

# Impact of Hydrocarbons on the Dual (Oxidation and SCR) Functions of Ammonia Oxidation Catalysts

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## ABSTRACT

Ammonia oxidation (AMOX) catalysts are critical parts of most diesel aftertreatment systems around the world. These catalysts are positioned downstream of selective catalytic reduction (SCR) catalysts and remove unreacted  $\text{NH}_3$  that passes through the SCR catalyst. In many configurations, the AMOX catalyst is situated after a diesel oxidation catalyst and catalyzed diesel particulate filter that oxidize CO and hydrocarbons. However, in Euro V and proposed Tier 4 final aftertreatment architectures there is no upstream oxidation catalyst. In this study, the impact of hydrocarbons is evaluated on two different types of AMOX catalysts. One has dual washcoat layers-SCR washcoat on top of PGM washcoat-and the other has only a PGM washcoat layer. Results are presented for  $\text{NH}_3$  and hydrocarbon oxidation,  $\text{NO}_x$  and  $\text{N}_2\text{O}$  selectivity, and hydrocarbon storage. The AMOX findings are rationalized in terms of their impact on the individual oxidation and SCR functions. Finally, these new results are compared to recent hydrocarbon conversion measurements made on vanadium-based SCR catalysts in order to estimate the potential system-level reduction of hydrocarbons possible with a combined V-SCR+AMOX aftertreatment.

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## INTRODUCTION

Diesel aftertreatment is an integral part of modern, new technology diesel engines that enables engine manufacturers and system integrators to meet regulatory emissions requirements. A highly complex system, today's aftertreatment requires the seamless integration of catalysts and filters including diesel oxidation catalysts (DOC), selective catalytic reduction (SCR) catalysts, ammonia oxidation (AMOX) catalysts, and diesel particulate filters (DPF), in addition to diesel exhaust fluid (DEF) dosers, hydrocarbon dosers, numerous gas and temperature sensors, and advanced packaging.

One key function of diesel aftertreatment is  $\text{NO}_x$  reduction, for which zeolite (Cu or Fe) and vanadium-based SCR catalysts are currently the most widely used technologies. Conversion over SCR technology is accomplished via the well documented catalytic reactions between  $\text{NO}_x$  and  $\text{NH}_3$  [1, 2]. Unreacted and un-stored  $\text{NH}_3$  then passes into the AMOX catalyst where it is converted into  $\text{N}_2$ , NO,  $\text{NO}_2$ , or  $\text{N}_2\text{O}$  depending on the catalyst and other relevant conditions including temperature and gas composition [3, 4, 5, 6]. Broadly, commercially available AMOX catalysts have either a single washcoat layer consisting of platinum-group metals (PGM) on an alumina support (PGM-only)-this type of catalyst can be considered a DOC with

significantly lower PGM loading-or they have a dual-layer configuration consisting of a zeolite-based (Cu or Fe) SCR layer on top of the PGM layer (PGM+SCR).

Both AMOX technologies have advantages. The PGM-only catalyst is capable of achieving high  $\text{NH}_3$  oxidation, is less expensive, and does not require the same level of controls sophistication since there is negligible  $\text{NH}_3$  storage and SCR desulfation is not an issue. The PGM+SCR catalyst has similar  $\text{NH}_3$  oxidation but is also highly selective to  $\text{N}_2$  since the SCR layer is capable of reacting undesired  $\text{NH}_3$  oxidation products (e.g., NO and  $\text{NO}_2$ ) with  $\text{NH}_3$  as they diffuse through the SCR layer. However, the additional complexity resulting from  $\text{NH}_3$  storage and SCR sulfation/desulfation on the dual-layer catalyst must be considered.

Similar to DOC and SCR catalysts, AMOX functions can be degraded through multiple mechanisms including hydrothermal aging, sulfation, hydrocarbon exposure, and multiple other contaminants. Kamasamudram et al. reported the effects of hydrothermal aging on both PGM-only and PGM+SCR AMOX catalysts [3]. The authors found that  $\text{NH}_3$  oxidation was relatively insensitive to 650°C aging, but that  $\text{NO}_x$  selectivity monotonically increased with aging.  $\text{N}_2\text{O}$  formation was less affected by hydrothermal aging and only slightly increased with the onset of aging. In addition, Girard et al. have studied the effect of PGM loading on  $\text{N}_2\text{O}$  and  $\text{NO}_x$  selectivity of AMOX

catalysts, and their results show that there is minimal impact of PGM loading except at the lowest temperatures investigated (less than 250°C) [4].

In addition to the effects of hydrothermal aging and sulfation, hydrocarbons can adversely affect the performance of the PGM and SCR AMOX layers. Especially in aftertreatment systems that do not contain an upstream DOC and DPF, the AMOX catalyst may be exposed to significant concentrations of hydrocarbons. In this study, a catalyst core reactor is used to measure and understand the effect of short and long-chain aliphatic hydrocarbons on practical AMOX performance metrics including  $\text{NH}_3$  and hydrocarbon oxidation,  $\text{NO}_x$  and  $\text{N}_2\text{O}$  selectivity, and hydrocarbon storage for both PGM-only and PGM+SCR AMOX catalysts.

## EXPERIMENTAL

Reactor performance measurements were made with a catalyst core reactor. The reactor has previously been described in detail, but a brief overview is provided below as some components of the system have been changed [7]. Briefly, the core-reactor used in this study consists of MKS™ mass flow controllers for gas metering, a Waters™ high performance liquid chromatography pump for water introduction, Bronkhorst™ vapor delivery system for hydrocarbon introduction, a Lindberg™ 3-zone tube furnace for reactor temperature control, and a MKS 2030 HS Fourier transform infrared spectrometer for gas analysis. All lines are heated to approximately 190°C to eliminate condensation of water and hydrocarbons and avoid the formation of undesirable low-temperature products such as ammonium nitrate. The quartz reactor tubes used in this study were 39 inches (90 cm) long with inner and outer diameters of 1.1 inches (28 mm) and 1.26 inches (32 mm), respectively. The inlet 10 inches (25.4 cm) of the reactor were filled with quartz beads to ensure that incoming gas is uniformly mixed and heated.

Three state-of-the-art AMOX catalysts were evaluated in this study, and their specifications are shown in Table 1. All samples were 1" diameter by 1" long and were coated on 300 cell per square inch (cps) cordierite substrates. The first sample consisted of only a PGM layer. The two PGM+SCR samples both contained an oxidation layer with a zeolite-based SCR over-coat, but the SCR zeolite pore sizes as well as the PGM loadings of the two catalysts were distinct. PGM+SCR\_LP had a PGM loading equivalent to the PGM-only sample and a large-pore (LP) zeolite SCR over-layer, and PGM+SCR\_SP has a lower PGM loading and a small-pore (SP) zeolite SCR over-layer.

Table 1. Details of AMOX catalysts evaluate

| Catalyst   | PGM loading | Zeolite ( $D_p$ ) | CPSI |
|------------|-------------|-------------------|------|
| PGM-only   | high        | n/a               | 300  |
| PGM+SCR_LP | high        | large             | 300  |
| PGM+SCR_SP | low         | small             | 300  |

Experiments were performed using the 3-step protocol previously defined by Kamasamudram et al. [3]. Briefly, this protocol permits the efficient measurement of key AMOX functions in three segments as shown in Figure 1.

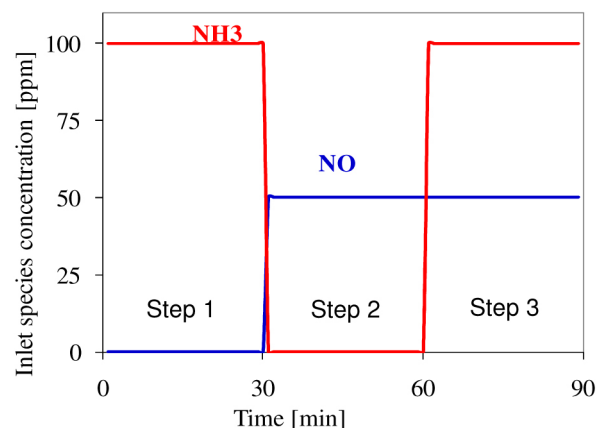


Figure 1. 3-step AMOX evaluation protocol [3]

Step 1 measures  $\text{NH}_3$  oxidation and product selectivity; Step 2 measures NO oxidation and  $\text{NH}_3$  storage; Step 3 evaluates the catalysts SCR performance and the effect of NO on product selectivity. Experiments were performed at a gas hourly space velocity (GHSV) of 100  $\text{hr}^{-1}$ , and background gas concentrations consisted of 8%  $\text{H}_2\text{O}$ , 7%  $\text{CO}_2$ , 10%  $\text{O}_2$ , and balance  $\text{N}_2$ .  $\text{CO}_2$  was not present during hydrocarbon experiments in order to better understand product formation from hydrocarbon oxidation. When flowing, concentrations of 100 ppm  $\text{NH}_3$ , 50 ppm NO, 330 ppm  $\text{C}_3\text{H}_8$ , and 100 ppm  $\text{C}_{12}\text{H}_{26}$  were used. Hydrocarbon concentrations of 1000 ppm carbon were targeted, and additional experiments were performed with 30, 70, and 200 ppm  $\text{C}_{12}\text{H}_{26}$  to measure the effect of concentration. All catalysts were degreened at 500°C for 2 hrs before experiments were performed.

Hydrocarbon storage experiments were also performed at temperatures from 100 to 450°C. For these tests, the catalyst was initially pretreated at 500°C in 10%  $\text{O}_2$ , and then brought to the desired storage temperature. Dodecane (100 ppm) was then introduced for 2 hrs in balance gases consisting of 10%  $\text{O}_2$ , 7%  $\text{H}_2\text{O}$ , and balance  $\text{N}_2$ . The catalyst was then maintained at the storage temperature for 30 minutes to evacuate any residual or loosely bound hydrocarbons from the reactor, and then the temperature was ramped to 500°C at 10°C/min in 10%  $\text{O}_2$ , 7%  $\text{H}_2\text{O}$ , and balance  $\text{N}_2$ .  $\text{CO}_2$  was not flowed during the desorption since stored  $\text{C}_{12}\text{H}_{26}$  releases primarily as  $\text{CO}_2$  in the presence of PGM.

## RESULTS

### Baseline AMOX Performance Comparison

Experiments were first performed in the absence of hydrocarbon to establish a baseline and to quantify the inherent differences in the three AMOX formulations. Results for  $\text{NH}_3$  oxidation and product formation during Step 1 are shown in Figure 2, and it is clear that  $\text{NH}_3$  oxidation is primarily

a function of PGM loading since the two formulations with higher PGM loading (PGM-only and PGM+SCR\_LP) have higher  $\text{NH}_3$  oxidation conversion between 250 and 450°C than PGM+SCR\_SP which has lower PGM loading. The two formulations with higher PGM loading both achieve 100%  $\text{NH}_3$  conversion by 300°C, whereas PGM+SCR\_SP only reaches this conversion at 500°C.

$\text{NO}_x$  formation is below 5 ppm over PGM+SCR\_LP and it is almost zero over PGM+SCR\_SP, while  $\text{NO}_x$  formation is significant for the catalyst with PGM-only as previously reported [3, 4, 5].  $\text{NO}_x$  formation increases for PGM-only with increasing temperature. Over 90% of  $\text{NH}_3$  is converted to  $\text{NO}_x$  at 500°C as shown in Figure 2b. The outlet  $\text{NO}_2:\text{NO}_x$  ratio is an important factor to consider for AMOX catalysts with high  $\text{NO}_x$  selectivity since  $\text{NO}_2$  contributes to ground level smog and is the most toxic of the seven nitrogen oxides [8]. The ratio is presented for PGM-only for steps 1 and 2 in Figure 3.  $\text{NO}_2$  formation, as a percentage of outlet  $\text{NO}_x$ , is approximately 18% lower at 300°C in step 1 than in step 2. This is reasonable since the catalyst achieves 100%  $\text{NH}_3$  conversion at 300°C and likely has fewer sites available for  $\text{NO}$  oxidation in step 1 than in step 2 when  $\text{NO}$  oxidation is not competing with  $\text{NH}_3$  oxidation. At high temperatures,  $\text{NO}_2$  formation is limited by equilibrium in both steps. A negligible amount of  $\text{NO}_2$  is present in the outlet gas of the two PGM+SCR AMOX catalysts since any  $\text{NO}_2$  formed over the PGM layer is consumed by the fast SCR reaction with  $\text{NH}_3$  in the SCR layer. It is also critical to understand the factors leading to  $\text{N}_2\text{O}$  formation because of its global warming effect. Without hydrocarbon,  $\text{N}_2\text{O}$  formation is highest on the catalyst with PGM-only, and is reduced on both of the formulations with SCR due to higher  $\text{N}_2$  selectivity of the SCR reactions between  $\text{NH}_3$  and  $\text{NO}_x$  than of the  $\text{NH}_3$  oxidation reaction over PGM. On all catalysts,  $\text{N}_2\text{O}$  peaks between 250 and 300°C. These results are similar to those previously reported by Kamasamudram et al [3].

$\text{NO}_x$  conversion results from the third step of experiments without hydrocarbons are shown in Figure 4. Because the PGM-only AMOX does not have SCR functionality, the  $\text{NO}_x$  conversion is zero below 250°C and it turns negative above 250°C, consistent with its significant oxidation of  $\text{NH}_3$  to  $\text{NO}_x$  as shown in Figure 2. As expected, substantial  $\text{NO}_x$  conversion was observed over both of the PGM+SCR catalysts. PGM+SCR\_SP catalyst displays higher  $\text{NO}_x$  conversion than PGM+SCR\_LP, while the opposite trend was seen for  $\text{NH}_3$  oxidation as shown in Figure 2. Even though there is less PGM on PGM+SCR\_SP, the SCR layer converts significantly more  $\text{NH}_3$  through the SCR reaction with  $\text{NO}_x$ . The difference in SCR activity is most evident at 200°C where  $\text{NH}_3$  oxidation over the PGM layer is only approximately 10% but the SCR catalysts are already active [1, 2]. At this temperature,  $\text{NO}_x$  conversion is 72% on PGM+SCR\_SP and only 31% on PGM+SCR\_LP.

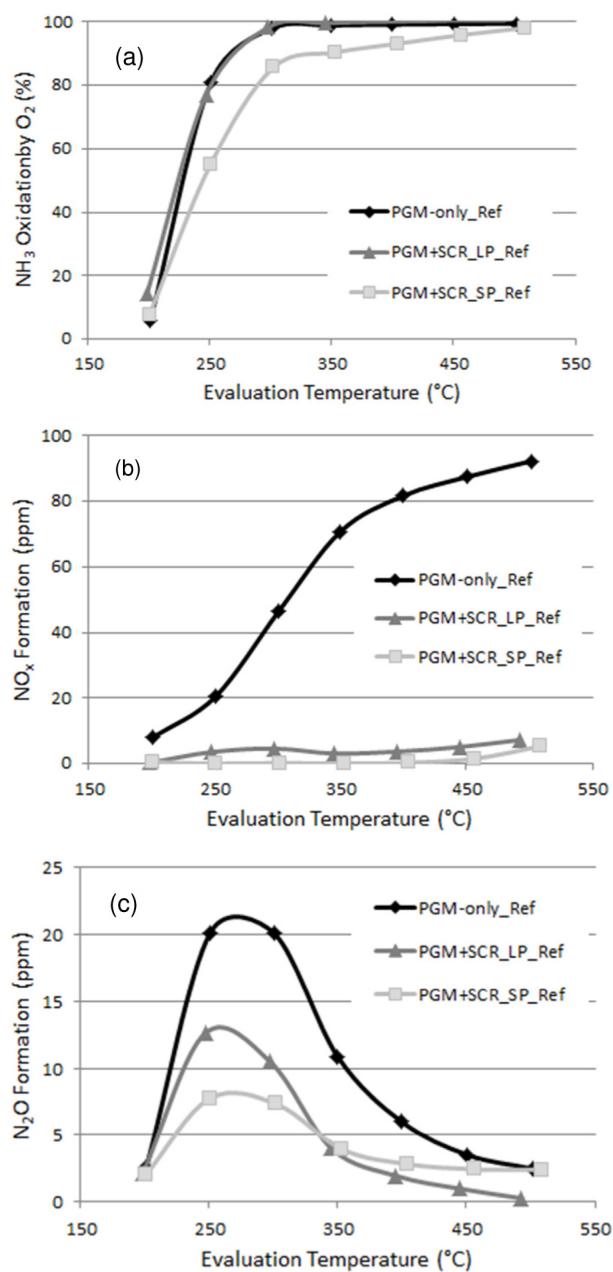


Figure 2.  $\text{NH}_3$  oxidation (a),  $\text{NO}_x$  formation (b), and  $\text{N}_2\text{O}$  formation (c) in the absence of hydrocarbons (step 1)

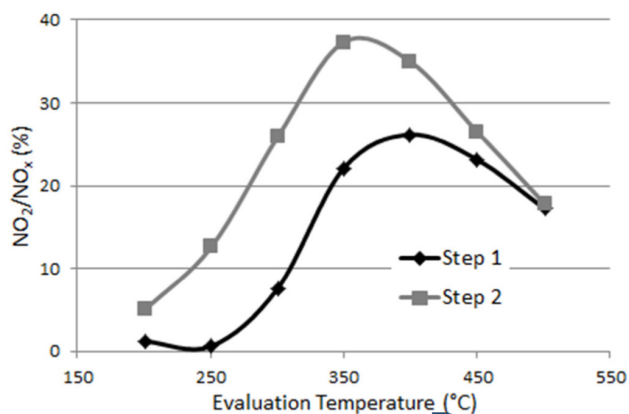


Figure 3.  $\text{NO}_2:\text{NO}_x$  on PGM-only AMOX during step 1 and step 2 in the absence of hydrocarbons