



Catalytic Aftertreatment Systems for Combustion Exhaust Gases from Future Hydrogen, Ammonia and e-HC Engines

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Abstract

Heavy-duty and marine transport will continue to rely on robust, high energy-density, combustion engine technology. Sustainable fuels, fuel-flexible engines and stricter future emission standards all call for further development of catalytic aftertreatment systems (ATSS). This paper reviews progress and evaluates emission removal methods, based on synthetic gas bench (SGB) experiments simulating characteristic lean and stoichiometric conditions in hydrogen, ammonia, methanol and methane engine exhaust gases. The oxidation reactivity of fuel compounds on tailored catalysts showed the following light-off temperatures (T_{50} , °C) in lean conditions: hydrogen(140) < methanol(170) ~ CO < diesel-hydrocarbons, reference(180) < ammonia(250) < methane(380). NO_x removal in mobile applications will be challenging, due to NO_x limits and varying fuel types/mixtures. Urea/ NH_3 -SCR will remain the main NO_x removal method, with an option of double SCR widening its temperature window. NO_x storage catalysts based on metal oxides or zeolites, increased NO_x removal at 100–200 °C by passive adsorption–desorption. NO_x reduction by hydrogen (H_2 -SCR) showed NO_x reduction of up to 60–70% on platinum catalysts at 100–160 °C, before NH_3 -SCR reactions at higher temperatures. Selective ammonia slip catalysts (ASCs) were effective to cut NH_3 emissions. High selectivity to N_2 with low N_2O formation was challenging with H_2 -SCR and ASC. Three-way catalysts, applied with stoichiometric hydrogen combustion, were operating below 200 °C. More efficient catalytic methods for methane and N_2O removal are required to improve the feasibility of methane and ammonia as future fuels. Integration of different properties in the same units is essential to minimise ATS volume and costs. The flexible use of green fuels requires flexible ATSS too.

Keywords Green fuels · Hydrogen · Ammonia · Methane · Methanol · Emissions · Nitrogen oxides · Catalysts · SCR

1 Introduction and Review

Population growth and global industrialisation have created a huge increase in energy consumption, accompanied by severe environmental issues, including fossil fuel depletion, pollution and increased content of greenhouse gases (GHG) [1]. The Paris agreement countries agreed to a reduction of 50–52% in carbon dioxide (CO_2) emissions by 2030, generation of carbon pollution-free electricity by 2035 and net zero GHG emissions by 2050. International low- or zero-GHG

emission targets create challenges for the development of combustion engines. It is believed that the risk of higher non- CO_2 GHG emissions, such as methane (CH_4), nitrous oxide (N_2O) and hydrofluorocarbons, will increase without specific limitations in the future [2]. In addition to electric vehicles and fuel cells, carbon-free fuels also offer an opportunity to reduce CO_2 emissions, particularly in heavy-duty applications. Renewable biofuels (methane, diesel, ethanol) may serve during an interim period before a move to fossil carbon-free fuels. Hydrogen (H_2) is a clean fuel, forming only water in combustion. However, current commercial “grey” hydrogen is produced mostly from fossil natural gas by methane reforming. Green hydrogen, produced using green electricity (solar, wind, hydro and possibly nuclear), is a key target fuel, with carbon-free emissions in the whole energy production path [3]. This green hydrogen is the main focus for the future, with development, production and

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Fig. 1 An estimation of energy sources in future transport applications (year 2050) [8]

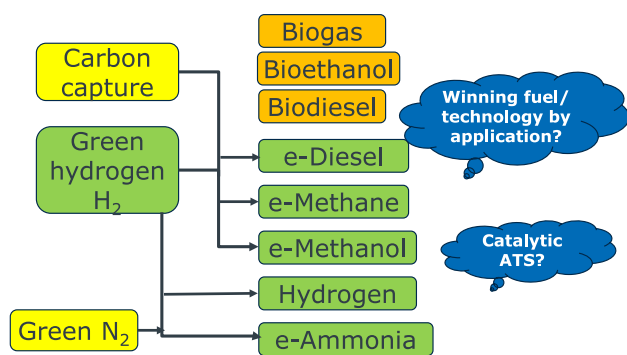


Fig. 2 Utilisation of hydrogen for green fuels

investments aimed at achieving worldwide carbon freedom during 2030–2060s.

Currently, there is growing interest in ammonia (NH_3) as an energy-dense hydrogen carrier. Easy storage and transport in compressed liquid form make it an attractive zero-carbon alternative for marine applications [4] (Fig. 1). Ammonia is a volumetrically efficient hydrogen carrier in comparison to any hybrids, hydrazine or hydrogen, which require low temperatures to be packed into practical volumes [5]. Ammonia is conventionally produced from fossil fuels and air, using the Haber–Bosch process [6]. This technology is well known, and ammonia has been widely used as a raw material, for example, in fertiliser, which has had a key role in food production capacity for the fast population growth during the last 60 years [6]. The raw materials for green ammonia production are green hydrogen and green nitrogen, which is separated from air. Therefore, in a green shift, ammonia production needs to be sufficiently large and economically viable to accommodate the needs of both food and energy sectors. The first ammonia-fuelled locomotive engine was introduced in 1822, followed by limited automotive implementations at the turn of the century [4]. For combustion enhancement, it is possible to convert ammonia

back to hydrogen on cracking catalysts, where ruthenium (Ru) was the most active metal among Ru, Rh, Pt, Pd, Ni, and Fe supported on carbon and metal oxides [7].

Synthetic hydrocarbon and alcohol fuels (e-methane, e-hydrocarbons/diesel, e-methanol,) produced in green ways by carbon capture, together with hydrogen, form a flexible route for future combustion and emission control (Fig. 2). However, the current research and development is very wide, seeking the optimal solutions for technology, raw material sources and economics for varying applications. Most of the fuels intended to replace fossil fuels are still more expensive to produce, their volumetric energy density is low, or their safe use is challenging.

Methanol (MeOH) and methane (CH_4) are C_1 fuels, and they are simpler and cheaper to manufacture than heavier green HCs (e.g. e-diesel). They are also well-matched to diesel engine combustion and marine applications, where commercial lean-burn engine technology has already been introduced. Alcohols and biomethane also have been prepared from recycled biological wastes with low net CO_2 emissions. Bioethanol has been used successfully in automotive gasoline blends (E5, E85) and applications, notably in Brasil since the 1990s. Methanol (MeOH) has a sufficiently high energy density (liquid) and an existing optimised production process with a high production capacity [9]. Replacing diesel oils with MeOH is reported to lead to cuts in NO_x emissions of 5–50%, depending on engine load, mainly due to lower combustion temperature [9]. Of course, the ultimate fossil-free fuel will be e-methanol produced by CO_2 hydrogenation, using H_2 (green electricity) and CO_2 (green carbon capture), replacing natural gas and coal-derived synthesis gas, which are still today the main raw material in synthesis [10]. The production of e-ethanol (EtOH) is possible by similar routes as for MeOH . The use of synthetic, low-C oxygenated hydrocarbons results also in very low PM (particulate matter—soot) and polyaromatic hydrocarbon (PAH) emissions. Alcohol, aldehyde and carbon acid emissions can be purified efficiently by oxidation catalysts [11].

Methane (CH_4) is the first, obvious C_1 e-hydrocarbon by chemistry when prepared by catalytic methanation process (Sabatier reaction: $\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$) and based on green CO_2 and H_2 [12, 13]. On-board methanation of CO_2 in vehicle exhaust gases is proposed technology to reduce CO_2 emissions, even though this is practically quite challenging. Methane has a greenhouse gas (GHG) factor 25 higher than CO_2 , so its emissions are also limited separately in addition to total hydrocarbon (THC) emissions [14]. Methane (natural gas) has been applied alone or in fuel combinations (dual- or bi-fuel) in both stoichiometric and lean combustion. Any resultant NO_x , CO, methane and often formaldehyde emissions, require active aftertreatment systems.

Large methane oxidation catalysts (MOC) with a high PtPd loading are necessary to activate methane oxidation in lean-burn conditions at 400–500 °C [14].

The properties of alternative fuels vary because they are dependent on their original sources, production methods, combustion properties and emission formation (Table 1). Those properties are also important in fuel storage, transport, combustion flexibility, thermal management, energy density and safety. Hydrogen, for example, has a very wide explosion range and high adiabatic combustion temperature in air, which might cause issues in safety and durability of components. The water content, calculated by comparable stoichiometric mixtures of fuels, is the maximum value, which will be diluted correspondingly by excess of air in lean mixtures (Table 1). However, the water content in exhaust gases will be still high, at 10–20%, after lean combustion with hydrogen-rich fuels (H_2 , NH_3 , CH_4), which is challenging for catalyst durability, for example. NO_x formation increases exponentially with the adiabatic flame temperature (stoichiometric air/fuel): this temperature will decrease in lean mixtures due to air dilution [15]. Fuels (alcohols, methane, e-diesel) composed of both hydrogen and carbon atoms have quite similar properties in combustion and emissions and they match existing engine technology. Due to ammonia's fuel-N, the formation of N_2O (a GHG) is usually much higher in ammonia combustion than with other fuels. Therefore, there are concerns with each studied fuel. The match of individual fuels in mixtures or when serving as alternative fuels in the same engines is part of a flexible fuel and combustion strategy.

Even if carbon-free fuels offer low particulate emissions, new fuels on a large scale pose challenges not only for combustion but also for catalysed aftertreatment systems (ATS) used for emissions removal. Planned, future emission legislation after 2026 for on-road (Euro VII) and off-road (Stage 6) applications will include new specific limits. For example, Euro VII for on-road trucks includes limits for NH_3 (60 mg/kWh), N_2O (200 mg/kWh) and methane (500 mg/kWh) in steady-state and transient test cycles. Euro VII

limits are challenging for exhaust gases from lean engines with diesel but also with any other fuels and their mixtures. The base for new ATS development in mobile, on-wheels applications is conventional diesel ATS, which includes pre-oxidat (located before DPF+SCR, ~DOC), DPF, SCR and post-oxidat (located after SCR, ~ASC) to remove CO, hydrocarbons, NO_x , PM and NH_3 [19]. Efficient NH_3 -SCR catalysts (e.g. Cu-zeolite, like Cu on chabazite) with a NO_2 promotion have been a key solution for low-temperature performance since Euro VI level (2014). However, urea dosing, evaporation and hydrolysis limit active SCR use below 200 °C and so alternative methods have been proposed for low-temperature NO_x control.

The passive NO_x adsorption (PNA) unit is designed to adsorb NO_x below 200 °C. The NO_x is desorbed naturally during warm-up phases in drive and then reduced downstream by NH_3 on a warmed SCR catalyst or by lean NO_x trap (LNT) [20–22]. Catalyst units can operate either passively (PNA, SCR) or actively (LNT with reduction peaks, NH_3 -SCR with urea dosing) [23, 24]. PNAs with precious group metals (PGM) like platinum (Pt) and palladium (Pd) as active metals have been based on metal oxides (Ce, La, Al) and zeolites (ZSM-5, Beta, CHA, Fer). The latest versions are confirmed to withstand high temperatures and SO_2 in exhaust gases [25, 26]. In addition, simultaneous NO_x and HC trapping can be applied for low temperature emission control [22]. Even if there are no heavy hydrocarbons as precursors for PM in CH_4 , MeOH, H_2 and NH_3 engines, the change of particulate number regulation from PN_{23} to PN_{10} (detection of particles larger than 10 nm) will be challenging, when there may be excessive formation of the smallest particulates coming from lubrication oil, sulphur oxides (SO_x), urea or metals/ash. If they exceed PM/PN limits, particulate emissions will be removed with wall-flow or partial filters.

A high water content (up to 15–25% in lean burn) in H_2 and NH_3 engine exhaust gases is challenging, particularly for zeolite-SCR catalysts, which are the mainstream NO_x removal method for on-road and machinery diesel

Table 1 The characteristics of common fuels: variables most related to evaluations of applications and emission control [16–18]

Property	Ammonia	Hydrogen	Methane	Methanol	Ethanol	Gasoline	Diesel
Formula	NH_3 (l)	H_2 (l)	CH_4 (l)	CH_3OH (l)	C_2H_5OH (l)	$C_nH_{1.87n}$ (l)	$C_nH_{1.8n}$ (l)
Density (liquid), kg/m^3	682	70	500	800	790	720–780	830–870
Boiling point, °C	~33	–255	–161.5	~65	78	33–190	180–370
Evaporation latent heat, kJ/kg	1370	446	511	1160	840	305	230–250
Low heating value, MJ/kg	18.8	120	50	50	47	44	42.6
Adiabatic flame temperature in air, °C	1800	2110	1963	1950	1965	1995	~2000–2050
Energy density, MJ/L	11.5	4.8	9.7	16	21.3	32	35.2
Explosion limit in air, vol-%	15–28	4.7–75	5–15	6.7–36	3.3–19	0.6–8	0.6–5.5
A/F(stoich), kg/kg	6.1	34.1	17	6.4	9.0	14.5	14.5
Water in exhaust (sto), vol-%	~28	~34	~19	~23	~18	~12	~12

sto stoichiometric

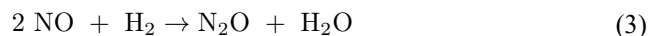
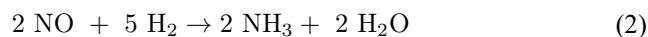
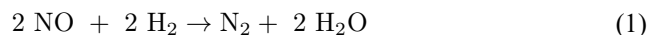
applications. Therefore, recent attention has switched to metal oxide-based SCR catalysts [3]. Sulphur-tolerant vanadium-SCR has been the principle deNO_x method in marine applications. Other metal oxide catalysts (e.g. Fe, Mn, Cu, Ce) still have weaknesses in terms of thermal durability, chemical deactivation, limited NO_x efficiency, and too-high NO₂ dependency or selectivity (N₂O), so they have not spread to wider commercial use. In addition to hydrothermal deactivation, a high water content also inhibits catalyst reactions.

Hydrogen (H₂) is a planned fuel for both heavy- and medium-duty applications, where leaner combustion mixtures might result in low exhaust gas temperatures. Double-/triple-deNO_x systems (SCR+SCR, LNT+SCR, LNT+LNT, PNA+LNT+SCR) have been introduced to improve low-temperature performance for NO_x reduction in mobile diesel and hydrogen applications [27–30]. An SCR catalyst in passive use is a good ammonia buffer, promoting NO_x conversion, enabling powerful enrichments through LNT and cutting ammonia emissions downstream. Within these concepts, twin-SCR (double-SCR) systems, together with thermal management, are the main proposed deNO_x solution to reach low NO_x emissions [30]. Twin-SCR and passive NO_x storage catalysts (NSC) by adsorption–desorption resulted in increased NO_x conversion in simulated hydrogen engine application at low temperatures (100–200 °C), when the efficient NO_x removal above 200 °C was based on NH₃-SCR catalysts [31]. It is also possible to intensify the ATS and utilise the DPF volume for different coatings, like SCR or adsorption catalysts [32].

NO_x reduction with hydrogen is an obvious, widely studied method, particularly for hydrogen engine applications, where H₂ is available as an on-board reductant or reaction promoter. However, typical NO_x conversion levels and selectivity to N₂ in H₂-SCR are not competitive with NH₃-SCR, which is the optimal solution to reach the required conversion rate of at least 90–95% with a reductant/NO_x ratio of 1/1 and with a low amount of side products or slip (NH₃, N₂O). Although with limited efficiency, selectivity to N₂ and higher H₂/NO_x requirements (→fuel economy), H₂-SCR on modified Pt and Pd catalysts was proven to create additional NO_x conversion, particularly below 200 °C [33]. Many other metal oxide- or zeolite-based catalysts (Ni, Co, Cu, Rh and W as active metals) also have been investigated [34, 35] but the current study focuses on durable H₂-SCR catalysts operating below 200–250 °C, where NH₃-SCR is not efficient, or ammonia slip is a risk.

Stoichiometric combustion is feasible for hydrogen or hydrogen-containing fuel blends and multi-fuel engines [36]. Three-way catalysts (TWCs) have been used since the 1970s, not only with λ-controlled, stoichiometric gasoline cars, but also with natural gas heavy-duty vehicles [37].

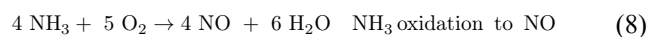
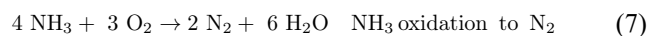
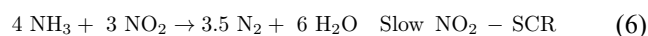
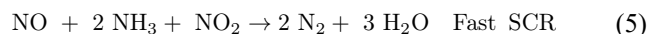
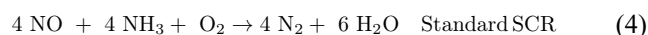
Hydrogen combustion at stoichiometric air/fuel ratios results in very high burnt gas temperatures, which are demanding for TWCs. Therefore, H₂-CH₄ or H₂-gasoline blends have been considered in bi-fuel engines. Due to the small H₂ molecule as the single reductant (no CO or HCs), the reaction mechanism is simpler than on gasoline-TWCs, but it is easier to have strong reducing reactions and form NH₃ [38].

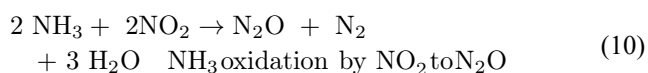


Ammonia engines are challenged by higher NO_x, NH₃ and N₂O emissions (→ fuel-N → fuel-NO_x/–N₂O) and combustion temperatures are usually higher (thermal-NO_x). NO_x can be removed by conventional NH₃-SCR, usually with vanadium-SCR catalysts in marine applications. However, possible higher engine-out NO_x emissions in NH₃ engines are challenging for SCR efficiency targets. Particulate matter emissions are so low that particulate filters are required to comply with PM limits only if diesel is a secondary fuel in combustion.

When the usual SCR catalysts (V, Cu, Fe) are very inert in ammonia oxidation up to high temperatures (>500 °C), a small ammonia slip catalyst (ASC) can be added in the rear part of SCR catalysts to cut remaining NH₃ after SCR, in NH₃ engine applications too [39]. ASC design is focused on the high selectivity of NH₃ to N₂. Conventional oxidation catalysts have a poor selectivity and NO_x and N₂O are also formed, even with a low Pt(Pd) loading. Base metal or Pd-only catalysts usually have insufficient activity and durability [19]. Principal concepts will also differ in on-wheels and marine applications due to fuel variation, emission limits, driving conditions and the criticality of fuel cost.

Important reactions for NH₃ removal in SCR-ASC systems:





Catalytic N₂O decomposition and reduction (deN₂O) is receiving more attention again due to the growing interest in NH₃ engines, even if catalytic N₂O removal, such as by Fe-zeolites, has been already widely investigated during the last decades [40–42].

The current study first reviewed and then investigated aftertreatment systems, methods and challenges for emissions removal with hydrogen, ammonia, methanol and methane engine exhaust gases. The investigations used small-scale laboratory experiments to find durable catalytic methods, mainly for NO_x removal, for future carbon-free applications.

2 Materials and Methods

The small-scale, proprietary catalyst samples were prepared and activity-tested in the Dinex catalyst R&D Centre laboratory. Palladium (Pd) and platinum (Pt) were used as active metals in oxidation catalysts (Pt, Pd, PtPd (4:1) as 10–60 g/cft (grams per cubic foot, 0.35–2.12 g/dm³) on DOC and H₂-SCR catalysts; in MOCs (PtPd (1:4) as 100–200 g/cft (3.5–7.0 g/dm³) and in NO_x storage catalysts (NSCs) as about 30 g/cft (1.06 g/dm³). Three-way catalysts (TWCs) contained Pt, Pd and rhodium (Rh) on aluminium oxide (Al₂O₃)-based supports and were promoted with thermal stabilisers zirconium (Zr) and lanthanum (La) and ceria-based oxygen storage capacity (OSC) materials. The catalysts in the SCR experiments were vanadium (V) on

titanium dioxide-tungsten oxide (TiO₂-WO_x); copper (Cu) on chabazite (CHA) zeolite; and iron (Fe) on beta zeolite.

The catalysts were coated at about 130–160 g/dm³ on cordierite or metallic supports (400/500 cells per in² (cpsi), 1 cpsi~0.155 cells per cm²) and their compositions were selected and developed for studied conditions based on our wide experience in emission catalyst applications. The ageing was conducted in tubular reactors in hydrothermal (HT) (10% water in air for 20 h) or sulphur accumulation (25 ppm SO₂ with water and air for 20 h at 400 °C) conditions ageing [43].

The activity of structured oxidation catalysts was evaluated in a synthetic gas bench (SGB) with metallic tubular reactors (diameter 14 mm) by simulated exhaust gases with relevant feed concentrations and space velocities (SV=flow rate/catalyst volume, mainly 50.000 h⁻¹) (Table 2). The feed of simulated gas compositions was controlled by a mass flowmeter and came from bottle gases (5%NO/N₂, 5%NO₂/N₂, 5%NH₃/N₂, 5%H₂/N₂, 5%C₃H₆/N₂, CH₄, CO₂, CO, air and N₂). Water and diesel HCs, toluene/decane/methanol/acetaldehyde, were injected by evaporators into the feed gases. Acetaldehyde, having the same functional group than formaldehyde, represented aldehydes in feed gases, when its injection control was easier into these SGB reactors [43]. Catalyst design experiments were made as a function of space velocity (SV) to confirm the required volume or active metal loadings for applications. NO_x adsorption capacity was detected at 120 °C by the step exchange method in the presence of 100/250 ppm NO and 6% water and adsorption strength by proceeding desorption (no O₂, 6% water) in a heating ramp [44]. The NSCs were pre-treated before measurements, using oxidising feed gas (13% O₂, 6% H₂O in N₂) at 500 °C/5 min. The activity of SCR

Table 2 Feed gas mixtures in experimental simulations

Compound	MeOH	H ₂ lean	H ₂ stoich	CH ₄ lean	ASC	NH ₃ -SCR	Diesel
NO, ppm	300	150/250	500	500	0/100	600/1000	200
NO ₂ , ppm	–	–	–	–	–	0/400	–
NH ₃ , ppm	–	0/250	0	–	100	1000	–
CH ₄ , ppm	–	–	–	1500	–	–	–
Ethane, ppm	–	–	–	300	–	–	–
Propane, ppm	–	–	–	100	–	–	–
Propene, ppm	–	–	–	–	–	–	80
Toluene, ppm	–	–	–	–	–	–	15
Decane, ppm	–	–	–	–	–	–	15
Acetaldehyde (AA), ppm	300	–	–	150	–	–	–
H ₂ , ppm	–	500/1000/3000	10000	–	–	–	–
CO, ppm	1200	–	–	1200	500	–	1500
Oxygen, %	12	13	0.22–1.02*	10	10	10	14
Water, %	10	10	15	8	10	10	6
CO ₂ , %	10	–	–	7.5	–	–	6
Nitrogen	Bal	Bal	Bal	Bal	Bal	Bal	Bal
SV**, h ⁻¹	50.000	50.000	50.000	50.000	100.000	50.000	30.000

*No oscillation or ±0.22%, 1 Hz, ** Space velocity varying in reaction studies

catalysts and ASC was investigated by steady-state experiments at 150–550 °C in a quartz reactor, heated by an infrared furnace [14, 45]. The inlet concentration in the standard SCR mixtures was stoichiometric by $\text{NH}_3/\text{NO}_x=1:1$ with 1000 ppm NO_x (NO only or $\text{NO}_2:\text{NO}=40:60$) and a space velocity (SV) of $50,000 \text{ h}^{-1}$. The inlet NH_3 concentration in ammonia removal experiments was 100 ppm in the absence or presence of NO . The gas compositions in three separate reactors, applied for different applications, were analysed with Fourier transform infrared spectroscopy (FTIR) using either a Gaset CR 2000 or MKS Multigas 2030, equipped with heated (180 °C) sampling lines, which prevent ammonia adsorption and condensations, for example. The varying combinatory catalyst systems were always tested in the single reactor equipped with a single FTIR analyser to find out their activity and selectivity in investigated reactions.

3 Results and Discussion

3.1 Aftertreatment System for Hydrogen Engine Emissions

3.1.1 Co-operation of NO_x Storage Catalyst and NH_3 -SCR to Promote NO_x Removal at Low Temperatures

Exhaust gas temperatures after lean hydrogen combustion have been reported to be below 200 °C for longer time in transient driving conditions, and NO_x removal is the only

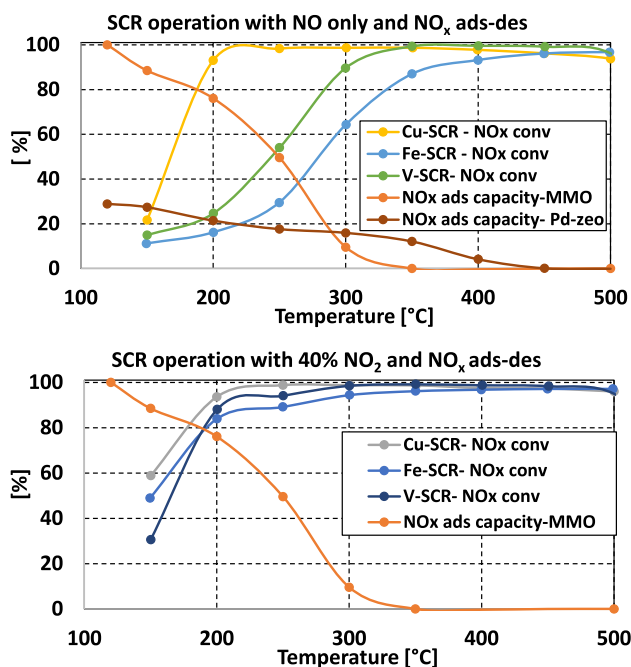


Fig. 3 NO_x conversion of Cu-, Fe- and V-SCR catalysts (140 g/L) as HT-aged and relative NO_x adsorption capacity of fresh NSCs (~30 g/cft Pt). SV over SCR: $50,000 \text{ h}^{-1}$, ceramic catalysts (400 cps)

aftertreatment required since $\text{CO}/\text{HC}/\text{PM}$ removal is not needed [3]. The use of urea-SCR below 180–200 °C is not practically possible, so passive NO_x storage catalysts (NSCs) have been proposed as a solution. Typical passive NSCs have a peak NO_x adsorption capacity at around 100–120 °C and then decreasing capacity and desorption as a function of increasing temperature. The match of NO_x adsorption capacity with different NH_3 -SCR catalysts' operation windows by temperatures was compared to optimise the ATS design (Fig. 3).

The Cu-SCR catalyst (zeolite) shows good low-temperature activity and stability at high temperatures. These properties are not affected by the NO_2 concentration. These characteristics make the Cu-SCR catalyst suitable for applications combining NSC and NH_3 -SCR, a common choice in mobile diesel and NG lean applications. However, long-term hydrothermal stability of zeolite catalysts with high H_2O content (>15%) remains a question for fuels with very high hydrogen content. This requires further studies of materials and conditions.

The Fe-SCR (zeolite) requires high NO_2 concentrations to reach suitable NO_x conversion efficiencies (above 80%) with temperatures below 250 °C (Fig. 3). Although the catalyst has good activity at high temperatures, its hydrothermal stability might be limited in the presence of a high H_2O content. V-SCR (TiO_2 - WO_x -based catalyst) has similar low-temperature characteristics as Fe-SCR. Its catalyst activation below 250 °C requires at least 20% NO_2 of NO_x to be utilised for NSCs or in CC-SCR (close-coupled SCR) applications. However, V-SCR is much more robust in terms of SO_x poisoning and should tolerate substantially higher water concentrations compared to zeolites. On the downsides, the thermal durability of V catalysts is limited to a maximum of 600 °C and low-temperature activity requires improvement for NSC+SCR applications in cold conditions.

The investigated NSCs for low temperatures were based on mixed metal oxides (MMO, Ce-based) and durable zeolites (chabazite) with palladium (Pd). Adsorption capacity was higher with fresh Pt-MMOs, but Pd-zeolites are known to have a higher thermal durability [26]. After HT700/20h and sulphation ageing, the investigated Pd-zeolites had kept the initial fresh NO_x adsorption capacity, whereas Pt-MMO had lost a substantial part of its capacity (no results shown). However, there was a greater focus on MMO adsorbents in this study due to low SO_2 and high water concentrations in H_2 engine exhaust gases. The high water content in hydrogen applications will require further durability research for zeolite-NSCs.

Building on the initial results shown in Fig. 3, an aftertreatment system consisting of Pt-NSC (70 g/cft), Pt-DOC (25 g/cft) and V-SCR catalyst was proposed. Pt-DOC promoted NO_2 formation, resulting in an improved low

temperature SCR performance. The results are based on a single catalyst (V-SCR1) or combinations of catalysts (NSC+DOC, NSC+DOC+V-SCR1) located inside the test reactor and NO_x conversions are based on FTIR analysis in each separate experiment. Ammonia for SCR was injected after DOC to detect the NO_x conversion performance of these combinations (NO_x trapping+ NH_3 -SCR) during a heating ramp (Fig. 4).

The V-SCR1 was developed for low-temperature performance, so had a high NH_3 oxidation property with the feed $\text{NH}_3/\text{NO}_x=1$ above 400 °C. In a real NH_3 -SCR system calibration, that drop can be adjusted near to 100% by increasing NH_3/NO_x ratios, even up to 1.5 above 400 °C. A NSC promotion was detected at 100–200 °C, before the NH_3 -SCR reaction initiated. A larger NSC volume (20 → 40 mm) was required to increase NO_x conversion from 30 to 60% with and without V-SCR1 in that transient condition around 130–150 °C. This concept is efficient during continuous heating and cooling periods (adsorption–desorption) but the total NO_x adsorption capacity limits practical use during long low-temperature periods.

3.1.2 NO_x Reduction with H_2 -SCR in Lean Conditions

We focused our studies on stable, low temperature H_2 -SCR catalysis to find supporting concepts for NH_3 -SCR. Noble metal catalysts have shown higher activities at low temperatures and therefore stable alumina-based Pt and Pd catalysts were selected for these studies.

The normal hydrogen concentrations (1000 ppm) in lean H_2 engine exhaust gas promoted NO_x conversions on a Pt catalyst only up to a maximum of 20% at 100–150 °C (Fig. 5). The H_2 to NO_x ratio in the feed was about 7. In addition, the selectivity to N_2O of converted NO_x was very high (>50%) in that low-temperature range. The additional

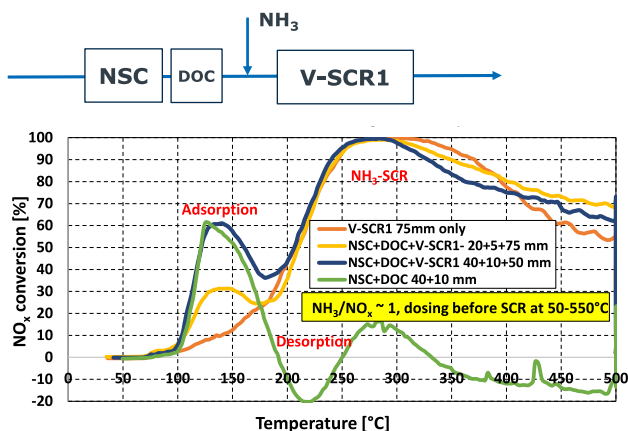


Fig. 4 NO_x conversion during a heating ramp (5 °C/min) with NSC+DOC+V-SCR1, NSC+DOC and V-SCR1 with varying catalyst lengths (ceramic 400 cpsi, SGB feed gas: 250ppm NO, 500ppm H_2 , 13% O_2 , 10% H_2O , bal. N_2 , 50.000 h⁻¹, 250 ppm NH_3 before SCR)

H_2 injection was simulated by increasing the H_2 concentration from 1000 to 3000 ppm ($\text{H}_2/\text{NO}=20$) and the maximum NO_x conversion was then over 65% at 105 °C. This higher H_2 concentration corresponds to an increase in hydrogen fuel consumption of roughly 5–10%. The increasing water content in the feed gas had slight inhibiting effects on reaction initiation (no data shown). A lower O_2 concentration (13 → 5%, lower λ) clearly promoted H_2 -SCR reactions, with the peak NO_x conversion rising from 68 to 91%. The main experiments were done in a very lean feed (13% O_2) but it was seen that H_2 -SCR will be more efficient if using lower λ values in the light-off phases. The studied H_2 -SCR catalyst (HSCR1) was also a good H_2 and NO oxidation catalyst. Therefore, H_2 -SCR and hydrogen/NO oxidation catalyst properties were fully integrated on this catalyst. The formed NO_2 is useful in promoting NH_3 -SCR reactions downstream.

The principal differences between Pt and Pd on the HSCR2 catalyst were seen in the temperature operation window and by N_2O and NO_2 formation (Fig. 6). The Pd catalyst has a higher kinetic barrier to activate H_2 for NO_x reduction, so its NO_x reduction window was shifted up to 220–400 °C. N_2O and NO_2 formation was negligible on the Pd catalyst, but the operation window of NH_3 -SCR catalysts covers the same temperature window with a lower total fuel penalty (fuel, plus urea as fuel equivalent). Therefore, there are no practical utilisation opportunities for Pd/HSCR catalysts, and poison tolerance is known to be significantly poorer with Pd than with Pt. However, oxidation catalysts in many emission applications are often composed of both Pt and Pd in zoned or layered structures, designed to cover required properties and in multi-fuel applications (H_2 , diesel, CH_4 , alcohols). Pd is required in conjunction of Pt for better oxidation of saturated hydrocarbons (CH_4), promote DPF regeneration, improve thermal durability in Pt-rich catalysts or limit $\text{NO}_2/\text{N}_2\text{O}$ formation.

The combined NO_x conversion was simulated by two separate experimental results with 20 g/cft Pt-HSCR1 and V-SCR2 (Fig. 7). H_2 -SCR was active at 100–170 °C and NH_3 -SCR above 170 °C. Both reactions were overlapping at around 150 °C, but useful activity of NH_3 -SCR operation will be limited at over 170–200 °C in practical terms. Due to a high NO_2 formation in this Pt catalyst, NH_3 -SCR performance on V-SCR2 was promoted, already achieving high NO_x conversion at 200 °C. Furthermore, this V-SCR2 did not show excessive ammonia oxidation at high temperatures, maintaining high NO_x efficiency up to 500 °C. Even if H_2 -SCR is aimed to be applied only in a narrow temperature range, the N_2O formation on Pt catalysts and the fuel penalty remain as drawbacks.

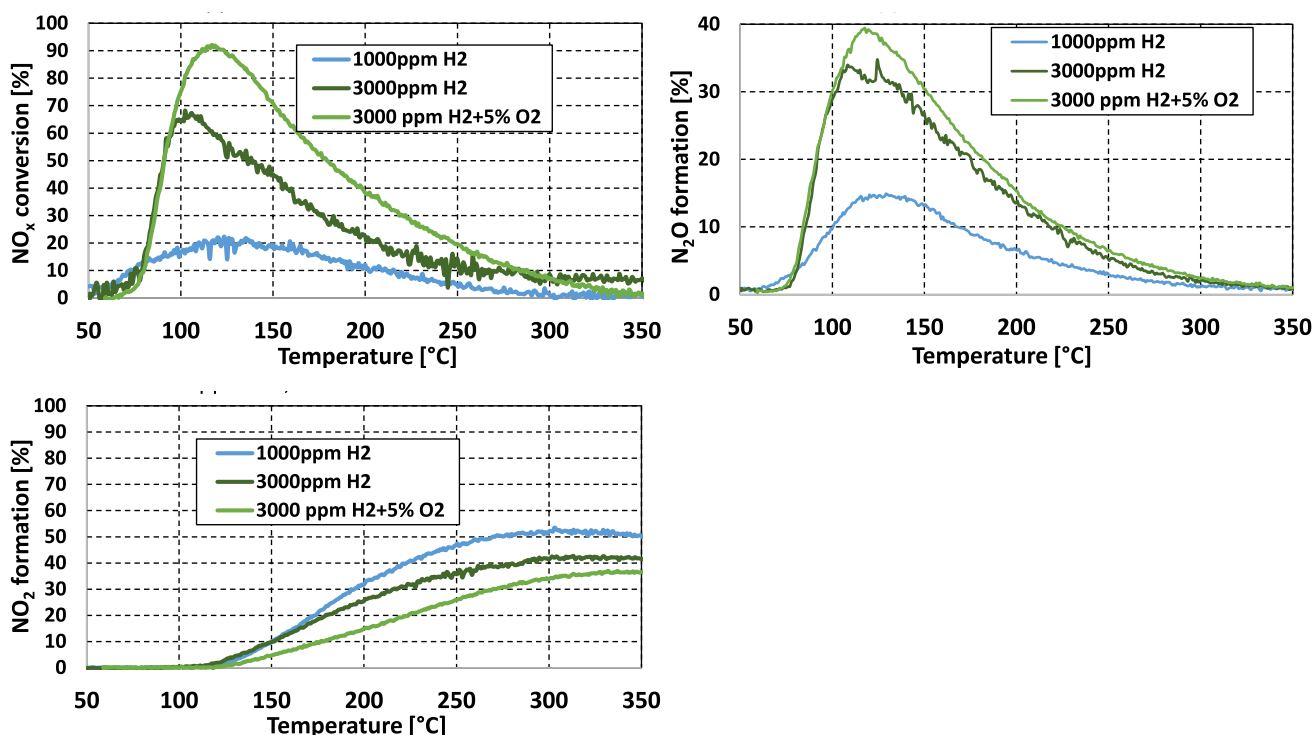


Fig. 5 NO_x conversion and $\text{N}_2\text{O}/\text{NO}_2$ formation in H_2 -SCR in simulated lean hydrogen engine exhaust gas on fresh 20 g/cft Pt/HSCR1 (ceramic 400 cps, feed H_2 lean—13% O_2 , $50,000 \text{ h}^{-1}$)

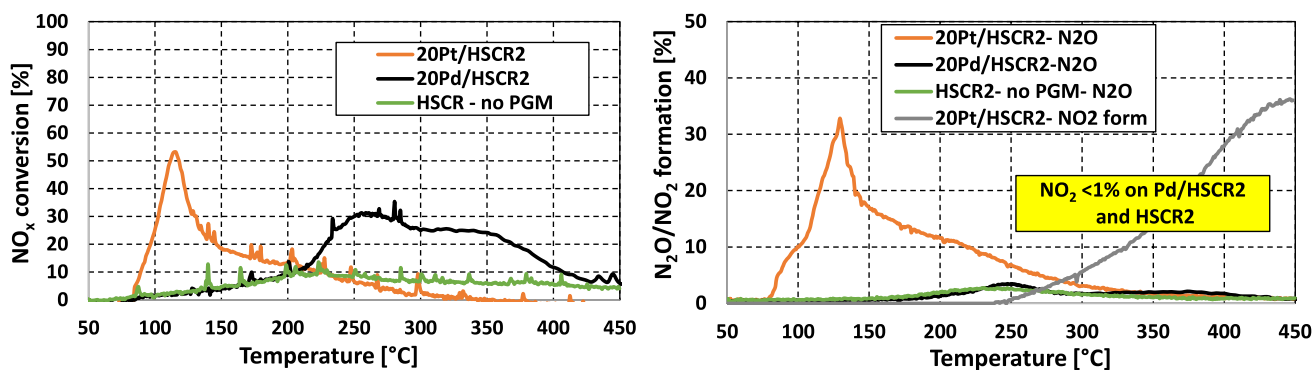


Fig. 6 NO_x conversion and $\text{N}_2\text{O}/\text{NO}_2$ formation in H_2 -SCR in simulated lean hydrogen engine exhaust gas with fresh Pt and Pd (both 20 g/cft) on HSCR2 (ceramic 400 cps, feed H_2 lean—13% O_2 , $50,000 \text{ h}^{-1}$)

3.1.3 Hydrogen Oxidation Activity in Lean Mixtures

Hydrogen is very reactive in the presence of excess of oxygen. The light-off temperature (T_{50}) of hydrogen was about 130 °C with $50,000 \text{ h}^{-1}$ and 160 °C with $100,000 \text{ h}^{-1}$ (Fig. 8). This was measured for both the fresh and mildly-aged HT500/20h oxidation catalyst, with a low-Pt loading (10 g/cft). In the case of H_2 -SCR, NO_x storage or NO oxidation catalysts, the Pt(Pd) loading usually will be higher (20–50 g/cft), giving improved H_2 oxidation activity at low temperatures (~ 100 – 120 °C with $50,000 \text{ h}^{-1}$). This can be indirectly concluded by results seen in earlier sections (Figs. 4 and 5), where NO_x reduction at low temperatures is

related to hydrogen consumption. The usual alumina-based oxidation catalysts are known to be well able to withstand water, but higher water concentrations (15–25%) in the gas stream will add inhibition and slightly increase light-off temperatures (T_{50} , when 50% conversion) in oxidation reactions [46]. Of course, water is also the reaction product in complete hydrogen oxidation. Additionally, the catalyst volume and Pt(Pd) loading should be high enough to reach H_2 conversions of over 90% at 200–300 °C. Possible higher H_2 emissions, and their consequences in engine start-up phases below 200 °C, will require further application-related studies. Additionally, hydrogen often will be a secondary fuel, together with, for example, diesel, CH_4 , NH_3 or alcohols.

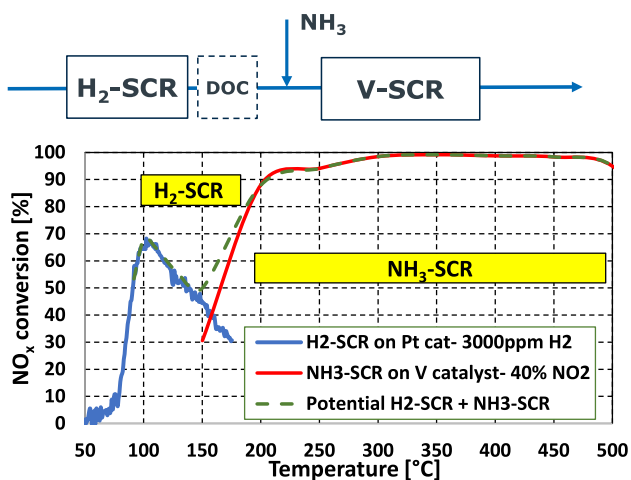


Fig. 7 Combined NO_x conversion with Pt/HSCR1+V-SCR2 (ceramic 400 cpsi, feeds: H₂ lean and SCR 40% NO₂, 50,000 h⁻¹)

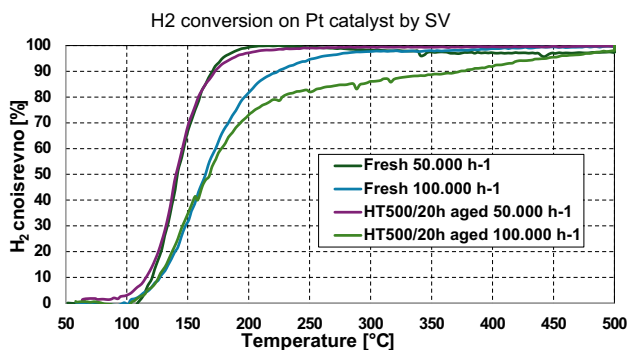


Fig. 8 H₂ conversion on Pt oxidation catalyst in simulated lean hydrogen engine exhaust gas by space velocity (h⁻¹) (ceramic 400 cpsi, 10 g/cft Pt, feed H₂ lean—13% O₂)

Future studies are planned to investigate the consequential co-reactions.

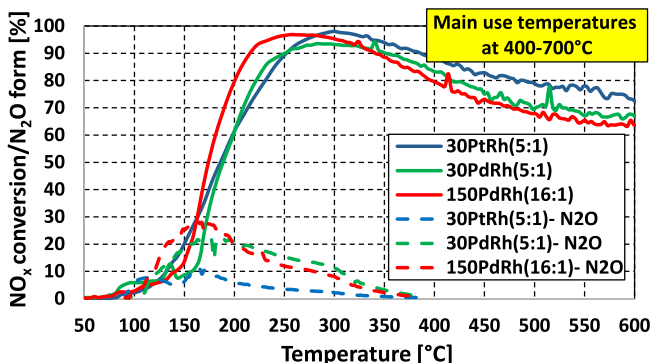
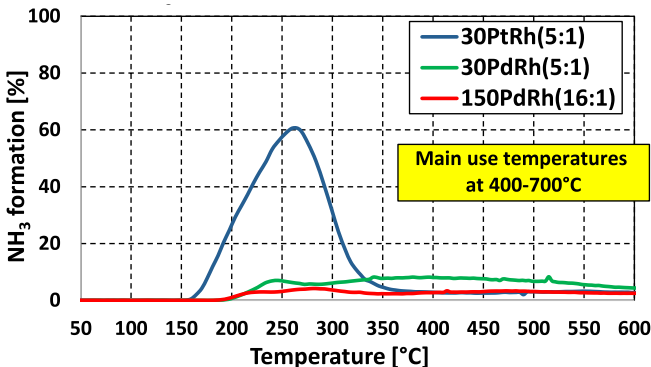


Fig. 9 NO_x conversion and NH₃/N₂O formation in λ oscillating, stoichiometric hydrogen engine exhaust gas conditions by light-off experiments (10 °C/min) with aged (Air 1050 °C/3h) 30 g/cft PtRh(5:1)/

3.1.4 NO_x Reduction by Hydrogen on Three-Way Catalysts in Stoichiometric Conditions

As discussed in the introduction, a three-way catalyst (TWC) requires stoichiometric conditions, which in the context of H₂ combustion, yields excessive exhaust gas temperatures. Thermally durable, alumina-based PtRh and PdRh catalysts were examined for this application, both as fresh and air-aged (1000 °C/5h) (Fig. 9). The investigation focused on NO_x conversion efficiency and side product emissions of NH₃ and N₂O under mixture conditions characteristic of λ-controlled spark-ignited engines (air–fuel ratio oscillating with 1Hz frequency around stoichiometry).

The NO_x light-off temperature (T₅₀) was about 175–180 °C with all three heavily air-aged TWCs. T₅₀ was as low as 100 °C for the fresh catalysts. Noble metal loading (PtRh or PdRh) of 30 g/cft (1.06 g/dm³) was sufficient: a PdRh loading of 150 g/cft (NG-TWC to activate CH₄) did not show much promotion. NO_x conversions were dropping as a function of temperature with this feed composition, due to excessive hydrogen oxidation above 350 °C. It was possible to increase NO_x conversion over 90% at high temperatures, but then NH₃ formation would increase. The same drop also was seen on fresh TWCs (results not shown). However, PtRh and PdRh showed quite different selectivity to NH₃ or N₂O with that mean, oscillating O₂ concentration (0.48±0.22%, 1 Hz) in light-off experiments. NH₃ formation showed a sharp, very high peak of 60% at 250 °C on aged PtRh catalysts (fresh 36%) and clearly λ was rich enough in the feed gas to form ammonia. However, that low temperature range with higher NH₃ relates only to short drive and TWC start-up periods, which will have a negligible cumulative effect on NH₃ emissions in overall driving conditions or test cycles. Conversely, NH₃ was no more than 5–10% on both PdRh catalysts at 150–350 °C. In fact, formation of both NH₃ and N₂O was lower on PtRh than on PdRh catalysts in normal driving conditions on the warm



TWC1, 30 g/cft PdRh(5:1)/TWC2 and 150 g/cft PdRh (16:1)/TWC3 (ceramic 400 cpsi, feed H₂ STOICH, O₂ (0.48±0.22)%, 50,000 h⁻¹)

TWC (>400–500 °C). Mean exhaust gas temperatures will be higher with hydrogen (high heating value) than in usual gasoline and natural gas stoichiometric combustion. Where there is no diluting air to decrease them, the maximum temperatures relate to the heating value of each fuel type and are reached in combustion and exhaust gas lines. In summary, even heavily thermally aged TWCs were working at lower temperatures (>200 °C) than with gasoline engines (>250 °C). High theoretical water content (34%) after stoichiometric combustion in cooling exhaust gases causes a condensation issue. This is difficult to control, and so H₂ often has been used as a secondary fuel with methanol, ammonia, diesel or other fuels [47–50].

The effect of λ oscillation (perturbation) on NO_x performance was evaluated only with PtRh-TWC catalysts (Fig. 10). As is known, the shape of NO_x conversion and reductant oxidations is very sharp without perturbation enabled by feedback λ control [51]. NO_x conversion remained near to 100% up to 0.42% O₂, and then dropped sharply at 400 °C. NH₃ formation was also higher without perturbation on the rich side, and dropped sharply after 0.32% O₂. No H₂ analysis was conducted during these TWC experiments, but it was apparent when the lack of hydrogen started to limit lean operation, and how much hydrogen was consumed to NO_x reduction and NH₃ formation on the rich side. Conversely, λ perturbation was able to maintain a wider operation window by oxygen concentration near stoichiometric conditions, which gives more freedom for control. PtRh-TWC was able to maintain higher NO_x conversion than Pd-TWC, with or without perturbation. High-PdRh (150 g/cft) was slightly better at 400 °C than PdRh with 30 g/cft on the rich side, but no promotion was seen on the lean side. However, the Pd/Rh ratio was also slightly different in these TWCs.

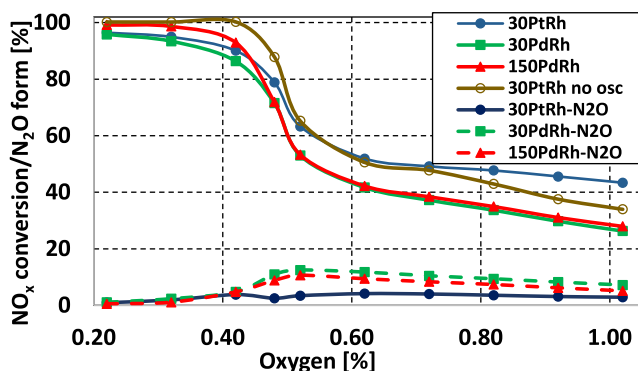
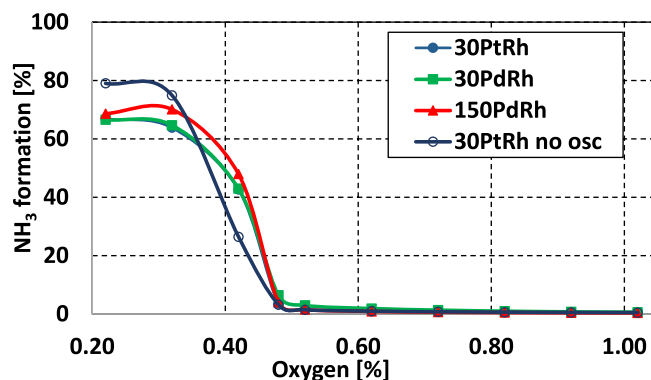


Fig. 10 NO_x conversion and NH₃/N₂O formation with oscillating (osc), stoichiometric hydrogen engine exhaust gas in λ window experiments at 400 °C with aged (air 1050 °C/3h) 30 g/cft PtRh(5:1)/TWC1,

3.2 Oxidation Catalysts for Methanol, Methane and Aldehyde Removal

When considering engines running on methanol and methane, unburned hydrocarbons or alcohols are a particular concern from the perspective of toxicity (MeOH) or GHG effect (CH₄). Additionally, flame quenching can cause partial oxidation, resulting in large quantities of CO and aldehyde emissions. Similar NH₃-SCR catalysts as used for NO_x reduction in diesel applications also will be applied, with tailored SCR system calibrations, for methanol and methane engine applications. CO and MeOH are very reactive and are oxidised at quite low temperatures (Fig. 11). Aldehyde conversions, represented by acetaldehyde in feed, had a similar temperature dependence as MeOH and CO, but higher space velocity (SV) dependency. Hydrothermal ageing (at 700 °C) did not majorly affect the light-off temperatures, implying thermal stability of Pt-rich catalysts, as in DOC applications.

Oxidation of methane is known to be challenging, due to its high molecular stability. It has been oxidised in lean conditions on a dedicated MOC. Even with high PtPd (1:4) loadings of up to 100–300 g/cft, high light-off temperatures like 360–400 °C with SV of 50,000 h⁻¹ are a normal activity level (Fig. 12). Note that the feed gas in these experiments also contains ethane (C₂H₆) and propane (C₃H₈), which are the next inert saturated HCs after methane and are present in natural gas. FTIR analysis showed their T₅₀ was as low as 300–350 °C. In addition, MOCs are very sensitive to even low SO₂ concentrations, originating from lubrication oil [43, 52, 53]. MOCs require periodic regeneration by desulphation, in low-O₂ and high-HC conditions above 550 °C for 10 min, for example. These Pd-rich MOCs are very active for CO and aldehyde oxidation, with light-off temperatures of around 200 °C also as sulphated with 25 ppm SO₂ for 20h. Much lower loadings, like 30–50 g/cft, and Pt-rich, smaller (e.g. 100,000 h⁻¹) oxidation catalysts



30 g/cft PdRh(5:1)/TWC2 and 150 g/cft PdRh (16:1)/TWC3 (ceramic 400 cps, feed H₂ stoich, O₂ 0.48±0.22% by 1 Hz, 50,000 h⁻¹)

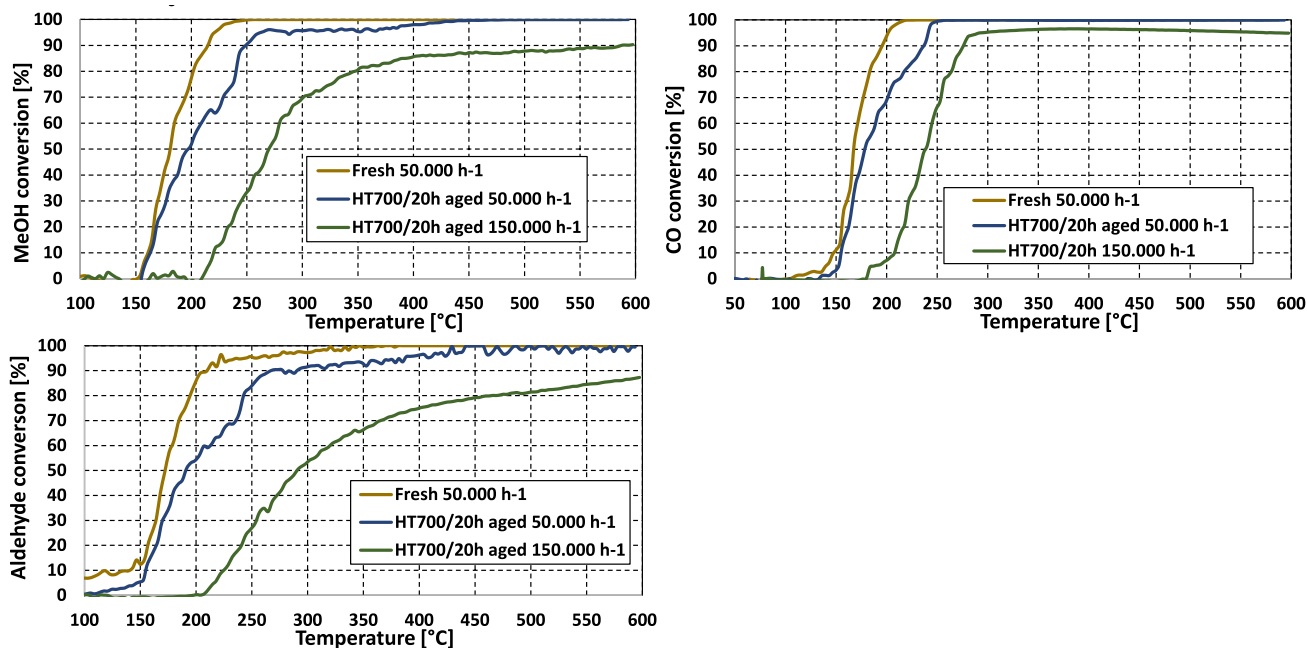


Fig. 11 Methanol, acetaldehyde and CO conversion on PtPd (4:1) oxidation catalyst in simulated lean MeOH engine exhaust gas with SV of 50,000 and 150,000 h^{-1} (ceramic 400 cpsi, feed MeOH– 1200 ppm MeOH, 300 ppm acetaldehyde (AA))

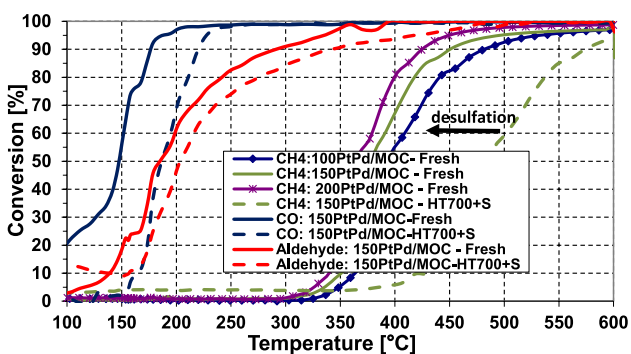


Fig. 12 Methane, CO and aldehyde conversions on PtPd (1:4)-MOC in simulated lean CH_4 exhaust gas (ceramic 400 cpsi, feed: 1500 ppm CH_4 , 300 ppm C_2H_6 , 100 ppm C_3H_8 , 150 ppm acetaldehyde (AA), 500 ppm NO, 50,000 h^{-1})

are sufficiently active if focusing only on CO and aldehyde removal in methane applications.

Stoichiometric combustion of natural gas (\rightarrow e- CH_4 in future) has been very popular in medium- sized on-road engines in trucks, where the ATS consists only of a TWC. Methane light-off temperature was reported to be, depending on ageing temperature, around 300–400 °C (TWC, 200 g/cft ($\sim 7.1 \text{ g/dm}^3$) PdRh, 50,000 h^{-1}) [46]. In addition, there are no or low sulphur deactivation issues in stoichiometric exhaust gas conditions. A heterogenous lean-rich engine calibration has been proposed to solve challenges (Pd state and sulphation) with lean NG engines or catalyst performance [46, 54]. Higher fuel consumption means that

stoichiometric calibration is not an economic solution for larger engines such as marine applications.

3.3 Ammonia and Nitrous Oxide Removal in Ammonia Engine Applications

Ammonia is as reactive on catalysts as, for example, CO or light unsaturated hydrocarbons, but selectivity in ammonia oxidation is challenging, because it must prevent reactions to NO, NO_2 or N_2O (Fig. 13). The ammonia oxidation catalyst (AMOX) is planned to convert selectively NH_3 to N_2 without the assistance of a SCR catalyst. Located after the SCR catalyst, the ASC has the task of oxidising the remaining NH_3 selectively to N_2 .

Layered Pt/metal oxide (bottom) and SCR catalyst (top) structures have given the best selectivity as ASCs [39] (Fig. 14). A low Pt loading, like 1–3 g/cft ($\sim 0.03\text{--}0.11 \text{ g/dm}^3$) in a thin bottom layer, together with a thick SCR coating layer, was applied to reach target selectivity. Pore diffusion through the top SCR layer was purposely designed to limit the access of NH_3 to Pt sites. A small catalyst volume, with high SV, was also used to limit excessive oxidation activity. A high ammonia adsorption (NH_3^*) capacity and strength in the top layer promote the SCR reaction paths. Part of the NH_3 remains adsorbed on the SCR catalyst surface and reacts with NO molecules formed in the bottom layer. This, of course, is challenging at high temperatures, where the NH_3 adsorption capacity on SCR catalysts is physically low. In addition, NH_3 adsorption on a large SCR

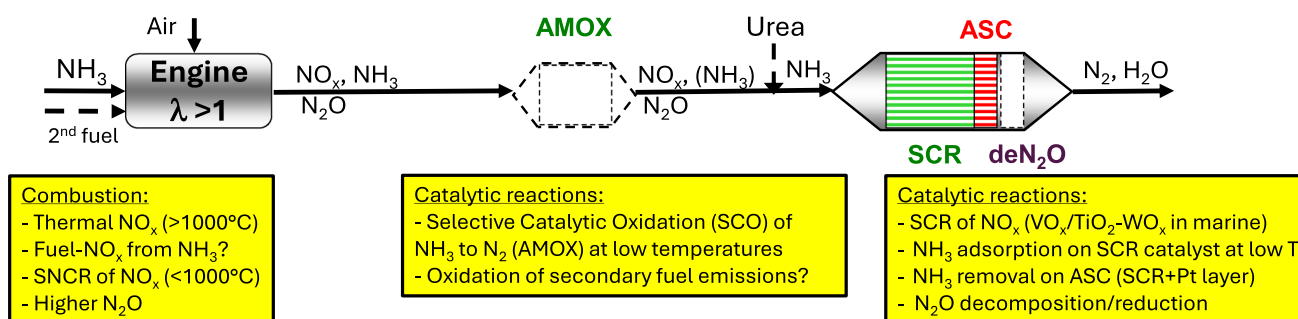


Fig. 13 Critical conditions, reactions, ATS and AMOX in ammonia engine applications

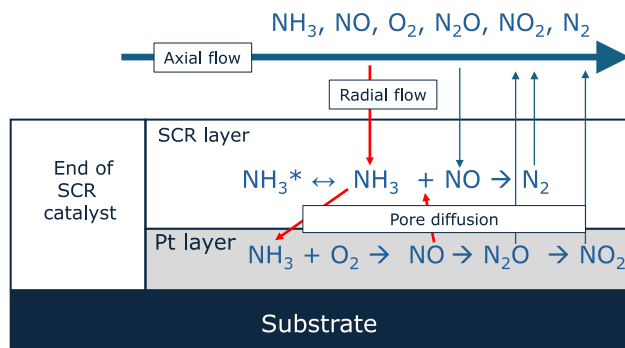


Fig. 14 NH_3 removal and reactions of nitrogen species in the two-layer ASC structure

catalyst (volume ratio: SCR/ASC $\sim 5\text{--}10$) upstream also has a buffering effect during NH_3 engine cold-start periods, before the NH_3 slip from engine starts to pass through the complete SCR+ASC system.

In real exhaust gas, as seen by the Cu-SCR catalyst results (Fig. 3), NO_x started to react more with NH_3 on the surface or in the gas phase above 150°C . Remaining NH_3 after the SCR unit is oxidised efficiently by the ASC. Related results were presented in our earlier studies for SCR+ASC concepts [39]. However, when the Pt loading and the ASC volume are both low, to keep a high selectivity to N_2 , the NH_3 light-off temperature (T_{50}) on a fresh ASC varied in the range of $150\text{--}300^\circ\text{C}$, depending on SV (Fig. 15). A two-layer CuSCR+Pt was even more efficient in NH_3 oxidation (steady state) than the pure oxidation catalyst with the same low loading of 2 g/cft . In addition, the use of that Pt oxidation catalyst alone results in harmful high selectivity to NO_x and N_2O formation (maxima of 34% and 64% respectively). Pt is known to be a strong dissociation catalyst for NO and NH_3 compounds, which is the preceding reaction in N_2O formation mechanism ($\text{N} + \text{NO} \rightarrow \text{N}_2\text{O}$) [38].

Cu-CHA zeolite catalysts have a higher ammonia adsorption capacity and stability than Fe-Beta zeolite or particularly TiO_2 -based V-SCR catalysts [23]. The buffering effect of ammonia adsorption was approximately evaluated by the adsorption capacity at 200°C , which is near to SCR reaction initiation, and the ammonia concentration (500

ppm in Table 3) in exhaust gas. SV can be assumed to be low ($\sim 10,000\text{ h}^{-1}$) in low-speed, cold drive conditions. The buffering time will be shorter if the NH_3 concentration or SV is higher. The buffering time was about 4.5 times longer on Cu-zeolite in comparison to a V-titanium SCR catalyst with 150 g/L coating. However, V-SCR catalysts are mainly extruded, particularly in marine applications, the first examples of ammonia engines. The total catalyst amount is about three times higher ($\sim 450\text{ g/L}$) in an extruded V-SCR than in the usual coated catalysts. In that case, the volumetric buffering reserve of extruded V-SCR catalysts will be near to that of coated zeolite SCR catalysts.

There is a catalytic method of handling ammonia emissions if they are continuously too high to manage only with SCR+ASC. From NH_3 -only or NH_3 -rich exhaust gas, it creates an appropriate feed with a $\text{NH}_3/\text{NO}_x \sim 1$ for the NH_3 -SCR catalyst [55]. NH_3 is partly oxidised on an AMOX (e.g., a PtPd oxidation catalyst) to NO_x , which reacts with by-passed gaseous or adsorbed NH_3 in the SCR catalyst unit (Fig. 16). After AMOX it was installed three-zone SCR catalysts (Fe-zeolite + V/ $\text{TiO}_2\text{-WO}_3$ + Fe-zeolite), where the larger V-SCR unit acts as a good base SCR catalyst and the Fe-SCR units are good in high-temperature ($>400^\circ\text{C}$) SCR, NO_2 -promoted SCR and N_2O decomposition. NO, NO_2 , N_2 and N_2O are formed on the AMOX. The by-pass of the oxidation catalyst had to be high ($>90\%$ of its frontal face area) to avoid excessive NO_x and N_2O formation. The by-pass in these experiments was passive, controlled by fluid dynamics in honeycomb structures (coated and uncoated parts), but valves are an alternative means of by-pass control.

Many different types of AMOX and SCR catalysts were investigated, either alone or in combinations, in these experiments [55]. However, the AMOX by-pass concept described above was the only one to achieve a wide operating window for N_2 formation and minimal unreacted NH_3 , formed NO_x and N_2O (Fig. 17). Its NH_3 light-off temperature (T_{50}) was below 200°C ; N_2 formation 63–88%; maximum N_2O formation 5%; maximum NO formation 8%; and NO_2 formation was 4% at $200\text{--}500^\circ\text{C}$. However, NO_x formation was negligible ($<2\%$) below 400°C . The best operating

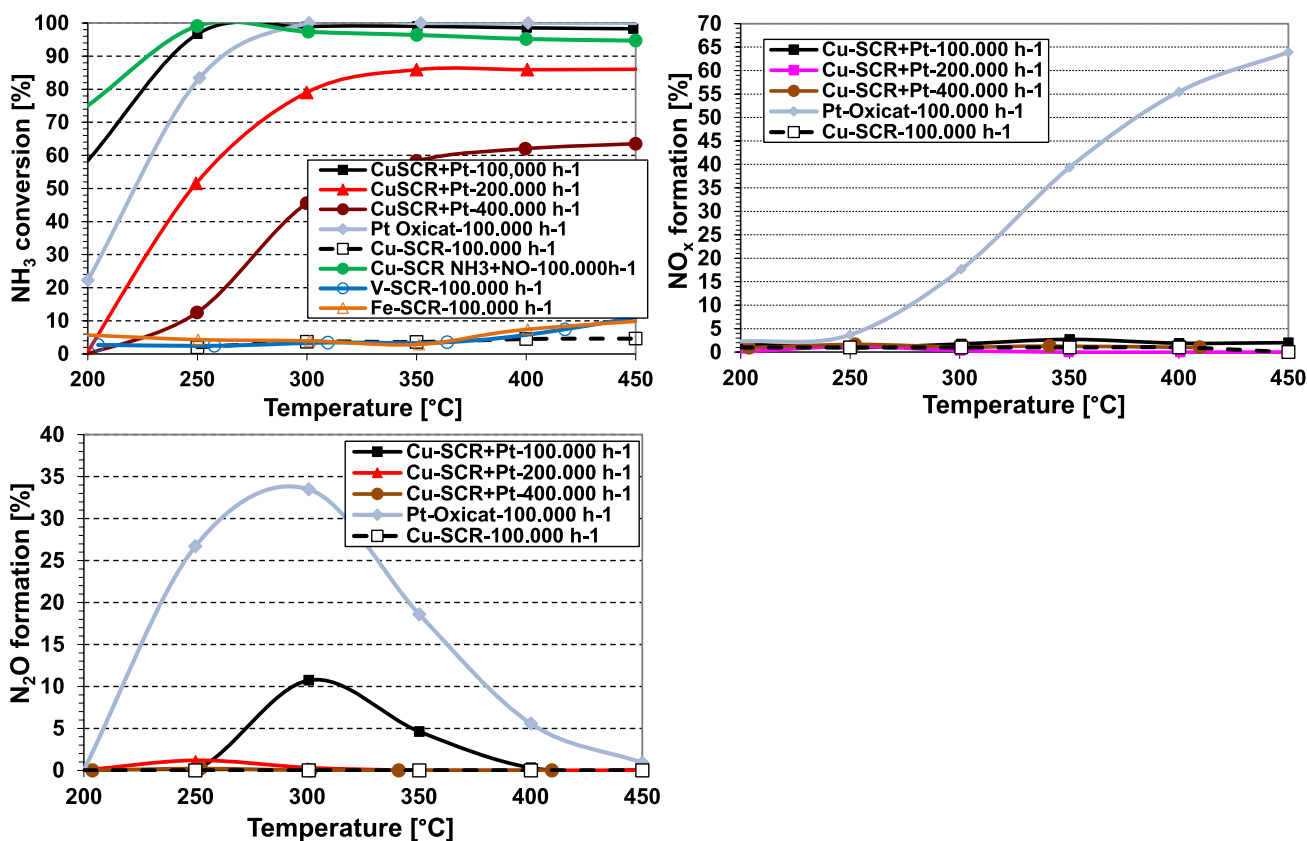


Fig. 15 NH₃ conversion and N₂O/NO_x formation by space velocity (h⁻¹) on fresh ASC (two-layer CuPt-ASC with Pt bottom layer), Pt oxidation catalyst (Oxicat) and SCR catalysts (Cu, V, Fe- no Pt) in

ASC feed with 100 ppm NH₃ only (all) and NH₃+NO (only for Cu-SCR) (2 g/cft (0.07 g/dm³) Pt when present)

Table 3 Ammonia adsorption capacity [23, 45] at 200 °C and resulting maximum buffering time with fresh, stabilised Cu-CHA, Fe-Beta and V-TiO₂-WO₃ catalysts (SV 10,000 h⁻¹, NH₃ adsorbed on SCR catalyst with a coating amount of 150 g/L)

SCR catalyst	NH ₃ ads capacity mg/g coating	Buffering time (s) if 500 ppm NH ₃
Cu-CHA	12.1	114
Fe-Beta	5.5	52
V-TiO ₂ -WO ₃	2.6	25/75*

*extruded V-SCR with 450 g/L catalyst material

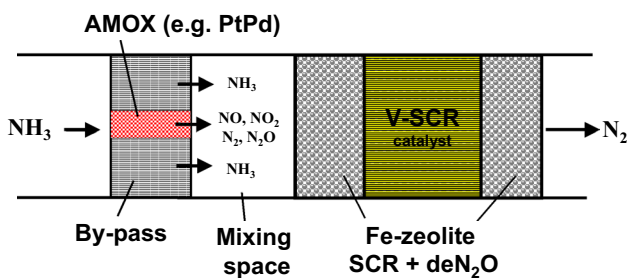


Fig. 16 Purification of ammonia-rich exhaust gases by forming an SCR feed gas composition

window, with 94–97% N₂ formation, was detected at around 370–450 °C. At 350 °C, the NH₃ light-off temperature of the reference catalyst (Fe+V+Fe SCR) with a good selectivity was too high for practical applications.

4 Conclusions

There are various challenges for engine emission removal in the future. In parallel to the move from fossil fuels (GHG) to green fuels and energy, future emission standards for conventional harmful pollutants will increase the pressure to further develop catalytic aftertreatment systems (ATS). Furthermore, specific emission limits will be set also for N₂O, NH₃, CH₄, aldehydes and smaller particles (PN₁₀). All light-duty applications like cars soon will be electric, but full electric solutions are not universally possible in heavy-duty applications. Therefore, green electricity-based fuels like e-H₂, e-NH₃, e-methanol, e-CH₄ or heavier e-hydrocarbons (C_i, i ≥ 2) are under wide international development and evaluation. This paper has evaluated potential catalytic aftertreatment systems for these new fuel candidates,

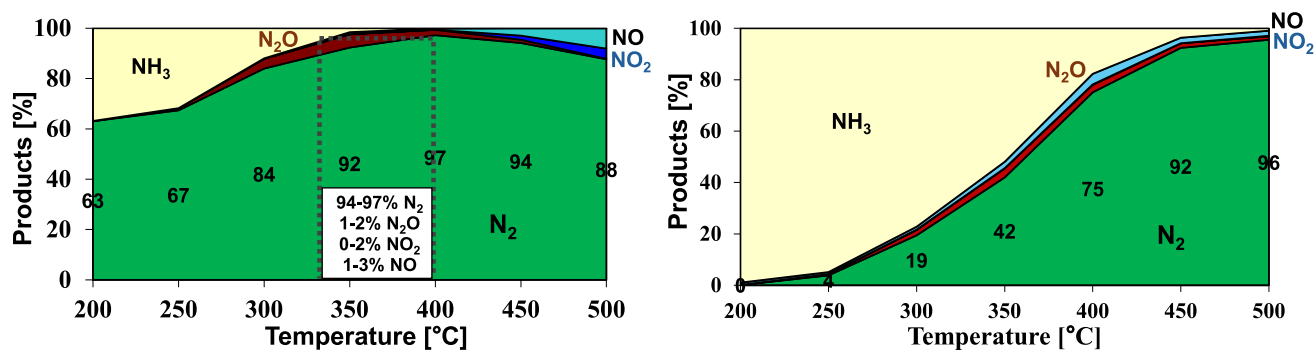


Fig. 17 NH₃ removal by reaction product fractions with Fe-Beta + VW/Ti + Fe/Beta (600 cpsi, 50,000 + 25,000 + 50,000 h⁻¹ → total 12,500 h⁻¹) together with (LEFT) and without (RIGHT = reference, SCR cata-

lysts only) the by-passed (98%) PtPd (1:1) AMOX (metallic 500 cpsi, 50 g/cft, 67,000 h⁻¹)—feed 1000 ppm NH₃ in lean by [55]

based on a review of literature and small-scale experimental results.

The oxidation reactivity of fuel compounds on optimised catalyst compositions in lean conditions without harmful side reactions (e.g. N₂O) was as follows, in order of their light-off temperature (T₅₀, °C): H₂ (140) < methanol (170) ~ CO < diesel-hydrocarbons (180) < NH₃ (250) < CH₄ (380). NO_x removal in lean mobile applications will be still most challenging for ATSs in future (Euro VII/Stage 6 and beyond), due to very strict emission limits, cold exhaust gases and varying fuel types/mixtures. Urea/NH₃-SCR will remain as the main NO_x removal method, and the double SCR is a solution to cover a wide temperature window. Passive NO_x adsorbents, H₂-SCR, ASC, NH₃ adsorption and oxidation catalysts, as well as thermal management, are methods to assist NH₃-SCR. Integration and intensification of different catalytic properties in the same units is necessary to save ATS volume and cost. A lower sulphur content in new fuels will help maintain high catalyst durability, but the high water content (15–25% with H₂, NH₃, and CH₄) will require additional deactivation/inhibition studies and catalyst development in future.

Stoichiometric combustion is also applied for hydrogen blends and three-way catalysts (TWC) with low PGM loadings (≤30 g/cft) are efficient, even as heavily thermally aged (1000°C), and at lower temperatures than with gasoline engines. The design objective is a catalytic ATS with sufficient flexibility to manage single and multi-fuel mixtures, together with varying exhaust gas compositions. Key targets for ATS development are minimisation of both total GHG emissions (CO₂, CH₄, N₂O) and fuel consumption too.

A demand for flexible green fuel use in the same engines will also require flexible and versatile ATS designs, able to handle short- and long-term variation in fuel grades and mixtures. Although already widely studied, improved methods for the removal of methane and N₂O are needed to enable more efficient use of emerging fuels and minimise total greenhouse gas emissions.

lysts only) the by-passed (98%) PtPd (1:1) AMOX (metallic 500 cpsi, 50 g/cft, 67,000 h⁻¹)—feed 1000 ppm NH₃ in lean by [55]

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Declarations

Conflict of interest The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

1. Di Nardo A, Calabrese M, Venezia V, Portarapillo M, Turco M, Di Nenetto A, Luciani G (2023) Addressing environmental challenges: the role of hydrogen technologies in a sustainable future. *Energies* 16:7908
2. Jablonska M, Palkovits R (2016) It is no laughing matter: nitrous oxide formation in diesel engines and advances in its abatement over rhodium-based catalysts. *Catal Sci Technol* 6:7671
3. Huth V, Virnich L, Pfortje A, Pischinger S, Sterlepper S, Wolff T, Moreno A, Georgiadis E, Geist M, Kallinen K, Maunula T, Chernyshev AN, The hydrogen combustion engine as zero impact emission powertrain concept, 30th Aachen Colloquium Sustainable Mobility 2021.
4. Dimitriou P, Javard R (2020) A review of ammonia as a compression ignition engine fuel. *Int J Hydrogen Energy* 45:7098

5. Hasan MH, Mahlia TMI, Mofijur M, Fattah IMR, Handayani F, Ong HC, Silitonga AS (2021) A comprehensive review on the recent development of ammonia as a renewable energy carrier. *Energies* 14:3732
6. Chehade G, Dincer I (2021) Review article: progress in green ammonia production as potential carbon-free fuel. *Fuel* 299:120845
7. Rizi HAY, Sin D (2022) Green hydrogen production technologies from ammonia cracking. *Energies* 15:8246
8. Ram M, Galimova T, Bogdanov D, Fasihi M, Gulagi A, Breyer C, Micheli M, Crone K (2020) Powerfuels in a renewable energy world - global volumes, costs, and trading 2030 to 2050. LUT University and Deutsche Energie-Agentur GmbH (dena), Lappeenranta
9. Parris D, Spinthiropoulos K, Ragazou K, Giovou A, Tsanaktsidis C (2024) Methanol, a plugin marine fuel for green house gas reduction - a review. *Energies* 17:605
10. Sollai S, Porcu A, Tola V, Ferrara F, Pettinau A (2023) Renewable methanol production from green hydrogen and captured CO₂: a techno-economic assessment. *J CO₂ Utiliz* 68:102345
11. Maunula T, Kinnunen T, Effect of oxygen containing biofuels on the emissions with exhaust gas catalysts, SAE Paper 2009-01-2737.
12. Murena F, Prati MV (2017) Catalytic Conversion of CO₂ to CH₄ with a Ru Catalyst: Application at Vehicle Exhaust. *Emiss Control Sci Tech* 3:220
13. Wang W, Gong J (2011) Methanation of CO₂: a review. *Front Chem Sci Eng* 5:nr1
14. Maunula T, Kallinen K, Kinnunen N, Keenan M, Wolff T (2019) Methane abatement and catalyst durability in heterogeneous lean-rich and dual-fuel conditions. *Topics Catal* 62:315
15. Zhao H, Direct injection NG engines in “advanced direct injection combustion engine technologies and development” book, Woodhead Publishing, 2009.
16. Ma F, Guo L, Li Z, Zeng X, Zheng Z, Li W, Zhao F, Yu W (2023) A review of current advances in ammonia combustion from the fundamentals to applications in internal combustion engines. *Energies* 16:6304
17. Martins J, Brito FP (2020) Alternative fuels for internal combustion engines. *Energies* 13:4086
18. Glaude P-A, Fornet R, Bounaceur R, Moliere M (2010) Adiabatic flame temperature from biofuels and derived effect on NO_x emissions. *Fuel Process Tech* 91:229
19. Maunula T, Lylykangas R, Lievonen A, Härkönen M, NO_x reduction by urea in the presence of NO₂ on metal substrated SCR catalysts for heavy-duty vehicles, SAE Technical Paper Series, SAE Paper 2003-01-1863.
20. Ryou Y, Lee J, Lee H, Kim CH, Kim DH (2018) Low temperature NO adsorption over hydrothermally aged Pd/CeO₂ for cold start application. *Catal Today* 307:93
21. Li J, Fan K, Shan Y, Wang S, Zhang J, Fan W, He H, Zhao X, Meng X, Xiao F-S (2023) Superior performance in passive NO_x adsorption over an Al-rich Beta zeolite supported palladium. *Appl Catal B* 339:123127
22. Chen H-Y, Mulla S, Weigert E, Camm K, Ballinger T, Cox J, Balkeman P, Cold start concept (CSCTM): a novel catalyst for cold start emission control, SAE Paper 2013-01-0535.
23. Maunula T, NO_x reduction with the combinations on LNT and SCR in diesel applications, SAE Paper 2013-24-0161.
24. Johnson T, Review of vehicle engine efficiency and emissions, SAE paper 2017-01-0907.
25. Theis JR, Lambert CK (2019) Effect of reductant on the NO_x storage performance of a Pd/CZO low temperature NO_x adsorber. *Emiss Control Sci Technol* 5:215
26. Wang Y, Yong X, Rong M, Zheng J, Zhao H (2020) Recent advances in catalytic automotive emission control: Passive NO storage at low temperatures. *J Chi Chem Soc* 67:1530
27. Kovacs D, Rezaei R, Menning M, Hayduk C, Delebinski T, Future HD diesel and hydrogen-fueled concepts: emissions challenges and system solutions, SAE Paper 2022-01-1011.
28. Seykens X, Kupper F, Mentink P, Ramesh S, Towards ultra-low NO_x emissions within GHG phase 2 constraints: main challenges and technology directions, SAE Paper 2018-01-0331.
29. Boerensen C, Roemer D, Nederlof C, Smirnov E, Linzen F, Goebel F, Carberry B, Twin-LNT system for advanced diesel exhaust gas aftertreatment, SAE Paper 2017-01-0935.
30. Joshi A, Review of vehicle engine efficiency and emissions, SAE Paper 2022-01-0540.
31. Wolff T, Geist M, Pfeifer M, Moreno A, Kallinen K, Huth V, Brucker E, Durand T, A path towards ultra-low NO_x emissions on hydrogen internal combustion engines, 19th FAD-Conference, Challenge – Exhaust Aftertreatment, 3–4 Nov 2022, Dresden.
32. Maunula T, Intensification of catalytic aftertreatment systems for mobile applications, SAE Technical Paper 2013-01-0530, 2013.
33. Esser E, Kureti S, Heckemuller L, Todt A, Eilts P, Marawietz T, Friedrich A, Waiblinger W, Hosseiny S, Bunar F, Low-temperature NO_x reduction by H₂ in diesel engine exhaust, SAE Paper 2022-01-0538.
34. Väliheikki A, Petallidou KC, Kalamaras CM, Kolli T, Huuhtanen M, Maunula T, Keiski RL, Efstathiou AM (2014) Selective catalytic reduction of NO_x by hydrogen (H₂-SCR) on WO_x-promoted Ce₂Zr_{1-z}O₂. *Appl Catal B: Env* 156–157(2014):72–83
35. Resitoglu IA, Keskin A (2017) Hydrogen applications in selective catalytic reduction of NO_x emissions from diesel engines. *Int J Hydrogen Energy* 42:23389
36. Yavuz M, Brinklow G, Cova B, Herreros JM, Wu D, Doustdar O, Zeraati-Rezaei S, Tsolakis A (2024) The suitability of the three-way catalyst for hydrogen fueled engines. *Johnson Matthey Technol Rev* 68:412
37. Nevalainen P, Kinnunen NM, Kirveslahti A, Kallinen K, Maunula T, Keenan M, Suvanto M (2018) Formation of NH₃ and N₂O in a modern natural gas three-way catalyst designed for heavy-duty vehicles: the effects of simulated exhaust gas composition and ageing. *Appl Catal A: General* 552:30
38. Maunula T, Ahola J, Salmi T, Haario H, Härkönen M, Luoma M, Pohjola V (1997) Investigation of CO oxidation and NO reduction on three-way catalysts with transient response techniques. *Appl Catal B* 12:287–308
39. Maunula T, Tuikka M, Wolff T (2020) The reactions and role of ammonia slip catalysts in modern urea-SCR systems. *Emission Control Sci Tech* 6:390
40. Kapteijn F, Rodrigues-Mirasol J, Mouljin JA (1996) Heterogeneous decomposition of nitrous oxide. *Appl Catal B* 9:25
41. Delahay G, Mauvezin M, Guzman-Vargas A, Coq B (2002) Effect of the reductant nature on the catalytic removal of N₂O on Fe-zeolite-beta catalysts. *Catal Comm* 3:385
42. Perez-Ramirez J, Kapteijn F, Mui G, Mouljin JA (2002) NO-assisted N₂O decomposition over Fe-based catalysts: effects of gas-phase composition and catalyst constitution. *J Catal* 208:211
43. Maunula T, Kallinen K, Savimäki A, Wolff T (2016) Durability evaluations and rapid ageing methods in commercial emission catalyst development for diesel, natural gas and gasoline applications. *Topics Catal* 59:1049–1053
44. Maunula T, Väliheikki A, Pfeifer M, Wolff T, Promotion of low temperature NO_x removal with NO_x storage and SCR catalysts in mobile diesel applications, MODEGAT VII Conference, Bad Herrenalb, Germany, 11–13 Sept 2022.
45. Maunula T, Wolff T, Durable copper and iron SCR catalysts for mobile diesel applications, SAE Paper 2016-01-2214.

46. Gholami R, Alyani M, Smith K (2015) Deactivation of Pd catalysts by water during low temperature methane oxidation relevant to natural gas vehicle converters. *Catalysis* 5:561
47. Klell M, Eishlseder H, Sartory M (2012) Mixtures of hydrogen and methane in the internal combustion engine - synergies, potential and regulations. *Int J Hydrogen Energy* 37:11531
48. Qi Y, Liu W, Wang W, Peng Y, Wang Z (2023) review on ammonia-hydrogen fueled internal combustion engines. *eTransportation* 18:100288
49. Alrazen HA, Abu Talib AR, Adnan R, Ahmad KA (2016) A review of the effect of hydrogen addition on the performance and emissions of the compression – ignition engine. *Renew Sust Ene Rev* 54:785
50. Purayil STP, Hamdan MO, Al-Omari SAB, Selim MYE, Elnajjar E (2023) Review of hydrogen–gasoline SI dual fuel engines: engine performance and emission. *Ene Rep* 9:4547
51. Muraki H, Shinjoh H, Sobukawa H, Yokota K, Fujitani Y (1985) Behavior of automotive noble metal catalysts in cycled feed streams. *Ind Eng Chem Prod Res Dev* 24:43
52. Kinnunen NM, Kallinen K, Maunula T, Keenan M, Suvanto M (2019) Fundamentals of sulfate species in methane combustion catalyst operation and regeneration—a simulated exhaust gas study. *Catalysts* 9:417
53. Kinnunen N, Kallinen K, Kinnunen T, Improved sulfur resistance of noble metal catalyst for lean-burn natural gas applications, SAE Paper 2013-24-0155.
54. Bounchada D, Groppi G, Forzatti P, Kallinen K, Kinnunen T (2012) Effect of periodic lean/rich switch on methane conversion over a Ce–Zr promoted Pd-Rh/Al₂O₃ catalyst in the exhausts of natural gas vehicles. *Appl Catal B* 119–120:91
55. Maunula T, Härkönen M, Novel catalytic method for ammonia removal from waste gases, 5th International Conference on Environmental Catalysis, 31Aug–3Sept 2008, Belfast, Ireland.

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