10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

CeO2 based catalysts for elemental mercury capture

Haitao Zhao[a, b, c], Shufan Yin[d], Quhan Chen[d], Xingduan Huang[d], Hongkun Chen[d], Lu Lu[d], Chenghang Zheng[a], Xiang Gao[a,*], Tao Wu[b, c, *]

[a] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, P. R. China.
[b] Municipal Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, P. R. China.
[c] New Materials Institute, The University of Nottingham Ningbo China, Ningbo 315042, P. R. China
[d] Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo 315042, P. R. China

Abstract

The alternative materials to remove Hg^0 from energy utilization sectors is crucial to mercury control in atmosphere. CeO_2 based catalysts were prepared by an incipient wetness impregnation (IWI) method. A novel Hg^0 and Hg^T temperature-programmed surface reaction (Hg^0-Hg^T-TPSR) was proposed in this study for the investigation of the prepared CeO_2 based catalysts with the qualitative and quantitative analyses. The characteristic temperatures, the areas of adsorption region and desorption region, and activation energy with reaction kinetics were investigated to evaluate the performance. It was found that 2wt% Ce catalyst has the best mercury removal performance with the highest Hg^0 removal ability and the lowest E_a. There was also small amount of Hg^{2+} detected which indicated the catalytic effect contributed. The results suggested that 2wt% Ce based binary catalysts could be the potential candidates to be investigated in the future study.

Keywords: CeO2 based catalysts; Hg0 removal; TPSR study

1. Introduction

Mercury is considered as a threat to both human health and environment due to its features of toxicity, volatility, persistence and bioaccumulation [1-3]. With the objective of protecting human health and environment from anthropogenic mercury emissions, more than 50 nations have officially participated in the Minamata Convention since 18th May, 2017 and this Convention has come into force on 16th August, 2017. The major mechanism by which mercury finds its way into atmosphere is anthropogenic emissions [4, 5].The Minamata Convention is concerned with controlling anthropogenic mercury emissions of five categories: Coal-fired power plants; Coal-fired industrial

boilers; Smelting and roasting processes used in the production of lead, zinc, copper and industrial gold, in the Convention and in this document as 'non-ferrous metals'; Waste incineration facilities; and Cement clinker production facilities. Therefore, effective techniques on controlling mercury emission, especially those five categories of sources listed above, is of utmost need.

Mercury released from anthropogenic sources has three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate bound mercury (Hg^p) [6, 7]. Among them, Hg^{2+} can be easily captured by the wet flue gas desulfurization (WFGD) system while Hg^p can be captured by particulate control devices [8, 9]. The problem arises from Hg^0 because it is highly volatile and hardly soluble in water [10-12], making it the most difficult to be removed. Therefore, removal of Hg^0 flue gas from emission gas is crucial to mercury control in atmosphere.

Activated carbon injection (ACI) is a mature technology to reduce Hg^0 emission [13-16]. Despite of its effectiveness to adsorb Hg^0, the high cost associated with usage [11, 17, 18] and the negative effects on the saleable by-product from coal combustion [19-21] have made the wide application of ACI to be undesirable. Furthermore, the ACI technology is limited because it requires low concentration of inlet mercury and low reaction temperature [14, 17]. To overcome the above limitations, other alternative methods on controlling Hg^0 emission should be introduced.

One of the alternative methods is catalytic oxidation of Hg^0 by using metallic oxides [7, 10, 11, 22] such as copper oxides (CuO_x), Cerium oxides (CeO_x) and manganese oxides (MnO_x) [22, 23]. Being oxidized to Hg^{2+}, mercury can then be easily removed by WFGD system. Based on previous research, CeO_2 is the most promising one among all of the transition metal oxides [24, 25]. The superiority of CeO_2 comes from its resistance to sulfur dioxide (SO_2), oxidization ability and outstanding oxygen storage capacity [24, 26]. Nevertheless, CeO_2 is not stable under high temperature[25]. In order to enhance thermal stability of CeO_2, γ-alumina (γ-Al_2O_3) is employed as the support because of its excellent mechanical properties, good thermal stability and low cost[27, 28]. Consequently, a combination of CeO_2 and γ-Al_2O_3 can be a feasible and effective catalyst for Hg^0 oxidation.

In this study, CeO_2 catalyst supported by γ-Al_2O_3 is to be synthesized to oxidize Hg^0. Experiments are carried out to investigate Hg^0 oxidation performance of this synthesized catalyst. Effects of different concentration for CeO_2 under different temperatures is also rapidly investigated to find the condition of optimum catalyst performance.

2. Material and methods

CeO_2 based catalysts were prepared by an incipient wetness impregnation (IWI) method in this study using γ-Al_2O_3 as the support, which was described in detail elsewhere. Rare earth Ce metal was selected as metal precursor with different concentrations of metal salts $Ce(NO_3)_3 \cdot 6H_2O$ (analytical grade, Sinopharm Chemical Reagent Co, Ltd.) used in this study.

A novel Hg^0 and Hg^T temperature-programmed surface reaction (Hg^0-Hg^T-TPSR) was proposed in this study for the investigation of the prepared CeO_2 based catalysts with the qualitative and quantitative analyses as described in our previous research. The characteristic temperatures, the areas of adsorption region and desorption region, and reaction kinetics were studied.

3. Results & Discussions

The temperature-programmed surface reaction (TPSR) was selected as an experimental method to analyse the performance of γ-Al_2O_3 supported CeO_2 catalysts. Figure 1 shows the temperature-programmed surface reaction (TPSR) profile of Hg^T and Hg^0.
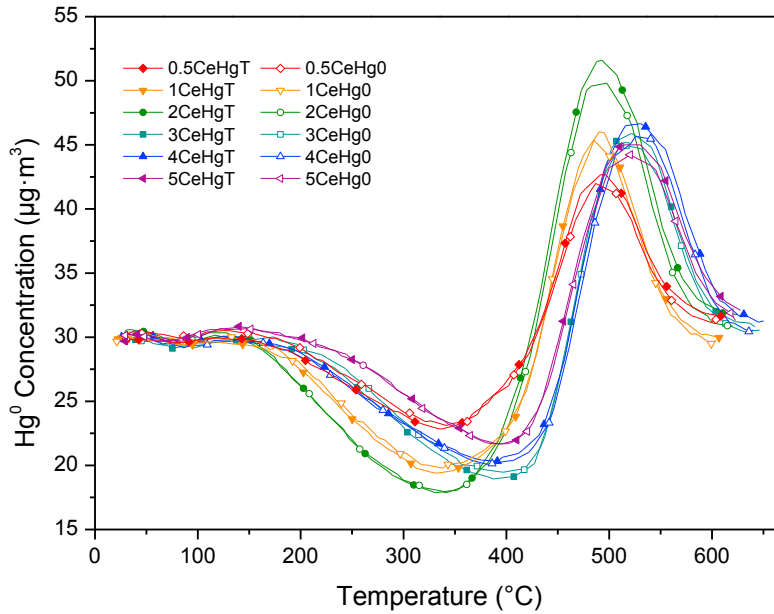
Fig. 1. Hg^T-TPSR and Hg^0-TPSR profiles of γ-Al2O3 supported Ce oxides.

As can be seen from Fig. 1, Ce based catalyst displays a vigorous mercury absorption ability at a relative low temperature. Lowest concentration of Hg^0 can be achieved with 2wt% Ce in catalyst. Therefore, 2wt% Ce catalyst has the best Hg^0 removal performance. There was also small amount of Hg^{2+} detected with the gap between Hg^T and Hg^0, which indicated the catalytic effect contributed. However, this phenomenon is of great important for the Ce based binary catalysts further study.

Table 1 Characteristic temperatures of CeO_2 based catalysts

Sample	T_{a0} (°C)	$T_{ra,peak}$ (°C)	$T_{a,peak}$ (°C)	T_{d0} (°C)	$T_{rd,peak}$ (°C)
0.5Ce	171.3	285.4	341.8	429.5	462.2
1Ce	148.8	234.3	338	433.3	444.8
2Ce	145.5	213.9	341.4	427.5	443.1
3Ce	196.9	271.9	397.1	459.8	472.7
4Ce	163.5	318	381	462.4	466.4
5Ce	190.6	282.3	400.2	453.6	460.5

During the process of TPSR, different types of characteristic temperature for each of these catalysts have been recorded. The result has been summarised in table 1 by qualitative analysis. Those different types of characteristic temperature included in table 1 are initial adsorption (T_{a0}), adsorption rate peak ($T_{ra,peak}$), adsorption peak ($T_{a, peak}$), initial desorption (T_{d0}), desorption rate peak ($T_{rd, peak}$) and desorption peak ($T_{d, peak}$).

All the characteristic temperatures can be selected as effective parameters to analyse the Hg^0 capture performance of all the catalysts. According to the data in table 1, catalyst with 2wt% Ce has the lowest temperature for most of the characteristic temperatures when in comparison with the value of other catalysts. Regarding T_{a0} and $T_{ra,peak}$, the value of 2wt% Ce catalyst is the lowest temperature, which indicate that less energy is needed for 2wt% Ce catalyst to capture Hg^0. Moreover, the $T_{a,peak}$ is relative higher than that of 1wt% Ce catalyst, which suggest the effect temperature window for Hg^0 capture extended.
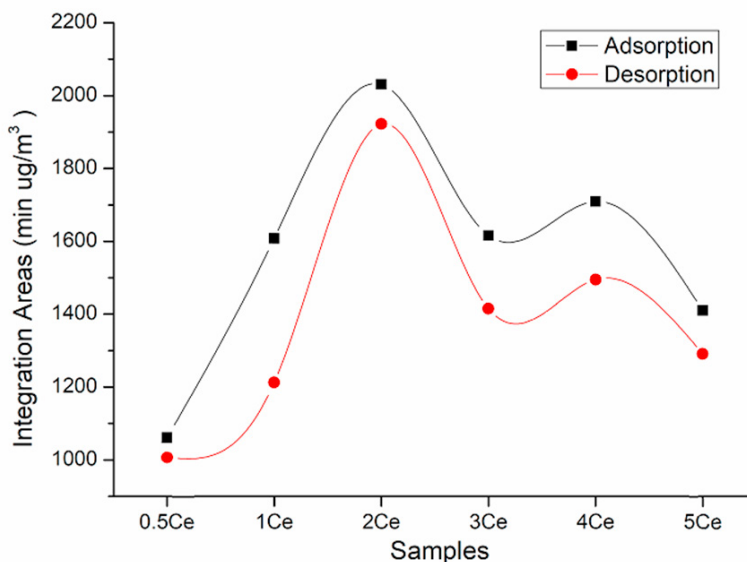
4

Fig. 2. Amount of Hg^0 adsorbed and desorbed over γ-Al_2O_3 supported Ce oxides

By quantitative analysis, the areas of adsorption region and desorption region (in the Fig. 1) were obtained via the integration calculation of the areas below/above the baseline concentration of Hg^0 as shown in Fig. 2. The calculated absolute adsorption areas enable the screening of the samples by identifying Hg^0 adsorption ability. It is obvious that the adsorption area for 2wt% Ce catalyst had the maximum amount of Hg^0 adsorbed. The catalysts with 1wt% Ce, 3wt% Ce and 4wt% Ce showed slightly the same performance whilst the Hg^0 adsorption ability decreased when catalysts with 0.5wt% Ce and 5wt% Ce with the shrinking of adsorption areas.

Furthermore, the values of absolute desorption areas are following the same trend with that of the absolute adsorption areas. However, there is a gap between the two curves, which indicate that the catalytic effect may happen with the Hg^{2+} generated. The phenomenon could also be observed from the Fig. 1. Further work is needed to study this phenomenon in the future.

Table 2 Reaction kinetics summary of γ-Al_2O_3 supported Ce oxides.

Sample	*Slope*	E_a (kJ/mol)	R^2	ΔX_{max} (%)
0.5Ce	-6917.78626	57.51724208	0.93598	24.88326286
1Ce	-6880.72017	57.20905978	0.91966	35.31628002
2Ce	-6376.60096	53.01761102	0.96012	41.02936347
3Ce	-7069.58075	58.77932219	0.99186	33.5344563
4Ce	-7375.21945	61.3205246	0.98361	33.19336765
5Ce	-8214.37654	68.2976123	0.95058	30.49307932

In this research, activation energy with kinetic study was also carried out to evaluate the potential of individual candidate Ce catalysts for Hg^0 capture, which was calculated using the modified Arrhenius plotting of Hg^0 -TPSR experimental data in Fig. 1. The data with initial removal efficiency below 10% were selected for the calculation and the correlation was strong with a R^2 above 0.95 as shown in the Table 2. It was found the 2wt% Ce catalyst had highest ΔX_{max} and the lowest E_a for Hg^0 capture. Fig. 3 also clearly indicated that E_a decreased with the increasing amount of Ce until 2 wt% when reached a peak. After that, the E_a increased with the increasing amount of Ce. Therefore, based on the above results, less energy is needed for 2wt% Ce catalyst to capture Hg^0, which results are useful for the Ce based binary catalysts study in the future.
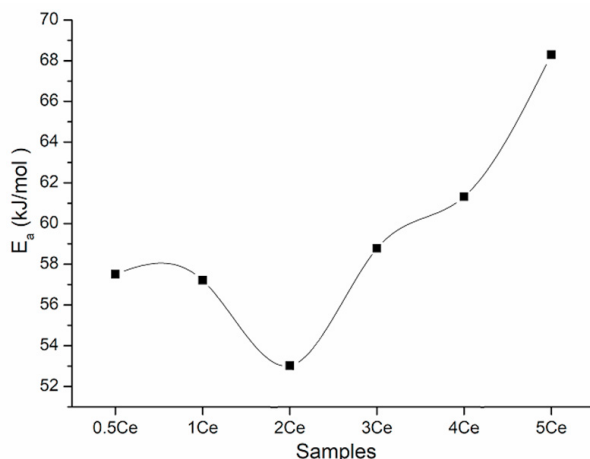
Fig. 3. Activation energy of Hg^0 oxidation over γ-Al$_2$O$_3$ supported Ce oxides

4. Conclusion

CeO$_2$ based catalysts were developed as alternative materials to mercury control in atmosphere. An incipient wetness impregnation (IWI) method was adopted to prepare the samples. For the investigation of the prepared catalysts, a novel Hg^0 and Hg^T temperature-programmed surface reaction (Hg^0-Hg^T-TPSR) was proposed in this study with the qualitative and quantitative analyses. The characteristic temperatures, the areas of adsorption region and desorption region, and activation energy with reaction kinetics were investigated to evaluate the performance. It was found that 2wt% Ce catalyst has the best mercury removal performance with the highest Hg^0 removal ability and the lowest E$_a$. There was also small amount of Hg^{2+} detected with the gap between Hg^T and Hg^0, which indicated the catalytic effect contributed. However, this phenomenon is of great important for the Ce based binary catalysts further study.

Acknowledgements

References

1.   Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; Pirrone, N., Mercury as a global pollutant: Sources, pathways, and effects. *Environmental Science and Technology* **2013,** *47*, (10), 4967-4983.
2.   Liu, J.; Qu, W.; Zheng, C., Theoretical studies of mercury–bromine species adsorption mechanism on carbonaceous surface. *Proceedings of the Combustion Institute* **2013,** *34*, (2), 2811-2819.
3.   Wei, Z. S.; Luo, Y. W.; Li, B. R.; Chen, Z. Y.; Ye, Q. H.; Huang, Q. R.; He, J. C., Elemental mercury oxidation from flue gas by microwave catalytic oxidation over Mn/γ-Al2O3. *Journal of Industrial and Engineering Chemistry* **2015,** *24*, 315-321.
4.   Stolle, R.; Koeser, H.; Gutberlet, H., Oxidation and reduction of mercury by SCR DeNOx catalysts under flue gas conditions in coal fired power plants. *Applied Catalysis B: Environmental* **2014,** *144*, 486-497.
5.   Wathen, J. B.; Lazorchak, J. M.; Olsen, A. R.; Batt, A., A national statistical survey assessment of mercury concentrations in fillets of fish collected in the U.S. EPA national rivers and streams assessment of the continental USA. *Chemosphere* **2015,** *122*, 52-61.
6.   Yang, Y.; Liu, J.; Wang, Z.; Zhang, Z., Homogeneous and heterogeneous reaction mechanisms and kinetics of mercury oxidation in coal-fired flue gas with bromine addition. *Proceedings of the Combustion Institute* **2017,** *36*, (3), 4039-4049.
7.   Zhang, B.; Liu, J.; Dai, G.; Chang, M.; Zheng, C., Insights into the mechanism of heterogeneous mercury

oxidation by HCl over V2O5/TiO2 catalyst: Periodic density functional theory study. *Proceedings of the Combustion Institute* **2015,** *35*, (3), 2855-2865.

8.   Zhang, B.; Liu, J.; Zheng, C.; Chang, M., Theoretical study of mercury species adsorption mechanism on MnO2(110) surface. *Chemical Engineering Journal* **2014,** *256*, 93-100.

9.   Wilcox, J.; Rupp, E.; Ying, S. C.; Lim, D.-H.; Negreira, A. S.; Kirchofer, A.; Feng, F.; Lee, K., Mercury adsorption and oxidation in coal combustion and gasification processes. *International Journal of Coal Geology* **2012,** *90*, 4-20.

10.   Wang, P.; Hu, S.; Xiang, J.; Su, S.; Sun, L.; Cao, F.; Xiao, X.; Zhang, A., Analysis of mercury species over CuO–MnO2–Fe2O3/γ-Al2O3 catalysts by thermal desorption. *Proceedings of the Combustion Institute* **2015,** *35*, (3), 2847-2853.

11.   Liu, Z.; Sriram, V.; Lee, J.-Y., Heterogeneous oxidation of elemental mercury vapor over RuO2/rutile TiO2 catalyst for mercury emissions control. *Applied Catalysis B: Environmental* **2017,** *207*, 143-152.

12.   Xue, L.; Liu, T.; Guo, X.; Zheng, C., Hg oxidation reaction mechanism on Fe2O3 with H2S: Comparison between theory and experiments. *Proceedings of the Combustion Institute* **2015,** *35*, (3), 2867-2874.

13.   Zhao, H.; Yang, G.; Gao, X.; Pang, C. H.; Kingman, S. W.; Wu, T., Hg0 Capture over CoMoS/γ-Al2O3 with MoS2 Nanosheets at Low Temperatures. *Environmental Science & Technology* **2016,** *50*, (2), 1056-1064.

14.   Shen, Z.; Ma, J.; Mei, Z.; Zhang, J., Metal chlorides loaded on activated carbon to capture elemental mercury. *Journal of Environmental Sciences* **2010,** *22*, (11), 1814-1819.

15.   Xu, H.; Qu, Z.; Zong, C.; Quan, F.; Mei, J.; Yan, N., Catalytic oxidation and adsorption of Hg0 over low-temperature NH3-SCR LaMnO3 perovskite oxide from flue gas. *Applied Catalysis B: Environmental* **2016,** *186*, 30-40.

16.   Krishnakumar, B.; Niksa, S., Predicting the impact of SO3 on mercury removal by carbon sorbents. *Proceedings of the Combustion Institute* **2011,** *33*, (2), 2779-2785.

17.   Aboud, S.; Sasmaz, E.; Wilcox, J., Mercury adsorption on PdAu, PdAg and PdCu alloys. *Main Group Chemistry* **2008,** *7*, (3), 205-215.

18.   Scala, F.; Anacleria, C.; Cimino, S., Characterization of a regenerable sorbent for high temperature elemental mercury capture from flue gas. *Fuel* **2013,** *108*, 13-18.

19.   Sjostrom, S.; Durham, M.; Bustard, C. J.; Martin, C., Activated carbon injection for mercury control: Overview. *Fuel* **2010,** *89*, (6), 1320-1322.

20.   Zhao, H.; Mu, X.; Yang, G.; George, M.; Cao, P.; Fanady, B.; Rong, S.; Gao, X.; Wu, T., Graphene-like MoS2 containing adsorbents for Hg0 capture at coal-fired power plants. *Applied Energy*.

21.   Zhao, H.; Yang, G.; Gao, X.; Pang, C.; Kingman, S.; Lester, E.; Wu, T., Hg0-temperature-programmed surface reaction and its application on the investigation of metal oxides for Hg0 capture. *Fuel* **2016,** *181*, 1089-1094.

22.   Gao, Y.; Zhang, Z.; Wu, J.; Duan, L.; Umar, A.; Sun, L.; Guo, Z.; Wang, Q., A Critical Review on the Heterogeneous Catalytic Oxidation of Elemental Mercury in Flue Gases. *Environmental Science & Technology* **2013,** *47*, (19), 10813-10823.

23.   Xu, H.; Ma, Y.; Huang, W.; Mei, J.; Zhao, S.; Qu, Z.; Yan, N., Stabilization of mercury over Mn-based oxides: Speciation and reactivity by temperature programmed desorption analysis. *Journal of Hazardous Materials* **2017,** *321*, 745-752.

24.   He, J.; Reddy, G. K.; Thiel, S. W.; Smirniotis, P. G.; Pinto, N. G., Ceria-Modified Manganese Oxide/Titania Materials for Removal of Elemental and Oxidized Mercury from Flue Gas. *The Journal of Physical Chemistry C* **2011,** *115*, (49), 24300-24309.

25.   Wen, X.; Li, C.; Fan, X.; Gao, H.; Zhang, W.; Chen, L.; Zeng, G.; Zhao, Y., Experimental Study of Gaseous Elemental Mercury Removal with CeO2/γ-Al2O3. *Energy & Fuels* **2011,** *25*, (7), 2939-2944.

26.   Li, H.; Wang, Y.; Wang, S.; Wang, X.; Hu, J., Removal of elemental mercury in flue gas at lower temperatures over Mn-Ce based materials prepared by co-precipitation. *Fuel* **2017,** *208*, 576-586.

27.   Hou, W.; Zhou, J.; Yu, C.; You, S.; Gao, X.; Luo, Z., Pd/Al2O3 Sorbents for Elemental Mercury Capture at High Temperatures in Syngas. *Industrial & Engineering Chemistry Research* **2014,** *53*, (23), 9909-9914.

28.   Du, W.; Yin, L.; Zhuo, Y.; Xu, Q.; Zhang, L.; Chen, C., Performance of CuOx–neutral Al2O3 sorbents on mercury removal from simulated coal combustion flue gas. *Fuel Processing Technology* **2015,** *131*, 403-408.