SYNTHESIS & CATALYTIC PROPERTIES OF TRANSITION METAL OXIDES FOR THE OXIDATION OF GASEOUS ELEMENTAL MERCURY

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ABSTRACT

Gaseous mercury (Hg) emissions from man-made sources pose a significant environmental concern. From the three species of mercury (Hg⁰, Hg²⁺, Hg³⁺) that are emitted, elemental mercury (Hg⁰), which emanates from coal powered power plants, ore processing and incineration, is the most common. Currently, the method for removing mercury from flue gases is based on carbon adsorption. Thus, determining an effective, efficient and economically viable substitute for the removal of mercury is highly desirable. An alternative method, which is utilised in this study, involves oxidising elemental mercury to its mercuric form (Hg²⁺) and capturing it in an aqueous solution. In this work, two transition metal oxides were investigated for their ability to catalyse the oxidation of elemental mercury. Nano particulate forms of hematite (α-Fe₂O₃) and Nickel Oxide (Ni₂O₃), were prepared and characterized using a range of techniques (X-Ray Diffraction, Transmission Electron Microscopy and BET Surface Area Analysis). The mercury oxidation efficiency of the synthesized nano transition oxides were investigated under varying conditions and compared with average % Hg oxidation values of 70.80% and 2.49% respectively.

INTRODUCTION

Gaseous mercury emissions have been identified as an important global chemical pollution issue (US EPA, 2000). According to Pacyna et al. (2003), Australia and Oceania reported 99.9 tonnes of mercury released from stationary combustion, with a 5.5% contribution to global emissions of total mercury. When burning Australian coal, a higher quantity of elemental mercury is released into the environment due to lower levels of chloride where elemental mercury contributes to 90-99% of atmospheric mercury. Because of the toxicity of elemental mercury, numerous mercury removal processes have been employed. The most widely used application for elemental mercury removal is Activated Carbon Injection (ACI) Technology. This technology is however expensive and leads to the generation of large amounts of toxic (mercury laden) waste that must be land filled.
Two alternative methods that have received significant interest include:

- Catalytic oxidation (conversion of $\text{Hg}^0$ to $\text{Hg}^{2+}$), where $\text{Hg}^{2+}$ has sufficient solubility in water and can therefore be captured by wet scrubbers.
- Adsorption using non-carbon based adsorbents such as platinum, titanium, gold or metal oxides.

Of the two aforementioned processes, catalytic oxidation has the potential to be the most effective as the final form in which the mercury can be captured (aqueous solution) can be easily concentrated for disposal. Additionally, such systems would be compatible with current technologies used by coal-fired power plants as similar systems are currently used to remove gases such as $\text{SO}_2$ from their effluent streams. The process of converting (catalysing) elemental mercury to an ionic form suitable for capture in aqueous solutions has been reported in several studies (Presto and Granite, 2006), (Dranga, 2012). Potential catalysts that have received attention are metal and metal oxide catalysts.

Presto and Granite reported that there are three possible reaction mechanisms for catalytic oxidation of elemental mercury vapour using a solid catalyst:

(1). Langmuir-Hinshelwood:

\[
\begin{align*}
\text{Hg}^0 (g) & \leftrightarrow \text{Hg} (\text{ads}) \\
\text{Cl}_2 (g) & \leftrightarrow \text{Cl} (\text{ads}) \\
\text{Hg} (\text{ads}) + \text{Cl} (\text{ads}) & \rightarrow \text{HgCl} (\text{ads}) \\
\text{HgCl} (\text{ads}) & \rightarrow \text{HgCl}_2 (g)
\end{align*}
\]

(2) Eley- Rideal Mechanism:

\[
\begin{align*}
\text{Hg}^0 (g) & \leftrightarrow \text{Hg} (\text{ads}) \\
\text{Hg} (\text{ads}) + \text{Cl}_2 (g) & \rightarrow \text{HgCl}_2 (g)
\end{align*}
\]

(3) Mars- Maessen Reaction:

\[
\begin{align*}
\text{Hg} (g) + \text{Surface} & \rightarrow \text{Hg} (\text{ads}) \\
\text{Hg} (\text{ads}) + M_xO_y & \rightarrow \text{HgO} (\text{ads}) + M_xO_{y-1} \\
\text{HgO} (\text{ads}) + M_xO_{y-1} + \frac{1}{2} O_2 (g) & \rightarrow \text{HgO} (\text{ads}) + M_xO_y \\
\text{HgO} (\text{ads}) + M_xO_y & \rightarrow \text{HgM}_xO_{y-1}
\end{align*}
\]
Recent studies on the heterogeneous oxidation of mercury have shown the importance of chlorine species and NO$_x$ (Wu et al. 2004) and that between 300-400 °C, Cl$_2$ can be catalytically produced and lead to more oxidation, according to the Deacon Process (Presto and Granite, 2006; Wu et al., 2004);

$$2\text{HCl}_{(g)} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{Cl}_2_{(g)} + \text{H}_2\text{O}_{(g)}$$

The conversion of HCl to Cl$_2$ enhances mercury oxidation when a suitable catalyst is present, the mechanism is most likely to be heterogeneous with low concentrations of Cl$_2(g)$. It has also been reported that the presence of HCl, air and VOC’s can have a considerable effect on catalytic oxidation of mercury, where studies involving the presence of HCl gas showed an increase in mercury oxidation.

The first detailed studies on catalytic oxidation of mercury were published in the open literature approximately ~10 years ago (Senior et al. 2000) and have steadily increased since then. These studies have involved testing on a number of materials including MoO$_3$, V$_2$O$_5$, Cr$_2$O$_3$, CuO, MnO$_2$, and Fe$_2$O$_3$. Although there have been some studies conducted on the activity of Cu, Fe and Mn transition metal oxides (in supported or non-supported form) there have been no systematic studies conducted on nickel oxide based catalysts. The main aim of this study was to investigate the removal (catalytic oxidation) of gaseous elemental mercury using iron oxide and nickel oxide based catalysts.

**MATERIALS AND METHODS**

**Materials**

The following chemicals were used as received to synthesise hematite, copper oxide and manganese oxide nanoparticles; ferric nitrate nonahydrate (Chem-Supply), hydrochloric acid (Merck), nitric acid (Ajax), potassium permanganate (Ajax), Sulphuric Acid (Merck), 1000 ppm AAS gold chloride solution standard (Ajax), potassium chloride (Chem Supply), sodium hydrogen carbonate (BDH Chemicals), 1000 ppm AAS mercury solution standard (Aldrich), quartz wool (Element Microanalysis), sodium hydroxide (Ajax), nickel(ii) nitrate hexahydrate (Aldrich Chemical company), potassium hydroxide (Sigma).

Ultrapure Milli-Q water was used for the preparation of all solutions.

**Methods**
Preparation of Hematite Nanoparticles

Hematite ($\alpha$-Fe$_2$O$_3$) was prepared using a known procedure (Schwertmann et al., 1991). 40 g of Fe(NO$_3$)$_3$.9H$_2$O was dissolved in Milli-Q water preheated to 90°C under magnetic stirring. Ferrihydrite was then precipitated by adding 300ml 1 M KOH to the Fe(NO$_3$)$_3$.9H$_2$O solution which was preheated to 90°C. To maintain the solution pH of 8-9, 50 ml 1 M NaHCO$_3$ preheated to 90°C was added to the brown ferrihydrite mixture and transferred to two 500ml Schott bottle and placed in an oven at 90°C for 48 hours.

Preparation of Nickel Oxide Nanoparticles

Nickel Oxide (NiO) was prepared using a precipitation method described in Li et al. (2006). 12 g of Ni(NO$_3$)$_2$.6H$_2$O was dissolved in 20ml Milli-Q water in a beaker and magnetically stirred for 5 minutes. To precipitate the Ni$_2$O$_3$, 200ml of 5M NaOH was added to the mixture and rapidly stirred at room temperature. The mixture was then left in the mother liquor for 3 days at room temperature. After 3 days, the precipitate was filtered, washed with Milli-Q water and dried in an oven at 60°C for 24 hours, where Ni$_2$O$_3$ was formed after calcination (350°C for 4 hours).

Characterisation methods

X-Ray Diffraction (XRD) analysis was conducted using a Bruker AXS D8 ADVANCE Wide Angle X-Ray Diffraction Instrument with a CuK$\alpha$ source (1.54 Å).

Transmission Electron Microscopy was conducted using a Jeol 2010 Transmission Electron Microscope.

An ASAP 2010 Surface Area Analyser was used to determine the surface area of the metal oxide nanoparticles. Prior to analysis, the nanoparticles were heated under vacuum for 24 hours at 250 °C.

Catalyst Testing and Mercury Analysis

Hematite and Nickel oxide nanoparticles were tested for their efficiency for the catalytic oxidation of mercury using a specially-built rig shown in figure 1, using the conditions reported. Prior to catalyst testing, a calibration was performed in order to confirm that the elemental mercury concentration exposed to the catalyst bed was consistently at 24 µg/m$^3$. In a Teflon reactor, 0.4g of catalyst material was placed in between two portions (1cm in length) quartz glass wool. At a reactor temperature of 150°C, elemental mercury (Hg$^\circ$) was run through at a total flow rate of 1 l/min. The catalyst tests performed involved the inclusion of HCl gas (calibrated at 64 mg/m$^3$). The inclusion of HCl gas in this experiment was designed to help increase the amount of elemental mercury oxidised during catalytic oxidation (Wu et al. 2004). These tests were repeated a minimum of three times to ensure reproducibility.
Mercury analyses of the treated gas streams were conducted using a modified version of the Ontario-hydro method (Sun 2003). The method used 40 mg/L KMnO₄ (with 2% H₂SO₄) and 0.1 M KCl. Samples were prepared with a matrix of 50 ppb% HAuCl₄ and 0.35% HNO₃. Samples were then analysed by ICP-MS Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) trace element analyser.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis
The phases of the prepared hematite and nickel oxide nanoparticles were analysed using XRD. The XRD patterns of hematite and nickel oxide nanoparticles are displayed in Figures 2(a) and 2(b) respectively. The patterns obtained confirmed that the phases prepared were rhombohedral Fe₂O₃ and cubic phase Ni₂O₃.
Figure 2(a) - XRD pattern of the synthesised hematite (Fe₂O₃) nanoparticles
Surface Area Analysis

The results obtained from surface area analysis by BET method are given in Table 1. Nickel oxide is reported to have the highest surface area with a reported value of 85.46 m²/g, with hematite having the lowest surface area of 36.94 m²/g.

Table 1- Surface and micropore area of the nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>Hematite</th>
<th>Nickel Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area</td>
<td>36.94 m²/g</td>
<td>85.46 m²/g</td>
</tr>
<tr>
<td>Micropore area</td>
<td>3.00 m²/g</td>
<td>2.33 m²/g</td>
</tr>
<tr>
<td>Average Pore Diameter</td>
<td>120 (Å)</td>
<td>100 (Å)</td>
</tr>
</tbody>
</table>

Transmission Electron Microscope Analysis

The particle size and morphology analysis from the TEM obtained are shown in Figures 2(a) and 2(b). For the hematite nanoparticles synthesised (Figure 2(a)), nanoplatelets are shown with a particle diameter of 35-40 nm. The nickel oxide nanoparticles synthesised by precipitation method (Figure 2(b)) show a cubic structure,
with a larger particle diameter of around 200 nm. The larger, nickel oxide nanoparticles reflect the larger surface area displayed in table 1.

![Figure 2(a) - TEM image of synthesised hematite](image)

![Figure 2(b) - TEM image of synthesised nickel oxide](image)

**Catalyst Testing**

The synthesised nanoparticles of hematite and nickel oxide were tested for their catalytic activity in the presence of HCl. A summary of the results obtained from the catalytic testing for amount of oxidised mercury (in $\mu$g/m$^3$) and percentage of oxidised mercury is given in Tables 2 & 3, respectively. Nano hematite was clearly a superior material for
catalysing the oxidation of gaseous elemental mercury under the conditions used with over 70% of the mercury in the inlet gas being catalytically oxidised by this material. The nano nickel oxide catalysed a significantly lower amount of gaseous elemental mercury (~4% of mercury in stream) compared to the nano hematite.

Table 2. Mercury analysis of trapping solutions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Exp.#</th>
<th>Oxidised Hg (µg/m³)</th>
<th>Elemental Hg (µg/m³)</th>
<th>Hg (µg/m³)</th>
<th>Total</th>
<th>Average Oxidised Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Trap 1</td>
<td>Trap 2</td>
<td>Trap 4</td>
<td>Trap 5</td>
<td>Trap 6</td>
</tr>
<tr>
<td>Hematite</td>
<td>1</td>
<td>12.33</td>
<td>4.82</td>
<td>5.83</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.98</td>
<td>4.93</td>
<td>5.81</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>12.04</td>
<td>4.87</td>
<td>5.73</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Nickel Oxide</td>
<td>4</td>
<td>1.00</td>
<td>0.02</td>
<td>21.06</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.97</td>
<td>0.08</td>
<td>20.87</td>
<td>0.68</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.98</td>
<td>0.08</td>
<td>21.99</td>
<td>0.67</td>
<td>0.67</td>
</tr>
</tbody>
</table>

\( T = 150 \, ^\circ \text{C} \) for gas matrix containing \( \text{Hg}^0 = 24 \, \mu \text{g/m}^3, \text{HCl} = 64 \, \text{mg/m}^3, \) balance N₂

Table 3- % Hg oxidation of nano transition metal oxides

<table>
<thead>
<tr>
<th>Nano-transition metal oxide</th>
<th>% Hg Oxidised</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite (α-Fe₂O₃)</td>
<td>70.80</td>
</tr>
<tr>
<td>Nickel Oxide (Ni₂O₃)</td>
<td>4.29</td>
</tr>
</tbody>
</table>

The lower activity of the nickel oxide catalyst compared to the iron oxide catalyst was clearly not due to the difference in surface areas of these materials as the nickel oxide catalyst had a significantly higher surface area than the iron oxide catalyst. It is possible however that the lower average pore diameter of the nickel oxide catalyst (100 Å) (compared to the iron oxide catalyst (120 Å)) may have hindered the activity of this catalyst through reducing access of mercury to a higher percentage of the surface sites of this material.

CONCLUSIONS

Under the conditions tested, hematite and nickel oxide produced catalytic efficiencies of 70.80% and 2.49% respectively. The main conclusions from this study were as follows:

- Hematite nanoparticles showed promising results for the catalytic oxidation of elemental mercury under the conditions tested.
- Nickel oxide was shown to have less catalytic efficiency for mercury oxidation under the conditions tested
The difference in activity of the catalysts tested was not significantly influenced by surface area however the lower average pore diameter of the nickel oxide catalyst may have hindered the activity of this material.

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REFERENCES


