

# A Critical Review on the Heterogeneous Catalytic Oxidation of Elemental Mercury in Flue Gases

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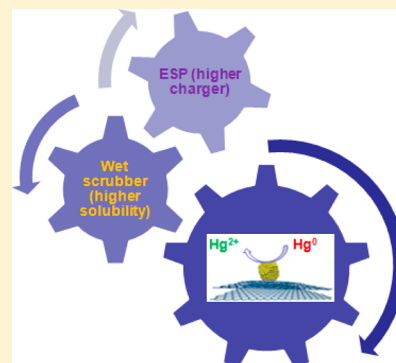
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## S Supporting Information

**ABSTRACT:** Nowadays, an increasing attention has been paid to the technologies for removing mercury from flue gases. Up to date, no optimal technology that can be broadly applied exists, but the heterogeneous catalytic oxidation of mercury is considered as a promising approach. Based on a brief introduction of the pros and cons of traditional existing technologies, a critical review on the recent advances in heterogeneous catalytic oxidation of elemental mercury is provided. In this contribution, four types of Hg oxidation catalysts including noble metals, selective catalytic reduction (SCR) catalysts, transition metals, and fly ash have been summarized. Both the advantages and disadvantages of these catalysts are described in detail. The influence of various acidic gases including SO<sub>2</sub>, SO<sub>3</sub>, NH<sub>3</sub>, NO<sub>x</sub>, HCl, Cl<sub>2</sub>, etc. have been discussed as well. We expect this work will shed light on the development of heterogeneous catalytic oxidation of elemental mercury technology in flue gases, particularly the synthesis of novel and highly efficient Hg<sup>0</sup> oxidation catalysts.



## 1. INTRODUCTION

Mercury is a leading concern among the air toxic metals because of its volatility, persistence, and bioaccumulation in the environment. Exposure to high levels of mercury has been associated with serious neurological and developmental effects in humans. Depending on the dose, the effects can range from subtle losses of sensory or cognitive ability to tremors, inability to walk, convulsions, and death.<sup>1,2</sup> Coal-fired utility boilers, which release more than 50 tons of mercury annually in the United States (59 tons in 1990 and 53 tons in 2005), are the largest source of mercury pollution.<sup>3</sup> However, on average only about 40% of the mercury entering a coal-fired power plant is captured and 60% emitted.<sup>4</sup> Since 1990, Hg had been listed as a hazardous and toxic pollutant under Title III of the Clean Air Act Amendments (CAAA) in the United States.<sup>5</sup> However, even after more than 20 years, no significant change has been made in Hg abatement. Thus, on December 16, 2011, the Environmental Protection Agency (EPA) finalized the first ever national standards to reduce mercury and other toxic air pollution from coal and oil-fired power plants. The final rule established that the power plant emission standards for mercury

is to prevent about 90% of the mercury in coal burned in power plants being emitted to the air.<sup>3</sup> Therefore, in order to meet the target, mercury abatement has attracted increasing and global attention nowadays.

Although mercury contents in coal are relatively low (approximately 0.1 ppm on average), the amount of mercury released into atmosphere from coal combustion is very large due to the great amount of coal combusted. At present, coal combustion is one of the main anthropogenic pollution sources of mercury emissions. Research by the U.S. Geological Survey indicated that much of the mercury in coal is associated with pyrite. Other forms of mercury that have been reported are organically bound, elemental, and in sulfide and selenide minerals. During combustion, mercury is released into the exhaust gas as elemental mercury vapor, Hg<sup>0</sup>. This vapor may then be oxidized to Hg<sup>2+</sup> via homogeneous (gas-gas) and

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heterogeneous (gas–solid, surface catalyzed) reactions. Consequently, mercury is present in the flue gases in several forms: elemental mercury vapor ( $\text{Hg}^0$ ), oxidized mercury species ( $\text{Hg}^{2+}$ ), and particulate-bound mercury ( $\text{Hg}_p$ ).<sup>6</sup> Among these forms,  $\text{Hg}^0$  is the most difficult to capture because of its high volatility and low solubility in water. The specific chemical form has a strong impact on mercury capture by boiler air pollution control equipments.<sup>5–7</sup>

The cost of mercury abatement can be highly reduced by combining catalytic oxidation of elemental mercury with particle controllers or flue gas desulfurization (FGD).  $\text{HgO}$  and  $\text{HgCl}_2$  have charge and lower volatility; thus they can be easily adsorbed on particles and removed in particle controllers.  $\text{HgCl}_2$  is more soluble in water, which can be removed by alkaline solution. Blythe<sup>8</sup> compared the cost of catalytic oxidation technology and conventional activated carbon injection (ACI). It was found that with a minimum removal of 55% and 2-year operating time, the cost for catalytic oxidation method is only 40% of ACI cost (sell ash and regenerate catalyst after 1 year use). Even without selling the ash, the cost (60% of ACI cost) is still greatly lower than ACI method.

Due to the essentiality of mercury abatement from flue gases, the related research has bloomed splendidly since 2005. In order to follow and aid its rapid development, a critical review of the recent advances in heterogeneous oxidation of mercury has been highly demanded. In the present work, we will first briefly review the background of the existing and current developing technologies for mercury removal; then highlight the heterogeneous catalytic oxidation of mercury technology. The types of potential catalysts and the influences of acidic gases are discussed in detail. This work will shed light on the development of heterogeneous catalytic oxidation of mercury in flue gases.

## 2. BACKGROUND OF MERCURY REMOVAL TECHNOLOGY

The control of mercury emissions from coal-fired boilers is achieved via existing controls used to remove particulate matter (PM), sulfur dioxide ( $\text{SO}_2$ ), and nitrogen oxides ( $\text{NO}_x$ ). This includes capture of particulate-bound mercury in PM control equipments such as electrostatic precipitator (ESP), fabric filter (FF), and soluble mercury compounds in wet FGD systems. The use of selective catalytic reduction (SCR) of  $\text{NO}_x$  control enhances the concentration of soluble mercury compounds in flue gas and results in increased mercury removal in the downstream wet FGD system.<sup>9</sup> Unfortunately, none of the aforementioned method can reach 90% of mercury removal alone.

ESP cold and ESP hot are significantly less effective than FF, because there is less contact between gaseous mercury and fly ash in ESPs. A FF can be very effective for mercury capture from both bituminous and subbituminous coals, which is one of the reasons that more and more FF units are being installed recently. However, this FF-only configuration only represents small percentage of (5–10% of the U.S.) coal burning capacity.<sup>6,10</sup> The wet FGD systems include the common limestone forced oxidation scrubber and the magnesium-enhanced lime scrubber. The dry FGD systems are typically spray dryer absorbers, which are usually installed in combination with FF. Mercury in its oxidized state ( $\text{Hg}^{2+}$ ) is highly water-soluble and thus would be expected to be captured efficiently in wet FGD systems. However, over 80% of total

mercury stays in elemental form, and easily escapes from wet FGD system.<sup>6</sup> All the traditional technologies for Hg abatement, and their advantages and disadvantages are summarized in Table 1.<sup>4,6,11</sup>

**Table 1. Traditional Existing Technologies for Hg Abatement from Flue Gases**

technologies	advantages	disadvantages
ESP cold	already existing device for PM abatement	low efficiency
ESP hot	already existing device for PM abatement	low efficiency; High temperature; high energy consumption
fabric filter	very effective for mercury capture	complex operation; periodical regeneration; high energy consumption
FGD	existing device for $\text{SO}_2$ abatement	only effective for oxidized Hg ( $\text{Hg}^{2+}$ )

In order to reach 90% of mercury control, an accelerating effort has been being made to develop cost-effective mercury control technologies that can be implemented by electric utilities. The main control options involve fuel blending, controlling unburned carbon content of the fly ash, sorbent injection, addition of oxidizing chemicals, SCR, and addition of a mercury-specific oxidizing catalyst downstream of the PM control device. Many of these options are shown in Figure 1.<sup>10</sup> Among them, powdered activated carbon (PAC) injection and SCR have already been commercially available now in the US. It is believed that many other enhanced multipollutant controls will also be commercially available in the near future, and the combination of coal type and control technology can potentially reduce 60–90% mercury. Presently, most of the work in this field is focused on modifying carbon-based sorbents, such as sulfur impregnated activated carbon, bromine, iodine and chlorine impregnated activated carbon, or exploring novel sorbent, such as petroleum coke, noncarbon novel sorbent, and chemical sorbent.<sup>12–14</sup> Deng et al.<sup>15</sup> reported that 99% of mercury and approximately 10–13% content of sulfur could be removed by S-loaded carbon. Alptekin et al.<sup>13</sup> developed a new sorbent that exhibited 7.5 to 11.0 mg/g mercury absorption capacity under representative flue gas streams. Tan et al.<sup>16</sup> developed an environmentally friendly and economical chemical sorbent, showed 80% of Hg removal for eastern bituminous coal. Up to date, there are tremendous amount of papers dealing with chemically promoted carbon-based and noncarbon based sorbents for mercury capture. However, the details will not be discussed in this contribution since we would like mainly focus on Hg oxidation catalysts.

Table 2 summaries some of the recent efforts reported in papers and patents.<sup>17–48</sup> However, although the development of new sorbents or additives has proceeded at a very rapid pace, and will likely continue to do so, and the sorbents injection system can be installed quickly in the near future, the cost needs to be further decreased to make it more commercially attractive. Among all the technologies, catalytic oxidation of mercury is the most promising method, which may lead to a high  $\text{Hg}^0$  conversion and low cost.

## 3. CATALYTIC OXIDATION OF MERCURY

It is well-known that the elemental form  $\text{Hg}^0$ , which is the main component of mercury in gas phase, is very hard to be removed due to their high volatility and low solubility in water. However, the oxidized mercury  $\text{Hg}^{2+}$  has much higher solubility in water,

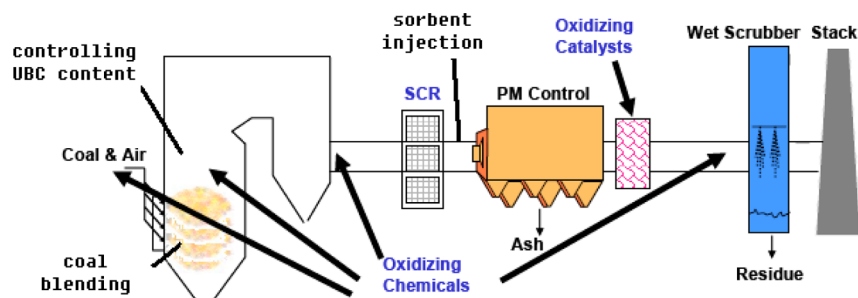


Figure 1. Options for enhancing mercury capture in existing air pollution controls.<sup>10</sup>

Table 2. Summary of the Recent Efforts on Mercury Abatement Reported in Papers or Patents<sup>17–41,43–45,47,48,92</sup>

	types	methods	references
sorbent injection	theory	modeling sorbents injection	21,22
	adding acids	sorbent injection with chlorine or bromine	32,47,48
		sorbent injection with H <sub>2</sub> S	31
	modifying carbon sorbent	iodine, bromine, and chlorine impregnated activated carbon	14,23,24
		sulfur impregnated activated carbon	25–30
novel sorbents	petroleum coke	33	
	noncarbon novel sorbent	34,35,44	
	Hg <sup>0</sup> oxidation	heterogeneous catalytic oxidation	17–20,45,92
Hg <sup>0</sup> oxidation		electro-catalytic oxidation	36
		photochemical oxidation	37,38
	others	membrane-based wet electrostatic precipitation	39
others		removal by reactive membranes	40,43
		advanced hybrid filter	41

and thus the oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> followed by the ESP and/or wet scrubbing processes became a promising method for mercury removal. Up to date, great efforts have been devoted and various types of catalysts for mercury oxidation have been developed, as summarized in Table 3. Currently,

Table 3. Summary of Reported Catalysts for Mercury Oxidation

catalyst type	potential catalysts
noble metals	Pd, Au, Pt, silver
SCR catalyst	VO <sub>x</sub> /TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> –WO <sub>3</sub> /TiO <sub>2</sub> , RuO <sub>2</sub> modified V <sub>2</sub> O <sub>5</sub> –WO <sub>3</sub> /TiO <sub>2</sub> , SiO <sub>2</sub> –TiO <sub>2</sub> –V <sub>2</sub> O <sub>5</sub> , MnO <sub>x</sub> /TiO <sub>2</sub> , MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> , Mo–MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> , and MnO <sub>x</sub> –CeO <sub>2</sub> /TiO <sub>2</sub> , etc
transition metal oxides	CuO, Cu <sub>2</sub> O, CuCoO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> , MoO <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub> , CeO <sub>2</sub> –TiO <sub>2</sub>
fly-ash	primarily silicon and aluminum oxides and certain amount of cations such as iron, sodium, potassium, calcium, and magnesium, etc.

there are mainly four groups of catalysts exist, including noble metals, SCR catalysts, transition metals, and fly ash. In the following section, both the advantages and disadvantages of these catalysts will be described in detail.

**3.1. Noble Metals Based Catalysts.** Noble metals including Pd, Au, Pt, and Ag have been investigated as potential Hg oxidation catalysts. Among them, Pd and Au are the most established catalysts, which have been tested in both bench and field scales.<sup>17</sup> It has been reported that Pd can

oxidize more than 95% of elemental Hg in the initial stage; its activity kept greater than 85% Hg oxidation after 3 months and 65% Hg oxidation after 20 plus months. The results also suggested that Pd could be readily regenerated to improve the oxidation activity by heating to approximately 315 °C for several hours. Hrdlicka et al.<sup>18</sup> also observed high performance over both Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, see SI Table S2. Due to its high activity, long stability and its regenerative ability, Pd has been considered as one of the most promising catalysts.

Gold has demonstrated its ability to adsorb mercury and form an amalgam, with which it has been widely used to adsorb mercury in different kinds of mercury analyzers and as a means of control in large-scale facilities. Zhao et al.<sup>49</sup> have shown that Au is a good mercury oxidation catalyst because it adsorbs mercury and chlorine, but does not adsorb other species such as nitric oxide, sulfur dioxide, and water. Because of the ultra low Hg concentration in flue gases (ppb level), Au shows great potential due to its high Hg adsorption and Hg catalytic oxidation properties. Presto et al.<sup>17</sup> reported a constant baseline reaction rate over a period of seven experiments, suggesting that there was no apparent catalyst deactivation. The mean baseline reaction rate was  $(2.2 \pm 0.3) \times 10^{-10}$  (mol Hg<sup>2+</sup>)/(g catalyst) s. The baseline reaction rate remained constant when the flow rate was raised from 8 standard liters per minute (slpm) to 10 slpm with no change in simulated flue gas composition, which suggests that the mercury oxidation reaction is not limited by mass transfer under their testing conditions.

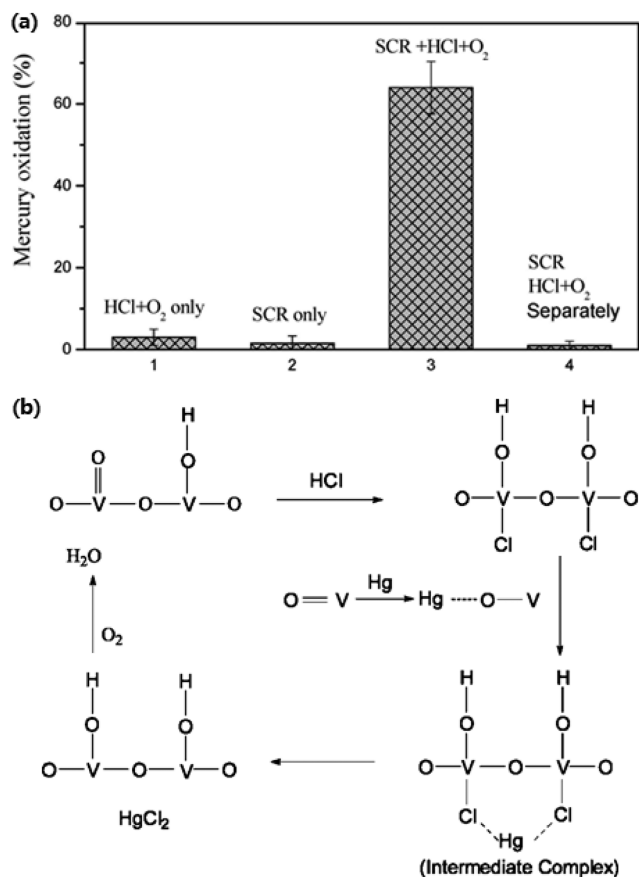
Both Pd and Au catalysts exhibited similar responses to changes in HCl concentration. Raising the HCl concentration from 50 ppm to 100 ppm had no impact on the reaction rate. Lowering the HCl concentration to 0 ppm slowed, but did not stop mercury oxidation. The oxidation rate decreased to ~45% of the baseline rate after 80 min, and ~42% of the baseline rate after 150 min. Pt catalyst has also been investigated and it exhibited a contrast behavior to Au and Pd. Unlike Au and Pd catalysts which continued to oxidize mercury at reduced rates when HCl flow stopped, an immediate halt to mercury oxidation was observed with Pt when the concentration of HCl was 0 ppm.<sup>17</sup>

**3.2. SCR Type Catalysts.** Since there is a trend for coal-fired power plants to install SCR systems for NO<sub>x</sub> reduction, the coprofit from the SCR catalyst in elemental Hg oxidation is highly desired.<sup>19</sup> This cobenefit from SCR also makes the cost of mercury control more economical than the ACI method. It was revealed that the operation of SCR units affects the speciation of mercury in the coal combustion flue gases, promoting the formation of Hg<sup>2+</sup> species. The extent of mercury oxidation across SCR heavily depends on the types of coal. For plants burning bituminous coal, the efficiency of

mercury oxidation across the SCR units varies widely from 30% to 98%, while in plants burning subbituminous, the mercury oxidation efficiency becomes much lower (<26%).<sup>50</sup>

Up to date, various types of SCR catalysts have been tested for Hg oxidation, as summarized in Table 3. Generally, according to their operating temperatures, the catalysts can be divided into high-temperature SCR catalysts (e.g.,  $V_2O_5$ -based) and low-temperature SCR catalysts (e.g.,  $MnO_x$ -based). For high-temperature SCR catalysts, several  $V_2O_5$ -based SCR catalysts including  $VO_x/TiO_2$ ,<sup>20</sup>  $V_2O_5-WO_3/TiO_2$ ,<sup>19,51</sup>  $RuO_2$  modified  $V_2O_5-WO_3/TiO_2$ ,<sup>52</sup> and  $SiO_2-TiO_2-V_2O_5$ <sup>53</sup> have been investigated. For low-temperature SCR catalysts, mainly  $MnO_x/Al_2O_3$ ,<sup>5</sup>  $Mo-MnO_x/Al_2O_3$ ,<sup>2</sup> and  $MnO_x-CeO_2/TiO_2$ <sup>54</sup> have been studied. In the following section, we will summarize their operating conditions, influencing parameters, advantages and disadvantages, and the overall performance in Hg oxidation within the SCR systems.

The effect of  $V_2O_5$ -based SCR catalysts for the oxidation of elemental mercury has been intensively investigated with different HCl concentrations, NO concentrations,  $NH_3/NO$  ratio, and reaction temperatures.<sup>55,56</sup> The SCR catalyst alone cannot ensure optimal mercury oxidation. It has been shown that HCl in the flue gas is critical for mercury oxidation. The extent of Hg oxidation increases with the increase in HCl content. For instance, He et al.<sup>56</sup> reported that 64% of the influent mercury can be oxidized over  $V_2O_5/TiO_2$  SCR catalyst in the presence of 50 ppmv HCl and 5%  $O_2$  (Figure 2(a)). However, the Hg oxidation efficiency significantly decreased

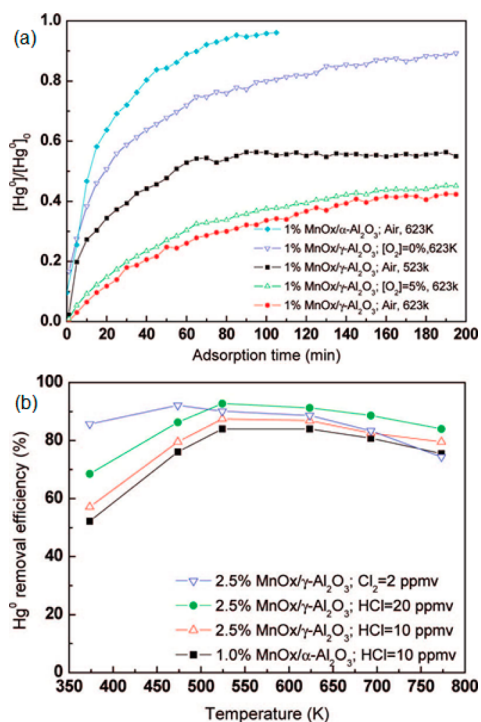


**Figure 2.** (a) Mercury oxidation over  $V_2O_5/TiO_2$  SCR catalyst with or without HCl +  $O_2$  at 300 °C. (b) Mechanism of the mercury oxidation on the vanadia-based SCR catalysts.<sup>56</sup>

with HCl+ $O_2$  or SCR only. In contrast,  $NH_3$  injection inhibits mercury oxidation within the SCR system. Although the exact mechanism for mercury oxidation by SCR catalysts is still not clear, some possibilities have been proposed. For instance, Niksa and Fujiwara<sup>57</sup> believed that the oxidation of  $Hg^0$  across an SCR catalyst occurs via adsorbed HCl on the  $V_2O_5$  active sites followed by reaction of the adsorbed HCl with either gas-phase  $Hg^0$  or weakly bound  $Hg^0$ . Senior<sup>58</sup> proposed a model that assumes an Eley–Rideal reaction between adsorbed  $Hg^0$  and gas-phase HCl. The Deacon process has been suggested as a means to produce chlorine ( $Cl_2$ ) in the gas via a reaction between  $V_2O_5$  and HCl. The gaseous  $Cl_2$  could then react with  $Hg^0$  in the gas phase to form  $HgCl_2$ . Later, Gao et al.<sup>59</sup> further confirmed that the mercury oxidation follows the Eley–Rideal mechanism involving chlorine compounds as the intermediates that subsequently oxidize mercury. Recently, He et al.<sup>56</sup> performed a series of tests for mercury oxidation across a laboratory-scale SCR system using a  $V_2O_5$ -based catalyst and proposed that the mercury oxidation on the SCR catalyst should be regarded as a heterogeneous reaction via the Langmuir–Hinshelwood mechanism (Figure 2(b)). According to the mechanism, first, HCl and  $Hg^0$  adsorb onto the vanadia sites to form  $HgCl_2$  and V–OH species; then, the reoxidation of the V–OH species by oxygen follows to form V–O and  $H_2O$ .<sup>56</sup>

The required operating temperature of conventional  $V_2O_5$ -based SCR catalysts is typically between 300–400 °C. Accordingly, it is necessary to locate the SCR unit upstream of the ESP/FF and WFGD immediately after the steam generator in order to avoid the cost for reheating the flue gas. However, this accelerates the catalyst deactivation through exposure to high concentrations of PM.<sup>60</sup> To avoid the deactivation by PM, it is therefore desirable to develop a SCR catalyst with high activity at low temperatures (100–250 °C), which would allow the SCR reactor to be located downstream of the PM control devices where the flue gas is relatively clean. Therefore, the Hg oxidation over low-temperature SCR catalysts is also of great interest to scientists.

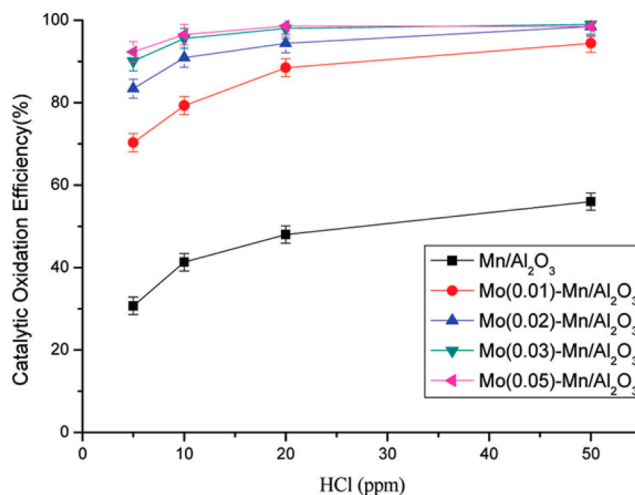
Qiao et al.<sup>5</sup> studied the adsorption and catalytic oxidation of gaseous elemental mercury in flue gas over  $MnO_x/Al_2O_3$ , as shown in Figure 3. The catalyst support has a significant effect on the adsorption of  $Hg^0$ , even with the same Mn loading (1.0 wt %). The half-breakthrough time (the time when the outlet  $Hg^0$  concentration is equal to 50% of that in the inlet) was only 15 min for  $MnO_x/\alpha-Al_2O_3$ , but it was more than 200 min for  $MnO_x/\gamma-Al_2O_3$ . In addition, the  $Hg^0$  adsorption capacity of the two catalysts at the point of 90% breakthrough at 350 °C was 1.6 and 75  $\mu g/g$ , respectively. The difference was explained by the surface areas.  $MnO_x$  could be well dispersed on the porous surface of  $\gamma-Al_2O_3$ , which is helpful to yield more active sites on catalysts for  $Hg^0$  adsorption. However,  $MnO_x$  tends to form a dense shell on  $\alpha-Al_2O_3$ , and most of the  $MnO_x$  in the deep layer is inaccessible to adsorb  $Hg^0$  because of the higher gas diffusion resistance. It was found that over 90% oxidation of  $Hg^0$  can be obtained with 20 ppm of HCl or 2 ppm of  $Cl_2$ . In addition, the catalysts with adsorbed mercury can be chemically regenerated by rinsing with HCl gas to strip off the adsorbed mercury in the form of  $HgCl_2$ .  $SO_2$  displayed inhibition to the adsorption of  $Hg^0$  on the catalyst, but the inhibition of the catalytic oxidation of  $Hg^0$  was lessened, especially in the presence of  $Cl_2$ . It was also found that the adsorbed mercury was mainly in the form of  $HgO$  and the weakly bonded speciation  $Hg-O-MnO_{x-1}$ , and the ratio of them varied with



**Figure 3.** (a) Breakthrough curves of elemental mercury across the catalysts. Air was used as the balance gas, and the packed volume of the catalyst was 3.2 mL (corresponding to 3.6 g of MnO<sub>x</sub>/α-Al<sub>2</sub>O<sub>3</sub> or 2.4 g of MnO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) if not indicated particularly. (b) Removal efficiency of Hg<sup>0</sup> in the presence of HCl or Cl<sub>2</sub> under various temperatures.<sup>5</sup>

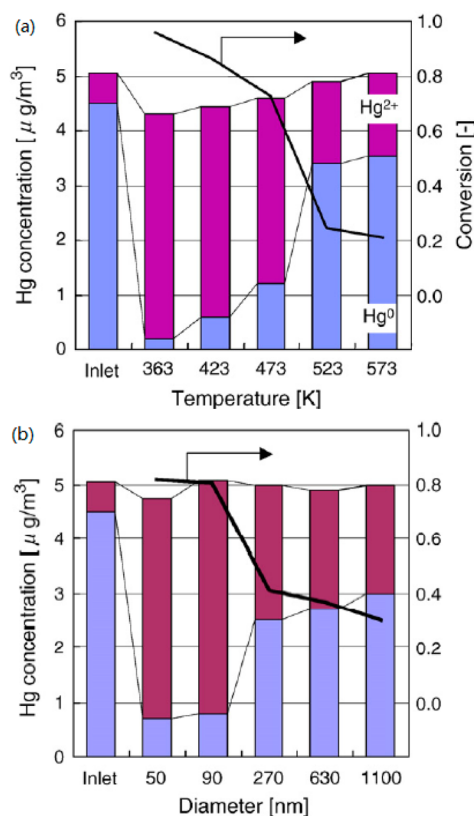
the adsorption amount and the content of MnO<sub>x</sub>. In order to further improve catalytic activity and the sulfur-tolerance of the catalysts at lower temperatures, several metal elements (Sr, W, Cu, and Mo) were employed as dopants to modify the catalyst of MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The best performance among the tested elements was achieved with molybdenum (Mo) as the dopant in the catalysts. Additionally, the Mo doped catalyst displayed excellent sulfur-tolerance performance at lower temperatures, and the catalytic oxidation efficiency for Mo(0.03)-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was over 95% in the presence of 500 ppm SO<sub>2</sub> versus only about 48% for the unmodified catalyst (see Figure 4). The apparent catalytic reaction rate constant increased by approximately 5.5 times at 150 °C.<sup>2</sup> Li et al.<sup>54</sup> observed a significant synergy for Hg<sup>0</sup> oxidation when MnO<sub>x</sub> and CeO<sub>2</sub> were combined. The MnO<sub>x</sub>-CeO<sub>2</sub>/TiO<sub>2</sub> catalyst was highly active for Hg<sup>0</sup> oxidation at low flue gas temperatures under either simulated flue gas or SCR conditions. Over 90% of Hg<sup>0</sup> oxidation was obtained on the MnO<sub>x</sub>-CeO<sub>2</sub>/TiO<sub>2</sub> catalyst under simulated flue gas at 200–250 °C, representing those from burning low-rank coals with a gas hourly space velocity (GHSV) of 60 000 h<sup>-1</sup> which is more than 10 times higher than the actual GHSV in SCR reactors.

**3.3. Transition Metal Oxides Based Catalysts.** In addition, some transition metal oxides have also been examined as catalytic materials for Hg oxidation, such as CuO, Cu<sub>2</sub>O, CuCoO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>, and CeO<sub>2</sub>-TiO<sub>2</sub>, etc.<sup>61–63</sup> Yamaguchi et al.<sup>64</sup> found that among all of the transition oxides, only CuO nanoparticles and MnO<sub>2</sub> were able to convert Hg<sup>0</sup> to Hg<sup>2+</sup> at low HCl concentration. The most efficient catalyst, CuO nanoparticles, showed a conversion rate of more than 80% at 2 ppm of HCl and 150 °C.



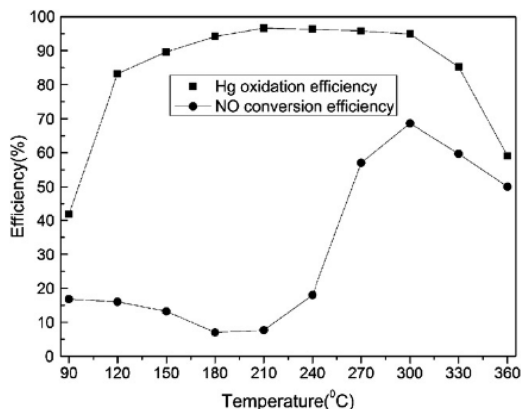
**Figure 4.** The effect of doped Mo content on the Hg<sup>0</sup> oxidation efficiency at various HCl concentrations and at 150 °C (with 500 ppm SO<sub>2</sub>).<sup>2</sup>

Over CuO nanoparticles, the conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> increased as the reaction temperature decreased from 300 to 90 °C, but the conversion decreased as the particle size increased (see Figure 5). Mercury oxidation with CuO nanoparticles of 50 nm in diameter was not significantly affected by area velocity in the range of 47 to 235 m<sup>3</sup>/(h m<sup>2</sup>), but the mercury oxidation with CuO particles of 1.1 μm was decreased over 100 m<sup>3</sup>/(h m<sup>2</sup>).



**Figure 5.** (a) Influence of temperature on mercury oxidation over CuO nanoparticles. (b) Influence of particle size on mercury oxidation at 423 K over CuO nanoparticles.<sup>64</sup>

Cobalt-based catalysts supported on different carriers were widely used for catalytic oxidation of NO,<sup>65–68</sup> CO,<sup>69</sup> and VOCs,<sup>70</sup> which showed high oxidation efficiency and long persistent activity. The presence of Co<sub>3</sub>O<sub>4</sub> was considered as the main reason of its high activity. Therefore, it is expected that cobalt-based catalysts could also have a good activity for Hg<sup>0</sup> oxidation. Furthermore, these catalysts may provide a potential for simultaneous removal of NO and Hg<sup>0</sup>. With a simultaneous oxidation of NO and Hg<sup>0</sup>, two contaminations could be both captured in the wet scrubbing process. Unlike SCR catalysts, there was no NH<sub>3</sub> in this system, which affected the adsorption of Hg<sup>0</sup>. Liu et al.<sup>71</sup> synthesized Co/TiO<sub>2</sub> catalyst via sol–gel method and revealed that the optimal loading of Co was 7.5 wt %, which yielded more than 90% oxidation efficiency within the temperature range of 120–330 °C. The high activity was mainly attributed to the enrichment of well dispersed Co<sub>3</sub>O<sub>4</sub>. It was also found that oxygen performed a key role in mercury oxidation process, while HCl could corrode the oxidized mercury and release it to gas phase. The combined oxidation of both Hg<sup>0</sup> and NO over 7.5 wt % Co/TiO<sub>2</sub> was also investigated, as shown in Figure 6. The NO conversion of

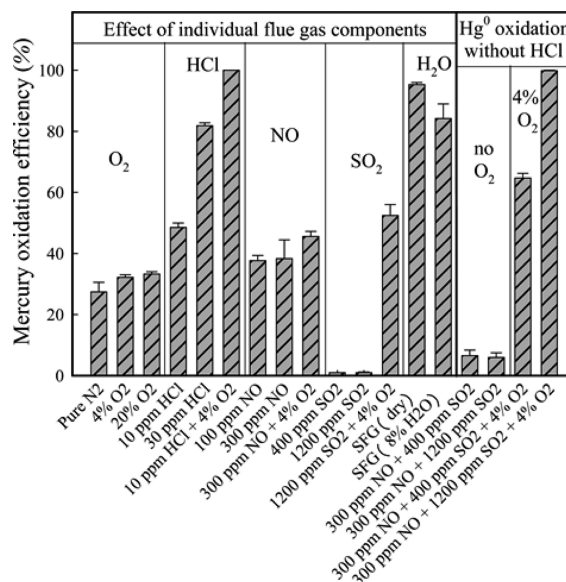


**Figure 6.** Co-oxidation of NO and mercury oxidation under experiment condition. Condition: [Hg<sup>0</sup>] = 180 ug/m<sup>3</sup>, balanced gas = N<sub>2</sub>, flow rate = 700 mL/min, GHSV = 105 000 h<sup>-1</sup>, O<sub>2</sub> = 3%, HCl = 29 ppm, NO = 300 ppm.<sup>71</sup>

68.8% was obtained at 300 °C with a GHSV of 105 000 h<sup>-1</sup>. Only a slight decrease in Hg<sup>0</sup> oxidation efficiency was found in the experiment compared with the NO free condition, suggesting both Hg<sup>0</sup> and NO could be simultaneously oxidized over the CoO<sub>x</sub>/TiO<sub>2</sub> catalyst. The introduction of high concentration of NO only slightly interrupted mercury oxidation. It was concluded that for their competitions in the consumption of the surface lattice oxygen during the combined oxidation process, the oxidation of Hg<sup>0</sup> must be superior to NO under the conditions investigated.<sup>71</sup>

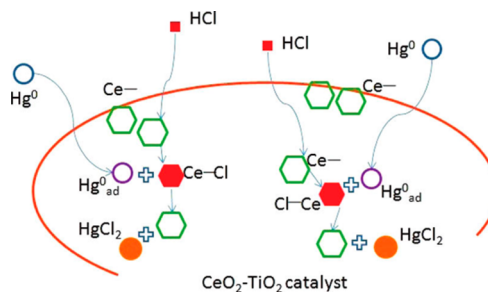
CeO<sub>2</sub> has been extensively studied as one of the catalyst components for SCR of NO<sub>x</sub> due to its large oxygen storage capacity and unique redox couple Ce<sup>3+</sup>/Ce<sup>4+</sup> with the ability to shift between CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> under oxidizing and reducing conditions, respectively.<sup>72</sup> Within the redox shift between Ce<sup>3+</sup> and Ce<sup>4+</sup>, labile oxygen vacancies and bulk oxygen species with relatively high mobility can be easily generated, which are active for oxidation processes. Furthermore, CeO<sub>2</sub> promotes the oxidation of NO to NO<sub>2</sub> which was reported to be more effective than NO for Hg<sup>0</sup> oxidation.<sup>73</sup> Similarly, HCl would probably be transformed to active chlorine species over CeO<sub>2</sub>

based catalysts even without gas-phase O<sub>2</sub>. In addition, CeO<sub>2</sub> based catalysts were reported to be more resistant to water vapor, the presence of which inhibits Hg<sup>0</sup> oxidation.<sup>74</sup> Therefore, CeO<sub>2</sub> based catalysts for the oxidation of Hg<sup>0</sup> is of great interest to researchers as well. Li et al.<sup>75</sup> investigated the oxidation of Hg<sup>0</sup> over CeO<sub>2</sub>/TiO<sub>2</sub> catalyst in simulated low-rank (sub-bituminous and lignite) coal combustion flue gas. The results showed that the CeO<sub>2</sub>/TiO<sub>2</sub> catalyst with a CeO<sub>2</sub>/TiO<sub>2</sub> weight ratio of 1–2 exhibited high Hg<sup>0</sup> oxidation activity from 150 to 250 °C. The high concentrations of surface cerium and oxygen are responsible for their superior performance. In the presence of O<sub>2</sub>, a promotional effect of HCl, NO, and SO<sub>2</sub> on Hg<sup>0</sup> oxidation was observed. Without O<sub>2</sub>, HCl and NO still promoted Hg<sup>0</sup> oxidation due to the surface oxygen, while SO<sub>2</sub> and water vapor inhibited Hg<sup>0</sup> adsorption and subsequent oxidation. HCl was the most effective flue gas component responsible for Hg<sup>0</sup> oxidation (see Figure 7). The possible mechanism is proposed in Figure 8.<sup>75</sup>



**Figure 7.** Effect of individual flue gas components and Hg<sup>0</sup> oxidation without HCl at 200 °C.<sup>75</sup>

For most of the base metal oxides such as MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, the influence of SO<sub>2</sub> poisoning is a major problem. One of the unresolved problems in replacing noble metals with base metal oxides to full-scale applications is how to improve their SO<sub>2</sub> antipoisoning ability and Hg<sup>0</sup> oxidation efficiency simultaneously. Mei et al.<sup>63</sup> investigated the vapor-phase Hg<sup>0</sup> oxidation



**Figure 8.** The possible catalytic reaction mechanism for the oxidation of Hg<sup>0</sup> over CeO<sub>2</sub>-TiO<sub>2</sub> in flue gas.<sup>75</sup>

over  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$ ,  $(\text{CuCoO}_4 + \text{NH}_4\text{Cl})/\text{Al}_2\text{O}_3$ , and  $(\text{CuCoO}_4 + \text{NH}_4\text{Br})/\text{Al}_2\text{O}_3$  in an attempt to produce more economical and effective sorbents for the control of  $\text{Hg}^0$  emission from combustion processes. It was reported that  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  doping showed a significantly higher  $\text{Hg}^0$  oxidation abilities than  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$ , and the optimal  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  adulteration value is 30%. The addition of  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  can improve the breakthrough time of  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$  from 26 to 158 h or 208 h, respectively. All these three catalysts possess outstanding  $\text{SO}_2$  antipoisoning ability. The N-doping technology does not have any adverse affect on either  $\text{Co}^{3+}$  or  $\text{Cu}^{2+}$ -octahedral cations structure of  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$ , which enables  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{Br}$  doping increase its  $\text{SO}_2$  resistant capability. It was suggested that the N atoms have been doped into  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$  crystal lattice and anion  $\text{Cl}^-$  or  $\text{Br}^-$  can be activated by N-doped AL-C  $\text{CuCoO}_4/\text{Al}_2\text{O}_3$  to oxidize elemental mercury.<sup>63</sup>

**3.4. Coal Fly Ash Based Catalysts.** Coal fly ash is a mixture of metal oxides found in both crystalline and amorphous forms. Glasses are common ash constituents, composed primarily of the oxides of silicon and aluminum that contain a significant amount of cations such as iron, sodium, potassium, calcium, and magnesium. Iron oxide (in the form of magnetite or hematite) is also as commonly found in ash as calcium oxide and calcium sulfate. Tests on actual fly ash samples with different coal ranks and iron contents in order to get a better understanding of the effects of iron in coal fly ashes on speciation of Hg were conducted by EPA.<sup>76</sup> It was observed that one subbituminous (3.7% iron) and three lignite coal fly ash (1.5 to 5.0% iron) samples tested with low iron content did not oxidize  $\text{Hg}^0$  in the presence of NO and HCl. However, a bituminous coal fly ash sample (Valmont Station) with a low iron content (2.3% iron) completely oxidized  $\text{Hg}^0$  in the presence of NO and HCl. It was also found that, upon adding  $\text{Fe}_2\text{O}_3$  to the low iron content subbituminous and lignite fly ash samples to reach an iron content similar to that of the Blacksville sample, significant  $\text{Hg}^0$  oxidation reactivity was measured (33–40% oxidation of  $\text{Hg}^0$ ) for these iron-doped samples. Bench-scale tests at EPA indicated two possible reaction pathways for fly ash-mediated oxidation of  $\text{Hg}^0$ . One possible pathway is the oxidation of gaseous  $\text{Hg}^0$  by fly ash in the presence of HCl, and the other is the oxidation of gaseous  $\text{Hg}^0$  by fly ash in the presence of  $\text{NO}_x$ . The research also reflected that the iron content of the ash appeared to play a key role in the oxidation of  $\text{Hg}^0$ .<sup>77</sup>

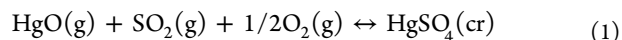
#### 4. EFFECT OF ACIDIC GASES ( $\text{SO}_2$ , $\text{SO}_3$ , $\text{NH}_3$ , $\text{NO}_x$ , $\text{HCl}$ , $\text{Cl}_2$ , ETC.)

It has been widely accepted that mercury oxidation is highly dependent on the compositions of the flue gases, especially the concentrations of acidic gases which include  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{HCl}$  and  $\text{Cl}_2$ . Here we are trying to clarify the effects of acidic gases by reviewing the recent reports, through which a proper mercury oxidation catalyst could be selected for certain type of flue gas.

Chemical equilibrium calculation predicts that gas-phase oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  starts at approximately 677 °C and is essentially complete by 427 °C. Based on these results, mercury should exist entirely as  $\text{Hg}^{2+}$  downstream of the air heater. However, flue-gas measurements of Hg at air heater outlets indicate that gaseous  $\text{Hg}^0$  is still present at this location, and that  $\text{Hg}^{2+}$  ranges from 5 to 95% of the gas-phase Hg. These

data suggest that the oxidation of  $\text{Hg}^0$  does not reach completion, due to kinetic limitations.

Frandsen et al.<sup>78</sup> reported that crystalline mercury sulfate ( $\text{HgSO}_4$ ) could be formed by reaction 1, and it is stable up to 242 °C. This effect might help the total Hg removal from flue gases.



Zhuang et al.<sup>79</sup> have reported that 7% and 20% mercury oxidation in SCR outlet flue gas were induced by 2000 ppm  $\text{SO}_2$  and 50 ppm  $\text{SO}_3$ , respectively (Figure 9). The marginally

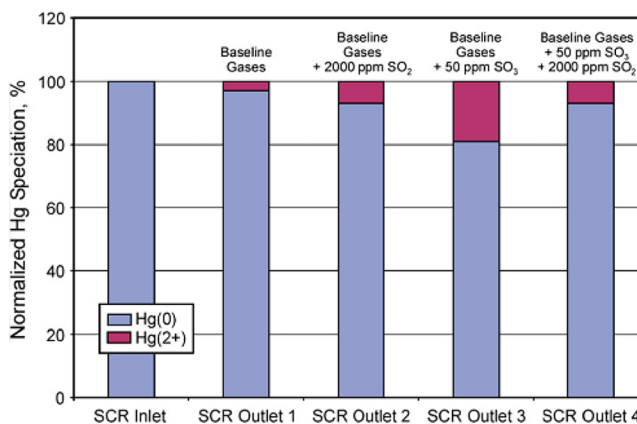


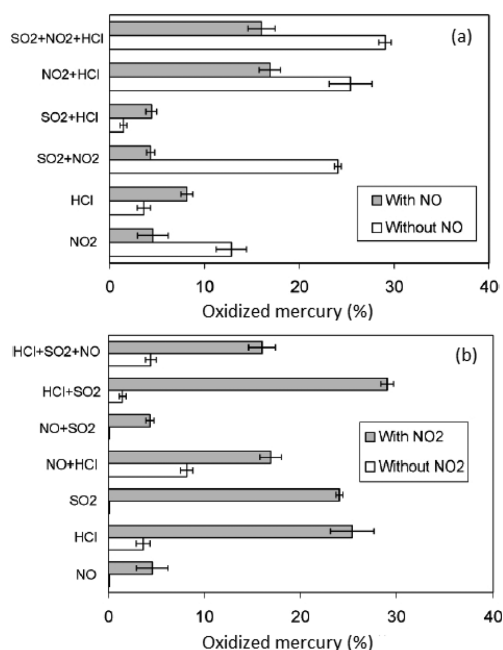
Figure 9. Effect of  $\text{SO}_2/\text{SO}_3$  on mercury oxidation across the SCR.<sup>79</sup>

promoting role of  $\text{SO}_3$  on mercury oxidation observed was somewhat unexpected, since  $\text{SO}_3$  was originally thought to compete for oxidation sites on the catalyst, thus decreasing mercury oxidation. It has been demonstrated that, in general mercury adsorption is only slightly decreased by  $\text{NH}_3$  and slightly increased by  $\text{SO}_2$ ; and  $\text{SO}_2$  has only a marginal effect and  $\text{NH}_3$  has a negative effect on the mercury oxidation. Recently, Li et al.<sup>80</sup> carried out a systematical investigation on the effect of  $\text{SO}_2$  on the  $\text{Hg}^0$  oxidation over a  $\text{CeO}_2\text{-TiO}_2$  catalyst.  $\text{SO}_2$  was found to have different, even contrary, effects on  $\text{Hg}^0$  oxidation under different flue gas conditions. In pure  $\text{N}_2$  atmosphere,  $\text{SO}_2$  inhibited  $\text{Hg}^0$  oxidation. In  $\text{N}_2 + \text{O}_2$  atmosphere, low concentration of  $\text{SO}_2$  promoted  $\text{Hg}^0$  oxidation, while high concentration of  $\text{SO}_2$  deteriorated  $\text{Hg}^0$  oxidation. The promotional effect of  $\text{SO}_2$  on  $\text{Hg}^0$  oxidation was probably due to  $\text{SO}_3$  generated from  $\text{SO}_2$  oxidation, and the inhibitive effect of  $\text{SO}_2$  on  $\text{Hg}^0$  oxidation was attributed to the competitive adsorption between  $\text{SO}_2$  and  $\text{Hg}^0$ .<sup>80</sup> However, base metal oxides such as  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  perform unsatisfactorily when  $\text{SO}_2$  exist; since they tend to react with  $\text{SO}_2$  to form metal sulfates.<sup>42,46</sup>

$\text{NO}_x$  seems to play a significant role for  $\text{Hg}^0$  oxidation in SCR, and chemisorption of  $\text{NO}_x$  creates active sites for  $\text{Hg}^0$  adsorption.<sup>73</sup> Li et al.<sup>53</sup> investigated the oxidation and capture of elemental mercury over  $\text{SiO}_2\text{-TiO}_2\text{-V}_2\text{O}_5$  SCR catalysts in simulated low-rank coal combustion flue gas. A promotional effect of NO on  $\text{Hg}^0$  oxidation was observed at 350 °C. With the addition of 100 and 300 ppm NO, the Hg oxidation efficiency was increased by ~15.4% and ~26.2%, respectively. It was reported that NO can be adsorbed on vanadia based catalysts in a molecular form, giving rise to active species such as  $\text{NO}^+$ ,  $\text{NO}_2^+$  and  $\text{NO}_2$  for  $\text{Hg}^0$  oxidation. However, the adsorption of NO on vanadia based catalysts is not strong. Thus, the observed promotional effect of NO was not

extraordinary.<sup>81</sup> It was further proved that introducing 4% O<sub>2</sub> together with 300 ppm NO can significantly improve the Hg oxidation efficiency up to ~52.9%.<sup>53</sup>

However, with non-SCR catalysts such as Blacksville fly ash, a different phenomenon was observed with NO<sub>x</sub>. Norton et al.<sup>82</sup> studied the heterogeneous catalytic oxidation of Hg<sup>0</sup> over Blacksville fly ash, and it was found that the presence of NO tended to suppress mercury oxidation. The NO inhibited mercury oxidation in four out of six cases as shown in Figure 10(a). In the two cases where this trend was not observed, very

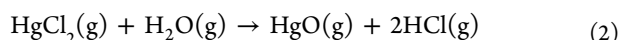


**Figure 10.** Effects of (a) NO and (b) NO<sub>2</sub> on mercury oxidation using Blacksville fly ash at 180 °C.<sup>82</sup>

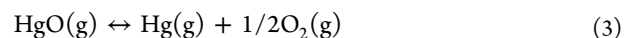
little oxidation occurred with or without NO. The suppression of mercury oxidation by NO was observed in all cases in which significant amounts of mercury oxidation were observed in the absence of NO. For example, when only NO<sub>2</sub> or SO<sub>2</sub> was added, the mercury oxidation efficiency was about 24%. However, after adding 300 ppm of NO, the amount of oxidized Hg<sup>0</sup> decreased to 4%. It was proposed that NO might react with the OH· radicals and thus inhibit mercury oxidation. In contrary to NO, Figure 10(b) shows that the Hg oxidation efficiency could be significantly increased by NO<sub>2</sub> in all the listed seven cases.<sup>82</sup>

Frandsen et al.<sup>78</sup> reported that in Hg/O/Cl system, gaseous mercury(II) chloride is stable between 82 and 402 °C. At 352 °C, the formation of Hg(g) begins. Above 402 °C, small amounts of HgO(g) are formed, which reaches a maximum occurrence around 502 °C. Above 652 °C, an equilibrium between Hg(g) and HgO(g), with elemental gaseous mercury, Hg(g), as the major stable form, is shifted gradually toward Hg(g) with increasing temperatures. If HgSO<sub>4</sub>(cr) is not considered in the calculation, HgCl<sub>2</sub>(g) is the stable form of mercury below 352 °C.

At higher temperatures HgCl<sub>2</sub>(g) reacts with H<sub>2</sub>O(g):



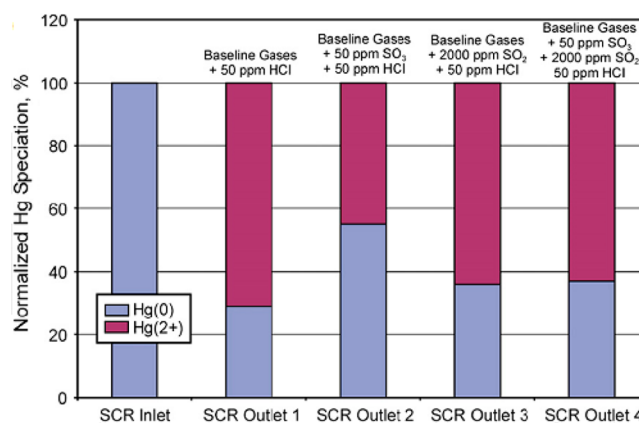
Above 652 °C, the equilibrium reaction is established and gradually shifts toward the right with increasing temperature.



Menke et al.<sup>83</sup> and Skare et al.<sup>84</sup> have confirmed that the reaction between mercury and chlorine gas is a slow gas-phase reaction, and it is kinetically limited by Cl concentration. The predicted distributions basing on equilibrium calculations of gas-phase oxidation of Hg<sup>0</sup> showed that 80% of gaseous Hg<sup>0</sup> is oxidized to HgCl<sub>2</sub> by 527 °C for bituminous coal; while no oxidation of Hg<sup>0</sup> at or above 527 °C for subbituminous coal. The difference in the equilibrium oxidation levels at 527 °C is attributed to the different chlorine levels in the model coals that were used in the calculations. The calculated data based on bituminous coal were with a relatively high chlorine concentration of several hundred ppm; in contrast, the calculated data based on subbituminous coal were with a relatively low chlorine content of 26 ppm.

The data for Au and Pd catalysts suggested that mercury reacts with HCl bound to the catalyst surface. This explains why mercury oxidation continues even in the absence of gas-phase HCl, but with a declining reaction rate. Cl<sub>2</sub> can chemisorb to Au surfaces and form AuCl<sub>3</sub>,<sup>85</sup> HCl dissociatively adsorbs to Pt surfaces, and similar behavior might be expected for Pd.<sup>86</sup> Thus, surface-bound Cl should be available for reaction on the Au and Pd surfaces. The Pt catalyst exhibited different behavior, and mercury oxidation stopped. This might be evidence of an Eley–Rideal mechanism for mercury oxidation across the Pt catalyst, with adsorbed Hg reacting with gas-phase HCl. Eley–Rideal kinetics would not suggest the zero-order dependence on [HCl] for concentrations greater than 50 ppm, but the overall reaction could exhibit a zero-order dependence on [HCl] if the Hg(ads) + HCl(g) step is not rate-limiting.<sup>17</sup>

It has been widely accepted that high chlorine content in coal general results in higher mercury oxidation across SCR.<sup>87</sup> Bench-scale data by Lee et al.<sup>88</sup> indicated that by adding 20 ppm HCl in flue gas, additional mercury oxidation occurred within the SCR in a subbituminous coal flue gas. Zhuang et al.<sup>79</sup> also observed that by adding HCl (1–50 ppm) in flue gas, mercury oxidation can be improved within an SCR catalyst, possibly because of the reactive chlorine species formed through catalytic reactions. Five ppm HCl in the simulated flue gas resulted in mercury oxidation of 45% across the SCR, and it reached 63% as the HCl concentration increased to 50 ppm, compared to less than 20% mercury oxidation without HCl (Figure 11). Pilot-scale combustion tests were completed



**Figure 11.** The influence of HCl on Hg oxidation in the presence of SO<sub>2</sub>/SO<sub>3</sub> across the SCR process.<sup>79</sup>



on three Illinois coals with varying sulfur (1.1%–3.5%) and chlorine (0.13%–0.29%) and one Powder River Basin (PRB) coal having 0.3% sulfur and <0.01% chlorine. The experimental data indicated higher mercury oxidation for the three Illinois bituminous coals tested, <12% of Hg<sup>0</sup> at the SCR outlet while Hg<sup>0</sup> accounted for 76%–88% of mercury species at the SCR outlet in the PRB test.<sup>89</sup>

According to the flue gas treatment processes and the Hg abatement requirement, there are several possible schemes of installing the Hg catalytic oxidation units. The Hg catalytic oxidation units can be installed in plants with or without FGD processes.<sup>90,91</sup> In order to prevent the catalyst deterioration problem, an NH<sub>3</sub> decomposing catalyst sometimes used before elemental mercury oxidation catalyst, preventing ammonium sulfate's formation. To achieve a higher Hg removal efficiency it is possible to install the mercury oxidation units in several different temperature zones. For example, it can be installed in a high temperature zone of 300 to 450 °C on the downstream side of NH<sub>3</sub> decomposition process, and/or a middle temperature zone of 120 to 200 °C on the downstream side of heating process, and/or the low temperature zone of 60 to 120 °C on the downstream side of heat recovery process. Shintaro et al.<sup>90</sup> reported that a NH<sub>3</sub> decomposing efficiency of 99% and a Hg removal efficiency of 95% can be achieved with such configuration. In addition, the Hg oxidizing catalyst can sometimes be used together with an adsorption agent (e.g., activated carbon). It was found that the amount of adsorption agent could be greatly decreased due to the existence of Hg oxidation catalyst. If low Cl content coal is used, the hydrochloric acid injection can be added upstream of the catalyst element as well. Hg<sup>0</sup> can be oxidized into HgO or HgCl<sub>2</sub>, and then adsorbed by carbon. The particles bounded with HgO or HgCl<sub>2</sub> could be removed by ESP. With such kind of configuration, a mercury removal efficiency of 90–99% can be achieved.<sup>91</sup>

## 5. CONCLUSIONS AND OUTLOOK

Heterogeneous catalytic oxidation of elemental mercury has been regarded as a very promising technology for efficiently and economically controlling the mercury emission from flue gases. In this contribution, four types of Hg oxidation catalysts including noble metals, SCR catalysts, transition metals, and fly ash have been summarized. Both the advantages and disadvantages of these catalysts are described in detail. Among different noble metals, Pd and Au are the most established catalysts, which have been tested on both bench and field scales. Since the emission regulations for NO<sub>x</sub> and SO<sub>2</sub> are becoming stricter, the use of SCR and scrubber systems at coal-fired utility boilers is expected to keep growing. Therefore, it is anticipated that the cobenefits from De-NO<sub>x</sub> and De-SO<sub>x</sub> catalysts and their combination with Hg<sup>0</sup> oxidation catalyst will continue to gain more attention. Several transition metal oxides including CuO, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub>, etc have also showed impressive Hg oxidation activity. One unresolved problem in replacing noble metals with base metal oxides to full-scale applications is how to improve their SO<sub>2</sub> antipointing ability and Hg<sup>0</sup> oxidation efficiency simultaneously. Besides, the influence of acidic gases including SO<sub>2</sub>, SO<sub>3</sub>, NH<sub>3</sub>, NO<sub>x</sub>, HCl, Cl<sub>2</sub>, etc is very significant. In general, HCl, Cl<sub>2</sub>, SO<sub>3</sub>, and NO<sub>2</sub> could greatly promote Hg oxidation, NO might slightly promote or inhibit Hg oxidation depending on its concentration and the catalyst type, while SO<sub>2</sub> and NH<sub>3</sub> always inhibit Hg oxidation.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Tables S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Zhang, H.; Zhao, J.; Fang, Y.; Huang, J.; Wang, Y. Catalytic oxidation and stabilized adsorption of elemental mercury from coal-derived fuel gas. *Energy Fuels* **2012**, *26* (3), 1629.
- (2) Li, J.; Yan, N.; Qu, Z.; Qiao, S.; Yang, S.; Guo, Y.; Liu, P.; Jia, J. Catalytic oxidation of elemental mercury over the modified catalyst Mn/alpha-Al<sub>2</sub>O<sub>3</sub> at lower temperatures. *Environ. Sci. Technol.* **2010**, *44* (1), 426.
- (3) EPA Mercury and air toxics standards (MATS): 16 December 2011.
- (4) Pavlish, J. H.; Sondreal, E. A.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A. Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **2003**, *82*, 89.
- (5) Qiao, S.; Chen, J.; Li, J.; Qu, Z.; Liu, P.; Yan, N.; Jia, J. Adsorption and catalytic oxidation of gaseous elemental mercury in flue gas over MnO<sub>x</sub>/alumina. *Ind. Eng. Chem. Res.* **2009**, *48* (7), 3317.
- (6) Brown, T. D.; Smith, D. N.; Hargis, J. R. A.; O'Dowd, W. J.; van Harreveld, A. P.; Heeres, P.; Harssema, H. Mercury measurement and its control: What we know, have learned, and need to further investigate. *J. Air Waste Manag. Assoc.* **1999**, *49*, 1.
- (7) Tan, Y.; Mortazavi, R.; Dureau, B.; Douglas, M. A. An investigation of mercury distribution and speciation during coal combustion. *Fuel* **2004**, *83*, 2229.
- (8) Blythe, G. Pilot testing of mercury oxidation catalyst for upstream WFGD. IN *Conference Proceedings-DOE/NETL's Mercury Control Technology R&D Program Review*, Pittsburgh, July 12–14, 2005.
- (9) Yudovich, Y. E.; Ketris, M. P. Mercury in coal: A review part 2. Coal use and environmental problems. *Int. J. Coal Geol.* **2005**, *62*, 135.
- (10) Srivastava, R. K. *Control of Mercury Emissions from Coal Fired Electric Utility Boilers: An Update*, EPA/600/R-10/006; U.S. Environmental Protection Agency: Washington, DC, 2010.
- (11) Heebink, L. V.; Hassett, D. J. Mercury release from FGD. *Fuel* **2005**, *84*, 1372.
- (12) Feng, W.; Kwon, S.; Borguet, E.; Vidic, R. Sulfur impregnation on activated carbon fibers by H<sub>2</sub>S oxidation for mercury control. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **2005**, *50*, 285.
- (13) Alptekin, G. O.; Dubovik, M.; Cesario, M. New sorbents for mercury removal from flue gases. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **2005**, *50*, 283.
- (14) Li, H.; Xu, Q.; Zhang, D. Removal of gas-phase elemental mercury by bromine-impregnated activated carbon. *Adv. Mater. Res.* **2011**, *356–360*, 1660.

- (15) Deng, X.; Jiang, J.-C. Development of S-loaded activated carbon applied to remove mercury. *J. Chem. Ind. Forest Prod.* **2004**, *38*, 13.
- (16) Tan, Y.; Mortazavi, R.; Lu, D.; Anthony, B.; Dureau, R.; Wong, J.; Douglas, M.; Thambimuthu, K. Development of a chemical sorbent for Hg removal in a condensing environment. *Proc. Int. Tech. Conf. Coal Util. Fuel Syst.* **2004**, 765.
- (17) Presto, A. A.; Granite, E. J. Noble metal catalysts for mercury oxidation in utility flue gas gold, palladium, platinum formulations. *Platinum Met. Rev.* **2008**, *52* (3), 144.
- (18) Hrdlicka, J. A.; Seames, W. S.; Mann, M. D.; Muggli, D. S.; Horabik, C. A. Mercury oxidation in flue gas using gold and palladium catalysts on fabric filters. *Environ. Sci. Technol.* **2008**, *42* (17), 6677.
- (19) Kamata, H.; Ueno, S.; Naito, T.; Yukimura, A. Mercury oxidation over the  $V_2O_5(WO_3)/TiO_2$  Commercial SCR Catalyst. *Ind. Eng. Chem. Res.* **2008**, *47* (21), 8136.
- (20) Kamata, H.; Ueno, S.; Naito, T.; Yamaguchi, A.; Ito, S. Mercury oxidation by hydrochloric acid over a  $VO_x/TiO_2$  catalyst. *Catal. Commun.* **2008**, *9* (14), 2441.
- (21) Flora, J. R. V.; Hargis, R. A.; O'Dowd, W. J.; Pennline, H. W.; Vidic, R. D. Modeling sorbent injection for mercury control in baghouse filters: II-pilot-scale studies and model evaluation. *J. Air Waste Manage. Assoc.* **2003**, *53*, 489.
- (22) Flora, J. R. V.; Hargis, R. A.; O'Dowd, W. J.; Pennline, H. W.; Vidic, R. D. Modeling sorbent injection for mercury control in baghouse filters: I-model development and sensitivity analysis. *J. Air Waste Manage. Assoc.* **2003**, *53*, 478.
- (23) Ghorishi, S. B.; Keeney, R. M.; Serre, S. D. Development of a Cl-impregnated activated carbon for entrained-flow capture of elemental mercury. *Environ. Sci. Technol.* **2002**, *36*, 4454.
- (24) Zeng, H.; Jin, F.; Guo, J. Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. *Fuel* **2004**, *83*, 143.
- (25) Karatza, D.; Lancia, A. Study of mercury absorption and desorption on sulfur impregnated carbon. *Exp. Therm. Fluid Sci.* **2000**, *21*, 150.
- (26) Hsi, H.; Rood, M. J.; Rostam-Abadi, M. Effects of sulfur impregnation temperature on the properties and mercury adsorption capacities of activated carbon fibers (ACFs). *Environ. Sci. Technol.* **2000**, *35*, 2785.
- (27) Hsi, H.; Rood, M. J.; Rostam-Abadi, M. Mercury adsorption properties of sulfur impregnated adsorbents. *J. Environ. Eng.* **2002**, *128*, 1080.
- (28) Hsi, H.; Chen, S.; Rostam-Abadi, M. Preparation and evaluation of coal-derived activated carbons for removal of mercury vapor from simulated coal combustion flue gases. *Energy Fuels* **1998**, *12*, 1061.
- (29) Liu, W.; Vidic, R. D.; Brown, T. D. Optimization of sulfur impregnation protocol for fixed-bed application of activated carbon-based sorbents for gas-phase mercury removal. *Environ. Sci. Technol.* **1998**, *32*, 531.
- (30) Liu, W.; Vidic, R. D.; Brown, T. D. Impact of flue gas conditions on mercury uptake by sulfur-impregnated activated carbon. *Environ. Sci. Technol.* **2000**, *34*, 154.
- (31) Wu, S.; Morimoto, T.; Uddin, M. A.; Togaki, N.; Nagamine, S.; Sasaoka, E. Characters of activated carbon for Hg removal of flue gas with H<sub>2</sub>S and iron oxide for Hg removal of coal derived fuel gas with H<sub>2</sub>S. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 234.
- (32) Hultbom, K. G., Industrially proven methods for mercury removal from gases. Proceedings of Sessions and Symposia held during the TMS Annual Meeting, San Diego, CA, United States, March 26, 2003, 147.
- (33) Yang, H.; Xu, Z.; Fan, M.; Bland, A. E.; Judkins, R. R. Adsorbents for capturing mercury in coal-fired boiler flue gas. *J. Hazard. Mater.* **2007**, *146*, 1.
- (34) Granite, E. J.; Pennline, H. W.; Hargis, R. A. Novel sorbents for mercury removal from flue gas. *Ind. Eng. Chem. Res.* **2000**, *39*, 1020.
- (35) Alptekin, G. O.; Dubovik, M.; Cesario, M.; Gershanovich, Y. Non-carbon sorbents for mercury removal from flue gases. *Powder Technol.* **2008**, *180*, 35.
- (36) Montgomery, J. L.; Whitworth, C. G.; Battleson, D. M.; Ray, I.; Buckley, W.; Reynolds, J.; Altman, R. Developments of the plasma-enhanced electrostatic precipitator for mercury removal in offgas. *Environ. Eng. Sci.* **2005**, *22*, 264.
- (37) McLarnon, C. R.; Granite, E. J.; Pennline, H. W. The PCO process for photochemical removal of mercury from flue gas. *Fuel Process. Technol.* **2005**, *87*, 85.
- (38) Granite, E. J.; Pennline, H. W. Photochemical removal of mercury from flue gas. *Ind. Eng. Chem. Res.* **2002**, *41*, 5470.
- (39) Bayless, D. J.; Shi, L.; Kremer, G.; Stuart, B. J.; Reynolds, J.; Caine, J. Membrane-based wet electrostatic precipitation. *J. Air Waste Manage. Assoc.* **2005**, *55*, 784.
- (40) DeBerry, D. W. Reactive membrane process for the removal of vapor phase contaminants. U.S. Patent 7306774, 2007.
- (41) Zhuang, Y.; Pavlish, J. H.; Holmes, M. J.; Benson, S. A., Pilot-scale study of advanced mercury control technologies for lignite-fired power plant in a retrofit advanced hybrid filter. *Proc. Int. Tech. Conf. Coal Util. Fuel Syst.*, **2004**, 753.
- (42) Yan, N.; Chen, W.; Chen, J.; Qu, Z.; Guo, Y.; Yang, S.; Jia, J. Significance of RuO<sub>2</sub> modified SCR catalyst for elemental mercury oxidation in coal-fired flue gas. *Environ. Sci. Technol.* **2011**, *45*, 5725.
- (43) Guo, Y.; Yan, N.; Yang, S.; Qu, Z.; Wu, Z.; Liu, Y.; Liu, P.; Jia, J. Conversion of elemental mercury with a novel membrane delivery catalytic oxidation system (MDCOs). *Environ. Sci. Technol.* **2011**, *45*, 706.
- (44) Yang, S.; Yan, N.; Guo, Y.; Wu, D.; He, H.; Qu, Z.; Li, J.; Zhou, Q.; Jia, J. Gaseous elemental mercury capture from flue gas using magnetic nanosized (Fe<sub>3-x</sub>Mn<sub>x</sub>)<sub>1-δ</sub>O<sub>4</sub>. *Environ. Sci. Technol.* **2011**, *45*, 1540.
- (45) Yang, S.; Guo, Y.; Yan, N.; Wu, D.; He, H.; Xie, J.; Qu, Z.; Yang, C.; Jia, J. A novel multi-functional magnetic Fe-Ti-V spinel catalyst for elemental mercury capture and callback from flue gas. *Chem. Commun.* **2010**, *46*, 8377.
- (46) Yang, S.; Guo, Y.; Yan, N.; Wu, D.; He, H.; Xie, J.; Qu, Z.; Jia, J. Remarkable effect of the incorporation of titanium on the catalytic activity and SO<sub>2</sub> poisoning resistance of magnetic Mn-Fe spinel for elemental mercury capture. *Appl. Catal., B* **2011**, *101*, 698.
- (47) Qu, Z.; Yan, N.; Liu, P.; Chi, Y.; Jia, J. Bromine chloride as an oxidant to improve elemental mercury removal from coal-fired flue gas. *Environ. Sci. Technol.* **2009**, *43*, 8610.
- (48) Liu, S.; Yan, N.; Liu, Z.; Qu, Z.; Wang, H. P.; Chang, S.; Miller, C. Using bromine gas to enhance mercury removal from flue gas of coal-fired power plants. *Environ. Sci. Technol.* **2007**, *41*, 1405.
- (49) Zhao, Y. X.; Mann, M. D.; Pavlish, J. H.; Mibeck, B. A. F.; Dunham, G. E.; Olson, E. S. Application of gold catalyst for mercury oxidation by chlorine. *Environ. Sci. Technol.* **2006**, *40* (5), 1603.
- (50) Chu, P.; Laudal, D. L.; Brickett, L.; Lee, C. W., Power plant evaluation of the effect of SCR technology on mercury. In *Proceedings of the Combined Power Plant Air Pollutant Control Symposium—The Mega Symposium*, Washington, DC, 2003.
- (51) Wan, Q.; Duan, L.; Li, J.; Chen, L.; He, K.; Hao, J. Deactivation performance and mechanism of alkali (earth) metals on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst for oxidation of gaseous elemental mercury in simulated coal-fired flue gas. *Catal. Today* **2011**, *175* (1), 189.
- (52) Yan, N. Q.; Liu, S. H.; Chang, S. G.; Miller, C. Method for the study of gaseous oxidants for the oxidation of mercury gas. *Ind. Eng. Chem. Res.* **2005**, *44* (15), 5567.
- (53) Li, H.; Li, Y.; Wu, C.-Y.; Zhang, J. Oxidation and capture of elemental mercury over SiO<sub>2</sub>-TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> catalysts in simulated low-rank coal combustion flue gas. *Chem. Eng. J.* **2011**, *169* (1-3), 186.
- (54) Li, H.; Wu, C. Y.; Li, Y.; Zhang, J. Superior activity of MnO<sub>x</sub>-CeO<sub>2</sub>/TiO<sub>2</sub> catalyst for catalytic oxidation of elemental mercury at low flue gas temperatures. *Appl. Catal., B* **2012**, *111*, 381.
- (55) Lee, C. W.; Srivastava, R.; Ghorishi, S.; Hastings, T.; Stevens, F. M. Investigation of selective catalytic reduction impact on mercury speciation under simulated NO<sub>x</sub> emission control conditions. *J. Air Waste Manage. Assoc.* **2004**, *54*, 1560.

- (56) He, S.; Zhou, J.; Zhu, Y.; Luo, Z.; Ni, M.; Cen, K. Mercury oxidation over a vanadia-based selective catalytic reduction catalyst. *Energy Fuels* **2009**, *23* (1), 253.
- (57) Niksa, S.; Fujiwara, N. A predictive mechanism for mercury oxidation on selective catalytic reduction catalysts under coal-derived flue gas. *J. Air Waste Manag. Assoc.* **2005**, *55* (12), 1866.
- (58) Senior, C. L. Oxidation of mercury across selective catalytic reduction catalysts in coal-fired power plants. *J. Air Waste Manag. Assoc.* **2006**, *56* (1), 23.
- (59) Gao, W.; Liu, Q.; Wu, C.-Y.; Li, H.; Li, Y.; Yang, J.; Wu, G. Kinetics of mercury oxidation in the presence of hydrochloric acid and oxygen over a commercial SCR catalyst. *Chem. Eng. J.* **2013**, *220*, 53.
- (60) Ettireddy, P. R.; Ettireddy, N.; Mamedov, S.; Boolchand, P.; Smirniotis, P. G. Surface characterization studies of TiO<sub>2</sub> supported manganese oxide catalysts for low temperature SCR of NO with NH<sub>3</sub>. *Appl. Catal. B: Environ.* **2007**, *76*, 123.
- (61) O'Dowd, W. J.; Hargis, R. A.; Granite, E. J.; Pennline, H. W. Recent advances in mercury removal technology at the national energy technology laboratory. *Fuel Process. Technol.* **2004**, *85*, 533.
- (62) Portzer, J. W.; Albritton, J. R.; Allen, C. C.; Gupta, R. P. Development of novel sorbents for mercury control at elevated temperatures in coal-derived syngas: Results of initial screening of candidate materials. *Fuel Process. Technol.* **2004**, *85*, 621.
- (63) Mei, Z.; Shen, Z.; Mei, Z.; Zhang, Y.; Xiang, F.; Chen, J.; Wang, W. The effect of N-doping and halide-doping on the activity of CuCoO<sub>4</sub> for the oxidation of elemental mercury. *Appl. Catal., B* **2008**, *78* (1–2), 112.
- (64) Yamaguchi, A.; Akiho, H.; Ito, S. Mercury oxidation by copper oxides in combustion flue gases. *Powder Technol.* **2008**, *180* (1–2), 222.
- (65) Wang, Q.; Park, S. Y.; Choi, J. S.; Chung, J. S. Co/K<sub>x</sub>Ti<sub>2</sub>O<sub>5</sub> catalysts prepared by ion exchange method for NO oxidation to NO<sub>2</sub>. *Appl. Catal., B* **2008**, *79* (2), 101.
- (66) Wang, Q.; Park, S. Y.; Duan, L.; Chung, J. S. Activity, stability and characterization of NO oxidation catalyst Co/K<sub>x</sub>Ti<sub>2</sub>O<sub>5</sub>. *Appl. Catal., B* **2008**, *85*, 10.
- (67) Wang, Q.; Chung, J. S.; Guo, Z. Promoted soot oxidation by doped K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> catalysts and NO oxidation catalysts. *Ind. Eng. Chem. Res.* **2011**, *50* (13), 8384.
- (68) Wang, Q.; Sohn, J. H.; Park, S. Y.; Choi, J. S.; Lee, J. Y.; Chung, J. S. Preparation and catalytic activity of K<sub>4</sub>Zr<sub>5</sub>O<sub>12</sub> for the oxidation of soot from vehicle engine emissions. *J. Ind. Eng. Chem.* **2010**, *16*, 68.
- (69) Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-temperature oxidation of CO catalysed by Co<sub>3</sub>O<sub>4</sub> nanorods. *Nature* **2009**, *458*, 746.
- (70) Wyrwalski, F.; Lamonier, J.-F.; Perez-Zurita, M. J.; Sifferta, S.; Aboukaias, A. Influence of the ethylenediamine addition on the activity, dispersion and reducibility of cobalt oxide catalysts supported over ZrO<sub>2</sub> for complete VOC oxidation. *Catal. Lett.* **2006**, *108*, 87.
- (71) Liu, Y.; Wang, Y.; Wang, H.; Wu, Z. Catalytic oxidation of gas-phase mercury over Co/TiO<sub>2</sub> catalysts prepared by sol-gel method. *Catal. Commun.* **2011**, *12* (14), 1291.
- (72) Reddy, B. M.; Khan, A.; Yamada, Y.; Kobayashi, T.; Lorient, S.; Volta, J. C. Structural characterization of CeO<sub>2</sub>-TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts by Raman and XPS techniques. *J. Phys. Chem. B* **2003**, *107*, 5162.
- (73) Li, Y.; Murphy, P. D.; Wu, C.-Y.; Powers, K. W.; Bonzongo, J.-C. Development of silica/vanadia/titania catalysts for removal of elemental mercury from coal-combustion flue gas. *Environ. Sci. Technol.* **2008**, *42*, 5304.
- (74) Xu, W.; Yu, Y.; Zhang, C.; He, H. Selective catalytic reduction of NO by NH<sub>3</sub> over a Ce/TiO<sub>2</sub> catalyst. *Catal. Commun.* **2008**, *9*, 1453.
- (75) Li, H.; Wu, C.-Y.; Li, Y.; Zhang, J. CeO<sub>2</sub>-TiO<sub>2</sub> catalysts for catalytic oxidation of elemental mercury in low-rank coal combustion flue gas. *Environ. Sci. Technol.* **2011**, *45* (17), 7394.
- (76) Lee, C. W.; Srivastava, R. K.; Kilgroe, J. D.; Ghorishi, S. B., Effects of iron content in coal combustion fly ashes on speciation of mercury. *94th Annual Meeting of the Air & Waste Management Association*, Paper #156, Orlando, FL, 2001.
- (77) Ghorishi, S. B.; Lee, C. W.; Kilgroe, J. D., Mercury speciation in combustion systems: Studies with simulated flue gases and model fly ashes. *92nd Annual Meeting of Air & Waste Management Association*, St. Louis, MO, 1999.
- (78) Frandsen, F.; Johansen, K. D.; Rasmussen, P. Trace elements from combustion and gasification of coal—an equilibrium approach. *Prog. Energy Combust. Sci.* **1994**, *20*, 115.
- (79) Zhuang, Y.; Laumb, J.; Liggett, R.; Holmes, M.; Pavlish, J. Impacts of acid gases on mercury oxidation across SCR catalyst. *Fuel Process. Technol.* **2007**, *88* (10), 929.
- (80) Li, H.; Wu, C.-Y.; Li, Y.; Li, L.; Zhao, Y.; Zhang, J. Impact of SO<sub>2</sub> on elemental mercury oxidation over CeO<sub>2</sub>-TiO<sub>2</sub> catalyst. *Chem. Eng. J.* **2013**, *219*, 319.
- (81) Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO<sub>x</sub> by ammonia over oxide catalysts: A review. *Appl. Catal., B* **1998**, *18*, 1.
- (82) Norton, G. A.; Yang, H. Q.; Brown, R. C.; Laudal, D. L.; Dunham, G. E.; Erjavec, J. Heterogeneous oxidation of mercury in simulated post combustion conditions. *Fuel* **2003**, *82* (2), 107.
- (83) Menke, R.; Wallis, G. Detection of mercury in air in the presence of chlorine and water vapor. *Am. Ind. Hyg. Assoc. J.* **1980**, *41*, 120.
- (84) Skare, A.; Johansson, R. Reactions between mercury vapor and chlorine gas at occupational exposure levels. *Chemosphere* **1992**, *24*, 1633.
- (85) Spencer, N. D.; Lambert, R. M. Chlorine chemisorption and surface chloride formation on Au(111). *Surf. Sci.* **1981**, *107*, 237.
- (86) Wagner, F. T.; Moylan, T. E. Hydrogen chloride adsorption and coadsorption with hydrogen or water on platinum (111). *Surf. Sci.* **1989**, *216*, 361.
- (87) Van Otten, B.; Buitrago, P. A.; Senior, C. L.; Silcox, G. D. Gas-phase oxidation of mercury by bromine and chlorine in flue gas. *Energy Fuels* **2011**, *25* (8), 3530.
- (88) Lee, C. W.; Srivastava, R.; Ghorishi, S. B.; Hastings, T. W.; Stevens, F. M., Study of speciation of mercury under simulated SCR NO<sub>x</sub> emissions control conditions. *ICAC Forum 03: Multi-Pollutant Controls & Strategies*, Nashville, TN, 2003.
- (89) Lee, C. W.; Srivastava, R. K.; Ghorishi, S. B.; Karwowski, J.; Hastings, T. W.; Hirschi, J. C. Pilot-scale study of the effect of selective catalytic reduction catalyst on mercury speciation in Illinois and powder river basin coal combustion flue gases. *J. Air Waste Manage.* **2006**, *56*, 643.
- (90) Shintaro, H.; Toru, T.; Kozo, I.; Tetsuya, I.; Koichiro, I.; Tatsuto, N., Method and equipment for removing mercury in exhaust gas. 2003, Japan Patent JP2003053142.
- (91) Couling, D. J.; Nguyen, H. V.; Green, W. H. Screening of metal oxides and metal sulfides as sorbents for elemental mercury at elevated temperatures. *Fuel* **2012**, *97*, 783.
- (92) Kamata, H.; Ueno, S.; Sato, N.; Naito, T. Mercury oxidation by hydrochloric acid over TiO<sub>2</sub> supported metal oxide catalysts in coal combustion flue gas. *Fuel Process. Technol.* **2009**, *90* (7–8), 947.