Catalytic Oxidation of Elemental Mercury over the Modified Catalyst Mn/α-Al2O3 at Lower Temperatures

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In order to facilitate the removal of elemental mercury (Hg0) from coal-fired flue gas, catalytic oxidation of Hg0 with manganese oxides supported on inert alumina (α-Al2O3) was investigated at lower temperatures (373–473 K). To improve the catalytic activity and the sulfur-tolerance of the catalysts at lower temperatures, several metal elements were employed as dopants to modify the catalyst of Mn/α-Al2O3. The best performance among the tested elements was achieved with molybdenum (Mo) as the dopant in the catalysts. It can work even better than the noble metal catalyst Pd/α-Al2O3. Additionally, the Mo doped catalyst displayed excellent sulfur-tolerance performance at lower temperatures, and the catalytic oxidation efficiency for Mo(0.03)–Mn(0.01)/α-Al2O3 was over 95% in the presence of 500 ppm SO2 versus only about 48% for the unmodified catalyst. The apparent catalytic reaction rate constant increased by approximately 5.5 times at 423 K. In addition, the possible mechanisms involved in Hg0 oxidation and the reaction with the Mo modified catalyst have been discussed.

Introduction

Mercury emitted from coal-fired power plants has become a major environmental issue because of its volatility, persistence, and bioaccumulation (1, 2). An agreement to launch United Nations Environment Programme (UNEP) Mercury Treaty Negotiations have been approved at UNEP’s 25th GC Session in 2009 (3). Worldwide, China is regarded as one of the larger emitters of mercury, and coal-fired utilities are believed to be the largest anthropogenic sources in China (4–6).

Mercury in coal combustion flue gas includes three forms: elemental mercury (Hg0), oxidized mercury (Hg2+), and particulate-bound mercury (Hg0) (7, 8). Hg2+ is water-soluble and therefore might be effectively captured by wet flue gas desulfurization (FGD) systems as a cobenefit (6–10). Most Hg0 can be collected by electrostatic precipitators (ESPs) or fabric filters together with fly ash. However, Hg0 is the most difficult to be removed because of its high volatility and low solubility in water. The conversion of Hg0 to its oxidized form can thus facilitate its capture from the flue gas. It has been reported that some catalysts used for the selective catalytic reduction of nitric oxides (SCR) were able to improve the oxidation of Hg0 to Hg2+ as an additional benefit when enough HCl was present in the flue gas (10–16). In order to develop the task-specific catalysts or sorbents for Hg0 removal, some noble metals or transition metal oxides were also investigated for such a purpose (13). Noble metal catalysts, such as gold (Au) and palladium (Pd), have been shown to assist the catalytic oxidation of Hg0 at lower temperatures, but they are considered too expensive for industrial applications. It has been found that manganese oxides on some carriers (e.g., titania or Al2O3) displayed significant catalysis for Hg0 oxidation at higher temperatures (10, 11). To meet such temperature demands, the catalyst unit must be installed upstream of the air preheater and the particulate control devices. This location may result in catalyst deactivation by exposure to high concentration of fly ash. The effect of fly ash can be minimized if the catalysts can be located downstream of the particulate control devices, where the temperature of the flue gas is relatively low. Therefore, developing higher activity catalysts operating at lower temperatures (373–523 K) has been of the great interest.

Recently, the authors have investigated the performance of the catalysts of manganese oxides (11). It was found that the catalysts were less active at lower temperatures and that SO2 had a significant negative effect on their performance. To improve their performance at lower temperatures, modification of the catalysts with several metal elements was investigated, and the catalysts were characterized by various techniques.

Experimental Section

Materials. It was found in our previous study that the catalysts with porous γ-Al2O3 as the carrier displayed very large adsorption capacity with Hg0 (11). The adsorption duration was very long, which would interfere with the test results for the net catalytic activity. In order to minimize this adsorption, inert alumina (α-Al2O3) pellets were used as the carrier in this study. The carrier consisted of pellets with a diameter of 1.5 ± 0.5 mm, and the BET surface area was 0.40 m2/g. All chemicals used for the catalysts preparation were of analytical grades, and purchased from Sigma-Aldrich Co. and Sino- pharm Chemical Reagent Co. Gases of SO2 (100%), NO (100%) and HCl (5000 ppm) were produced by Dalian Special Gas Co. The original gases were diluted to 200–1000 ppm by nitrogen, and then were added to the simulated gas through the mass flow controllers (MFCs). Compressed air and nitrogen in gas cylinders were used for the balance of the gases to prepare the simulated flue gases.

Catalysts Preparation. The manganese based catalysts were all prepared by the wet impregnation methods as follows. The aqueous solution of Mn(NO3)2 and the doped metal precursors, e.g., Sr(NO3)2, Na2WO4, 2H2O, Cu(NO3)2, and (NH4)6Mo7O24·4H2O were dissolved in deionized water at the room temperature, then the dried α-Al2O3 pellets were added to the solutions. After impregnation for 2 hours (h), the pellets were dried at 333 K for 12 h; then followed by calcination in air at 573 K for 1 h and at 673 K for 3 h. The doped catalysts were expressed as M(y)–Mn/α-Al2O3, in which M represents the added metals, and y represents the mole ratio of the added metal to Mn, the weight percentage of the impregnated Mn to α-Al2O3 was set at 1% in this study if it was not stated clearly. In order to evaluate the effect of the modified catalysts, the noble metal catalyst Pd(1%)/α-Al2O3 was used for comparison, it was prepared by the same method as Mn(1%)/α-Al2O3.

Catalytic Activity Evaluation. The catalytic activity was evaluated in a fixed-bed reactor, which was similar to that in our previous study (11). The reactor (i.d., 6 mm) consisted of...
of two quartz tubes: one was filled with 1.25 g of the catalysts, and the other contained the same amount of α-Al2O3 without any catalysts, as the reference. The simulated flue gas compositions were prepared in situ. The inlet flow rate of each gas stream was accurately controlled by MFCs. Hg0 vapor was prepared from the Hg0 permeation unit (placed in an oil bath with a temperature of 333 K) and was blended with the gases before they entered the reactor. Hg0 in the effluent stream was continuously monitored with an online mercury analyzers, and the data was recorded with a data acquisition system (N-2000). The reactions were mainly performed under atmospheric pressure at 373–523 K which was controlled by a tubular furnace. The total flow rate was 50 L/h and a space velocity (SV) of 4.4 × 104 h−1 was obtained. The tests consisted of the adsorption and catalytic oxidation processes. The catalyst was first exposed to the simulated flue gas for hours or days, until the Hg0 breakthrough in the outlet gas reached at least 80% of inlet Hg0 concentration. This was followed by the tests on catalytic activity in the presence of HCl.

A cold vapor atomic absorption spectrophotometry analyzer (SG921, Jiangfen, China) was used as the continuous emission monitor to measure Hg0 concentration continuously. The Ontario Hydro Method (OHM) was used to test the balance of mercury before and after the conversion. The OHM samples analysis and the adsorbed mercury on the catalysts were determined by a RA-915® mercury analyzer (Lumex, Russia) equipped with a liquid analysis unit and a solid pyrolysis unit (RP-91C), respectively.

Characterization of the Catalysts. To determine the crystals species distribution in the catalyst, X-ray diffraction (XRD) measurements were carried out with a diffractometer (D/max-2200/PC, Rigaku, Japan) using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA) measurements were used to determine the Mn 2p and O 1s binding energies with Mg Kα radiation (hν = 1253.6 eV). The Cls line at 284.6 eV was taken as a reference for the binding energy calibration. Transmission electron microscopy (TEM) was used to investigate microstructures of the catalysts with an electron microscope (JEM-2010, JEOL, Japan) and the selected area electron diffraction (SAED) patterns were obtained at the same time. Hydrogen temperature program reduction (H2–TPR) experiments were carried out on a CHEMBET 3000 (Quantachrome, U.S.) by increasing the temperature from 60 to 700 °C at a rate of 10 °C/min. The specific surface area of the catalysts was tested using Brunauer—Emmett—Teller (BET) method (ASAP 2010, Micromeritics Inc., U.S.).

Results and Discussion
Performance of Mn/α-Al2O3 at Lower Temperatures. As shown in Figure 1, the increasing of the adsorption temperature from 423 to 523 K was unfavorable for the adsorption of Hg0. The half breakthrough time of Hg0 dropped from about 240 min at 423 K to 35 min at 523 K in the absence of SO2. This result was different from our previous tests on the catalysts with γ-Al2O3, as the carrier (11). Additionally, the effect of SO2 on adsorption was remarkable, especially for the adsorption at lower temperatures. The presence of 500 ppm SO2 in the flue gas resulted in the reduction of the half breakthrough time to 30 and 18 min at 423 K and 523 K, respectively. The results indicated that the presence of SO2 could inhibit the adsorption of Hg0 onto the catalyst especially at lower temperatures.

Once the Hg0 adsorption breakthrough efficiency was over 80%, HCl was continuously injected into the gas to investigate the performance of catalytic oxidation of Hg0 over various catalysts. These results are also shown in Figure 1(b). It was obvious that the presence of HCl enhanced the removal of Hg0. It was also observed that the removal of Hg0 by catalytic oxidation with 20 ppm HCl at 423 K (73%) was lower than that at 523 K (84%), and the catalyst Mn/α-Al2O3 was less active below 523 K. The balance of mercury with OHM indicated that almost all the removed Hg0 in the presence of HCl was converted to oxidized mercury, with the balance of 95(±10)% for the total mercury between in the inlet gas (Hg0) and the outlet (Hg2+ and Hg0). The presence of SO2 also showed a significant inhibition to Hg0 catalytic conversion at lower temperatures.

Temperature Dependence of the Catalysts with Various Doping Elements. Since Mn/α-Al2O3 catalyst was less active for Hg0 conversion at lower temperatures or in the presence of SO2, several metal elements (Sr, W, Cu, and Mo) were tentatively doped into Mn/α-Al2O3 to improve the performance of the catalysts, and Pd(1%)/α-Al2O3 catalyst was employed as a reference as well.

The adsorption and catalytic behavior for Mo–Mn/α-Al2O3 is also illustrated in Figure 1. As can be seen, the adsorption and the catalytic performance at lower temperatures were both significantly improved by the addition of Mo. The half breakthrough time for Hg0 adsorption in the absence of SO2 increased to about 2000 min versus about 240 min for the Mn/α-Al2O3 catalyst at 423 K. However, the Hg0 half breakthrough for sole Mo/α-Al2O3 was only 120 min.

The catalytic oxidation efficiency of Hg0 by Mo(0.01)–Mn/α-Al2O3 with 20 ppm HCl (without SO2) was about 95% at 423 K, with an increase of about 20% over Mn/α-Al2O3 (as the baseline). Furthermore, the Hg0 oxidation efficiencies for the catalysts with other doping elements at different temperatures are shown in Figure 2 (with 10 ppm HCl). It was seen that the doping of other elements into Mn/α-Al2O3 could also improve the catalytic activity at lower temperatures. Mo was
found to be the best among the tested dopants, and the addition Mo (0.01) to the catalyst can decrease the operation temperature by at least 80 K while still achieving the same Hg⁰ oxidation efficiency (Figure 3). By comparison, Mo(0.01) – Mn/α-Al₂O₃ showed higher Hg⁰ catalytic oxidation efficiency than Pd/α-Al₂O₃ under similar conditions. However, the Hg⁰ oxidation efficiency on sole Mo(1%)/α-Al₂O₃ at 423 K was about 30% with 20 ppm HCl. Therefore, Mo just acted as the promoter in Mn/α-Al₂O₃ because the catalysis of its sole was rather low. In addition, the effect of NO (0–400 ppm) on the catalysts was observed to be insignificant.

The Effect of SO₂ on Various Catalysts. Manganese based materials have been found to be able to adsorb sulfur dioxide at lower temperature (17), which might deteriorate the catalyst’s performance for Hg⁰ conversion. The activity of each catalyst was investigated in the simulated flue gas with 500 ppm SO₂. For the adsorption, the addition of Mo and W can increase the t₁/₂, obviously. The t₁/₂ for Mn/α-Al₂O₃ in the presence of SO₂ at 423 K was only about 30 min, but it was more than 350 min when Mo(0.01) was doped into the Mn/α-Al₂O₃ catalyst.

The effects of SO₂ on the Hg⁰ oxidation with various catalysts are shown in Figure 3. As can be seen, the inhibition effect of SO₂ varied for different catalysts. The Hg⁰ oxidation efficiency of Mn/α-Al₂O₃ with 20 ppm HCl dropped from 93 to 78% (in Figure 1), a loss of about 15% at 573 K in the presence of SO₂. However it sharply decreased from about 73 to 48% at 423 K, with a loss of 25%. This indicated that the inhibition of SO₂ on the activity of Mn/α-Al₂O₃ was more remarkable at lower temperatures. Among the modified catalysts, Mo(0.01) – Mn/α-Al₂O₃ showed the best resistance to the inhibition of SO₂. Hg⁰ oxidation efficiency decreased from about 95 to 88% (7% loss) at 423 K in the presence of 500 ppm SO₂. Doping Sr into Mn/α-Al₂O₃ can also improve its catalytic activity at lower temperatures, but its performance against the inhibition of SO₂ was relatively weak. Mo(0.01) – Mn/α-Al₂O₃ also showed higher tolerance to SO₂ than Pd/α-Al₂O₃, which was only about 80% at 423 K in the presence of 500 ppm SO₂.

Additional tests were performed to determine the possible reasons that SO₂ influenced on catalysts’ activities. First, the Mn/α-Al₂O₃ catalyst was continuously pretreated with 500 ppm SO₂ (dry air as the balance) at 423 K for 10 h before their catalytic activity tests. It was found the Hg⁰ conversion efficiency decreased by about 16% comparing with the untreated fresh catalyst in the absence of SO₂, and further dropped to about 26% in the presence of 500 ppm SO₂. Meanwhile, the effect of SO₂ on the Hg⁰ adsorption on Mn/α-Al₂O₃ was more remarkable, and Hg⁰ adsorption capacity would loss over 80% in the coexistence of 500 ppm SO₂. The above results indicated that SO₂ could cause a permanent activity loss maybe by the combination with catalyst elements. And a possible temporary and reversible effect maybe resulted in the competitive adsorption between SO₂ and Hg⁰ on the catalyst’s active sites, which has ever been proposed in the similar study (14). Therefore, it can been regarded that the doped Mo in catalysts might be helpful to diminish the competitive adsorption of SO₂ with Hg⁰ or the permanent coverage by SO₂ on Mn-base active sites because the larger affinity of Mo to sulfur would minimize the chance of the contact of sulfur and Mn (18–20). However, further investigations are required to support the hypothesis.

Effect of the Doped Content Mo and HCl Concentration. The effect of the doped content of Mo into the catalysts was also investigated and the results are shown in Figure 4. As expected, the catalytic oxidation efficiency of Hg⁰ increased with the increase of the doped amount of Mo. Hg⁰ oxidation efficiency at 423 K with 20 ppm HCl in the presence of 500 ppm SO₂ was only 48% for the Mn/α-Al₂O₃ without Mo addition, but it was about 87% and 95% when the doped mole ratios of Mo to Mn were 0.01 and 0.03, respectively. The enhancement effect tended to be flat as the doped mole ratios of Mo to Mn exceeded 0.03.

Meanwhile, the effect of HCl concentration on the Hg⁰ oxidation efficiency is also shown in Figure 4. Higher HCl concentration was favorable for the catalytic oxidation of
the values of 
and the main results are listed in Table 1. It can be seen that data obtained by graphing with the data obtained above, be obtained with eq 1.

the consumed HCl was almost negligible, HCl concentration more clearly, powdered γ-Al2O3 appeared too weak to identify the crystals of Mn
5 oxidation.

Both of them slightly decreased after 24 h tests (by about 0.5% for the catalyst of Mo(0.03). The XRD patterns of the catalysts with the higher Mo amount. Only 5 ppm of Hg0. The required HCl concentration was lower using the modified catalysts with the higher Mo amount. 5 ppm of HCl was needed to obtain 90% Hg0 oxidation efficiency when the doped mole ratios of Mo to Mn was about 0.03. Additionally, since γ-Al2O3 was more porous than α-Al2O3, a better performance was expected if γ-Al2O3 was employed as the catalyst carrier.

Kinetics for the Typical Catalytic Reaction. Equation 1 is tentatively used to express the rate of Hg0 catalytic oxidation.

\[ r_A = K[HCl]^{\beta}[Hg^0] \] (1)

in which, \( r_A \) is the specific reaction rate for Hg0 oxidation on the catalyst, mg/(m2·s), \( K \) is the apparent catalytic reaction rate constant, m/s., and \( \beta \) is the reaction order with regard to HCl concentration, dimensionless. Since the employed HCl concentration in the reactor was far higher than Hg0 and the consumed HCl was almost negligible, HCl concentration could be regarded as a constant (21, 22). Therefore, eq 2 can be obtained with eq 1.

\[ \frac{[Hg^0]}{[Hg^0]_0} = \exp[-K_\beta[HCl]^{\beta}] \] (2)

Where \( \varepsilon \) is the specific area per unit volume of the catalyst, m2/m3. The relationship of ln(−ln([Hg0]/[Hg0]0))~[HCl] should be linear if eq 1 was suitable for the description of the kinetics. As expected, it was observed that the ln(−ln([Hg0]/ [Hg0]0))~[HCl] curves for the tested catalysts showed linear performance, which indicated that the catalytic reaction conformed to the pseudo first order with respect to Hg0. Then \( \beta \) and \( K_\beta \) in eq 2 can be obtained by graphing with the data obtained by graphing with the data obtained above, and the main results are listed in Table 1. It can be seen that the values of \( \beta \) for various catalysts were very close to one other (0.36 ± 0.02), but the value of \( K_\beta \) varied significantly. The enhanced factor, defined as the \( K_\beta \) ratio of the doped catalyst to the unmodified (baseline), can also be employed to assess the performance of the catalyst, and it was about 5.5 for the catalyst of Mo(0.03)−Mn/α-Al2O3 at 423 K in the presence of 500 ppm SO2.

Characterization of the Catalysts. The BET area were determined to be about 0.57 m2/g, 0.87 m2/g, 1.10 m2/g, and 1.18 m2/g for the sloe Mn/Al2O3, Mo(0.01)−Mn/Al2O3, Mo(0.03)−Mn/Al2O3, and Mo(0.05)−Mn/Al2O3, respectively. Both of them slightly decreased after 24 h tests (by about 5~10%). The XRD patterns of the catalysts with α-Al2O3 as the carrier appeared too weak to identify the crystals of Mn or Mo on the catalysts because of lower load content (~2%). In order to explain the effect of Mo on the Mn/α-Al2O3 catalyst more clearly, powdered γ-Al2O3 was used as the catalyst carrier to obtain a higher load content of Mn and Mo in the catalyst. Figure 5 shows XRD patterns of (20%)Mn/Al2O3 and Mo(0.15)−Mn(20%)/Al2O3. It can be seen that Mn mainly presented in the form of MnO2, and the peak for MnO2 can also been observed. The Mn in the doped catalyst was mainly found as MoO3. It was found that the full width at half maximum (fwhm) of MnO2 and Mo3O8 peaks slightly increased after doping with Mo. The higher XRD fwhm of the crystalline indicated the smaller size of the particles, which indicated that Mo can improve the dispersion of MnO2 particles by inhibiting the agglomeration.

It was also observed from the TEM micrograph of Mn/Al2O3 (Figure 6) that the particles were not well dispersed. However, for the Mo−Mn/Al2O3 catalyst, the observed particles appeared to be smaller. Also, the SAED patterns of the two catalysts (at the right down corner of TEM pictures) also showed the Mn/Al2O3 appeared to be the single crystal diffraction spots and the Mo/Mn/Al2O3 had the poly crystal diffraction rings within the same scanned surface area. This indicated that the crystalline of Mn catalyst was larger than the Mo doped one. The result agrees well with the XRD fwhm results.

Figure 7 shows the temperature program reduction (TPR) curves of the catalysts by hydrogen. It was shown that the addition of Mo to the catalyst resulted in the flattening of the TPR curves. The reduction startup temperature decreased to about 423 K, though the peak was relatively low. Meanwhile, the main TPR curves of the modified catalyst shifted to a higher temperature. Although the lower TPR reduction startup temperature can be used to explain why the catalyst showed better catalytic activity at lower temperatures, it should not be the only factor considered to interpret such remarkable results for Hg0 conversion. Meanwhile, the shift of TPR curves might implicate that Mo−Mn complex was formed on the catalysts, which would result in a better tolerance to SO2 (18~20). The XPS analysis results for Mn2p (Figure 8) indicated that doping Mo into the catalysts can increase the ratio of Mn4+/Mn3+, which was favorable for the reaction with Hg0, and this effect of the change were consistent with the Deacon process described below. The increase of binding energy of O1s may implicate that the ratio of lattice oxygen (O2−) to other oxygen species (e.g. oxygen in O22− or hydroxide) dropped when Mo was doped in the catalysts.

<table>
<thead>
<tr>
<th>catalysts</th>
<th>temperature (K)</th>
<th>SO2</th>
<th>( \beta )</th>
<th>( \varepsilon K_0 ) (mg/m3·s)</th>
<th>constant ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn/α-Al2O3 (baseline)</td>
<td>423</td>
<td>W/o</td>
<td>0.37 ± 0.02</td>
<td>4.2 ± 0.3</td>
<td>1</td>
</tr>
<tr>
<td>Mo(0.01)−Mn/α-Al2O3</td>
<td>423</td>
<td>W/o</td>
<td>0.36 ± 0.02</td>
<td>11.4 ± 0.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Mn/α-Al2O3</td>
<td>423</td>
<td>W</td>
<td>0.37 ± 0.02</td>
<td>2.1 ± 0.2</td>
<td>1</td>
</tr>
<tr>
<td>Mo(0.01)−Mn/α-Al2O3</td>
<td>423</td>
<td>W</td>
<td>0.36 ± 0.02</td>
<td>6.5 ± 0.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Mo(0.03)−Mn/α-Al2O3</td>
<td>423</td>
<td>W</td>
<td>0.36 ± 0.02</td>
<td>11.7 ± 0.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Mo(0.01)−Mn/α-Al2O3</td>
<td>373</td>
<td>W</td>
<td>0.36 ± 0.02</td>
<td>5.4 ± 0.5</td>
<td>1</td>
</tr>
<tr>
<td>Mo(0.01)−Mn/α-Al2O3</td>
<td>473</td>
<td>W</td>
<td>0.36 ± 0.02</td>
<td>7.2 ± 0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

W/o: in the absence of SO2 in the gas; W: with 500 ppm SO2 in the gas. The ratio of the apparent catalytic reaction rate constant to the baseline. Mn: Mn/α-Al2O3.
Speculation on the Mechanism for the Modified Catalysts.

From the tests results of the catalysts, the low-temperature catalytic activity and the ability to tolerate poisoning from sulfur dioxide can be remarkably improved by the doping of Mo oxide. According to our preliminary tests, Cl₂ was apparently detectable when it was over 573 K, and the yield of Cl₂ with Mo doped catalyst was about 50% higher than Mn catalyst at the similar test condition. Therefore, the doping of Mo in the catalyst was proved to be favorable to the Deacon reaction (22). In addition, the shift of the main TPR curves to higher temperature may indicate that more stable compound formed after Mo was doped. Thus based on the above experimental results, the mechanism for the functions of Mo in the catalyst can be speculated as follows: First, the impregnated manganese precursor on the Al₂O₃ carrier would be converted to particles of manganese oxides as the catalyst was calcined. These particles would tend to agglomerate and then form crystalline Mn oxides during the sintering process. The crystalline Mn oxides were unfavorable for the catalytic activity and the sulfur tolerance. The doped Mo in the catalysts could partly form Mo oxides among the particles of Mn oxides or Mo-Mn compound and the agglomeration of particles would be effectively inhibited. In addition, the presence of Mo-Mn complex was supposed to improve the sulfur resistance performance (18–20). These might promote the Deacon reaction to form reactive chlorine species (e.g., Cl₂ or Cl). The first step in the Deacon mechanism is the hydrogen abstraction from HCl leading to adsorbed activated chlorine and hydroxyl species (21). Then, Hg⁰ can be quickly oxidized by the activated chlorine. The series reactions in the presence of Mo-Mn complex can be speculated as follows, in which eq 12 can be regarded as the overall Deacon reaction (21). The effect of
Mo^{6+} to the catalysis might be attributed to its promotion on the cycle between Mn^{3+} and Mn^{4+}, which would speed the transfer of oxygen and the formation of the reactive chlorine species (eqs 3–8).

\[
\begin{align*}
\text{Mn}^{4+} + \text{O}^2- + \text{HCl} & \rightarrow \text{Mn}^{3+} + \text{OH}^- + \text{Cl}^- \quad (3) \\
\text{OH}^- + \text{OH}^- & \rightarrow \text{H}_2\text{O} + \text{O}^2- \quad (4) \\
\text{Cl}^- + \text{Cl}^- & \rightarrow \text{Cl}_2 \quad (5) \\
2\text{Mn}^{3+} + 0.5\text{O}_2 & \rightarrow 2\text{Mn}^{4+} + \text{O}^2- \quad (6) \\
\text{Mo}^{6+} + \text{Mn}^{3+} & \rightarrow \text{Mn}^{4+} + \text{Mo}^{5+} \quad (7) \\
2\text{Mo}^{5+} + 0.5\text{O}_2 & \rightarrow 2\text{Mo}^{6+} + \text{O}^2- \quad (8) \\
\text{Hg}^0 + \text{Cl}^- & \rightarrow \text{HgCl}^- \quad (9) \\
\text{HgCl}^- + \text{HCl} & \rightarrow \text{HgCl}_2 + \text{H} \quad (10) \\
\text{Hg}^0 + \text{Cl}_2 & \rightarrow \text{HgCl}_2 \quad (11) \\
\text{Hg}^0 + 2\text{HCl} + 0.5\text{O}_2 & \rightarrow \frac{\text{Mo-MnO}_x}{\text{HgCl}_2 + \text{H}_2\text{O}} \quad (12)
\end{align*}
\]

In conclusion, the Mo doped catalyst Mn/e-Al_2O_3 displayed excellent performance for Hg^0 catalytic conversion. The apparent catalytic reaction rate constant increased by about 5.5 times in the presence of SO_2 at 423 K. The doping of Mo into the catalysts might improve the dispersion of MnO_2 particles and form more stable compound that have stronger sulfur-tolerance. The Mo doped catalysts appear to have potential for Hg^0 oxidation from coal fired flue gas in industrial applications.

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Literature Cited