Supplementary Material

Using rice-husk-derived porous silica modified with recycled Cu from industrial wastewater and Ce to remove Hg\(^0\) and NO from simulated flue gases

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Detailed descriptions on Hg\(^0\) and NO removal tests

The experiment apparatus for Hg\(^0\)/NO removal tests is shown in Figure S1. The Hg\(^0\) removal tests were carried out in a fixed-bed reactor using a simulated coal-combustion flue gas containing 30, 65, 100 ± 5 \(\mu\)g m\(^{-3}\) Hg\(^0\) at 150, 250 and 350°C (Chiu et al., 2015, 2017; Liu et al., 2017; Lin et al., 2019). In the testing apparatus, Hg\(^0\) was generated with a certificated Hg\(^0\) permeation tube (VICI Metronics) in a gas generator at 70 ± 0.1°C to ensure a constant Hg\(^0\) diffusion rate. The N\(_2\) flow carrying

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gaseous Hg$^0$ at constant concentration was mixed with other gases. The simulated flue gas also contained 12% CO$_2$, 10% H$_2$O, 6% O$_2$, 50 ppm HCl, 200 ppm SO$_2$, 200 ppm NO, and balanced N$_2$ prepared from standard gas cylinders. The composition of the simulated flue gas was selected to reflect the typical condition of Taiwan’s coal-fired power plants, in which low-sulfur bituminous and subbituminous coal blends are typically burned. The resulting gas stream passed through a temperature-controlled fixed-bed column (0.5-in i.d.) containing a 10 mg sample. The gas flow through an empty column was about 1.5 l min$^{-1}$ at 25°C. The column length of the sample/sand mixture was about 1.5 cm, the time for gas stream to pass the mixture was approximately 0.03 s and the space velocity was approximately 120,000 hr$^{-1}$. The effluent gas from the fixed-bed column flowed through heated lines to an impinger containing SnCl$_2$(aq) that reduced any oxidized Hg compounds to Hg$^0$; therefore, the concentration of total Hg (Hg$^0$ and Hg$^{2+}$) could be determined. Gas exiting the impinger solutions flowed through a gold amalgamation column housed in a tubular furnace where the Hg$^0$ in the gas was adsorbed. The Hg$^0$ that was concentrated on the gold was then thermally desorbed and sent as a concentrated Hg$^0$ stream to a cold-vapor atomic fluorescence spectrophotometer (CVAFS; Brooks Rand Lab Model III) for analysis. The experiment was performed for 900 min or ceased until 100% breakthrough achieved. The Hg adsorption capacities of raw and treated samples were then calculated based on the breakthrough results obtained from the CVAFS measurements.

The average total Hg removal efficiency can be calculated as follow:

$$\text{Percentage of average total Hg removal} = \frac{1}{n} \sum \frac{[\text{CHg}_{\text{in}}^0 - \text{CHg}_{\text{out}}^0]}{\text{CHg}_{\text{in}}^0} \times 100\% \quad (1)$$

where $\text{CHg}_{\text{in}}^0$ is the concentration of inlet Hg$^0$ (μg Nm$^{-3}$) and $\text{CHg}_{\text{out}}^0$ is the concentration of outlet Hg$^0$ (μg Nm$^{-3}$). The total test number $n$ also is 180 because 5
min was required to obtain one data point within the 900 min experiment.

NO concentrations was continuously monitored with a flue gas component analyzer (Sick Maihak S710). The resulting gas stream passed through a temperature-controlled fixed-bed column (1-in i.d.) containing a 1 g sample, and the sample was dispersed by glass wool. The gas flow through an empty column was about 1.5 l min⁻¹ at 25°C. The test temperature was from 200 to 400°C. The column length of the sample/glass wool mixture was about 5 cm, the time for gas stream to pass the mixture was approximately 1 sec and the space velocity was 3600 hr⁻¹. Because a portion of the downstream NO was captured by the cooler/condenser located prior to the flue gas analyzer, the NO removal was determined respectively by:

\[
\text{NO conversion (\%)} = \left( \frac{c_{\text{NO, blank}} - c_{\text{NO, out}}}{c_{\text{NO, blank}}} \right) \times 100\%
\]  

for here \(c_{\text{NO, blank}}\) is NO concentrations obtained from blank tests. The blank tests were performed under simulated flue gas condition and without the presence of metal oxide-incorporated SiO₂. \(c_{\text{NO, out}}\) is the NO concentrations in the outlet stream, respectively, when mesoporous particles are in the fixed-bed reactor.
(1) Gas mixing chamber-1
(2) Gas mixing chamber-2
(3) Mercury vapor generator
(4) Temperature-controlled; adsorbent fixed bed
(5) Gold/amalgamation/CVAFS
(6) Computer system
(7) Cooler/condenser
(8) SO₂/NO continuously monitored system
(9) Water pump

Fig. S1 Experimental system for fixed-bed testing of raw and metal-incorporated SiO₂ catalysts (Chiu et al., 2015, 2017; Liu et al., 2017; Lin et al., 2019)
Fig. S2 O1s XPS spectra of raw and metal-oxide SiO$_2$
Fig. S3 Cu2p XPS spectra of raw and metal-oxide SiO2
Fig. S4 H₂-TPR profiles of metal-oxide SiO₂
Fig. S5 NH$_3$-TPD profiles of metal-oxide SiO$_2$
**Table S1.** Select applications of transition metal oxide surface-modified materials on NO and Hg$^0$ removal

<table>
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<tr>
<th>Material</th>
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| SiO$_2$–TiO$_2$–V$_2$O$_5$       | 1. 10 ppm HCl, 300 ppm NO, 400 ppm SO$_2$, 4% O$_2$, 8% H$_2$O, 12% CO$_2$ balanced by N$_2$  
  2. Flow rate: 1000 ml min$^{-1}$  
  3. GHSV: 80000 h$^{-1}$  
  4. Temperature: 135–400°C  
  5. Hg$^0$ concentration: 70 μg m$^{-3}$ | Hg$^0$           | 1. Hg$^0$ oxidation activity over STV catalysts decreased from 135 to 300°C due to the impact of water vapor.  
  2. At typical SCR operating temperatures, Hg$^0$ oxidation efficiency increased as the titania loading of the STV increased up to 18wt%. | Li et al. (2011)         |
| MnO$_x$/CeO$_2$–TiO$_2$          | 1. 400 ppm NO, 400 ppm CO, 30–50 ppbv Hg$^0$ and balanced N$_2$  
  2. GHSV: 5000–10200 h$^{-1}$  
  3. Temperature: 175 and 200°C | NO/Hg$^0$        | 1. After impregnation with MnO$_x$, the Ce$^{3+}$ content increased compared to that of the CeO$_2$–TiO$_2$ support.  
  2. The NO removal capacity of MnO$_x$/CeO$_2$–TiO$_2$ decreased only slightly, from 160 to 152 mg g$^{-1}$, in the presence of Hg$^0$, while the Hg$^0$ capacity decreased from 37 to 5.1 mg g$^{-1}$ when NO was added. | He et al. (2013)          |
| 8% CuO/AC-H                      | 1. 500 ppm NO, 5% O$_2$ balanced by N$_2$  
  2. Flow rate: 300 ml min$^{-1}$  
  3. GHSV: 23000 h$^{-1}$  
  4. Temperature: 80–200°C  
  5. Hg$^0$ concentration: 50 μg m$^{-3}$ | Hg$^0$           | 1. 8%CuO loading and 300°C calcination for 3 hours was found to be the optimal material for mercury removal, achieving around 73% average efficiency at 120°C.  
  2. The increase of reaction temperature would enhance the removal efficiency when it was below 160°C, but had a negative effect with further increase. | Zhao et al. (2016)        |
| CeO$_2$/TiO$_2$–SiO$_2$ (Mass ratio of Ti/Si=3/1) | 1. 500 ppm NO, 500 ppm NH$_3$, 200 ppm SO$_2$, 10% H$_2$O, 3% O$_2$ balanced by N$_2$  
  2. Flow rate: 300 ml min$^{-1}$  
  3. GHSV: 28000 h$^{-1}$  
  4. Temperature: 150–500°C | NO               | 1. With the addition of SiO$_2$ into TiO$_2$, the activity temperature range was broadened.  
  2. Ce/Ti-Si (3:1) showed the best activity, its NO$_x$ conversion was greater than 90% in the temperature range of 250–450°C. | Liu et al. (2012)         |
Compared to Ce/Ti, the stability of SCR activity over Ce/Ti–Si (3:1) was greatly improved in the presence of SO₂.

| Fe₂O₃-SiO₂ | 1. 12% CO₂, 6% O₂, 500, 1000, 2000, 3000 ppm SO₂, 0, 1, 3, 6, 10% H₂O balanced by N₂ | Hg⁰ | 1. The FS catalyst with loading value of 10% showed the best performance at 350°C. | Tan et al. (2012) |
|           | 2. Flow rate: 2.1 min⁻¹ |   | 2. High concentration SO₂ (>1500 ppm) is not conducive to Hg⁰ removal by FS catalyst. |
|           | 3. Temperature: 80–450°C |   |                                           |
|           | 4. Hg⁰ concentration: 40 μg m⁻³ |   |                                           |

| Ce-Cu modified V₂O₅/ TiO₂ based SCR catalysts | 1. 500 ppm NO, 500 ppm NH₃, 1000 ppm SO₂, and 5% O₂ balanced by N₂ | Hg⁰/NO | 1. 7%Ce-1%Cu/SCR showed the best removal efficiency on mercury and NO. | Chi et al. (2017) |
|                                              | 2. Flow rate: 1.5 L min⁻¹ |   | 2. Commercial SCR modified with 7%Ce-1%Cu improved the SCR activity in the presence of SO₂ (recover from 65% to 90%). |
|                                              | 3. GHSV: 45,000 h⁻¹ |   |                                           |
|                                              | 4. Temperature: 150–400°C |   |                                           |
|                                              | 5. Hg⁰ concentration: 30 μg m⁻³ |   |                                           |

| Cu-Mn/ordered mesoporous carbon (prepared by three different method: self-assembly (S), ultrasound-assisted impregnation (I), and mechanical mixing (M)). | 1. 500 ppm NO, 500 ppm NH₃, 5% O₂ balanced by N₂ | NO | 1. Cu-Mn/OMC(S) performed the highest NO conversion (88%) at 250°C. | Yu et al. (2017) |
|                                                                 | 2. Flow rate: 0.06 L min⁻¹ |   | 2. XRD indicated manganese oxides are highly dispersed on the surface of the Cu-Mn/OMC(S). |
|                                                                 | 3. GHSV: 36,000 h⁻¹ |   | 3. According to XPS, the self-assembly method provided the highest ratio of Mn⁴⁺/Mn³⁺, Cu²⁺/Cu⁺, and chemisorbed oxygen. |
|                                                                 | 4. Temperature: 100–300°C |   |                                           |

| MnOx(12%)/Zr–Ce–PILC(30) | 1. 600 ppm NO, 600 ppm NH₃, 8% O₂, 3% H₂O balanced by N₂ | NO | 1. The MnOₓ(12%)/Zr–Ce–PILC(30) catalyst can reach 96% of NOₓ conversion at 200°C | Boxiong et al. (2014) |
|                          | 2. Flow rate: 300 ml min⁻¹ |   | 2. NOₓ conversion decreased as the GHSV increased; however, the change was negligible in the GHSV range from 20000 h⁻¹ to 35000 h⁻¹. |
|                          | 3. GHSV: 20000–50000 h⁻¹ |   | 3. The inhibition effect of H₂O on the adsorption of NH₃ and NOₓ was mainly caused by the competitive adsorption of H₂O on the surface of the catalyst. |
|                          | 4. Temperature: 80–280°C |   |                                           |