

Supporting Information

Highly Dispersed Mn–Ce Binary Metal Oxides Supported on Carbon Nanofibers for Hg⁰

Removal from Coal-Fired Flue Gas

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I. Sorbent Preparation

II. Sorbent Characterization

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I. Sorbent Preparation

Commercial carbon nanofibers (CNFs, purity 99.9%) were purchased from Beijing Dk nano S&T Ltd. The CNFs were pretreated before being used as the support. The CNFs were mixed with concentrated nitric acid for 3 h with ultrasonic oxidation treatment. Then, the mixture was separated by a centrifuge, washed by deionized water, and dried at 75 °C. The pretreated CNFs were named CNFs(OX).

The metal-oxide-loaded sorbents were prepared by a wet chemistry method. CNFs(OX) were mixed with deionized water and the mixture were stirred continuously at 40 °C for 30 min. Then, citric acid solution was added, and the mixture was stirred for another 20 min. Later, the nitrates were added to the beaker and stirred for 4 h continuously. The mixed solution was evaporated at 75 °C, and the dried samples were calcined at 450 °C for 4 h under a N₂ atmosphere. The calcined samples were ground and sieved to 0.45–0.2 mm for activity tests.

The synthesized sorbents were named $\alpha\text{MnO}_x\text{-}\alpha\text{CeO}_2/\text{CNFs(OX)}$, where α represents the mass percentage of MnO₂ and CeO₂ in the sorbents. The mass ratio of Mn/Ce was set as 1:1. Sorbents of five different loading values ($\alpha = 6\%$, 9%, 12%, 15%, and 18%) were prepared.

II. Sorbent Characterization

The crystallinity and dispersity of the active metals in the different sorbents were analyzed by X-ray powder diffraction (XRD, PANalytical B.V., Holland). The surface physical characteristics of different sorbents were analyzed using N₂ adsorption–desorption measurements at 77 K by utilizing Brunauer–Emmett–Teller (BET, TriStar, micromeritics, USA). The valence of surface elements and surface atomic concentrations of different loading value sorbents were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, Japan). The spent sorbent was used to carry out the Hg-TPD test with a carrier gas. The heating rate was 10 °C/min. A Sirion 200 scanning electron microscope (FEI, Holand) was used for detecting the topography.

III. Supplementary Tables

Table S1. Experimental conditions.

Set	Sorbents	Flue gas components	Temperature (°C)
I	CNFs, CNFs(OX), α MnO _x - α CeO ₂ /CNFs(OX) (α =6%-18%)	N ₂ +6% O ₂	170
II	15% MnO _x - 15% CeO ₂ /CNFs(OX)	N ₂ +6% O ₂	70, 120, 170, 220
III	15% MnO _x - 15% CeO ₂ /CNFs(OX)	N ₂ N ₂ +12% CO ₂ N ₂ +3%, 6% O ₂	120
IV	15% MnO _x - 15% CeO ₂ /CNFs(OX)	N ₂ +500, 1000, 1500ppmSO ₂ N ₂ +6% O ₂ +500, 1000, 1500ppmSO ₂	120
V	15% MnO _x - 15% CeO ₂ /CNFs(OX)	N ₂ +100, 200, 300ppmNO N ₂ +6% O ₂ +100ppmNO	120
VI	15% MnO _x - 15% CeO ₂ /CNFs(OX)	N ₂ +8% H ₂ O N ₂ +6% O ₂ +8% H ₂ O	120

Table S2. A comparison of the Hg⁰ removal efficiency in this study and that of other Mn–Ce-based composites reported in the literature.

Support	Temperature (°C)	Q/M (ml·h ⁻¹ ·g ⁻¹)	Reaction time (h)	Atmosphere	Efficiency (%)	Ref.
TiO ₂	200	120,000	-	N ₂ +4% O ₂ +75μg/m ³ Hg	75	[1]
γ-Al ₂ O ₃	250	200,000	-	N ₂ +4.5% O ₂ +75μg/m ³ Hg	60	[2]
Ti-PILCs	100-200	120,000	2	N ₂ +5% O ₂ +45μg/m ³ Hg	>98	[3]
Activated	190	3,333	3	N ₂ +6% O ₂ +80μg/m ³ Hg	95	[4]
coke			3	N ₂ +9% O ₂ +80μg/m ³ Hg	~95	
CNFs	120	300,000	9	N ₂ +3% O ₂ +95μg/m ³ Hg	81.9	<i>Present</i>
			9	N ₂ +6% O ₂ +95μg/m ³ Hg	>99	

V. Supplementary References

- [1] Li H, Wu C-Y, Li Y, Zhang J. Superior activity of MnO_x-CeO₂/TiO₂ catalyst for catalytic oxidation of elemental mercury at low flue gas temperatures. *Appl. Catal., B* 2012,111-112,381-8.
- [2] He C, Shen B, Chen J, Cai J. Adsorption and Oxidation of Elemental Mercury over Ce-MnO_x/Ti-PILCs. *Environ. Sci. Technol.* 2014,48(14),7891-8.
- [3] Wang P, Su S, Xiang J, You H, Cao F, Sun L, et al. Catalytic oxidation of Hg⁰ by MnO_x-CeO₂/γ-Al₂O₃ catalyst at low temperatures. *Chemosphere* 2014,101,49-54.
- [4] Xie Y, Li C, Zhao L, Zhang J, Zeng G, Zhang X, et al. Experimental study on Hg⁰ removal from flue gas over columnar MnO_x-CeO₂/activated coke. *Appl. Surf. Sci.* 2015,333,59-67.