

Towards Carbon Neutrality - Synthetic Gas Bench Study of Performance of Potential Aftertreatment Components for H₂ Internal Combustion Engine

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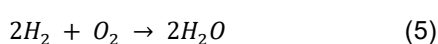
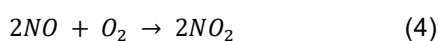
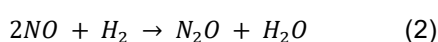
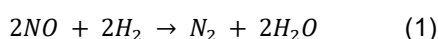
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Abstract

Hydrogen internal combustion engines (H₂ ICE) present a cost-effective, durable, and reliable pathway toward carbon neutrality and compliance with zero-emission regulations, offering fast refueling and resilience across climates while avoiding issues tied to critical mineral mining and battery waste. To address tailpipe NO_x emissions, selective catalytic reduction (SCR) can significantly reduce emissions and support in achieving Low-NO_x standards. Our study evaluated diesel aftertreatment catalysts under simulated H₂ ICE exhaust using a synthetic gas bench (SGB) setup, which accurately reproduced conditions with high repeatability and greater flexibility than engine benches. Key features of H₂ ICE exhaust include low engine-out NO_x, negligible soot and sulfur, lower temperatures, higher water content, and challenges such as increased N₂O at 120–250 °C and potential H₂ slip.

1 Introduction

As the transition toward full decarbonization progresses, a key advancement involves utilizing hydrogen as a carbon-free fuel in lean-burn internal combustion engines. In such engines, NO_x emissions become the primary environmental concern, with only trace amounts of CO, unburned hydrocarbons, and lubricant-derived ash generated during combustion. Although advanced engine control strategies can substantially reduce NO_x emissions in hydrogen-fueled engines, increasingly stringent emission standards may still necessitate the integration of an efficient exhaust aftertreatment system like modern diesel engines. Given the onboard availability of hydrogen, its application as a reducing agent in SCR (Selective Catalytic Reduction) of NO_x presents an elegant solution (shown in Equation (1)). This approach is particularly attractive if the formation of undesired byproducts that are outlined in Equations (2)–(5)—can be effectively minimized.



Hydrogen has been reported to be very active as a reducing agent for the NO/H₂ reaction and could potentially be used to reduce NO_x emissions from stationary sources. Hydrogen is already available in many industrial units in which various hydrotreating and fuel-combustion processes for heat supply are operated. Moreover, hydrogen demand is expected to increase at a compound growth rate of about 10% per year and therefore hydrogen availability in the industrial sector is expected to increase more in the following years. Therefore, a H₂-SCR of NO_x catalytic technology might be considered as a breakthrough technology against any H₂-SCR catalytic processes that might evolve in the future⁽²⁾.

2 Experiments and Results:

The catalytic activity measurements were performed at ITCA (Isuzu Technical Center of America, Inc.) synthetic gas bench (Figure 1), specially designed for the evaluation of catalytic activity of the small core samples extracted from the aftertreatment modules, under emulated H₂ engine exhaust conditions, i.e. higher H₂O content (10% → 15%) and H₂ concentration in the exhaust (maximum up to 3.5%) in addition to the other exhaust species that are similar to diesel exhaust. The gas bench consists of three regions: the gas feed, the reactor, and the gas analysis system. The

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gas feed region contains the reactant gases, the mass flow controllers for mixing the gases, valves such as check, on/off, and three-way for controlling the direction of the flows and the water pump to pump the water into the boiler for steam introduction to the gas mixture. The gas mix finally is fed into the reactor placed inside the three-zone furnace. After that gas passes through the analyzer systems depending on

the components interested in the measurement of the concentration of gases, as schematically illustrated in Figure 2. The monolith is wrapped in quartz glass wool and placed in tubular stainless-steel reactor flanked by two thermocouples approximately 1 cm upstream and downstream of the monolith.

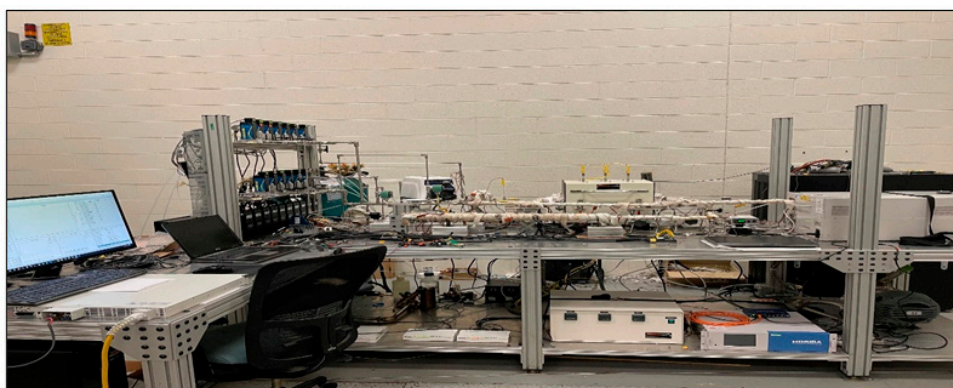


Figure 1 Picture of Synthetic Gas Bench at ITCA

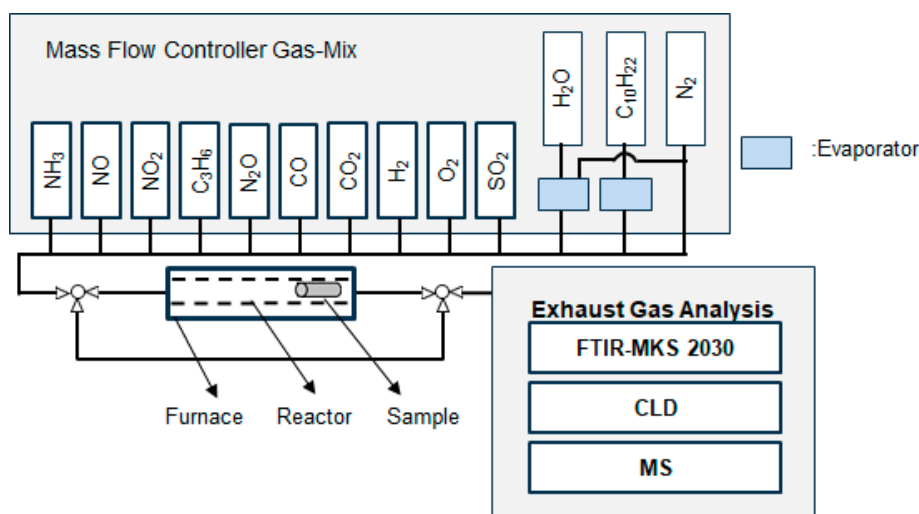


Figure 2 Schematic of the Synthetic Gas Bench at ITCA

Conversion of the gases and selectivity were calculated based on gas analysis by an FT-IR spectrometer (MultiGas 2030, MKS Instruments) operating at 1 Hz. Light-off experiments with 5C/min from 100 °C to 300 °C with a GHSV (Gas Hourly Space Velocity) of 60,000 h⁻¹ provide information on the catalytic activity in a temperature range that is considered relevant for H₂-SCR.

2.1 Experiment 1 (uf_SCR_aged)

A series of experiments were conducted on the aged uf_SCR (Underfloor Selective Catalytic Reduction) catalyst following the standard SCR testing protocol. The study focused on varying the ANR (Ammonia-to-NO_x Ratio) at values of 1.0, 0.5, 0.25, and 0.0, to assess the effect of reductant availability on NO conversion and byproduct formation. The gas mixture included 200 ppm NO, 1% H₂, 10% O₂, with the balance composed of N₂, and the tests were performed at a GHSV of 60,000 h⁻¹. The influence of water vapor content

in the feed gas, specifically at 10% and 15% H₂O, was systematically examined. Table 1 details the gas compositions employed across the test matrix. As shown in Figure 3, presence of water was found to enhance NO conversion during H₂-SCR, demonstrating a beneficial effect on catalytic

performance. However, as shown in Figure 4, increasing the water content from 10% to 15% at 200°C resulted in a 5% decrease in NO conversion, indicating an optimum water level beyond which performance may decline.

Table 1 Volumetric inlet gas compositions for the catalytic activity measurements at 200°C with 10% and 15% water content

| Gas mix | NH ₃ (ppm) | NO(ppm) | ANR | H ₂ (%) | O ₂ (%) |
|---------|-----------------------|---------|------|--------------------|--------------------|
| A | 200 | 200 | 1 | 1 | 10 |
| B | 100 | 200 | 0.5 | 1 | 10 |
| C | 50 | 200 | 0.25 | 1 | 10 |
| D | 0 | 200 | 0 | 1 | 10 |

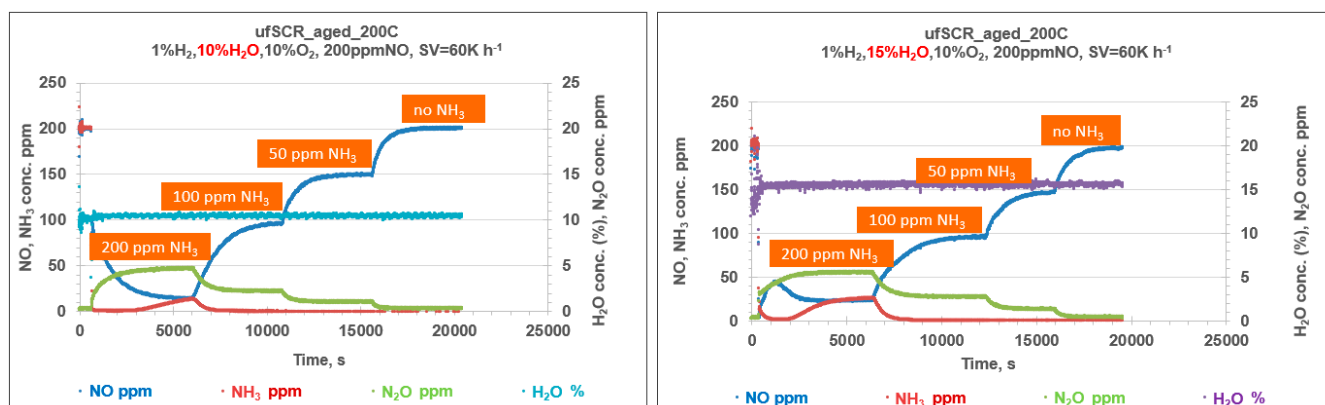
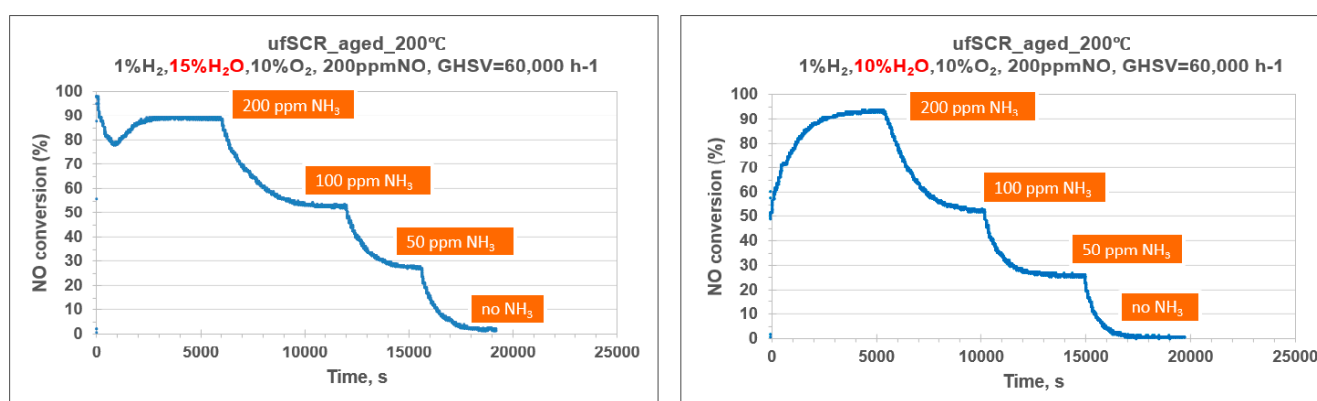


Figure 3 ufSCR_aged : NO, NH₃, and N₂O concentration at two different water content



**Figure 4 ufSCR_aged: At ANR=1.0 the water content influences NO conversion at 200°C
An increase of 5% H₂O content reduces NO conversion by around 5%**

Notably, NO_x conversion performance decreased by 10-20% below 200°C sample inlet temperature with 20% H₂O in the feedgas in comparison to 7% H₂O in the feedgas. However, N₂O formation remained largely unaffected by the increase in H₂O content between 10% and 15%, suggesting minimal impact on selectivity under these conditions. These

observations are similar to the results observed by Sharp et al.⁽³⁾. Additional experiments were performed under ANR = 1.0, across eight temperature points ranging from 150°C to 450°C. The resulting data, presented in Figure 5, show that N₂O formation peaked at 200°C, highlighting a critical temperature window for byproduct generation.

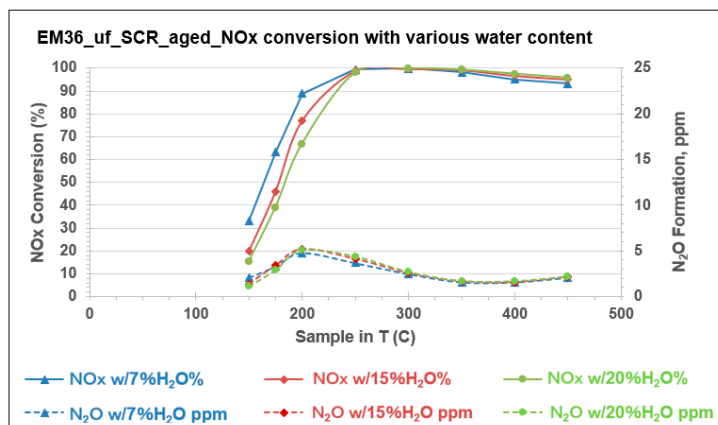


Figure 5 ufSCR_aged: NO_x conversion and N₂O formation impact various H₂O content in feedgas at ANR 1.0 in the presence of 1% H₂

2.2 Experiment 2. (DOC_Degreened).

The influence of hydrogen concentration in the feed stream on the catalytic activity of the degreened DOC (Diesel Oxidation Catalyst) was investigated under NO/H₂/O₂ reaction conditions. The primary objective was to evaluate whether localized exotherms could be induced at the catalyst inlet via H₂ injection, as shown in Figure 6, and to determine if such thermal effects could help mitigate N₂O formation. The test matrix, shown in Table 2, involved varying the hydrogen content in between hydrogen and oxygen, as represented in Equation (5), which provides localized heating and may alter downstream catalytic reactions. The feed while maintaining a constant 15% H₂O concentration. Experiments were conducted at a GHSV of 110,000 h⁻¹. Results demonstrated that a significant exothermic response could be achieved even at temperatures as low as 70°C. This behavior is attributed to the exothermic reaction.

Table 2 Volumetric inlet gas compositions for the catalytic activity measurements at 80°C and 70°C with 15% water content

| Gas mix | NO (ppm) | O ₂ (%) | H ₂ O(%) | H ₂ (%) |
|---------|----------|--------------------|---------------------|--------------------|
| A | 500 | 10 | 15 | 2 |
| B | 500 | 10 | 15 | 2.5 |
| C | 500 | 10 | 15 | 3 |
| D | 500 | 10 | 15 | 3.5 |

A series of experiments were conducted to evaluate the potential for inducing localized exotherms at the catalyst inlet by varying hydrogen concentration in the feed over a degreened DOC. Initial tests were performed with 2% H₂, with subsequent increments up to 3.5% H₂. Hydrogen was introduced at an inlet temperature of 80°C, and the gas mixture consisted of 500 ppm NO, 10% O₂, and 15% H₂O, at a space velocity of 110,000 h⁻¹. As shown in Figure 6, a significant exothermic response was observed at 80°C. To determine the lowest inlet temperature at which an exotherm could still be generated, a second test series was performed by injecting hydrogen at 70°C, while keeping the gas composition constant. Hydrogen concentrations were varied at 2.5%, 3.0%, and 3.5%, respectively. Results in Figure 7 demonstrate that even at 70°C, substantial exothermic activity was observed, particularly at 3.5% H₂, which also resulted in a notable reduction in N₂O formation. These observations are similar to the results observed by Sharp et al.⁽³⁾. These findings highlight the potential of H₂ dosing as a strategy for low-temperature catalyst activation and N₂O mitigation.

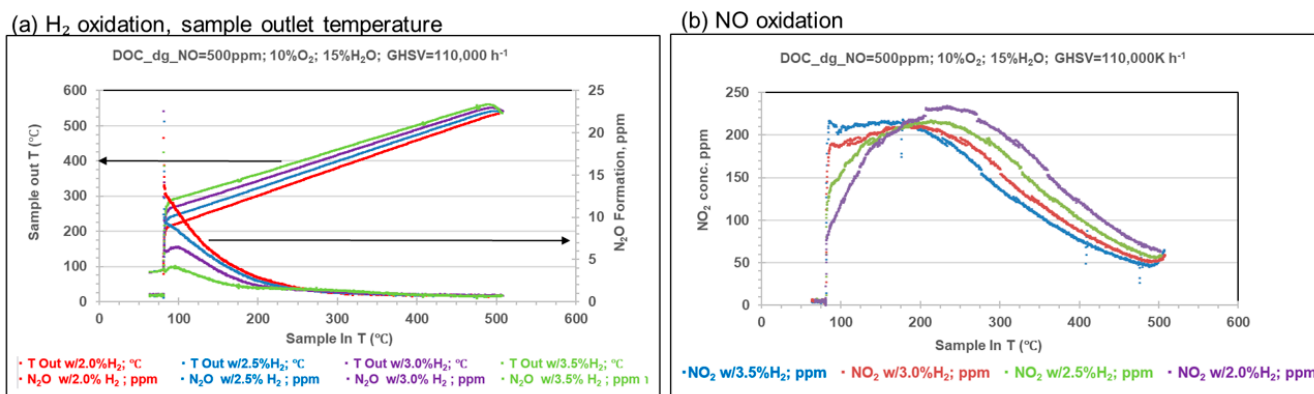


Figure 6 H₂ oxidation, sample outlet temperature, and NO oxidation with H₂ injection at 80°C

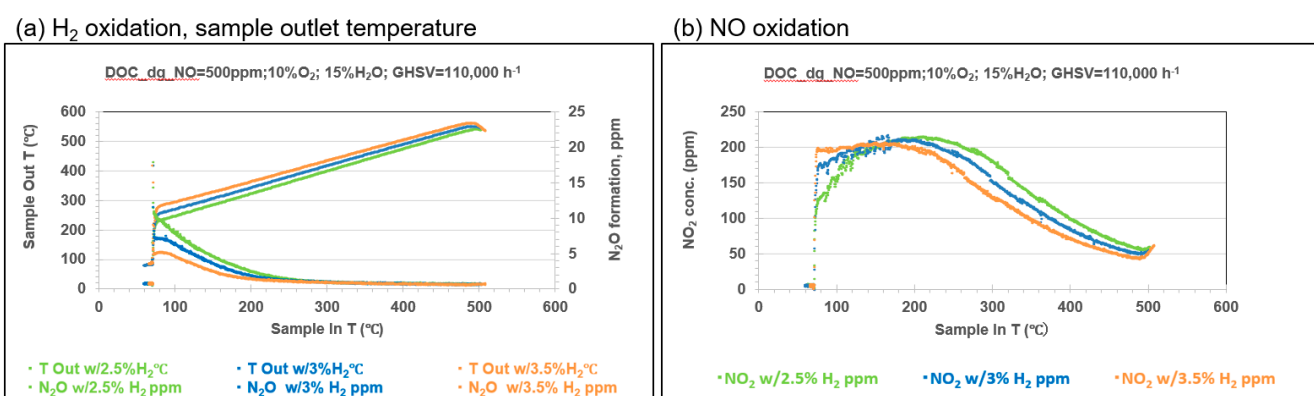


Figure 7 H₂ oxidation, sample outlet temperature, and NO oxidation with H₂ injection at 70°C

2.3 Experiment 3. (ASC_aged - H₂-SCR_concept : NO_x conversion with varying H₂)

A series of experiments were carried out on the aged ASC (Ammonia Slip Catalyst) catalyst to investigate the effect of hydrogen injection at the ASC inlet on N₂O formation. The test conditions included 200 ppm NO, 8% O₂, and 15% H₂O, with a space velocity of 110,000 h⁻¹. The detailed test matrix is presented in Table 3. As shown in Figure 8, the graph includes both the measured NO conversion and the corrected NO_x conversion, which accounts for secondary emissions by including the nitrogen content of N₂O as unconverted NO_x. This corrected value was calculated by attributing the two nitrogen atoms in each N₂O molecule to NO_x that was not effectively reduced.

At 215°C, the introduction of 1,800 ppm H₂ led to the formation of approximately 3 ppm N₂O. Increasing the hydrogen concentration to 3,800 ppm resulted in about 6 ppm N₂O. At elevated temperatures, a noticeable decline in NO conversion was observed,

which can be attributed to the exothermic nature of the H₂ and O₂ reaction (see Equation (5)), potentially altering reaction pathways and active site availability. Interestingly, both catalyst activity and N₂ selectivity improved with increasing H₂ concentration in the feed. However, this trend was not strictly monotonic. At higher H₂ levels, the promotion of NH₃ formation (as described by Equation (3)) can reduce N₂ selectivity. In this study, no NH₃ was detected, even at the highest tested H₂ concentration of 5,500 ppm, suggesting that under the given operating conditions, the formation of unwanted ammonia slip was effectively avoided.

Table 3 Volumetric inlet gas compositions for the ASC catalytic activity measurements

| Gas mix | NO(ppm) | O ₂ (%) | H ₂ O(%) | H ₂ (%) |
|---------|---------|--------------------|---------------------|--------------------|
| A | 200 | 8 | 15 | 0.18 |
| B | 200 | 8 | 15 | 0.38 |
| C | 200 | 8 | 15 | 0.55 |

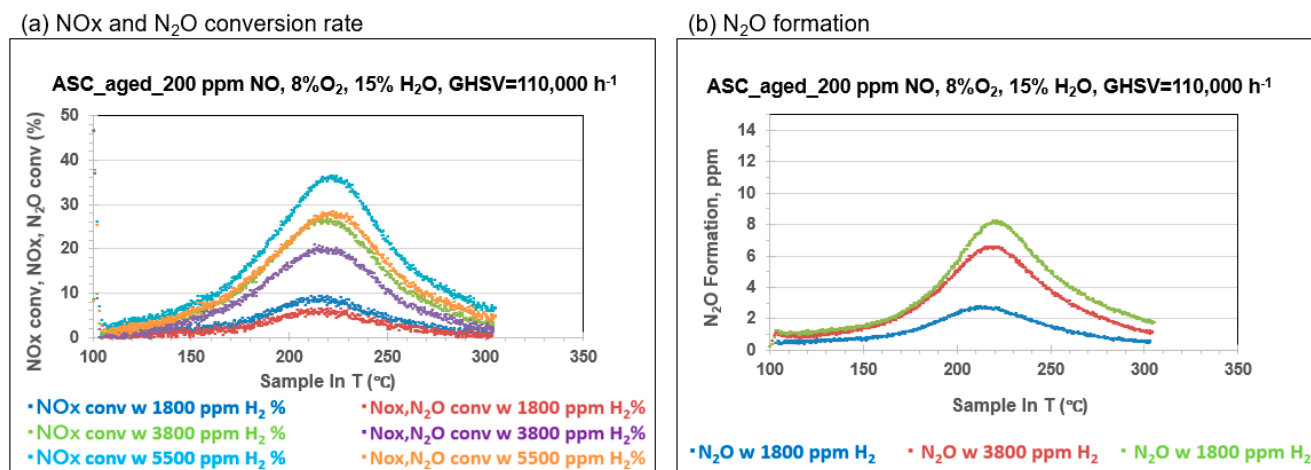


Figure 8 N₂O formation increases with the increase of H₂ at the exhaust

A set of experiments was conducted under ANR = 1.0 conditions, with 500 ppm NH₃ in the feed, to assess the impact of hydrogen presence on ammonia conversion. Tests were performed at a space velocity of 110,000 h⁻¹, both with and without H₂ in the gas stream. As shown in Figure 9(a), the presence of H₂ was found to have a beneficial effect, resulting in lower N₂O formation during the SCR reaction, while maintaining effective NH₃ conversion. In a complementary test sequence, NH₃-only feed experiments were performed to compare performance

with and without H₂. Results, shown in Figure 9(b), indicate that in the presence of hydrogen, NH₃ light-off occurs at a lower temperature, demonstrating enhanced reactivity at reduced thermal conditions. Additionally, the temperature at which the N₂O formation peak occurs also shifts to a lower range when H₂ is included in the stream. These findings suggest that hydrogen not only facilitates earlier NH₃ activation but also alters the temperature profile of byproduct formation.

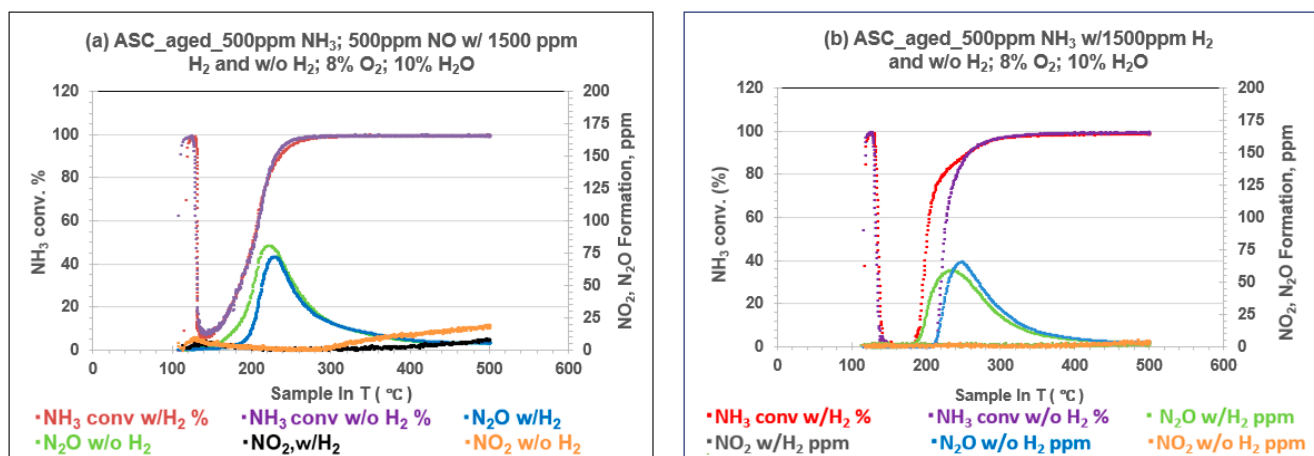


Figure 9 (a) NH₃ conversion at ANR=1 with and without H₂. (b) NH₃ oxidation w/ and w/o H₂

3 Conclusion

A comprehensive series of experiments was conducted using the catalysts typical of diesel engine aftertreatment under exhaust conditions representative of H₂ ICE (Internal Combustion Engine) and supporting aftertreatment system. Catalytic activity was evaluated on aged and degreened samples across various configurations (SCR, DOC, and ASC) to understand the role of hydrogen, higher water content, and temperature in NO_x conversion and N₂O formation.

The results indicate that the presence of hydrogen in the feedgas significantly influences both the catalytic activity and selectivity of the system. For the aged SCR catalyst (uf_SCR_aged), excessive water content (15% H₂O) resulted in a slight performance drop at 200°C. However, N₂O formation remained largely unaffected by water content but exhibited a temperature-dependent profile, peaking at approximately 200°C. The degreened DOC (DOC_deg) demonstrated that localized exotherms could be effectively induced at low inlet temperatures (as low as 70°C) through controlled hydrogen dosing, offering potential for low-temperature catalyst activation. Furthermore, these exotherms were correlated with reductions in N₂O formation, suggesting a thermally mediated enhancement in reaction pathways. For the aged ASC catalyst (ASC_aged), modest N₂O generation was observed with increased H₂ concentrations while the overall NO_x conversion performance improved. No ammonia slip was detected, even at elevated hydrogen levels (up to 5,500 ppm), demonstrating that H₂-SCR could be implemented without compromising downstream ammonia management.

These findings collectively highlight the promising potential of hydrogen as a reductant and thermal promoter in future decarbonized aftertreatment strategies, supporting improved NO_x conversion efficiency and reduced secondary emissions across a broad temperature window. Further optimization of H₂ dosing strategies, in conjunction with tailored catalyst formulations, could enable robust compliance with tightening emission regulations in hydrogen-fueled or hybrid diesel powertrains.

References

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