

Development of Advanced Ultra-Low PGM DOC for BS VI DOC+CDPF+SCR System

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ABSTRACT

Stricter regulatory standards are continuously adopted worldwide to control heavy duty emissions, and at the same time, fuel economy requirements have significantly lowered exhaust temperatures. The net result is a significant increase in Precious Group Metal (PGM) usage with current Diesel Oxidation Catalyst (DOC) technology. Therefore, the design and development of advanced DOC with ultra-low PGM to achieve highly beneficial emission performance improvement is necessary. The advanced DOC is synergized PGM (SPGM) with Mixed Metal Oxide (MMO). The presence of MMO in SPGM is responsible for NO oxidation to NO₂ which is critical for the passive regeneration of the downstream filter and SCR function.

This paper outlines the development of MMO for application in modern DOCs and addresses some specific challenges underlying this application. Lab and flow reactor data demonstrates MMO by itself owns great oxidation properties with high surface area available for NO oxidation reaction. In addition, SPGM DOC with reduced PGM levels indicated thermal resistance and sensitivity to type of hydrocarbon in gas stream. This paper summarizes the results of engine dyno and on-road testing of SPGM DOC versus OEM DOCs. The engine testing indicated high level of NO₂ production at significantly reduced PGM levels. On-road testing on DOC/CDPF/SCR system showed no change or deterioration of the system performance after the switch OEM DOC to SPGM DOC. Field data logging during on-road testing showed identical exotherms for both systems and great NO_x conversion and enough NO₂ formation when ultra-low SPGM used as advanced DOC. Specific challenges remain in the development of the SPGM DOC which is under investigation based on formulation and mechanism of MMO.

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INTRODUCTION

The most commonly used PGM strategy for DOCs are based on high loading of Pt or Pd, or a combination of both; which shows high level of oxidation performance, some NO₂ make as well as sulfur resistance [1, 2, 3]. NO oxidation to NO₂ is critical for the passive regeneration of a downstream filter and SCR operation. Numerous studies consistently showed that Lean NO_x Trap (LNT) or NO_x-selective catalytic reduction (NSR) catalysts have better performance if NO₂ is the dominant NO_x component entering the catalyst [4]. Traditionally, a reduction in PGM loading causes a significant decrease in performance of DOC and specifically, NO₂ make. Therefore, there is a growing need to provide DOC systems employing reduced amounts of PGM materials that exhibit catalytic properties substantially similar to or exceeding the catalytic properties exhibited by conventional systems.

Recently, base metal oxides have attracted more attention as potential partial substitutes for PGM because of their low cost and excellent oxidation activity. For example, Co₃O₄, NiO and MnO₂ showed

beneficial hydrocarbon oxidation, whereas mixed oxides such as Cu-Cr (Co), MnO_x-CeO₂ and CuMoO₄ are found to be advantageous for diesel soot oxidation [4, 5, 6]. In addition, perovskite oxides, such as La_{1-x}Ce_xCoO₃ and La_{1-x}Sr_xMnO₃ have drawn particular interest because of their flexible structure, adaptable to various crystal chemical substitutions, showing NO oxidation reaching 86% at 300 °C; similar to or higher than Pt/Pd based catalysts [7, 8, 9, 10].

This paper focuses on advanced MMO used in combination with ultra-low Pt/Pd in SPGM catalyst to achieve a high performance DOC. Lab and flow reactor tests were used to characterize the efficiency of MMO within SPGM DOCs and to evaluate the sensitivity of catalyst performance to PGM level and hydrothermal aging as well as type of hydrocarbon in feed stream. In addition, the SPGM catalyst with ultra-low PGM was evaluated in engine dyno tests, in comparison with OEM DOCs with high loading of PGM. The on-road testing on a regional transit bus with extra urban drive cycle was performed in order to evaluate SPGM DOC in DOC/CDPF/SCR system in real world conditions.

EXPERIMENTS AND TEST RESULTS

Mixed Metal Oxide Powder Lab Test

MMO composition was deposited on ZrO_2 based support oxide by incipient wetness method and calcined at 800 °C for different duration, including 30 min, 60min and 90min. A CO-TPR experiment and DOC Light-Off (LO) test were used to evaluate performance and oxidation property of MMO and investigate how calcination condition affect the oxidation property of MMO. The CO-TPR test was performed on Micrometrics Auto Chem II 2920 apparatus with thermal conductive detector by passing 1%CO/He (flow rate 50 ml/min) over a 100 mg supported MMO powder at heating rate of 10°C/min to 900°C. To do LO test, the Zero-PGM (ZPGM) catalyst was built on a honeycomb substrate with a wash coat layer of supported MMO powder with target loading of 130 g/L and cored out in size of 1" diameter by 3" length. ZPGM cores tested in a flow reactor for DOC light off from 100 °C to 400 °C at a rate of about 20°C/min and SV of 54,000 h⁻¹. A gas feed employed for the test includes a composition of 100 ppm of NO, 1,500 ppm of CO, 4% CO₂, 4% of H₂O, 14% of O₂, and 200 ppm decane C₁, 80 ppm toluene C₁, 120 ppm propylene C₁, 30 ppm methane C₁ and balance N₂.

Figure 1 shows CO-TPR data on MMO/ ZrO_2 - based support oxide powder which calcined at 800 °C for 30 min, 60 min and 90 min. The results shows the reduction property of MMO will change by increasing the duration of calcination, as main reduction peak shift to higher temperature when powder calcined at 800 °C for 90 min. As shown in Figure 2, the BET surface area of supported MMO powder shows similar trend, i.e., decreasing BET by increasing the calcination time. On the other hand, Figure 3 shows NO conversion light offs for supported MMO powder which calcined 800 °C for 30 min, 60 min and 90 min. The results clearly shows the sensitivity oxidation property of MMO composition to calcination condition. The maximum value of NO conversion decreased by increasing the duration of calcination. Both CO-TPR and NO light-off data show that 30 min calcination at 800 °C is adequate for activation of MMO/support oxide. In addition, these data clearly confirm MMO is active composition for DOC and shows great NO oxidation performance even without adding PGM.

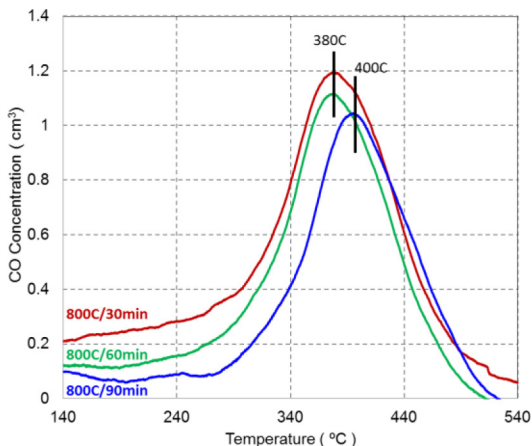


Figure 1. CO-TPR data for supported MMO powder at different calcination conditions.

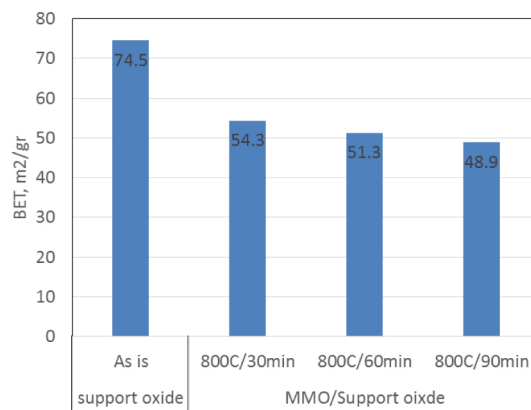


Figure 2. BET data for support oxide and MMO/support oxide powder at different calcination conditions.

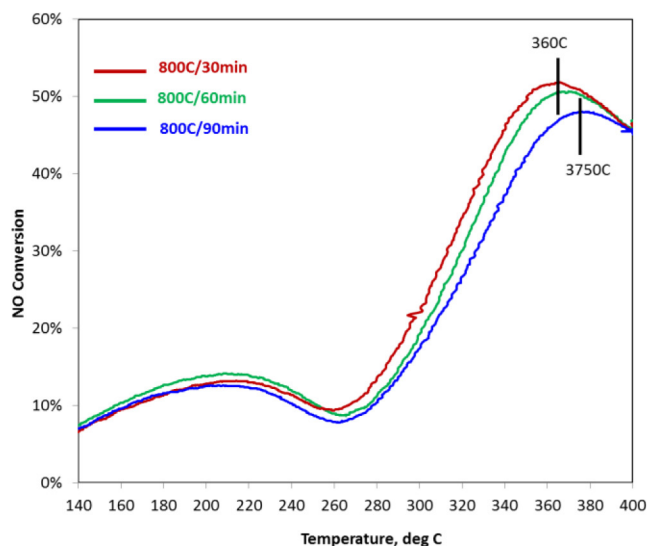


Figure 3. Comparison NO conversion of MMO/Support oxide calcined at different conditions.

SPGM DOC Flow Reactor Test

The SPGM catalysts were built on a honeycomb substrate with the combination of a wash coat layer of doped MMO/ ZrO_2 -based support oxide (100 g/L) and an overcoat layer of ultra-low PGM with alumina-based support oxide (100 g/L). The total PGM loading used in SPGM catalyst are 4.75 g/ft³ and 15 g/ft³ where the Pt: Pd ratio is 8.5:1. SPGM catalysts were cored out in size of 1" diameter by 3" length and tested in a flow reactor for DOC light off from 100 °C to 400 °C at a rate of about 20°C/min and SV of 54,000 h⁻¹. A gas feed employed for the test includes a composition of 100 ppm of NO, 1,500 ppm of CO, 4% CO₂, 4% of H₂O, 14% of O₂, and 200 ppm decane C₁, 80 ppm toluene C₁, 120 ppm propylene C₁, 30 ppm methane C₁ and balance N₂. SPGM catalysts were hydrothermally aged at 650°C for 50 hr with 5 ml/min water in a tube furnace prior to flow reactor testing.

Figure 4 a and b describe NO and HC oxidation light off from flow reactor test for two SPGM catalysts with total PGM loading of 4.75 g/ft³ and 15 g/ft³ before and after hydrothermal aging (F & A). The SPGM DOC with 15 g/ft³ PGM shows significant maximum conversion, about 76% at fresh condition and 65% after aging at.