The characterization of γ-alumina supported manganese oxide as an incineration catalyst for trichloroethylene

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Abstract

Trichloroethylene (TCE) decomposed over a MnO/γ-Al2O3 catalyst in a fixed bed reactor was conducted in this study. The MnO/γ-Al2O3 powders were prepared by the incipient wetness impregnation method with aqueous solution of manganese nitrate. The catalyst was characterized by TGA, X-ray diffraction, porosity analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The products and reactants distribution from the oxidation of TCE over MnO/γ-Al2O3 were observed. A life test of the catalyst on TCE was performed to identify the chlorine poisoning effect. The catalysts were characterized by porosity analysis and elemental analysis before and after the tests.

1 Introduction

Halogenated volatile organic compounds emissions are associated to a wide range of industrial processes; for instance, trichloroethylene (TCE) is mainly used in metal degreasing processes and known to be hazardous to the environment and public health. Some people believe that the best technique to eliminate these toxic materials in the waste stream is catalytic oxidation. [1] Therefore, heterogeneous catalytic incineration has been paid the most attention lately because it is a final disposal and energy saving process. [2, 3] The present study focuses on the characterization of supported manganese oxide catalysts on the activity and product yield in the vapor-phase oxidation of TCE under excess of air between 175°C and 500°C, with the aim of enhancing our understanding of the reaction pathway.
2 Experimental

2.1 Catalyst preparation

The commercial γ-alumina spherical support, which supplied by Macherey Nagel, was used in this study. From the surface and pore size analysis, the following properties were obtained: BET surface area, 127.7 m²g⁻¹; pore volume, 0.24 cm³g⁻¹; and average pore radius, 7.50 nm.

The active materials (MnNO₃) was incorporated by adsorption from aqueous solution of the salts—Mn(NO₃)₂·4H₂O. To do so, 0.61 cm³ of the 1.4 M solution was sprayed on each gram of γ-alumina. The nominal compositions of the prepared catalysts of Mn was 5 wt%. After drying for 1h at room temperature followed by drying for 24h at 120°C in an oven, the supported catalysts were activated by calcining at 600°C in a furnace with air stream for 8 hours, and reducing at 600°C with a N₂/H₂ = 10/1 stream for eight additional hours.

2.2 Catalyst characterization (BET, TGA, XRD, XPS)

The catalysts' surface areas and average pore diameters were measured through N₂ adsorption at liquid-nitrogen temperature by a surface area analyzer (Micromeritics ASAP 2400).

The TGA analysis was carried out in air (100 ml/min) on a thermogravimetric analyzer (model SDT 2960 and Thermo analysis 2000, TA instruments); the temperature cycle was programmed from 40 to 800°C at a rate of 10°C/min.

An X-ray diffractometer (Rigaku D/max III V XRD) was employed to analyze the catalysts' structures. The radiation source was Cu Kα. The applied current and voltage were 30 mA and 40 kV, respectively. During the analysis, the sample was scanned from 20° to 80° at a speed of 0.4°/min.

The XPS chemical analyzing instrument is a VG Micro Lab. MKIII XPS analyzing instrument (where Mg Kα was the radiation source). The sample was initially tapped on a sample supporting plate. The plate was then placed in a pretreatment chamber attached to the instrument. The chamber pressure was then decreased from 100 to 1.33 × 10⁻¹⁰ kPa via a turbo pump. The time needed to reach the final pressure was approximately 4 h. A gate valve between the pretreatment chamber and a vacuum chamber was then opened after the pre-treatment. The sample was moved to the vacuum chamber for analysis. The pressure in the vacuum chamber was maintained at 1.33 × 10⁻¹⁰ kPa via an ion pump. The following analyzing conditions were utilized: resolution= 0.1 eV; number of scans= 100. The binding energy spectra were obtained under the above-mentioned conditions and a pre-determined scanning range.
2.3 Activity measurement

The catalytic incineration of this study was conducted in a bench scale fixed bed reactor under atmospheric pressure. It consisted of a 1.6 cm i. d., 2.0 cm o. d., and 45 cm length stainless steel tube located inside an electrical furnace. A 200-mesh SS316 sieve was set in the reactor, 24 cm below the top of the tube, to support the catalyst. The weight of catalyst packing was 1.7g (thickness 0.75 cm). Two K type thermocouples were inserted into the reactor to the positions on the top and bottom of the catalyst packing, respectively, to control (up position) and measure (down position) the inlet and outlet temperature.

To start an experimental run, after the catalyst bed temperature had decreased to the desired reaction temperature (172~590°C), a gas mixture containing 100 ppm TCE balanced by dry air was passed through the catalyst bed. The gas hourly space velocity (GHSV) was set at 80,000 hr⁻¹.

The conversion of TCE and C₂Cl₄ concentration were determined by analyzing inlet and outlet gases by a GC unit (Shimadzu, GC-14B) with an FID detector and the concentration of CO and CO₂ in the effluent gas was measured with a CO/CO₂/O₂ analyzer (Model 300 type). Carbonaceous material change of the catalyst samples was determined by an elemental analyst (EA, Elementar Analysensysteme GmbH), metal composition and surface changes of the catalysts were analyzed by a SEM/EDS analyzer (Hitachi S-2500). The conversion ($X$) of TCE and the yield ($Y_C$ and $Y_{Cl}$) of carbon and chlorine products are defined as follows:

$$X = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

(1)

$$Y_{C(ClO,CO_2,C_2Cl_4)} = \frac{C_{CO}}{2C_{in}} \times 100\% \quad \quad \frac{C_{CO_2}}{2C_{in}} \times 100\% \quad \quad \frac{2C_{C_2Cl_4}}{2C_{in}} \times 100\%$$

(2)

$$Y_{Cl(Cl_2,HCl,C_2Cl_4)} = \frac{2C_{Cl_2}}{3C_{in}} \times 100\% \quad \quad \frac{C_{HCl}}{3C_{in}} \times 100\% \quad \quad \frac{4C_{C_2Cl_4}}{3C_{in}} \times 100\%$$

(3)

3 Results and discussion

3.1 The Porosity of the catalysts at various status

Table 1 shows the physical properties of the catalysts at various status, such as γ-Al₂O₃, impregnated catalyst, calcined catalyst, reduced catalyst, and 365°C incinerated catalyst.
Table 1. The basic properties of MnO2/γ-Al2O3 catalyst.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Average Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al2O3</td>
<td>127.7</td>
<td>0.239</td>
<td>74.96</td>
</tr>
<tr>
<td>Impregnated Catalyst</td>
<td>120.1</td>
<td>0.211</td>
<td>70.39</td>
</tr>
<tr>
<td>Calcined Catalyst</td>
<td>105.3</td>
<td>0.219</td>
<td>83.20</td>
</tr>
<tr>
<td>Reduced Catalyst</td>
<td>106.1</td>
<td>0.223</td>
<td>83.89</td>
</tr>
<tr>
<td>365°C Incinerated Catalyst</td>
<td>100.9</td>
<td>0.216</td>
<td>85.64</td>
</tr>
</tbody>
</table>

As this table reveals, the surface area decreases slightly by the impregnation and high temperature treatment. However, for the average pore diameter (Figure 1), an opposite phenomenon occurs. The above observations reveal that the impregnation material and the high temperature status block some small pores.

3.2 Surface property (characterized by XRD, TGA/DTA, XPS, SEM/EDS)

The x-ray diffraction spectra of the catalysts calcined at various temperatures were performed. The principal peaks at θ = 32.88° and 55.04° in the spectrum of 600°C calcination temperature do not appear in those of calcination temperatures 300 to 500°C, and the peak intensity of the 700°C calcination temperature are much less than the 600°C calcination temperature. According to the Joint Committee on Powder Diffraction System (JCPDS) file, the principal peaks
Air pollution X

represent Mn₂O₃ [78-0390]. The result suggests that the best calcination
temperature of the impregnated catalyst converted to supported Mn₂O₃ catalyst is
600°C.

The x-ray diffraction spectra of the catalysts at various status were also
examined. The principal peaks at 2θ = 34.96° and 40.59° in the spectrum of
reduced catalyst do not appear in those of calcined catalyst. According to the
Joint Committee on Powder Diffraction System file, the principal peaks represent
MnO [78-0424].

The result suggests that the calcined catalyst reduced by H₂ in the reducing
processes let the manganese oxide on γ-Al₂O₃ support become amorphous. In
addition, small peaks representing the manganese oxide crystal phase appear in
the spectra of the impregnated catalyst. According to the Joint Committee on
Powder Diffraction System file, the small peaks represent Mn₃O₈ [72-1427].
From this observation, we infer that the major part of Mn₃O₈ of the impregnated
catalyst is converted to Mn₂O₃ after the 600°C calcination process and form the
MnO by the reducing process.

The result of TGA analysis at a heating rate of 10°C/min for the impregnated
catalyst is shown in Figure 2. From this figure, the TGA curve indicates that the
weight loss of impregnated catalyst declines from 98.5% to 90%, and two
principal losses at 100°C (373K) and 600°C (873K) appears in the TGA curve.
This finding suggests that the weight loss phenomenon might be due to the loss of
moisture adsorbed by impregnated catalyst and the manganese oxide crystal
changes at 100°C and 600°C, respectively. According to the XRD spectra, the
result demonstrates that the crystal forming temperature of Mn₂O₃ is 600°C.

Figure 2: The DTA-TGA curve of the impregnated catalyst.
The XPS spectra for the impregnated, calcined, and reduced catalysts were recorded. The binding energy (BE) values for the Mn2P3/2 peak in impregnated and calcined catalysts are compiled in Figure 3. For the impregnated sample, value at 642.6 eV is consistent with the expected BE for Mn4+ species. This suggests that the impregnated precursor during the drying for 24h at 120°C in an oven, the manganese is oxidized to Mn4+ or Mn3+ species. For the calcined catalyst, exposed to a air pulse, the Mn2P3/2 profile changes to a value at 641.7 eV which is consistent with the expected BE for Mn3+ species. This finding suggests that the manganese is oxidized to Mn2O3 during the 600°C calcination process. These results were also observed earlier on the XRD spectra. For the reduced catalyst, the Mn2P3/2 profile resolves three peaks. The manganese species corresponding to the BE at 641.2 eV for the major peak would be Mn2+ species. [4]

According to the results of XRD and XPS spectra, such a phase change (MnO2 or Mn3O4-Mn2O3-MnO) has also been found in other studies. [5]

Figure 4 presents SEM photographs of the impregnated and calcined catalysts. For the impregnated catalyst, some spherical particles are formed. After the 600°C calcination process, small needle-shape particles are formed. Although it is impossible to carry out a quantitative EDX analysis of the catalysts, the semi-quantitative information can be obtained. Table 2 shows the results corresponding to the catalysts at various status. For example, the Al content and Mn content of the calcined catalyst are higher and lower than the impregnated catalyst, respectively.

![Figure 3: The Mn2P3/2 XPS spectra of the catalysts at various status.](image-url)
3.3 Product Distributions of TCE decomposition

Figure 5 shows the distributions the products and reactants for the oxidation of TCE over 5 wt% MnO/γ-Al₂O₃. The conversion of TCE was extremely slow below 300°C. As the temperature exceeds 325°C the conversion rapidly increases and CO₂, HCl and Cl₂ are the main products, with only some trace amounts of incomplete combustion products (e.g., C₂Cl₄ and CO). According to this figure, the C₂Cl₄ is formed from the beginning, presenting a peak at 395°C, 34.9 ppm. The concentration of CO is peaked at 425°C, 34.2 ppm.

From the results shown in Figure 5, to correlate concentrations of different components in the figure, the following reaction scheme can be proposed for the destruction of TCE:

\[
\begin{align*}
\text{C}_2\text{HCl}_3 + 2\text{O}_2 & \rightarrow 2\text{CO}_2 + \text{HCl} + \text{Cl}_2 & (4) \\
\text{C}_2\text{HCl}_3 + \text{O}_3 & \rightarrow 2\text{CO} + \text{HCl} + \text{Cl}_2 & (5) \\
\text{C}_2\text{HCl}_3 + \text{O}_2 + \text{HCl} & \rightarrow \text{C}_2\text{Cl}_4 + \text{H}_2\text{O} & (6) \\
\text{C}_2\text{Cl}_4 + \text{O}_2 & \rightarrow 2\text{CO} + 2\text{Cl}_2 & (7) \\
\text{CO} + \text{O}_2 & \rightarrow \text{CO}_2 & (8)
\end{align*}
\]

as well as the Deacon reaction [6] since water and chlorine are present in the reaction environment.

The TCE conversion and product yield against the change of reaction of 5 wt% MnO/γ-Al₂O₃ catalyst. To thoroughly understand the reaction pathway of the decomposition of TCE, the mass balance on C and Cl atoms was performed.

Figure 4: The SEM photographs of the catalysts (A) impregnated and (B) calcined.
Table 2. The EDX analysis for the catalysts at various status.

<table>
<thead>
<tr>
<th>Element mass percentage (%)</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>86.5</td>
<td>0.0</td>
<td>13.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Impregnated Mn(NO$_3$)$_2$/γ-Al$_2$O$_3$</td>
<td>5.5</td>
<td>85.8</td>
<td>8.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Calcined Mn$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>8.9</td>
<td>83.8</td>
<td>7.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Reduced MnO/γ-Al$_2$O$_3$</td>
<td>18.4</td>
<td>73.0</td>
<td>8.6</td>
<td>0.0</td>
</tr>
<tr>
<td>365°C Incinerated catalyst</td>
<td>11.8</td>
<td>80.5</td>
<td>7.4</td>
<td>0.0</td>
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</table>

The TCE simulation conversion ($X_s$) and the yields ($Y_i$) of products are defined as the equation (9).

$$X_{s(C,Cl)} = \sum Y_{i(C,Cl)}$$

(9)

As shown in Table 3 that the TCE simulation conversions are attached with the raw TCE conversion Data. It reveals that carbon atoms (C) measured at outlet and inlet of the reactor remains balanced at all temperatures. This finding consists with equations (4) to (8) that the reactant is TCE and the products containing carbon atoms are CO, CO$_2$, and C$_2$Cl$_4$. The dominant product is CO$_2$.

From Table 4 shows that the TCE simulation conversions do not fit well with the raw TCE conversion data. It reveals that the chlorine atoms (Cl) measured at outlet and inlet of the reactor are not balanced at high temperatures.

![Figure 5: The product distributions of the TCE decomposed on the 5 wt% MnO/γ-Al$_2$O$_3$ catalyst.](image-url)
Table 3. The relationship between the yield of CO, CO₂, and C₂Cl₄ and the conversion of TCE.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>CO₂(%)</th>
<th>CO(%)</th>
<th>C₂Cl₄ (%)</th>
<th>X(%)</th>
<th>X(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>445.5</td>
<td>1.78</td>
<td>0.19</td>
<td>0.00</td>
<td>1.97</td>
<td>3.13</td>
</tr>
<tr>
<td>551.5</td>
<td>11.49</td>
<td>2.11</td>
<td>0.82</td>
<td>14.41</td>
<td>13.48</td>
</tr>
<tr>
<td>598.5</td>
<td>17.23</td>
<td>4.98</td>
<td>3.84</td>
<td>26.05</td>
<td>26.17</td>
</tr>
<tr>
<td>638.5</td>
<td>23.54</td>
<td>7.46</td>
<td>27.46</td>
<td>58.47</td>
<td>56.24</td>
</tr>
<tr>
<td>668.5</td>
<td>34.31</td>
<td>13.01</td>
<td>34.78</td>
<td>82.10</td>
<td>78.85</td>
</tr>
<tr>
<td>698.5</td>
<td>51.33</td>
<td>15.50</td>
<td>30.07</td>
<td>96.90</td>
<td>93.86</td>
</tr>
<tr>
<td>725.5</td>
<td>74.65</td>
<td>14.93</td>
<td>7.97</td>
<td>97.55</td>
<td>98.01</td>
</tr>
<tr>
<td>750.5</td>
<td>88.05</td>
<td>11.87</td>
<td>0.00</td>
<td>99.92</td>
<td>99.43</td>
</tr>
<tr>
<td>773.5</td>
<td>93.79</td>
<td>8.81</td>
<td>0.00</td>
<td>102.60</td>
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<td>793.5</td>
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<td>5.17</td>
<td>0.00</td>
<td>101.79</td>
<td>100.00</td>
</tr>
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<td>0.00</td>
<td>99.97</td>
<td>100.00</td>
</tr>
<tr>
<td>863.5</td>
<td>98.82</td>
<td>0.00</td>
<td>0.00</td>
<td>98.82</td>
<td>100.00</td>
</tr>
</tbody>
</table>

A change in color of the catalyst from black to light green was observed at the end of the activity tests. These colors fit quite well with those reported in the literatures for metal chloride complexes. [7] Therefore, the interaction of chlorine with the metal in presence of halocarbons or adsorption of chlorine on the γ-Al₂O₃ support could explain the unfitted chlorine balance.

Table 4. The relationship between the yield of Cl₂, HCl, and C₂Cl₄ and the conversion of TCE.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>C₂Cl₄ (%)</th>
<th>Cl₂ (%)</th>
<th>HCl (%)</th>
<th>X(%)</th>
<th>X(%)</th>
</tr>
</thead>
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<tr>
<td>445.5</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>3.13</td>
</tr>
<tr>
<td>551.5</td>
<td>1.09</td>
<td>0.81</td>
<td>0.00</td>
<td>1.90</td>
<td>13.48</td>
</tr>
<tr>
<td>598.5</td>
<td>5.11</td>
<td>7.13</td>
<td>0.00</td>
<td>12.24</td>
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</tr>
<tr>
<td>638.5</td>
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<td>15.72</td>
<td>0.00</td>
<td>52.70</td>
<td>56.24</td>
</tr>
<tr>
<td>668.5</td>
<td>47.09</td>
<td>31.16</td>
<td>0.52</td>
<td>78.77</td>
<td>78.85</td>
</tr>
<tr>
<td>698.5</td>
<td>40.18</td>
<td>45.55</td>
<td>2.81</td>
<td>88.54</td>
<td>93.86</td>
</tr>
<tr>
<td>725.5</td>
<td>10.54</td>
<td>55.62</td>
<td>8.08</td>
<td>74.24</td>
<td>98.01</td>
</tr>
<tr>
<td>750.5</td>
<td>0.00</td>
<td>60.68</td>
<td>15.92</td>
<td>76.60</td>
<td>99.43</td>
</tr>
<tr>
<td>773.5</td>
<td>0.00</td>
<td>63.54</td>
<td>21.00</td>
<td>84.54</td>
<td>100.00</td>
</tr>
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<td>793.5</td>
<td>0.00</td>
<td>64.28</td>
<td>25.05</td>
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</tr>
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<td>64.49</td>
<td>26.62</td>
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<td>65.65</td>
<td>29.77</td>
<td>95.42</td>
<td>100.00</td>
</tr>
</tbody>
</table>

At 452°C (725K), high conversion of TCE (above 95%) is obtained with some amounts of C₂Cl₄ (which is destroyed by reaction (7) in the range of 425-477°C
Air Pollution X

(698-750K)) and a yield to Cl$_2$ around 61% and a yield to HCl around 16% at 477°C (750K). The side reaction associated with the chlorination of the feed (TCE) to tetrachloroethylene was also observed by Wang et al. [8] over 1.5% platinum on γ-alumina with 95.6% conversion at 450°C but low yield to HCl in the range 20-23% at temperatures between 350°C and 450°C. These authors [9] also studied the TCE oxidation over PdO on γ-Al$_2$O$_3$ that reported 95.6% conversion at 550°C with yield to HCl of 31% and selectivity to C$_2$Cl$_4$ of 1.43%. Thus, the catalyst studied in this work produces higher yield to the desirable Cl$_2$ and HCl than those reported elsewhere. [8, 9]

Formation of CO from incomplete oxidation of TCE, reaction (5), can be observed over MnO/γ-Al$_2$O$_3$ catalysts at lower temperatures around 278°C (551K) but not found at high temperature, due to the reaction (8). The peak around 425°C (698K) obtained with the catalyst corresponds to the oxidation of C$_2$Cl$_4$, reaction (7), since formation of CO coincides with the decrease of C$_2$Cl$_4$.

All of our work was performed under dry inlet conditions such that water vapor effects were not examined. The effects of water vapor are beyond the scope of this study, deserving further attention in the future, although it is well known that on the one hand water can sinters the precious metal inhibiting the catalyst activity, and on the other hand is a source of hydrogen in the TCE oxidation promoting the selectivity to HCl. [8, 9]

4 Conclusions

TCE decomposed over a Mn$_2$O$_3$/γ-Al$_2$O$_3$ catalyst in a fixed bed reactor was conducted in this study. The Mn$_2$O$_3$/γ-Al$_2$O$_3$ powders were prepared by the incipient wetness impregnation method with aqueous solution of manganese nitrate. The catalyst was characterized by TGA, XRD, porosity analysis, SEM, EDX, and XPS. The results show that the main distinct weight loss is found at the temperatures around 373K and 873K, the Mn$_2$O$_3$ peaks (2θ= 32.5° and 55°) are only observed on the fresh catalyst, the SEM image of the Mn$_2$O$_3$ impregnated γ-Al$_2$O$_3$ support is much different from the calcined catalyst, and the Al element quantity on the catalyst surface is higher than that of the impregnated support.

The products and reactants distributions from the oxidation of TCE over Mn$_2$O$_3$/γ-Al$_2$O$_3$ were observed. The results show that the TCE conversion starts from 5% at 443K and rises to very high values in the 673-873K ranges, the CO$_2$ yield also pushes to 99% at the same temperature ranges. HCl and Cl$_2$ are the other main products with little halogenated VOC intermediates.
References


