

Cold Start Concept (CSC™): A Novel Catalyst for Cold Start Emission Control

Hai-Ying Chen, Shadab Mulla, Erich Weigert, Kenneth Camm, Todd Ballinger, Julian Cox and Phil Blakeman
Johnson Matthey Inc.

ABSTRACT

Catalytic emission control systems are installed on nearly all automobiles and heavy duty trucks produced today to reduce exhaust emissions for the vehicles to meet government regulations. Current systems can achieve very high efficiencies in reducing tailpipe emissions once the catalytic components reach their operating temperatures. They are, however, relatively ineffective at temperatures below their operating temperature windows, especially during the cold start period of the vehicles. With the increasingly stringent government regulations, reducing the emissions during the cold start period before the catalytic components reach their operating temperatures is becoming a major challenge.

For cold start HC control, HC traps based on zeolites have been investigated and commercialized for certain applications. For cold start NO_x control, especially in lean burn engine exhaust, NO_x storage and release catalysts have been evaluated. In this paper we will introduce a novel catalyst which we refer to as Cold Start Concept (CSC™) catalyst technology. This cold start catalyst not only stores HC and NO_x at low temperatures with very high storage efficiencies, but also converts a significant portion of the stored HC/NO_x during the warm-up period before the rest of the HC/NO_x is thermally released from the catalyst. The HC/NO_x release temperature in a cold start catalyst is high enough that the released HC/NO_x can be further converted by the downstream catalytic components. In addition, the cold start catalyst also exhibits excellent CO, HC, and NO oxidation activity under normal lean conditions. Both laboratory and engine evaluation results of this new concept will be presented.

CITATION: Chen, H., Mulla, S., Weigert, E., Camm, K. et al., "Cold Start Concept (CSC™): A Novel Catalyst for Cold Start Emission Control," *SAE Int. J. Fuels Lubr.* 6(2):2013, doi:10.4271/2013-01-0535.

INTRODUCTION

Nearly all automobiles and heavy duty trucks produced today are equipped with emission control catalysts to reduce tailpipe emissions in order to meet government regulations [1]. On stoichiometric-burn gasoline engine powered vehicles, Three-Way Catalysts (TWCs) are installed in the exhaust system to reduce CO/HC/NO_x emissions. On lean-burn diesel engine powered vehicles, Diesel Oxidation Catalysts (DOCs) are installed in the tailpipe to reduce CO/HC emissions, which are followed by Diesel Particulate Filters (DPFs) to reduce particulate matter emissions. Different technologies have been developed to reduce the NO_x emission in the lean-burn exhaust. Two of the leading technologies are the Selective Catalytic Reduction of NO_x with urea (urea-SCR) and the NO_x Adsorber Catalysts (NACs, or Lean NO_x Traps (LNTs)). Both of these catalysts are very effective for reducing the tailpipe emissions once they reach their operating temperature, which is typically

above 200°C. At temperatures below their operating temperature windows, however, these catalysts are relatively ineffective. As a result, a majority of the tailpipe emissions are emitted during the cold start period of the vehicles before the catalytic components reach their operating temperatures [2].

To meet the stringent emission standards, controlling the emissions during the cold start period is critical. On a gasoline engine, with the relatively high engine-out exhaust temperature, the TWC component can quickly reach its operating temperature when it is placed closer to the engine-out position [3]. On a diesel engine, which generates relatively lower exhaust temperatures, it can take more than 100 seconds for the catalytic component to reach its operating temperature. Therefore, controlling the cold start emissions on a diesel engine is even more challenging [4, 5].

One approach to reduce the cold start emissions on a diesel engine is to use storage components to store pollutants such as HC and NO_x during the cold start period. The stored

HC and NO_x are released from the storage components and subsequently converted when the rest of the catalytic components reach their operating temperature.

Zeolites, with their unique porous crystalline structure and large surface area, can adsorb and store a considerable amount of HCs at temperatures below 200°C. DOCs containing zeolite components have already been commercialized to reduce the cold start HC emissions from the diesel exhaust [6]. To meet the future emission standards, further improvement of the HC storage during the cold start period and the subsequent HC conversion efficiency during the warm-up period is needed.

Although a NAC can store a large amount of NO_x when it is fully regenerated, this type of catalyst is not suitable for cold start applications because the NAC regeneration has to be carried out under rich conditions and at temperatures above 200°C [7]. For most diesel engines, it is difficult to achieve rich conditions. Even on diesel engines that are capable of performing rich regeneration events, the control strategy can be complicated. As an alternative, Passive NO_x Adsorber catalysts (PNA) were developed [8]. This type of catalyst can store NO_x at low temperatures. Different from a NAC, a PNA can release the stored NO_x under normal lean operation conditions after the cold start period. Beyond that point, the downstream NO_x control catalyst reaches its operating temperature and becomes active enough to convert the released NO_x.

Increasingly stringent regulations require low emissions for both HC and NO_x. For example, the US EPA Tier 2 Bin 2 standards limit NMOG (Non-Methane Organic Gases) = 0.01 g/mile and NO_x = 0.02 g/mile. To meet such low emission standards, both HC and NO_x have to be well controlled during the cold start period. With a projected engine-out NO_x at 0.4 g/mile under the US FTP cycle and assuming that the SCR catalyst could achieve 97% NO_x reduction efficiency once the engine-out exhaust temperature exceeded 200°C, Henry et al. estimated that more than 50% NO_x removal was needed during the initial ~200-second cold start period of the FTP cycles [4]. As well, a similar level of HC removal is also required to meet the cycle HC emission target.

The requirement of controlling both NO_x and HC during the cold start period led to our development of Cold Start Concept (CSCTM) catalysts. This type of cold start catalyst combines the functions of HC trapping and passive NO_x adsorption and release into one component, so that it can store both HC and NO_x simultaneously during the cold start period. In addition, the cold start catalyst can convert a portion of the stored HC/NO_x during the warm-up period before the rest of the HC/NO_x is released from the catalyst. Furthermore, the cold start catalyst also functions as an oxidation catalyst: converting CO to CO₂, oxidizing HC after warm-up, and oxidizing NO to NO₂ after warm-up to improve the catalytic efficiency of the downstream catalytic components. Besides the functional advantages, the cold start catalyst can have a reduced thermal mass compared to the

combination of a DOC/HC trap followed by a separate PNA, allowing quicker temperature increase for the downstream catalytic components to improve the overall efficiency of the system.

In this paper, results generated on a laboratory reactor will be presented to illustrate the concept of cold start catalyst technology and to demonstrate its advantages compared to a DOC and a PNA. Preliminary cold start FTP75 LA-4 evaluation results on an engine with a cold start catalyst combined with a SCR catalyst will also be reported.

EXPERIMENTAL

Catalysts

To illustrate the concept and to demonstrate the advantages of the cold start catalyst technology, a cold start catalyst was compared to a diesel oxidation catalyst (DOC) that contains zeolites as the HC trapping component and a passive NO_x adsorber catalyst (PNA). All the catalysts were prepared as monoliths with a cell density of 62 cell/cm² (or 400 cpsi) in a size of (12.7 cm - diameter × 15.2 cm - length) = 2L of volume. For laboratory study, cores of 2.54-cm in diameter and 7.62-cm in length were cut from the monoliths.

The DOC is a typical zeolite-containing diesel oxidation catalyst with a PGM loading of Pt = 70 g/ft³ and Pd = 35 g/ft³. The PNA catalyst is similar to the catalysts disclosed in reference [8]. The PGM loading is Pt = 100 g/ft³ and Pd = 100 g/ft³. The cold start catalyst contains Pt = 50 g/ft³ and Pd = 90 g/ft³.

It is worth noting that, in this study, the cold start catalyst contains less Pt than the DOC and less total PGM than the PNA catalyst.

Hydrothermal Aging

For the laboratory reactor study, core samples of 2.54-cm diameter × 7.62-cm long were hydrothermally aged in a tubular furnace at 750°C for 16 hours in a flow of 5% H₂O mixed with air. For engine evaluation, full size DOC and cold start catalysts were hydrothermally aged in a retort oven at 750°C for 48 hours in a flow of 10% H₂O mixed with air. These aging conditions represent the typical hydrothermal stability requirement for catalysts located at the engine-out position.

Laboratory Reactor Evaluation

After aging, the 2.54-cm × 7.62-cm cores were tested in a laboratory reactor. Different feed gases were prepared by adjusting the mass flow of the individual gas components. The gas flow rate was maintained at 21.2 L/minute resulting in a Gas Hourly Space Velocity of 30,000 h⁻¹ (GHSV= 30,000 h⁻¹).

The catalysts were first pre-heated to 650°C in a flow of 10% O₂, 5% CO₂, 5% H₂O and balance N₂ (volume %) to clean the surfaces. The pre-treated catalysts were

subsequently cooled to 80°C. Once the temperature was stabilized, 200 ppm NO, 200 ppm CO, 500 ppm (on C₁ basis) decane were added into the above feed gas to mimic the cold start exhaust. The catalysts were exposed to the feed gas for 100 seconds to simulate the cold start period. Thereafter, the temperature was increased linearly to 650°C at a ramping rate of 100°C/minute. The NO_x, CO, and HC concentration at the reactor outlet was measured during the 80°C holding and the subsequent temperature ramping sections. Additional tests were also conducted to examine the NO oxidation activity and the sulfur tolerance/regeneration properties of the catalysts. The details of those testing conditions will be described in the later sections.

Engine Evaluation

Engine evaluation under FTP75 LA-4 testing cycles of the aged full-size cold start catalyst was performed on a 2011 MY light heavy-duty diesel engine. The cold start catalyst (2 L in volume) was paired with a downstream Cu-SCR catalyst (10 L in volume) to form a system. A diesel particulate filter was not included in the system in these tests. The space velocity during the LA-4 testing cycles was around 30,000-300,000 hr⁻¹ over the cold start catalyst and around 5,000-60,000 hr⁻¹ over the SCR catalyst.

As will be shown below, with the current cold start catalyst formulation, NO_x begins to release from the catalyst when the exhaust temperature exceeds 150°C. In order for the SCR catalyst to convert the released NO_x at this temperature, gaseous NH₃ would be needed. Since the available exhaust system did not have the capability of performing gaseous NH₃ injection, the SCR catalyst was pre-conditioned with urea at a higher temperature so that a consistent amount of NH₃ was stored on the SCR catalyst. With the pre-stored NH₃, the SCR catalyst was able to effectively convert NO_x at temperatures above ~150°C.

As a comparison, a similar system with an aged and identically-sized DOC was also tested in place of the cold start catalyst. In addition, a third system with two bricks of the aged cold start catalysts (4L in total volume) in front of same SCR catalyst was tested to examine the impact of increasing the cold start catalyst volume.

RESULTS

NO_x Storage, Release and Conversion under Laboratory Testing Conditions

The cold start NO_x storage behavior of the catalysts is probed by the first 100-second storage phase of the laboratory reactor test with the inlet gas temperature kept isothermal at 80°C. Figure 1 shows the NO_x concentration at the catalyst outlet. The feed gas contains 200 ppm NO. A small amount of NO_x storage is seen on the DOC at the beginning of the experiment. After about 20 seconds of exposure, the outlet concentration reaches the same level as

the feed gas, suggesting no additional NO_x storage occurs on the DOC. Although the NO_x storage on the PNA catalyst is substantially higher compared to the DOC, there is still about 120 ppm NO_x slipping through the PNA without being trapped during the test. A significant improvement of the NO_x storage efficiency on the cold start catalyst is evident; less than 40 ppm is passing through the catalyst for the duration of the 100-second test.

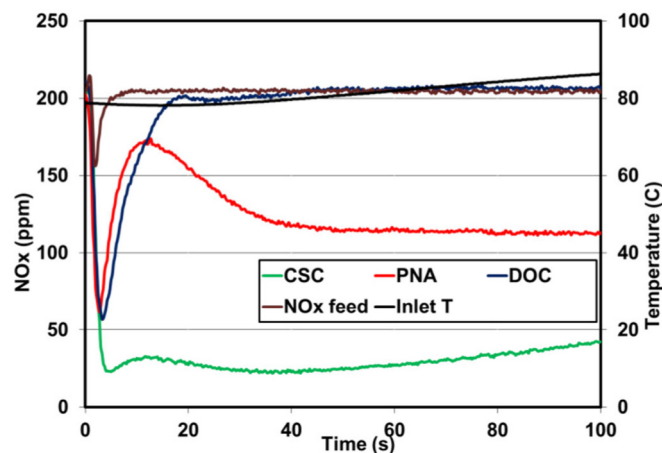


Figure 1. NO_x trace at the catalyst outlet when the catalyst is exposed to 200 ppm NO at 80°C for 100 seconds

To further illustrate the difference in the NO_x storage behavior of these catalysts, Figure 2 plots the instantaneous NO_x trapping efficiency as a function of the cumulative NO_x storage of the catalyst during the 100-second test. The instantaneous NO_x trapping efficiency is defined as the percentage of NO_x being removed by the catalyst at each time instant, while the cumulative NO_x storage is calculated by integrating the amount of NO_x being removed by the catalyst from the beginning of the test to this time instant. As the temperature (80°C) is too low for any NO_x reduction reactions to occur, it is reasonable to consider the amount of NO_x removed from the stream as being equivalent to the amount of NO_x stored on the catalysts. The cumulative NO_x storage is expressed as equivalent grams of NO₂ stored per liter of the catalyst (g NO₂/L cat).

It is evident from Figure 2 that, after 100 seconds of 200 ppm NO_x exposure, the DOC stores a negligible amount of NO_x (0.02 g NO₂/L cat) at very low NO_x trapping efficiencies. The PNA stores a moderate amount of NO_x (0.13 g NO₂/L cat) at NO_x trapping efficiencies never exceeding 50%, while the cold start catalyst shows the highest NO_x storage (0.29 g NO₂/L cat) at NO_x trapping efficiencies greater than 80%. Although the cold start catalyst has a lower PGM loading compared to the PNA, it effectively stores significantly higher amounts of NO_x under low temperature (cold start) conditions.