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Passive-ammonia selective catalytic reduction (SCR): Understanding NH_3 formation over close-coupled three way catalysts (TWC)

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ABSTRACT

NH_3 formation was examined under steady-state and lean/rich cycling conditions over four commercial catalysts including: (1) a Pd-only, high precious metal loading (HPGM) three-way catalyst, (2) a Pd/Rh + CeO_2, low precious metal loading (LPGM) three-way catalyst, (3) a combination of a HPGM and a LPGM (Dual-Zone) catalyst and (4) a lean NO_X trap (LNT) catalyst. The goal of this work was to evaluate these catalysts for their potential use as the upstream component in a passive-NH_3 SCR configuration. NH_3 formation during steady-state operation was found to be dependent on the air-to-fuel ratio (AFR), temperature and catalytic formulation used. While all of the formulations produced significant amounts of NH_3 when operated under sufficiently rich conditions, in general the steady-state NH_3 yield decreased in the following order: HPGM $\geq$ Dual-Zone » LPGM $\approx$ LNT. Under lean-rich cycling conditions that would be required for this mode of operation, lower air-to-fuel ratios were required to generate the same amount of NH_3 as under steady-state conditions. Results obtained with the LNT catalyst demonstrated that at moderate temperatures (i.e., 275–500 °C) NO_X storage capacity significantly increased the amount of NH_3 produced in relation to the amount of NO_X slipped. Consequently, the addition of an "optimum" amount of NO_X storage capacity in addition to well-controlled lean-rich timing, could significantly improve the performance of the three-way catalyst used as the upstream component in a passive-NH_3 SCR configuration. When the CO, C_3H_6 and N_2O concentrations in the effluent were considered in addition to the NH_3 formation, an optimum temperature of 400–450 °C was determined for the operation of these catalysts.

1. Introduction

Lean-burn engines are more fuel efficient and produce less CO_2 than traditional, stoichiometric-burn engines [1–3]. Full commercial implementation of lean-burn engines, however, requires the development of cost effective catalysts capable of meeting current emissions regulations under lean-burn exhaust conditions, which still represents a major technical challenge. Since the late 1970s, three-way catalysts (TWC) have been employed for the simultaneous reduction of nitrogen oxides (NO_X) and the oxidation of unburned hydrocarbons and carbon monoxide (CO) present in the exhaust of stoichiometric burn engines. However, these TWCs only sufficiently remediate pollutants if operated in a very narrow region near the stoichiometric combustion regime and exhibit very low NO_X conversion if operated under the much higher O_2 concentrations encountered in lean-burn engine exhausts [4]. Two existing solutions for the reduction of NO_X in this case include lean NO_X trap (LNT) and NH_3-selective catalytic reduction (NH_3-SCR) catalysts, where operation of these systems has been summarized in recent reviews [4–9].

Briefly, LNTs are designed for operation in periodic lean (~60 s) and rich (~5 s) environments. During lean periods, NO_X is oxidized to NO_2 over the precious metal component of these catalysts (e.g., Pt, Pd, Rh) and then is subsequently stored in the form of nitrites or nitrates on an alkali or alkali-earth storage component (e.g., Ba) [10,11]. The storage component eventually becomes saturated with NO_X and a brief rich period must be employed to convert the stored NO_X to N_2 and regenerate the storage capacity of the catalyst. Typical LNT formulations contain relatively high weight loadings of Pt (≈2–3 wt%), with smaller amounts of Pd and/or Rh also present, supported on a Ba-containing high surface area support, typically γ-Al_2O_3 [12,13]. Conversely, NH_3-SCR catalysts do

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not rely on a cycling strategy, but instead operate through the selective reaction of NH_3 with NO_X in the presence of excess oxygen, with NH_3 typically provided via on-board storage of urea—which is rapidly hydrolyzed to NH_3 under automotive exhaust conditions [5]. SCR catalytic formulations for automotive applications are usually either V_2O_5-WO_3/TiO_2 type or Cu/Fe exchanged zeolites [4,5,7,9]. In Europe, V_2O_5-WO_3/TiO_2-based formulations were introduced in 2005 for heavy-duty diesel applications. However, the high activity for SO_2 oxidation of these catalysts, the toxicity of volatile vanadia species (>650 °C) and their poor activity and selectivity above 550 °C, generally make the zeolite-based formulations more attractive for lean-gasoline applications [9]. Furthermore, zeolite-based catalysts can also store significantly more NH_3 than their V_2O_5-based counterparts [14,15]. Initially, commercial application of zeolite-based SCR catalysts was limited because of poor hydrothermal stability, but recent advances in zeolite technology have led to the discovery of hydrothermally stable zeolites that are active over a broad temperature range [16,17]. Stabilization of the zeolite structure using a metal oxide coating has also been demonstrated [18].

Both LNT and NH_3-SCR technologies suffer from different, but significant drawbacks. For example, LNT catalysts require high platinum group metal (PGM) loadings, resulting in a significant cost per catalyst. They are also particularly susceptible to sulfur poising, requiring periodic, high-temperature regenerations schemes, which eventually lead to partial degradation of LNT performance [7,8]. NH_3-SCR catalysts are less expensive, but the dosing system required to deliver urea to the exhaust stream adds to the total cost of the exhaust system and may represent a technical challenge for smaller gasoline engines. These systems also require on-board storage of urea (e.g., a 30-litre tank) and customer resistance to an additional “fuel” tank, the lack of existing urea “fueling” infrastructure, and a relatively high freezing point (approx. −12 °C) and long-term stability issues (>32 °C) for urea are topics of considerable concern. Additionally, in lean-burn gasoline applications the potential for high NOx outputs would require an even larger urea tank than its diesel counterpart [19]. Despite these problems, NH_3-SCR is emerging as the key technology for large diesel vehicle applications, while LNT catalysts have been favored for smaller engines.

Recently, researchers at GM have demonstrated a new technology referred to as the “passive-ammonia” or “urealess” SCR approach [1–3,20–22]. As in the case of LNT systems, the passive-NH_3 SCR approach is based on periodic lean-rich cycling, but does not include an LNT catalyst. Instead, a TWC is used to generate NH_3 during periods of rich operation. The NH_3 thus generated is subsequently stored on a downstream, under-floor SCR catalyst. After a sufficient amount of NH_3 has been stored, the engine switches back to lean operation and the stored NH_3 is used to reduce NO_X that slips un-reacted from the upstream TWC. This is particularly attractive in gasoline applications, because it allows the vehicle to periodically resort to stoichiometric operation when necessary. Ultimately, the successful operation of the passive-NH_3 SCR approach relies on the following factors: (1) robust and selective NH_3 generation over the TWC, (2) significant storage of NH_3 on the downstream SCR catalyst, (3) efficient utilization of stored NH_3 for NO_X reduction and (4) optimization of the required lean/rich engine timing, with a higher ratio of lean to rich time increasing efficiency gains.

Of these, the selective generation of NH_3 over the TWC is arguably the most important aspect of the passive-NH_3 approach. While the potential for NH_3 formation over TWCs is well known [23], early research efforts were focused on avoiding NH_3 formation. Even so, subsequent reactor screening experiments [24–26], engine chassis dynamometer studies [27–31] and tunnel investigations [32–35] confirmed NH_3 slip from vehicles equipped with TWCs, where NH_3 generation was not necessarily expected under typical operating conditions. Heeb et al. [30,31] further demonstrated that NH_3 was produced as a secondary pollutant over the TWC and was not generated by the engine and argued that NH_3 standards should be included in future regulations. While NH_3 slip from TWCs may be unfavorable in the traditional sense, in the passive-NH_3 SCR approach the main goal is to produce NH_3 over the TWC for use in a downstream SCR catalyst.

In this manuscript, we focus on NH_3 generation over a series of TWCs including: a high PGM, a low PGM, a dual-zone TWC and a lean NO_X trap catalyst (LNT) evaluated under identical conditions as the TWCs. Commercial monolithic cores of these catalysts were evaluated under both steady-state and lean-rich cycling conditions in a laboratory flow reactor. The effects of catalytic formulation, temperature and steady-state vs. cycling conditions on NH_3 generation were considered and will be discussed in detail below.

2. Experimental

2.1. Materials

Four fully formulated cores (wash-coated honeycomb cordierite monoliths) were used in the present investigation. Their properties are summarized in Table 1. Three of the cores were obtained from a commercial 1.3 L TWC that is employed in a 6-speed, Chevy Malibu vehicle (Model Year: 2009). The commercial catalyst design in this case was constructed using a dual-zone approach, where the front and rear sections were intentionally synthesized using different formulations: the first 62 mm (0.6 L) section of the monolith was a high platinum group metal (HPGM), Pd-only TWC (0/7.3/0 g/L of Pt/Pd/Rh, respectively) and the rear 73 mm (0.7 L) section was a low platinum group metal (LPGM), Pd/Rh TWC (0/1.14/0.3 g/L Pt/Pd/Rh, respectively), which also contained CeO_2. The HPGM catalyst, the LPGM catalyst and the “Dual-Zone” combination of the two were independently evaluated, where the HPGM catalyst was placed upstream of the LPGM catalyst in the Dual-Zone designation—as is the case on the vehicle.

In addition to the TWCs, a lean NO_X trap catalyst (LNT) was also evaluated under identical conditions as the TWCs. Obviously, the LNT catalyst includes a significant amount of NO_X storage capacity (NSC). The LNT core was obtained from a commercial LNT catalyst that is employed in a lean-gasoline BMW 120i vehicle (Model year: 2009). This is the same catalyst that has been selected as the new representative commercial LNT catalyst in the Crosscut Lean Exhaust Emissions Reduction Simulations (CLEERS) research community [36]. More detailed information regarding the characterization of this catalyst can be found elsewhere [37]. Briefly, semi-quantitative metals screening via inductively coupled plasma mass spectroscopy (ICP-MS) measurements conducted at Galbraith Laboratories confirmed the presence of Mg, Al, Ce and Ba as major components, with other elements of interest including: Zr, La, Pt, Pd, and Rh. Subsequent electron microscopy with complementary elemental analysis measurements exposed three compositionally distinct regions including: a Ce/Zr mixed oxide domain, a Mg/Al mixed oxide domain and an Al oxide domain. The Pt, Pd and Ba active components all seemed to be preferentially deposited on the Ce/Zr domain.

2.2. Catalytic evaluation

Catalytic activity measurements were performed using a laboratory flow reactor, described in more detail elsewhere [37,38]. Briefly, the monolithic cores were tightly wrapped in Zetex insulation tape and inserted into a horizontal quartz tube reactor. The quartz tube was heated using a horizontal bench-top furnace (Lindberg/Blue M). Gas mixtures were prepared using pressurized gas