Effect of Molybdenum on the Activity Temperature Enlarging of Mn-Based Catalyst for Mercury Oxidation

Bo Zhao 1,2, Xiaojiong Zhao 2, Yangshuo Liang 1, Yu Wang 1, Linbo Qin 1,* and Wangsheng Chen 1

1 Hubei Key Laboratory for Efficient Utilization and Agglomeration of Metallurgic Mineral Resources, Wuhan 430081, China; zhaobo87@wust.edu.cn (B.Z.); liangyangshuo@126.com (Y.L.); yuwang@wust.edu.cn (Y.W.); chenwangsheng@wust.edu.cn (W.C.)
2 Industrial Safety Engineering Technology Research Center of Hubei Province, Wuhan University of Science and Technology, Wuhan 430081, China; jiongwust@163.com

* Correspondence: qinlinbo@wust.edu.cn

Received: 11 January 2020; Accepted: 20 January 2020; Published: 22 January 2020

Abstract: The MnO2/TiO2 (TM5) catalyst modified by molybdenum was used for mercury oxidation at different temperatures in a fixed-bed reactor. The addition of molybdenum into TM5 was identified as significantly enlarging the optimal temperature range for mercury oxidation. The optimal mercury oxidation temperature of TM5 was only 200 °C, with an oxidation efficiency of 95%. However, the mercury oxidation efficiency of TM5 was lower than 60% at other temperatures. As for MnO2–MoO3/TiO2 (TM5Mo5), the mercury oxidation efficiency was above 80% at 200–350 °C. In particular at 250 °C, the mercury oxidation efficiency of TM5Mo5 was over 93%. Otherwise, the gaseous O2, which could supplement the lattice oxygen in the catalytic reaction, played an important role in the process of mercury oxidation over TM5Mo5. The results of X-ray photoelectron spectroscopy (XPS) suggested that mercury oxidized by O2 over TM5Mo5 followed the Mars–Maessen mechanism.

Keywords: mercury oxidation; MnO2–MoO3/TiO2; temperature; mars–maessen mechanism

1. Introduction

Coal-fired power plants are among the largest mercury emission sources from anthropogenic activities [1]. Because of its toxicity to the environment and human health, mercury emission from coal-fired power plants has been strictly limited in the United States [2]. In China, a mercury emission limitation of 0.03 mg/m3 was announced in the Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011). Additionally, the Chinese government deposited the ratification of the Minamata Convention on Mercury, and became the 30th country of the Convention on August 31st, 2016. This means that the limit of mercury emission from coal-fired power plants in China will be stricter [3].

Mercury exists as three forms in coal combustion flue gas: elemental mercury (Hg0), oxidized mercury (Hg2+), and particle-bound mercury (HgP) [4]. Hg2+ and HgP can be easily eliminated by wet flue gas desulphurization (WFGD) and electrostatic precipitator (ESP) [5], respectively. However, Hg0 is difficult to capture by existing air pollution control devices due to its water insolubility and volatility. In the past 20 years, the methods of mercury removal, such as adsorption by sorbents [6,7] and oxidation by oxidants [8] or catalysts [9,10], have been widely investigated. Catalytic oxidation of Hg0 was in the spotlight when the selective catalytic reduction (SCR) system in coal-fired power plants was found to be beneficial for elemental mercury oxidation [11,12]. Hence, a variety of catalysts for mercury oxidation have been developed recently. Metal oxides, such as V2O5 [13,14], Fe2O3 [15], CeO2 [16], MnO2 [17], CuO [18], etc., have been loaded as active ingredients on the catalysts for mercury
oxidation. Peña et al. [19] found that the catalytic activity of the catalysts followed the sequence Mn > Cu > Cr > Co > Fe > V > Ni, which indicated that an Mn-based catalyst was an excellent choice for mercury oxidation. Ji et al. [20] reported that MnO2/TiO2 was available for Hg0 oxidation and NO reduction simultaneously at 200 °C, with a mercury oxidation efficiency of 90% and NO conversion efficiency of 97%. Wu et al. [21] indicated that Mn-based catalysts were beneficial for mercury oxidation, and elemental mercury removal efficiency follows the order 4% Mn/MK10 (montmorillonite K 10) > 4% Mn/SiO2 > 4% Mn/TiO2 > 4% Mn/Al2O3. In particular for the Mn/montmorillonite K 10, the mercury removal efficiency was greater than 90% [22]. However, mercury oxidation ability of MnO2/TiO2 was significantly restrained in the presence of SO2, and more than 80% of Hg0 escaped [20]. The optimal temperature of the Mn-based catalyst for mercury oxidation was always lower than 250 °C, and the formation of NH4HSO4 was the main reason for the catalyst deactivation at low temperature [23].

One way to enhance mercury oxidation ability was to add various auxiliary metal components into the Mn-based catalyst and keep low-temperature activity. Ce [17,24,25], Fe [3,15], and Co [16] were extensively loaded into the Mn-based catalyst. Li et al. [19] reported that the Mn–Ce/Ti catalyst exhibited high mercury oxidation ability at 150–250 °C. He et al. [25] stated that 6% Ce–6% MnO2/Ti–PILC exhibited optimal mercury oxidation ability at 250 °C, with a mercury oxidation efficiency of 72%.

Another way to avoid NH4HSO4 being deposited on the catalyst was to enhance the activity temperature of the Mn-based catalyst for mercury oxidation. In general, less NH4HSO4 was formed on the catalyst after the temperature rose above 300 °C, so enhancing the activity temperature of Mn-based catalyst to above 300 °C might be valuable. Existing research proves that molybdenum is a beneficial auxiliary component in V2O5/TiO2. Mercury oxidation efficiency of V2O5–MoO3/TiO2 was higher than that of V2O5/TiO2. More importantly, the active temperature range was enlarged to 350°C [26]. SCR activity of V2O5/ Mo3/TiO2 was higher than that of V2O5/WO3/TiO2 at 300 °C [27]. Fewer sulfates were considered to deposit on V/Mo/Ti–S catalyst [28]. Furthermore, more acid sites were also discovered after the addition of Mo into Ce/Ti catalyst, which contributed to the enhancement of SCR activity [29]. Therefore, to increase the active temperature of MnO2/TiO2 for mercury oxidation, the addition of molybdenum to this catalyst may be feasible. Moreover, few studies have focused on the mercury oxidation over Mn–Mo/Ti catalyst, and no research about the role of molybdenum in the catalyst for mercury oxidation has been reported. To develop a more widely applicable Mn-based catalyst, it is worth investigating whether the addition of molybdenum to MnO2/TiO2 enlarge the active temperature range of this Mn-based catalyst.

To clarify this question, in this study, Mn–Mo/Ti catalyst was prepared and the performance of this catalyst on mercury oxidation in simple O2/N2 atmosphere at different temperature was investigated. In addition, the mechanism of mercury oxidized by O2 over Mn–Mo/Ti was also examined.

2. Results and Discussion

2.1. Catalyst Characterization

2.1.1. Brunauer–Emmett–Teller (BET)

The pore structure parameters of the three catalysts are listed in Table 1. BJH is the abbreviation of “Barrett Joyner Halenda”, meaning the pore size distribution, which refers to the percentage of pore size at all levels in the material calculated by quantity or volume. The Brunauer–Emmett–Teller (BET) surface area of TM5 was 81 m2/g, and this value decreased to 56 m2/g after the addition of 5 wt. % MoO3 into the catalyst. Moreover, the BET surface area of TM05 was only 26 m2/g. Figure 1 was the pore diameter distribution of the three catalysts. The pore volume of TM5 Mo5 (0.0507 cm3/g) was lower than that of both TM5 (0.0936 cm3/g) and TM05 (0.0639 cm3/g). The addition of molybdenum to TM5 caused both the surface area and pore volume to decrease, which indicated that the interaction might be held between these compositions.
Table 1. The BET surface area of the three catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET Surface Area/m²/g</th>
<th>BJH Pore Volume/cm³/g</th>
<th>BJH Average Diameter/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM5</td>
<td>80.8678</td>
<td>0.0936</td>
<td>4.5871</td>
</tr>
<tr>
<td>TM5Mo5</td>
<td>55.7141</td>
<td>0.0507</td>
<td>3.8020</td>
</tr>
<tr>
<td>TMo5</td>
<td>25.9037</td>
<td>0.0639</td>
<td>9.3176</td>
</tr>
</tbody>
</table>

Figure 1. The pore diameter distribution of the catalysts.

2.1.2. Scanning Electron Microscopy (SEM)

Figure 2 shows the scanning electron microscopy (SEM) images of TM5 and TM5Mo5. It is clearly revealed that the addition of molybdenum can significantly change the morphology of the catalyst. Comparing these two catalysts, the surface morphology of TM5Mo5 was much smoother than that of TM5, and roughly melted materials were exhibited on the surface of TM5Mo5. This is mainly because molybdenum tends to aggregate during the process of catalyst preparation, where molybdenum was added to calcine titanic acid [30]. Few pores existed at the surface of both catalysts, which was consistent with the results of BET analysis.

Figure 2. The scanning electron microscopy (SEM) images of (a) TM5 and (b) TM5Mo5.

2.1.3. X-ray Powder Diffraction (XRD)

Figure 3 displays the X-ray powder diffraction (XRD) patterns of the three catalysts. Only two types of crystalline were identified in both TM5Mo5 and TM5, which were the anatase and rutile of
TiO$_2$. The crystalline at 25.2$^\circ$ was the typical peak of anatase [26], which was in all three catalysts. No crystal phase of MoO$_3$ and MnO$_2$ was discovered on the surface of TM$_5$Mo$_5$ and TM$_5$. However, a crystalline at 32$^\circ$ was found in TMo$_5$, which was the peak of MoO$_3$ according to the result of the joint committee on power diffraction standards (JCPDS). This indicates that the crystal phase of MoO$_3$ tends to change into a non-crystalline state after Mn and Mo are both present in the catalysts. This may be caused by the interaction of Mn and Mo during the process of catalyst preparation [30]. As for TM$_5$Mo$_5$ and TM$_5$, both molybdenum and manganese oxides were present in either as small crystallites (less than 4 nm in diameter) or non-crystalline state [27].

![X-ray powder diffraction (XRD) results of the three catalyst.](image)

**Figure 3.** The X-ray powder diffraction (XRD) results of the three catalyst.

2.1.4. X-ray Photoelectron Spectroscopy (XPS)

Mn 2p results of TM$_5$ and TM$_5$Mo$_5$ are shown in Figure 4. Two peaks of Mn 2p 3/2 are exhibited at 636–647 eV, which are respectively Mn$^{2+}$ at 641 eV and Mn$^{4+}$ at 642.4 eV on the surface of TM$_5$ in Figure 4a [8,31]. Two peaks of Mn 2p 3/2 are also noted at 636–647 eV on the surface of TM$_5$Mo$_5$ after the addition of MoO$_3$, which are Mn$^{3+}$ at 641.7 eV and Mn$^{4+}$ at 642.8 eV [8]. Comparing the results in Figure 4a,b, higher valence manganese was discovered on the surface of TM$_5$Mo$_5$. It should be noted that the addition of molybdenum enhanced the binding energy of manganese oxide transformed to high electron bit. Research into typical SCR catalysts (V–Mo/Ti) clarified that the presence of both molybdenum and vanadium in the catalyst cause the formation of stronger acid sites because of the interaction of Mo and V on surface of the catalysts [27], and molybdenum oxide could assist in oxidization of vanadium in low valence to higher valence [26]. As for TM$_5$Mo$_5$, the same effect of molybdenum might cause the change of electron bit of manganese in TM$_5$ and TM$_5$Mo$_5$, since the interaction of Mn and Mo during the process of catalysts preparation may occur depending on the results of XRD analysis.
Figure 4. The XPS analysis of Mn 2p for (a) TM₅; and (b) TM₅Mo₅.

Figure 5 shows the O 1 s results of the three catalysts. Four peaks of O 1 s are discovered at 526–534 eV on the surface of TM₅, which are TiO₂ at 529 eV and 530.1 eV, Ti₂O₃ at 531.1 eV, MnOₓ at 529.5 eV, respectively. In Figure 5b, three peaks, which are TiO₂ at 529.7 eV, MoO₃ at 530.4 eV and Ti₂O₃ at 531.1 eV, were consulted on the surface of TMo₅. Four peaks, which are TiO₂ at 530 eV and 529.3 eV, MoO₃ at 530.48 eV and TiO₄.₇₃ at 531.5 eV, are found on the surface of TM₅Mo₅. The addition of MnO₂ significantly weakened the intensity of TiO₂, which means that the surface of TM₅Mo₅ became complex for the interaction between manganese and molybdenum. In Figure 5c, the Mn–O component disappeared, but this does not mean that there were no Mn–O components on the surface of TM₅Mo₅. During the X-ray photoelectron spectroscopy (XPS) analysis of O 1 s, the binding energy of peaks for TiO₂ and MnOₓ was partly overlapped, e.g., the peak of 529.3 eV was TiO₂ and the peak at 529.5 eV was MnOₓ, and TiO₂ accounts for most of the catalyst. Mn–O components on the surface of TM₅Mo₅ were hidden, especially after the addition of Mo, because of the binding energy of peaks for TiO₂ was transferred to near 529.5 eV. Therefore, XPS analysis of Mn 2p in Figure 6 was the main basis for the following results.

Figure 5. The XPS analysis of O 1 s for (a) TM₅; (b) TMo₅ and (c) TM₅Mo₅.
2.2. Effect of Temperature

Figure 6 exhibits the effect of temperature on mercury oxidation over these catalysts in 6% O$_2$/N$_2$. The mercury oxidation efficiency of TM$_5$ increased as the temperature rose from 100 °C to 200 °C. However, this value of TM$_5$ decreased immediately when the temperature was above 200 °C. The optimal temperature range of TM$_5$ for mercury oxidation was only at the point of 200 °C, with mercury oxidation efficiency over 95%. Mercury oxidation efficiency of TM$_5$ decreased to 60% at 250 °C, 49% at 300 °C, and 27% at 350 °C, respectively. As for TM$_5$Mo$_5$, the mercury oxidation efficiency rose as the temperature increased. Mercury oxidation efficiency of TM$_5$Mo$_5$ was over 80% when the temperature was above 200 °C, and the optimal mercury oxidation efficiency was 93% at 250 °C. Moreover, this value was 88% at 300 °C and 77% at 350 °C, respectively. As for TM$_5$Mo$_5$, the best mercury oxidation efficiency of Mn-based catalyst was over 90%. Reporting on the above research, the Mn-based catalyst in this work also had similar mercury oxidation ability.

The results in Figure 6 indicate that the addition of molybdenum to TM$_5$ not only enhances the mercury oxidation ability, but also expands the optimal temperature range of mercury oxidation over TM$_5$Mo$_5$. Marshneva et al. [13] points out that molybdenum could improve the activity of the SCR catalyst in the De–NO$_x$ process. The sulfur resistance of molybdenum was discovered in the Mn/α-Al$_2$O$_3$ catalyst for mercury oxidation [32]. The primary result was that the addition of molybdenum could optimize the structure of the catalyst and promote the main active site transformation to a more active state. Additionally, other curious phenomena were also displayed in Figure 6. When the temperature was below 200 °C, the mercury oxidation ability of the three catalysts followed in the order TM$_5$ > TM$_5$Mo$_5$ > TM$_5$Mo$_5$. However, the order was changed to TM$_5$Mo$_5$ > TM$_5$Mo$_5$ > TM$_5$, when the temperature was over 250 °C. Existing research states that mercury oxidation over catalyst follows two primary steps: Hg$^0$ should be first adsorbed on the catalyst surface, and then the adsorbed mercury is oxidized by the oxidizing components on the catalyst surface. The BET surface area of the three catalysts follows the order TM$_5$ > TM$_5$Mo$_5$ > TM$_5$, and this was consistent with the mercury oxidation ability of the three catalysts at temperatures below 200 °C. This implies that the first step determines the mercury oxidation efficiency of the catalysts when the temperature is below 200 °C. During this temperature range, Hg$^0$ is more easily physically adsorbed on the surface of TM$_5$ due to having the highest surface area of the three catalysts. When the temperature is above 250 °C, the advantage of the BET surface area is weakened. Instead, oxidizing components on the catalyst surface play a primary role in the process of mercury oxidation over these catalysts. The XPS analysis results suggest that a much higher quantity of manganese is in the high-valance state on the surface of TM$_5$Mo$_5$, which is the core component for
mercury oxidation. Therefore, mercury oxidation efficiency of TM$_5$Mo$_5$ is higher than that of other two catalysts at temperatures above 250 $^\circ$C.

2.3. Effect of O$_2$

Figure 7 shows the mercury oxidation efficiency of TM$_5$Mo$_5$ in two conditions, with or without 6% O$_2$ at 250 $^\circ$C. It shows that the mercury oxidation efficiency of TM$_5$Mo$_5$ in 6% O$_2$/N$_2$ is 93% and the value is only 45% in pure N$_2$ after 2 h. It suggests that O$_2$ plays an important role in the process of Hg$^0$ oxidation over TM$_5$Mo$_5$. It has been shown that Hg$^0$ oxidized by O$_2$ over catalyst mainly follows the Mars–Maessen mechanism [5,8,26]. Equations (1)–(4) describe the reaction process. Besides the primary two steps mentioned in Section 3.2, the third step highlights the effect of oxygen in the circle of the catalytic reaction. As for TM$_5$Mo$_5$, elemental mercury is first adsorbed on the catalyst surface; subsequently, the adsorbed elemental mercury is oxidized by manganese in high valance, such as MnO$_2$ and Mn$_2$O$_3$. The manganese in high valance itself is reduced to the lower valance, which mainly is MnO. In pure N$_2$ condition, no oxidizing substance is supplied in the atmosphere; after MnO$_2$ or Mn$_2$O$_3$ is reduced to MnO, the reduced manganese cannot be re-oxidized to a high-valance state. Therefore, mercury oxidation efficiency of TM$_5$Mo$_5$ decreases and the value is lower than 45% after 2 h. In 6% O$_2$/N$_2$, as the oxidability of O$_2$, MnO could be re-oxidized to MnO$_2$ or Mn$_2$O$_3$. Accordingly, more elemental mercury could be oxidized by the oxidizing substance on the surface of TM$_5$Mo$_5$ and the value was even higher than 93% after 2 h tests.

\[
A(g) \leftrightarrow A(\text{ads}) \quad (1)
\]
\[
A(\text{ads}) + M_xO_y \rightarrow AO(\text{ads}) + M_xO_{y-1} \quad (2)
\]
\[
M_xO_{y-1} + 1/2O_2 \rightarrow M_xO_y \quad (3)
\]
\[
AO(\text{ads}) \rightarrow AO(g) \quad (4)
\]

Figure 7. The effect of oxygen on mercury oxidation over TM$_5$Mo$_5$.

2.4. Stability Test

To clarify the mechanism of mercury oxidation over TM$_5$Mo$_5$, a type of 20 h tests in 6% O$_2$/N$_2$ atmosphere at 200 $^\circ$C and 300 $^\circ$C was designed. It represents the low-temperature mercury oxidation ability of TM$_5$Mo$_5$ at 200 $^\circ$C, while it represents the high-temperature mercury oxidation ability of TM$_5$Mo$_5$ at 300 $^\circ$C. Figure 8 shows that mercury oxidation efficiency of TM$_5$Mo$_5$ was in the range of 88% to 93% at 300 $^\circ$C, while the value was 78% to 83% at 200 $^\circ$C during the 20 h tests. This indicates that the mercury oxidation ability of TM$_5$Mo$_5$ is much stronger at 300 $^\circ$C than at 200 $^\circ$C. In addition, mercury oxidation efficiency of TM$_5$Mo$_5$ is steady at both temperatures. To explain this phenomenon,
XPS was introduced to characterize the tested samples. Figure 9 shows the Mn 2p results of the two tested samples. MnO, Mn$_2$O$_3$, and MnO$_2$ were discovered on the surface of both samples. The result of Figure 4b shows that no MnO exists on the surface of initial TM$_5$Mo$_5$. This illustrates that elemental mercury is mainly oxidized by Mn$_2$O$_3$ and MnO$_2$ on the surface of TM$_5$Mo$_5$, and partial MnO is formed on the catalyst surface. Additionally, peak area ratio of Mn$_2$O$_3$ and MnO$_2$ in Figure 9a was 0.31, and the ratio increased to 0.79 in Figure 9b. This was in accordance with the results of the mercury oxidation ability at these two temperatures. When the catalytic reaction was steady, more Mn$^{4+}$ on the surface participated in the reaction at 300 °C than that at 200 °C. Therefore, the quantity of MnO$_2$ at 300 °C was less than that at 200 °C and the mercury oxidation ability was to the contrary. This proves that the main active component for mercury oxidation is manganese in high valance and the addition of molybdenum enhanced the mercury oxidation ability of MnO$_2$–MoO$_3$/TiO$_2$.

![Figure 8. Long time test of the mercury oxidation over TM$_5$Mo$_5$ at 200 and 300 °C.](image)

![Figure 9. XPS results of long-term test samples: (a) 20 h test at 200 °C; (b) 20 h test at 300 °C.](image)

3. Experimental

3.1. Catalyst Preparation

The catalysts were prepared by sol–gel method, and a detailed synthesis process is shown in Figure 10. Main raw materials were tetrabutyl titanate, ethanol, ammonia, nitric acid, molybdenum trioxide, and Mn(NO$_3$)$_2$ solution. All the chemical reagents were analytically pure. The tetrabutyl titanate was first dissolved in isometric volume ethanol solution to develop the sol. Then ammonia, nitric acid, manganese nitrate, and molybdenum were successively included in the solution. After
blending, drying, calcining, and grinding, the catalysts were pulverized to 45–100 µm. Three kinds of catalysts, named TM₅ (5 wt. % MnO₂), TM₅Mo₅ (5 wt. % MnO₂ and MoO₃) and TMo₅ (5 wt. % MoO₃) were prepared in this study.

3.2. Characterization Equipment

The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were controlled by ASAP 2020 (Micromeritics, America) [33–35]. X-ray photoelectron spectroscopy (XPS) and XRD of the three catalysts were determined by VG Multilab 2000 X-ray Photoelectron Spectroscopy and X’pert PRO X-ray powder diffraction (PANalytical, Holland) [36–38], respectively. Sirion 200 scanning electron microscope (FEI, Holland) was used to characterize the SEM of the three catalysts [39].

3.3. Experimental Conditions

Mercury oxidation ability of the three catalysts was tested on a laboratory scale fixed-bed experimental system. As showed in Figure 11, the experimental system was made up of three parts: a fixed-bed reactor, a mercury permeation source, and a mercury detection device. Detailed information of the fixed-bed reactor and mercury permeation source has been described in other research [26]. The fixed-bed reactor was a vertical furnace, and a quartz tube (ID: 16 mm) with a length 550 mm was equipped in the furnace. A sieve plate used to load the catalyst was in the middle of the quartz tube. The mercury permeation source was a U-shaped quartz tube, which was placed in a thermostat-controlled water bath. The mercury permeation tube was positioned in the U-shaped quartz tube, and mercury was transported out by N₂. The elemental mercury concentration was determined by QM201G (measuring ranges: 0–100 µg/L, Sensitivity: 0.1 µg/L, Qing’an Inc. Changzhou, China). Before each test, the mercury content standard curve of QM201G was determined. The initial Hg₀ concentration in the experimental flue gas was 55 ± 2 µg/m³. The total flow rate of each experiment was 1 L/min, and elemental mercury was transported by 0.5 L/min N₂. The weight of the catalyst in each run was 0.15 g, and the gas reciprocal space velocity was over 180,000 h⁻¹, which was calculated by dividing the volume of the catalyst by the volume of gas passing through the reactor in one hour. The experimental conditions are listed in Table 2.
Table 2. The experimental conditions.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Catalysts</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact of temperature</td>
<td>TM5Mo5/TM3/TMo5</td>
<td>6% O2/N2, 100 °C/150 °C/200 °C/250 °C/300 °C/350 °C</td>
</tr>
<tr>
<td>Impact of oxygen</td>
<td>TM5Mo5</td>
<td>100% N2/6% O2/N2, 250 °C</td>
</tr>
</tbody>
</table>

Mercury oxidation efficiency was used to describe Hg\(^0\) oxidized ability of the catalysts. This was determined by Equation (5), and a detailed introduction of this equation has been made in other research \[10,17,26,40\]. When the mercury content at the outlet of the reactor was varied below the range of 5% in 1 h, it could be assumed that the experiment reached a stable state. To ensure the accuracy of the results, every experiment was replicated three times.

\[ \eta = \frac{\Delta Hg\(^0\)_{out} - Hg\(^0\)_{in}}{Hg\(^0\)_{in}} \times 100\% \]  

\( \eta \): The mercury oxidation efficiency of the catalyst  
\( Hg\(^0\)_{in} \): The elemental mercury concentration at the inlet of the reactor  
\( Hg\(^0\)_{out} \): The elemental mercury concentration at the outlet of the reactor

4. Conclusions

This work focused on the unique performance of mercury oxidation over MnO\(_2\)–(MoO\(_3\))/TiO\(_2\). XPS was put in place to clarify the mechanism of mercury oxidation over this catalyst. Molybdenum enhanced manganese transference from a low-valance state to a high-valance state, which increased the active sites on the surface of the catalyst for mercury oxidation. Molybdenum effectively widened the optimal temperature range of the catalyst for mercury oxidation. The optimal temperature of TM\(_5\) for mercury oxidation was only a point at 200 °C, while the best temperature range of TM\(_5\)Mo5 for mercury oxidation was 200 to 350 °C. O\(_2\) plays an important role for mercury oxidation over TM\(_5\)Mo5, and this process follows the Mars–Maessen mechanism. Long-term tests indicated that the oxygen component of the catalyst surface was more active at 200 °C than that at 300 °C.

Author Contributions: Writing—review & editing, B.Z.; Data curation, X.Z.; Writing—original draft, Y.L.; Methodology, Y.W.; Resources, L.Q. & W.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China, grant number 51906182; The Open Project Foundation of Hubei Key Laboratory for Efficient Use and Agglomeration of Metallurgical Mineral
Resources grant number 2019zy003; The Open Project Foundation of Hubei Key Laboratory for Efficient Use and Agglomeration of Metallurgical Mineral Resources grant number 2019zy007.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**

2. Han, J.; Xiong, Z.; Zhao, B.; Liang, Y.; Wang, Y.; Qin, L. A prediction of arsenic and selenium emission during the process of bituminous and lignite coal co-combustion. *Chem. Pap.* 2020. [CrossRef]
20. Ji, L.; Sreekanth, P.M.; Smirniotis, P.G.; Thiel, S.W.; Pinto, N.G. Manganese oxide/titania catalysts with enhanced performance and reactivity of V/Mn-based catalysts for NH3-SCR of NOx and elemental mercury from flue gas. *Energy Fuels* 2008, 22, 2299–2306. [CrossRef]


35. Qin, L.; Xing, F.; Zhao, B.; Chen, W.; Han, J. Reducing polycyclic aromatic hydrocarbon and its mechanism by porous alumina bed material during medical waste incineration. *Chemosphere* 2018, 212, 200–208. [CrossRef]


