Development and Evaluation of Nanoscale Sorbents for Mercury Capture from Warm Fuel Gas

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Raja A. Jadhav, Ph.D.
Howard Meyer

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U.S. Department of Energy, National Energy Technology Laboratory (NETL)
Ronald Breault, Project Manager
3610 Collins Ferry Road, P.O. Box 880
Morgantown, WV 26507-0880

Submitted by

Gas Technology Institute (GTI)
1700 S. Mount Prospect Road
Des Plaines, IL 60018
GTI Project Number **20162**

Subcontractor

NanoScale Materials, Inc.
1310 Research Park Dr., Manhattan, KS 66502

Technical Point of Contact

Raja A. Jadhav, Ph.D.
Engineer, GTI
Phone: (847) 768-0807, Fax: (847) 768-0600
E-mail: raja.jadhav@gastechnology.org

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ABSTRACT

Several nanocrystalline sorbents were evaluated for their mercury-sorption capacity in GTI's mercury-sorbent testing facility. These preliminary tests were carried out in mercury-laden N₂ stream at 423 and 533 K. Desorption tests on the post-sorbed sorbents were carried out to understand the mechanism of interaction between mercury and the sorbent. Of the eight nanocrystalline sorbents evaluated, NanoActive Cr₂O₃ was the most effective sorbent at both 423 and 533 K. NanoActive MnO₂ and CuO sorbents also showed promise for capture of mercury from N₂ stream. Desorption tests indicated that the capture of mercury took place by a combination of physical and chemical adsorption. It is speculated that the NanoActive metal oxides oxidized mercury to HgO form that was immobilized on the sorbent surface. Presulfidation of NanoActive CuO increased its Hg-sorption capacity at 423 K; however, presulfided NanoActive MnO₂ sorbent became ineffective for Hg capture at both 423 and 533 K.

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EXECUTIVE SUMMARY

Gas Technology Institute (GTI), in collaboration with Nanoscale Materials, Inc. (NanoScale), is developing and evaluating several nanocrystalline sorbents for capture of mercury from coal-gasifier (such as IGCC) warm fuel gas. The focus of this study is on the understanding of fundamental mechanism of interaction between mercury and nanocrystalline sorbents over a range of fuel gas conditions. Detailed chemical and structural analysis of the sorbents will be carried out using an array of techniques, such as XPS, SEM, XRD, N₂-adsorption, to understand the mechanism of interaction between the sorbent and mercury.

The proposed nanoscale oxides have significantly higher reactivities as compared to their bulk counterparts, which is a result of high surface area, pore volume, and nanocrystalline structure. These metal oxides/sulfides will be evaluated for their mercury-sorption potential in an experimental setup equipped with state-of-the-art analyzers. Initial screening tests will be carried out in N₂ atmosphere, and two selected sorbents will be evaluated in simulated fuel gas containing H₂, H₂S, Hg and other gases. The focus will be on development of sorbents suitable for higher temperature (420–640 K) applications.

Activities in Task 3 were focused on preliminary evaluation of eight nanocrystalline metal oxide sorbents for mercury capture. The sorbents were synthesized by NanoScale and sent to GTI for evaluation in GTI's mercury-sorbent testing facility. The preliminary sorbent testing was carried out in Hg-laden N₂ stream at 423 and 533 K to screen effective sorbents for detailed evaluation in simulated fuel gas. The concentration of mercury was maintained about 135 µg/m³ in 3 lpm of N₂ stream. The metal oxide sorbents were also presulfided to understand the effect of sulfur in capture of mercury. The screening tests concluded that NanoActive Cr₂O₃ was the most effective sorbent for Hg removal from N₂ stream at both 423 and 533 K. During a 6-h exposure to Hg at 423 K, NanoActive Cr₂O₃ captured nearly 100% of the Hg with a Hg-loading of 720 µg/g sorbent. At 533 K, the sorbent captured 73% of exposed mercury giving a Hg loading of 530 µg/g sorbent. NanoActive MnO₂ and CuO also showed promise for Hg capture. Desorption tests on post-sorption sorbents indicated a combination of physical and chemical sorption mechanisms. Detailed mechanistic studies on the metal oxides suggested catalytic oxidation and subsequent capture of Hg by the sorbent. Presulfidation of NanoActive CuO increased its Hg-sorption capacity at 423 K; however, presulfided NanoActive MnO₂ sorbent became ineffective for Hg capture at both 423 and 533 K.

1. Experimental Methods

Nanocrystalline Sorbents

Seven different nanocrystalline metal oxides (viz., NanoActive® TiO₂, CeO₂, ZnO, CuO and NanoActive®-D MoO₃, Cr₂O₃, and MnO₂) were synthesized by NanoScale using their proprietary techniques. In addition, a NanoActive-D MnO₂/alumina was also synthesized, which is a supported sorbent with about 30 wt.% MnO₂ on a high surface area alumina support. The nanomaterials were pelletized by pressure-compaction method and ground to the desired size range (180–250 µm).

Experimental Setup

The sorbents are evaluated in a lab-scale, fixed bed reactor with the outlet mercury concentration monitored by a semi-continuous mercury analyzer. As shown in Figure 1, the mercury sorbent testing unit essentially consists of a quartz reactor shell and a quartz reactor insert that are externally heated by a three-zone electric furnace. The setup is complete with equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, monitoring the reactor pressure and the pressure drop across the bed, off-gas sampling and analysis, and an automated data acquisition system. The reactor system is configured for upward gas flow, and the three-zone furnace is positioned with respect to the sorbent bed to accomplish feed gas preheating. Certified elemental mercury (Hg⁰) permeation tube from VICI Metronics is used to generate the Hg⁰ vapor. The permeation tube is housed in a VICI Metronics U-tube, heated in a constant temperature water bath. The reactor insert has a 2.3 cm O.D. and a 1.8 cm I.D. sorbent bed cage of a 1 cm height. The top of the cage is a fixed porous frit, while the bottom consists of a similar, but removable porous frit to allow for placement of the sorbent. The height of the sorbent bed is maintained around 0.5 cm, with the bed sandwiched between quartz wool packing. A “semi-continuous” gas-phase mercury analyzer (PSA Sir Galahad II) is used to monitor the concentration and speciation of mercury in the gas stream.

Experimental Procedure

Approximately 0.2 g of the sorbent (size range 180–250 µm) is mixed with 1.8 g of inert alumina (size range 250–425 µm) to prevent channeling of mercury within the sorbent bed. The sorbent is loaded in the quartz reactor insert and the sorbent bed is supported by quartz wool and porous frit on both sides. Next, the reactor is inserted in the shell and preheated to the desired temperature in flowing 2.6 lpm of N₂ stream. A mercury permeation tube is used as a source of mercury with 0.4 lpm N₂ used as a mercury carrier stream. When the temperature, flow rate, and bypass mercury concentration values are stabilized, the mercury is sent to the sorbent, and the outlet concentration (including mercury speciation) is monitored and recorded by the PSA analyzer. The mercury loading on the sorbent is calculated based on the area above the breakthrough curve. For selected experiments, this result is confirmed using a DMA-80 Direct Mercury Analyzer from Milestone, Inc., which measures total mercury loaded on the sorbent.

Presulfidation of Sorbents

To evaluate Hg capture by nanocrystalline metal sulfides, NanoActive CuO and MnO₂ sorbents were presulfided in the presence of 0.5 slpm of 10% H₂S/N₂ stream for 3 h. The sulfidation of NanoActive CuO and MnO₂ was carried out at 423 K and 573 K, respectively.

Figure 1: Schematic of GTI's experimental setup for mercury sorbent testing

2. Results and Discussion

Evaluation of NanoActive Sorbents for Mercury Capture

Mercury sorption capacities of the eight NanoActive metal oxides were determined by following the procedure given earlier. The sorption studies were carried out at two different temperatures of 423 and 533 K with 3 slpm of Hg-laden N₂ stream. The inlet mercury concentration varied over the range of 125–140 µg/m³ for these experiments, believed to be due to the day-to-day variation of the analyzer calibration.

NanoActive TiO₂, CeO₂, ZnO and MoO₃ sorbents were ineffective in capturing mercury, and their Hg-sorption capacities were negligible at both the temperatures. Table 1 gives a summary of the results for the NanoActive CuO, MnO₂, MnO₂/alumina, and Cr₂O₃ sorbents. It should be noted that the Hg-sorption capacity given in the table represents the sorbent capacity for the duration for which the sorbent was exposed to mercury, and not the saturation sorption capacity. In this table, the total mercury captured as a percentage is calculated by dividing the total mercury captured by the sorbent by the total mercury exposed to the sorbent.

Table 1: Comparison of Hg-sorption capacities of NanoActive® sorbents

	423 K				533 K			
	CuO	MnO ₂	MnO ₂ /alumina	Cr ₂ O ₃	CuO	MnO ₂	MnO ₂ /alumina	Cr ₂ O ₃
Inlet Hg conc., $\mu\text{g}/\text{m}^3$	130	125	138	130	140	132	135	133
Final outlet Hg conc., $\mu\text{g}/\text{m}^3$	97	45	10	4	140	106	75	56
Sorption time, h	6	6	4	6	2.5	5	6	6
Hg-sorption capacity, $\mu\text{g}/\text{g}$	250	490	480	720	74	230	500	530
Total Hg captured, %	36	73	97	~100	21	32	70	73

Of the eight nanocrystalline sorbents evaluated so far in this work, NanoActive-D Cr₂O₃ was the most effective at both the temperatures. Increasing the NanoActive MnO₂ sorbent surface area by supporting it on a high surface area alumina increased the Hg-sorption capacity of the sorbent, which suggest that the sorption of Hg takes primarily at the surface. Although the Hg-capacities of NanoActive Cr₂O₃ and MnO₂/alumina are similar, the surface area of the latter is more than twice that of the former (240 vs. 103 m²/g). Since Hg-sorption is a surface phenomenon, Hg-sorption capacities should be compared based on the sorbent surface area. Therefore, it can be concluded that the Hg-sorption capacity of Cr₂O₃ is higher than that of MnO₂.

Figure 2 shows a typical Hg breakthrough plot for NanoActive MnO₂/alumina sorbent at 423 K.

Figure 2: Mercury breakthrough plot for NanoActive-D MnO₂/alumina sorbent at 423 K

Mechanism of Mercury Capture by Sorbents

Results in Table 1 indicate that mercury-sorption capacity of the sorbents decrease at higher temperature, suggesting that physical adsorption is the controlling mechanism of mercury capture. As outlined below, further studies were carried out to understand the mechanism of interaction between mercury and the sorbents.

NanoActive MnO₂ Sorbent: To further confirm the physical adsorption mechanism for NanoActive® MnO₂ sorbent, an experiment was carried out in which the sorbent, after exposure to the mercury stream, was exposed to mercury-free N₂ stream. Figure 3 shows the adsorption and desorption cycle for NanoActive® MnO₂ sorbent. In this experiment, approx. 0.1 gm of the sorbent was mixed with 1.9 gm of inert alumina and exposed to 115 µg/m³ of Hg/N₂ stream at 423 K. After 1 h of exposure, the mercury stream was diverted to the vent and only N₂ was passed over the sorbent. At approx. 2.75 h into the desorption stage, temperature of the sorbent was increased to 468 K. This temperature increase resulted in further release of adsorbed mercury from the sorbent. The amount of Hg released by sorbent in the N₂ stream was recorded by the PSA mercury analyzer. Calculations indicate that about 16 µg of Hg was captured by the sorbent during adsorption, whereas, only 3.6 µg of total Hg was released during desorption. Therefore, it is concluded that Hg is adsorbed on the sorbent surface by physical (weak van der Waal's forces) as well as strong chemical forces, and a much higher temperature is required for its complete release from the sorbent surface.

Figure 3: Adsorption/desorption studies on NanoActive MnO₂ sorbent

NanoActive Cr₂O₃ sorbent: Adsorption/desorption studies were also carried out for NanoActive Cr₂O₃ sorbent. As shown in Figure 4, after Hg adsorption for 1 h at 423 K in N₂, the sorbent temperature was gradually increased to 443, 473, and 523 K in Hg-free N₂ stream. The amount of mercury released increased with the desorption temperature. However, of the 22.6 µg of Hg captured during the 1-h adsorption, only 2.7 µg of Hg was released during desorption, suggesting that the balance Hg is captured on the sorbent surface by stronger chemical forces.

Figure 4: Adsorption/desorption studies on NanoActive Cr_2O_3 sorbent

Figure 5: Mercury breakthrough plot for NanoActive CuO at 423 K

An oxidation mechanism has been suggested by Granite et al.¹ for capture of Hg by metal oxide catalysts such as MnO₂ and Cr₂O₃. According to the proposed mechanism, in the first step of the capture process, gas phase Hg is physically adsorbed on the sorbent surface, which in the second step is oxidized to HgO by the lattice oxygen of the metal oxide (M_xO_y) catalyst. The mechanism can be given as:

During the desorption stage, the physically adsorbed mercury on the surface Hg_(ad) is released, however, the chemically adsorbed mercury (HgO_(ad)) remains on the sorbent surface.

NanoActive CuO sorbent: An unusual shape of the breakthrough curve was obtained when mercury was exposed to 0.2 gm of NanoActive CuO sorbent at 423 K (see Figure 5). It can be seen that the outlet mercury concentration reached a steady value of approx. 92 µg/m³ at the end of 30 min exposure to mercury, suggesting that a complete breakthrough could never be obtained. To investigate this further, the experiment was repeated under identical conditions. A similar behavior was observed even for the repeat experiment. It is speculated that the NanoActive CuO sorbent has some catalytic activity that results in oxidation of a certain fraction of incoming elemental mercury. This oxidized mercury is captured by the same sorbent. Since the sorbent remains catalytically active for the duration of the experiment, mercury breakthrough is not observed. To reduce the experimental time so that a complete breakthrough could be observed, an experiment was carried out at 423 K with only 0.05 gm of the sorbent mixed with 1.95 gm of inert alumina. The sorbent achieved near saturation during the 4 h exposure to Hg.

Mercury Sorption on Presulfided Sorbents

Presulfided NanoActive CuO and MnO₂ sorbents were evaluated for Hg capture in N₂ stream at 423 and 533 K following the procedure given earlier. Presulfided NanoActive MnO₂ was not effective at either of the temperatures, whereas, presulfided NanoActive CuO was effective only at 423 K. During the 5-h exposure to mercury, the presulfided NanoActive CuO captured nearly 370 µg Hg/g sorbent, which corresponded to 71% of total exposed mercury. Comparison with the Hg-capacity of NanoActive CuO given in Table 1 indicates that sulfided CuO has higher capacity and efficiency for Hg capture. The increased capacity of the sulfided sorbent is due to the formation of CuS during presulfidation, which has increased affinity towards Hg.

3. Conclusion

Preliminary evaluation of nanocrystalline metal oxide and sulfide sorbents was carried out in N₂ stream to screen effective mercury sorbents for further evaluation in simulated fuel gas. Of the eight sorbents evaluated in this work, NanoActive Cr₂O₃ was the most effective at 423 and 533 K. NanoActive MnO₂ and CuO sorbents also showed promise in capturing Hg from N₂ stream. Mechanistic studies suggested that Hg was captured on the sorbent surface by a combination of physical and chemical sorption mechanisms. Sulfidation of NanoActive CuO sorbent increased its Hg-sorption capacity at 423 K, however, the sulfided CuO was not effective at 533 K.

4. Reference

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