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 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 SiO_2, TiO_2, ZrO_2, Al_2O_3 or zeolites.[1-3]

The real world requirements include catalysts activity over a large temperature range (250-450ºC), tolerant to high levels of water and SO_2. Silver based catalysts work best above 300ºC but the low temperature activity can be improved by adding H_2 to the emission streams. This improvement however is limited in with high amounts of SO_2 in the stream and is not always practical in all applications. Clearly, improving the silver performance at low temperature with 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 a 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 Al_2O_3 based materials have performed well (See Figure 2a) at higher temperatures. The addition of 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 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%.

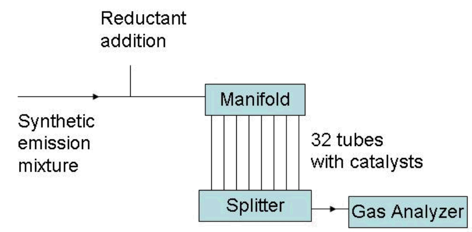

Figure 1. Simplified reactor scheme for 32-tube HTS reactor

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.

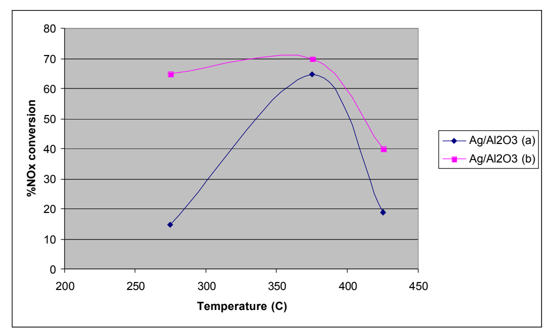

Figure 2. %NOx conversion with O_2 (13%), NO (200 ppm), H_2O (7%), SO_2 (ppm), hydrocarbon reductant at C1:NO of (8:1). a) 0 ppm H_2, b) 1900 ppm H_2.

References

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