Oxidation of Elemental Mercury over SCR Catalysts

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Experiments were conducted in the simulated flue gas system containing the selective catalytic reduction (SCR) catalyst to investigate the Hg^0 oxidation in different flue gas components, such as H$_2$O, SO$_2$ and HCl. The results show that Hg^0 oxidation over SCR catalysts increased from 8% to 24% with increase of V$_2$O$_5$ content in the SCR catalyst from 0.5% to 2.7wt% in the absence of HCl. Higher vanadium content leads to a higher oxidation activity. The inhibitory effect of H$_2$O on Hg^0 was measured and there is a 6% decrease under the condition of 7.5% H$_2$O due to its competitive adsorption with Hg^0 on the active sites. 12% of promotional effect of SO$_2$ on Hg^0 oxidation is shown by adding 50 ppm SO$_2$ that can enhance the Hg^0 adsorption slightly. Furthermore, the Hg^0 oxidation significantly achieves up to 80% with 4.5 ppm HCl via the chemisorption reaction. In short, the SCR catalyst with 2.7wt% V$_2$O$_5$ and 4.5 ppm HCl demonstrates the best Hg^0 oxidation efficiency.

Keywords: Oxidation, Elemental mercury, SCR catalyst

1. INTRODUCTION

Mercury (Hg) is a toxic heavy metal that bioaccumulates in the human body through the food chain and impacts neurological health[1]. Hg is emitted to the air by natural sources, such as volcanoes, forest fires, and anthropogenic activities including coal combustion and oil burning. Presently, Hg in flue gas discharge from coal-fired power plants has been recognized as a major anthropogenic source in most countries[1]. According to the US Environmental Protection Agency, power plants accounts for about 50% of the total anthropogenic emissions and the government agencies promulgated the Clean Air Mercury Rule in 2005[2]. 5.0 μg/m^3 of Hg emission standard for the existing coal fired power plants in Taiwan was announced by Taiwan Environmental Protection Administration in 2015[3].

Typically, Hg is released from combustion processes into the atmosphere in three forms: particulate-bound Hg (Hg$_p$), oxidized Hg (Hg^{2+}), and elemental Hg (Hg^0)[4,5]. For the Hg$_p$, it can be captured by particulate matter control devices, such as the electrostatic precipitator or bag filter[5]. Hg^{2+} is soluble in water which can be effectively removed by a wet scrubber or wet flue gas desulfurization system (WFGD)[6]. However, Hg^0 is difficult to collect by conventional air pollution control devices (APCDs) due to the high volatility and low solubility in water[1,5,6]. To date, the activated carbon injection is the best method for capturing Hg^0 from the flue gas, but the utilization rate of activated carbon is low. At the same time, the used activated carbons need to be treated carefully to avoid secondary pollution[1,5]. For that reason, the conversion of Hg^0 to oxidized form is a good approach to improve mercury collection efficiency in the present APCDs[1,5,7].

Normally, many coal-fired power plants are equipped with selective catalytic reduction (SCR) for controlling NOx emissions. Recent studies have demonstrated that the SCR catalysts that consisted of titanium dioxide (TiO$_2$), vanadium pentoxide (V$_2$O$_5$), tungsten trioxide (WO$_3$), molybdenum trioxide (MoO$_3$) are efficient to convert Hg^0 into the oxidized form that can be subsequently removed in downstream WFGD systems[1,5,8]. The catalyst provides a very active oxidizing surface that can activate the mercury in order to achieve mercury oxidation[8]. Hg^0 can come through either heterogeneous or homogeneous reactions on the SCR system. However, heterogeneous oxidation, for instance the Deacon process, has a faster reaction rate than homogeneous oxidation[9,10]. Generally, the interaction of Hg^0 and V$_2$O$_5$ surface includes physisorption and chemisorption depending on different sites. Hg^0 adsorption on top sites tends to be physisporption, while that on bridge sites tends to be chemisorption[11].

Besides, the Hg^0 oxidation efficiency depends on the composition of flue gas. H$_2$O has been reported to obstruct Hg oxidation over the catalysts due to competitive adsorption[9,12]. The competitive adsorption of H$_2$O on active sites may prohibited the adsorption of reactive species[9]. The impact of SO$_2$ on Hg^0 oxidation was not conclusive, and it may be a promotional or inhibitory effect. Many studies reported that HCl plays the most important role in oxidization of Hg^0[9,13]. There were two possible mechanisms for the interaction of Hg and HCl.

Firstly, Hg^0 and HCl may bind to an adjacent active site to react with each other. Secondly, Hg^0 and HCl compete to bind on an active site and the bound HCl reacts with gaseous Hg^0 [14].

In this study, a bench-scale system with SCR catalyst was established. The object of this research was to investigate the Hg^0 oxidation over various compositions of SCR catalysts in the simulated flue gas conditions, and the effects of different flue gas components, such as SO_2, H_2O, HCl on Hg^0 oxidation were also evaluated.

2. EXPERIMENTAL METHOD

2.1 SCR catalyst

The SCR catalysts were prepared by this method[15]. The solution contains a metallic oxide including a metallic nitric-acid-precursor, a metallic acetic-acid-precursor, and a titanium dioxide as a support to form a catalyst solution. Then, a titrating process and a calcining process are performed in sequence to form the catalysts. The catalysts were ground to mesh size 18 (1.00 mm) and dried for 4 h at 150°C before the test. Both the microstructure and the pattern of the SCR catalysts were detected by a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS).

2.2 A bench-scale system

The simulated flue gas system consisting of the individual flue gas, a gas mixer, a catalytic reactor, a Hg analyzer, and exhaust gas treated devices is shown in Fig.1. All individual flue gas components were from cylinder gases and the Hg^0 vapor was generated by the Dynacal Hg^0 permeation device (VICI Metronics Dynacalibrators). The desired flue gas flowed through an impinger (Na_2CO_3) and a moisture trap to remove acidic gases such as HCl or SO_2, and H_2O, respectively, before entering the Hg instrument. The Hg^0 concentration at both the inlet and outlet of the reactor was measured by a Hg^0 analyzer (Nippon Instruments Corporation-AM4, a cold vapor atomic adsorption spectrometer). Unreacted Hg^0 gas passed through the filter and the activated carbon device before exiting to the hood.
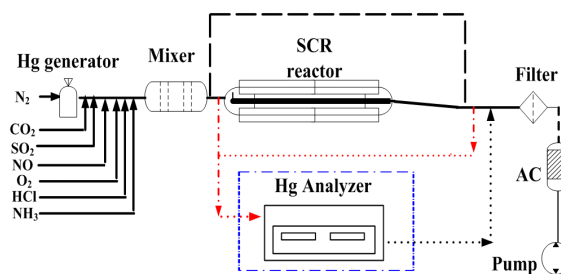

Fig.1. Schematic diagram of a bench-scale system.

2.3 The simulated flue gas for mercury oxidation

The simulated flue gas components and the test conditions are listed in Table 1. In set A, N_2, 8.0%O_2 and Hg^0 (1.85 μg/m³) was used to establish the baseline. The effect of H_2O (2-7.5%) on Hg^0 oxidation was tested in set B, while the impact of SO_2 (30-80 ppm) on Hg^0 oxidation was tested in Set C. Lastly, the influence of HCl (1.5-4.5 ppm) on Hg^0 oxidation was tested in Set D. The Hg^0 oxidation was defined as E_{Hg0}, and calculated according to the Eq. (1).

$$E_{Hg0} = \frac{\Delta[Hg^0]}{[Hg^0]_{in}} = \frac{[Hg^0]_{in} - [Hg^0]_{out}}{[Hg^0]_{in}} \quad \text{..................(1)}$$

Where $[Hg^0]_{in}$ and $[Hg^0]_{out}$ representd Hg concentration at the inlet and outlet of the reactor, respectively, which was measured by the Hg analyzer (NIC AM4).

3. RESULTS AND DISCUSSION

3.1 Characterization of SCR catalysts

Table 2 summarizes characteristic data of different composition of SCR catalysts used in this study. Those catalysts included 0.51wt% V_2O_5-9.02wt% WO_3/TiO_2, 0.98wt% V_2O_5-9.01wt% WO_3/TiO_2, and 2.72wt% V_2O_5-6.89wt% WO_3/TiO_2 are representing catalyst A, catalyst B, and catalyst C, respectively. As shown in Table 2, the BET surface areas of catalyst A, catalyst B, and catalyst C are 61.50, 59.58, and 51.47 m²/g, individually, which indicates that the BET surface area of the catalyst decreased with the increasing of the vanadium

Table 1 Experimental conditions of SCR catalyst test.

Test	Catalyst (g)	Gas components	T (°C)	GHSV (hr⁻¹)
A	0.5	N_2+O_2(8.0%)+Hg^0 (1.85 μg/m³)	300	76,000
B	0.5	N_2+O_2(8.0%)+Hg^0 (1.84 μg/m³)+H_2O(2, 4, 7.5%)	300	76,000
C	0.5	N_2+O_2(8.0%)+Hg^0(1.87 μg/m³)+SO_2(30, 50, 80 ppm)	300	76,000
D	0.5	N_2+O_2(8.0%))+Hg^0(1.85 μg/m³)+HCl(1.5, 2.5, 4.5ppm)	300	76,000

Table 2   Characteristic data of SCR catalysts.

	A	B	C
V_2O_5 content (wt%)	0.51	0.98	2.72
WO_3 contents (wt%)	9.02	9.01	6.89
Pore size (nm)	10.78	11.10	15.12
BET surface (m²/g)	61.50	59.58	51.47

content. Nevertheless, catalyst C has the biggest pore size compared with the others. Figure 2 shows the SCR catalyst aggregation and the profile of Ti, V, W detected by SEM/EDS and illustrated in figure 3.
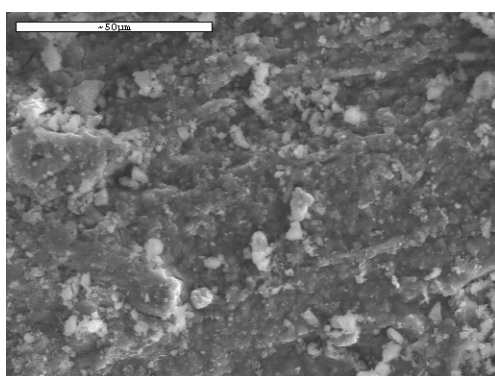

Fig. 2.   SEM images of the SCR catalyst C.
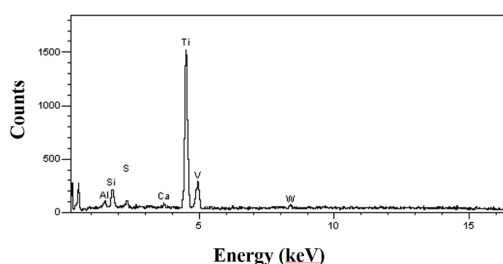
Fig. 3.   SEM/EDS pattern of the SCR catalyst C.

### 3.2 Stability of Hg^0 concentration

The Hg^0 concentration was generated from a permeation tube and its stability facilitated in a 5 hour test. As shown in Fig.4, the Hg^0 concentration was generated to maintain 1.85 ± 0.02 μg/m³ after 110 mins operation. Hence, further studies should be to stabilize the Hg^0 concentration for at least 120 minutes before entering the reactor.

3.3 Effect of the V_2O_5 content on Hg^0 oxidation over SCR catalyst

In order to clarify the effect of the SCR catalyst
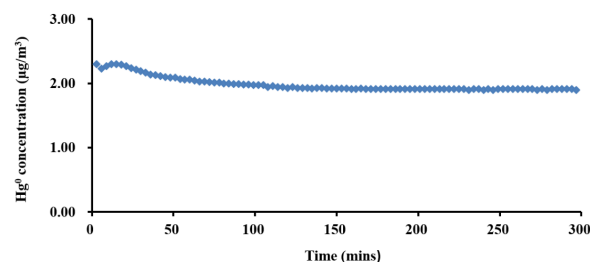
Fig.4.   Stability of feed Hg^0 concentration.

composition on Hg^0 oxidation, the V_2O_5 content varied from 0.5 to 2.7wt%. In the absence of HCl, the result of Hg^0 oxidation over SCR catalysts at 300°C in test condition A is shown in Fig.5. The Hg^0 oxidation was 8%, 12%, and 24% for catalyst A, catalyst B and catalyst C, respectively. Hg^0 oxidation increased with increasing V_2O_5 content in the SCR catalyst. The Hg^0 oxidation shows a good correlation with V_2O_5 content, and the linear regression correlation coefficient (R^2) is calculated as 0.9979 which agrees with the previous studies that an increase in Hg^0 oxidation is almost linear with VOx loading up to 10wt%[16,17]. Furthermore, both monomeric and polymeric vanadyl sites were found to be active for Hg^0 oxidation[17]. On the other hand, Hg^0 adsorption increased with increasing V_2O_5 content from 2.5-4.5wt% which involved chemisorption and the formation of Hg-O bonding on the SCR catalyst surface[18].
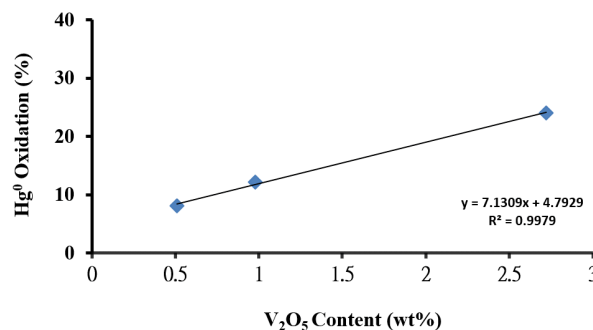
Fig.5. Hg^0 oxidation at different V_2O_5 content.

The Hg^0 oxidation potential was expressed by the Hg oxidation activity O_{Hg} according to Eq. (2), in a

similar manner for the De-NOx activity of the catalyst:

$$O_{Hg} = -AV \ln (1- \eta) \quad (2)$$

O_{Hg} is the Hg oxidation activity (m/h); AV is the area velocity (m/h); η is the efficiency of Hg oxidation (%).

By calculating the mercury oxidation activity, the mercury oxidation activity of 13 m/h was measured for catalyst C that was higher than an oxidation factor of 6, 4 m/h for catalyst B and A. Higher vanadium content leads to a higher oxidation activity.

3.4 Effect of H₂O on Hg⁰ oxidation over SCR catalyst

An effect of H_2O on Hg^0 oxidation over SCR catalyst was displayed in Fig.6. When H_2O content increases from 0% to 7.5%, the Hg^0 oxidation decreases from 24% to 16%, which indicated the competitive adsorption of H_2O with the mercury[9,12]. The Hg^0 oxidation shows that a negative correlation with H_2O content and the linear regression correlation coefficient (R^2) is calculated as 0.9895. 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 flue gas[9]. In addition, physically adsorbed Hg^0 can be desorbed from the surface of SiO_2-TiO_2 composition by water vapor, which suggested that Hg^0 is just barely adsorbed on the sorbent surface[19].
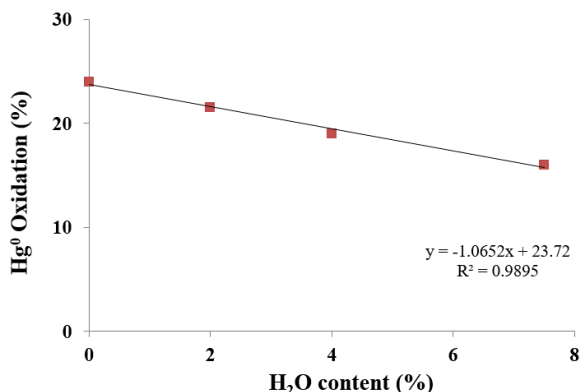

Fig.6. Hg^0 oxidation at different H_2O content.

3.5 Effect of SO₂ on Hg⁰ oxidation over SCR catalyst

As shown in Fig.7, SO_2 was found to increase Hg^0 oxidation from 24% to 29%, 36% by adding 33 and 50 ppm SO_2 respectively. However, Hg^0 oxidation decreases from 36% to 28% when SO_2 concentration increased from 50 to 83 ppm. The promotional effect of SO_2 on Hg^0 oxidation over the catalyst under 50 ppm agrees with a previous report that Hg^0 adsorption slightly increased when SO_2 was present[12,18]. The sulfate

species that was formed from SO_2 were adsorbed on a catalyst surface to enhance the catalyst activation because of the newly formed sulfate adsorption acid sites[20]. On the contrary, the negative impact of SO_2 on Hg oxidation due to the competitive adsorption between SO_2 and Hg^0 on the active site[21].
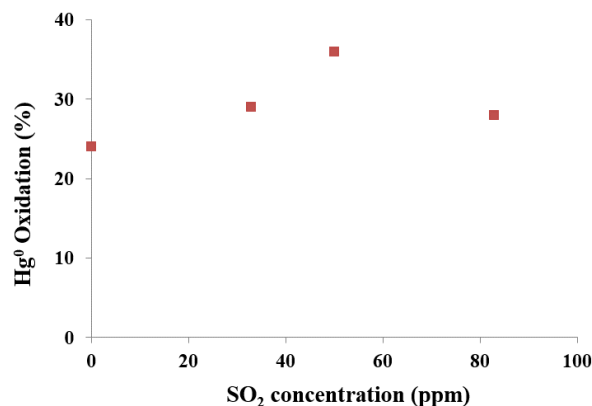

Fig.7. Hg^0 oxidation at different SO_2 concentration.

The mechanism was proposed as shown in Eq. (3) and (4)[22].

$$SO_2 + 1/2\, O_2 \rightarrow SO_3 \quad (3)$$

$$Hg + SO_3 + 1/2\, O_2 \rightarrow HgSO_4 \quad (4)$$

3.6 Effect of HCl on Hg⁰ oxidation over SCR catalyst

The Hg^0 oxidation over SCR catalyst A, B, C by adding a different concentration of HCl is shown in Fig. 8. The order of Hg^0 oxidation was Catalyst C > catalyst B > catalyst A. For SCR catalyst C, the Hg^0 oxidation over catalyst was 24%, 38%, 62%, 80% by adding 0, 1.5, 2.5, and 4.5 ppm HCl in flue gas, respectively. Hg^0 oxidation increases with accumulating the HCl concentration significantly. The above results are similar to the previous report that the SCR catalyst with 1.1-1.2% of vanadate showed about 90% of the Hg^0 oxidation at 10 ppm HCl, while the other with about 0.5% of vanadate was under 40%[23]. The Hg^0 is adsorbed by the V_2O_5 surface and then has a chemisorption reaction to form HgCl and $HgCl_2$. Finally, $HgCl_2$ desorbs from the V_2O_5 surface[9]. The Eley-Ridel mechanism was proposed to explain the interaction between Hg^0 and the adsorbed species as in Eq. (5) and (6)[13,24].

$$Hg^0 + HCl + 1/4\, O_2 \rightarrow HgCl + 1/2 H_2O \quad (5)$$

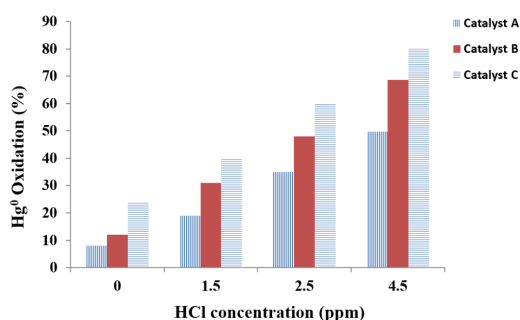$$HgCl + HCl + 1/4\, O_2 \rightarrow HgCl_2 + 1/2 H_2O \quad (6)$$

Fig.8. Hg^0 oxidation at different HCl concentration.

4. CONCLUSIONS

The BET surface areas of SCR catalysts decrease with increasing the vanadium contents. In the absence of HCl, the Hg^0 oxidation over SCR catalyst performed better at a high loading vanadium catalyst due to its strong adsorption on a SCR catalyst surface. An inhibitory effect of H$_2$O on Hg^0 oxidation over a SCR catalyst was observed due to its competitive adsorption with Hg^0 on the active site. Hg^0 oxidation was slightly promoted by low SO$_2$ concentration because of the sulfate species were formed to enhance the catalyst activation. By adding 4.5 ppm HCl, the Hg^0 oxidation increased to 80%. Significantly that occurred via an Eley-Ridel mechanism, which adsorbed HCl reacts with gas phase Hg^0.

REFERENCES

1. J. H. Pavlish, E. A. Sondreal, M. D. Mann, E. S. Olson, K. C. Galbreath, D. L. Laudal, S. A. Benson: Fuel Process. Technol., 2003, vol. 82, pp. 89-165.
2. US EPA, Mercury and Air Toxic Standards (MATS) (2021), http://www.epa.gov/mats/cleaner-power-plants. (Accessed on 15 June 2021)
3. Taiwan EPA, Mercury emission regulation for coal-fired electricity generating units, 2014, https://law.moj.gov.tw/Law-Class/LawAll.aspx?pcode=O0020026. (Accessed on 15 June 2021)
4. K. C. Galbreath, and C. J. Zygarlicke: Environ Sci Technol., 1996, vol. 30, pp. 2421-5609.
5. A. A. Presto, and E. J. Granite: Environ Sci Technol., 2006, vol. 40, pp. 5601-5609.
6. M. Diaz-Somoano, S. Unterberger, K. R. G. Hein: Fuel Process. Technol., 2007, vol. 88, pp. 259-263.
7. C. L. Senior: J Air Waste Manage., 2006, vol. 56, pp. 23-31.
8. B. A. Dranga, L. Lazar, H. Koeser: Catal., 2012, vol. 2, pp. 139-170.
9. L. Zhao, C. Li, X. Zhang, G. Zeng, J. Zhang, Y. Xie: Catal Sci Technol., 2015, vol. 5, pp. 3459-3472.
10. R. K. Srivastava, N. Hutson, B. Martin, F. Princiotta, J. Staudt: Environ Sci Technol., 2006, vol. 40, pp. 1385-1393.
11. J. Liu, M. He, C. Zheng, M. Chang: Proc Combust Inst., 2011, vol. 33, pp. 2771-2777.
12. Y. Li, P. Murphy, C. Y. Wu: Fuel Process. Technol., 2008, vol. 89, pp. 567-573.
13. S. Niksa, and N. Fujiwara: J Air Waste Manage., 2005, vol. 55, pp. 1866-1875.
14. C. Senior: DOE Quarterly Progress Report, 2004.
15. C. W. Young, C. L. Chen, S. S. Huang, H. L. Bai, G. H. Huang, S. Y. Yu, S. Y. Liou: Taiwan Patient., 2015, TW 201515707.
16. R. Stolle, H. Koeser, H. Gutberlet: Appl. Catal B-Environ., 2014, vol. 144, pp. 486-497.
17. H. Kamata, S. I. Ueno, T. Naito, A. Yamaguchi, S. Ito: Catal Commum., 2008, vol. 9, pp. 2441-2444.
18. S. Straube, T. Hahn, H. Koeser: Appl. Catal B-Environ., 2008, vol. 79, pp. 286-295.
19. Y. Li, C.Y. Wu: Environ Sci Technol., 2006, vol. 40, pp. 6444-6448.
20. O. Krocher, M. Elsener: Appl. Catal B-Environ., 2008, vol. 77, pp. 215-227.
21. H. L. Li, C. Y. Wu, Y. Li, J. Y. Zhang: Environ Sci Technol., 2011, vol. 45, pp. 7394-7400.
22. S. Eswaran, H.G. Stenger: Energ Fuel., 2005, vol. 19, pp. 2328-2344.
23. J. B. Lee, S. M. Lee, I. Y. Lee: Proc. World Acad. Sci. Eng. Technol., 2008, vol. 40, pp. 256-257.
14. H. Kamata, S. Ueno, N. Sato, T. Naito: Fuel Process. Technol., 2009, vol. 90, pp. 947-951.