

SCR Atmosphere Induced Reduction of Oxidized Mercury over CuO–CeO₂/TiO₂ Catalyst

Hailong Li,^{†,||} Shaokang Wu,[†] Chang-Yu Wu,[‡] Jun Wang,[§] Liqing Li,^{*,†} and Kaimin Shih^{*,||}

[†]School of Energy Science and Engineering, Central South University, Changsha, China, 410083

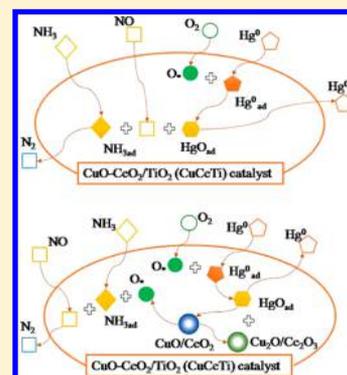
[‡]Department of Environmental Engineering Sciences, Engineering School of Sustainable Infrastructure and Environment, University of Florida, Gainesville, Florida 32611, United States

[§]Department of Occupational and Environmental Health, College of Public Health, University of Oklahoma Health Sciences Center, Oklahoma City, Oklahoma 73126, United States

^{||}Department of Civil Engineering, The University of Hong Kong, Hong Kong SAR, China

S Supporting Information

ABSTRACT: CuO–CeO₂/TiO₂ (CuCeTi) catalyst synthesized by a sol–gel method was employed to investigate mercury conversion under a selective catalytic reduction (SCR) atmosphere (NO, NH₃ plus O₂). Neither NO nor NH₃ individually exhibited an inhibitive effect on elemental mercury (Hg⁰) conversion in the presence of O₂. However, Hg⁰ conversion over the CuCeTi catalyst was greatly inhibited under SCR atmosphere. Systematic experiments were designed to investigate the inconsistency and explore the in-depth mechanisms. The results show that the copresence of NO and NH₃ induced reduction of oxidized mercury (Hg²⁺, HgO in this study), which offset the effect of catalytic Hg⁰ oxidation, and hence resulted in deactivation of Hg⁰ conversion. High NO and NH₃ concentrations with a NO/NH₃ ratio of 1.0 facilitated Hg²⁺ reduction and therefore lowered Hg⁰ conversion. Hg²⁺ reduction over the CuCeTi catalyst was proposed to follow two possible mechanisms: (1) direct reaction, in which NO and NH₃ react directly with HgO to form N₂ and Hg⁰; (2) indirect reaction, in which the SCR reaction consumed active surface oxygen on the CuCeTi catalyst, and reduced species on the CuCeTi catalyst surface such as Cu₂O and Ce₂O₃ robbed oxygen from adjacent HgO. Different from the conventionally considered mechanisms, that is, competitive adsorption responsible for deactivation of Hg⁰ conversion, this study reveals that oxidized mercury can transform into Hg⁰ under SCR atmosphere. Such knowledge is of fundamental importance in developing efficient and economical mercury control technologies for coal-fired power plants.



INTRODUCTION

The concentration of mercury (Hg) in coal matrix is much less than that of other abundant elements.^{1,2} However, coal combustion, most notably in utility boilers, has been targeted as a major source accounted for anthropogenic mercury emissions, as more than 7 billion tons of coal are burned globally each year.³ Because of the extreme toxicity, persistence, and bioaccumulation of methyl mercury transformed from emitted mercury,⁴ China and United States (U.S.) already had adopted national/federal mercury standards to limit mercury emission from coal-fired power plants by December 2011.^{5,6} In addition, more than 20 U.S. states had either proposed or adopted their own mercury emission regulations to regulate mercury emission from coal-fired power plants.⁷ Therefore, various technologies including activated carbon injection (ACI) have been developed for controlling mercury emissions from coal-fired power plants to meet the requirements of these mercury regulations.

In the near future, more and more coal fired power plants are expected to install a wet flue gas desulfurization (WFGD) system,^{8,9} which offers a cost-effective alternative to ACI,

because oxidized mercury (Hg²⁺) can be effectively removed by WFGD slurry with no additional cost.¹⁰ As such, a selective catalytic reduction (SCR) system which facilitates elemental mercury (Hg⁰) oxidation combining with WFGD would be promising for mercury removal from flue gas. The efficiency of this method largely depends on the conversion of Hg⁰ to Hg²⁺ over SCR catalysts.¹¹ Therefore, a variety of studies have been conducted to investigate Hg⁰ conversion over SCR catalysts.^{12–19}

Among these SCR catalysts, vanadium (V₂O₅)-based commercial SCR catalysts, which are originally developed for reducing nitrogen oxides (NO_x) to nitrogen (N₂) by ammonia (NH₃), have been demonstrated to be active for Hg⁰ conversion.²⁰ However, Hg⁰ conversion efficiency greatly depends on the hydrogen chloride (HCl) concentration of flue gas.^{12,21} Hg⁰ conversion less than 30% was achieved over a

Received: March 4, 2015

Revised: May 5, 2015

Accepted: May 11, 2015

Published: May 11, 2015

Table 1. List of Experimental Conditions^a

experiments	catalyst	flue gas atmosphere (1000 mL·min ⁻¹)
Set I	CuCeTi	N ₂ , N ₂ + 4% O ₂ ; N ₂ + 500 ppm of NO, N ₂ + 1000 ppm of NO, N ₂ + 1000 ppm of NO + 4% O ₂ ; N ₂ + 500 ppm of NH ₃ , N ₂ + 1000 ppm of NH ₃ , N ₂ + 1000 ppm of NH ₃ + 4% O ₂ ; N ₂ + 1000 ppm of NO + 1000 ppm of NH ₃ ; N ₂ + 1000 ppm of NO + 1000 ppm of NH ₃ + 4% O ₂
Set II	CuCeTi	N ₂ + 0, 250, 500, 750, 1000 ppm of NH ₃ + 1000 ppm of NO + 4% O ₂
Set III	CuCeTi	N ₂ + 0, 250, 500, 750, 1000 ppm of NO + 1000 ppm of NH ₃ + 4% O ₂
Set IV	pretreated CuCeTi	N ₂ , N ₂ + 1000 ppm of NO; N ₂ , N ₂ + 1000 ppm of NH ₃ ; N ₂ , N ₂ + 1000 ppm of NO + 1000 ppm of NH ₃ ; N ₂ , N ₂ + 1000 ppm of NO + 1000 ppm of NH ₃ + 4% O ₂
Set V	CuCeTi	N ₂ + 0, 250, 500, 750, 1000 ppm (NO and NH ₃) + 4% O ₂
Set VI	0.40 g HgO	500 ppm of NO + 500 ppm of NH ₃ (without Hg ⁰ , 200 and 250 °C)

^aTemperature was 200 °C, Hg⁰ concentration was about 75 μg·m⁻³ when used, the dosage of CuCeTi catalyst was 0.20 g. Pretreated CuCeTi: fresh CuCeTi saturated by Hg⁰ at 200 °C under 4% O₂ plus 300 μg·m⁻³ Hg⁰ balanced in N₂ for 5 days, then purged with pure N₂ until Hg⁰ discharged from the reactor outlet was below the detection limit.

V₂O₅-based SCR catalyst under sub-bituminous coal combustion flue gas with low concentrations of HCl.²² Moreover, artificially injected NH₃ for NO reduction is known to play a detrimental role in Hg⁰ oxidation over metal oxide catalysts²³ through competitive adsorption with HCl²⁴ and/or Hg⁰.²⁵ Besides these limitations in Hg⁰ conversion, V₂O₅-based commercial SCR catalysts have other drawbacks in NO reduction, where improvements can be made,²⁶ such as high operating temperature (300–400 °C). The high operating temperature requirement for V₂O₅-based commercial SCR catalysts demands that the SCR unit to be located upstream of the particulate matter control devices (PMCDs) immediately after the steam generator to avoid the cost of reheating the flue gas. To reduce reactor volume and prevent the deactivation of these catalysts due to exposure to high concentrations of particulate matter, ideally catalysts should be placed downstream of the PMCDs where flue gas temperature is relatively low.²⁷ Thus, catalysts with high SCR activity at low temperatures (100–250 °C) would be more promising for industrial applications, and hence of great interest for research.

Recently, a variety of low temperature SCR catalysts have been extensively investigated and reported facilitating NO_x reduction.²⁸ Among these low temperature SCR catalysts, CeO₂–TiO₂-based SCR catalysts are of most interest, because they are nontoxic and highly effective for Hg⁰ oxidation even under low-rank coal combustion flue gas conditions.^{29,30} However, cerium (CeO₂)-based catalysts are sensitive to sulfur poisoning, because sulfur dioxide (SO₂) can react with CeO₂ to form cerium(III) sulfate (Ce₂(SO₄)₃) and/or cerium(IV) sulfate (Ce(SO₄)₂) under different conditions.^{31,32} To facilitate the application of CeO₂–TiO₂-based catalysts on low temperature NO_x reduction, copper-modified CeO₂–TiO₂ (CuO–CeO₂/TiO₂) was recently developed as an alternative SCR catalyst with extraordinarily high SCR performance and SO₂ poisoning resistance.^{33,34} However, no research on Hg⁰ conversion over low temperature CuO–CeO₂/TiO₂ (CuCeTi) catalysts was yet conducted.

In this study, CuCeTi catalyst prepared by a sol–gel method was employed to accelerate Hg⁰ conversion under various flue gas conditions at low temperature. During the study, we found an interesting phenomenon, that is, in the presence of O₂, both NO and NH₃ promoted Hg⁰ conversion, individually, while the copresence of NO and NH₃ inhibited Hg⁰ conversion. Accordingly, we hypothesized that the copresence of NO and NH₃ induced reduction of oxidized mercury, which takes place in parallel with and may partially offset Hg⁰ oxidation, and hence resulted in lower Hg⁰ conversion efficiency. The focus of this work is to prove the reduction of oxidized mercury on the

CuCeTi catalyst, which has mostly been neglected thus far. HgO was selected as the oxidized mercury species which was reduced to be Hg⁰ under SCR atmosphere, because it is less volatile than HgCl₂ and it probably is the initial product of Hg⁰ oxidation on the metal-based catalyst regardless the presence of HCl.²³ The ultimate goal is to gain a deeper understanding of mechanisms involved in mercury conversion across SCR catalysts. This knowledge will lead to a more effective and economic technology for controlling mercury emission from coal-fired power plants.

EXPERIMENTAL SECTION

Preparation and Characterization of Catalysts. CuCeTi catalyst was synthesized by a sol–gel method. The fresh catalyst was characterized by Brunauer–Emmett–Teller (BET) surface area analysis, X-ray diffraction (XRD) measurement, and X-ray photoelectron spectroscopy (XPS) analysis. (Please refer to Synthesis of Catalyst and Material Characterization Methods in the Supporting Information for further details.)

Identification of Mercury Species on Catalyst Surface. XPS analysis for identifying mercury species on the catalyst surface was conducted on an Escalab 250Xi (Thermo Fisher Scientific, USA), with a monochromatized Al K α radiation ($h\nu = 1486.6$ eV) as the excitation source. The catalyst was cooled and dried in a desiccator prior to the XPS analysis. The degree of vacuum in the XPS equipment was maintained at 10⁻⁶ Pa. The carbonaceous C 1s line (284.8 eV) was used as reference for the calibration of binding energy values.

Catalytic Activity Measurement. Mercury oxidation and reduction experiments were conducted in a laboratory-scale experimental system shown in Supporting Information, Figure S1. All flue gas components including N₂, O₂, NO, and NH₃ were from cylinder gases and were precisely controlled by mass flow controllers (MFCs), with a total flow rate of 1 L per minute (Lpm). A Dynacal mercury permeation device (VICI Metronic, Inc. USA) sealed in a U shaped glass tube holder was used to generate a constant feed of Hg⁰ vapor (~75 μg·m⁻³). High purity N₂ acted as carrier gas to introduce vapor-phase Hg⁰ to the inlet of the gas mixer. During each test, 0.20 g of CuCeTi catalyst was loaded into a borosilicate glass reactor with an inner diameter of 10 mm, corresponding to a gas space hourly velocity (GHSV) of 21 600 h⁻¹. The reactor was vertically placed in a temperature controlled tubular furnace to control the reaction temperature at 200 °C with a variation less than 1 °C. Hg⁰ concentrations at both the inlet and outlet of the reactor were online monitored by a VM3000 mercury analyzer (Mercury Instruments Inc., Germany). The interferences from the reactor itself and individual flue gas components

on the Hg^0 measurement were verified to be negligible. Before proceeding to the mercury analyzer, a trace amount of water vapor was removed by silica, which had been demonstrated to be inert for Hg^0 conversion in preliminary experiments. An OPTIMA7 flue gas analyzer (MRU Emission Monitoring Systems, Germany) was employed to measure NO concentrations at both the inlet and outlet of the reactor. To avoid the influence caused by oxidation of NH_3 , the gas stream passed through an ammonia trap containing phosphoric acid solution before entering the flue gas analyzer.

Five sets of experiments were conducted, and the details are summarized in Table 1. Homogeneous Hg^0 conversion was identified to be negligible in preliminary experiments conducted under different atmosphere without catalyst. Set I experiments were designed to study the effect of O_2 , NO, NH_3 , and the copresence of O_2 , NO, and NH_3 , that is, SCR atmosphere (SCRA), on Hg^0 conversion, respectively. In Set II, Hg^0 conversion was investigated in the presence of 1000 ppm of NO and 4% O_2 with different NH_3 concentrations. Similarly, Hg^0 conversion in the presence of 1000 ppm of NH_3 and 4% O_2 with different NO concentrations was studied in Set III. Set IV experiments aimed at identifying the reduction of oxidized mercury using pretreated CuCeTi catalyst (saturated by Hg^0 at 200 °C under 4% O_2 plus 300 $\mu\text{g}\cdot\text{m}^{-3}$ Hg^0 balanced in N_2 for 5 days, then purged with pure N_2 until Hg^0 discharged from the reactor outlet was below the detection limit). In Set V, NO and NH_3 with a fix NO/ NH_3 ratio of 1 but different concentrations were adopted to investigate the impact of NO and NH_3 concentration on Hg^0 conversion. A NO reduction experiment was explored over pure HgO in Set VI for demonstrating a possible mercury reduction mechanism. In all experiments, triplicates were conducted, and their mean values and standard deviations were reported.

At the beginning of each test, the gas stream bypassed the reactor, and the inlet gas was monitored until the desired inlet Hg^0 concentration ($[\text{Hg}^0]_{\text{inlet}}$) with variation less than 5% had been obtained for at least 30 min. The gas flow was then taken from the exit of the reactor to measure the outlet Hg^0 concentration ($[\text{Hg}^0]_{\text{outlet}}$). $[\text{Hg}^0]_{\text{outlet}}$ was recorded after the catalytic process had reached equilibrium, which was defined as having a fluctuation of Hg^0 concentration less than 5% for more than 30 min. At the end of each experiment, the inlet gas was sampled again to verify the $[\text{Hg}^0]_{\text{inlet}}$. In an adsorption experiment conducted at room temperature, 0.50 g of CuCeTi catalyst was penetrated in less than 5 min when N_2 gas flow containing 75 $\mu\text{g}\cdot\text{m}^{-3}$ Hg^0 passed through it, demonstrating that the Hg^0 physical adsorption capacity of the CuCeTi catalyst was negligible. Therefore, the variation of Hg^0 concentration during an experiment was ascribed to the net sum of Hg^0 oxidation and Hg^{2+} reduction.^{35,36} Accordingly, Hg^0 conversion efficiency (E_{con}) in this study was calculated by the following equation:

$$E_{\text{con}}\% = ([\text{Hg}^0]_{\text{inlet}} - [\text{Hg}^0]_{\text{outlet}})/[\text{Hg}^0]_{\text{inlet}} \times 100 \quad (1)$$

Similarly, NO reduction efficiency (E_{red}) in Set VI experiments was calculated as follow.

$$E_{\text{red}}\% = ([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}})/[\text{NO}]_{\text{inlet}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Hg^0 Conversion under Different Flue Gas Conditions.

Effects of flue gas atmosphere on Hg^0 conversion over the

CuCeTi catalyst are summarized in Figure 1, in which SCRA was defined as 4% O_2 , 1000 ppm of NO, and 1000 ppm of NH_3 balanced in N_2 .

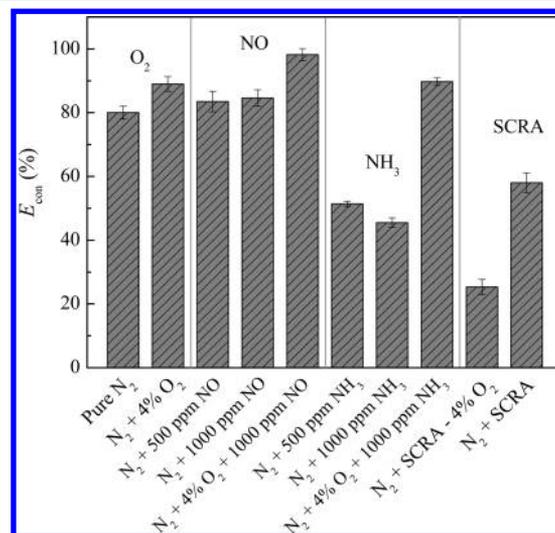


Figure 1. Effect of flue gas atmosphere on Hg^0 conversion (SCRA represents 1000 ppm of NO + 1000 ppm of NH_3 + 4% O_2).

Effect of O_2 on Hg^0 Conversion. E_{con} over CuCeTi catalyst was observed to be 80.0% at 200 °C under pure N_2 gas flow, which is higher than the E_{con} of 27.4% observed over 1.0 g $\text{CeO}_2/\text{TiO}_2$ catalyst under similar flue gas conditions.³⁷ The result indicates that the Hg^0 catalytic conversion performance of $\text{CeO}_2/\text{TiO}_2$ catalyst was enhanced by the addition of CuO, which was well incorporated into the catalyst matrix and/or highly dispersed on the $\text{CeO}_2/\text{TiO}_2$ support (demonstrated by the XRD profile in Supporting Information, Figure S2). This likely resulted from the rich stored oxygen on the CuCeTi catalyst, including lattice oxygen and chemisorbed oxygen (as shown in Figure S3 and Table S1). When 4% gas-phase O_2 was introduced to the gas flow, E_{con} increased to 89.0%. Gas-phase O_2 regenerated the lattice oxygen and replenished the chemisorbed oxygen, which served as Hg^0 oxidants.

Effect of NO on Hg^0 Conversion. NO can be oxidized on the surface of metal oxides-based catalysts, giving rise to species like NO^+ and NO_2 which can cause oxidation of Hg^0 .³⁷ On the contrary, NO can cover active sites³⁸ and consume surface oxygen,³⁹ thus inhibiting Hg^0 oxidation. In the absence of O_2 , the promotional and the inhibitive effects of NO on Hg^0 conversion over the CuCeTi catalyst were almost at a steady state. Therefore, no obvious effect of NO on Hg^0 conversion was observed when gas-phase O_2 was absent. The application of 500 ppm of NO and 1000 ppm of NO resulted in E_{con} values of 83.5% and 84.6%, respectively, which are just slightly higher than that observed under pure N_2 atmosphere. In the presence of gas-phase O_2 , more adsorbed NO can be oxidized to form abundant active species like NO_2 , which are active for Hg^0 oxidation,³⁷ while the consumed surface oxygen can be replenished by gas-phase O_2 . Therefore, E_{con} increased up to 98.2% when 4% O_2 was introduced to gas flow containing 1000 ppm of NO. This is also higher than the E_{con} of 89.0% when NO was absent, indicating that NO possessed a promotional effect on Hg^0 conversion with the aid of O_2 .

Effect of NH_3 on Hg^0 Conversion. As a potential low temperature NH_3 -SCR catalyst,³³ CuO/ CeO_2 - TiO_2 catalyst

would probably be used under SCR conditions where NH_3 is present. Therefore, it is indispensable to investigate Hg^0 conversion activity in the presence of NH_3 . As shown in Figure 1, an addition of NH_3 into pure N_2 exhibited an inhibitive effect on Hg^0 conversion over the CuCeTi catalyst. After reaching equilibrium (about 1 h), 500 ppm of NH_3 balanced in N_2 resulted in E_{con} of 51.4%, which is lower than the 80.0% Hg^0 conversion under pure N_2 condition. An E_{con} of 45.5% was observed when NH_3 concentration further increased to 1000 ppm. This was probably due to (a) NH_3 consumed the surface oxygen⁴⁰ which is responsible for Hg^0 oxidation in pure N_2 atmosphere and/or (b) NH_3 inhibited Hg^0 adsorption^{41,42} which is crucial for Hg^0 oxidation through different mechanisms.¹⁰ However, NH_3 exhibited no obviously inhibitive effect on Hg^0 conversion in the presence of O_2 . A 1000 ppm sample of NH_3 plus 4% O_2 balanced in N_2 resulted in an E_{con} of 89.7%, which is statistically the same as the E_{con} under N_2 plus 4% O_2 condition. This indicates that the presence of gas-phase O_2 offsets the greater part of the inhibitive effect of NH_3 . Therefore, it can be concluded that the consumption of surface oxygen by NH_3 was mostly responsible for the deactivation of Hg^0 conversion in the absence of O_2 .

Effect of the Co-presence of NO and NH_3 on Hg^0 Conversion. As stated above, NO never possessed a prohibitive effect on Hg^0 conversion over the CuCeTi catalyst regardless of the presence of O_2 . However, introduction of 1000 ppm of NO to a gas flow containing 1000 ppm of NH_3 without O_2 yielded a decrease of E_{con} from 45.5% to 25.3%. Neither NO nor NH_3 exhibited an inhibitive effect on Hg^0 conversion in the presence of O_2 . However, the copresence of NO and NH_3 resulted in a huge deactivation of Hg^0 conversion over the CuCeTi catalyst. As shown in Figure 1, E_{con} decreased from 89.0% to 58.0% when 1000 ppm of NO and 1000 ppm of NH_3 were introduced to gas flow containing 4% O_2 .

To further confirm this interesting phenomenon, mercury conversion was studied under several SCR conditions with different NH_3/NO ratios. As shown in Figure 2, an E_{con} of

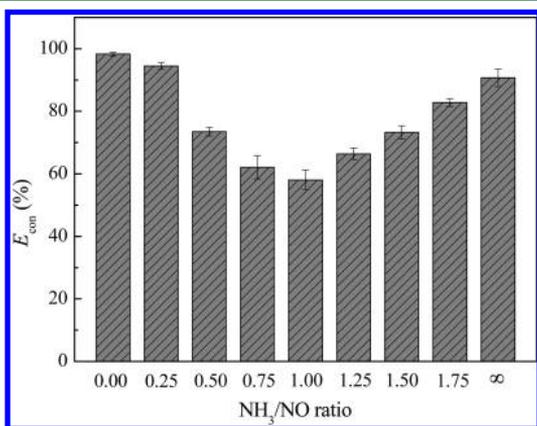


Figure 2. Effect of NH_3/NO ratio on Hg^0 conversion.

98.3% was observed when the gas flow contained 4% O_2 and 1000 ppm of NO without NH_3 ($\text{NH}_3/\text{NO} = 0$). An additional 250 ppm of NH_3 ($\text{NH}_3/\text{NO} = 0.25$) resulted in an E_{con} of 94.5%, which is lower than the 98.3% Hg^0 conversion at $\text{NH}_3/\text{NO} = 0$. When NH_3/NO ratios were smaller than 1, an increase of the NH_3/NO ratio (i.e., maintaining NO concentration at 1000 ppm while increasing NH_3 concentration from 0 to 1000 ppm) resulted in less NO remaining in the gas

flow, which was demonstrated to be promotional in Hg^0 conversion. Therefore, a further increase of NH_3/NO ratio to 1 yielded less Hg^0 conversion. The surplus NO should facilitate Hg^0 oxidation when the NH_3/NO ratio was smaller than 1. If there was only Hg^0 oxidation, Hg^0 conversion should be higher than the E_{con} of 89.0% under 4% O_2 plus N_2 condition when the NH_3/NO ratio was smaller than 1. However, E_{con} values were observed to be 73.5% and 62.1% for NH_3/NO ratios of 0.5 and 0.75, respectively. The inconsistency indicates that other processes like reduction of oxidized mercury should be taken into account in the Hg^0 conversion.³⁵ The lowest Hg^0 conversion of 58.0% was observed in the presence of 4% O_2 , 1000 ppm of NH_3 , and 1000 ppm of NO, that is, when the NH_3/NO ratio was 1. A further increase of the NH_3/NO ratio (i.e., keeping NH_3 concentration at 1000 ppm, while lowering NO concentration from 1000 to 0 ppm) raised the E_{con} . A sample of 4% O_2 and 1000 ppm of NH_3 balanced in N_2 ($\text{NH}_3/\text{NO} = \text{infinity}$) resulted in an E_{con} of 90.7%, which is about the same as that under N_2 plus 4% O_2 condition. This is in line with the results presented above that NH_3 exhibited an insignificant effect on Hg^0 conversion in the presence of O_2 . However, the increase of E_{con} with the increase of NH_3/NO ratio from 1 to infinity was due to the decrease of NO concentration, because other experimental parameters like NH_3 concentration remained constant. This phenomenon seems totally opposite as compared to the results observed without NH_3 that NO exhibited a promotional effect on Hg^0 oxidation with the aid of O_2 . Above inconsistency indicates again that there must be some other reactions besides Hg^0 oxidation when both NO and NH_3 were presence. As the observed Hg^0 conversion reflects the net sum of Hg^0 oxidation and Hg^{2+} reduction on the catalyst, it is reasonable to hypothesize that the copresence of NO and NH_3 could probably lead to reduction of oxidized mercury.

Identification of Oxidized Mercury Reduction. As stated above, it is very likely that the copresence of NO and NH_3 induced reduction of oxidized mercury, which offset part of Hg^0 oxidation and hence resulted in lower Hg^0 conversion observed. The reduction of oxidized mercury on the CuCeTi catalyst was demonstrated by desorption experiments in Set IV, the results of which are shown in Figure 3. Pretreated CuCeTi catalyst was used in these experiments. Prior to Set IV experiments, an XPS analysis was carried to identify the valence state of mercury on the pretreated catalyst. The Hg 4f spectrum

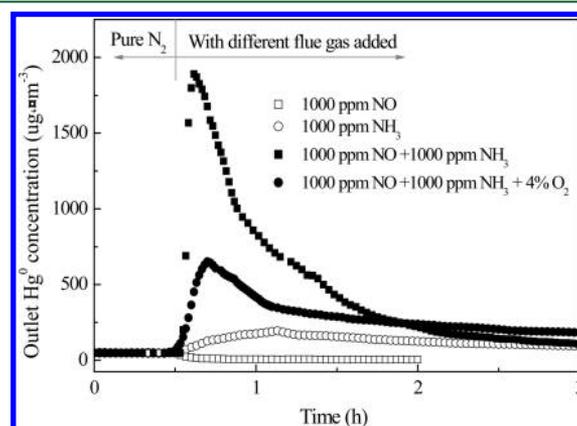


Figure 3. Desorption of Hg^0 from pretreated CuCeTi by different gas components.

of the pretreated catalyst is presented in Figure 4. As shown, the Hg 4f spectrum of the pretreated catalyst possesses two

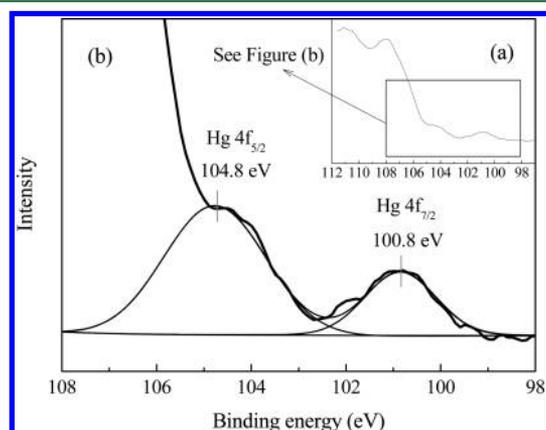
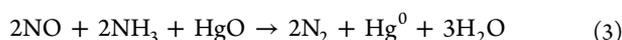


Figure 4. XPS spectra of Hg 4f of pretreated CuCeTi.

peaks at 100.8 and 104.8 eV, respectively. This is in agreement with the difference in energy predicted by the spin–orbit splitting.⁴³ There was no detectable Hg⁰ on the surface of the pretreated catalyst, because no obvious peak around 99.9 eV (characteristic peak for Hg 4f_{7/2} associated with Hg⁰) was observed.⁴⁴ The binding energies of 100.8 (4f_{7/2}) and 104.8 eV(4f_{5/2}) confirmed that the dominating mercury species on the pretreated catalyst surface was HgO.⁴³ This is in accordance with our preliminary study that negligible Hg⁰ can be physically adsorbed on the CuCeTi catalyst even at temperatures lower than 200 °C. Even if some Hg⁰ physically adsorbed on the CuCeTi catalyst surface, most of it would have been flushed away during the pretreatment. Therefore, Hg⁰ discharged from the reactor outlet was negligible when pure N₂ passed through the pretreated catalyst (as shown in Figure 3). An addition of 1000 ppm of NO resulted in less Hg⁰ emission. This is in accordance with the result presented in Figure 1 that NO slightly facilitated Hg⁰ conversion. The addition of 1000 ppm of NH₃ caused no obvious desorption of Hg⁰ from the pretreated catalyst in 2 h. This was probably due to the competitive adsorption between NH₃ and trace amount Hg⁰ on the pretreated catalyst.⁴⁵ In sum, no obvious Hg⁰ concentration increase was observed when NO or NH₃ was added alone. However, a huge spike of Hg⁰ was observed after adding 1000 ppm of NO and 1000 ppm of NH₃ simultaneously to a N₂ gas flow passing through the pretreated catalyst. As the most abundant mercury species on the pretreated catalyst was identified to be HgO, it is reasonable to believe that HgO was reduced by NO and NH₃ to form Hg⁰. The overall pathway summarized below is likely responsible for HgO reduction in the copresence of NO and NH₃.



If this reaction pathway is feasible, more NO and NH₃ should facilitate HgO reduction, which is adverse to Hg⁰ oxidation, and hence resulted in less Hg⁰ conversion. This is in accordance with the results of the Hg⁰ conversion experiment conducted under SCR atmosphere with NH₃/NO ratio of 1. As shown in Figure 5, Hg⁰ conversion decreased while NO and NH₃ concentration increased from 0 to 1000 ppm. This consistency further demonstrated that the proposed pathway is appropriate. When 4% O₂ was added with NO and NH₃, the spike of Hg⁰ was smaller than that without O₂. This probably occurred

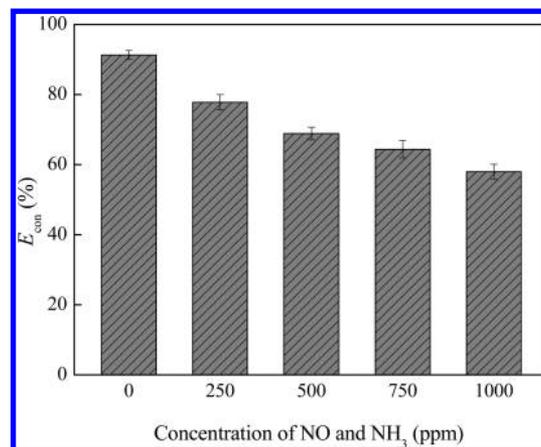
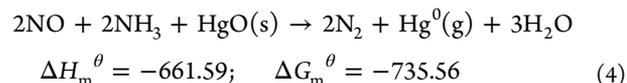


Figure 5. Effect of NO and NH₃ concentration (NH₃/NO = 1) on Hg⁰ conversion.

because (1) the oxidizing atmosphere inhibited HgO reduction; (2) part of Hg⁰ from HgO reduction was reoxidized by active sites on the catalyst surface, which can be continuously replenished by gas-phase O₂.

Mechanisms of Oxidized Mercury Reduction. Two mechanisms can possibly be responsible for mercury reduction over the CuCeTi catalyst in the copresence of NO and NH₃; that is, eq 3 could proceed through two different ways.

For the first mechanism, the CuCeTi catalyst is not involved in the HgO reduction process; that is, NO and NH₃ reacted directly with HgO to form N₂ and Hg⁰. Hence, this is called a direct reaction. The reaction process is as follows.



According to the thermodynamic, both the enthalpy and the Gibbs free energy variations of reaction 4 are far less than 0, indicating reaction 4 is spontaneous and favorable from the thermodynamic perspective. To further verify this mechanism, NO reduction experiments were conducted over pure HgO without CuCeTi catalyst and gas-phase O₂. As shown in Figure 6, NO can be reduced by NH₃ with the aid of HgO, indicating that reaction 4 was at least partly responsible for HgO reduction over the CuCeTi catalyst. With the variation of Gibbs free energy being much lower than 0, reaction 4 is a kinetic

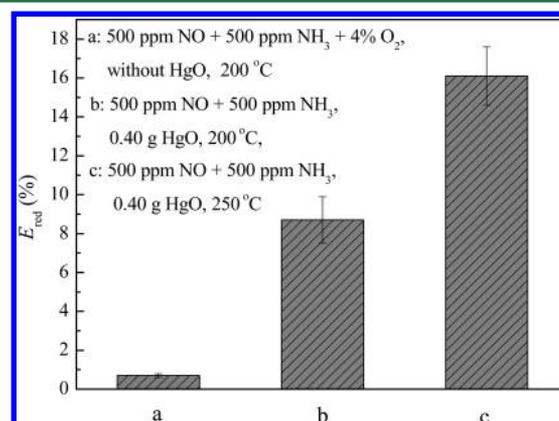
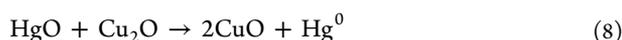
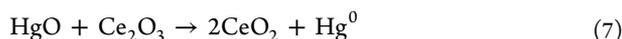
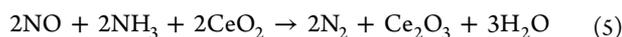


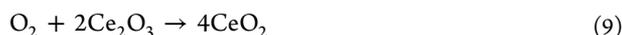
Figure 6. NO reduction over pure HgO.

control process. Therefore, an increase of temperature from 200 to 250 °C resulted in a higher E_{red} (as shown in Figure 6).

On the CuCeTi catalyst, Ce^{4+} can be reduced to Ce^{3+} in the DeNOx cycle and then reoxidized back to Ce^{4+} by gas-phase O_2 in the flue gas.³³ Besides Ce^{4+} , Cu^{2+} also can be reduced to Cu^+ in the oxidation process and then reoxidized back to Cu^{2+} by gas-phase O_2 .⁴⁶ The reduced cerium and copper species probably also react with other oxidizing matters such as oxidized mercury to return to the original oxidation state. Meanwhile, the oxidized mercury is reduced to elemental mercury, which is discharged from the reactor outlet in the desorption experiments. In summary, HgO reduction over the CuCeTi catalyst could also proceed through another pathway, in which HgO reacts with other reducing species from the NH_3 DeNOx cycle rather than NO and NH_3 themselves. Therefore, this mechanism is called indirect reaction. The possible heterogeneous reactions over the CuCeTi catalyst without gas-phase O_2 are proposed to be the following steps:



In the presence of gas-phase O_2 , O_2 rapidly reoxidizes a portion of reduced cerium and copper species (reaction 9 and 10), which is crucial for HgO reduction through the indirect reaction mechanism. Moreover, the regenerated CeO_2 and CuO from reactions 9 and 10 are more active than HgO for NO reduction, NO and NH_3 will preferentially react with CeO_2 and CuO rather than HgO. These were verified by less Hg^0 detected at the reactor outlet.



■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis of catalysts, material characterization methods, one table and three figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01104.

■ AUTHOR INFORMATION

Corresponding Authors

*Phone: 86-18670016725; fax: 86-731-88879863; e-mail: lienergycsu@gmail.com.

*E-mail: kshih@hku.hk

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (No. 51206192, 51476189) and the China Postdoctoral Science Foundation (No. XJ2014033), and the Foundation of State Key Laboratory of Coal Combustion (FSKLCCA1505).

■ REFERENCES

- (1) Zhang, J. Y.; Zheng, C. G.; Ren, D. Y.; Chou, C. L.; Liu, J.; Zeng, R. S.; Wang, Z. P.; Zhao, F. H.; Ge, Y. T. Distribution of potentially hazardous trace elements in coals from Shanxi province, China. *Fuel* **2004**, *83*, 129–135.
- (2) Yudovich, Y. E.; Ketris, M. P. Mercury in coal: A review: Part I. *Geochemistry. Int. J. Coal Geol.* **2005**, *62*, 107–134.
- (3) Schofield, K. Mercury emission control from coal combustion systems: A modified air preheater solution. *Combust. Flame* **2012**, *159*, 1741–1747.
- (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*, 89–165.
- (5) Ministry of Environmental Protection of China, Emission Standard of air pollutants for thermal Power plants, <http://www.zhb.gov.cn/gkml/hbb/bgg/201109/W020120113518288046763.pdf> (accessed Feb 2015).
- (6) U.S. Environmental Protection Agency, Air Toxics Standards for Utilities, <http://www.epa.gov/ttn/atw/utility/utilitypg.html> (accessed Feb 2015).
- (7) Milford, J. B.; Pienciak, A. After the Clean Air mercury rule: Prospects for reducing mercury emissions from coal-fired power plants. *Environ. Sci. Technol.* **2009**, *43*, 2669–2673.
- (8) Strivastava, R. *Control of Mercury Emissions from Coal Fired Electric Utility Boilers: An Update*; U.S. Environmental Protection Agency: Cincinnati, OH, 2010.
- (9) Zhao, Y.; Wang, S. X.; Duan, L.; Lei, Y.; Cao, P. F.; Hao, J. M. Primary air pollutant emissions of coal-fired power plants in China: Current status and future prediction. *Atmos. Environ.* **2008**, *42*, 8442–8452.
- (10) Presto, A. A.; Granite, E. J. Survey of catalysts for oxidation of mercury in flue gas. *Environ. Sci. Technol.* **2006**, *40*, S601–S609.
- (11) Pritchard, S. Predictable SCR co-benefits for mercury control. *Power Eng.* **2009**, *113*, 42.
- (12) Eswaran, S.; Stenger, H. G. Understanding mercury conversion in selective catalytic reduction (SCR) catalysts. *Energy Fuels* **2005**, *19*, 2328–2334.
- (13) Richardson, C.; Machalek, T.; Miller, S.; Dene, C.; Chang, R. Effect of NO_x control processes on mercury speciation in utility flue gas. *J. Air Waste Manage. Assoc.* **2002**, *52*, 941–947.
- (14) Gao, W.; Liu, Q. C.; Wu, C. Y.; Li, H. L.; Li, Y.; Yang, J.; Wu, G. F. Kinetics of mercury oxidation in the presence of hydrochloric acid and oxygen over a commercial SCR catalyst. *Chem. Eng. J.* **2013**, *220*, 53–60.
- (15) Liu, J.; He, M. F.; Zheng, C. G.; Chang, M. Density functional theory study of mercury adsorption on V_2O_5 (0 0 1) surface with implications for oxidation. *Proc. Combust. Inst.* **2011**, *33*, 2771–2777.
- (16) He, C.; Shen, B.; Chen, J.; Cai, J. Adsorption and oxidation of elemental mercury over Ce-MnOx/Ti-PILCs. *Environ. Sci. Technol.* **2014**, *48*, 7891–7898.
- (17) Pudasainee, D.; Lee, S. J.; Lee, S. H.; Kim, J. H.; Jang, H. N.; Cho, S. J.; Seo, Y. C. Effect of selective catalytic reactor on oxidation and enhanced removal of mercury in coal-fired power plants. *Fuel* **2010**, *89*, 804–809.
- (18) Senior, C. L. Oxidation of mercury across selective catalytic reduction catalysts in coal-fired power plants. *J. Air Waste Manage. Assoc.* **2006**, *56*, 23–31.
- (19) Yan, N.; Chen, W.; Chen, J.; Qu, Z.; Guo, Y.; Yang, S.; Jia, J. The significance of RuO_2 modified SCR catalyst for elemental mercury oxidation in coal-fired flue gas. *Environ. Sci. Technol.* **2011**, *45*, S725–S730.
- (20) 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. *Environ. Sci. Technol.* **2013**, *47*, 10813–10823.
- (21) Kamata, H.; Ueno, S.; Naito, T.; Yukimura, A. Mercury oxidation over the $\text{V}_2\text{O}_5(\text{WO}_3)/\text{TiO}_2$ commercial SCR catalyst. *Ind. Eng. Chem. Res.* **2008**, *47*, 8136–8141.

- (22) Cao, Y.; Gao, Z.; Zhu, J.; Wang, Q.; Huang, Y.; Chiu, C.; Parker, B.; Chu, P.; Pan, W. P. Impacts of halogen additions on mercury oxidation, in a slipstream selective catalyst reduction (SCR), reactor when burning sub-bituminous coal. *Environ. Sci. Technol.* **2008**, *42*, 256–261.
- (23) Straube, S.; Hahn, T.; Koeser, H. Adsorption and oxidation of mercury in tail-end SCR-DeNO_x plants—Bench scale investigations and speciation experiments. *Appl. Catal., B* **2008**, *79*, 286–295.
- (24) Niksa, S.; Fujiwara, N. A predictive mechanism for mercury oxidation on selective catalytic reduction catalysts under coal-derived flue gas. *J. Air Waste Manage. Assoc.* **2005**, *55*, 1866–1875.
- (25) Eom, Y.; Jeon, S. H.; Ngo, T. A.; Kim, J.; Lee, T. G. Heterogeneous mercury reaction on a selective catalytic reduction (SCR) catalyst. *Catal. Lett.* **2008**, *121*, 219–225.
- (26) Liu, Z.; Li, J.; Woo, S. I. Recent advances in the selective catalytic reduction of NO_x by hydrogen in the presence of oxygen. *Energy Environ. Sci.* **2012**, *5*, 8799–8814.
- (27) Li, H. L.; Wu, C. Y.; Li, Y.; Li, L. Q.; Zhao, Y. C.; Zhang, J. Y. Role of flue gas components in mercury oxidation over TiO₂ supported MnO_x-CeO₂ mixed-oxide at low temperature. *J. Hazard. Mater.* **2012**, *243*, 117–123.
- (28) Li, J. H.; Chang, H. Z.; Ma, L.; Hao, J. M.; Yang, R. T. Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts: A review. *Catal. Today* **2011**, *175*, 147–156.
- (29) Li, H. L.; Wu, C. Y.; Li, Y.; Zhang, J. Y. CeO₂-TiO₂ catalysts for catalytic oxidation of elemental mercury in low-rank coal combustion flue gas. *Environ. Sci. Technol.* **2011**, *45*, 7394–7400.
- (30) Li, H. L.; Wu, C. Y.; Li, L. Q.; Li, Y.; Zhao, Y. C.; Zhang, J. Y. Kinetic modeling of mercury oxidation by chlorine over CeO₂-TiO₂ catalysts. *Fuel* **2013**, *113*, 726–732.
- (31) Casapu, M.; Kröcher, O.; Elsener, M. Screening of doped MnO_x-CeO₂ catalysts for low-temperature NO-SCR. *Appl. Catal., B* **2009**, *88*, 413–419.
- (32) Xu, W. Q.; He, H.; Yu, Y. B. Deactivation of a Ce/TiO₂ catalyst by SO₂ in the selective catalytic reduction of NO by NH₃. *J. Phys. Chem. C* **2009**, *113*, 4426–4432.
- (33) Du, X. S.; Gao, X.; Cui, L. W.; Fu, Y. C.; Luo, Z. Y.; Cen, K. F. Investigation of the effect of Cu addition on the SO₂-resistance of a CeTi oxide catalyst for selective catalytic reduction of NO with NH₃. *Fuel* **2012**, *92*, 49–55.
- (34) Liu, Z.; Yi, Y.; Li, J.; Woo, S. I.; Wang, B.; Cao, X.; Li, Z. A superior catalyst with dual redox cycles for the selective reduction of NO_x by ammonia. *Chem. Commun.* **2013**, *49*, 7726–7728.
- (35) Madsen, K. Mercury oxidation over selective catalytic reduction (SCR) catalysts. Ph.D. Dissertation, Technical University of Denmark, Kongens Lyngby, Denmark, 2011.
- (36) Stolle, R.; Koeser, H.; Gutberlet, H. Oxidation and reduction of mercury by SCR DeNO_x catalysts under flue gas conditions in coal fired power plants. *Appl. Catal., B* **2014**, *144*, 486–497.
- (37) Li, Y.; Murphy, P. D.; Wu, C. Y.; Powers, K. W.; Bonzongo, J. C. J. Development of silica/vanadia/titania catalysts for removal of elemental mercury from coal-combustion flue gas. *Environ. Sci. Technol.* **2008**, *42*, 5304–5309.
- (38) Qi, G. S.; Yang, R. T. Characterization and FTIR studies of MnO_x-CeO₂ catalyst for low-temperature selective catalytic reduction of NO with NH₃. *J. Phys. Chem. B* **2004**, *108*, 15738–15747.
- (39) Jin, R. B.; Liu, Y.; Wu, Z. B.; Wang, H. Q.; Gu, T. T. Low-temperature selective catalytic reduction of NO with NH₃ over Mn-Ce oxides supported on TiO₂ and Al₂O₃: A comparative study. *Chemosphere* **2010**, *78*, 1160–1166.
- (40) Qi, G. S.; Yang, R. T.; Chang, R. MnO_x-CeO₂ mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH₃ at low temperatures. *Appl. Catal., B* **2004**, *51*, 93–106.
- (41) He, S.; Zhou, J. S.; Zhu, Y. Q.; Luo, Z. Y.; Ni, M. J.; Cen, K. F. Mercury oxidation over a vanadia-based selective catalytic reduction catalyst. *Energy Fuels* **2009**, *23*, 253–259.
- (42) Lee, C. W.; Srivastava, R. K.; Ghorishi, S. B.; Hastings, T. W.; Stevens, F. M. Investigation of selective catalytic reduction impact on mercury speciation under simulated NO_x emission control conditions. *J. Air Waste Manage. Assoc.* **2004**, *54*, 1560–1566.
- (43) NIST XPS Database. <http://srdata.nist.gov/xps/> (accessed Feb 2015).
- (44) Lee, W. J.; Bae, G. N. Removal of elemental mercury (Hg(0)) by nanosized V₂O₅/TiO₂ catalysts. *Environ. Sci. Technol.* **2009**, *43*, 1522–1527.
- (45) Li, H. L.; Wu, C. Y.; Li, Y.; Zhang, J. Y. Superior activity of MnO_x-CeO₂/TiO₂ catalyst for catalytic oxidation of elemental mercury at low flue gas temperatures. *Appl. Catal., B* **2012**, *111–112*, 381–388.
- (46) Moreno, M.; Bergamini, L.; Baronetti, G. T.; Laborde, M. A.; Marino, F. J. Mechanism of CO oxidation over CuO/CeO₂ catalysts. *Int. J. Hydrogen Energy* **2010**, *35*, 5918–5924.