

Article pubs.acs.org/est

# Comparison of Elemental Mercury Oxidation Across Vanadium and Cerium Based Catalysts in Coal Combustion Flue Gas: Catalytic Performances and Particulate Matter Effects

Qi Wan,<sup>†,‡</sup> Qiang Yao,<sup>‡</sup> Lei Duan,<sup>\*,§</sup> Xinghua Li,<sup>§</sup> Lei Zhang,<sup>§</sup> and Jiming Hao<sup>§</sup>

<sup>†</sup>School of Renewable Energy, North China Electric Power University, Beijing 102206, China

<sup>‡</sup>Key Laboratory of Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

<sup>§</sup>State Key Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

ABSTRACT: This paper discussed the field test results of mercury oxidation activities over vanadium and cerium based catalysts in both coal-fired circulating fluidized bed boiler (CFBB) and chain grate boiler (CGB) flue gases. The characterizations of the catalysts and effects of flue gas components, specifically the particulate matter (PM) species, were also discussed. The catalytic performance results indicated that both catalysts exhibited mercury oxidation preference in CGB flue gas rather than in CFBB flue gas. Flue gas component studies before and after dust removal equipment implied that



the mercury oxidation was well related to PM, together with gaseous components such as NO, SO<sub>2</sub>, and NH<sub>3</sub>. Further investigations demonstrated a negative PM concentration-induced effect on the mercury oxidation activity in the flue gases before the dust removal, which was attributed to the surface coverage by the large amount of PM. In addition, the PM concentrations in the flue gases after the dust removal failed in determining the mercury oxidation efficiency, wherein the presence of different chemical species in PM, such as elemental carbon (EC), organic carbon (OC) and alkali (earth) metals (Na, Mg, K, and Ca) in the flue gases dominated the catalytic oxidation of mercury.

# 1. INTRODUCTION

Mercury emissions from anthropogenic sources, such as coal combustion, nonferrous metal smelting, and cement production, have aroused widespread public concern due to their adverse effects on human health and the ecosystem.<sup>1,2</sup> Nearly 40% and about 33% of the known anthropogenic mercury emissions are derived from coal combustion in China and the United States, respectively.<sup>3</sup> Accordingly, more and more countries, including the two aforementioned ones, have formulated relevant laws or regulations to strictly control mercury emissions from industrial coal-fired sources.<sup>4-6</sup> For example, the Ministry of Environmental Protection of the People's Republic of China released the new Emission Standard of Air Pollutants for Thermal Power Plants in July 2011, which proposed a mercury and its compounds emission limit to 0.03 mg/m<sup>3.7</sup> The U.S. Environmental Protection Agency also promulgated a federal Mercury and Air Toxics Standards (MATS) to cap power plant mercury emissions in December 2011.8

To meet the process demands in the presence of these regulations, effective and economical mercury emission control technologies for coal-fired power plants have been recently developed, including sorbent injection,9,10 catalytic oxidation of elemental mercury (Hg<sup>0</sup>),<sup>11,12</sup> photochemical oxidation,<sup>13,14</sup>

and scrubbers.<sup>15</sup> Among these, catalytic oxidation has proven to be one of the most effective technologies in power plants, <sup>5,16</sup> in that the oxidized mercury can be removed downstream in scrubbers. Some investigations have demonstrated how the use of certain catalysts, such as V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>, in the selective catalytic reduction (SCR) process enhanced the catalytic oxidation of Hg<sup>0,17,18</sup> Recent research examined several transition metal oxides, such as Fe<sub>2</sub>O<sub>3</sub>, CuO, Co<sub>3</sub>O<sub>4</sub>, and  $MnO_{2}$ , <sup>16,19,20</sup> for Hg<sup>0</sup> oxidation under various simulated flue gas conditions. MnO<sub>2</sub> and CuO exhibited high Hg<sup>0</sup> catalytic oxidation efficiencies at low HCl concentrations,<sup>19,2</sup> wherein acidic gases, including NO and HCl promoted mercury oxidation over these catalysts. In comparison, alkaline gases, such as NH<sub>3</sub>, weakened their catalytic activities.<sup>20</sup>

The study of rare earth metals for Hg<sup>0</sup> oxidation, including Ce, has recently garnered great interest.<sup>19–22</sup> Moreover, Celoaded metal oxides can replace the toxic V<sub>2</sub>O<sub>5</sub> as an efficient SCR catalyst while achieving  $NO_x$  reduction and  $Hg^0$  oxidation. Recent scientific and laboratory evaluations have indicated that

Received:	November 22, 2017
Revised:	February 6, 2018
Accepted:	February 7, 2018
Published:	February 7, 2018



Figure 1. Schematic of the setup for the field tests.

Hg<sup>0</sup> oxidation efficiencies over Ce-loaded catalysts exhibited high values at specific reaction temperature ranges.<sup>21,22</sup> In addition, the characterizations of CeO<sub>2</sub> indicate the presence of oxygen vacancies on the catalyst surface, thereby resulting in an abundance of surface active oxygen, which is highly participatory in catalytic reactions.<sup>23,24</sup> Previous bench-scale studies have demonstrated the significant effectiveness of the Ce-loaded catalyst for the oxidation of Hg<sup>0</sup> in the presence of simulated flue gas.<sup>25</sup> Water vapor exhibits competitiveness with Hg<sup>0</sup> for the active adsorption sites, thus inhibiting the oxidation of Hg<sup>0.17</sup> However, all of these studies focus on laboratory simulations and thus lack real-life verification in actual combustion flue gas, thereby resulting in more complex reaction conditions in the presence of SO<sub>2</sub>, NO, HCl, NH<sub>3</sub>, and water vapor. Especially, they rarely exhibits the effects of particulate matter (PM), which is inevitably present in real flue gas but has not yet to be generated in laboratory simulations. To further investigate the oxidation efficiencies over these catalysts in real flue gas conditions and to examine the effects of PM, it is necessary to perform field tests in the presence of coal combustion flue gas.

In this paper, mercury oxidation activities over honeycomb  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> and CeO<sub>2</sub>- $WO_3$ /TiO<sub>2</sub> were tested in two full-scale coal-fired boilers, the samples of the tested catalysts were characterized, and the effects of the flue gas components, such as HCl, NO, SO<sub>2</sub>, NH<sub>3</sub>, and PM, particularly the chemical species of PM, were discussed. The significance of this work aids in the evaluation of the actual catalytic oxidation performances over the catalysts in the real flue gas, thereby revealing the contributions of separate PM chemical species in the oxidation of mercury. Moreover, acquired knowledge on different types of coal-fired boilers improves the research and application of catalysts in both bench-scale and field tests.

### 2. MATERIALS AND METHODS

**2.1. Catalyst Preparation.** Commercial honeycomb  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> and noncommercial honeycomb CeO<sub>2</sub>- $WO_3$ /TiO<sub>2</sub> were employed as the two types of test catalysts. Both catalyst samples, prepared prior to testing, were obtained from China Guodian, Jiangsu Longyuan Catalyst Co., Ltd. (Wuxi, China).<sup>26</sup> The catalysts tested and discussed in this work were  $V_2O_5(1)$ - $WO_3(9)$ /TiO<sub>2</sub> and CeO<sub>2</sub>(1)- $WO_3(9)$ /

 $TiO_2$ , wherein the numbers in the brackets represented the mass percentage. They were abbreviated as V1–W9/Ti and Ce1–W9/Ti, respectively.

2.2. Activity Measurements. Field tests were conducted in the presence of flue gas from two real coal-fired boilers. One of the boilers is a circulating fluidized bed boiler (CFBB), equipped with an electrostatic precipitator (ESP) and a wet flue gas desulfurization (WFGD) at a power plant located in Hebei Province, and the other is a chain grate boiler (CGB), equipped with a fabric filter (FF) and WFGD at a heating plant located in Beijing, China. The field tests were conducted by pumping flue gas out through a packed bed reactor filled with prepared honeycomb catalysts. The assemblies of the packed bed reactor consisted of a flue gas sampling probe, a temperature controller, an online mercury analyzer, and a suction pump. The schematic was presented in Figure 1. A stable flow of flue gas was pumped through the packed bed reactor, which was heated and maintained at a constant temperature of 300 °C used in most SCR reactions by the temperature controller. A quartz tube was placed in the center of the reactor (760 mm in length with an outer diameter of 50 mm and an inner diameter of 45 mm) and surrounded by a large clam-shell furnace. Then, pumped flue gas was passed through the mercury analyzer, wherein a portion of the flue gas was diverted to the flue gas composition detector. The test sites were selected before and after ESP/FF equipment, wherein the same fresh catalysts were employed to investigate the effects of PM. Each boiler test continued for about 2 weeks using two catalyst samples.

The Hg<sup>0</sup> concentrations of the influent and effluent were measured based on Zeeman atomic absorption spectrometry using a Lumex RA 915+ Hg analyzer (Lumex Instruments Company, St. Petersburg, Russia), which provided a real-time response of Hg<sup>0</sup> every 1 s. The Hg<sup>0</sup> catalytic oxidation efficiency ( $E_{oxi}$ ) over the catalysts was expressed and calculated by the inlet/outlet Hg<sup>0</sup> concentrations as follows:

$$E_{\text{oxi}}(\%) = \frac{[\text{Hg}^{0}]_{\text{inlet}} - [\text{Hg}^{0}]_{\text{outlet}}}{[\text{Hg}^{0}]_{\text{inlet}}} \times 100\%$$

An online detector was applied to measure the continuous concentration of the flue gas components, such as HCl, SO<sub>2</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and O<sub>2</sub> (Gasmet Dx4000 FTIR Analyzer,

#### **Environmental Science & Technology**

Gasmet Technologies Inc., Helsinki, Finland). The PM samples were collected using quartz fiber filters, and then directly determined by weighing the mass before and after sampling. A thermal/optical carbon analyzer (DRI, Model 2001, Desert Research Institute, Reno, NV) was employed to analyze the organic carbon (OC) and elemental carbon (EC) on the quartz fiber filter by the thermal/optical reflectance method. The elements were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, IRIS Intrepid II XSP, Thermo Electron Corporation, Franklin, MA). To convert the samples into the solution for element analysis, the samples were digested using a microwave accelerated reaction system (Mars, CEM Corporation, Matthews, NC) with high-purity reagents, specifically subboiled HNO3, HCl, and HF. Ionic species, including chloride, nitrate, sulfate, and ammonium, were quantified by ion chromatography (Dionex DX-600, Conquer Scientific, San Diego, CA). Quality control and quality assurance procedures were routinely applied for all of the elemental, ion, and OC/EC analyses.<sup>2</sup>

**2.3. Catalyst Characterization.** All of the catalyst samples were characterized by Brunauer, Emmett, and Teller (BET) surface area and X-ray photoelectron spectroscopy (XPS). The BET surface area, pore size, and pore volume were measured by  $N_2$  adsorption at 77 K using a Quantachrome AutoSorb AS-1 System (Quantachrome Instruments, FL). The XPS data were collected using a PHI Quantera SXM (ULVAC-PHI Inc., Kanagawa, Japan). The binding energies were referenced to the C 1s line at 284.8 eV for adventitious carbon.

#### 3. RESULTS AND DISCUSSION

**3.1. Catalytic Mercury Oxidation.** *3.1.1. CFBB and CGB Flue Gases.* Field tests results showed that the average concentrations of Hg<sup>0</sup> in CFBB and CGB flue gases before ESP/FF were 84  $\mu$ g/m<sup>3</sup> and 78  $\mu$ g/m<sup>3</sup>, respectively, higher than the average (56  $\mu$ g/m<sup>3</sup>) according to 30 previous on-site measurements in coal-fired power plants and industrial boilers.<sup>28</sup> Figure 2 presents the Hg<sup>0</sup> catalytic oxidation



Figure 2. Field tests results of the Hg<sup>0</sup> oxidation efficiencies.

efficiencies over honeycomb V1–W9/Ti and Ce1–W9/Ti before and after ESP/FF in the flue gases of two boilers. The mercury oxidation efficiency in the CGB flue gas was around 80%, which was higher than that observed in the CFBB flue gas (74%). The mercury oxidation efficiencies over the honeycomb V1–W9/Ti and Ce1–W9/Ti catalysts were 76% and 77%, respectively. The results indicated the enhanced possibility of exhibiting mercury oxidation in the CGB flue gas rather than in the CFBB flue gas. In addition, the honeycomb V1–W9/Ti and Ce1–W9/Ti catalysts exhibited comparable Hg<sup>0</sup> catalytic oxidation activities, wherein the honeycomb V1–W9/Ti catalyst was widely used in coal-fired power plants to reduce flue gas NO<sub>x</sub> levels and was also considered an important catalyst for mercury oxidation in flue gas.<sup>29,30</sup>

3.1.2. before and After ESP/FF. To study the effects of the flue gas components, specifically that of PM on the catalytic oxidation activity, contrast tests were conducted in the flue gas before and after ESP/FF of the two boilers. The results are presented in Figure 2. The mercury oxidation efficiencies in CGB flue gas after FF (averagely 87%) were higher than that before FF (73%). In addition, the mercury oxidation efficiencies in CFBB flue gas after ESP (83%) were higher than those before ESP (65%). The observation of more elemental mercury being oxidized in the flue gas after ESP/FF suggested that low PM condition could improve mercury oxidation over both catalysts. The presence of PM in the flue gas was previously reported as a major concern for SCR catalysts because it plugged the pores and excessively covered the catalyst surface.<sup>4</sup> The above results validated the negative effects of PM on the elemental mercury catalytic oxidation activity in the real flue gas conditions.

**3.2. Catalyst Characterization.** The catalytic performances were generally determined by the physical and chemical properties of the catalyst.<sup>31</sup> The present study characterized the BET surface area and XPS results of the two tested catalysts for further investigation.

3.2.1. BET Surface Area. The physical properties of the honeycomb V1-W9/Ti and Ce1-W9/Ti catalysts, specifically the BET surface area, pore volume, and pore diameters were characterized. The results indicated that both catalysts exhibited similar surface characteristic levels. The V1-W9/Ti and Ce1-W9/Ti catalysts exhibited mean BET surface areas of 73  $m^2/g$ and 48 m<sup>2</sup>/g, respectively. The V1–W9/Ti catalyst exhibited a pore volume and average pore diameter of 0.32 cm<sup>3</sup>/g and 25 nm, respectively, whereas those of the Ce1-W9/Ti catalyst were measured to be 0.39  $\text{cm}^3/\text{g}$  and 37 nm, respectively. In other words, the V1-W9/Ti catalyst exhibited a larger surface area, whereas the Ce1-W9/Ti catalyst exhibited a higher optimal pore volume and average pore size. In comparison with the Hg<sup>0</sup> oxidation activities, the surface characteristics did not significantly affect the catalytic oxidation efficiencies and were not the main contributors to elemental mercury oxidation over vanadium and cerium based catalysts.

3.2.2. XPS of V 2p and Ce 3d. XPS is an effective way to detect the atomic concentration of catalyst surface. The XPS results for V1-W9/Ti and Ce1-W9/Ti catalysts showed that the surface atomic concentrations of V and Ce were 1.45% and 1.39%, respectively, representing that V and Ce were evenly spread and effectively covered on the catalyst surface. Further photoelectron spectra of the V 2p of V1-W9/Ti and the Ce 3d of Ce1-W9/Ti catalysts are presented in Figure 3. The V 2p spectrum exhibited a clear V1-W9/Ti XPS pattern. In addition, several obvious peaks were observed in the range of 515.0-517.0 eV. According to literature,<sup>32</sup> the binding energies at around 517.2, 516.2, and 515.2 eV correlated to V<sub>2</sub>O<sub>5</sub>, VO<sub>4</sub> and V<sub>2</sub>O<sub>3</sub>, respectively, which suggested the presence of V in the  $V^{5+}$ ,  $V^{4+}$  and  $V^{3+}$  mixtures on the catalyst surface, thereby indicating a stronger oxidation capacity given that the higher oxidation states exhibited higher binding energies and narrower V 2p lines.<sup>32</sup> Therefore, the high catalytic oxidation efficiency of elemental mercury over the V1-W9/Ti catalyst might be



Figure 3. XPS spectra of V 2p and Ce 3d.

attributed to the mixture of  $V^{5+}$ ,  $V^{4+}$ , and  $V^{3+}$ , especially the large amount of  $V^{5+}$  on the catalyst surface with a stronger oxidation capacity.

The Ce 3d spectrum also exhibited a clear Ce1-W9/Ti XPS pattern and had eight peaks labeled u and v, respectively. According to Benjaram,<sup>33</sup> the Ce 3d spectrum was assigned as follows: the bands labeled as u/v, u2/v2, and u3/v3 were attributed to the 3d<sup>10</sup>4f<sup>0</sup> state of Ce<sup>4+</sup> and the other doublets, specifically u1/v1, representing the 3d<sup>10</sup>4f<sup>1</sup> initial electronic state, which corresponded to Ce<sup>3+</sup>. The Ce 3d spectrum basically denoted a mixture of  $Ce^{3+}/Ce^{4+}$  oxidation states giving rise to a myriad of peaks, which indicated that the surface of both samples was not fully oxidized. In addition, Ce<sup>4+</sup> oxide was a mainly formed based on the peak areas of both catalysts, which was beneficial for the oxidation reactions.<sup>33,34</sup> Both monomeric and polymeric Ce<sup>4+</sup> sites were reportedly active for Hg<sup>0</sup> oxidation,<sup>25</sup> thereby suggesting that the Hg<sup>0</sup> oxidation activity over the honeycomb Ce1-W9/Ti catalyst was mainly based on the Ce4+ sites on the catalyst surface. In addition, a significantly high Ce1-W9/Ti binding energy was detected around 902.0 and 917.0 eV, which might be due to the addition of W with a strong electronegativity, thereby withdrawing the electron atmosphere of Ce-O. Hence, W was most likely beneficial for the transformation of Ce4+ to Ce3+. In addition, the presence of the Ce<sup>3+</sup> species created a charge imbalance, vacancies, and unsaturated chemical bonds on the catalyst surface, thereby resulting in an increase in chemisorbed oxygen on the surface.<sup>35</sup> Therefore, it might be concluded that good catalytic oxidation performance to elemental mercury over the Ce1-W9/Ti catalyst might be attributed to two aspects, specifically Ce4+ on the catalyst surface, which had a strong oxidation capacity, and partially oxidized Ce<sup>3+</sup> on the catalyst surface, which increased the amount of chemisorbed oxygen and enhanced the catalyst adsorption capacity.

3.2.3. XPS of O 1s. XPS O 1s is also a good way to characterize the redox potential of the catalyst surface, and the results of V1–W9/Ti and Ce1–W9/Ti catalysts are shown in Figure 4. It exhibited that significant peaks of O 1s were



Figure 4. XPS results of O 1s.

detected in both catalyst samples, and these peaks could be fitted into two types referred to lattice oxygen at 529.3-531.0 eV (hereafter, denoted as  $O\beta$ ) and chemisorbed oxygen belonging to the defect-oxide or the hydroxyl-like group at 531.3–531.9 eV (hereafter, denoted as  $O\alpha$ ).<sup>36</sup> Preston and Granite<sup>5</sup> studied various metal oxides for Hg<sup>0</sup> catalytic oxidation and proposed that lattice oxygen in the metal oxides could serve as an oxidant, impelling to form mercuric oxide (HgO). It was also reported that surface chemisorbed oxygen was a kind of most active oxygen and played an important role in oxidation reactions, whereas the relatively high concentration ratio of  $O\alpha/(O\alpha+O\beta)$  on catalyst surface might be correlated with high oxidation activity.<sup>37</sup> The O $\alpha$  ratio of V1–W9/Ti and Ce1-W9/Ti catalysts were 26% and 25%, respectively, and the calculated  $O\alpha/(O\alpha+O\beta)$  ratio of the two catalysts were nearly in the same level. Based on this, it could explained that the comparable elemental mercury oxidation efficiencies between vanadium and cerium based catalysts were partly due to the similar ratio of lattice oxygen and surface chemisorbed oxygen in the two catalysts.

3.3. Effects of the Flue Gas Components. To examine the relationship of the catalytic activity with the various flue gas components, specifically the concentration of PM, the major flue gas component concentrations, notably O2, H2O, HCl, SO<sub>2</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, and PM, from the two boiler flue gases were characterized, as presented in Table 1. Because the promotive effect of O2 and inhibitory role of H2O on the oxidation process has been widely studied and accepted, herein the effects of other flue gas components were concerned and discussed. The major components, such as the HCl, SO<sub>2</sub>, NO, NO2, NH3, and PM concentrations, exhibited significant different concentrations in the two tested boiler flue gases. Compared the flue gas components concentrations to mercury oxidation efficiencies over catalysts in the flue gas of two boilers, indicating that relatively higher concentrations of HF (3.3 ppm), NO (146 ppm) and NO<sub>2</sub> (4.0 ppm) in CGB flue gas might result in higher Hg<sup>0</sup> catalytic oxidation efficiencies, whereas high concentrations of SO<sub>2</sub> (937 ppm), NH<sub>3</sub> (1.9 ppm), and PM (13.4  $g/m^3$ ) in CFBB flue gas might result in

 
 Table 1. Flue Gas Temperature and Averages of Components Concentration

parameter/component	in CFBB	in CGB
temperature (°C)	138	127
$Hg^0 (\mu g/m^3)$	84	78
O <sub>2</sub> (%)	4.0	5.0
H <sub>2</sub> O (%)	6.6	5.9
HCl (ppm)	7.6	0.6
HF (ppm)	2.5	3.3
NO (ppm)	67	146
NO <sub>2</sub> (ppm)	0.1	4.0
SO <sub>2</sub> (ppm)	937	305
NH <sub>3</sub> (ppm)	1.9	0.1
PM before ESP/FF (g/m <sup>3</sup> )	13.4	8.4
PM after ESP/FF (g/m <sup>3</sup> )	0.004	0.006

lower catalytic oxidation efficiencies. Higher HCl concentrations generally result in better mercury oxidation performances.<sup>5,31</sup> HCl was a source of Cl<sup>-</sup> and Cl<sub>2</sub> through Deacon Reactions on the catalyst surface, and the reactive forms of chlorine could oxidize Hg<sup>0</sup> and would react favorably with ash components such as Na and Ca.<sup>16</sup> Although the CFBB flue gas exhibited a higher HCl concentration it did not exhibit a higher mercury oxidation efficiency. One possible explanation was, for the CFBB flue gas that having relatively high contents of Ca and Na, the reactive forms of Cl were likely consumed by Ca and Na, whereas in the CGB flue gas there was much less Na and Ca, leaving more reactive Cl to oxidize the Hg<sup>0</sup>. The above results therefore implied that some flue gas components, such as HCl, HF, NO, and NO<sub>2</sub>, enhanced mercury oxidation, whereas SO<sub>2</sub> and NH<sub>3</sub>, exhibited inhibitory effects on the oxidation of elemental mercury.

However, gaseous components of flue gas could only partly explain the observed differences of elemental mercury oxidation efficiency between the two boilers. The differences in concentration and composition of PM in the flue gas before and after ESP/FF might be more significant contributory factors. According to the tests before and after ESP/FF, the PM concentration in the CFBB flue gas before ESP was 13.4  $g/m^3$ , which was higher than that in the CGB flue gas before FF (8.4  $g/m^3$ ). In addition, the PM concentration in the CFBB flue gas after ESP was 0.004  $g/m^3$ , which was a little lower than that in the CGB flue gas after FF (0.006  $g/m^3$ ). Correspondingly, the mercury oxidation efficiencies in the CFBB flue gas before ESP (65%) were lower than those in the CGB flue gas before FF (73%). In addition, the mercury oxidation efficiencies in the CFBB flue gas after ESP (83%) were still lower than those in the CGB flue gas after FF (87%). Comparisons of the mercury catalytic oxidation performances and the PM concentrations in the flue gases before and after ESP/FF indicated that a higher PM content before ESP/FF resulted in a much lower oxidation efficiency. In contrast, a lower PM content after ESP/FF did not exhibit a higher oxidation efficiency. Many studies reported various combustion-induced PM concentrations in different coal combustion flue gases at varying chemical species proportions.<sup>38,39</sup> In general, particulate matter in flue gas plugged catalyst pores, and the active ingredient of PM reacted with the active phases of the catalysts.<sup>4</sup> Based on the results, it implied that the catalytic oxidation performance in high PM content before the precipitator was significantly affected by the surface cover of PM, whereas the oxidation efficiency at low PM levels after the precipitator did not appear to be directly

related to the PM concentration. Other dominant factors required further investigation.

**3.4. Chemical Species of PM.** To gain more insights on the effects of active ingredients in PM on the catalytic activity, further studies on the major chemical species of PM, including carbonaceous materials, such as OC and EC, elements (Na, Mg, K, Ca, Al, Fe, Si, and S), and ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>), were conducted. For convenient comparison to the aforementioned PM concentrations, the absolute concentrations of PM chemical species were converted and presented in Table 2, wherein the OC, EC, alkali (earth) metals (Na, Mg, K,

Table 2. Concentration	n of PM	Chemical	Species
------------------------	---------	----------	---------

	in CFBB		in CGB	
chemical species	before ESP (g/m <sup>3</sup> )	after ESP (mg/m <sup>3</sup> )	before FF (g/m <sup>3</sup> )	after FF (mg/m <sup>3</sup> )
EC	1.86	0.80	2.07	1.28
OC	2.89	0.67	1.55	0.52
Na	0.27	0.06	0.02	0.01
Mg	0.04	0.02	0.02	0.01
K	0.32	0.09	0.07	0.04
Ca	0.24	0.06	0.08	0.02
Al	0.64	0.14	0.17	0.04
Fe	0.20	0.06	0.06	0.03
Si	0.48	0.22	0.66	0.10
S	0.60	0.25	0.39	0.77
Cl <sup>-</sup>	0.35	0.06	0.11	0.01
$NO_3^-$	0.03	0.01	0.08	0.01
SO4 <sup>2-</sup>	1.50	0.61	0.76	2.12
$\mathrm{NH_4}^+$	0.29	0.17	0.15	0.19

and Ca) and salts were widely present in the collected PM. With the exception of OC, EC, and the alkaline (earth) metals, such as Na, Mg, K, and Ca, the concentrations of the remaining PM chemical species were not consistent with the mercury oxidation efficiencies. Based on these findings, the closely related species were the focus of further investigation.

The results of absolute concentration of EC before and after FF in the CGB flue gas  $(2.07 \text{ g/m}^3 \text{ and } 1.28 \text{ mg/m}^3)$ , respectively) were higher than those before and after ESP in the CFBB flue gas  $(1.86 \text{ g/m}^3 \text{ and } 0.80 \text{ mg/m}^3, \text{ respectively})$ , indicating that the EC of PM in flue gases of both boilers be well consistent with the mercury oxidation efficiency. The coal burning-derived EC particles were reported in the form of honeycombs and played as reaction beds or catalysts toward those adsorbed air pollutants.<sup>35</sup> According to the mercury oxidation performances in the flue gas of the two boilers, the EC significantly affected the mercury catalytic oxidation process and improved the elemental mercury oxidation efficiency due to its adsorption. Additionally, the result of absolute concentration of OC in both boiler flue gases presented opposite features as that compared to the EC, which implied the OC in the boiler flue gas might negatively affect the catalytic oxidation activity over the catalysts. It was considered that the carbonaceous matter was involved in most of the interactions between mercury and fly ash, and the organic matter played an important role in Hg<sup>0</sup> retention,<sup>40</sup> thereby inhibited the mercury oxidation process as observed in the field tests.

According to the remaining chemical species in Table 2, the Na, Mg, K, and Ca concentrations in flue gas between the two boilers differed significantly and exhibited opposite profiles as

compared to the EC. The absolute concentrations of Na, Mg, K, and Ca in the CGB flue gas were obviously lower than those in the CFBB flue gas, respectively. In addition, the concentrations of Na, Mg, K, and Ca after ESP/FF (in magnitude of  $mg/m^3$ ) were also much lower than those before ESP/FF (in magnitude of  $g/m^3$ ) in both boiler flue gases, respectively. Compared to the mercury catalytic oxidation efficiencies, the results exhibited that the Na, Mg, K, and Ca concentrations in flue gas of both boilers were negatively correlated with the mercury oxidation efficiencies. The alkali (earth) metals and salts were also reported as major dust components that could strongly decrease the catalytic activity.<sup>41</sup> Research indicated that the deactivation effects caused by alkali (earth) metals over the SCR catalysts were well-associated with the alkalinity value and were presence in the sequence as K > Na  $\sim$  Ca > Mg, thereby also illustrating that the deactivation effects increased proportionately with the alkali (earth) metal amounts.<sup>41</sup> The similarities in the observed results also evinced the significance of the alkali (earth) metals (Na, Mg, K, and Ca) of PM on the elemental mercury catalytic oxidation activity in real flue gas of coal-fired boilers, and in this study, these alkali (earth) metals exhibited obvious deactivating effects on the catalytic oxidation of elemental mercury.

Based on the combined mercury catalytic oxidation performances and the effects of PM, it might be concluded that in the high PM concentration flue gases before the dust removal, mercury catalytic oxidation activities were negatively affected by the PM concentration, which was attributed to the surface coverage by the large amount of PM, whereas in the low PM concentration flue gases after the dust removal, the PM concentrations in different boiler flue gases failed in determining the mercury oxidation efficiency, wherein the chemical species of PM, such as EC, OC and alkali (earth) metals (Na, Mg, K, and Ca), dominated the catalytic oxidation of elemental mercury.

## AUTHOR INFORMATION

## **Corresponding Author**

\*Phone: +86-010-6277 1403; fax: +86-010-6277 3650; e-mail: lduan@tsinghua.edu.cn.

## ORCID 💿

Qi Wan: 0000-0002-9366-8805 Lei Duan: 0000-0001-9965-4618 Xinghua Li: 0000-0003-0187-7720

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This study was supported by the National Key Research and Development Program of China (2017YFC0210500), the National Basic Research Program of China (2013CB430000), and the Fundamental Research Funds for the Central Universities (2018MS036).

#### REFERENCES

(1) Pacyna, E. G.; Pacyna, J. M.; Sundseth, K.; Munthe, J.; Kindbom, K.; Wilson, S.; Steenhuisen, F.; Maxson, P. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* **2010**, *44* (20), 2487–2499.

(2) Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason, R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G.; Telmer, K. Global mercury emissions to the atmosphere from

anthropogenic and natural sources. Atmos. Chem. Phys. 2010, 10 (13), 5951-5964.

(3) Wu, Y.; Wang, S. X.; Streets, D. G.; Hao, J. M.; Chan, M.; Jiang, J. K. Trends in anthropogenic mercury emissions in China from 1995 to 2003. *Environ. Sci. Technol.* **2006**, *40* (17), 5312–5318.

(4) Pavlish, J. H.; Sondreal, E. A.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A. Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **2003**, 82 (2–3), 89–165.

(5) Presto, A. A.; Granite, E. J. Survey of catalysts for oxidation of mercury in flue gas. *Environ. Sci. Technol.* **2006**, *40* (18), 5601–5609. (6) You, C. F.; Xu, X. C. Coal combustion and its pollution control in China. *Energy* **2010**, *35* (11), 4467–4472.

(7) Ministry of Environmental Protection of the People's Republic of China. http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqgdwrywrwpfbz/201109/t20110921 217534.htm.

(8) U.S. Environmental Protection Agency Website; https://www.epa. gov/mats/regulatory-actions-final-mercury-and-air-toxics-standardsmats-power-plants.

(9) Yang, H. Q.; Xu, Z. H.; Fan, M. H.; Bland, A. E.; Judkins, R. R. Adsorbents for capturing mercury in coal-fired boiler flue gas. *J. Hazard. Mater.* **2007**, *146* (1–2), 1–11.

(10) Xu, H.; Qu, Z.; Zong, C.; Quan, F.; Mei, J.; Yan, N. Catalytic oxidation and adsorption of  $Hg^0$  over low-temperature  $NH_3$ -SCR LaMnO<sub>3</sub> perovskite oxide from flue gas. *Appl. Catal., B* **2016**, *186*, 30–40.

(11) He, S.; Zhou, J.; Zhu, Y.; Luo, Z.; Ni, M.; Cen, K. Mercury oxidation over a vanadia-based selective catalytic reduction catalyst. *Energy Fuels* **2008**, *23* (1), 253–259.

(12) Yan, N. Q.; Chen, W. M.; Chen, J.; Qu, Z.; Guo, Y. F.; Yang, S. J.; Jia, J. P. Significance of RuO<sub>2</sub> modified SCR catalyst for elemental mercury oxidation in coal-fired flue gas. *Environ. Sci. Technol.* **2011**, 45 (13), 5725–5730.

(13) Granite, E. J.; Pennline, H. W.; Hargis, R. A. Photochemical removal of mercury from flue gas. *Ind. Eng. Chem. Res.* **2002**, *41*, 5470–5476.

(14) O'Dowd, W. J.; Hargis, R. A.; Granite, E. J.; Pennline, H. W. Recent advances in mercury removal technology at the National Energy Technology Laboratory. *Fuel Process. Technol.* **2004**, 85 (6–7), 533–548.

(15) 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. *Int. J. Coal Geol.* **2012**, *90*, 4–20.

(16) Gao, Y. S.; Zhang, Z.; Wu, J. W.; Duan, L. H.; Umar, A.; Sun, L. Y.; Guo, Z. H.; Wang, Q. A critical review on the heterogeneous catalytic oxidation of elemental mercury in flue gases. *Environ. Sci. Technol.* **2013**, 47 (19), 10813–10823.

(17) Lee, W.; Bae, G. N. Removal of elemental mercury (Hg(0)) by nanosized  $V_2O_5/TiO_2$  catalysts. *Environ. Sci. Technol.* **2009**, 43 (5), 1522–1527.

(18) Kamata, H.; Ueno, S-i.; Naito, T.; Yukimura, A. Mercury oxidation over the  $V_2O_5(WO_3)/TiO_2$  commercial SCR catalyst. *Ind. Eng. Chem. Res.* **2008**, *47*, 8136–8141.

(19) Wang, Y. Y.; Shen, B. X.; He, C.; Yue, S. J.; Wang, F. M. Simultaneous removal of NO and Hg-0 from flue gas over Mn-Ce/Ti-PILCs. *Environ. Sci. Technol.* **2015**, 49 (15), 9355–9363.

(20) Li, H. L.; Wu, S. K.; Wu, C.-Y.; Wang, J.; Li, L. Q.; Shih, K. M. SCR atmosphere induced reduction of oxidized mercury over CuO-CeO<sub>2</sub>/TiO<sub>2</sub> catalyst. *Environ. Sci. Technol.* **2015**, *49* (12), 7373–7379. (21) Fan, X. P.; Li, C. T.; Zeng, G. M.; Zhang, X.; Tao, S. S.; Lu, P.; Tan, Y.; Luo, D. Q. Hg-0 removal from simulated flue gas over CeO<sub>2</sub>/HZSM-5. *Energy Fuels* **2012**, *26* (4), 2082–2089.

(22) Wen, X. Y.; Li, C. T.; Fan, X. P.; Gao, H. L.; Zhang, W.; Chen, L.; Zeng, G. M.; Zhao, Y. P. Experimental study of gaseous elemental mercury removal with  $CeO_2/gamma-Al_2O_3$ . *Energy Fuels* **2011**, 25 (7), 2939–2944.

## **Environmental Science & Technology**

(23) Liu, X. W.; Zhou, K. B.; Wang, L.; Wang, B. Y.; Li, Y. D. Oxygen vacancy clusters promoting reducibility and activity of ceria nanorods. *J. Am. Chem. Soc.* **2009**, *131* (9), 3140–3141.

(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. *J. Phys. Chem. C* 2011, 115 (49), 24300–24309.

(25) Wan, Q.; Duan, L.; He, K. B.; Li, J. H. Removal of gaseous elemental mercury over a CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> nanocomposite in simulated coal-fired flue gas. *Chem. Eng. J.* **2011**, *170* (2–3), 512–517.

(26) China Guodian, Jiangsu Longyuan Catalyst Co., Ltd. http://www.jslychj.cn/hxyw.aspx?cateid=66.

(27) Li, X.; Wang, S.; Duan, L.; Hao, J.; Li, C.; Chen, Y.; Yang, L. Particulate and trace gas emissions from open burning of wheat straw and corn stover in China. *Environ. Sci. Technol.* **2007**, *41* (17), 6052–6058.

(28) Zhang, L.; Wang, S.; Wu, Q.; Wang, F.; Lin, C.; Zhang, L.; Hui, M.; Yang, M.; Su, H.; Hao, J. Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review. *Atmos. Chem. Phys.* **2016**, *16* (4), 2417–2433.

(29) Li, Y.; Murphy, P. D.; Wu, C. Y.; Powers, K.; Bonzongo, J. C. Development of silica/vanadia/titania catalysts for removal of elemental mercury from coal-combustion flue gas. *Environ. Sci. Technol.* **2008**, 42 (14), 5304–5309.

(30) Straube, S.; Hahn, T.; Koeser, H. Adsorption and oxidation of mercury in tail-end SCR-DeNOx plants - Bench scale investigations and speciation experiments. *Appl. Catal., B* **2008**, *79*, 286–295.

(31) Dranga, B. A.; Lazar, L.; Koeser, H. Oxidation catalysts for elemental mercury in flue gases - a review. *Catalysts* **2012**, *2* (1), 139–170.

(32) Silversmit, G.; Depla, D.; Poelman, H. Determination of the V2p XPS binding energies for different vanadium oxidation states ( $V^{5+}$  to  $V^{0+}$ ). *J. Electron Spectrosc. Relat. Phenom.* **2004**, *135* (2–3), 167–175.

(33) Benjaram, M.; Ataullah, K.; Yusuke, Y.; Tetsuhiko, K.; Stephane, L.; Jean-Claude, V. Structural characterization of  $CeO_2$ -Ti $O_2$  and  $V_2O_5/CeO_2$ -Ti $O_2$  catalysts by Raman and XPS techniques. *J. Phys. Chem. B* **2003**, *107*, 5162–5167.

(34) Reddy, B. M.; Lakshmanan, P.; Khan, A. Investigation of surface structures of dispersed  $V_2O_5$  on CeO<sub>2</sub>-SiO<sub>2</sub>, CeO<sub>2</sub>-TiO<sub>2</sub>, and CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides by XRD, Raman, and XPS techniques. *J. Phys. Chem. B* **2004**, *108* (43), 16855–16863.

(35) He, C.; Shen, B. X.; Chen, J. H.; Cai, J. Adsorption and oxidation of elemental mercury over Ce-MnOx/Ti-PILCs. *Environ. Sci. Technol.* **2014**, 48 (14), 7891–7898.

(36) Chen, L.; Li, J.; Ge, M.; Zhu, R. Enhanced activity of tungsten modified  $CeO_2/TiO_2$  for selective catalytic reduction of NOx with ammonia. *Catal. Today* **2010**, *153* (3–4), 77–83.

(37) Kang, M.; Park, E. D.; Kim, J. M.; Yie, J. E. Manganese oxide catalysts for NOx reduction with  $NH_3$  at low temperatures. *Appl. Catal., A* **2007**, 327 (2), 261–269.

(38) Duan, L.; Xiu, G.; Feng, L.; Cheng, N.; Wang, C. The mercury species and their association with carbonaceous compositions, bromine and iodine in  $PM_{2.5}$  in Shanghai. *Chemosphere* **2016**, *146*, 263–271.

(39) Lee, S. J.; Seo, Y. C.; Jang, H. N.; Park, K. S.; Baek, J. I.; An, H. S.; Song, K. C. Speciation and mass distribution of mercury in a bituminous coal-fired power plant. *Atmos. Environ.* **2006**, 40 (12), 2215–2224.

(40) Abad-Valle, P.; Lopez-Anton, M. A.; Diaz-Somoano, M.; Martinez-Tarazona, M. R. The role of unburned carbon concentrates from fly ashes in the oxidation and retention of mercury. *Chem. Eng. J.* **2011**, 174 (1), 86–92.

(41) Chen, L.; Li, J. H.; Ge, M. F. The poisoning effect of alkali metals doping over nano  $V_2O_5$ -WO<sub>3</sub>/TiO<sub>2</sub> catalysts on selective catalytic reduction of NOx by NH<sub>3</sub>. *Chem. Eng. J.* **2011**, 170 (2–3), 531–537.