

Supplementary Material

Using rice-husk-derived porous silica modified with recycled Cu from industrial wastewater and Ce to remove Hg⁰ and NO from simulated flue gases

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Detailed descriptions on Hg⁰ and NO removal tests

The experiment apparatus for Hg⁰/NO removal tests is shown in Figure S1. The Hg⁰ removal tests were carried out in a fixed-bed reactor using a simulated coal-combustion flue gas containing 30, 65, 100 ± 5 μg m⁻³ Hg⁰ at 150, 250 and 350°C (Chiu *et al.*, 2015, 2017; Liu *et al.*, 2017; Lin *et al.*, 2019). In the testing apparatus, Hg⁰ was generated with a certificated Hg⁰ permeation tube (VICI Metronics) in a gas generator at 70 ± 0.1°C to ensure a constant Hg⁰ diffusion rate. The N₂ 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_2O , 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 $120,000 \text{ hr}^{-1}$. The effluent gas from the fixed-bed column flowed through heated lines to an impinger containing $\text{SnCl}_{2(\text{aq})}$ 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 CHg_{in}^0 is the concentration of inlet Hg^0 ($\mu\text{g Nm}^{-3}$) and $\text{CHg}_{\text{out}}^0$ is the concentration of outlet Hg^0 ($\mu\text{g Nm}^{-3}$). 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 were continuously monitored with a flue gas component analyzer (Sick Mairhak 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:

$$\text{NO conversion (\%)} = \frac{[C_{\text{NO}}^{\text{blank}} - C_{\text{NO}}^{\text{out}}]}{C_{\text{NO}}^{\text{blank}}} \times 100\% \quad (2)$$

for here $C_{\text{NO}}^{\text{blank}}$ 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 SiO_2 . $C_{\text{NO}}^{\text{out}}$ is the NO concentrations in the outlet stream, respectively, when mesoporous particles are in the fixed-bed reactor.

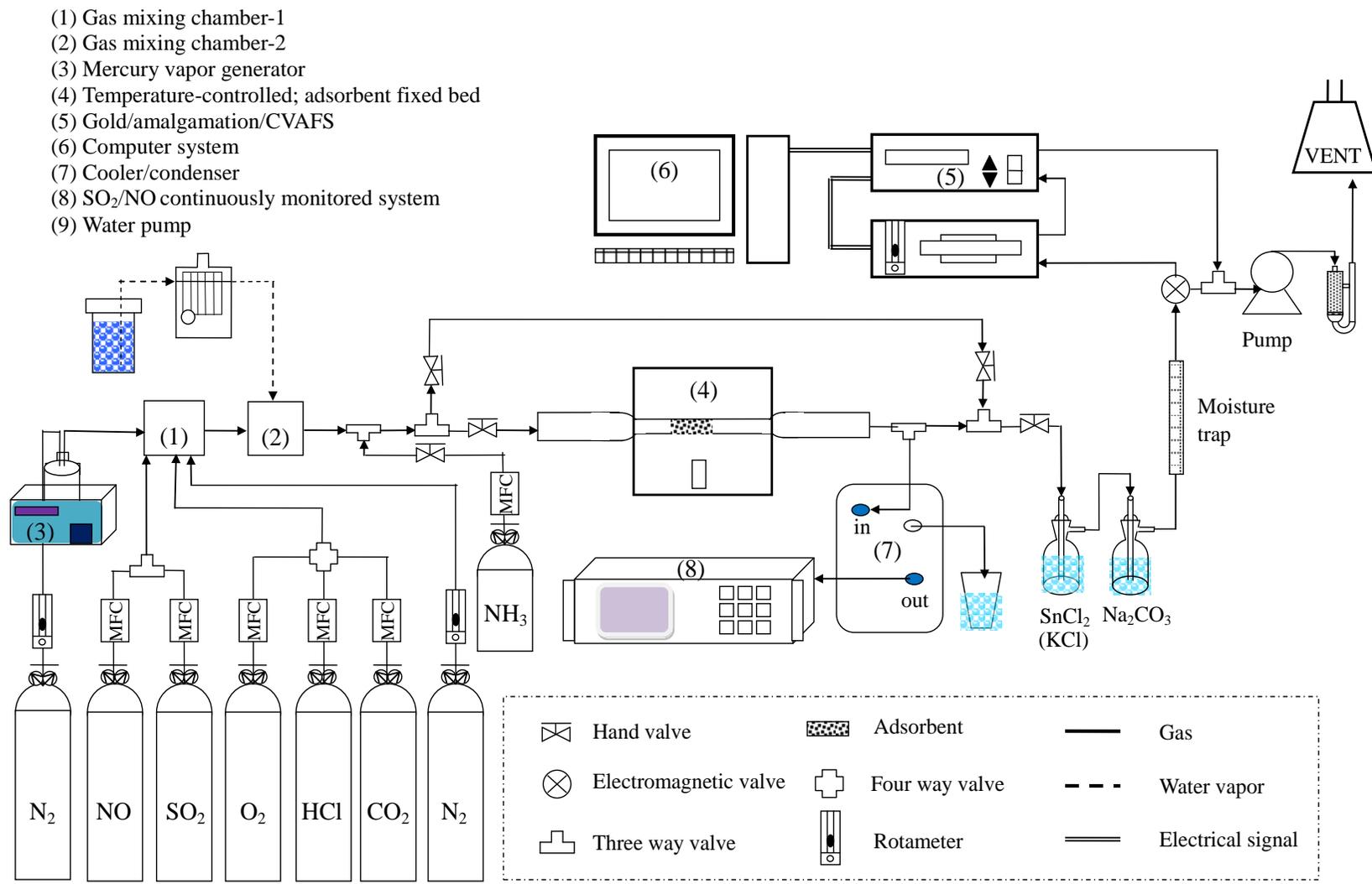


Fig. S1 Experimental system for fixed-bed testing of raw and metal-incorporated SiO₂ catalysts (Chiu *et al.*, 2015, 2017; Liu *et al.*, 2017; Lin *et al.*, 2019)

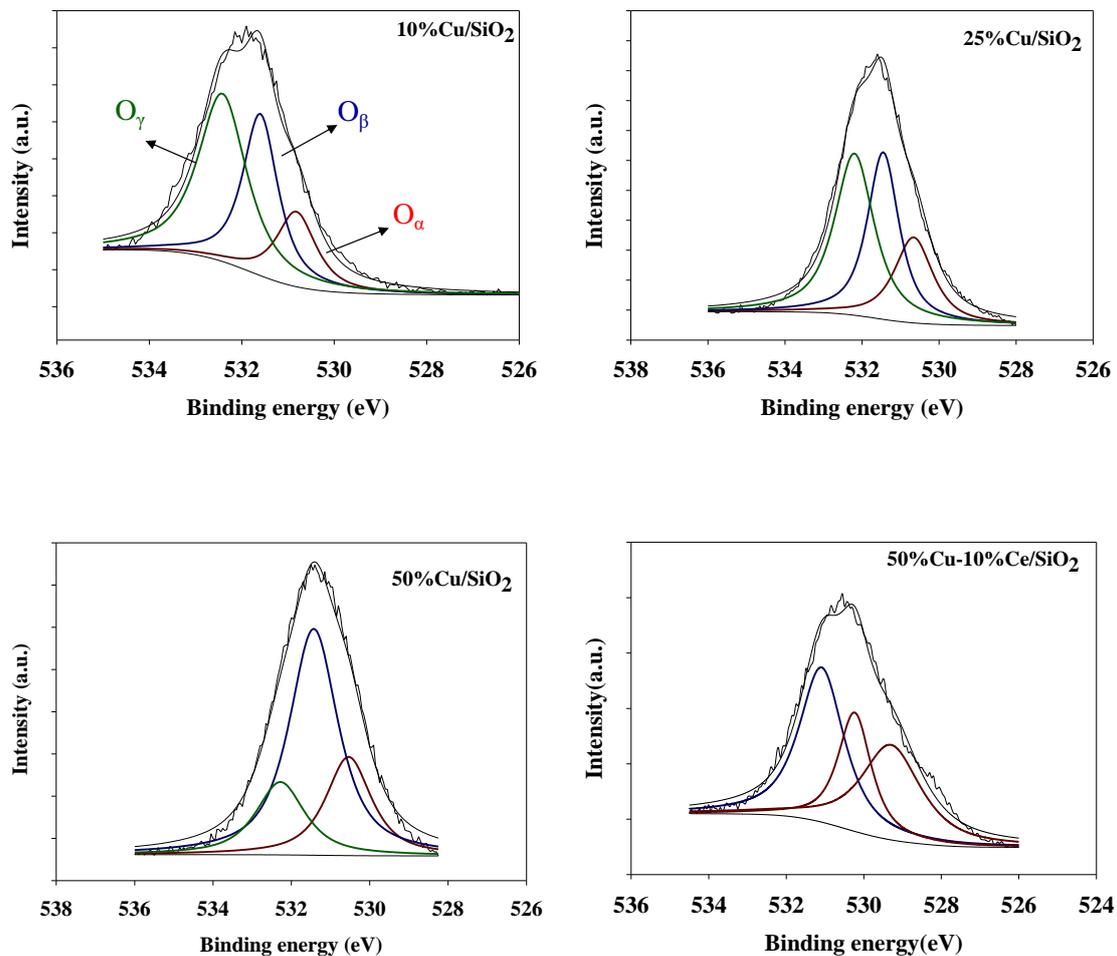


Fig. S2 O1s XPS spectra of raw and metal-oxide SiO₂

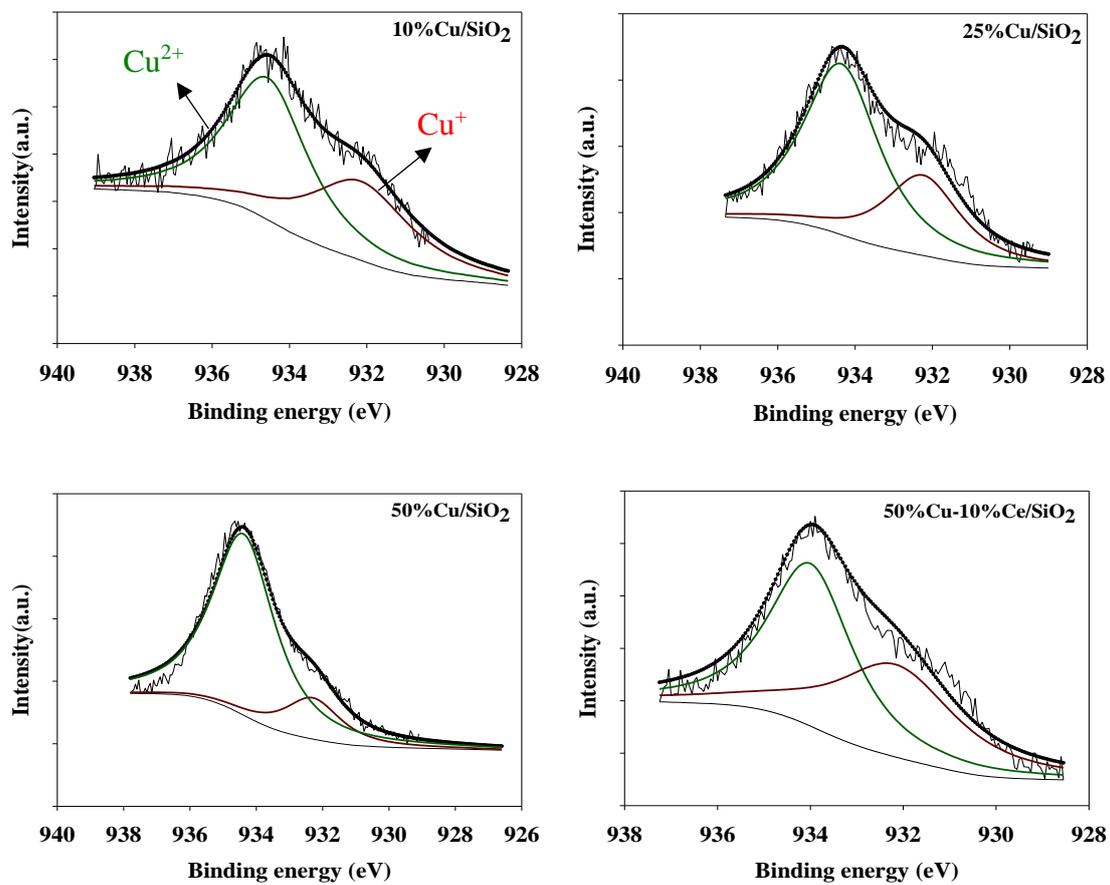


Fig. S3 Cu₂p XPS spectra of raw and metal-oxide SiO₂

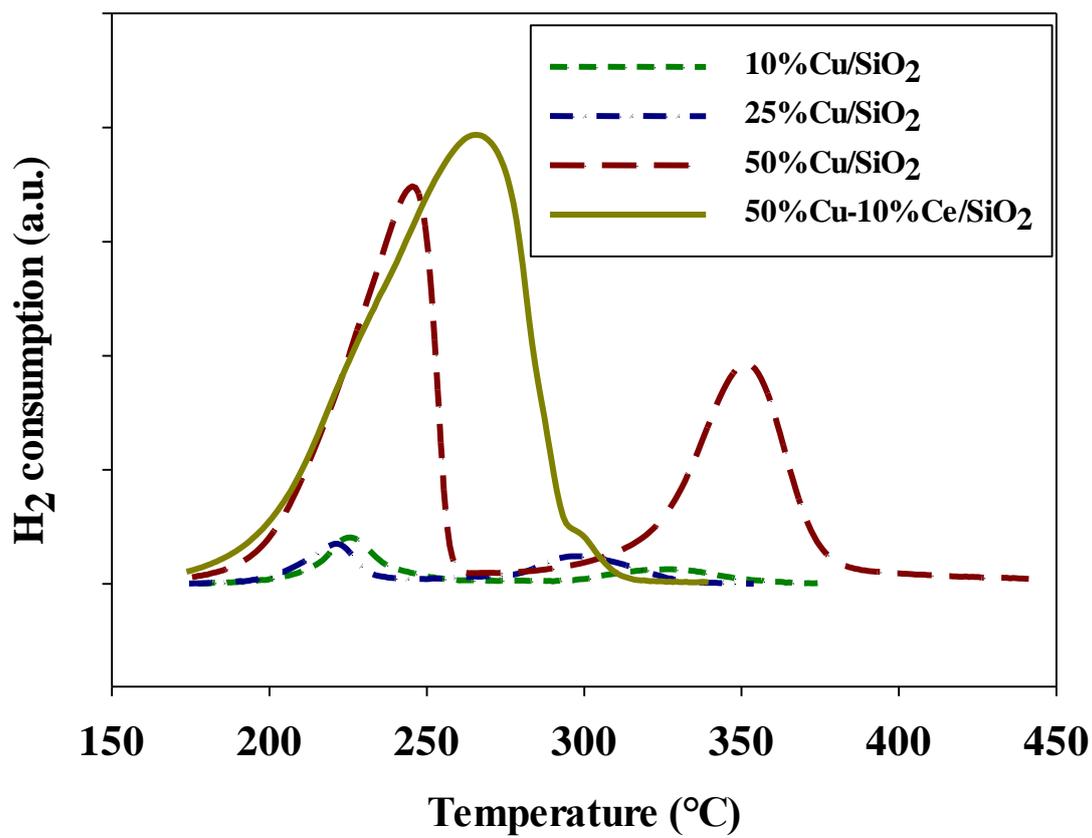


Fig. S4 H₂-TPR profiles of metal-oxide SiO₂

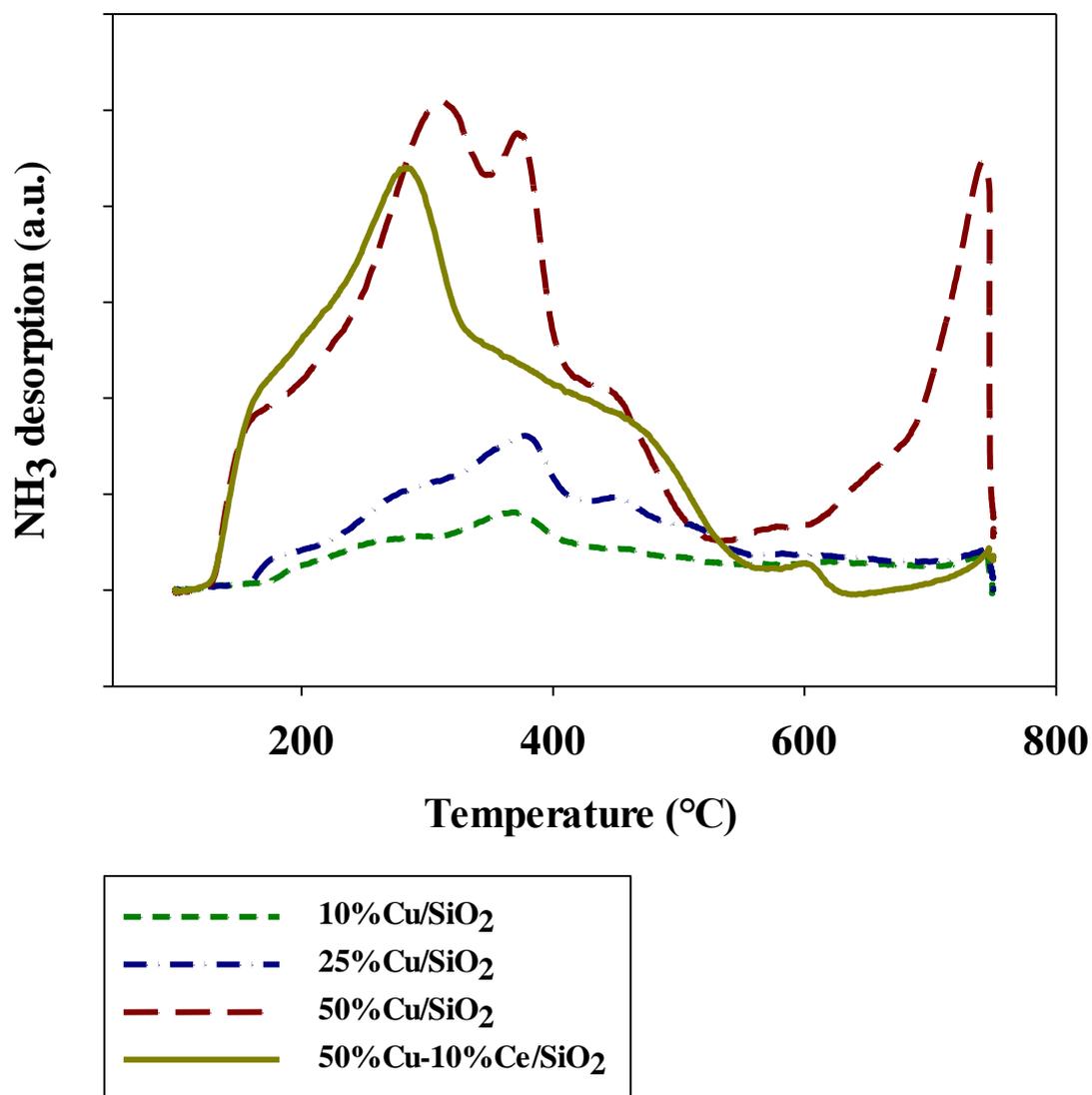


Fig. S5 NH₃-TPD profiles of metal-oxide SiO₂

Table S1. Select applications of transition metal oxide surface-modified materials on NO and Hg⁰ removal

Material	Reaction condition	Target pollutant	Experimental results	References
SiO ₂ -TiO ₂ -V ₂ O ₅	<ol style="list-style-type: none"> 10 ppm HCl, 300 ppm NO, 400 ppm SO₂, 4% O₂, 8% H₂O, 12% CO₂ balanced by N₂ Flow rate: 1000 ml min⁻¹ GHSV: 80000 h⁻¹ Temperature: 135-400°C Hg⁰ concentration: 70 μg m⁻³ 	Hg ⁰	<ol style="list-style-type: none"> Hg⁰ oxidation activity over STV catalysts decreased from 135 to 300°C due to the impact of water vapor. At typical SCR operating temperatures, Hg⁰ oxidation efficiency increased as the titania loading of the STV increased up to 18wt%. 	Li <i>et al.</i> (2011)
MnO _x /CeO ₂ -TiO ₂	<ol style="list-style-type: none"> 400 ppm NO, 400 ppm CO, 30-50 ppbv Hg⁰ and balanced N₂ GHSV: 5000-10200 h⁻¹ Temperature: 175 and 200°C 	NO/Hg ⁰	<ol style="list-style-type: none"> After impregnation with MnO_x, the Ce³⁺ content increased compared to that of the CeO₂-TiO₂ support. The NO removal capacity of MnO_x/CeO₂-TiO₂ decreased only slightly, from 160 to 152 mg g⁻¹, in the presence of Hg⁰, while the Hg⁰ capacity decreased from 37 to 5.1 mg g⁻¹ when NO was added. 	He <i>et al.</i> (2013)
8%CuO/AC-H	<ol style="list-style-type: none"> 500 ppm NO, 5% O₂ balanced by N₂ Flow rate: 300 ml min⁻¹ GHSV: 23000 h⁻¹ Temperature: 80-200°C Hg⁰ concentration: 50 μg m⁻³ 	Hg ⁰	<ol style="list-style-type: none"> 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. 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 <i>et al.</i> (2016)
CeO ₂ /TiO ₂ -SiO ₂ (Mass ratio of Ti/Si=3/1)	<ol style="list-style-type: none"> 500 ppm NO, 500 ppm NH₃, 200 ppm SO₂, 10% H₂O, 3% O₂ balanced by N₂ Flow rate: 300 ml min⁻¹ GHSV: 28000 h⁻¹ Temperature: 150-500°C 	NO	<ol style="list-style-type: none"> With the addition of SiO₂ into TiO₂, the activity temperature range was broadened. 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 <i>et al.</i> (2012)

			3. Compared to Ce/Ti, the stability of SCR activity over Ce/Ti–Si (3:1) was greatly improved in the presence of SO ₂ .	
Fe₂O₃-SiO₂	<ol style="list-style-type: none"> 12% CO₂, 6% O₂, 500, 1000, 2000, 3000 ppm SO₂, 0, 1, 3, 6, 10% H₂O balanced by N₂ Flow rate: 2 l min⁻¹ Temperature: 80–450°C Hg⁰ concentration: 40 μg m⁻³ 	Hg ⁰	<ol style="list-style-type: none"> The FS catalyst with loading value of 10% showed the best performance at 350°C. High concentration SO₂ (>1500 ppm) is not conducive to Hg⁰ removal by FS catalyst. 	Tan <i>et al.</i> (2012)
Ce-Cu modified V₂O₅/TiO₂ based commercial SCR catalysts	<ol style="list-style-type: none"> 500 ppm NO, 500 ppm NH₃, 1000 ppm SO₂, and 5% O₂ balanced by N₂ Flow rate: 1.5 L min⁻¹ GHSV: 45,000 h⁻¹ Temperature: 150–400°C Hg⁰ concentration: 30 μg m⁻³ 	Hg ⁰ /NO	<ol style="list-style-type: none"> 7%Ce-1%Cu/SCR showed the best removal efficiency on mercury and NO. Commercial SCR modified with 7%Ce-1%Cu improved the SCR activity in the presence of SO₂ (recover from 65% to 90%). 	Chi <i>et al.</i> (2017)
Cu-Mn/ordered mesoporous carbon (prepared by three different method: self-assembly (S), ultrasound-assisted impregnation (I), and mechanical mixing (M)).	<ol style="list-style-type: none"> 500 ppm NO, 500 ppm NH₃, 5% O₂ balanced by N₂ Flow rate: 0.06 L min⁻¹ GHSV: 36,000 h⁻¹ Temperature: 100–300°C 	NO	<ol style="list-style-type: none"> Cu-Mn/OMC(S) performed the highest NO conversion (88%) at 250°C. XRD indicated manganese oxides are highly dispersed on the surface of the Cu-Mn/OMC(S). According to XPS, the self-assembly method provided the highest ratio of Mn⁴⁺/Mn³⁺, Cu²⁺/Cu⁺, and chemisorbed oxygen. 	Yu <i>et al.</i> (2017)
MnO_x(12%)/Zr–Ce–PILC(30)	<ol style="list-style-type: none"> 600 ppm NO, 600 ppm NH₃, 8% O₂, 3% H₂O balanced by N₂ Flow rate: 300 ml min⁻¹ GHSV: 20000–50000 h⁻¹ Temperature: 80–280°C 	NO	<ol style="list-style-type: none"> The MnO_x(12%)/Zr–Ce–PILC (30) catalyst can reach 96% of NO_x conversion at 200°C NO_x conversion decreased as the GHSV increased; however, the change was negligible in the GHSV range from 20000 h⁻¹ to 35000 h⁻¹. The inhibition effect of H₂O on the adsorption of NH₃ and NO_x was mainly caused by the competitive adsorption of H₂O on the surface of the catalyst. 	Boxiong <i>et al.</i> (2014)