SCR Atmosphere Induced Reduction of Oxidized Mercury over CuO–CeO\textsubscript{2}/TiO\textsubscript{2} Catalyst

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Supporting Information

ABSTRACT: CuO–CeO\textsubscript{2}/TiO\textsubscript{2} (CuCeTi) catalyst synthesized by a sol–gel method was employed to investigate mercury conversion under a selective catalytic reduction (SCR) atmosphere (NO, NH\textsubscript{3} plus O\textsubscript{2}). Neither NO nor NH\textsubscript{3} individually exhibited an inhibitive effect on elemental mercury (Hg\textsubscript{0}) conversion in the presence of O\textsubscript{2}. However, Hg\textsubscript{0} 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 NH\textsubscript{3} induced reduction of oxidized mercury (Hg\textsuperscript{2+}, HgO in this study), which offset the effect of catalytic Hg\textsubscript{0} oxidation, and hence resulted in deactivation of Hg\textsubscript{0} conversion. High NO and NH\textsubscript{3} concentrations with a NO/NH\textsubscript{3} ratio of 1.0 facilitated Hg\textsuperscript{2+} reduction and therefore lowered Hg\textsubscript{0} conversion. Hg\textsuperscript{2+} reduction over the CuCeTi catalyst was proposed to follow two possible mechanisms: (1) direct reaction, in which NO and NH\textsubscript{3} react directly with HgO to form N\textsubscript{2} and Hg\textsubscript{2}O\textsubscript{3}; (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 Cu\textsubscript{2}O and Ce\textsubscript{2}O\textsubscript{3} robbed oxygen from adjacent HgO. Different from the conventionally considered mechanisms, that is, competitive adsorption responsible for deactivation of Hg\textsubscript{0} conversion, this study reveals that oxidized mercury can transform into Hg\textsubscript{0} 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.\textsuperscript{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.\textsuperscript{3} Because of the extreme toxicity, persistence, and bioaccumulation of methyl mercury transformed from Hg\textsubscript{0}, which offsets the effect of catalytic oxidation and hence resulted in deactivation of Hg\textsubscript{0} conversion. High NO and NH\textsubscript{3} concentrations with a NO/NH\textsubscript{3} ratio of 1.0 facilitated Hg\textsuperscript{2+} reduction and therefore lowered Hg\textsubscript{0} conversion. Hg\textsuperscript{2+} reduction over the CuCeTi catalyst was proposed to follow two possible mechanisms: (1) direct reaction, in which NO and NH\textsubscript{3} react directly with HgO to form N\textsubscript{2} and Hg\textsubscript{2}O\textsubscript{3}; (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 Cu\textsubscript{2}O and Ce\textsubscript{2}O\textsubscript{3} robbed oxygen from adjacent HgO. Different from the conventionally considered mechanisms, that is, competitive adsorption responsible for deactivation of Hg\textsubscript{0} conversion, this study reveals that oxidized mercury can transform into Hg\textsubscript{0} under SCR atmosphere. Such knowledge is of fundamental importance in developing efficient and economical mercury control technologies for coal-fired power plants.

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V_2O_5-based SCR catalyst under sub-bituminous coal combustion flue gas with low concentrations of HCl. Moreover, artificially injected NH_3 for NO reduction is known to play a detrimental role in Hg_0 oxidation over metal oxide catalysts through competitive adsorption with HCl and/or Hg_0.23 Besides these limitations in Hg_0 conversion, V_2O_5-based commercial SCR catalysts have other drawbacks in NO reduction, where improvements can be made, such as high operating temperature (300–400 °C). The high operating temperature requirement for V_2O_5-based commercial SCR catalysts demands that the SCR unit 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. 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 NOx industrial applications, and hence of great interest for research.

### 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 Kα radiation (hv = 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 N_2, O_2, NO, and NH_3 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 Hg_0 vapor (~75 μg·m⁻³). High purity N_2 acted as carrier gas to introduce vapor-phase Hg_0 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. Hg_0 concentrations at both the inlet and outlet of the PMCD were monitored online using a VM3000 mercury analyzer (Mercury Instruments Inc., Germany). The concentrations in the reactor outlet were below the detection limit.

#### Table 1. List of Experimental Conditions

<table>
<thead>
<tr>
<th>experiments</th>
<th>catalyst</th>
<th>flue gas atmosphere (1000 mL·min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set I</td>
<td>CuCeTi</td>
<td>N_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+4% O_2</td>
</tr>
<tr>
<td>Set II</td>
<td>CuCeTi</td>
<td>N_2+0, 250, 500, 750, 1000 ppm of NH_3+1000 ppm of NO+4% O_2</td>
</tr>
<tr>
<td>Set III</td>
<td>CuCeTi</td>
<td>N_2+0, 250, 500, 750, 1000 ppm of NO+1000 ppm of NH_3+4% O_2</td>
</tr>
<tr>
<td>Set IV</td>
<td>CuCeTi</td>
<td>N_2+N_2+1000 ppm of NO, N_2+N_2+1000 ppm of NH_3, N_2+1000 ppm of NO+1000 ppm of NH_3+4% O_2</td>
</tr>
<tr>
<td>Set V</td>
<td>CuCeTi</td>
<td>N_2+0, 250, 500, 750, 1000 ppm (NO and NH_3)+4% O_2</td>
</tr>
<tr>
<td>Set VI</td>
<td>HgO</td>
<td>500 ppm of NO+500 ppm of NH_3 (without Hg_0, 200 and 250 °C)</td>
</tr>
</tbody>
</table>

“Temperature was 200 °C, Hg_0 concentration was about 75 μg·m⁻³” when used, the dosage of CuCeTi catalyst was 0.20 g. Pretreated CuCeTi: fresh CuCeTi saturated by Hg_0 at 200 °C under 4% O_2 plus 300 μg·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.
on the Hg\textsuperscript{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\textsuperscript{0} conversion in preliminary experiments. An OPTIMA\textsuperscript{a} 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\textsubscript{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\textsuperscript{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\textsubscript{2}, NO, NH\textsubscript{3}, and the copresence of O\textsubscript{2}, NO, and NH\textsubscript{3} that is, SCR atmosphere (SCRA), on Hg\textsuperscript{0} conversion, respectively. In Set II, Hg\textsuperscript{0} conversion was investigated in the presence of 1000 ppm of NO and 4% O\textsubscript{2} with different NH\textsubscript{3} concentrations. Similarly, Hg\textsuperscript{0} conversion in the presence of 1000 ppm of NH\textsubscript{3} and 4% O\textsubscript{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\textsuperscript{0} at 200 °C under 4% O\textsubscript{2} plus 300 μg·m\textsuperscript{-3} Hg\textsuperscript{0} balanced in N\textsubscript{2} for 5 days, then purged with pure N\textsubscript{2} until Hg\textsuperscript{0} discharged from the reactor outlet was below the detection limit). In Set V, NO and NH\textsubscript{3} with a fix NO/NH\textsubscript{3} ratio of 1 but different concentrations were adopted to investigate the impact of NO and NH\textsubscript{3} concentration on Hg\textsuperscript{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\textsuperscript{0} concentration ([Hg\textsuperscript{0}]\textsubscript{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\textsuperscript{0} concentration ([Hg\textsuperscript{0}]\textsubscript{outlet}). [Hg\textsuperscript{0}]\textsubscript{outlet} was recorded after the catalytic process had reached equilibrium, which was defined as having a fluctuation of Hg\textsuperscript{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 [Hg\textsuperscript{0}]\textsubscript{inlet}. In an adsorption experiment conducted at room temperature, 0.50 g of CuCeTi catalyst was penetrated in less than 5 min when N\textsubscript{2} gas flow containing 75 μg·m\textsuperscript{-3} Hg\textsuperscript{0} passed through it, demonstrating that the Hg\textsuperscript{0} physical adsorption capacity of the CuCeTi catalyst was negligible. Therefore, the variation of Hg\textsuperscript{0} concentration during an experiment was ascribed to the net sum of Hg\textsuperscript{0} oxidation and Hg\textsuperscript{2+} reduction.\textsuperscript{15,36} Accordingly, Hg\textsuperscript{0} conversion efficiency (E\textsubscript{con}) in this study was calculated by the following equation:

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

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

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

\section*{RESULTS AND DISCUSSION}

**Hg\textsuperscript{0} Conversion under Different Flue Gas Conditions.** Effects of flue gas atmosphere on Hg\textsuperscript{0} conversion over the CuCeTi catalyst are summarized in Figure 1, in which SCRA was defined as 4% O\textsubscript{2}, 1000 ppm of NO, and 1000 ppm of NH\textsubscript{3} balanced in N\textsubscript{2}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Effect of flue gas atmosphere on Hg\textsuperscript{0} conversion (SCRA represents 1000 ppm of NO + 1000 ppm of NH\textsubscript{3} + 4% O\textsubscript{2}).}
\end{figure}

**Effect of O\textsubscript{2} on Hg\textsuperscript{0} Conversion.** E\textsubscript{con} over CuCeTi catalyst was observed to be 80.0% at 200 °C under pure N\textsubscript{2} gas flow, which is higher than the E\textsubscript{con} of 27.4% observed over 1.0 g Ce\textsubscript{O}/TiO\textsubscript{2} catalyst under similar flue gas conditions.\textsuperscript{37} The result indicates that the Hg\textsuperscript{0} catalytic conversion performance of Ce\textsubscript{O}/TiO\textsubscript{2} catalyst was enhanced by the addition of CuO, which was well incorporated into the catalyst matrix and/or highly dispersed on the Ce\textsubscript{O}/TiO\textsubscript{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\textsubscript{2} was introduced to the gas flow, E\textsubscript{con} increased to 89.0%. Gas-phase O\textsubscript{2} regenerates the lattice oxygen and replenishes the chemisorbed oxygen, which serves as Hg\textsuperscript{0} oxidants.

**Effect of NO on Hg\textsuperscript{0} Conversion.** NO can be oxidized on the surface of metal oxides-based catalysts, giving rise to species like NO\textsuperscript{+} and NO\textsubscript{2} which can cause oxidation of Hg\textsuperscript{0}.\textsuperscript{37} On the contrary, NO can cover active sites of Hg\textsuperscript{0}.\textsuperscript{37} A NO reduction experiment conducted at room temperature, 0.50 g of CuCeTi catalyst was penetrated in less than 5 min when N\textsubscript{2} gas flow containing 75 μg·m\textsuperscript{-3} Hg\textsuperscript{0} passed through it, demonstrating that the Hg\textsuperscript{0} physical adsorption capacity of the CuCeTi catalyst was negligible. Therefore, the variation of Hg\textsuperscript{0} concentration during an experiment was ascribed to the net sum of Hg\textsuperscript{0} oxidation and Hg\textsuperscript{2+} reduction.\textsuperscript{15,36} Accordingly, Hg\textsuperscript{0} conversion efficiency (E\textsubscript{con}) in this study was calculated by the following equation:

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

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

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

**Effect of NH\textsubscript{3} on Hg\textsuperscript{0} Conversion.** As a potential low temperature NH\textsubscript{3}–SCR catalyst,\textsuperscript{33} CuO/CeO\textsubscript{2}–TiO\textsubscript{2} catalyst...
would probably be used under SCR conditions where NH₃ is present. Therefore, it is indispensable to investigate Hg⁰ conversion activity in the presence of NH₃. As shown in Figure 1, an addition of NH₃ into pure N₂ exhibited an inhibitive effect on Hg⁰ conversion over the CuCeTi catalyst. After reaching equilibrium (about 1 h), 500 ppm of NH₃ balanced in N₂ resulted in an $E_{\text{con}}$ of 51.4%, which is lower than the 80.0% Hg⁰ conversion under pure N₂ condition. An $E_{\text{con}}$ of 45.5% was observed when NH₃ concentration further increased to 1000 ppm. This was probably due to (a) NH₃ consumed the surface oxygen which is responsible for Hg⁰ oxidation in pure N₂ atmosphere and/or (b) NH₃ inhibited Hg⁰ adsorption which is crucial for Hg⁰ oxidation through different mechanisms. However, NH₃ exhibited no obviously inhibitive effect on Hg⁰ conversion in the presence of O₂. A 1000 ppm sample of NH₃ plus 4% O₂ balanced in N₂ resulted in an $E_{\text{con}}$ of 89.7%, which is statistically the same as the $E_{\text{con}}$ under N₂ plus 4% O₂ condition. This indicates that the presence of gas-phase O₂ offsets the greater part of the inhibitive effect of NH₃. Therefore, it can be concluded that the consumption of surface oxygen by NH₃ was mostly responsible for the deactivation of Hg⁰ conversion in the absence of O₂.

**Effect of the Co-presence of NO and NH₃ on Hg⁰ Conversion.** As stated above, NO never possessed a prohibitive effect on Hg⁰ conversion over the CuCeTi catalyst regardless of the presence of O₂. However, introduction of 1000 ppm of NO to a gas flow containing 1000 ppm of NH₃ without O₂ yielded a decrease of $E_{\text{con}}$ from 45.5% to 25.3%. Neither NO nor NH₃ exhibited an inhibitive effect on Hg⁰ conversion in the presence of O₂. However, the co-presence of NO and NH₃ resulted in a huge deactivation of Hg⁰ conversion over the CuCeTi catalyst. As shown in Figure 1, $E_{\text{con}}$ decreased from 89.0% to 58.0% when 1000 ppm of NO and 1000 ppm of NH₃ were introduced to gas flow containing 4% O₂.

To further confirm this interesting phenomenon, mercury conversion was studied under several SCR conditions with different NH₃/NO ratios. As shown in Figure 2, an $E_{\text{con}}$ of 98.3% was observed when the gas flow contained 4% O₂ and 1000 ppm of NO without NH₃ (NH₃/NO = 0). An additional 250 ppm of NH₃ (NH₃/NO = 0.25) resulted in an $E_{\text{con}}$ of 94.5%, which is lower than the 98.3% Hg⁰ conversion at NH₃/NO = 0. When NH₃/NO ratios were smaller than 1, an increase of the NH₃/NO ratio (i.e., maintaining NO concentration at 1000 ppm while increasing NH₃ concentration from 0 to 1000 ppm) resulted in less NO remaining in the gas flow, which was demonstrated to be promotional in Hg⁰ conversion. Therefore, a further increase of NH₃/NO ratio to 1 yielded less Hg⁰ conversion. The surplus NO should facilitate Hg⁰ oxidation when the NH₃/NO ratio was smaller than 1. If there was only Hg⁰ oxidation, Hg⁰ conversion should be higher than the $E_{\text{con}}$ of 89.0% under 4% O₂ plus N₂ condition when the NH₃/NO ratio was smaller than 1. However, $E_{\text{con}}$ values were observed to be 73.5% and 62.1% for NH₃/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 Hg⁰ conversion.

**Identification of Oxidized Mercury Reduction.** As stated above, it is very likely that the copresence of NO and NH₃ induced reduction of oxidized mercury, which offset part of Hg⁰ oxidation and hence resulted in lower Hg⁰ 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...
of the pretreated catalyst is presented in Figure 4. As shown, the Hg 4f spectrum of the pretreated catalyst possesses two peaks at 100.8 and 104.8 eV, respectively. This is in agreement with the difference in energy predicted by the spin–orbit splitting. There was no detectable Hg⁰ on the surface of the pretreated catalyst, because no obvious peak around 99.9 eV (characteristic peak for Hg 4f7/2 associated with Hg⁰) was observed. The binding energies of 100.8 (4f7/2) and 104.8 eV(4f5/2) confirmed that the dominating mercury species on the pretreated catalyst surface was HgO. This is in accordance with our preliminary study that negligible Hg⁰ can be physically absorbed 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. 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.

$$2\text{NO} + 2\text{NH}_3 + \text{HgO} \rightarrow 2\text{N}_2 + \text{Hg}^0 + 3\text{H}_2\text{O}$$

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 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.

$$2\text{NO} + 2\text{NH}_3 + \text{HgO} \rightarrow 2\text{N}_2 + \text{Hg}^0 + 3\text{H}_2\text{O}$$

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
control process. Therefore, an increase of temperature from 200 to 250 °C resulted in a higher $E_{\text{red}}$ (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. 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 $O_2$. 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:

$$2\text{NO} + 2\text{NH}_3 + 2\text{CeO}_2 \rightarrow 2\text{N}_2 + 2\text{Ce}_2\text{O}_3 + 3\text{H}_2\text{O}$$ (5)

$$2\text{NO} + 2\text{NH}_3 + 2\text{CuO} \rightarrow 2\text{N}_2 + 2\text{Cu}_2\text{O} + 3\text{H}_2\text{O}$$ (6)

$$\text{HgO} + 2\text{Ce}_2\text{O}_3 \rightarrow 2\text{CeO}_2 + \text{Hg}^0$$ (7)

$$\text{HgO} + 2\text{Cu}_2\text{O} \rightarrow 2\text{CuO} + \text{Hg}^0$$ (8)

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 Ce$^{4+}$ and Cu$^{2+}$ from reactions 9 and 10 are more active than HgO for NO reduction, NO and NH$_3$ will preferentially react with Ce$^{4+}$ and Cu$^{2+}$ rather than HgO. These were verified by less Hg$^0$ detected at the reactor outlet.

$$O_2 + 2\text{Ce}_2\text{O}_3 \rightarrow 4\text{CeO}_2$$ (9)

$$O_2 + 2\text{Cu}_2\text{O} \rightarrow 4\text{CuO}$$ (10)

## 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.

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