Study on the characteristics of V₂O₅-WO₃/TiO₂ denitration catalyst synergistic mercury removal

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Abstract. Ti-V₁W₉ catalyst obtained the best 68.18 % elemental mercury (Hg⁰) oxidation efficiency at the temperature of 250 °C, the elemental mercury (Hg⁰) oxidation efficiency can be maintained above 60 % in the reaction temperature range of 250-350 °C, indicating that V₂O₅-WO₃/TiO₂ catalyst has certain oxidizing ability to elemental mercury (Hg⁰); SO₂ inhibits Ti-V₁W₉ catalyst's ability to oxidize elemental mercury (Hg⁰), and the toxicity of Ti-V₁W₉ catalyst cannot be reversed to some extent; O₂ has a very obvious promoting effect on the oxidation performance of Ti-V₁W₉ catalyst elemental mercury (Hg⁰). Increasing the concentration of O₂ can significantly improve the elemental mercury (Hg⁰) oxidation efficiency; Low concentration of NO contributes to the adsorption oxidation of elemental mercury (Hg⁰) by Ti-V₁W₉ catalyst, while high concentration of NO significantly inhibits oxidation of elemental mercury (Hg⁰) on the surface of catalyst; NH₃ inhibits the adsorption and oxidation of elemental mercury (Hg⁰) on the surface of catalyst; H₂O(g) has very obvious inhibitory effect on elemental mercury (Hg⁰) adsorption oxidation.

1. Introduction

In order to achieve sustainable development of the environment, the former Ministry of Environmental Protection promulgated the "Emission Standards of Air Pollutants for Thermal Power Plants" (GB13223-2011) for the first time clarified the emission limit of 0.03 mg/m³ of mercury and its compounds from coal-fired boilers in thermal power plants. Implemented on January 1, 2015 [1-2].

Mercury and its compounds in flue gas are transformed from mercury in coal during combustion, and exist in three forms of Hg⁰, Hg²⁺ and Hg⁸⁺ in flue gas. Hg⁰ is highly volatile and insoluble in water, so it cannot be removed in subsequent flue gas treatment facilities; Hg²⁺ has strong water solubility and can be removed in the subsequent wet flue gas treatment facilities; Hg⁸⁺ can be removed together with the smoke and dust in the dust collector system[3-4]. Therefore, mastering the transformation law of Mercury forms in flue gas becomes the key factor and effective control method to control mercury emission concentration. Studies have proved[5-8], that the SCR denitration catalyst can convert Hg⁰ to Hg²⁺, so that it can be removed synergistically in subsequent wet desulfurization facilities. Therefore, researching and improving the Hg⁰ oxidation performance of SCR denitration catalysts can efficiently remove mercury and its compounds in flue gas. This experiment is based on the research of the removal characteristics of Hg⁰ by V₂O₅-WO₃/TiO₂ catalyst.
2. Experimental method

2.1. Preparation of catalyst sample
The catalyst prepared in this experiment is supported by TiO$_2$ and supported by V$_2$O$_5$ and WO$_3$ as active components. In the laboratory, V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst is prepared by ultrasonic assisted equal amount impregnation method. The preparation of mixed samples of V$_2$O$_5$ and 9% WO$_3$ is marked Ti-V$_1$W$_9$; The preparation load content of V$_2$O$_5$ sample was marked Ti-V$_1$; The sample with 9% WO$_3$ load was labeled Ti-W$_9$; The pure TiO$_2$ was prepared as a sample labeled TiO$_2$.

2.2. Oxidation performance test of Hg$^0$
The oxidation performance test of Hg$^0$ catalyst is completed in the gas-solid micro reactor. The catalyst test system is shown in Figure 1. The simulated flue gas components are 400 ppm-1200 ppm SO$_2$, 0-300 ppm NO, 5% O$_2$ (volume fraction, the same below), about 8% H$_2$O (g) and 0-530 ppm NH$_3$ (when required), N$_2$ (purity ≥ 99.99%), Hg$^0$ is provided by mercury vapor generating device.

Each component of the simulated flue gas is controlled by a mass flow meter. During the experiment, first turn on N$_2$, and control the Hg$^0$ content in the system by adjusting the carrier gas flow of the Hg$^0$ vapor generator. After the Hg$^0$ content in the inlet and outlet of the reaction device is stable, then according to the operating conditions required by the experiment, adjust the N$_2$, SO$_2$, NO, O$_2$ gas content in the simulated flue gas, and control the total flow of the simulated flue gas at 1.0 L/min; adjust the temperature according to the experimental requirements, and start testing the Hg$^0$ inlet and outlet concentration after the program is heated to the set temperature.

3. Experimental results and discussion

3.1. Hg$^0$ efficiency test of series catalyst samples
At 250 ℃, 5% O$_2$, 400 ppm SO$_2$, 300 ppm NO, mercury vapor (100 ml/min high purity N$_2$ as carrier gas) and equilibrium gas N$_2$ were introduced into the system. The oxidation performance of V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst series samples prepared in the laboratory for Hg$^0$ was tested under simulated flue gas experimental conditions. The comparison results are shown in Figure 2.

The experimental results show that the oxidation efficiency of Hg$^0$ is less than 20% and stable when TiO$_2$ is used as catalyst alone. The oxidation efficiency of Ti-V$_1$ and Ti-W$_9$ increased to a certain extent when V$_2$O$_5$ and WO$_3$ were loaded on TiO$_2$, but the oxidation efficiency of both Ti-V$_1$ and Ti-W$_9$ was still lower than 50%. Ti-V$_1$W$_9$ loaded with V$_2$O$_5$ and WO$_3$ at the same time showed good Hg$^0$ oxidation efficiency, and more than 60% of Hg$^0$ oxidation efficiency lasted for 3h. This may be due to the synergistic effect of V$_2$O$_5$ and WO$_3$ on Hg$^0$ adsorption and oxidation.
3.2. Effect of reaction temperature on Hg0 oxidation efficiency of catalyst

The oxidation properties of V2O5-WO3/TiO2 series samples for Hg0 were tested in the temperature range of 150-400 °C. According to the experimental results in Figure 3, the oxidation performance of TiO2 to Hg0 is poor, and the oxidation efficiency of Hg0 is maintained at 10%. The oxidation efficiency of Ti-V1W9, Ti-V1 and Ti-W9 catalysts increased with the increase of temperature from 150 °C to 250 °C, and the best performance of Hg0 oxidation was achieved at 250 °C. The results show that the oxidation efficiency of Ti-V1W9 reaches 68.18% at 250 °C, which is the highest oxidation efficiency of Hg0 in this series of samples. After that, the oxidation efficiency of Ti-V1W9 decreases. However, Ti-V1W9 has good activity in the reaction temperature range of 250 ~ 350 °C, and the oxidation efficiency of Hg0 can still maintain above 60%.

3.3. Effect of flue gas composition on Hg0 oxidation efficiency of catalyst

Effect of No: the effect of NO on the Hg0 oxidation removal efficiency of the catalyst is shown in Figure 4. It can be seen that when 100 ppm NO is injected into the simulated flue gas, the oxidation efficiency of Ti-V1W9 catalyst for Hg0 is significantly higher than that of pure N2. However, when the concentration of NO is continuously increased from 100 ppm to 300 ppm, the oxidation efficiency of Ti-V1W9 catalyst for Hg0 is significantly decreased, even lower than that of pure N2, indicating that low concentration of NO is conducive to the adsorption and oxidation of Hg0. The oxidation of Hg0 was inhibited by high concentration of NO; When 5% O2 was added into 300 ppm NO flue gas, it was observed that the oxidation efficiency of Ti-V1W9 catalyst for Hg0 increased. This was mainly due to the existence of O2. NO was adsorbed on the surface of Ti-V1W9 catalyst in molecular form and
reacted with O$_2$ to form intermediate active substances such as NO$_2$, NO$^+$, NO$_2^+$, etc. these active substances were more likely to react with Hg$^0$, thus increasing the oxidation efficiency of Hg$^0$.

Fig 4. Effect of NO on Oxidation Efficiency of Catalyst Hg$^0$.

Effect of SO$_2$: the oxidation performance of Ti-V$_1$W$_9$ catalyst for Hg$^0$ was investigated under the conditions of pure N$_2$ and 400-1200 ppm SO$_2$ at 250 °C, and the results are shown in Figure 5. Figure 5 (a) shows that with the increase of SO$_2$ concentration, the oxidation efficiency of Hg$^0$ gradually decreases, indicating that the catalytic oxidation activity of Ti-V$_1$W$_9$ catalyst is obviously inhibited. When 5% O$_2$ was injected at 1200 ppm SO$_2$ concentration, it was observed that the oxidation efficiency of Hg$^0$ increased significantly, indicating that O$_2$ had a positive role in promoting the adsorption and oxidation of Hg$^0$. The sulfur resistance of Ti-V$_1$W$_9$ catalyst was tested in Figure 5 (b). After adding 400 ppm SO$_2$, the oxidation efficiency of Hg$^0$ decreased rapidly. When the oxidation efficiency of Hg$^0$ decreased to 40% and was basically stable, SO$_2$ was shut down. It can be seen that the oxidation efficiency of Hg$^0$ increased to a certain extent, but could not return to the initial level in a short time. The results showed that the toxicity of SO$_2$ to Ti-V$_1$W$_9$ catalyst could not be reversed to some extent. The results show that [14], there is a competitive relationship between SO$_2$ and SO$_3$. SO$_3$ can promote the oxidation of Hg$^0$ to a certain extent, and high concentration of SO$_3$ can significantly inhibit the oxidation of Hg$^0$, reducing the oxidation efficiency of Hg$^0$.

Fig 5. Effect of SO$_2$ on Hg$^0$ oxidation efficiency.

Influence of H$_2$O: water vapor is introduced into dry flue gas to form wet flue gas with humidity of 8%. The Hg$^0$ oxidation efficiency of Ti-V$_1$W$_9$ catalyst is tested, and the results are shown in Figure 6. Comparing and analyzing the Hg$^0$ oxidation efficiency of dry and wet flue gas, it can be seen that the Hg$^0$ oxidation efficiency of Ti-V$_1$W$_9$ catalyst in wet flue gas is significantly reduced, indicating that H$_2$O (g) in flue gas has a very obvious inhibition effect on Hg$^0$ adsorption and oxidation, because H$_2$O
(g) on the catalyst surface affects the physical and chemical adsorption process of Hg\textsuperscript{0}, hinders the reaction process of Hg\textsuperscript{0} on the catalyst surface, resulting in catalyst deactivation \cite{7}.

![Fig 6. Effect of H\textsubscript{2}O on Oxidation Efficiency of Hg\textsuperscript{0} Oxidation Efficiency.](image)

Influence of NH\textsubscript{3}: NH\textsubscript{3} is the most commonly used reducing agent in SCR Flue Gas Denitration Process. In this experiment, the activity of catalyst in the presence of NH\textsubscript{3}, NH\textsubscript{3}, NO and O\textsubscript{2} was investigated, and the results are shown in Figure 7. In the absence of O\textsubscript{2} and NO, the Hg\textsuperscript{0} oxidation efficiency of Ti-V\textsubscript{1}W\textsubscript{9} catalyst decreased gradually with the increase of NH\textsubscript{3} concentration. When NH\textsubscript{3} concentration reached 300 ppm, the Hg\textsuperscript{0} oxidation ability of Ti-V\textsubscript{1}W\textsubscript{9} catalyst was obviously inhibited, and then 5% O\textsubscript{2} was added, the Hg\textsuperscript{0} oxidation efficiency increased obviously; When 300 ppm NO is added, the activity of Ti-V\textsubscript{1}W\textsubscript{9} decreases slightly with the increase of NH\textsubscript{3}/NO ratio from 1:3 to 1:1, which is mainly caused by the inhibition of Hg\textsuperscript{0} adsorption and oxidation by NH\textsubscript{3} on the catalyst surface. The oxidation efficiency of Hg\textsuperscript{0} increases significantly after 5% O\textsubscript{2} is added.

![Fig 7. Effect of NH\textsubscript{3} on Hg\textsuperscript{0} oxidation efficiency.](image)

Through the above conditions, it can be found that the addition of O\textsubscript{2} has a positive effect on the Hg\textsuperscript{0} adsorption and oxidation efficiency. After the addition of 5% O\textsubscript{2}, the Hg\textsuperscript{0} oxidation efficiency of the samples under the above conditions is slightly improved. The reason may be that O\textsubscript{2} provides oxygen atoms for the oxidation reaction, or supplements the oxygen vacancies formed after the oxidation of Hg\textsuperscript{0}. Hg\textsuperscript{0} can be oxidized by O\textsubscript{2} or lattice oxygen, but the reaction energy barrier is very high, and the reaction is difficult to occur \cite{11}. However, O\textsubscript{2} still has a positive effect on the catalytic oxidation of Hg\textsuperscript{0}.
3.4. Analysis of Hg\textsuperscript{0} oxidation mechanism of catalyst
According to the above test results of Hg0 oxidation efficiency of the catalyst, based on the Mars Maessen mechanism, the following mechanism analysis of Hg0 adsorption and catalytic oxidation reaction process under the action of Ti-V1W9 sample in this experimental study was made: firstly, after Hg0 in the flue gas was adsorbed on the surface of the catalyst, Hg0 in the gas phase was adsorbed on the surface of the catalyst. The active component VOx in the catalyst can provide lattice oxygen or oxygen atoms in the valence reduction of V5+ and V4+, and the latter can react with Hg0 adsorbed to produce stable oxidized Hg0. The supply of oxidant components such as O atoms in the catalytic oxidation process is the focus of the catalytic oxidation process of elemental mercury Hg0.

In the above experiments, the oxidation ability of Ti-V1W9 was obviously inhibited after adding certain concentration of SO\textsubscript{2}, NH\textsubscript{3} and other gases into the system. After adding 5% O\textsubscript{2}, it was observed that the O\textsubscript{2} in the simulated gas filled the oxygen consumed in the oxidation reaction of Hg0, which increased the catalytic oxidation ability of Ti-V1W9 to a certain extent and improved the oxidation efficiency of Hg0, which confirmed the above mechanism.

4. Conclusion
(1) Under the experimental conditions, the Ti-V1W9 catalyst prepared in the laboratory has the best Hg0 oxidation efficiency of 68.18% in the series of samples at 250 °C. It has good activity in the reaction temperature range of 250 ~ 350 °C, and the Hg0 oxidation efficiency can maintain more than 60%. It shows that V\textsubscript{2}O\textsubscript{3}-WO\textsubscript{3}/TiO\textsubscript{2} catalyst has a certain oxidation ability for Hg0.

(2) The results show that the influence of flue gas components on the Hg0 oxidation ability of Ti-V1W9 catalyst is quite different, and SO\textsubscript{2} can obviously inhibit the Hg0 oxidation of Ti-V1W9 catalyst; Low concentration of no is helpful to the adsorption and oxidation of Hg0 on Ti-V1W9 catalyst, while high concentration of no obviously inhibits the oxidation of Hg0; The oxidation efficiency of Ti-V1W9 catalyst can be improved by increasing the concentration of O\textsubscript{2}.

(3) H\textsubscript{2}O(g) on the catalyst surface affects the physical and chemical adsorption process of Hg0, hinders the reaction process of Hg0 on the catalyst surface, resulting in the deactivation of the catalyst.

References
[1] Wang Lei, Wang Lijuan. Status quo and suggestions of mercury pollution control in coal-fired power plants in China [J]. Environmental science and technology, 2014 (S2): 285-289.
[2] Chinese Academy of Environmental Sciences. Emission standard of air pollutants for thermal power plants: GB 13223-2011 [M]. China Environmental Science Press, 2012.
[3] LIU Fasheng, XIA Yongjun, XU Rui, et al. Experimental Study on Mercury Removal Effect and Mercury Emission Characteristics of Pollution Control Equipment in Coal-Fired Power Plants[J]. Electric Power, 2017, 50(4): 162-166.
[4] YANG Ligu, DUAN Yufeng, YANG Xianghua, et al. Mercury emission characteristics from coal-fired power plants [J]. Journal of Southeast University(Natural Science Edition), 2007, 37(5):817-821.
[5] CAI Xingfei, NIU Tianwen, ZHANG Yubin, et al. Progress in the Field of Low-temperature SCR of Flue Gas Denitrification Technology [J]. Boiler Technology, 2014, 45(2):77-80.
[6] XU Yueyang, XUE Jianming, WANG Hongliang, et al. Research on Mercury Collaborative Control by Conventional Pollutants Purification Facilities of Coal-fired Power Plants [J]. Proceedings of the CSEE, 2014, 34(23):3924-3931.
[7] TAO Li, ZHANG Xunan, LI Caiting, et al. Oxidation and capture of elemental mercury over SCR catalyst in simulated flue gas [J]. Chinese Journal of Environmental Engineering, 2015, 9(6):2925-2932.
[8] ZHENG Yiwu, DUAN Yufeng, TANG Hongjian, et al. Characteristics of the existing air pollutant control devices on Hg synergistic removal in a coal-fired power plant [J]. China Environmental Science, 2018, 38(3): 862-870.
[9] ZHANG Xunan. Experimental Study on Simultaneous Removal of HgO and NO in Flue Gas with CeO2 Modified SCR Catalyst[D]. Hunan University, 2015.

[10] YANG Jian, YANG iang, SUN Jian, et al. Effects of mercury oxidation on V2O5-WO3/TiO2 catalyst properties in NH3-SCR process[J]. Catalysis Communications, 2015, 59: 78–82.

[11] Gao W, Liu Q, Wu C Y, et al. Kinetics of mercury oxidation in the presence of hydrochloric acid and oxygen over a commercial SCR catalyst[J]. Chemical Engineering Journal, 2013, 220(11):53-60.

[12] SUAREZ NEGREIRA A, WILCOX J. DFT study of Hg oxidation across vanadia-titania SCR catalyst under flue gas conditions[J]. The Journal of Physical Chemistry C, 2013, 117(4): 1761–1772.

[13] ZHAO Li, LIU Yu, WU Yangwen, et al. Review on Theoretical Research of the Catalytic Oxidation of Hg0 in Coal-Fired Flue Gas [J]. Electric Power, 2018, 51(3): 170-176.

[14] Ye Z, Laumb J, Liggett R, et al. Impacts of acid gases on mercury oxidation across SCR catalyst[J]. Fuel Processing Technology, 2007, 88(10):929-934.

[15] Pudasainee D, Kim J H, Yoon Y S, et al. Oxidation, reemission and mass distribution of mercury in bituminous coal-fired power plants with SCR, CS-ESP and wet FGD[J]. Fuel, 2012, 93(1):312-318.

[16] WANG Zhen, LIU Jing, ZHANG Bingkai, et al. Mechanism of heterogeneous mercury oxidation by HBr over V2O5/TiO2 catalyst[J]. Environmental Science & Technology, 2016, 50(10): 5398–5404.

[17] JIANG Ye, GAO Xiang, WU Weihong, et al. Review of the deactivation of selective catalytic reduction De NOx catalysts[J]. Proceedings of the CSEE, 2013, 33(14):18–31.

[18] QU Litao, LI Chao, YU Honghai, et al. I Impact Analysis and Countermeasures on Coal Fired Units In-depth Peak Regulation of Environmental Protection Facilities [J]. Northeast Electric Power Technology, 2016, 37(10):38-40.

[19] LI H, YING L, WU C Y, et al. Oxidation and capture of elemental mercury over SiO2–TiO2 – V2O5, catalysts in simulated low-rank coal combustion flue gas[J]. Chemical Engineering Journal, 2011, 169(1):186-193.

[20] LI H, WU C Y, LI Y, et al. Superior activity of MnOx -CeO2 /TiO2, catalyst for catalytic oxidation of elemental mercury at low flue gas temperatures[J]. Applied Catalysis B Environmental, 2012, 111(3):381-388.

[21] YAN N, CHEN W, CHEN J, et al. Significance of RuO2 Modified SCR Catalyst for Elemental Mercury Oxidation in Coal-fired Flue Gas[J]. Environmental Science & Technology, 2011, 45(13):5725-30.

[22] Zhao Lingkui. Experimental and theoretical study on simultaneous denitrification and mercury removal by selective catalytic reduction catalyst [D]. Hunan University, 2017.

[23] GUO Pan, GUO Xin, ZHENG Chuguan. Computational insights into interactions between Hg species and α-Fe2O3 (001)[J]. Fuel, 2011, 90(5): 1840–1846.