of the catalyst changes inversely. For instance, the specific surface areas of the Mn\(_2\)O\(_3\)-425 and Mn\(_2\)O\(_3\)-500 catalysts are 105.8 m\(^2\)/g and 45.1 m\(^2\)/g, respectively, and the pore sizes of these two catalysts are 6.5 nm and 17.5 nm, respectively. This is a typical sintering phenomenon, suggesting that the manganese oxide crystalline grains aggregate during the calcination process. In addition, the specific surface areas of the catalysts with the crystal structures of the Mn\(_2\)O\(_3\)
and Mn$_3$O$_4$ are similar, but the specific surface areas of the MnCO$_3$-350 and MnCO$_3$-425 catalysts with the crystal structure of the $\gamma$-MnO$_2$ are very large. The above results indicate that the precipitated precursor has a strong influence on the morphology of the catalyst. Moreover, almost no changes can be observed in the microstructure of the catalysts after the benzene oxidation.

| Catalyst       | Specific Surface Area (m$^2$/g) | Pore Size (nm) | Pore Volume (cm$^3$/g) | O$_{ads}$ | O$_{latt}$ |
|----------------|---------------------------------|----------------|------------------------|-----------|------------|
| MnCO$_3$-350   | 153.2                           | 5.6            | 0.29                   | 0.698     | 0.302      |
| MnCO$_3$-425   | 105.8                           | 6.5            | 0.24                   | 0.587     | 0.413      |
| MnCO$_3$-425 (B) | 104.1                         | 6.6            | 0.25                   | 0.295     | 0.705      |
| MnCO$_3$-425 (DCE) | 37.6                         | 17.5           | 0.22                   | 0.271     | 0.729      |
| MnCO$_3$-500   | 45.1                            | 17.5           | 0.24                   | 0.382     | 0.618      |
| MnCO$_3$-575   | 43.9                            | 17.4           | 0.29                   | 0.282     | 0.718      |
| Mn$_2$O$_4$-350 | 58.6                            | 9.6            | 0.24                   | 0.285     | 0.715      |
| Mn$_2$O$_4$-425 | 47.7                            | 9.6            | 0.24                   | 0.299     | 0.701      |
| Mn$_2$O$_4$-500 | 33.8                            | 17.7           | 0.22                   | 0.375     | 0.625      |
| Mn$_2$O$_4$-500 (B) | 33.3                         | 17.4           | 0.20                   | 0.272     | 0.728      |
| Mn$_2$O$_4$-500 (DCE) | 24.2                        | 31.1           | 0.32                   | 0.261     | 0.739      |
| Mn$_2$O$_4$-575 | 25.2                            | 31.5           | 0.19                   | 0.274     | 0.726      |
| Mn(OH)$_2$-350 | 30.3                            | 31.0           | 0.23                   | 0.433     | 0.567      |
| Mn(OH)$_2$-425 | 30.1                            | 30.5           | 0.21                   | 0.304     | 0.696      |
| Mn(OH)$_2$-425 (B) | 37.1                         | 30.9           | 0.23                   | 0.212     | 0.788      |
| Mn(OH)$_2$-425 (DCE) | 17.2                           | 46.4           | 0.24                   | 0.264     | 0.736      |
| Mn(OH)$_2$-500 | 27.0                            | 31.2           | 0.36                   | 0.275     | 0.725      |
| Mn(OH)$_2$-575 | 21.6                            | 46.3           | 0.85                   | 0.296     | 0.704      |

Table 2. Characterization data for the manganese oxide catalysts.

a After evaluation as a catalyst for the catalytic oxidation of benzene. b After evaluation as a catalyst for the catalytic oxidation of 1,2-DCE. c O$^-$, O$_2^-$ and O$_{22}^-$ species, and OH groups. d Lattice oxygen species (O$^{2-}$).

The MnCO$_3$-425, Mn$_2$O$_4$-500 and Mn(OH)$_2$-425 catalysts were characterized by SEM and TEM, and Figure 3 shows the representative micrographs. As shown in Figure 3a, the MnCO$_3$-425 catalyst consists of spherical particles approximately 0.3–1 µm in diameter. The manganese oxide crystalline grain size is approximately 5–7 nm (Figure 3b), and the lattice spacing is 0.21 nm, corresponding to the (101) crystal plane of the $\gamma$-MnO$_2$ (Figure 3c). As shown in Figure 3d, the Mn$_2$O$_4$-500 catalyst consists of spherical particles similar to those observed in the MnCO$_3$-425 catalyst. The manganese oxide crystalline grain size, which is much larger, is approximately 20–50 nm (Figure 3e), and the lattice spacing is 0.27 nm, corresponding to the (222) crystal plane of the Mn$_2$O$_3$ (Figure 3f). As shown in Figure 3g, the Mn(OH)$_2$-425 catalyst consists of large cubic particles approximately 10–20 µm in diameter. The manganese oxide crystalline grain size is slightly smaller than that of the Mn$_2$O$_4$-500 catalyst (Figure 3h), and the lattice spacing is 0.25 nm, corresponding to the (211) crystal plane of the Mn$_3$O$_4$ (Figure 3i).
Figure 3. Representative SEM, TEM micrographs of the (a–c) MnCO$_3$-425, (d–f) MnC$_2$O$_4$-500 and (g–i) Mn(OH)$_2$-425 catalysts. The high resolution TEM micrograph shows the yellow dotted area in the corresponding TEM micrograph of the catalyst.

The H$_2$-TPR analyses were conducted to investigate the reducibility of the manganese oxide catalysts, and the results are shown in Figure 4. The reduction of the manganese oxides can be described as follows: MnO$_2$ → Mn$_3$O$_4$ → Mn$_2$O$_3$ → MnO [34]. As shown in Figure 4, each H$_2$-TPR profile of the manganese oxide catalyst shows two or three main peaks that can be attributed to the reduction of the manganese species in different valence states. In general, the peaks in the temperature range from 270 °C to 370 °C can be assigned to the reduction of MnO$_2$ to Mn$_2$O$_3$ or Mn$_3$O$_4$ to Mn$_2$O$_3$, and the peak in the temperature range of 370 °C to 460 °C can be assigned to the reduction of Mn$_3$O$_4$ to MnO. Specifically, the MnCO$_3$-350 and MnCO$_3$-425 catalysts with the crystal structure of the γ-MnO$_2$ show strong reduction peaks at approximately 280 °C and 310 °C, which can be attributed to the Mn$^{4+}$ and Mn$^{3+}$ reduction, respectively, and the peaks at approximately 420 °C can be attributed to the reduction of Mn$_3$O$_4$ to MnO (Figure 4a). For the Mn(OH)$_2$-350 and Mn(OH)$_2$-425 catalysts with the crystal structure of the Mn$_3$O$_4$, the characteristic peaks at 450 °C can be assigned to the reduction of Mn$_3$O$_4$ to MnO, but the peaks in the temperature range from 270 °C to 370 °C are quite weak, indicating that the reducibility of the Mn$_3$O$_4$ is poor due to the lack of the high valance manganese species (Figure 4c). The reduction profiles of the other manganese oxide catalysts with the crystal...
structure of the Mn$_2$O$_3$ are similar, showing two strong peaks assigned to the reduction of the Mn$_2$O$_3$ and Mn$_3$O$_4$ at approximately 340 °C and 450 °C, respectively.

![Figure 4](image)

**Figure 4.** H$_2$-TPR profiles of the manganese oxide catalysts obtained by calcining (a) MnCO$_3$, (b) MnC$_2$O$_4$ and (c) Mn(OH)$_2$.

In addition to the abovementioned peaks, characteristic peaks in the temperature range from 210 °C to 270 °C can be assigned to the reactive oxygen species (mainly the surface oxygen species and highly reactive lattice oxygen species). It can be seen that the peak intensity of these species decreases with the increase in the calcination temperature for all the catalysts, and these peaks are barely observable when the catalyst is calcined at a temperature exceeding 500 °C. The main reduction peaks of the manganese species also shift to higher temperatures. For instance, the main reduction peaks at 312 °C and 417 °C for the MnCO$_3$-350 catalyst gradually shift to 350 °C and 441 °C for the MnCO$_3$-575 catalyst. It should also be noted that the initial reduction temperature has increased as well. All the above phenomena indicate that the crystal structures of the manganese oxides gradually become more intact, and the oxygen mobility and thus the reducibility of the catalyst decrease with the increase in the calcination temperature. Similar phenomena are observed in many transition metal oxide catalysts [15,35], in which these processes decrease the availability of the reactive oxygen species in the oxidation reactions. It is well known that the Mars-van-Krevelen mechanism is operational in the transition metal oxide catalysts during the oxidation reactions, which involves the process of releasing and replenishing lattice oxygen. Therefore, the reducibility of the catalyst will be closely related to the catalytic activity. Overall, the reducibility of the manganese oxides with different crystal structures is $\gamma$-MnO$_2$ > Mn$_2$O$_3$ > Mn$_3$O$_4$, which shows a strong correlation with the main valence states of the manganese oxides.

The surface manganese species and oxygen species of the manganese oxide catalysts were investigated by XPS. Figure 5 shows the XPS spectra of the Mn 2p for these catalysts. The determination of the different oxidation states of manganese by XPS is not trivial because of the relative importance of the intra and inter-atomic effects [36], so Mn 2p has not been treated as a peak separation. However,
it can be seen that the peak shifts to the low binding energy region with the increase in the calcination temperature, indicating that the amount of the high valent manganese species decreases. Figure 6 shows the XPS spectra of the O 1s for these catalysts, and the relative content of the different surface species was calculated and shown in Table 2. As presented in Figure 6, the peak of O 1s can also be divided into three peaks [23,25]. The peak at 529.4 ± 0.2 eV can be assigned to lattice oxygen species (O2−) in a fully coordinated environment [23,25]. The peak at 531.3 ± 0.2 eV can be attributed to the surface oxygen species (O−, O2− and O22−) in the vicinity of the surface defects [37], and the peak at 533.4 ± 0.2 eV can be described as the OH groups [23,25], together known as the adsorbed oxygen species. From the calculated data in Table 2, it can be concluded that the catalyst calcined at high temperatures has a higher ratio of the lattice oxygen species, and a lower ration of the surface oxygen species, indicating that the crystal structure of the catalyst gradually becomes more intact, and the surface defects are reduced. Therefore, increasing the calcination temperature causes a reduction in the catalyst specific surface area, leading to a decrease in the catalytic reaction interface. It has been widely reported that the surface defect sites exhibit a high oxidation activity [38–40] because they are prone to produce active oxygen species, such as the surface oxygen species and highly reactive lattice oxygen species. In addition, these species are easily involved in the catalytic reaction. Thus, increasing the calcination temperature will have adverse effects on the catalyst activity.

![XPS spectra of Mn 2p](image1)

**Figure 5.** XPS spectra of Mn 2p for the manganese oxide catalysts obtained by calcining (a) MnCO3, (b) MnC2O4 and (c) Mn(OH)2.

![XPS spectra of O 1s](image2)

**Figure 6.** XPS spectra of O 1s for the manganese oxide catalysts obtained by calcining (a) MnCO3, (b) MnC2O4 and (c) Mn(OH)2.

Figure 7 summarizes the catalytic properties for the manganese oxide catalysts. The results show a complex structure-activity relationship of the manganese oxidation catalysts. The high activity can be attributed to the large specific surface area and more abundant surface oxygen species. These catalyst characteristics are related to the oxygen mobility and the reducibility of the catalyst, which is significantly influenced by the manganese oxide crystal structure and the calcination temperature.
As shown in Figure 8, the bands at 1572 cm\(^{-1}\) (C=O stretching vibration) and 1236 cm\(^{-1}\) (C-O stretching vibration) can be assigned to a surface phenolate species \([41]\), and the bands at 1425 and 1313 cm\(^{-1}\) can be assigned to the maleate species (Olefin rocking vibration), consistent with the former reports \([42–44]\). In addition, the bands at 1561 cm\(^{-1}\) (asymmetric stretching vibration of COO\(^{-}\)), 1377 cm\(^{-1}\) (CH\(_2\) stretching vibration), 1368 cm\(^{-1}\) (C–C stretching vibration) and 1354 cm\(^{-1}\) (CH\(_3\) stretching vibration) can be assigned to the acetate species \([43,45,46]\), and the band at 1478 cm\(^{-1}\) can be assigned to the adsorbed benzene (C=C stretching vibration) \([46]\). In the adsorption process of benzene over MnCO\(_3\)-425, only the band at 1561 cm\(^{-1}\) can be observed, while other bands that are assigned to the adsorbed benzene or other intermediate products cannot be observed (Figure 8a). For the MnC\(_2\)O\(_4\)-500 and Mn(OH)\(_2\)-425 catalysts, not only benzene but also the phenolate, maleate and acetate species can be observed (Figure 8b,c). Notably, in the adsorption process of benzene over the MnCO\(_3\)-425 catalyst, there is an inverse peak in the 1300–1500 cm\(^{-1}\) region. This peak may arise because the MnCO\(_3\)-425 catalyst has a residual MnCO\(_3\), which absorbs the infrared light in the range of 1300–1500 cm\(^{-1}\), and these species are covered by intermediates. This phenomenon is confirmed the XRD hypothesis.

The band at 1478 cm\(^{-1}\) that is assigned to the C=C vibration of the adsorbed benzene over the MnC\(_2\)O\(_4\)-500 and the Mn(OH)\(_2\)-425 catalysts decreases somewhat during the exposure of the adsorbed species to a flowing 20 vol% O\(_2\)/N\(_2\) stream (Figure 8a,c), indicating that benzene is gradually removed or converted to the intermediate products. In contrast, the bands assigned to the intermediate products do not decrease but increase somewhat, indicating that the catalytic oxidation performance of the catalysts is weak at a low temperature, hindering the conversion of the intermediate products to the final products. Nevertheless, the adsorbed benzene can be oxidized under the action of the active oxygen or lattice oxygen on the catalyst surface, resulting in the accumulation of the intermediate products. Clearly, the peak strength of the adsorbed benzene and intermediate products shows the rule of MnCO\(_3\)-425 < MnC\(_2\)O\(_4\)-500 < Mn(OH)\(_2\)-425, which is related to the catalytic oxidation performance of the catalysts. When benzene is adsorbed on the surface of the manganese oxide catalysts with a stronger oxidation ability, it can be rapidly converted to the intermediate or final products.
R spectra of the adsorption and desorption process of

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ability for benzene, which can cause the benzene ring pyrolysis at low temperatures.

intermediate products are mainly the phenolate, aldehyde, maleate, that the catalytic oxidation mechanism of benzene over di

...catalysts cannot be detected, indicating that there is no adsorbed benzene at these temperatures. In comparison to Figure 8, similar bands at 1561, 1425, 1377, 1368 and 1313 cm

region
due to different organic species are found in Figure 9 [46]. For the MnC

O2/N2 stream. Figure 9 shows the in-situ FTIR spectra collected at different temperatures in a 1000 ppm benzene/20 vol.% O2/N2 stream over the MnCO

MnC

Mn(OH)

MnCO

C stretching vibration) can be assigned to the C=C vibration of the adsorbed benzene over the MnC

Mn(OH)

MnCO

C–O stretching vibration) emerged [45,46]. For the Mn(OH)

C–C stretching vibration) can be assigned

different crystalline manganese oxide catalysts are essentially the same, and the intermediate products are mainly the phenolate, aldehyde, maleate, and acetate species. Additionally, the manganese oxide catalysts have a strong catalytic oxidation ability for benzene, which can cause the benzene ring pyrolysis at low temperatures.
Nevertheless, the vibration 002 scattering vibration) in the 1,2-DCE oxidation process. However, the manganese oxide catalyst ultimately reaches the catalyst [47]. Hence, we speculated that the catalyst channel was blocked by the newly formed structure in the 1,2-DCE oxidation process. However, the manganese oxide catalyst ultimately reaches a stable catalytic state, indicating that it has some ability to resist the chlorine poisoning by achieving an equilibrium state of chlorination and dechlorination.

Figure 9. In-situ FTIR spectra of the (a) MnCO$_3$-425 (b) MnC$_2$O$_4$-500 (c) Mn(OH)$_2$-425 catalysts collected at 200 °C during oxidation at 30 min in a 1000 ppm benzene/20 vol% O$_2$/N$_2$ stream followed by the temperature programmed to 250 °C, 300 °C and 350 °C.

To evaluate the catalytic properties of the manganese oxide catalysts in the catalytic oxidation of CVOCs, MnCO$_3$-425, MnC$_2$O$_4$-500 and Mn(OH)$_2$-425 catalysts with the crystal structures (γ-MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$) were chosen as representatives, and the catalytic oxidations of 1,2-DCE by these catalysts were studied, as shown in Figure 10. Due to the reason that the catalyst deactivation was observed in the oxidation process, three identical activity tests were performed. Figure 10a–c shows the 1,2-DCE conversion and reaction temperature as a function of time. As shown, the activity of the catalysts decreases continuously when the temperature is below 300 °C in the first experiment. After increasing the catalytic temperature above 300 °C, all the catalysts can reach stable states, and 1,2-DCE can be completely converted at 400 °C. In the second and third experiments, the activity of the catalysts are very similar, although inevitably lower than that in the first experiment, indicating that these manganese oxide catalysts are able to resist the chlorine poisoning. However, the porous structure of the catalysts appears to have been damaged (Table 2). For example, the specific surface area of the MnCO$_3$-425 catalyst decreases from 105.8 m$^2$/g to 37.6 m$^2$/g. This decrease may be related to the effects of the chlorine poisoning. During the catalytic oxidation of the CVOCs, the catalyst is inevitably chlorinated, even causing changes in the specific surface area or the crystal structure of the catalyst [47]. Hence, we speculated that the catalyst channel was blocked by the newly formed structure in the 1,2-DCE oxidation process. However, the manganese oxide catalyst ultimately reaches a stable catalytic state, indicating that it has some ability to resist the chlorine poisoning by achieving an equilibrium state of chlorination and dechlorination.
was mainly reflected in two aspects. Firstly, it destroyed the structure of the catalyst, resulting in a significant reduction of the specific surface area and reduction of the catalytic reaction interface. Notably, the selectivity of CO could the activity of the catalyst be stable. It suggested that a higher reaction temperature could facilitate the removal of the chlorine species. However, the reduction of the catalyst interface was irreversible.

Figure 10 shows the 1,2-DCE conversion and CO₂ selectivity as a function of the temperature in the third experiment. As shown, the MnCO₃-425 catalyst demonstrates the best activity in the 1,2-DCE oxidation, followed by the MnC₂O₄-500 and Mn(OH)₂-425 catalysts. This result is similar to that for the benzene oxidation. However, the selectivity of CO₂ for these catalysts is not 100%. This observation may also be related to the effects of the chlorine poisoning, which can directly affect the capacity of the catalyst to provide the reactive oxygen species [48]. Therefore, CO is released as an incomplete oxidation product. Notably, the selectivity of CO₂ can gradually increase to 100% for all the catalysts after the total conversion of 1,2-DCE. Moreover, almost no by-products were observed.

3. Experimental

3.1. Catalysts Preparation

All the chemicals used in this study were purchased from Aladdin (Shanghai, China) without further purification. Mn(NO₃)₂ (50 wt% in H₂O) was used as a manganese precursor, and NH₄HCO₃
(>99.9%), (NH₄)₂C₂O₄·H₂O (>99.8%) and NaOH (>96%) were used as precipitants. First, 0.8 mol NH₄HCO₃, 0.096 mol (NH₄)₂C₂O₄·H₂O and 0.192 mol NaOH were dissolved in 400 mL of deionized H₂O respectively, and a 85.89 g Mn(NO₃)₂ solution (0.08 mol Mn(NO₃)₂) was diluted in the 1.2 L deionized H₂O and then divided into three equal parts. Typically, the NH₄HCO₃ solution was added dropwise into the Mn(NO₃)₂ solution under stirring at room temperature (R.T.), resulting in the formation of a precipitate. After stirring for 0.5 h, the precipitate was aged for 4 h under static conditions and then filtered and washed with the deionized water and dried at 100 °C overnight. Subsequently, the precipitate was calcined at 350–575 °C in air, generating the manganese oxide catalyst MnCO₃- T, where T is the calcination temperature. Similarly, the manganese oxide catalysts obtained using (NH₄)₂C₂O₄ and NaOH as precipitants are denoted as MnC₂O₄-T and Mn(OH)₂-T, respectively.

3.2. Catalyst Characterizations

3.2.1. X-ray Diffraction (XRD)

XRD patterns of the samples were recorded on a powder diffractometer (Rigaku D/Max-RA, Shimadzu, Kyoto, Japan) using the Cu Kα radiation (40 kV and 120 mA). The diffractograms were recorded from 10° to 80° with a step size of 0.02° and a step time of 8 s.

3.2.2. N₂ Adsorption/Desorption

The porous structures of the catalysts were characterized using the N₂ adsorption at 77 K in an automatic surface area and porosity analyzer (Autosorb iQ, Quantachrome, Boynton, FL, USA). The specific surface areas of the catalysts were calculated from the N₂ adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation, and the pore sizes and pore volumes of the catalysts were determined from the N₂ desorption isotherms using the Barrett–Joyner–Halenda (BJH) method.

3.2.3. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The SEM analyses were performed with a JEOL JSM-7500F Field Emission scanning electron microscope (JEOL, Tokyo, Japan) at 5 kV. The TEM analyses were collected on an FEI Tecnai G² F20 field emission electron microscope (FEI, Hillsboro, OR, USA) at 200 kV.

3.2.4. X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were collected on a photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific, Waltham, MA, USA) using the Al Kα (1486.8 eV) radiation as the excitation source (powered at 10 mA and 15 kV). Charging of the samples was corrected by setting the binding energy of the adventitious carbon (C1s) at 284.6 eV.

3.2.5. H₂-Temperature-Programmed Reduction (H₂-TPR)

The H₂-TPR measurements were conducted on an automated chemisorption analyzer (ChemBET Pulsar TPR/TPD, Quantachrome, Boynton, FL, USA). The sample (30 mg) was pretreated in He at 300 °C for 1 h. After being cooled to R.T., the TPR experiments were carried out in a flow of 10% H₂/Ar from R.T. to 600 °C at a ramp of 10 °C·min⁻¹.

3.3. Catalytic Oxidation of VOCs

Catalytic evaluations were carried out in a quartz tube, single-pass fixed-bed microreactor (4 mm i.d.) with a 200 mg catalyst (40–60 mesh). The reactor was heated by an electric furnace, and the temperature was monitored through a K-type thermocouple next to the sieve plate. Benzene and 1,2-DCE were introduced into the reaction flow directly from the gas cylinders. The total flow rate of the mixed stream was 100 mL·min⁻¹ with a gas composition of 1000 ppm benzene/20 vol% O₂/N₂ or 100 ppm 1,2-DCE/20 vol% O₂/N₂ (corresponding weight hourly space velocity (WHSV) was 30,000 mL·g⁻¹·h⁻¹). The reactants and products (CO₂ and CO) were analyzed on-line with a gas
chromatograph (GC 2010 Plus, Shimadzu, Kyoto, Japan), which was equipped with a methanizer (MTN, Shimadzu, Kyoto, Japan) and two flame ionization detectors. Additionally, the relative error was less than ±1%.

The conversion of benzene and 1,2-DCE was calculated by Equation (1):

\[
x(\%) = \frac{[C(\text{in}) - C(\text{out})]}{C(\text{in})} \times 100
\]

where \(x\) is the conversion, and \(C(\text{in})\) and \(C(\text{out})\) are the inlet and outlet concentrations, respectively.

The CO\(_2\) selectivity was calculated using Equation (2):

\[
S(\text{CO}_2) (\%) = \frac{C(\text{CO}_2)}{C(\text{CO}_2) + C(\text{CO})} \times 100
\]

where \(S(\text{CO}_2)\) is the CO\(_2\) selectivity, and \(C(\text{CO}_2)\) and \(C(\text{CO})\) are the outlet concentrations of the CO\(_2\) and CO, respectively.

3.4. In-Situ Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were collected with a FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA). The FTIR spectrometer was equipped with an MCT (mercury-cadmium-telluride) detector and a stainless-steel IR cell. The powder sample was pressed into a self-supported disk, and the sample was pretreated at 400 °C for 1 h in a 20 vol% O\(_2\)/N\(_2\) stream before the experiment. After being cooled to a desired temperature, the spectra of the clean sample surfaces were collected as the background. In addition, the spectra of the in-situ reactions of the sample in specific mixed streams at given temperatures were collected.

4. Conclusions

A series of manganese oxides were synthesized and used as catalysts for the benzene and 1,2-DCE oxidation. The complete conversion temperatures for the benzene and 1,2-DCE are lower than 300 °C and 400 °C, respectively. Generally, the \(\gamma\)-MnO\(_2\) exhibits the highest activity, followed by Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\), and Mn\(_2\)O\(_3\) shows the best thermal stability. Additionally, there is no essential difference in the benzene oxidation processes for \(\gamma\)-MnO\(_2\), Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\). The high activity of the manganese oxides is associated with the large specific surface area, abundant surface oxygen species and excellent low-temperature reducibility, and increasing the calcination temperature has obvious adverse effects. During the catalytic oxidation of 1,2-DCE, the catalyst structure is irreversibly damaged, which leads to the decrease of the reaction interface and activity. A higher reaction temperature could facilitate the removal of the chlorine species to maintain the catalyst activity. These results indicate that, in addition to increasing the catalytic activity, further improvements in the thermal stability and chlorine resistance of the manganese oxide catalysts are essential.

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