Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2014

Supporting Information

Efficient Removal of Elemental Mercury (Hg⁰) by SBA-15-Ag Adsorbents

Yijun Xie^a, Bin Yan^a, Chong Tian^b, Yuxi Liu^a, Qingxia Liu^a and Hongbo Zeng^a, *

^aDepartment of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2V4, Canada.

^bState Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, P.R.China.

*Email: <u>hongbo.zeng@ualberta.ca;</u> phone: +1-780-492-1044; fax: +1-780-492-2881

1. Experimental methods

1.1 Chemicals

Pluronic P-123, tetraethyl orthosilicate (TEOS), sodium citrate (Na₃Cit) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37%), ammonia hydroxide (28%), silver nitrate (AgNO₃) were obtained from Fisher Scientific. All chemicals were directly used without further purification. Ultrapure water prepared with a Millipore Milli-Q water purification system (MA, USA) was used for all experiments.

1.2 Synthesis of mesoporous silica (SBA-15)

2.0 g of P123 was dissolved in 62 mL of 2 M HCl at the room temperature. After P123 was completely dissolved, 4.2 g of TEOS was added to this solution and the synthesis was carried out by stirring for 24 h at 40 °C. Then the mixture was transferred into an autoclave and aged at 100 °C for 24 h. After that, the white precipitate was collected by filtration and dried at 80 °C. The product was obtained by removing the P123 template via calcining at 550 °C for 5 h.

1.3 Synthesis of Ag loaded mesoporous silica (SBA-15-Ag)

To prepare 10 wt% Ag loaded SBA-15, 300 mg of SBA-15 powder was soaked in 10 mL silver ammonia solution containing 52 mg AgNO₃ for a day. Silver ammonia solution was prepared by adding ammonia aqueous solution (2 wt.%) into AgNO₃ solution until brown precipitation was just dissolved. Then, 30 mL of trisodium citrate aqueous solution containing 90 mg trisodium citrate was added to this mixture and stirred magnetically for 6 h at 80 °C. The dried solid was centrifuged with ultrapure water twice and then dried at 60 °C to obtain 10 wt% Ag loaded SBA-15 sample. 5 wt% Ag loaded SBA-15 was synthesized by using the same procedure with 26 mg AgNO₃ and 45 mg trisodium citrate, respectively. For comparison, AgNO₃ solution was also used as the Ag source in place of silver ammonia solution accordingly.

2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RU-200B Xray diffractometer with a rotating anode X-ray generator, Cu Kα radiation (40 kV, 110 mA). The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were performed on a Philips (FEI) Morgagni 268 TEM operated at 80 kV and JEOL JAMP 9500F Auger Microscope. The samples are coated with gold film for SEM characterization. The X-ray mapping was analyzed on an energy dispersive X-ray spectroscopy (EDS) system from Oxford Instruments. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis spectrometer with monochromatized Al Ka. C 1s peak at 284.6 eV was used to correct all XPS spectra. Fourier transform infrared (FT-IR) spectra were collected on Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) using an ATR diamond crystal. Nitrogen adsorption/desorption isotherms were determined using a surface analysis system (iQ2MP, Quantachrome) at -196 °C. Before measurements, the samples were degassed at 3 h at 200 °C. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area in a relative pressure range of 0.05 to 0.15. Pore size was obtained from the adsorption branch of N₂ adsorption-desorption isotherms. The Barrett-Joyner-Halenda (BJH) analysis provided the pore size distributions, and total pore volume was determined at P/P₀ = 0.975.

3. Mercury breakthrough test

Elemental mercury (Hg⁰) breakthrough test were performed on a Tekran model-2500 cold vapour atomic fluorescence spectrophotometer (CVAFS). The experimental setup was shown in Scheme S1. In summary, 30 mg of adsorbents were loaded into a borosilicate glass u-tube with 4 mm inside diameter, held into a GC oven. The GC oven was used to control the temperature for the adsorbents to capture Hg⁰. 200 μ L of Hg⁰ standard vapour at room temperature was injected at port 1 with an argon flow rate of 40 mL/min. The gold beads (GB) trap was used as a standard mercury preconcentration device to capture remaining Hg^0 vapour which was not adsorbed by the adsorbents. After 3 min, the gold trap was rapidly heated by the heat coil to release the Hg^0 . The Hg^0 signal was further detected by CVAFS. The Hg^0 breakthrough was calculated as the ratio between the amounts of captured Hg^0 by gold trap and injected Hg^0 vapour. Regeneration of the adsorbents was achieved by heating under 350 °C for 10 min after capturing Hg^0 vapour.

4. Mercury capture in flue gas

In the test, 14 mg of adsorbents were exposed on continuous flue gas (flow rate: 1.2 L/min) with a composition of 4% O_2 , 12% CO_2 , 400 ppm SO₂, 300 ppm NO and 77.6 μ g/m³ Hg⁰ under different temperature. The concentration of Hg⁰ from the outlet of the flue gas was determined by the VM-3000 mercury vapour detector (Mercury Instruments, Germany).



Figure S1. TEM image of SBA-15-10% Ag.



Figure S2. SEM images of (a) SBA-15, (b) SBA-15-5% Ag, (c) SBA-15-10% Ag when using silver ammonia solution as the Ag source.



Figure S3. TEM images of (a) SBA-15-5% Ag, (b) SBA-15-10% Ag when using $AgNO_3$ solution as the Ag source.



Figure S4. SEM images of (a) SBA-15-5% Ag, (b) SBA-15-10% Ag when using $AgNO_3$ solution as the Ag source.



Figure S5. (a) The backscattered electron (BSE) image of SBA-15-10% Ag using AgNO₃ solution as the Ag source and its corresponding EDX pattern in the red rectangular area. (b) X-ray mapping image of Ag element according to the BSE image.



Figure S6. FTIR spectra of (a) SBA-15, (b) SBA-15-5% Ag, (c) SBA-15-10% Ag.



Figure S7. UV-vis adsorption spectra of (a) SBA-15, (b) SBA-15-5% Ag, (c) SBA-15-10% Ag.



Figure S8. TEM image of (a) SBA-15-10% Ag sample treated at 200 °C for 2h, (b) the regenerated SBA-15-10% Ag at 350 °C.



Figure S9. Mercury capture by SBA-15-10% Ag over a 5-min exposure in the flue gas under different temperatures.



Scheme S1. Experimental setup of mercury breakthrough test.