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ARTICLE TYPE

A review on oxidation of element mercury from coal-fired flue gas with selective catalytic reduction catalysts

Lingkui Zhao^{a,b}, Caiting Li^{*a,b}, Xunan Zhang^{a,b}, Guangming Zeng^{a,b}, Jie Zhang^{a,b}, Yin'e Xie^{a,b}
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Catalytic technologies present a more environmentally and financially sound option in the removal of element mercury (Hg^0) from coal-fired flue gas. However, developing novel and efficient catalysts for Hg^0 oxidation is still in challenge. This paper reviews the catalytic oxidation of Hg^0 over a new kind of catalysts which were developed from selective catalytic reduction (SCR) catalysts of NO_x . In this review, both noble metal catalysts and non-noble metal catalysts for Hg^0 oxidation were summarized. An overview of mercury emissions including transformation and speciation of mercury in coal-fired flue gas was also presented. The possible mechanisms and kinetics of mercury oxidation, space velocity as well as the effects of flue gas components on activity and stability of the catalysts were examined. We expect this work will serve as a theoretical underpinning for the development of Hg^0 oxidation technology in flue gas.

1 Introduction

Mercury (Hg) has been known for a long time to be an environmental contaminant which is toxic to human beings and other organisms. It is well known that, in anthropogenic activities, coal combustion is a major source of Hg emission¹. Due to the harmful environmental impacts, Hg emission legislation becomes increasingly stringent. In 2013, the US Environmental Protection Agency (USEPA) updated the emission limits of Mercury and Air Toxics Standards (MATS), which requires that total emission of mercury from new coal-fired units burning low rank virgin coal must be controlled below the level of 0.003 lb/GWh^{2,3}. Furthermore, in January 2013, 140 nations adopted the first legally binding international treaty to set enforceable limits on emissions of Hg and exclude, phaseout, or restrict some products that contain Hg⁴.

To meet the stringent regulation, various technologies for controlling Hg emissions, including adsorption technology, corona discharge plasma technology, and electrocatalytic oxidation combined treatment technology, have been investigated⁵⁻⁷. Unfortunately, it is difficult to apply these technologies widely because of the unaffordable cost. Hence, developing a low cost option for controlling Hg emissions from coal-fired power plants is indispensable. Due to the strict regulations for air pollution, most of the coal-fired power plants have been equipped with air pollution control devices (APCDs), such as fabric filters (FF) and electrostatic precipitators (ESPs) for particulate control, wet flue gas desulfurization (WFGD) for SO_2 control and selective catalytic reduction (SCR) for NO_x emission control⁸. In flue gas, Hg primarily exists in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-associated mercury (Hg^p). It has been reported that the existing

APCDs can achieve the co-benefits of Hg capture^{9,10}. For example, Hg^p can be collected by ESPs and FF together with fly ash¹¹. Highly water-soluble Hg^{2+} might be effectively captured by WFGD¹²⁻¹⁴. However, it is difficult to remove Hg^0 directly by existing APCDs because it's highly volatile and nearly insoluble in water¹⁵⁻¹⁸. Therefore, combination of Hg^0 oxidation and WFGD is considered as an effective option for Hg emission control¹⁹⁻²¹.

SCR catalysts for NO_x removal were proved to be able to oxidize Hg^0 to Hg^{2+} and lots of full-scale tests were carried out to evaluate the performances of these SCR catalysts on Hg^0 oxidation²²⁻²⁴. It is found that a combination of ESP, SCR and FGD is effective in removing appreciable levels of Hg^0 ¹⁹. Overall mercury removal efficiency of APCDs, on average, was about 61% and 47% with and without SCR system, respectively²². Blythe²⁵ compared the cost of catalytic oxidation technology and activated carbon injection (ACI). It was proved that the co-benefit effect of SCR system for oxidizing Hg^0 makes the cost of Hg^0 removal lower than that of ACI. Hence, combining SCR system with WFGD is thought to be one of the most economic approaches for controlling Hg emissions from coal-fired power plants. Some researches on researching selective catalytic reduction of NO_x and Hg^0 removal have been done in our group^{17,26-29}.

Understanding the transformation and speciation of Hg throughout the coal-fired process is crucial to the design of effective technologies for Hg^0 removal. The oxidation of Hg^0 is helpful to obtain greater mercury capture efficiency with the APCDs. Accordingly, this paper introduces the research progress on Hg^0 oxidation over a new kind of catalysts which were developed from selective catalytic reduction (SCR) catalysts of NO_x . The transformation and speciation of Hg in coal-fired flue gas will be considered first, followed by a review on mechanistic

pathways and kinetics of mercury oxidation. At last, the influence of flue gas components, space velocity and temperature are summarized and reviewed.

2 Mercury emissions in flue gas

2.1. Mercury emissions

Table.1 Contribution of sources of anthropogenic mercury emissions expressed as a percentage (%) of total emissions [34]

Emission type		USA	China	Canada	Europe	Africa	Global
Coal combustion	Power plants	32.6	12.7	3.6	26.1	51.5	-
	Industrial	13.1	19.3	-	-	-	-
	Residential	-	3.7	-	26.1	0.1	-
	Total	45.7	35.7	3.6	52.2	51.6	65.0
Waste incineration ^a	33.8	1.1	9.4	2.8	-	3.0	
Base metal smelting ^b	0.1	36.9	66.0	4.5	2	6.8	
Gold production ^c	-	13.6	9.4	-	44.6	11.3	
Mercury production	0.3	1.6	-	-	-	1.1	
Chlor-alkali plants	4.5	0.04	1.4	12.1	0.1	3.0	
Cement production	3.1	4.2	3.0	8.4	1.3	6.4	
Iron & steel industry	-	-	0.8	3.4	0.1	1.4	
Other	12.5	6.9	28.0	16.6	0.4	2.0	

a Includes municipal, medical, sewage sludge and hazardous waste incineration.

b Includes copper, lead and zinc smelting.

c Includes artisanal and large-scale gold mining.

After 19th century, a large amount of Hg is emitted into the environment due to anthropogenic activities, leading to considerably increasing Hg level in atmosphere³⁰. According to United Nations Environment Programme (UNEP), the global Hg emissions to air from anthropogenic sources were estimated as 1960 tonnes in 2010³¹. Coal combustion, waste incineration, base metal smelting, large-scale and artisanal gold production and cement production are the most important anthropogenic sources of Hg emissions^{32,33}. As listed in Table.1³⁴, coal combustion is the biggest contributor to Hg emissions. As a big coal consumer, Hg emissions from coal-fired power plant can't be ignored and has been studied by many researchers. Streets *et al.*³⁵ estimated that China's emissions in 1999 were 536 (± 236) tons, and approximately 38% of the Hg comes from coal combustion. At the same time, Wu *et al.*³⁶ also estimated that total Hg emissions from all anthropogenic sources increased at an average annual rate of 2.9% during the period 1995-2003, reaching 696 (± 307) tons in 2003. The USEPA estimated that approximately 75 tons of Hg are found during the process of coal transportation in the United States each year and about two thirds of the mercury is emitted to the air³⁷. Using South Africa specific and toolkit based emission factors, coal-fired power plants were estimated to be the largest contributor of Hg emissions, viz. 27.1 to 38.9 tonnes y⁻¹ in air³⁸.

2.2 transformation and speciation of mercury in flue gas

In order to understand the transport and fate of Hg in the air pollution control systems, it is necessary to investigate Hg transformations and speciation in coal-fired flue gas. Hg was found to be the most volatile element in coal. It can volatilize at

temperature as low as *c.a.* 150°C. The volatility of Hg increased with the increasing of temperature above 400°C. Fikleman *et al.*³⁹ showed that the volatilization rate of Hg in the Argonne Premium Coal Samples is about 40%-75% at 550°C. Rizeq *et al.*⁴⁰ suggested that Hg could be volatilized completely when temperature was higher than 800°C. Therefore, while entering the furnace, most of Hg is rapidly volatilized. It moves through the convective section and economizer of the boiler island before exchanging heat in the air pre-heater. With the temperature of

flue gas decreasing, gaseous Hg is predicted to react with the component of flue gas. Eventually, the principal forms of Hg in coal combustion flue gas are assumed to be Hg⁰⁴¹. Fig. 1 presents the migration mechanism of mercury in coal combustion process and flue gas⁴¹. At furnace exit temperatures (1700K), all of mercury is expected to remain as the favoured elemental form of thermodynamics in the gas⁴². However, Hg⁰ vapor undergoes several chemical and physical processes changes in the post combustion section, where the gas temperature decreases. It reacts with other flue gas constituents to convert to gaseous Hg²⁺ and Hg^p as the temperature of flue gases falls down below 600°C. Hence, the forms of Hg in coal-fired flue gas are Hg⁰, Hg²⁺, and Hg^p^{43,44}.

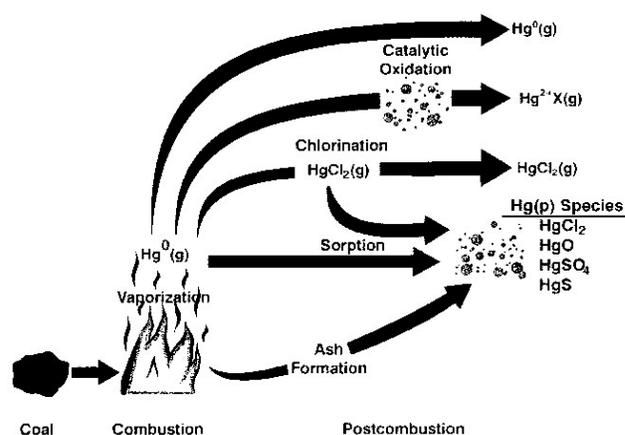


Fig 1. Migration mechanism of mercury in coal combustion process and flue gas [41].

Researchers have proposed different Hg reaction mechanisms to describe Hg transformations in coal-fired flue gas⁴⁵⁻⁴⁷. To date, it has been widely accepted that both heterogeneous and homogeneous reactions play important roles in mercury-flue gas chemistry. The fate of Hg species in coal flue gas is determined by the results of heterogeneous and homogeneous reactions occurring in utility systems. Meanwhile, the formation

of various Hg species is affected by many parameters, including the component of flue gas, combustion environment and plant operating condition. Therefore, some researchers focused on understanding the mechanisms of Hg oxidation by injection of Hg⁰ into gas fuel flame or simulated flue gas. The experimental data obtained by Boot *et al.*⁴⁸ indicated that most of mercury vaporized and either left the reactor as a vapor or was captured by residual carbon. The equilibrium predicted HgO might form and condense on the ash. In the presence of NO₂, HCl, and SO₂ exhibited promotional effect on Hg⁰ oxidation, while NO inhibited Hg⁰ oxidation⁴⁹. Nevertheless, the extent of homogeneous Hg⁰ oxidation is highly dependent upon the coal rank, the content of Cl in the coal, and the conditions of the utility boiler (e.g., air-to-fuel ratio and temperature)⁵⁰. Thermodynamic calculation has predicted that Hg will be in the form of Hg⁰ and HgCl₂ at typical temperatures in flue dusts (80–250°C). HgCl₂ is stable mercury species followed by HgO_(g) in a chlorine-laden flue gas at temperatures lower than 400°C. Meanwhile, a literature survey revealed that Hg⁰ oxidation occurs at temperatures below 700°C and that mercury will be completely oxidized at (or below) 450°C⁴². However, Hg⁰(g) is the only thermodynamically stable species above 750°C⁵¹. Consequently, Hg is mainly distributed in gaseous (Hg⁰ and Hg²⁺) form⁵². Generally, more than half of the gas phase Hg exists as Hg²⁺ which is likely to be HgCl₂ (50–80%), and the remaining is Hg⁰ (20–50%)^{53–55}.

3. The catalytic oxidation of Hg⁰ on SCR catalysts

Catalyst type	Potential catalysts	Gas composition							T °C	Space velocity h ⁻¹	Hg ⁰ Oxidation %	Reference
		O ₂ vol. %	H ₂ O vol.%	HCl ppm	NO ppm	NH ₃ ppm	SO ₂ ppm	Hg ⁰ µg/Nm ³				
Noble metal-based catalysts	Pd/Al ₂ O ₃	-	-	10	-	-	-	70	200-350	1200	>90	[57]
	Au/TiO ₂	4	10	50	100	-	1000	20-30	150	1200	40-60	[58]
	Pd/Al ₂ O ₃	0-5.25	-	0-100	500	-	1000	6-18	138-160	8-10 ^{**}	1.6×10 ⁻¹⁰ [■]	[61]
Non-noble metal-based catalysts	V ₂ O ₅ /TiO ₂	1.6	8	10	160	52.8	160	1.2 [◇]	250-400	170	>90	[74]
	MnO _x /TiO ₂	2	-	-	400	-	-	15-66 [◇]	175-200	5000	>90	[12]
	MnO _x -CeO ₂ /TiO ₂	4	8	10	300	300	400	75	100-400	6×10 ⁵	0-90	[75]
	Mo-Mn/α-Al ₂ O ₃	7.1	6.8	0-20	400	-	500	-	100-250	4.4×10 ⁴	70-100	[11]
	CeO ₂ -WO ₃ /TiO ₂	8	8	10	-	-	500	80-100	100-500	1.0×10 ⁵	>80	[82]
	CeO ₂ -TiO ₂	4	8	10	300	-	400	50	120-400	6×10 ⁵	>90	[84]
	Commercial SCR catalysts	6	-	50	400	400	-	36-39	350	4000	3-91	[64]
	-	15	0.3-3	400	300	70	160	260-320	170	50-90	[91]	
	3	-	500	250	275	2000	120	300-350	1800	<80	[94]	

Table.2 Elemental mercury oxidation on SCR-DeNO_x catalysts

• gas space velocity (L/h); ** gas space velocity (L/min); ■ reaction rate in the presence of HCl and O₂ in (mol Hg²⁺) × (g catalyst)⁻¹ × s⁻¹; ◇ PPb

The SCR technology for control of NO_x emissions from flue gas is the best developed and world-wide used technology since 1980s⁵⁶. The main overall reactions can be expressed as:



In addition to NO_x control, SCR catalysts exhibit the co-benefit of promoting Hg oxidation in coal-fired power plants¹⁹.

Two types of catalysts have been developed, including noble metal-based catalysts and non-noble metal-based catalysts. As summarized in Table. 2, these two types of catalysts have been primarily studied for heterogeneous catalytic oxidation of Hg⁰.

3.1 Noble metal-based catalysts

Noble metals, such as Au, Pd, Pt, and Rh, which are used as potential Hg⁰ oxidation catalysts, have been used to test their Hg adsorption abilities because of their regeneration potential and good stability at high temperatures. In order to maximize specific surface areas of the catalysts, the noble metals used for the Hg⁰ oxidation are supported by various porous materials, including alumina, silica, zirconia, titania, carbons, and zeolite. For example, a mass loading of 8% Pd supported by alumina can remove over 90% of mercury for operating temperatures up to 270°C⁵⁷. Au/TiO₂ was also effective, yielding Hg oxidation ranges of 40–60%⁵⁸.

In particular, Pd has been considered the most attractive option for controlling Hg⁰ emissions^{59,60}. In the study of Presto⁶¹, the Pd catalyst exhibited no apparent catalyst deactivation with HCl concentration changed. When the HCl concentration increases from 50 to 100 ppm, little impact on the Hg⁰ oxidation rate was observed. In the absence of HCl, however, it was observed that Hg⁰ oxidation still continues on the catalysts, while with a declining reaction rate. From this observation, it was suggested that the reactions between mercury and HCl are bound to the catalyst surface. This explains why Hg⁰ oxidation continues in the absence of HCl, but with a declining reaction rate.

Au has been considered as a very promising candidate

catalyst for Hg⁰ oxidation because Au can adsorb and react with Hg⁰ to form amalgam^{61,62}. Lim *et al.*⁶² suggested that adsorbed Hg⁰ on the Au catalyst reacts with Cl₂ (or HCl) in accordance with a Langmuir-Hinshelwood mechanism. Activation energies for Hg oxidation were calculated assuming the possible reaction pathways: three-step Hg oxidation (Hg→HgCl→HgCl₂) with transition states TS₁ and TS₂ (Fig. 2). In this Hg⁰ oxidation, the first Cl attachment step is exothermic, while the second Cl attachment step is endothermic. It is implied that Hg⁰ oxidation prefers a pathway in which HgCl and HgCl₂ are formed, rather than a pathway directly oxidizing Hg to HgCl₂. Another literature mentioned the similar Hg⁰ oxidation trend⁶³. Atomic Cl is the key species for Hg⁰ oxidation on the surfaces of gold. That is, Hg⁰ first reacts with one atomic Cl to form HgCl, which, in turn,

is oxidized into HgCl_2 by the other Cl.

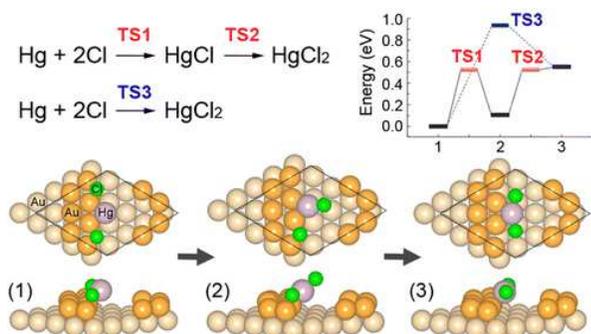


Fig.2 Reaction pathways of Hg oxidation on perfect Au(111)-p(4x4) surfaces [62]. Reprinted (adapted) with permission from (D.H. Lim and J. Wilcox, *Environ Sci Technol*, 2013, 47, 8515-8522.). Copyright (2013) American Chemical Society.

3.2 Non-noble metal-based catalysts

Noble metal catalysts used as catalysts for SCR of NO in flue gas is still an area of active study. However, they are too expensive to apply in industry. Consequently, noble metal catalysts were soon replaced by non-noble metal catalysts for SCR of NO. Non-noble catalysts, especially some transition metal catalysts have been observed to be beneficial to oxidize Hg^0 to Hg^{2+} when sufficient HCl exists in the flue gas. Therefore, various metal catalysts materials have been investigated for Hg^0 oxidation in recent years^{11, 64-67}.

3.2.1 Transition metal oxide catalysts

To date, lots of researches involving transition metal oxide catalysts, such as V_2O_5 , MnO_2 , Co_3O_4 , CuO and TiO_2 have been extensively conducted to develop effective Hg^0 oxidation technologies⁶⁸⁻⁷². Compared with noble metal catalysts, the lower-cost transition metal catalysts exhibit high catalytic oxidation activity. Transition metal oxide catalysts for Hg^0 oxidation are usually supported by various materials, including alumina, silica, titania, carbons and zeolite, etc. Generally, alumina and titania are used as carriers for these transition metal oxide catalysts. It is well known that the role of the supporter not only stabilize and ensure a high metal dispersion degree, but also in certain cases to participate in the Hg^0 oxidation reaction⁷³. Kamata *et al.*⁷⁴ investigated Hg^0 oxidation by HCl over the metal oxides (1 w.t.% MO_x where $\text{M}=\text{V}$, Cr , Mn , Fe , Ni , Cu , and Mo) supported on anatase type TiO_2 . The metal oxides added to the catalyst were observed to be dispersed well on the TiO_2 surface. Meanwhile, the catalyst such as $\text{V}_2\text{O}_5/\text{TiO}_2$ showed high NO reduction activity and high Hg^0 oxidation activity.

Among several metal oxide catalysts^{67, 75}, the manganese-based catalysts were found to be one of the best candidates for Hg^0 oxidation owing to their excellent catalytic activity, easy manufacturing and low cost. It has been studied extensively as low-temperature SCR catalysts because they possessed various types of labile oxygen which played an important role in the catalytic reaction^{76, 77}. Meanwhile, MnO_x based SCR catalysts can also serve as catalysts for Hg^0 oxidation. Ji *et al.*¹² reported that MnO_x supported on titania was effective for both elemental mercury capture and low temperature SCR. The results indicated that $\text{MnO}_x/\text{TiO}_2$ catalyst could achieve 97% NO conversion and capture approximately 90% of the incoming Hg. However, for

manganese-based catalysts, the influence of SO_2 poisoning is a major problem. In order to further improve the sulphur tolerance of catalysts at low temperature, several metal elements (CeO_2 , W , Mo) were employed as dopant to modify the manganese-based catalysts. The CeO_2 doped catalyst displayed excellent sulfur tolerance performance at low temperature⁷⁸. In particular, Mn-Ce mixed-oxide exhibited an excellent Hg^0 removal capacity. Li *et al.*⁷⁵ found that the combination of MnO_x and CeO_2 resulted in significant synergy for Hg^0 oxidation. The Mn-Ce/Ti catalyst was highly active for Hg^0 oxidation at low temperatures (150-250°C) under both simulated flue gas and SCR flue gas (see Fig 3). The Mo doping also resulted in high Hg^0 oxidation in gases with 60 ppm HCl, even in the presence of SO_2 ¹¹.

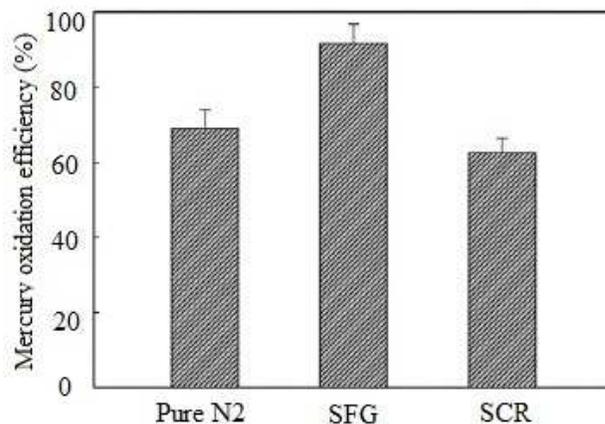


Fig.3 Hg^0 oxidation under different atmospheres at 200°C [75]

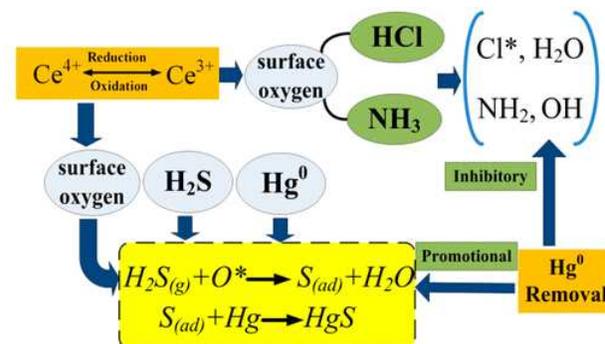


Fig.4 Mechanism of CeO_2 - TiO_2 Catalysts for elemental mercury removal [83]. Reprinted (adapted) with permission from (J. Zhou, W. Hou, P. Qi, X. Gao, Z. Luo and K. Cen, *Environ Sci Technol*, 2013, 47, 10056-10062.). Copyright (2013) American Chemical Society.

As is well known, cerium has received considerable attention due to its prominent ability to store/release oxygen as an oxygen reservoir via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions, respectively^{69, 79}. Besides, Cerium oxide-based catalysts were reported to have good resistance to water vapor⁸⁰. And the doping of CeO_2 greatly enhanced the SO_2 resistance of the catalyst⁸¹. Therefore, Cerium oxide is considered as a very promising candidate for mercury oxidation. Wan *et al.*⁸² studied the removal of Hg^0 over a CeO_2 - WO_3/TiO_2 nano-composite in simulated coal-fired flue gas. About 95% of the Hg^0 could be removed by HCl in the presence of O_2 . The Hg^0 removal efficiency was found to be slightly affected by H_2O addition, while SO_2 promoted the Hg^0 oxidation.

Remarkably, the CeO₂-TiO₂ materials exhibited excellent single and simultaneous capture capacities⁸¹. Most likely cerium can occupy two oxidation states [CeO₂ (Ce⁴⁺) ↔ Ce₂O₃ (Ce³⁺)], allowing ceria from the CeO₂-TiO₂ support to accommodate more surface lattice oxygen species. Consequently, Hg⁰ adsorbed on the ceria surface can react with the lattice oxygen to form HgO. Zhou et al.⁸³ believed that Hg⁰ oxidation over CeO₂-TiO₂ catalysts could be explained by Mars-Maessen mechanism, in which active surface sulfur reacts with gas-phase Hg⁰. The possible mechanism was proposed in Fig 4. However, the research of Li *et al.*⁸⁴ showed different results. It proposed that Hg⁰ oxidation over CeO₂-TiO₂ catalysts was proposed to follow the Langmuir-Hinshelwood mechanism whereby reactive species from adsorbed flue gas components react with adjacently adsorbed Hg⁰.

3.2.2 Commercial SCR catalysts

Recent years, SCR system has been extensively used in coal-fired plant to remove NO_x because of its higher efficiency, selectivity and economic feasibility. Generally, typical commercial SCR catalysts composed of TiO₂, the catalytically active component V₂O₅, WO₃ and/or MoO₃ as promoter. The vanadia phase V₂O₅ not only catalyzes NO_x reduction but also catalyzes Hg⁰ oxidation. Stolle *et al.*⁸⁵ observed that Hg⁰ oxidation activity increased with increasing V₂O₅ concentration on SCR-DeNO_x-catalyst (Fig. 5). The highest Hg⁰ oxidation activity was measured as 86.6 m/h on the H7 catalyst with 2.6 w.t.% V₂O₅, while the lowest oxidation factor was measured as 8.2 m/h on the almost vanadium-free test catalyst H8. This was consistent well with the previously reported literatures⁸⁶ where an increase in Hg⁰ oxidation almost linearly with VO_x loadings up to 10w.t.%. WO₃ inhibits the initial sintering of TiO₂ and improves SO₂ resistance. On the other hand, WO₃ increases the amounts of Lewis acid. For V₂O₅-MoO₃/TiO₂ catalysts, Hg⁰ oxidation was found to follow the Mars-Maessen mechanism. MoO₃ could not directly oxidize Hg⁰, but molybdenum in high valence could assist to oxidize vanadium in low valence to increase the number of lattice oxygen for mercury oxidation².

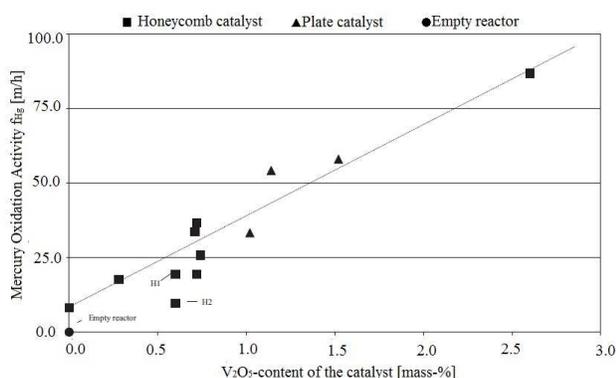


Fig. 5. Mercury oxidation activity fHg of commercial SCR DeNO_x catalysts as function of their V content (influent model flue gases with 40 μg/m₃ elemental mercury, 100 mg/m₃ HCl, 4% by volume (dry) O₂, 7% by volume H₂O and no NO, NH₃ and SO₂, 390°C) [85].

SCR system is effective in controlling NO_x emissions as well as oxidizing Hg⁰ in coal-fired flue gas. Nevertheless, it has some disadvantages, such as narrow active temperature window, toxicity to environment and human health due to the loss of

vanadium during the preparation and operation processes⁸⁷. Moreover, the conventional SCR catalysts were not effective enough for Hg⁰ oxidation with low HCl concentrations. In addition, SO₂ and NH₃ have been observed to inhibit the oxidation of Hg⁰ over the conventional SCR catalysts⁶⁵. Hence, in order to overcome these disadvantages, many efforts have been paid to modify the catalysts. RuO₂ have been studied for modifying conventional SCR catalysts⁸⁸. RuO₂ not only showed rather high catalytic activity on Hg⁰ oxidation by itself, but also appeared to be well cooperative with the commercial SCR catalyst for Hg⁰ conversion. Besides, the modified commercial SCR catalyst with RuO₂ displayed an excellent tolerance to SO₂ and NH₃ without any distinct negative effects on NO_x reduction and SO₂ conversion. At the same time, the Hg⁰ oxidation activity of commercial SCR catalysts impregnated with different metal oxides (Cr₂O₃, ZnO, CuO, NiO, MnO) were also investigated⁸⁹. Results showed that the Hg⁰ oxidation efficiency of metal oxide-impregnated commercial SCR catalysts was higher than that of the non-impregnated reference commercial SCR catalyst. In especial, CuO/SCR catalyst exhibited the best Hg⁰ oxidation activity.

4. Proposed mechanism for the catalytic oxidation of elemental mercury

Hg adsorption and oxidation on catalyst surfaces has been studied in a number of researches^{64, 90-92}. It is well known that Hg⁰ can undergo either heterogeneous or homogeneous reactions on the SCR systems. SCR catalysts are believed to facilitate heterogeneous oxidation, which have faster reaction rate than homogeneous oxidation⁹³. However, the exact mechanisms for Hg oxidation on SCR catalysts and their dependence on flue gas properties were not yet well understood. In order to obtain an understanding of the mechanisms governing Hg⁰ oxidation, the effect of SCR catalysts for Hg⁰ oxidation has been widely studied^{90, 91, 94}. Several mechanisms, including the Deacon process, the Eley-Rideal mechanism, the Langmuir-Hinshelwood mechanism and the Mars-Maessen mechanism, have been used to explain the heterogeneous Hg⁰ oxidation.

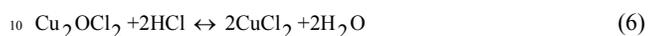
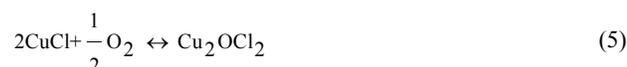
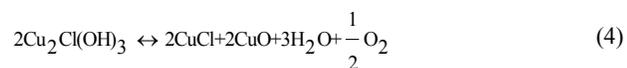
4.1 Deacon reaction

The Deacon process⁹⁵ generates Cl₂ by catalytic oxidation of HCl with air or oxygen, which takes place at about 300-400°C (Eqs 3).



In the presence of an appropriate catalyst, the Deacon process could convert the large concentrations of HCl into Cl₂, and the generated Cl₂ is the key factor of Hg oxidation in the flue gas. Copper, iron, and manganese salts are suitable catalysts for the Deacon process. Hisham and Benson et al.⁹⁶ studied the basic thermochemistry of the Deacon reaction over a large number of groups and transition metal oxides. The process comprises a catalytic cycle which can be examined in terms of two independent steps: (1) HCl absorption by the metal oxide to form the metal chloride (or oxychloride) plus water and (2) oxidation of chloride by O₂ to regenerate the metal oxide and free Cl₂. However, the Deacon reaction was described by a Mars-van Krevelen type mechanism involving five steps: hydrogen

abstraction from HCl, recombination of atomic chlorine, hydroxyl recombination, water desorption and dissociative oxygen adsorption⁹⁷. By invoking the Deacon mechanism, Du⁹⁸ suggested that Cu₂Cl(OH)₃ formed on the surface of adsorbents and decomposed to CuCl in the reaction of Hg removal, and then CuCl react with HCl (or O₂) to form little Cl₂. The mechanism is described as follows:



4.2 Eley-Rideal Mechanism

Senior and Linjewile⁹⁹ proposed that the mercury oxidation could occur via an Eley-Rideal mechanism. HCl competes with NH₃ for surface active sites, and adsorbed HCl reacts with gaseous (or as a weakly adsorbed) Hg⁰ (Eqs 16-17).



On the other hand, Senior¹⁰⁰ suggested that the Eley-Rideal type mechanism in which Hg⁰ adsorption was in competition with NH₃ adsorption and adsorbed Hg⁰ reacts with gaseous HCl. Recently the V₂O₅-based SCR catalysts was found to oxidize Hg⁰ to Hg²⁺, which might follow the Eley-Rideal mechanism^{65, 101}. According to this mechanism, HCl is dissociatively adsorbed on V₂O₅-active sites. Then the chemically adsorbed Cl species reacts with gas-phase Hg⁰ to generate an intermediate HgCl species, which further reacts with chlorine species to form HgCl₂. Interestingly, the reaction between Hg⁰ and H₂S was in a similar manner, whereby active surface sulfur reacts with gas phase Hg⁰ to form stable HgS⁸³. The possible reactions are proposed as follows:



Where S_(ads) and O* are active surface sulphur and surface oxygen

of the sorbent, respectively.

4.3 Langmuir-Hinshelwood Mechanism

The bimolecular reaction between two species adsorbed to a surface can be described by a Langmuir-Hinshelwood mechanism¹⁰². Wang *et al.*¹⁰³ suggested that mercury oxidation on MnCe catalyst surface followed the Langmuir-Hinshelwood mechanism, where reactions took place between the adsorbed active species and adsorbed Hg⁰ to form Hg²⁺. It has also been reported that Hg⁰ oxidation over V₂O₅-based catalyst occurred via Langmuir-Hinshelwood mechanism. On the basis of this mechanism, gas-phase Hg⁰ and HCl adsorbed onto the vanadia sites to form HgCl₂ and V-OH species. Then, the reoxidation of the V-OH species by oxygen follows to form V=O and H₂O⁶⁶. The possible path way responsible for mercury oxidation over V₂O₅-based catalyst is described in Fig. 6. A similar mercury oxidation mechanism over Ce-Ti catalyst was proposed by other authors^{84, 104}. Specifically, in Suarez Negreira's works^{105, 106}, it was showed that Hg⁰ had a negligible interaction with the vanadia oxide dimer, while HgCl⁰ had the strongest adsorption, followed by HCl. The proposed Hg⁰ oxidation mechanism may contain the following two steps: first, Langmuir-Hinshelwood step between HCl and HgCl to produce HgCl₂. second, Eley-Rideal step between gas-phase Hg⁰ and adsorbed HCl to produce HgCl. Based on these results, the mechanism of Hg⁰ oxidation through the formation of HgCl₂ was proposed in Figure 7.

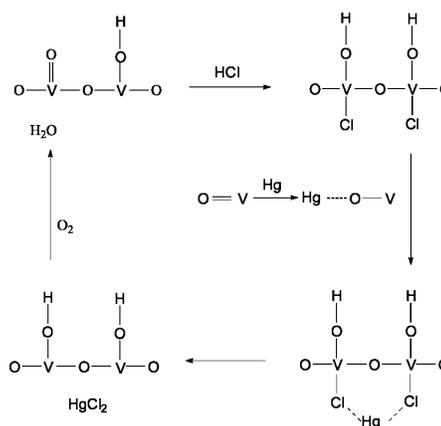


Fig. 6. Mechanism of the mercury oxidation on the vanadia-based SCR catalysts [66]. Reprinted (adapted) with permission from (S. He, J. S. Zhou, Y. Q. Zhu, Z. Y. Luo, M. J. Ni and K. F. Cen, *Energ Fuel*, 2009, 23, 253-259.). Copyright (2009) American Chemical Society.

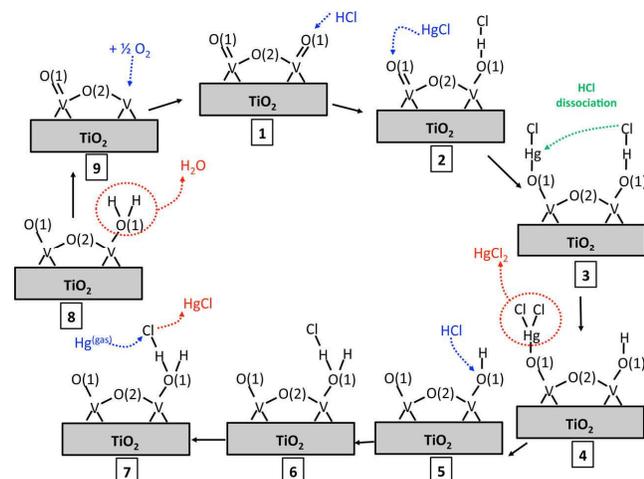
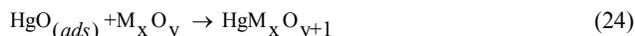
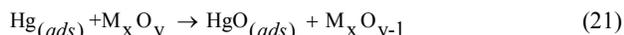


Fig. 7. Proposed mechanism of mercury oxidation on vanadia-titania SCR catalyst. Blue arrows indicate an adsorption step, green arrows indicate a dissociation step, and red arrows indicate a desorption step [105].

Reprinted (adapted) with permission from (A. Suarez Negreira and J. Wilcox, *J Phy Chem C*, 2013, 117, 1761-1772.). Copyright (2013) American Chemical Society.

4.4 Mars-Maessen Mechanism

Initially, Zhang *et al.*¹⁰⁷ proposed that Hg⁰ oxidation on Co_xMn_yTi catalyst can be interpreted by the Mars-Maessen mechanism, where Hg⁰ bonds with lattice oxygen and/or chemisorbed oxygen of the catalyst surface to form weakly bonded speciation Hg–O–M–O_{x-1} (M = Mn or/and Co) and then formed mercuric oxide (HgO). The consumed lattice oxygen and/or surface oxygen can be replenished by the gas-phase O₂. Mars-Maessen mechanism has been widely used for illustrating the Hg⁰ oxidation process on metal oxides catalysts^{68, 108-111}. In this mechanism, adsorbed Hg⁰ would react with a lattice oxidant (either O or Cl) that is replenished from the gas phase, forming a binary mercury oxide⁵⁹. Reaction Eqs 20-24 showed the Mars-Maessen mechanism for the reaction of adsorbed Hg⁰ with lattice oxidant.



5 Kinetics

It is known that Hg conversions in flue gas are kinetically, but not thermodynamically, controlled¹¹². A kinetics model is a useful tool to simulate the mercury oxidation and evaluate the mercury oxidation efficiency for various operational conditions. It can hopefully facilitate the predictions of the effectiveness of different mercury control measures and strategies. Lots of works had been done for researching the mechanisms and kinetics of Hg⁰ oxidation.

Table.3 Rate Constants in Hg⁰ Oxidation Mechanism [113].

No	Reactions	A cm ³ /mol-sec	β	E_a kcal/mol
1	Hg+Cl+M=HgCl+M	2.40×10^8	1.4	-14.4
2	Hg+Cl ₂ =HgCl+Cl	1.39×10^{14}	0.0	34.0
3	HgCl+Cl ₂ =HgCl ₂ +Cl	1.39×10^{14}	0.0	1.0
4	HgCl+Cl+M=HgCl ₂ +M	2.19×10^{18}	0.0	3.10
5	Hg+HOCl=HgCl+OH	4.27×10^{13}	0.0	19.0
6	Hg+HCl=HgCl+H	4.94×10^{14}	0.0	79.3
7	HgCl+HCl=HgCl ₂ +H	4.94×10^{14}	0.0	21.5
8	HgCl+HOCl=HgCl ₂ +OH	4.27×10^{13}	0.0	1.0

As tabulated in Table. 3, formulation of a reaction mechanism began with the kinetic framework of Widmer¹¹³. The reaction controlling of the Hg conversion is between Hg⁰ and the chlorine atom¹¹⁴. Though such mechanisms can give plausible qualitative results, they are generally not suitable for examining the effects of other flue gas constituents on Hg chlorination⁴⁵. It should be recognized that Hg oxidation would be subject to kinetic control under actual combustion conditions. As a result, it is necessary to develop mercury chemical kinetics for application in real combustion systems¹¹⁴. Presto *et al.*¹¹⁵ researched a kinetic approach to the catalytic oxidation of Hg⁰ in flue gas. They proposed a method for analysing Hg⁰ oxidation catalyst results in a kinetic framework using the bulk reaction rate for oxidized mercury formation normalized by either the catalyst mass or surface area. The bulk Hg⁰ oxidation reaction rate (R_{cat}) can be described as an apparent gas-phase reaction as shown in Eqs (25):

$$R_{cat} = R_{gas} \left(\frac{V_{cat}}{m_{cat}} \right) = k_{cat} [\text{Hg}^0]^\alpha [\text{Oxidant}]^\beta \quad (25)$$

Where, R_{gas} is the bulk reaction rate for Hg²⁺ formation across the catalyst bed, V_{cat} is the catalyst volume, and m_{cat} is the catalyst mass; k_{cat} is the catalyst-normalized rate constant. Results reported for fractional mercury oxidation are strongly influenced by the specific experimental conditions and therefore difficult to translate from experiment to experiment.

Li *et al.*¹¹⁶ developed and evaluated a kinetic modelling of Hg⁰ oxidation by chlorine over CeO₂-TiO₂ catalysts. Based on the conditions of experiment and assuming Hg⁰ oxidation over CeTi catalysts follows the Langmuir–Hinshelwood mechanism, the bulk Hg⁰ oxidation reaction rate under flue gas containing HCl can be described as:

$$R_{cat} = -k [\text{Hg}^0]^s \theta_{\text{HCl}} = -k [\text{Hg}^0]^s \frac{k_{\text{HCl}} [\text{HCl}]}{1 + k_{\text{HCl}} [\text{HCl}]} \quad (26)$$

Where K is the overall reaction rate constant, $[\text{Hg}^0]^s$ is the concentration of surface-phase Hg⁰, θ_{HCl} is the fraction of the active sites occupied by HCl, k_{HCl} is the Langmuir adsorption constant of HCl, and $[\text{HCl}]$ is the gas-phase HCl concentration, respectively. Experimental data were analyzed using a kinetic model incorporating mass transfer, adsorption equilibrium and mass balance with key variables of interest being residence time, catalyst type as well as HCl concentration in simulated coal

combustion flue gas. The experimental data verification for the proposed kinetic model was satisfactory, indicating the validity of the model for describing the mechanism of Hg^0 oxidation by chlorine over CeTi catalysts.

The reaction mechanisms and catalytic oxidation kinetics in the oxidizing flue gas was also evaluated by Gao *et al.*¹¹⁷. In their study, the kinetic model following the Eley-Rideal mechanism was implemented. The reaction rate of Hg^0 oxidation (r) defined in Eqs 27 can be expressed as the change of reactant concentration:

$$\gamma = k_2 C_{\text{Hg}^0}^x C_{\text{O}_2}^y \gamma_1 = k_2 C_{\text{Hg}^0}^x C_{\text{O}_2}^y \left(-\frac{d\eta_{\text{HCl}}}{d_w} \right) = K^* C_{\text{Hg}^0}^x C_{\text{O}_2}^y \quad (27)$$

Where k^* is the overall rate constant for oxidation, k_2 is the reaction rate constant for Hg^0 , x and y are the reaction order with respect to Hg^0 and O_2 , respectively. The results showed that the rate of Hg^0 oxidation over commercial SCR catalyst was zeroth order with respect to O_2 and nearly first order with respect to Hg^0 . In agreement with the experimental results, the kinetic model well described the rate of Hg^0 oxidation in the presence of HCl and O_2 at different conditions. According to the kinetic model, the apparent activation energy for Hg^0 oxidation over the commercial SCR catalyst was 37.73 kJ/mol.

6 Effect of flue gas constituents (HCl, H_2O , SO_2 , O_2 , NO , NH_3) on Hg^0 oxidation

Hg^0 oxidation efficiency highly depended on the composition of flue gas. Although SCR catalyst is active for Hg^0 oxidation, its effectiveness was found to depend on the halide species and their concentration¹¹⁸. Many studies suggested that HCl plays the most important role in oxidization of Hg^0 ^{74, 119-121}. It could remarkably increase Hg^0 oxidation. He *et al.*⁶⁶ analyzed the effect of HCl on the Hg^0 oxidation across the SCR unit, as shown in Fig. 8. The results indicated that the monomeric vanadyl sites on the catalyst surface were found to be responsible for the adsorption of both Hg^0 and HCl, which meant they were active for mercury oxidation. The detailed Langmuir-Hinshelwood mechanism was proposed to explain the Hg oxidation on vanadia-based SCR catalyst, where reactive Cl generated from adsorbed HCl reacts with adjacent Hg^0 . At the same time, it has been recognized that the oxidation of Hg^0 over catalysts in the presence of HCl might experience a series of reactions, such as Deacon reaction, Mars-Maessen or Eley-Rideal mechanism^{11, 65, 122, 123}. Meanwhile, the reaction of HCl and the active component V_2O_5 of the SCR catalysts was also investigated. For example, Liu *et al.*¹²⁴ studied the HCl adsorption on different sites of V_2O_5 (0 0 1) surface, and the comparison between HCl and Hg adsorptions was made. The results showed that Hg^0 adsorption on V_2O_5 surface is stronger than that of HCl. The Hg^0 in the flue gas is adsorbed by the V_2O_5 surface as an intermediate which reacts fairly rapidly with chlorine species to form surface HgCl , and then reacts with chlorine species to form surface HgCl_2 . Finally, HgCl_2 desorbs from the V_2O_5 surface.

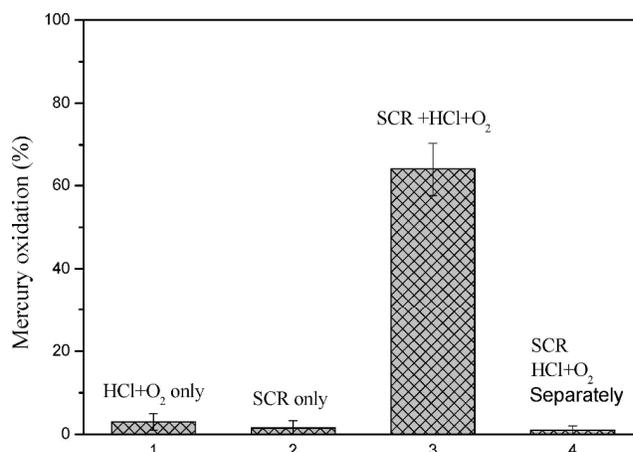


Fig. 8. The effect of HCl on the heterogeneous oxidation of Hg across the SCR unit [66]. Reprinted (adapted) with permission from [S. He, J. S. Zhou, Y. Q. Zhu, Z. Y. Luo, M. J. Ni and K. F. Cen, *Energ Fuel*, 2009, 23, 253-259.]. Copyright (2009) American Chemical Society.

It should be note that HBr also show a very strong impact in increasing Hg^0 oxidation¹²⁵. Results by Cao *et al.*¹²⁶ suggest that the promotional effect of HBr is far more pronounced than that of HCl. On cooling of the gases, the diatomic and molecular form of the halogens become stable according to the Deacon type of reactions^{41, 127}:



However, the depletion of Cl_2 would occur by the enriched SO_2 in the coal-derived flue gases¹²⁷. Br_2 oxidize the typical amounts of mercury in the coal flue gases through direct mercury bromination. This explains why HBr is a more effective mercury oxidizer than HCl.



H_2O has been reported to inhibit Hg^0 oxidation over metal oxide catalysts due to competitive adsorption^{101, 128}. The competitive adsorption of water vapor on active site may have prohibited the adsorption of reactive species that have promotional effect on Hg^0 oxidation such as O_2 , HCl and NO_x ¹²⁹⁻¹³¹. For instance, the conversion of Hg^0 to Hg^{2+} may decrease due to competition between the O and OH when both water vapor and oxygen co-exist in the simulated flue gas. Furthermore, a high concentration of water vapor in the flue gas would diminish the adsorption of HCl, which is a crucial flue gas component responsible for Hg^0 oxidation.

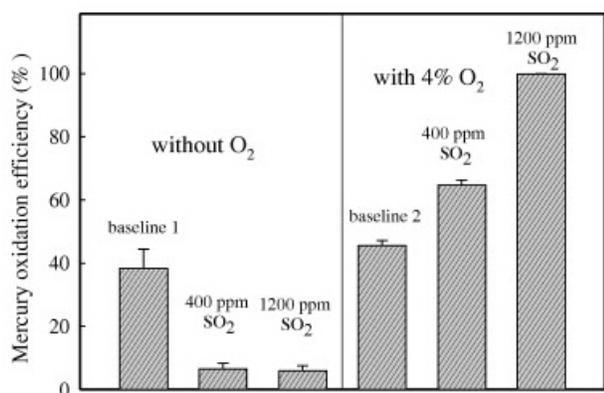


Fig. 9. Effect of SO₂ on Hg⁰ oxidation in the presence of NO [136].

The effect of SO₂ on Hg⁰ oxidation in flue gas were not conclusive, either promotional or inhibitory^{49, 132}. Wan *et al.*⁸² would like to define SO₂ as a promoter because the addition of 800ppm SO₂ slightly enhanced the Hg conversion under dry conditions. It might be supposed that the sulfate species could be more easily formed since SO₂ was introduced into the reaction. The formed sulfate species adsorbed on catalyst surface could also enhance the catalytic activation because of the newly formed sulfate adsorption acid sites¹³³. On the contrary, the inhibitory effect of SO₂ on Hg⁰ oxidation had been shown in many literatures^{61, 103, 121, 134, 135}. On one hand, SO₂ had a large inhibitory effect on Hg⁰ oxidation mainly via the elementary reactions and to eliminate OH radicals¹³⁵. On the other hand, SO₂ negatively affect Hg⁰ oxidation due to the competitive adsorption between SO₂ and Hg⁰ on active sites^{61, 121}. In particular, Li *et al.*^{84, 136} showed that SO₂ had different effects on Hg⁰ oxidation under different flue gas conditions. SO₂ inhibited Hg⁰ oxidation without O₂, while SO₂ had a promotional effect on Hg⁰ oxidation in the presence of O₂. As shown in Fig. 9, without O₂, addition of SO₂ into gas flow containing 300 ppm NO decreased Hg⁰ oxidation efficiency from 38.3% to about 6.5%. With the aid of 4% O₂, the addition of 400 ppm SO₂ into gas flow containing 300 ppm NO increased Hg⁰ oxidation efficiency from 45.6% to 64.7%. Conversion of SO₂ to SO₃ not only relieved the prohibitive effect related to the competitive adsorption between SO₂ and Hg⁰ but also yielded active SO₃ for Hg⁰ oxidation, and hence have an obvious the promotional effect.

O₂ plays a crucial role in Hg⁰ oxidation¹³⁷. To obtain higher Hg⁰ oxidation efficiency, the presence of O₂ is normally necessary, especially for metal oxide catalysts^{68, 69}. Some researchers believed that Hg⁰ oxidation with the presence of O₂ can be explained by the Mars-Maessen mechanism¹⁰⁷. Hg⁰ reacts with the lattice oxygen on the catalyst surface to form weakly bonded species and then formed HgO. The consumed lattice oxygen can be replenished by the gaseous O₂. Yet researchers believed that adsorbed O₂ could oxidize Hg⁰ to HgO directly¹³⁸. However, Xu *et al.*⁴⁵ found that O₂ showed little effect on Hg⁰ oxidation alone. It should be noted that O₂ has a synergistic effect on mercury oxidation via SO₂, NO or HCl^{84, 130, 139}.

NO can achieve significant promotional effect on Hg⁰ oxidation. It has been reported that adsorbed NO can be oxidized by the surface oxygen of catalysts to give rise to species like

NO⁺, NO₂, nitrite, and nitrate, which are likely responsible for Hg⁰ oxidation^{101, 134}. In contrast, the effect of NO on Hg⁰ oxidation over the Mn-Ce/Ti catalyst was found to be inhibitory¹⁴⁰. In the absence of O₂, NO is weakly adsorbed on the MnOx-CeO₂ mixed oxides¹⁴¹, and a fraction of it reacts with the surface oxygen to form limited NO₂, nitrite, and nitrate species⁷⁷. It was hypothesized that NO covered the active sites and consumed surface oxygen. Therefore, NO could cause a significant deteriorate effect on Hg⁰ oxidation without the aid of O₂. Nevertheless, more adsorbed NO can be oxidized on the Mn-Ce/Ti catalyst to form abundant active species like NO₂ with the present of O₂, which are more active than NO for Hg⁰ oxidation.

The effect of NH₃ on Hg⁰ oxidation has been analyzed several times with different results. A large number of studies suggested that NH₃ could cause a significant deteriorate effect on Hg⁰ oxidation by competing for active sites with Hg⁰^{142, 143}. However, it was pointed out that the oxidation rate of Hg⁰ at the outlet of the SCR unit is not influenced by the injection of stoichiometric amounts of NO and NH₃¹⁴⁴. Recently some studies have reported Hg²⁺ is reduced by NH₃^{79, 145}. Thorwarth *et al.*⁷⁹ found that not only does Hg⁰ oxidation not occur when NH₃ is present, but also NH₃ can reduce Hg²⁺ to Hg⁰. At temperatures higher than 325°C, NH₃ may also reduce Hg²⁺ in accordance with the following reaction¹⁴⁵:



In addition to this effect, the DeNO_x reaction may also cause a reduction of Hg²⁺⁸⁵. It is assumed that the reduction of the Hg²⁺ is caused by the intermediate reduced vanadium species produced by the DeNO_x reaction in the catalysts. The sum reaction involving DeNO_x and mercury could be formulated as:



7 Effect of space velocity and temperature

Some studies suggest that increasing space velocity reduces Hg⁰ oxidation activity across the SCR unit. For instance, Machalek *et al.*¹⁴⁶ observed that the extent of Hg⁰ oxidation was reduced from 40% to 5% as the gas space velocity increased from 3000 to 7800 h⁻¹ in flue gases derived from subbituminous coal. Another study of Lee *et al.*¹⁴⁷ reported that Hg⁰ oxidation decreased from 88 to 53% as space velocity increased from 2000 to 4000 h⁻¹ at 350°C.

Reaction temperature has a strong influence on Hg⁰ oxidation. The efficiency of Hg⁰ oxidation increased with the increasing of temperature in SCR condition¹⁴⁸. However, some studies suggest that Hg⁰ oxidation decreased with the increasing of temperature. Rallo *et al.*¹⁴² observed a decrease in Hg⁰ oxidation from 70% at 280°C to 50% at 350°C.

8 Conclusions and outlook

This work focused on catalytic oxidation of elemental mercury by SCR catalysts in coal-fired flue gas. Mercury is a global pollutant which is emitted into the atmosphere from natural and various anthropogenic sources. Coal-fired power plants are considered to be a major source of mercury emission from anthropogenic activities. Mercury transformations and

speciation in combustion flue have been studied intensively. Hg in coal was found to be volatile. Most of them entering the furnace were rapidly volatilized and present in the gas phase. In the post combustion section, Hg reacts with flue gas constituents to convert to gaseous oxidized forms and particulate-bound mercury. Eventually, the principal forms of Hg in coal combustion flue gas are assumed to be Hg⁰, Hg²⁺, and Hg^p.

In addition to NO_x control, SCR catalysts affect the Hg speciation by altering Hg⁰ to Hg²⁺. Increasing the emission of Hg²⁺ across SCR catalyst allows for high reduction of Hg emission because Hg²⁺ can be removed in downstream equipment such as WFGD systems. A review on the recent advances in catalytic oxidation of Hg⁰ by SCR catalysts in flue gas was provided. SCR catalysts including noble metals and non-noble metals catalysts have been summarized. Among different noble metals, Pd and Au are the most attractive option for controlling Hg⁰ emissions. Several non-noble metals including MnO₂, CeO₂, V₂O₅, etc have also showed impressive Hg⁰ oxidation activity. One unresolved problem is how to improve their SO₂ resistance and Hg⁰ oxidation efficiency simultaneously. Meanwhile, the influence of flue gas constituents, space velocity and temperature is very significant.

Different mercury reaction mechanisms including Deacon mechanism, Eley-Rideal mechanism, Langmuir-Hinshelwood mechanism, and Mars-Maessen mechanism were also proposed to describe Hg⁰ oxidation in flue gas. At the same time, various kinetics models have been developed to simulate mercury oxidation. Although the assumptions were very different, the experimental data verification for the proposed kinetic model was satisfactory.

The catalytic mercury oxidation in flue gases is actively researched area. But there are still many challenges, such as the conventional SCR catalysts were not effective enough for Hg⁰ oxidation in the absence of HCl. What is more, mercury oxidation under SCR atmosphere was not effective enough because of the inhibitory effect of ammonia. It should be note that the conversion of SO₂ to SO₃ over SCR catalysts should not improve when promoting Hg⁰ oxidation activity. Furthermore, the exact mechanisms for Hg⁰ oxidation by SCR catalysts and their dependence on flue gas properties were not yet well understood. Therefore, further investigation is necessary for developing new and efficient SCR catalysts with a low SO₂/SO₃ conversion rate. The role of flue gas components and the mechanism of Hg⁰ oxidation need to better understand as well.

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Notes

^a College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

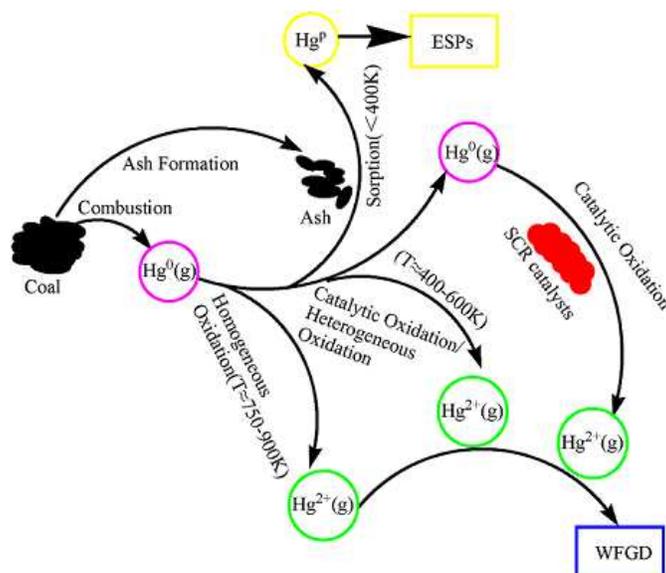
^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
Email: ctli@hnu.edu.cn, ctli3@yahoo.com
Fax: +86-731-88649216; Tel: +86-731-88649216

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Transformation and speciation of Hg in coal-fired flue gas, mechanism and kinetics for oxidizing Hg⁰ with SCR catalysts were discussed.