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# Removal of elemental mercury from simulated coal-combustion flue gas using a SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite

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# ABSTRACT

A novel silica-titania (SiO<sub>2</sub>-TiO<sub>2</sub>) nanocomposite has been developed to effectively capture elemental mercury (Hg<sup>0</sup>) under UV irradiation. Previous studies under room conditions showed over 99% Hg<sup>0</sup> removal efficiency using this nanocomposite. In this work, the performance of the nanocomposite on Hg<sup>0</sup> removal was tested in simulated coal-fired power plant flue gas, where water vapor concentration is much higher and various acid gases, such as HCl, SO<sub>2</sub>, and NO<sub>x</sub>, are present. Experiments were carried out in a fix-bed reactor operated at 135 °C with a baseline gas mixture containing 4%  $O_2,\,12\%$   $CO_2,\,and$  8%  $H_2O$  balanced with  $N_2$ . Results of Hg speciation data at the reactor outlet demonstrated that  $Hg^0$  was photocatalytically oxidized and captured on the nanocomposite. The removal efficiency of Hg<sup>0</sup> was found to be significantly affected by the flue gas components. Increased water vapor concentration inhibited Hg<sup>0</sup> capture, due to the competitive adsorption of water vapor. Both HCl and SO<sub>2</sub> promoted the oxidation of Hg<sup>0</sup> to Hg(II), resulting in higher removal efficiencies. NO was found to have a dramatic inhibitory effect on Hg<sup>0</sup> removal, very likely due to the scavenging of hydroxyl radicals by NO. The effect of NO2 was found to be insignificant. Hg removal in flue gases simulating low rank coal combustion products was found to be less than that from high rank coals, possibly due to the higher H<sub>2</sub>O concentration and lower HCl and SO<sub>2</sub> concentrations of the low rank coals. It is essential, however, to minimize the adverse effect of NO to improve the overall performance of the SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite.

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# 1. Introduction

As a highly toxic pollutant, mercury (Hg) tends to bioaccumulate in the food chain and exerts adverse effects on human health [1]. Coal-fired utility boilers are currently the largest single-known source of anthropogenic Hg emissions in the United States, accounting for approximately one-third of the 150 tons of mercury emitted annually [2]. In 2005, the U.S. EPA issued the Clean Air Mercury Rule (CAMR) to permanently cap and reduce Hg emissions from coal-fired power plants [3]. CAMR will be implemented in two phases, with a first phase cap of 38 tons in 2010 followed by a final cap of 15 tons in 2018 (approximately 70% reduction from 1999 emission levels). Consequently, various technologies have been developed to offer high levels of Hg control for utility boilers burning different types of coals. Mercury speciation studies showed that elemental mercury (Hg<sup>0</sup>) is the dominant species present in flue gas when burning low rank (subbituminous or lignite) coals. However, oxidized mercury [Hg(II)] is preferable to Hg<sup>0</sup> in that Hg(II) is water soluble and is readily collected in air

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pollution control devices (APCDs) such as  $SO_2$  scrubbers. Thus, the need exists for a low cost Hg oxidation/capturing process that can be applied for flue gas treatment.

A novel methodology using titanium dioxide (TiO<sub>2</sub>) nanoparticles as a photocatalyst has been recently developed to effectively remove  $Hg^0$  [4–10]. Under ultraviolet (UV) irradiation, hydroxyl (OH) radicals can be generated on the surface of TiO<sub>2</sub> and then oxidize  $Hg^0$  into mercury oxide (HgO), which is retained on the particle surface due to its low vapor pressure [9]. The reaction mechanism is described as follows [5,6]:

$$TiO_2 + hv \rightarrow e^- + h^+$$
 [R1]

$$H_2O \leftrightarrow H^+ + OH^-$$
 [R2]

$$h^+ + OH^- \rightarrow \cdot OH$$
 [R3]

 $h^+ + H_2 O \rightarrow \cdot OH + H^+$  [R4]

$$OH \cdot +Hg^0 \xrightarrow{\text{overall}} HgO$$
 [R5]

Removal of  $Hg^0$  has been achieved using photocatalysts in the form of either in-situ generated  $TiO_2$  particles [4,9] or a high surface area silica gel doped with  $TiO_2$  nanoparticles ( $SiO_2$ - $TiO_2$  nanocomposite) [5–8]. The  $SiO_2$ - $TiO_2$  nanocomposite is advantageous due to its high surface area and open structure, which allows effective irradiation by UV light and thus minimizes the mass-transfer resistance for  $Hg^0$  [7].

The efficiency of  $Hg^0$  removal using a SiO<sub>2</sub>–TiO<sub>2</sub> nanocomposite was able to reach 99% at low relative humidity at room temperature [7]. However, studies conducted at room temperature but higher water vapor concentrations (up to 23,000 ppm<sub>v</sub>)

demonstrated that  $Hg^0$  capturing on the nanocomposite was hindered by the competitive adsorption of water vapor on the active sites, and the extent of decrease in Hg<sup>0</sup> removal was proportional to the water vapor concentration [5,6]. It should be noted that in coal-fired boiler flue gas, the concentration of water vapor typically accounts for 6 to 12% in volume, much higher than that at normal room conditions. Thus, it is expected that water vapor may have a greater inhibitory effect on Hg<sup>0</sup> removal in flue gas. One the other hand, the catalyst developed in this work was designed for application at the cold-end of the boiler convective pass (e.g. between the electrostatic precipitator and the wet scrubber), where the typical flue gas temperature is in the range of 120 to 150 °C. Because adsorption of water vapor is favored at lower temperature, it is expected that the inhibitory effect of a certain concentration of water vapor would be less significant at flue gas temperature than at room temperature. These two counteracting effects warrant further investigation on the performance of the SiO2-TiO2 nanocomposite for  $\mathrm{Hg}^{\mathrm{0}}$  removal in flue gas at higher water vapor concentrations and process temperature.

Typical coal-derived flue gas consists of various trace gas components such as HCl, SO<sub>2</sub>, and NO<sub>x</sub>. Their concentrations are dependent on the type of coal burned, coal firing systems, boiler operating conditions, and/or NO<sub>x</sub> control processes. It has been reported that these trace gases are important to the heterogeneous adsorption and/or oxidation of Hg<sup>0</sup> on activated carbons or fly ash under flue gas conditions [11,12]. Carey et al. [11] reported that the adsorption capacity for both Hg<sup>0</sup> and HgCl<sub>2</sub> by Darco FGD carbon dramatically increases as HCl concentration increases from 0 to 50 ppm<sub>v</sub>. Norton et al. [12] reported that in the presence of fly ash, NO<sub>2</sub>, HCl, and



Fig 1-Schematic diagram of the experimental system.

 $SO_2$  result in greater levels of Hg oxidation, while NO inhibits Hg oxidation. It is expected that the nature of Hg capture on the  $SiO_2$ -TiO<sub>2</sub> nanocomposite would be different under flue gas conditions from that reported under room conditions in

our previous studies [5,6]. In this work, a photocatalytic reactor packed with SiO<sub>2</sub>– TiO<sub>2</sub> nanocomposite was installed. The goal of this research was to investigate the oxidation and capture of Hg<sup>0</sup> by the SiO<sub>2</sub>–TiO<sub>2</sub> nanocomposite under flue gas conditions and to identify the effects of individual flue gas components on Hg<sup>0</sup> removal. An improved understanding of the role of the flue gas components on Hg<sup>0</sup> oxidation can help evaluate the potential of applying this novel material as an effective Hg emission control strategy for coal-fired power plants.

# 2. Experimental methods

#### 2.1. Synthesis of the SiO<sub>2</sub>–TiO<sub>2</sub> nanocomposite

The SiO<sub>2</sub>–TiO<sub>2</sub> nanocomposite was made by a sol–gel method using deionized water, ethanol and tetraethyl orthosilicate (TEOS). Nitric acid (HNO<sub>3</sub>) and hydrogen fluoride (HF) were used as catalysts to increase the hydrolysis and condensation rates. A detailed procedure has been described in our previous study [6]. The nanocomposite was prepared in the form of cylindrical pellets approximately 5 mm in length and 3 mm in diameter. The weight fraction of TiO<sub>2</sub> in the prepared SiO<sub>2</sub>–TiO<sub>2</sub> pellets was approximately 12%, which corresponded to the optimum performance of Hg<sup>0</sup> removal at room conditions [7]. The average BET (Brunauer, Emmett, and Teller equation) surface area of the nanocomposite was measured to be 280 m<sup>2</sup> g<sup>-1</sup> using a Quantachrome NOVA 1200 Gas Sorption Analyzer (Boynton Beach, FL).

#### 2.2. Experimental setup and procedure

A schematic diagram of the experimental setup is shown in Fig. 1. The simulated flue gas consisted of three major gases: O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>. The N<sub>2</sub> flow was divided into three branches. One of the N<sub>2</sub> streams converged with the  $O_2$  and  $CO_2$  to form the main gas flow, which was allowed to pass through a heated water bubbler to introduce water vapor into the system. The second stream of N<sub>2</sub> served to dilute the main flow so as to adjust the humidity of the total gas stream. The third stream of N<sub>2</sub> passed through a Dynacal® Hg<sup>0</sup> permeation tube (VICI Metronics) and introduced the saturated Hg<sup>0</sup> vapor into the system. The permeation tube was placed in a U-shape glass tube which was immersed in a constanttemperature (90 $\pm$ 0.2 °C) water bath to ensure a constant Hg<sup>0</sup> permeation rate. Hg<sup>0</sup> concentration in the system was controlled in the range of 75  $\sim$  80  $\mu g$  m  $^{-3}.$  Minor gases including HCl, SO<sub>2</sub>, NO, and NO<sub>2</sub> were introduced into the main flow individually or in combination. Mass flow controllers (MFCs) were used to control each of the gas flows, with a total gas flow rate controlled at 2.0 L/ min. The gas concentrations were designed to be within the range of typical coal-fired flue gas composition [13]: 4% O2, 12% CO2,  $4 \sim 16\%$  H<sub>2</sub>O,  $10 \sim 50$  ppm<sub>v</sub> HCl,  $400 \sim 1200$  ppm<sub>v</sub> SO<sub>2</sub>,  $50 \sim 300$  ppm<sub>v</sub> NO,  $10 \sim 30$  ppm<sub>v</sub> NO<sub>2</sub>, and balanced with N<sub>2</sub>. The experimental conditions for investigation of the flue gas effects are listed in Table 1.

Downstream of all the gas flows is the packed-bed photocatalytic reactor placed horizontally. The  $SiO_2$ -TiO<sub>2</sub> pellets were packed in a U-shape quartz tube with an inner diameter of 13 cm. A heating cord was wrapped around the U-tube so that the flue gas temperature can be controlled at around 135 °C, which was monitored by a Teflon thermocouple (Type K, Omega). A UV lamp Table 1 – Experimental conditions for investigation of the flue gas effects\*

	H <sub>2</sub> O (%)	HCl (ppm)	SO <sub>2</sub> (ppm)	NO (ppm)	NO <sub>2</sub> (ppm)
Set 1 (baseline)	8	-	-	-	-
Set 2	0, 4, 12, 16				
Set 3	8	10, 30, 50	-	-	-
Set 4	8	-	400, 800, 1200	-	-
Set 5	8	-	-	50, 100, 300	-
Set 6	8	-	-	-	10, 20, 30
Set 7 (Flue Gas 1)	8	30	1200	300	10
Set 8 (Flue Gas 2)	12	10	400	300	10

 $^*$  All the conditions contained 4% O<sub>2</sub>, 12% CO<sub>2</sub>, 75  $\sim$  80  $\mu g$  m $^{-3}$  Hg $^0$  (inlet), and balanced with N<sub>2</sub>; the temperature was controlled at approximately 135 °C.

wavelength of 365 nm with an intensity of 4 mW/cm<sup>2</sup> measured by a UVX radiometer (with a UVX-36 sensor probe). A stream of cooling air was continuously purged through the UV lamp to lower the lamp temperature to around 60 °C. The entire reactor was placed inside an aluminum cylinder so that the UV light could be reflected back to the pellets and a maximum utilization of the UV energy could be achieved.

A wet-chemistry conversion system [14,15] and a RA-915+Hg analyzer (OhioLumex) were used to measure gas-phase Hg speciation (Hg<sup>0</sup> and Hg(II)) downstream the reactor. The Hg analyzer is based on Zeeman Atomic Absorption Spectrometry (ZAAS), which is selective only for  $Hg^0$ . In the conversion system, the sampling gas was divided into two streams, one for measuring  $Hg^0$  and the other for total Hg ( $Hg^T$ ). The solution used for  $Hg^0$ measurement consisted of 10% potassium chloride (KCl), which captures Hg(II) and allows only Hg<sup>0</sup> to pass through. Hg<sup>T</sup> measurement was accomplished using an acidic 10% stannous chloride (SnCl<sub>2</sub>) solution, which reduces Hg(II) to Hg<sup>0</sup>, thus producing Hg<sup>T</sup>. The concentration of Hg(II) can then be calculated by the difference between  $Hg^{T}$  and  $Hg^{0}$ . The two streams converged to a 10% sodium hydroxide (NaOH) solution before entering the Hg analyzer. The NaOH solution captured acid gases, such as HCl and SO<sub>2</sub>, to prevent corrosion of the detecting cell in the Hg analyzer. In addition, as part of the conversion process, a NaOH solution was used to remove SO<sub>2</sub> before the sampling gas entered the SnCl<sub>2</sub> solution, as SO<sub>2</sub> can interfere with the reduction of Hg(II) by SnCl<sub>2</sub> [15]. A condenser was installed upstream of the Hg analyzer to remove excess moisture in the gas stream. This aimed to avoid condensation of water vapor inside the Hg detection cell and thus to minimize possible interference from water vapor. The Hg analyzer is capable of providing a real-time response every 1 s. The calibration of the Hg analyzer was conducted by the manufacturer using a Dynacal® permeation device. In this study, the high-concentration mode of the Hg analyzer was used (with a detection limit of 0.5  $\mu g \ m^{-3}$  and an upper measurable concentration of 200  $\mu$ g m<sup>-3</sup>). Finally, the gas stream was passed through a carbon trap before it was exhausted into the fume hood. The entire system was Teflon lined. To avoid condensation of the water vapor along the pathway, all the lines before the condenser were heated by heating tapes to above 90 °C.

#### 3. Results and discussion

### 3.1. Baseline test

Tests were first conducted to examine any possible interference caused by the flue gas components on the measurements by the Hg analyzer. Balanced with pure N<sub>2</sub>, 8% H<sub>2</sub>O, 50 ppm<sub>v</sub> HCl, 1200 ppm<sub>v</sub> SO<sub>2</sub>, 300 ppm<sub>v</sub> NO, and 30 ppm<sub>v</sub> NO<sub>2</sub> were individually introduced to the system without the presence of Hg. In all cases, no significant Hg readings were observed (i.e. the interference was less than the detection limit,  $0.5 \,\mu g \, m^{-3}$ ) with or without UV irradiation. This indicated negligible interference by the flue gas components in the concentration ranges studied in this paper. In addition, tests were performed by introducing 80  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup> to an empty reactor (i.e. no catalyst) without UV irradiation for 2 h and subsequently with UV irradiation for another 2 h. Without UV, Hg<sup>0</sup> concentration remained constant with a small fluctuation (± 3%), which is probably associated with the errors of the Hg permeation device and the Hg analyzer. With UV, averagely less than 0.5% reduction in Hg<sup>0</sup> concentration was observed compared to without UV. These testes indicated that the loss of Hg<sup>0</sup> on the reactor wall was negligible either with or without UV irradiation.

Before examining the effect of individual flue gas components, a baseline test without the trace gases (Set 1) was first conducted. While a larger amount of  $SiO_2$ -TiO<sub>2</sub> pellets could be used to achieve a Hg removal efficiency greater than 90%, only 8 g of pellets (~ 1 g TiO<sub>2</sub>) were used to better manifest possible enhancement by the minor gases in subsequent tests. As shown in Fig. 2, the inlet Hg concentration was measured within the first 10 min when the gas stream bypassed the reactor (Period A). Next, the gas stream was passed through the reactor without UV light for another 10 min (Period B) and then the UV light was turned on to activate the photocatalytic reaction (Period C). The concentrations of Hg<sup>T</sup> and Hg<sup>0</sup> at the outlet of the reactor were recorded in alternation and were averaged every 2 min for Periods A and B and every 10 min for Period C.

In Period A, the concentration of Hg<sup>T</sup> was equal to that of Hg<sup>0</sup>, confirming that the Hg source in this study was only Hg<sup>0</sup>. In Period B when the gas passed through the reactor, the outlet Hg concentration first dropped by approximately 10%, probably due to the physical adsorption by the porous SiO<sub>2</sub>-TiO<sub>2</sub> pellets. However, it quickly recovered to the same level of the inlet concentration indicating the adsorption was saturated. A significant decrease in Hg concentration was detected only when the UV light was turned on in Period C. The concentration of Hg<sup>T</sup> dropped to 59% of the inlet level during the first 10 min of UV irradiation and slowly decreased to 53% in the next 80 min. At 100 min, the rate of the decrease of Hg<sup>T</sup> was approaching zero, and thus it was assumed that the performance of the catalyst reached a relatively stable level at this point. At 100 min, the outlet concentration of Hg<sup>0</sup> decreased to 34% of the inlet Hg<sup>0</sup> level while Hg(II) slowly increased to 19%. The efficiency of Hg capture on the pellets can be expressed as:

$$E_{cap}(\%) = \frac{Hg_{in}^{T} - Hg_{out}^{T}}{Hg_{in}^{T}} \times 100\%$$
<sup>(1)</sup>



Fig 2 – Hg speciation at the outlet of the reactor in the baseline test.

where  $Hg_{in}^{T}$  and  $Hg_{out}^{T}$  represent  $Hg^{T}$  at the inlet and outlet of the reactor, respectively. Since the inlet Hg source is 100%  $Hg^{0}$ and negligible  $Hg^{0}$  capture was observed without UV, it is reasonable to assume that the captured Hg species under UV irradiation was only Hg(II) due to the photocatalytic oxidation. Hence, the efficiency of  $Hg^{0}$  oxidation can be expressed as:

$$E_{oxi}(\%) = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \times 100\%$$
(2)

where  $Hg_{in}^0$  and  $Hg_{out}^0$  represent  $Hg^0$  at the inlet and outlet of the reactor, respectively. It should be noted that  $Hg_{in}^T$  was equal to  $Hg_{in}^0$  in this study. In the baseline test,  $E_{oxi}$  was calculated to be 66%, while  $E_{cap}$  was 47% and the rest (19%) of the Hg(II) passed through the reactor.

# 3.2. Effects of individual flue gas components

The effects of individual flue gas components were examined and the results were compared with the baseline. At least two runs were performed at each of the experimental condition listed in Table 1. The average values of Hg capture ( $E_{cap}$ ) and oxidation ( $E_{oxi}$ ) efficiencies are calculated from Eqs. 1 and 2 and are illustrated in Fig. 3, where the error bars represent the envelope of minimum and maximum values.

An inhibitory effect of water vapor on Hg removal was observed as shown in Fig. 3a. Experiments were first conducted in a relatively dry condition (<0.1%) by bypassing the water bubbler and then in humid conditions, with increasing water vapor concentrations. The efficiencies of both Hg capture and oxidation reached over 99% in the relatively dry condition. In this case, the water vapor concentration, even though at a very low level, was still several orders of magnitude higher than Hg concentration, and thus enough OH radicals can be generated to oxidize Hg<sup>0</sup> [5]. As the water vapor concentration increased from 4% to 16% (baseline was 8%), the Hg capture efficiency decreased from 73% to 18%, and the Hg oxidation efficiency decreased from 88% to 32%. The inhibitory effect of water vapor is due to its competitive adsorption with  $Hg^0$  on the active sites [5,6], and as shown in Fig. 3a, the extent of inhibition on Hg removal is proportional

significant even at higher temperatures (135 °C in this work). It should also be noted that penetration of oxidized Hg from the reactor (i.e. the difference between Hg oxidized and captured) occurred in humid conditions (4–16% H<sub>2</sub>O) but not in the dry condition. This can be explained by the competitive adsorption of water vapor with the gas-phase oxidized Hg. It was reported in our previous study [5] that physically adsorbed Hg<sup>0</sup> can be desorbed from the surface of SiO<sub>2</sub>–TiO<sub>2</sub> composite by water vapor at high concentrations, which suggested that Hg<sup>0</sup> is only weakly adsorbed on the sorbent surface. Hence, it is very possible that a portion of the oxidized Hg, which is the product of the reaction between Hg<sup>0</sup> and OH radicals, existed in the gas phase in the vicinities of the reaction sites. In the dry condition, the oxidized Hg in the gas phase was adsorbed and, thus, there was no penetration. However, under humid conditions, water vapor competes with the oxidized Hg and consequently not all oxidized Hg in the gas phase can be adsorbed. The superhydrophilic surface of  $TiO_2$  after exposure to UV irradiation can further enhance the adsorption of water vapor [5,16–18] but reduce the capture of oxidized Hg. As a result, penetration of oxidized Hg was usually observed in humid conditions in this work.

The effect of HCl on Hg removal was found to be promotional (Fig. 3b). In the range of 10 to 50 ppm<sub>v</sub> HCl, Hg capture efficiency increased to approximately 75% and Hg oxidation efficiency increased to over 90%. However, the extent of promotion was not apparently related to the HCl concentration in the range studied. The promotional effect of HCl is consistent with reports in the literature that HCl promotes heterogeneous Hg oxidation [19]. It has been reported that in the presence of an appropriate catalyst (e.g. metal oxides), a Deacon process [20] could convert HCl in the flue gas to  $Cl_2$  at high temperatures (300–400 °C), thereby enhancing Hg<sup>0</sup> oxidation (or chlorination). Niksa et al. [21,22] proposed that Hg oxidation occurs via an Eley-Rideal mechanism, where adsorbed HCl reacts with gas-phase (or weakly



Fig 3–Effects of flue gas components on Hg capture and oxidation under various conditions of a) H<sub>2</sub>O, b) HCl, c) SO<sub>2</sub>, d) NO, e) NO<sub>2</sub>, and f) simulated flue gases.

adsorbed) Hg<sup>0</sup>; however, the specific reaction pathway was not given. The mechanism was also consistent with the observation of enhanced Hg<sup>0</sup> sorption to halogen-promoted sorbents and fly ashes in the literature [23,24]. In this work, the Deacon process was less likely to occur because of the relatively low flue gas temperature (135 °C). Instead, it is more likely to follow the Eley-Rideal mechanism, where HCl may first be adsorbed on the surface of SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite, and then react with gasphase Hg<sup>0</sup>. Parfitt et al. [25] conducted an infra-red study of HCl adsorption on rutile TiO2 surface and found an increase in surface OH groups due to the introduction of HCl. The OH groups can further react with excess HCl to form Cl and H<sub>2</sub>O. With the hypothesis that HCl adsorption on the SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite occurs following a similar pathway, the observed enhancing effect of HCl can be explained by the formation of additional Cl species on the surface which also contributes to Hg<sup>0</sup> oxidation. Further investigation is needed to identify the exact reaction mechanism.

As shown in Fig. 3c, SO<sub>2</sub> was found to have a promotional effect on Hg capture and oxidation and the promotion was proportional to the concentration of SO<sub>2</sub> in the range of  $0 \sim 1200$  ppm<sub>v</sub>. The Hg capture and oxidation efficiencies reached 73% and 91% respectively at 1200 ppm<sub>v</sub> SO<sub>2</sub>. The effect of SO<sub>2</sub> on heterogeneous Hg oxidation is not conclusive in the literature. It has been reported that SO<sub>2</sub> competes with HCl for sites on activated carbon and fly ash sorbents and, thus, inhibits mercury oxidation and adsorption in flue gas [26,27]. Carey et al. [11] reported that the adsorption capability of a Darco FGD carbon for both Hg<sup>0</sup> and HgCl<sub>2</sub> decreases as the  $SO_2$  concentration increases from 0 to 500 ppm<sub>v</sub> but neither capacity changes significantly above 500 ppm<sub>v</sub> SO<sub>2</sub>. However, in some cases,  $SO_2$  appears to enhance  $Hg^0$  oxidation [12,28]. Eswaran and Stenger reported a promotional effect of SO<sub>2</sub> on Hg<sup>0</sup> oxidation over a selective catalytic reduction (SCR) catalyst [28]. The mechanism was proposed as:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$
 [R6]

$$Hg + SO_3 + \frac{1}{2}O_2 \rightarrow HgSO_4$$
 [R7]

A similar mechanism can be used to explain the promotional effect of  $SO_2$  in this work, where  $SO_3$  could be formed through the oxidation of  $SO_2$  by OH radicals [29], which were generated on the  $SiO_2$ -TiO<sub>2</sub> pellets under UV irradiation.

The effect of NO on Hg removal was found to be inhibitory at a significant but relatively constant level in the concentration range of  $50 \sim 300 \text{ ppm}_{v}$  NO (Fig. 3d). The Hg capture and oxidation efficiencies both decreased to around 10% in the presence of NO. NO has been reported as an inhibitor for heterogeneous Hg<sup>0</sup> oxidation on fly ash [12], but the mechanism is not clear. In this study, it is very likely that the scavenging of OH radicals by NO hindered the photocatalytic oxidation of Hg<sup>0</sup>. The inhibition may have occurred via [30]

$$OH + NO + M \rightarrow HONO + M$$
 [R8]

In the presence of  $10 \sim 30 \text{ ppm}_v \text{NO}_2$ , the efficiencies of Hg capture and oxidation were slightly lower than those in the baseline (Fig. 3e). However, the effect of NO<sub>2</sub> in this range can be considered as insignificant compared to the other flue gas components. It has been reported in the literature that NO<sub>2</sub>

can enhance heterogeneous oxidation of Hg<sup>0</sup> in the presence of fly ash [12] or iron oxides [31,32], though this effect is often considered of minor importance compared to chlorination.

#### 3.3. Hg removal in simulated flue gases

The performance of the SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite was finally tested in two simulated flue gases, the compositions of which were in line with those reported in literature [33]. Flue Gas 1 (Set 7) represents flue gas from high rank (bituminous) coals that contain higher chlorine and sulfur content. Flue Gas 2 (Set 8) represents flue gas from low rank (subbituminous and lignite) coals, which contain less chlorine and sulfur but more moisture. As shown in Fig. 3f, Hg removal in the Flue Gas 1 was close to that in the baseline, indicating that the prohibitory effect of 300  $ppm_v$  NO counteracted the promotional effects of  $30~\text{ppm}_v$  HCl and  $1200~\text{ppm}_v$  SO\_2. Hg removal in the Flue Gas 2 was less than in the Flue Gas 1, very likely due to the higher concentration of  $H_2O$  and lower concentrations of HCl and  $SO_2$ . Hence, high rank coals are preferable to low rank coals for the application of the SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite. Minimizing the adverse effect of NO so as to improve the overall performance of the catalyst would be an important task for future research.

# 4. Conclusions

A novel SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite has been synthesized for the removal of  $Hg^0$  from simulated coal-fired power plant flue gas. The flue gas components were found to have significant effects on Hg removal efficiency in a fixed bed study. HCl and SO<sub>2</sub> promoted Hg oxidation and capture, while H<sub>2</sub>O and NO inhibited Hg removal and the effect of NO<sub>2</sub> was not significant. Experiments of Hg removal in simulated flue gases showed that high rank coals are preferable to low rank coals because of the lower moisture and higher HCl and SO<sub>2</sub> concentrations in the flue gas. It is essential, however, to minimize the adverse effect of NO to improve the catalytic performance of the SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite.

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