

**Title:**           **Integrated Removal of NO<sub>x</sub> with Carbon Monoxide as Reductant, and Capture of Mercury in a Low Temperature Selective Catalytic and Adsorptive Reactor**

**Author(s):**   Panagiotis (Peter) G. Smirniotis and Neville G. Pinto  
University of Cincinnati, Dept. of Chemical & Materials Engineering  
P.O. Box 210012  
Cincinnati, OH, 45221-0012  
Phone:           (513) 556-2770  
Fax:             (513) 556-3930  
e-mail:          [Neville.pinto@uc.edu](mailto:Neville.pinto@uc.edu)  
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**OBJECTIVES(s):**

A three-year investigation is underway to develop a novel, advanced Low Temperature Selective Catalytic and Adsorptive Reactor (LTSCAR) for the simultaneous removal of NO<sub>x</sub> and mercury (elemental and oxidized) from coal-fired flue gases in a single unit. It is anticipated that the proposed system will lower removal costs for the targeted pollutants by an order of magnitude relative to current technologies. Recent advances in adsorption and catalysis research at Cincinnati will be combined to develop an integrated removal process for both pollutants. The specific project objectives are: (1) Tailoring existing bi-metallic catalysts for low temperature NO<sub>x</sub> removal with carbon monoxide as reductant; (2) The development of the above catalyst(s) for extended tolerance to SO<sub>2</sub> and H<sub>2</sub>O; (3) Tailoring a novel existing adsorbent for the capture of Hg<sup>0</sup> and Hg<sup>2+</sup> at high capacity in a LTSCAR; (4) A study of speciation of Hg in the LTSCAR; and (5) Performance evaluations of the LTSCAR in simulated coal-fired utility flue gases.

**ACCOMPLISHMENTS TO DATE:**

This project is a continuation of a Phase I project that ended on March 31, 2006; a three-month overlap with the current Phase II project. The accomplishments reported here are for the last quarter of the Phase I project. The Phase II project work has effectively started April 1, 2006.

A series of high surface area anatase titania supported Mn-Cu, Mn-Cr and Mn-Ni bimetallic oxide catalysts were prepared by wet impregnation method using their nitrate salts. The SCR of NO with CO was carried out at atmospheric pressure using a fixed bed quartz reactor (I.D. 6 mm) containing 0.05g of catalyst. The reaction was carried out at the space velocity of 50,000 h<sup>-1</sup> at 175 °C for various concentrations of NO and CO. Prior to the catalytic experiments, the catalysts were activated *in-situ* by passing oxygen for 2 hrs at 673 K. Under the above operating conditions prepared bimetallic oxide catalysts showed good performance giving more than 40% NO conversion with 100% N<sub>2</sub> selectivity. Studies are in progress to improve the NO conversion, by changing the reaction conditions and various metal oxide combinations and concentrations. The specific surface areas of the prepared catalysts were significantly lower than the pure TiO<sub>2</sub> support. The surface and bulk properties of the catalysts will be examined using X-ray diffraction, BET-surface area, FT-IR, ammonia-TPD and TPR techniques. These characterization results will be correlated with activity results.

A variety of chelating adsorbents have been tested for the capture of  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  in a fixed adsorbent bed. The temperature range selected for these tests has been 160-175 °C using a simulated flue gas. Specifically, three silica-based Hg-chelating adsorbents, 3-mercaptopropyltrimethoxysilane (MPTS), 2-mercaptobenzothiazole (APTS-MBT) and dithizone (DZ), which are thermally stable to 175°C, have been tested for  $\text{Hg}^{2+}$  capture. While all have been effective, it has been concluded that the MPTS version is most promising, because it is simplest to synthesize and has excellent Hg capture characteristics. At 160°C this adsorbent has been demonstrated to have a minimum operating capacity of  $\approx 58$  mg  $\text{Hg}^{2+}$ /g adsorbent. The MPTS adsorbent has been modified to also enable the removal of  $\text{Hg}^0$  from the flue gas. An oxidative capacity has been built into the surface nano-layer to convert  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  for subsequent capture. This has been accomplished while retaining a high specific surface area (130-150  $\text{m}^2/\text{g}$ ), specific pore volume (0.6  $\text{cm}^3/\text{g}$ ) and large pores (16 nm). The modified MPTS material is being tested in a fixed-bed adsorber under simulated flue gas conditions to measure  $\text{Hg}^0$  capture characteristics.

#### **FUTURE WORK:**

The project will focus on fundamental and applied research to develop and test catalysts and adsorbents suitable for use in the LTSCAR. Bi- and tri-metallic titania supported catalysts will be synthesized for low temperature  $\text{NO}_x$  removal using CO as the reductant. Targeted characteristics will be operation in the 140-160°C range with complete transformation of  $\text{NO}_x$  to  $\text{N}_2$ , time stability, durability and low cost. Particular emphasis will be placed on achieving extended tolerance to  $\text{SO}_2$  and  $\text{H}_2\text{O}$  at expected flue gas concentrations. In parallel, a high capacity chelating adsorbent for mercury will be developed for use in the LTSCAR. The adsorbent will achieve the removal of both elemental and oxidized mercury. Porous silica substrates will be used to support an engineered nano adsorbent layer that can oxidize elemental mercury and strongly and selectively bind the oxidized mercury through chelation. The influence of the adsorbent, catalyst and reductant on mercury speciation will also be evaluated. The effectiveness of the catalyst and the adsorbent will be determined separately and in combination in a simulated flue-gas flow system.

#### **STUDENTS SUPPORTED UNDER THIS GRANT:**

- 1) Hong Lu, PhD student in Chemical Engineering
- 2) Lei Ji, PhD student in Chemical Engineering