High-Throughput Screening of NOx HC-SCR Catalysts

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Introduction
Regulatory agencies are continuing to reduce the allowable NOx and particulate matter (PM) emissions that are allowed for diesel vehicles. The selective catalytic reduction (SCR) of NOx to \( \text{N}_2 \) is a key technology to meet these requirements. The use of hydrocarbons or oxygenates (HC-SCR) has a number of advantages over urea/ammonia based technologies including ability to create the hydrocarbon reductant from the fuel in mobile applications. Many systems have been explored to do this chemistry. A stand out system in the field is Ag loaded on a support such as \( \text{SiO}_2 \), \( \text{TiO}_2 \), \( \text{ZrO}_2 \), \( \text{Al}_2\text{O}_3 \) or zeolites.\(^1\)\(^3\)

The real world requirements include catalysts activity over a large temperature range (250-450°C), tolerant to high levels of water and \( \text{SO}_2 \). Silver based catalysts work best above 300°C but the low temperature activity can be improved by adding \( \text{H}_2 \) to the emission streams. This improvement however is limited in with high amounts of \( \text{SO}_2 \) in the stream and is not always practical in all applications. Clearly, improving the silver performance at low temperature with \( \text{SO}_2 \) is a significant goal for HC-SCR for mobile applications.

The potential chemical space available for new catalysts is very large. Variables for testing catalysts include catalysts formulations (active metals, supports and method of preparation), temperature, reductant, space velocity, time on stream etc. The large chemical and process space has led to the need for high-throughput screening of NOx SCR catalysts.

Materials and Methods
We have developed a multi-channel flow reactor for rapidly evaluating the NOx reduction of catalysts at various temperatures and in the presence of various reductants (See Figure 1). Using a multi-channel splitter the effluent stream from each tube is sequentially passed through a NOx sensor and CO/CO\(_2\) sensor (both from California Analytical Instruments).

The catalysts are prepared in parallel using either wet chemical impregnation or chemical exchange procedures. The catalysts can be prepared using conventional automated liquid handling equipment and then pretreated in a 3-tube 3-zone furnace where the temperature and gas composition can be varied. Each catalyst can be processed under 3 temperatures and 3 gas compositions (9 conditions) simultaneously.

Results and Discussion
Hundreds of catalysts and conditions have been tested using hydrocarbons as the reductant. Silver on \( \text{Al}_2\text{O}_3 \) based materials have performed well (See Figure 2a) at higher temperatures. The addition of \( \text{H}_2 \) to the stream improves the lower temperature performance (Figure 2b). In order to achieve similar performance to that seen in Figure 2b without \( \text{H}_2 \) new metal catalysts have been screened with and without added silver as well as in dual bed configurations. In particular the use of Li and K as low level (0.05% wt) additives was seen to increase the low temperature performance by 10-15%.

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<tr>
<th>Temperature (°C)</th>
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<tr>
<td>200</td>
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<tr>
<td>%NOx conversion</td>
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<td>80</td>
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![Figure 1. Simplified reactor scheme for 32-tube HTS reactor](image)

**Significance**
Ammonia SCR is the competing technology to HC-SCR for NOx reduction. Ammonia SCR is well developed but has a couple of disadvantages. First, this technology can have ammonia slip actually making the emissions worse. Second, there is no infrastructure for providing ammonia for mobile applications. HC-SCR where the reductant is the fuel or derived from the fuel overcomes these disadvantages. The performance HC-SCR catalysts need to be improved across the temperature range of interest.

- **Figure 1.** Simplified reactor scheme for 32-tube HTS reactor
- **Figure 2.** %NOx conversion with \( \text{O}_2 \) (13%), \( \text{NO} \) (200 ppm), \( \text{H}_2\text{O} \) (7%), \( \text{SO}_2 \) (ppm), hydrocarbon reductant at C1:NO of (8:1). a) 0 ppm \( \text{H}_2 \), b) 1900 ppm \( \text{H}_2 \).

References