What about the development of catalytic after-treatment processes as part of the transition from vehicles powered by liquid fuels to gaseous fuels

Yuanshuang Zheng, Amaury Decoster, Vasile Parvulescu and Pascal Granger

More stringent regulations on air pollutant emissions from engines fuelled by diesel and gasoline inevitably raise the question of the future of this type of motorization. Indeed, significant additional economic efforts by car manufacturers would be needed for compliant, that could be detrimental for their competitiveness. The promising alternatives are associated to the generalization of electric motorization. However, it will not be effective in the short and medium term. An intermediate scenario lies in the development of internal combustion engines powered by less harmful gaseous fuels towards environment. This review examines the different schemes and scenarios associated to this transition regarding the necessary adaptations on the existing catalytic after-treatment technologies.

1. Normative, economic context and alternatives to reduce air pollution from the automotive sector

Air quality is altered by the emissions of atmospheric pollutants from the global transportation sector. Up to now, the compliance with successive worldwide regulations led globally to successful achievements to improve air quality. The continuous implementation of more and more stringent atmospheric pollutant emission regulations by the European Community led to significant practical developments (see Table 1). Both, the improved engine efficiency and the implementation of sophisticated catalytic after-treatment systems have largely contributed to lower emission limits from Euro 0 to Euro 6 with NOx emissions divided by 36, unburnt hydrocarbons (HC) by 18 and particles by 35. The strategies implemented to comply with these regulations have also combined the use of less harmful liquid fuels to the environment, reducing the emissions of NOx, CO, unburnt hydrocarbons, particulate matter (PM) as well as CO2. All these technical advances needed important investments by car manufacturers as illustrated in Table 2.

Despite these strong technological advances, abnormally high levels of NOx emissions still persist in urban areas which suggest new costly technical adaptations for liquid fuelled vehicles. The implementation of more restrictive standard regulations in the frame of the Euro 7 regulations has been already envisioned by the European Commission stipulating a reduction of NOx emissions from light vehicles by 35% for 2035. For heavy goods vehicles, NOx emissions should be reduced by 56% compared to the Euro 6 standard. PM emissions should be reduced by 13% for light vehicles and 39% for heavy vehicles. Alongside, a more accurate detection of air pollution levels for light-duty vehicles from on-board analysis systems through the procedure of worldwide harmonized light vehicle testing in the world (WLTP) will induce extra efforts from car manufacturers. More realistic certifications could lead to extra costs that potentially may alter their competitiveness. This could encourage them to develop alternatives motorizations. According to this hypothesis, a loss of market share for vehicles powered by liquid fuels could emerge.

1.1. Methane: a promising fossil fuel for the future?

The transition toward zero emission limit jointly to the decline in the use of liquid fuels will probably take more longer time in accordance with scenarios predicted for 2050. Indeed, the number of global vehicles should be multiplied by a factor of 2–2.5 whereas alternative fuels will only count as half of the overall quantity. This could mean that oil could be still the major source of energy in 2050. Among fossil resource’s, the market share of natural gas should rise according to future projections with a double consumption from 2020 to 2030 and price maintained to the level observed during the period 2005–2008 thanks to abundant shell gas reserves. Other arguments seem in favour of the development of natural gas fuelled engines. Indeed, despite extra cost due
to compression and a lower thermal efficiency compared to gasoline and diesel, the chain production of natural gas is much cheaper compared to liquid fuels which need complex refining processes. As a consequence, significant cost advantages characterize the development of compressed natural gas (CNG) engines (see Fig. 1).

Sustained efforts towards the development of renewable fuels, i.e. bioethanol and biodiesel, have been beneficial in terms of reducing greenhouse gas emissions and reducing the carbon footprint for the transportation sector. In contrast, their benefits in terms of air quality are more questionable. Indeed, a deterioration of air quality can be envisioned as bioethanol blended with liquid fuels promotes the deleterious formation of formaldehyde and acetaldehyde. Besides, NO\textsubscript{x} and unburnt hydrocarbons are still released significantly.

Based on various scenarios, previous overviews pointed out the relevance in the use of natural gas especially for the transportation sector. Indeed, a more homogeneous combustion leads to lower atmospheric pollutant emissions that is particularly true for particulates emitted by buses (see Table 3). The lower adiabatic temperature from combustion using natural gas compared to liquid fuelled engines should in principle lead to lower NO\textsubscript{x} emissions. In practice, the evolutions are more contrasted than expected and can be questioned in some extent. By way of illustration, a reduction of CO\textsubscript{2} emissions clearly appears as exemplified in Table 3. Moreover, the octane number of natural gas is higher than that of gasoline (95–98) improving the compression ratio and the thermal efficiency. CNG engines would reduce CO\textsubscript{2} emissions by 20% compared to gasoline engines thanks to a higher H-to-C ratio. In the opposite, CO emission levels increase especially under stoichiometric conditions. Particular attention must be also paid on methane emissions recognized as potent greenhouse gas with a global warming potential around 25 times higher than that of CO\textsubscript{2} over a 100-year time period.\textsuperscript{8} Methane concentration increases with a much higher rate than CO\textsubscript{2} from pre-industrial of 0.76 ppm to 1.8 ppm nowadays representing 16% of the global warming impact.\textsuperscript{9} 60% emissions come from anthropogenic activity. Previous comparisons of on-road and laboratory emissions of NO, NO\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}O and CH\textsubscript{4} from late-model European light duty vehicles found average CH\textsubscript{4} emissions ranging from 18–45 mg km\textsuperscript{−1} corresponding to <1 g km\textsuperscript{−1} CO\textsubscript{2} for CNG engines. Some discrepancies appear by comparing on-road and laboratory emissions by considering greenhouse gas emissions being higher in the former case possibly due to longer period of urban driving and also a poorer accuracy related to data synchronisation, flow measurements and variability in traffic conditions.\textsuperscript{10} Hence, the development of CNG fuelled engines either for light and heavy-duty vehicles should be jointly related to the implementation of robust and efficient catalytic after-treatment systems for the simultaneous removal of unburnt methane, CO and NO\textsubscript{x}. Currently, this motorization system is more widespread in the Asia-Pacific region\textsuperscript{6} but is still emerging in Europe and North America despite natural gas is recognized as a cheap and cleaner fuel.

Some attempts consisting in hybrid bi-fuel and dual-fuel vehicles are considered as mid-term strategy.\textsuperscript{11} Indeed, an improved efficiency of CNG fuelled engines needs a better optimization of the ignition temperature related to the slower

### Table 1

<table>
<thead>
<tr>
<th>Standard</th>
<th>European directive</th>
<th>Implementation date</th>
<th>NO\textsubscript{x}</th>
<th>CO\textsubscript{2}</th>
<th>HC\textsuperscript{a}</th>
<th>PM\textsubscript{x}\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 0</td>
<td>88/77</td>
<td>01/10/1990</td>
<td>14.4</td>
<td>11.2</td>
<td>2.4</td>
<td>—</td>
</tr>
<tr>
<td>Euro 1</td>
<td>91/542 (B)</td>
<td>02/10/1993</td>
<td>9</td>
<td>4.9</td>
<td>1.23</td>
<td>0.36</td>
</tr>
<tr>
<td>Euro 2</td>
<td>91/542 (A)</td>
<td>03/10/1996</td>
<td>7</td>
<td>4.0</td>
<td>1.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Euro 3</td>
<td>1999/96</td>
<td>04/10/2001</td>
<td>5</td>
<td>2.1</td>
<td>0.66</td>
<td>0.13</td>
</tr>
<tr>
<td>Euro 4</td>
<td>1999/97</td>
<td>05/10/2006</td>
<td>3.5</td>
<td>1.5</td>
<td>0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>Euro 5</td>
<td>1999/98</td>
<td>06/10/2009</td>
<td>2</td>
<td>1.5</td>
<td>0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>Euro 6</td>
<td>595/2009</td>
<td>31/12/2013</td>
<td>0.4</td>
<td>1.5</td>
<td>0.13</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\textsuperscript{a} g kW\textsuperscript{−1} h\textsuperscript{−1}. \textsuperscript{b} Particulate matter.

### Table 2

<table>
<thead>
<tr>
<th>European regulations</th>
<th>NO\textsubscript{x} limits (g km\textsuperscript{−1})</th>
<th>Emission control cost (US dollar per vehicle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 3</td>
<td>0.5</td>
<td>−392</td>
</tr>
<tr>
<td>Euro 4</td>
<td>0.25</td>
<td>−513</td>
</tr>
<tr>
<td>Euro 5</td>
<td>0.18</td>
<td>−822</td>
</tr>
<tr>
<td>Euro 6</td>
<td>0.08</td>
<td>−1239</td>
</tr>
</tbody>
</table>

**Fig. 1** Cost advantages provided by the replacement of liquid fuels, i.e. gasoline and diesel, by compressed natural gas (CNG). This figure has been adapted/reproduced from ref. 7 with permission from Elsevier, copyright 2015.
burning rate of methane. However, natural gas mixed with liquid fuels would have unique features under lean conditions that are associated to the wide flammability limits and high flame propagation speed. Hence, a gain in thermal efficiency as compared to conventional fuels can be expected by combining these specific features with a high compression ratio. On this basis, a lower fuel consumption, nearly 25%, would compensate the incremental cost due to the technical adaptations of conventional diesel and gasoline engines.

### 1.2. Prospects in hydrogen powered combustion engines

Next opportunities come from hydrogen as vector of energy. Hydrogen is recognized as a clean fuel in terms of atmospheric pollution with a beneficial carbon balance because the principal combustion product is H$_2$O. Nonetheless, some obstacles are still remaining to qualify hydrogen as a green fuel because the most profitable production sector comes from the oil refining. In fact, hydrogen is mostly produced from the catalytic reforming at industrial scale. Presently, the steam reforming of methane stands for a benchmark low cost process. However, a strong focus on alternative biomass reforming processes are studied at the lab-scale. Emerging solar driven catalytic technologies for H$_2$ production from water splitting also arise. Alternative production from water using the electricity power from nuclear plants is not presently cost efficient. Nevertheless, intensive researches agree with the fact that the production of hydrogen should not be a technical problem anymore thanks to the wide availability of electrolyzers for this production.

Actually, the competition between H$_2$-fuelled internal engines and fuel cells fuelled by hydrogen seems in favour of the second option, at least for light duty vehicles. But some arguments make attractive the former option thanks to a better robustness with a weak sensibility to the quality of hydrogen. The use of large quantities of critical materials of strategic importance for batteries and fuel cells is questionable. Indeed, the European Community strongly encourages their substitution. Clearly, this issue will not be resolved in a short term. Their recyclability is still a current point of debate. According to the experts in this field, the recharging speed, autonomy and ability to meet the high power required by batteries actually limit their competitiveness. This opens other perspectives in the development of internal combustion engines fuelled with hydrogen. The prospects in the use of hydrogen and parallel routes for the production of alternative fuels from H$_2$, such as ammonia or methanol from the capture and the hydrogenation of CO$_2$ by H$_2$, could offer an efficient pathway to decarbonize the shipping industry. Indeed, an agreement for reducing greenhouse gas by 50% in 2050 emitted from marine engines has been adopted by the International Maritime Organisation.

Hydrogen can be used as fuel alone or mixed with natural gas, gasoline or diesel. H$_2$ + CNG blend may present a good compromise compared to conventional liquid fuels leading to lower CO, CO$_2$ and NO$_x$ emissions. Regarding the comparison with CNG, a significant decrease is expected on the CO and NO$_x$ emissions up to 80%. Hydrogen blended with liquid fuels can be a good strategy to improve the ignition of the gas mixture and promote the reduction of CO, unburnt hydrocarbons and PM emissions. However, NO$_x$ emissions increase with abnormally high NO$_2$/NO ratios for H$_2$ composition up to 40% which largely exceed those usually observed for diesel. The mechanism of the extra production of NO$_x$ emissions from H$_2$-diesel powered engines has been already investigated. The conversion of NO to NO$_2$ is related to the formation of HO$_2$ radicals in the H$_2$ combustion process above a limit temperature. In parallel, a subsequent increase in the population of the active radicals in the combustion zone leads to a faster oxidation of CO and unburnt hydrocarbons. For dual-fuel engines, the combination of hydrogen fuel (20% H$_2$) with the exhaust gas recirculation (EGR) could be implemented without any alteration of the combustion efficiency to reduce NO$_x$ emission levels. However, a good compromise is required because a decrease in NO$_x$ emissions by lowering the temperature and the pressure, thanks to an increase of the EGR rate, would lead correlatively to a decrease in the oxygen concentration. As a result, the complete elimination of CO and unburnt hydrocarbons would be no longer guaranteed.

Important technical issues for H$_2$-powered engines are based on the on-board storage and transportation of hydrogen. Indeed, the gravimetric density of energy for H$_2$ (120 MJ kg$^{-1}$) is higher than that of gasoline (120 MJ kg$^{-1}$ vs. 44 MJ kg$^{-1}$ respectively). In contrast, the volumetric density of energy is four times lower for gasoline which underlines significant drawbacks for on board H$_2$ storage. In practice, different strategies have been implemented for H$_2$-storage as metal hydride, compressed or liquefied gas, all taking advantages and drawbacks in terms of safety and energy saving. The balance between advantages and drawbacks for these different technical options has been recently discussed by Ravi et al. in a comprehensive review. The protocol chosen for the injection of hydrogen and air into the combustion chamber, separate or mixed, can have different impacts. For instance, the direct injection of cryogenic

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**Table 3** Emissions from diesel buses and CNG buses. This comparison is for all exhaust after treatment and driving cycles. Data adapted from ref. 1.

<table>
<thead>
<tr>
<th>Emission</th>
<th>Diesel</th>
<th>CNG</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0.31 ± 0.04 (97)</td>
<td>11.87 ± 0.98 (165)</td>
</tr>
<tr>
<td>NMHC</td>
<td>0.17 ± 0.05 (45)</td>
<td>0.80 ± 0.12 (87)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.00 ± 0.00 (37)</td>
<td>8.17 ± 1.07 (90)</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>14.30 ± 1.01 (130)</td>
<td>12.39 ± 0.89 (178)</td>
</tr>
<tr>
<td>CO</td>
<td>1.98 ± 041 (114)</td>
<td>4.12 ± 0.53 (156)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1417 ± 87 (58)</td>
<td>1236 ± 60 (98)</td>
</tr>
<tr>
<td>PM</td>
<td>102.24 ± 11.91 (131)</td>
<td>15.68 ± 1.51 (162)</td>
</tr>
</tbody>
</table>

Data reported in g km$^{-1}$ except for PM in mg km$^{-1}$. Number of measurements in bracket.
hydrogen can lower the residual temperature leading to a substantial reduction of the NO\textsubscript{x} production.\textsuperscript{29} Alternative approaches have also recently emerged considering the use of ammonia as an energy source. Ammonia stands for a hydrogen carrier with H\textsubscript{2} released from its decomposition. Firstly, its lower volumetric density of the energy eases its storage as a liquid phase (~33 °C vs. ~253 °C at 1 atm for hydrogen). Another important argument is related to the fact that the infrastructure for ammonia production exists as NH\textsubscript{3} is an important chemical intermediate in the production of fertilizers. On this basis, the substitution of the fossil fuels and/or hydrogen by ammonia can be attractive notably to decarbonize shipping industry. The H\textsubscript{2}–NH\textsubscript{3} dual-fuels can be also envisioned.\textsuperscript{30,31} However, this technical approach presents a significant disadvantage inducing much higher NO\textsubscript{x} emissions compared to the emission level in the case of the combustion of NH\textsubscript{3}. Ammonia is also recognized for its corrosive nature. In practice, NH\textsubscript{3} could be blended to liquid fuels to minimize the corrosion processes and to ignite the blend at lower temperatures. Indeed, the combustion of ammonia occurs with a slow flame propagation\textsuperscript{32} that is well related to the slow kinetics. Finally, the use of ammonia must be safe due to its intrinsic toxicity. This apparent disadvantage due to ammonia leaks opens the discussion on subsequent usages. Indeed, NH\textsubscript{3} leaks could feed end-of-pipe catalytic after-treatment systems for NO\textsubscript{x} reduction according to a classical ammonia-SCR technology.

1.3. Which would be the best approaches for the abatement of typical atmospheric pollutants from CNG and H\textsubscript{2}-powered vehicles

The guidelines and the objectives of this review are focused on future adaptations for CNG and H\textsubscript{2}-powered engines on existing after-treatment technologies dedicated to gasoline and diesel engines. For both alternatives motorizations an important factor is related to the weak formation of particulates due to improved homogeneous combustion irrespective of the richness conditions. However, large number of ultra-fine nanoparticles are generally emitted by low-carbon fuels. Basically, this concerns CNG engines and/or H\textsubscript{2}-enriched CNG vehicles. Earlier investigation found that intrinsically such motorizations do not produce significant emissions of particulates. However, the presence of lubricant in the combustion engines can have a deleterious effect in the production of nanoparticles.\textsuperscript{33} Recent investigation demonstrated a high reduction nearly 70% in the frame of world harmonized transient cycles simply by optimizing lube formulation.\textsuperscript{34} Contrast observations come from the comparison of H\textsubscript{2}-enriched CNG vehicles and CNG engines particulates emissions with higher number of nanoparticles but lower particles mass in the former case.\textsuperscript{35,36} Such a trend is also verified for ultrafine particulates. By considering size threshold of 23 nm, emissions from CNG engines are one order of magnitude lower compared to gasoline engines. However, this difference strongly attenuates by decreasing the threshold to 10 nm or 2.5 nm.\textsuperscript{36} The reduction of ultrafine particulates is a key point and the filtration efficiency of current particulate filter technologies must be improved thank to more optimized microstructure.\textsuperscript{34}

Hence, the suppression of the particulates would simplify the architecture of current catalytic after-treatment technologies especially those dedicated for running under lean conditions. Future technical adjustments on the existing catalytic after-treatment technologies, and/or implementation of novel systems, are closely related to the temperature of the exhaust and the richness. This is particularly true for natural gas fuelled engines because the exhaust temperatures are lower (<400 °C) than that of gasoline or diesel operating at higher temperatures in the range 400–700 °C. Therefore, lower temperatures mean slower kinetics for methane removal, which represents a significant challenge regarding the high energy required to break the C–H bond and to activate the methane molecules.\textsuperscript{37} For CNG fuelled-engines the abatement of trace amount of methane is a challenging issue especially near the stoichiometry or in an oxygen-depleted environment because the kinetics will be unfavoured. Under stoichiometric and slight rich conditions various reactions can occur such as reforming or water-gas-shift reactions leading to an extra production of CO. Carbon monoxide generally strongly adsorbs on PGMs and can further inhibit methane oxidation at low temperature.

Palladium is the metal of choice in the catalytic devices for methane abatement. Most of the studies dedicated to the catalytic methane combustion have been performed in lean conditions (in an excess of oxygen) emphasizing PdO as the active phase in these operating conditions. Under stoichiometric or slight rich conditions, oxygen depletion slows the kinetics and alters the stability of PdO decomposing more easily into less active Pd metal.\textsuperscript{38} The fast autothermal sintering is also an important issue particularly in the presence of steam in the exhaust.\textsuperscript{39} Presently, the strategies envisioned to suppress the related detrimental effects due to PdO decomposition and particle sintering are quite unclear. For three-way catalytic applications the best option would lie in a better stabilization of palladium as well as in the reduction of PGM content. For lean burn applications, the kinetics of methane combustion is much faster. In such a case, the best alternative could be a complete or partial replacement of PGMs. On the other hand, the simultaneous removal of NO\textsubscript{x} is uneasy because methane and CO are none selective being preferentially oxidized by O\textsubscript{2} resulting in a low availability of reductants for NO\textsubscript{x} reduction. To manage properly this problem, commercialized strategies consist in the injection of an extra-reducing agent or the application of transient regimes to store and reduce NO\textsubscript{x}, e.g. the urea-selective-catalytic-reduction (SCR) and lean-NO\textsubscript{x} trap applications (LNT).\textsuperscript{40,41}

Many reviews already pointed out advantages and drawbacks in the use of hydrogen fuelled thermal engines.\textsuperscript{42} Specific cautions and recommendations are related to significant levels of NO\textsubscript{x} emissions due to high flame
temperature. Hence, catalytic after-treatment technologies are still required to treat the NOx emissions. In this specific case, simple technology could be envisioned because NOx, as unique atmospheric pollutant in the exhaust, could be simply catalytically decomposed without the use of extra reducing agent. However, previous investigations shown that this technology suffers from significant kinetic limitations which prevented any further practical developments. Probably the catalystic decomposition of NOx in the exhausts of H2-fuelled engines would offer more development breaking with existing technologies. In contrast, NH3 leakage must be considered for ammonia-fuelled engines. As previously said, this apparent drawback could be helpful to remove NOx thanks to the installation of ammonia-SCR technology.

Different scenarios for each type of motorization will be compared based on their advantages and drawbacks. An important aspect with regard to the composition of the catalyst will be related to the urgent need to reduce the use of critical materials of strategic importance. Platinum group metals are evidently concerned.

### 2. Catalytic after-treatment systems: present status and future trends

#### 2.1. Pollution control in exhaust from natural gas vehicles engines

As previously emphasized, the implementation of CNG fuelled engines is related to the development of efficient catalytic after-treatment technologies for the methane removal. The simultaneous removal of CO and NOx for this type of motorization still represents an important target. To date, noble metals are extensively used as catalysts in these processes. Their performances mainly depend on the nature and composition of the residual gases as well as the air-to-fuel ratio.37 Basically, palladium–rhodium three-way catalysts met standard regulations for natural gas-powered engines running near the stoichiometry. In contrast, platinum–palladium compositions are more suitable for methane oxidation under lean conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition of the reaction mixture</th>
<th>GHSV ( \text{a} )</th>
<th>( t^\circ )</th>
<th>CH4 conv.</th>
<th>( E_a ) ( \text{b} )</th>
<th>TOF ( \text{c} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_x \text{CoO}_3 )</td>
<td>( \text{CH}_4/\text{O}_2 = 1/20 )</td>
<td>30000</td>
<td>640</td>
<td>96</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11%Sn/Al2O3</td>
<td>1 vol% CH4 + 0.5% O2</td>
<td>30000</td>
<td>534</td>
<td>2.7</td>
<td>151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 vol% CH4 + 0.5% O2</td>
<td>30000</td>
<td>534</td>
<td>10.2</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt% Pd/Na-ZSM-5</td>
<td>1500 ppm CH4 5 mol% O2</td>
<td>60000</td>
<td>343</td>
<td>95</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/ZSM-5</td>
<td>1 vol CH4, 20 vol% O2</td>
<td>30000</td>
<td>352</td>
<td>90</td>
<td>0.14</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>0.85 wt% Pd/CeO2–ZrO2</td>
<td>1500 ppm CH4 5 mol% O2</td>
<td>60000</td>
<td>340</td>
<td>99</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt% Pd/Na-ZSM-5</td>
<td>4 mol% CH4 8 mol% O2</td>
<td>14000</td>
<td>520</td>
<td>90</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe2O4</td>
<td>1 vol% CH4 42 vol% O2</td>
<td>24000</td>
<td>427</td>
<td>90</td>
<td>0.003 ( d )</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>BaO–MnO</td>
<td>1 vol% CH4 in air</td>
<td>30000</td>
<td>379</td>
<td>90</td>
<td>116</td>
<td>0.02</td>
<td>50</td>
</tr>
<tr>
<td>1 wt% Pd/H-ZSM-5</td>
<td>1 vol% CH4 in air</td>
<td>30000</td>
<td>315</td>
<td>90</td>
<td>0.18</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>2 wt% Pd/H-ZSM-5-K</td>
<td>1 vol% CH4 in air</td>
<td>30000</td>
<td>315</td>
<td>90</td>
<td>0.18</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>0.95 wt% Pd/CoO2–ZrO2</td>
<td>1 vol CH4 20 vol% O2</td>
<td>60000</td>
<td>345</td>
<td>90</td>
<td>0.09</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Gas hourly space velocity (mL g\(^{-1}\) h\(^{-1}\)). \( b \) Reaction temperature. \( c \) Activation energy. \( d \) \( T = 400 ^\circ \text{C} \).
more realistic modelling studies. Generally, lab-scale experiments carried out under simulated inlet gas mixture compositions underestimate the amounts of water and CO₂ produced in real exhausts in spite of water exerts a strong inhibiting effect ascribed to a high OH bond adsorption coming from the dissociation of H₂O.

2.1.1 Understanding reaction mechanisms for methane abatement and related surface properties of doped and undoped metal oxides supports with PGMs. A better understanding of reaction mechanisms is often a prerequisite to further improve the efficiency of existing catalysts and/or to develop alternative catalyst compositions. On this basis, this methodology appears suitable to find some guidelines for lowering the PGMs content or synthesized PGM-free catalysts.

New reaction mechanisms insights can be obtained from kinetic studies, molecular modelling and/or spectroscopic studies leading to key information on the energetic features of elementary steps over Pd single crystal model catalysts as well as on polycrystalline supported Pd catalysts. In this latter case, the contribution of the support can be significant. It can disperse nanosized palladium particles and/or participate in the catalytic cycle through the production of highly reactive oxygen species. This last feature concerns support materials exhibiting oxygen storage properties. Important information related their specific affinity toward adsorption on the active sites is also useful in case of competitive adsorptions of various atmospheric pollutants. According to this, deleterious effects can occur in case of strong inhibitions. By way of illustration, a strong accumulation of the OH groups onto support materials having high oxygen storage capacity will suppress the oxygen exchange. Recent investigations pointed out that the deposition of palladium onto hydrophobic support materials could reduce the detrimental effect of water. In this context the use of zeolite-based materials could offer new prospects. However, despite significant improvements in the thermal stability related to an optimal adjustment of the Si/Al ratio, they still exhibit a significant susceptibility to the water exposure at high temperature that can provoke structural deteriorations. Enhanced performances were obtained on Pd/γ-Al₂O₃ promoted by NiAl₂O₄ containing relatively low amount of palladium, i.e. 0.4 wt%.

The authors observed a suppression of the PdO aggregation as well as a decrease of OH accumulation in the course of methane combustion thanks to the NiAl₂O₄ interface.

The presence of sulphur also induces a strong poisoning effect. Interestingly, the sulphur poisoning of CNG catalysts can be weakened in the presence of water thanks to compensation effect associated to a strengthening of acid properties. More relevant information on thermal stability and poisoning effects of commercial Pd/CeO₂-ZrO₂ CNG three-way catalyst were obtained from monolith reactors working in real exhaust conditions. Indeed, the authors found on thermally aged three-way catalysts, exposed to high sulphur fuel, a promotional effect on the catalytic activity related to the growth of the following interface: (Pd⁰-SO₄²⁻)⁺ with Ce³⁺-V₆O. However, this promotional effect is sensitive to the accumulation of sulphate which then blocks the exchange of oxygen on the surface and in the bulk.

In brief, palladium stabilized as PdO has been suggested as the best active phase and largely inspired molecular modelling investigations on single crystals. On the other hand, a shift from lean to rich conditions, typically for three-way catalysts working in switch mode near the stoichiometry, is accompanied by a sharp loss of conversion. This deactivation could be jointly explained by changes in the kinetics disfavoured under these operative conditions and the relative instability of PdO. As explained, PdO can decompose into less active metallic Pd particles during a rise in temperature under rich atmosphere. Sulphur poisoning leads to the formation of stable PdSO₄ that can be decomposed only at high temperature. At elevated temperature, once regenerated PdO is enough unstable to decompose and produce less active Pd⁰ particles. Interestingly enough, Pt/Al₂O₃ behaves oppositely becoming more active when the O₂/CH₄ ratio tends to low values corresponding to oxygen depleted environments (see Fig. 2). At first glance, one can hypothesize that platinum would be more suited to the conditions of a three-way catalysis close to stoichiometry than PdO. But this assertion did not lead to a clear consensus. Hick et al. found the CH₄/O₂ reaction is structure-sensitive over platinum and palladium in a mixture containing 50 Torr CH₄ and 110 Torr O₂ in a temperature range 260–370 °C which can be explained on platinum by the coexistence of platinum oxide PdO dispersed on alumina and adsorbed oxygen species on platinum crystallites. The same trend is observed with palladium. Turn-over-frequency values recorded on dispersed PdO and PdO are 0.005 s⁻¹ and 0.02 s⁻¹ respectively on small
particles and shift to 0.08 s\(^{-1}\) and 1.3 s\(^{-1}\) on large particles which underline a significant particle size dependency on the reaction rate. Such comparisons also evidence that Pd outperforms Pt-based catalysts even near stoichiometric conditions. In practise, bimetallic Pd–Rh containing high amount of PGM with loading above 200 g ft\(^{-3}\) are requested to reach high level of methane combustion at the lowest temperature and to insure NO\(_x\) reduction to nitrogen.\(^{37}\)

So far, the reaction mechanisms for the combustion of methane in an oxygen-depleted environment are widely discussed because PdO becomes unstable. A first examination consists in developing theoretical approaches to probe the intrinsic activity of metallic Pd atoms. We must confess that most of those studies investigated PdO (ref. 64 and 65) especially the PdO(101) surface leading to the lowest activation barrier for the C–H breaking.\(^{64,76}\) Stotz et al.\(^{65}\) developed a two-site mean field microkinetic model on PdO(101) in agreement with a Mars–van-Krevelen mechanism involving reactive oxygen species from PdO and the formation of lattice oxygen vacancies. They observed a good agreement with light-off curves recorded on Pd/Al\(_2\)O\(_3\) in a mixture containing 1000 ppm CH\(_4\), 10 vol% O\(_2\) and 0–12 vol% H\(_2\)O capturing water inhibition. Hence, two different sequences have been identified under dry and wet atmospheres represented in Fig. 3. They were found sensitive to the temperature conditions.

Regarding the intrinsic catalytic properties of metallic Pd, the unity bond index-quadratic exponential potential (UBI-QEP) is a useful method to get energetics on the most relevant elementary steps. A closed-packed Pd(111) surface characterized by the prevalence of three-fold hollow sites has been considered in the calculations of activation barrier and heat of reaction.\(^{77}\) The calculation of the activation barrier \(E\) for C–H bond breaking assumed a nearest neighbor vacant site or occupied by chemisorbed O atoms according to step (1) and (2) respectively where * stands for a metallic Pd\(^0\) adsorption site.

\[
\text{CH}_4,\text{ads} + \ast \rightarrow \text{CH}_3,\text{ads} + \text{H}_{\text{ads}} \quad (1)
\]

\[
\text{CH}_4,\text{ads} + \text{O}_{\text{ads}} \rightarrow \text{CH}_3,\text{ads} + \text{OH}_{\text{ads}} \quad (2)
\]

As exemplified in Fig. 4, step (2) leads to a lower \(E\) value when the O-coverage is up to 40%. This seems in good agreement with kinetic features on PdO reflecting the assistance of surface lattice O atoms to break the C–H bond in methane. In the particular case of Pd(111), O-adsorbed species from gaseous O\(_2\) adsorption would assist the C–H bond scission. Another, kinetic feature appears related to the negative impact of OH-coverage inducing an increase of the activation barrier. This result is interesting because the detrimental effect of water would not only result from thermodynamic considerations, related to strong water adsorption, but would also involve kinetic factors related to loss of reactivity of key intermediates.

In the particular case of supported Pd catalysts, the support can participate in the supply of more reactive oxygen species.\(^{78}\) The performance of three-way Pd/Al\(_2\)O\(_3\)–CeO\(_2\) catalyst in a monolith reactor were evaluated in a representative exhaust gas composition on samples calcined from 550 °C to 950 °C. These two calcination temperatures correspond to PdO particles size in the range 1.9–8.5 nm. The 1.9 nm PdO particles strongly interact with Ce then decomposing more readily to metallic Pd\(^0\) particles which leads to improved catalytic performance in methane combustion. These improved catalytic properties have been assigned to the Pd–Ce interface. On the other hand, this interface deteriorates when the calcination proceeds at 950 °C leading to 8.5 nm PdO particles which corresponds to a predominant stabilization of the Pd–PdO interface and lower catalytic properties. Fig. 5 highlights the two kinetic regimes involving the Pd–PdO and Pd–Ce interfaces governed by the stability of PdO and corresponding to improved performance.

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**Fig. 3** Schematic of the considered C\(_1\)-pathways containing carbonaceous intermediates. Red arrows indicate the preferential reaction pathway at dry conditions before the light-off (low temperature path) while blue arrows indicate the preferential reaction pathway after the light-off at dry and mainly during wet conditions (high temperature path). This figure has been adapted/reproduced from ref. 65 with permission from Elsevier, copyright 2019.

**Fig. 4** Surface oxygen and OH coverage dependency on the activation barrier of step (2) O coverage (○) and OH coverage (▲). This figure has been adapted/reproduced from ref. 77 with permission from Elsevier, copyright 2022.
for the Pd–Ce interface likely due to the involvement of more reactive oxygen species from ceria.

The participation of reactive oxygen species from perovskite materials has been also envisioned on Pd/La0.7MnO3.77 However, the presence of steam was found to suppress the surface oxygen mobility of the perovskite. The loss of Pd-perovskite interface led to changes in the reaction mechanism shifting from a dual-sites reaction mechanism involving the cooperation of lattice oxygen species from the perovskite with metallic Pd sites, to a single site mechanism involving only palladium. Previous investigations pointed out the detrimental effect of OH groups accumulation on metal oxide supports neutralizing oxygen mobility and inducing deactivation.69

Recently, a novel strategy was implemented to create a new type of highly active SmMn2O5 mullite from acid etching (see Fig. 6). This one includes unsaturated-coordination Mn4+–O–PdOx sites in SmMn2O5 mullite which ease the C–H bond scission in CH4 molecules. The sharp gain in performances with TOF multiplied by 6 in comparison to a conventional supported Pd catalyst has been explained by an improved thermal stability and a better tolerance of water inhibition.79

Infrared spectroscopic measurements performed in the course of the reaction can complement data from molecular modelling or kinetic studies. However, they must be subjected to caution as only specific methodologies allow the identification of real intermediates. Jodłowski et al.80 investigated the catalytic methane combustion on Co, Ce, and Pd mixed oxides deposited on a steel surface. These authors assumed a metal oxide surface containing Co, Ce and Pd and hypothesized the reaction mechanism depicted in Fig. 7 in which [MeO] stands for a metal oxide adsorption site. It must be pointed out that either Pd-undoped or doped metal oxides are active for methane combustion. Oxygen is assumed dissociated onto the surface. On this basis, the authors suggested the following reaction pathway involving the formation of methoxy groups. [MeO] sites are restored after releasing CO and CO2 in the gas phase. CO can subsequently interact with OH groups of the alumina support. Let us not that this mechanism proposal does not underline strong difference with that presented in Fig. 3 from a microkinetic model on PdO(101) leading to the intermediate formation of adsorbed formaldehyde, methoxy groups and formate species.

The substitution of PGMs has been widely investigated on various single and mixed metal oxides. Particular attention was paid to perovskite structures with nominal composition ABO3. A and B are usually trivalent cations responsible respectively of the structural stability and the redox properties. Both properties can be improved through various substitutions of A- or B-sites creating possible electronic imbalances and geometric distortions. The restoration of the electroneutrality can be insured through either the stabilization of the B cation in unusual oxidation state or through the adjustment of the oxygen stoichiometry. By way of illustration, Taguchi et al.81 explained improved catalytic performances on La1−xMxCoO3 with M = Ca, Sr and Ba for x = 0.6 due to the stabilization of Co4+ and an increase of the Co–O–Co bond angle. Generally, the catalytic properties of perovskite-type structures depend on various parameters such as the specific surface area, oxygen mobility, textural properties, lattice oxygen concentration and reducibility of
the B-cation. The study of the reaction mechanism for methane combustion on LaCoO$_3$ showed that the relative position of the O-p band centre and the d-band centre for the B-cation governs the kinetics. A negative relative position value agrees with a preferential suprafacial reaction mechanism associated to the reactivity of surface adsorbed oxygen species. Conversely, an intraphac reaction mechanism involving oxygen lattice species at high temperature will be privileged according to a positive value. Fig. 8 illustrates the corresponding Eley–Rideal and Mars–van-Krevelen mechanisms involving respectively the gaseous O$_2$ adsorption and surface lattice oxygen species. Regarding this latter case, CH$_4$ dissociates once adsorbed and resulting abstracted H atoms react with oxygen lattice species creating oxygen vacancies subsequently refilled by gaseous O$_2$. Lanthanum manganite perovskites have been studied in the presence of an excess of Mn. Single MnO$_x$ oxides segregate corresponding to a higher oxidation state than cationic Mn species stabilized in the perovskite lattice. The improved reducibility of segregated oxidic Mn species coincides with a sharp gain in methane conversion.

Spinel structures exhibit similarly to perovskite efficient catalytic properties in mild reaction conditions for oxidation reactions. These catalytic features are generally ascribed to their high specific surface area and high cobalt concentration in Co–Mn-oxide spinel catalysts. These structures are also characterized by oxygen storage properties that can be profitably used for methane combustion. Their electronic structure plays an important role in defining their potential catalytic properties depending on the position of the metal d-band centre compared to the O p-band centre. A greater metallic character of the metal centre is associated to improved oxygen dissociation in agreement with a suprafacial Eley–Rideal reaction mechanism for oxidation reactions. Conversely, a higher position of the O p-band would preferentially correspond to an intraphac Mars–van-Krevelen reaction mechanism involving the participation of lattice oxygen species. The redox properties of cobalt spinels depend on the ease of forming active oxygen species. It was found that the reactivity of surface oxygen species differs on (111) to (110) facets, which explains the strong dependence of redox properties on aggregate morphology. Operando spectroscopic studies on spinel structures revealed the central role played by oxygen vacancies to abstract hydrogen recognized as the slow step in the course of methane combustion. These authors found that nickel ferrite NiFe$_2$O$_4$ exhibits superior performances than Cu, Co and Zn ferrites correlated to a synergy effect between oxygen vacancies and partially reduced metal sites with improved stability of spinel structures.

2.1.2 Catalytic technologies for the removal of NO$_x$ from CNG engines. NO$_x$ removal must be envisioned equally for CNG fuelled engines running near the stoichiometry or in lean operating conditions. In the former case, NO$_x$ and CH$_4$ are removed simultaneously typically on a TWC. On the other hand, a sequential process is generally preferred for lean-burn applications as NO$_x$ cannot be reduced in an excess of oxygen. The classical configuration consists in the installation of a selective NO$_x$ reduction process downstream the oxidation catalyst. Basically, the existing diesel oxidation catalyst technologies (DOC) used for diesel applications can be still suitable. As previously described, palladium exhibits the highest efficacy to oxidize both methane and CO in an excess of oxygen. On this basis, neither CH$_4$ nor CO will be available for further NO$_x$ reduction. In fact, NO$_x$ will be preferentially oxidized to NO$_2$ on the DOC and subsequent reduction to nitrogen will take place on a downstream ammonia-SCR catalyst thanks to an extra injection of a reductant, e.g. urea. This technology competes with lean-NO$_x$ trap reduction process (LNT)$^{[96,97]}$ which includes a NO$_x$ trapping system in lean conditions and a regeneration step by creating artificially rich conditions thanks to fuel injection. The optimization of both systems is complex. For urea-SCR, its decomposition into ammonia, acting as selective reducing agent, must be finely calibrated to avoid ammonia leakage. Complex dosage strategies must be implemented. For the LNT technology, both strong kinetic and thermodynamic limitations must be correctly apprehended to speed up the formation of NO$_2$ and decompose stored nitrates at moderate temperature in
order to avoid fuel penalties. Some differences characterize both systems. LNT systems use extensively PGMs. In contrast, the efficacy of PGMs is restricted to a narrow temperature range on SCR catalyst as exemplified in Fig. 9. In this latter case, the best catalytic technologies involve the use of PGM-free catalysts such as vanadium or doped zeolite catalysts.100

Ammonia-SCR is a powerful catalytic technology to reduce NO\textsubscript{x} in nitrogen in a large excess of oxygen according to the following eqn (3):

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 = 4\text{N}_2 + 6\text{H}_2\text{O} \text{ Standard-SCR (3)} \]

Vanadia–titania based catalysts are suited for this catalytic application.\textsuperscript{102–104} They combine acid and redox functionalities to adsorb ammonia and reduce NO\textsubscript{x}. These functionalities are assigned to V\textsuperscript{5+}–OH and V\textsuperscript{5+}≡O groups. A dual site reaction mechanism in the Fig. 10 is commonly accepted in which the reoxidation of V\textsuperscript{5+}–OH to V\textsuperscript{5+}≡O is the slow step.\textsuperscript{105}

For the automotive exhaust depollution, V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} is a benchmark SCR-catalyst. The reaction temperature is a key parameter for the stability of well-dispersed VO\textsubscript{x} species as an elevation can promote their coalescence leading to unreactive V\textsubscript{2}O\textsubscript{5} clusters.\textsuperscript{40} The volatilization of V\textsubscript{2}O\textsubscript{5} at high temperature inducing deactivation limits the applications to moderate temperatures. The catalyst efficiency is also sensitive to the ratio NO\textsubscript{2}/NO. Optimal performance are obtained for a ratio close to 1 that corresponds to the fast-SCR conditions in agreement with eqn (4). In such conditions, the presence of NO\textsubscript{2} favours the reoxidation of V\textsuperscript{5+}–OH to V\textsuperscript{5+}≡O. However, they also correspond to more complex reaction mechanism as illustrated in Fig. 11 with the involvement of nitrates and nitrites intermediates species.\textsuperscript{106}

\[ 2\text{NH}_3 + \text{NO} + \text{NO}_2 = 2\text{N}_2 + 3\text{H}_2\text{O} \text{ Fast-SCR (4)} \]

Recent advances offer alternatives, in particular with metal-doped zeolites that are more thermally stable.\textsuperscript{107–112} Their catalytic performances are reported and compared in Table 5. A remarkable thermal stability has been observed for Cu-SSZ-13 exhibiting high resistance to deactivation after aging in 8 vol% O\textsubscript{2} with 5 vol% H\textsubscript{2}O at 900 °C.\textsuperscript{112} An improved stabilization of vanadium can be obtained in bulk undoped and W-doped CeVO\textsubscript{4} ammonia SCR systems.\textsuperscript{113,114} Despite their low specific surface area these systems were found intrinsically highly active.

Biofuels contain alkalines which provoke a depletion of the catalyst efficiency.\textsuperscript{117} Indeed, the alkali metals neutralize Bronsted acid sites thus preventing the adsorption of ammonia. Noteworthy, the W–OH groups are more sensitive to this neutralization.\textsuperscript{118} Based on these, the doped-zeolite catalysts are preferred to the traditional V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} ammonia-SCR catalysts. Indeed, these materials exhibit higher specific surface areas, higher density of acid sites and improved thermal stability.\textsuperscript{119} Cu and Fe-doped zeolites SCR catalysts also exhibit a good sulphur tolerance and a high sensitivity to the NO\textsubscript{2}/NO\textsubscript{x} ratio.\textsuperscript{120–122} However, even though the metal-doped zeolites exhibit an improved stability against the alkali poisoning, this one is not completely suppressed and cumulative effects can finally alter the stability of the isolated doped zeolite cations.\textsuperscript{59,123,124}

In the particular case of automotive applications, the competition between the adsorption of unburnt hydrocarbons (HC), ammonia, and water during the cold start engine may generate inhibition effects on the NO\textsubscript{x} adsorption and reduction. Hence, the acid properties of zeolites should be optimized to store HC and suppress the HC leakage at low temperature.

Interestingly enough, ZSM-5 zeolite-based catalysts can be also considered for the methane removal under lean conditions. In general, their adsorption capacity is strongly deteriorated after water pre-adsorption but such a competition can be modulated by the addition of indium.\textsuperscript{125}
The catalytic performance of Pd will be also sensitive to the presence of sulphur from lubricants under real exhaust conditions. These catalysts exhibit a weak tolerance to SO\textsubscript{2} poisoning and to water inhibition. In this latter case a restoration of catalytic properties may occur when the water supply is cut off. The regeneration of the catalyst thanks to the removal of the accumulated sulphates onto the surface is more challenging for lean-burn applications.

### 2.2. Recommendations for the depollution of exhaust gas combustion from engines fuelled by CNG and or CH\textsubscript{4} blended with liquid fuels

The architecture of the catalytic after-treatment technologies depends on the richness determined by the air-to-fuel ratio. Under typical three-way conditions, the most important criteria are related to the activation of the methane combustion at low temperature and the ammonia leaks under rich conditions. Cross-fertilization with previous studies reporting passive ammonia technologies including TWC coupled with the SCR system can at least lead to some practical guidelines\textsuperscript{126}

The concept including cycling lean/rich conditions is based on the promotion of the formation of ammonia on TWC in rich conditions\textsuperscript{41}, then ammonia can react with NO by switching in lean conditions. Ammonia production on TWC can be promoted by the water-gas-shift reaction or steam reforming leading to a H\textsubscript{2}-rich atmosphere more suited to reduce NO\textsubscript{x} to NH\textsubscript{3}. In practice ammonia can be stored in rich conditions on downstream SCR catalysts. Subsequent lean exposure would promote the NO oxidation to NO\textsubscript{2} on TWC and then the NO/NH\textsubscript{3} reaction onto the SCR catalyst leading selectively to N\textsubscript{2}. Instead of the installation of two sequential monoliths associated to the TWC and the SCR function, an alternative would consist in the development of a dual-layer SCR + TWC monolith configuration. This option has been recently explored by coupling transient experiments and kinetic modelling\textsuperscript{127}. According to this approach, the emission of ammonia during the rich condition step can be suppressed at a low temperature through its trapping by adsorption onto the SCR catalysts. Afterwards, it reacts in a lean NO + O\textsubscript{2} gas mixture. On the contrary, the direct ammonia oxidation to nitrogen prevails at high temperature. The intrinsic properties of each active catalyst component are important for the optimization of the overall efficiency of the system. This is well demonstrated for CeO\textsubscript{2} characterized by high oxygen storage properties. CeO\textsubscript{2} has been also investigated in the particular case of the WGS reaction sometimes with controversial recommendations. By way of illustration, Thomas et al\textsuperscript{128} found that the performance of Pd/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} were weakly sensitive to the ceria content which led the authors to the conclusion that ammonia is preferentially produced via the hydrolysis of isocyanates instead of the NO/H\textsubscript{2} reaction. Previous comparisons of model Pd/Al\textsubscript{2}O\textsubscript{3} and Pd/Ce/Al\textsubscript{2}O\textsubscript{3} catalysts with a commercial TWC found that the production of ammonia is lowest on this latter system and delayed under the rich cycle in the presence of Rh. In contrast, Pd/Ce/Al\textsubscript{2}O\textsubscript{3} offers the best performances\textsuperscript{129}. Useful recommendations for the production and the valorisation of ammonia have been suggested consisting in the installation of a passive ceria-based ammonia-SCR catalyst to promote the water-gas-shift reaction. In parallel, the OSC properties of ceria must be modulated to avoid undesired oxidation reactions.

Finally, it seems obvious that the combination of cooled exhaust gas recycling (EGR) to TWC is an efficient way to reduce the NO\textsubscript{x} concentration in the exhaust prior to their post catalytic treatment. The installation of an additional catalytic selective oxidation device to resolve a possible ammonia leak is recommended to comply with the Euro 6 emission standard\textsuperscript{130}.

### 2.3. Pollution control in exhaust from hydrogen fuelled engines

The main target for H\textsubscript{2}-fueled engines lies in the abatement of high NO\textsubscript{x} concentrations. The reduction of NO by H\textsubscript{2} has been studied for a long time as this reaction can occur on the three-way catalysts\textsuperscript{131,132} and in lean-burn conditions\textsuperscript{133–135}. Previous attempts concerned supported...
PGM catalysts extensively used in post combustion catalysis. The kinetics of this process was found dependent on the thermal pre-treatment of the catalyst prior to the reaction. Indeed, the reduction of NO is enhanced when the catalyst is pre-oxidized avoiding the deleterious formation of ammonia.

The promotion of Pd/Al₂O₃ and Pd/Al₂O₃ model catalysts by transition metal oxides, such as WO₃, CoO₃, MoO₃, has been examined by Mergler and Nieuwenhuyse.136 Despite these authors studied the NO/H₂ reaction at much higher NO and H₂ concentrations subsequent comparison with a commercial three-way catalyst highlight the role played by the cobalt oxide on the selectivity to nitrogen production. They observed improved performance for the NO/H₂ reaction on pre-reduced Pt/SiO₂-CoO₃ while the bimetallic PtRh/Al₂O₃ system was found more efficient after a pre-oxidation step following the model of Hecker and Bell for Rh/SiO₂. The results emphasized the fact that Rh is preferentially involved in the reduction of NO on the bimetallic system. Hence, an improved selectivity towards N₂ production was obtained on Pt/SiO₂ thanks to the CoO₃ incorporation. In contrast, the three-way catalyst model was more selective once the catalyst was pre-treated in an oxidative atmosphere. When the reaction is performed near the stoichiometry then the competitive H₂/O₂ reaction becomes insignificant. In that case the most important issue lies in the competitive formation of N₂, undesired N₂O and ammonia (under slight rich conditions). As a matter of fact, the selectivity of these different products is intrinsically related to the strength in the NO adsorption. This is a peculiar feature of rhodium to adsorb more strongly and dissociate more readily adsorbed NO molecules. In the presence of CO, the NO/H₂ reaction is usually delayed reflecting a significant inhibiting effect of CO.132

Under lean conditions, in large excess of oxygen, both the NO/H₂ and H₂/O₂ reactions compete. Support effects can broaden the operating temperature window for the NO/H₂ reaction.133,134 A remarkable catalytic behaviour for this reaction has been observed on Pt/Laₐ₀.₃₅Srₐ₀.₆Ce₁₋ₐO₉ containing extremely low amount of platinum, i.e. 0.1 wt%.134 This beneficial effect was explained by a dual-site reaction mechanism involving NO adsorbed onto Pt dissociating on a nearest-neighbour oxygen vacancy. Similarly, to stoichiometric conditions, the nature of the catalyst pre-treatment prior to reaction influences the performances. This is particularly true for bimetallic catalysts or single metals promoted by a metallic oxide phase. Indeed, Hamada et al.137 investigated the reactivity of Pt-W and Pt-Mo in the presence of 0.08% NO, 0 or 10% O₂ and 0.28% H₂. Pre-reduction led to the formation of inactive intermetallic Pt-Mo aggregates for the NO/H₂ reaction. In contrast, Pt-Mo is readily oxidized in a large excess of oxygen to more active Pt-MoO₅ with a conversion taking place at 40 °C. On the other hand, N₂O is predominantly formed. Park et al.138 reported similar tendencies on Pt-MnO₂ catalysts. The peculiar properties of both Pt-MnO₂ and oxidized Pt-Mo systems can be reasonably explained by the involvement of a dual-site reaction mechanism with hydrogen activated on Pt and NO activated on MoO₃. In this configuration the high activity and selectivity to nitrogen production can be explained by the intermediate ammonia formation which enhances the NH₃-SCR. However, a rise in the temperature above 125 °C is accompanied to a loss in the NO conversion. In the absence of MoO₃, platinum is much less selective reproducing a similar trend observed by Hamada emphasizing the deterioration of the adsorptive properties of Pt possibly ascribed to a stronger NO adsorption leading to a high NO coverage.

Generally, the competition is more in favour of the H₂/O₂ reaction in an oxygen excess when the H₂/O₂ ratio decreases (see Fig. 12). Two ranges of NO conversion are often observed in these operating conditions. At low temperature, the NO reduction would proceed on metallic sites while the oxidized surface would be preferentially involved at high temperatures.139 The detection of ammonia with a rise in the temperature could be also explained by a different reaction pathway. Macleod et al.141 observed a broader range of NO conversion on Pd/TiO₂/Al₂O₃ catalysts in a reaction mixture composed of NO, CO, H₂ and O₂. They observed the in situ production of ammonia in the whole range of the NO conversion but provided different explanations as at low temperature ammonia would come from the hydrolysis of NCO species while at high temperature NH₃ would form thanks to the reaction between H₂ and nitrate species. Interestingly, the catalyst composed of alumina and titania would conserve the peculiar properties of both metallic and single oxide. Accordingly, Pd/TiO₂ would activate the production of ammonia further hydrolysed on alumina.

The support plays an important role modifying the adsorptive properties of noble metals through geometric or electronic effects and/or being involved directly in the catalytic cycle. The textural properties can improve the efficiency when using mesoporous support materials emphasizing the importance of the pore structure to disperse Pt on Si-MCM41.142 The chemical composition of the support materials is also an important criterion especially in the case...
of reducible support materials. By way of illustration, perovskite type mixed oxides exhibit redox properties that can be directly involved in the NO\textsubscript{x} reduction. The pre-activation thermal treatment can also influence the kinetics. Indeed, a pre-reduction of Pt/LaCoO\textsubscript{3} at moderate temperature, i.e. 250 °C, will not alter the structural properties of the perovskite. Hence, the reaction will take place over metallic Pt sites. On the other hand, a pre-reduction at high temperature leads to an extensive reduction of the perovskite. As a consequence, the growth of the Pt–CoO\textsubscript{x} interface modifies the kinetics of the NO/H\textsubscript{2} reaction shifting from single to a dual site reaction mechanism.

Important kinetic features come from a combined theoretical and experimental approach, especially to explain the high reactivity of the noble metals which activate the NO/H\textsubscript{2} reaction below 100 °C. A particular attention was paid to the potential assistance of chemisorbed H atoms to dissociate NO molecules (see Scheme 1). This step is generally slow in the overall reaction process. Fig. 14 reports DFT calculations emphasizing a decrease in the activation free energy when H atoms are involved in the NO dissociation step. The resulting adsorbed HNO\textsubscript{2} intermediate can undergo several transformations leading to adsorbed NH and O species while the subsequent H-addition can produce HNOH with a lower Gibbs energy, i.e. 40 kJ mol\textsuperscript{-1} instead of 135 kJ mol\textsuperscript{-1}. In this latter case, a bridging site is needed for the stabilization. Subsequent scenarios can be envisioned regarding the dissociation of chemisorbed HNOH intermediates producing either N ads and H\textsubscript{2}O or adsorbed NH and OH groups. The calculations of the activation barrier lead to lower values in this later case. Let us note that the preferential formation of the adsorbed NH intermediates can give rise ultimately to N\textsubscript{2}, N\textsubscript{2}O and ammonia.

In case of supported bimetallic catalysts, multiple interactions can be envisioned between the two metals and/ or each metal at the interface with the support. These can exert specific interactions. The strength corresponding to these different interactions will drive differently the kinetics corresponding to different types of reaction mechanism. It was also found that the catalytic NO/H\textsubscript{2}/O\textsubscript{2} reaction on supported Pd and Pd–Rh catalysts on alumina obeys to different kinetic routes. The dissociation of adsorbed NO molecules is rate-limiting on Pd/Al\textsubscript{2}O\textsubscript{3} occurring on free neighbour Pd sites released thanks to the rapid intervention of the H\textsubscript{2}/O\textsubscript{2} reaction. On the other hand, chemisorbed H atoms at the vicinity of adsorbed NO molecules will ease the N–O bond breaking on Pd–Rh/Al\textsubscript{2}O\textsubscript{3}. Consistently, N\textsubscript{2} and N\textsubscript{2}O formation only involves Rh sites and the selectivity is governed by the strength of the NO adsorption over Rh as above-mentioned. Let us note that this latter kinetic feature is in accordance with preferential adsorptions of NO on Rh while H\textsubscript{2} would adsorbed dissociatively on Pd.

Pd–Ir/TiO\textsubscript{2} catalyst also develops a high catalytic activity for the NO/H\textsubscript{2}/O\textsubscript{2} reaction under lean conditions in comparison to Pd/TiO\textsubscript{2} with a much broader operating
2.4. Possible recommendations for the development of efficient catalytic after-treatment systems for H₂-fueled engines

NOx abatement from H₂-fueled engine could proceed thanks to the selective catalytic reduction using hydrogen (H₂-SCR) as reducing agent. Up to now, PGM catalysts have been essentially developed as described. In practice, no commercial application relies on this technology, probably due to a narrow operating window. For the three-way catalysts the feasibility to remove efficiently NOx is closely related to the temperature and the H₂/NO ratio. Indeed, Lin-Zhi et al. claimed from a TWC simulation model, using a perfectly stirred tank model and experimental measurements from a 2.3 L turbocharger hydrogen engine, that a quasi-complete NO removal can be achieved when the temperature reaches 400 °C for a H₂-to-NO ratio equal to 1.5. The main drawback under slight rich conditions is reflected to ammonia production as undesired side product due to its toxicity. The weak selectivity of hydrogen also limits the efficiency for lean-burn applications. It is well illustrated in Fig. 13 a loss of NOx conversion occurs in large excess of oxygen with a rise in temperature. The practical solution in that case mimics those already described for methane application with dual systems consisting in coupling LNT with the SCR process. The key point lies in the regeneration step with hydrogen producing NH₃ that can be further stored and used in ammonia-SCR catalysts. In such a configuration a gain in efficacy to NOx removal is expected. As shown in Fig. 15, improved NOx conversion, accompanied by an enhanced formation of ammonia, is obtained with a rise in the H₂ composition during the regeneration step of the LNT. This may open new opportunities in the valorisation of in situ formed NH₃ through the downstream LNT of the NH₃-SCR system. According to previous discussion a dual-layer system could be envisioned to promote on the same monolith both the NOx storage/reduction to ammonia and selective catalytic reduction reaction during periodic lean period. In the particular case of H₂ blended with ammonia a simpler catalytic NOx abatement system could be envisioned in lean conditions associated to unique ammonia-SCR catalyst.

Returning to H₂-SCR systems, there is a renewed interest thanks to the emergence of hydrogen internal combustion engines. PGMs exert high activity but often restricted to low temperature, i.e. below 200 °C. The preservation of their metallic state, recognized as active phase to promote fast dissociation of H₂ and NO and prevent the formation of undesired nitrate species, in a broader operating window is a key point under lean conditions. A careful monitoring of the hydrogen coverage is prerequisite to insure a fast reduction of NO which means that the energy barrier for H₂ dissociative adsorption on metallic noble metal particles must be lower than that of direct NO dissociation. As described in section 3.2, great efforts have been provided through support effects and doping strategies to preserve the metallic state of Pt, Pd and Rh in active phases. However, finding relevant methodologies to broaden the operating windows of PGM at high temperature and also improve their selectivity to nitrogen production still remain grand challenges. Indeed, at low temperature, the significant production of N₂O acting as potent greenhouse gas must be avoided. The presence of SO₂ and H₂O can lead to detrimental effects through poisoning effects. Hence, the resistance to contaminant must be better considered by academia especially with the perspective to lower the metal loading targeting below 0.5 wt%. Compensation effects need to be found out thanks to novel approaches to increase the turn-over-number of PGMs. This can imply a careful control of the size and the morphology of PGM nano-sized particles. Indeed, the segregation of smaller Pd particles onto CeO₂ led to improved catalytic activity in the temperature range 130–220 °C. A salient observation is provided from DFT calculations on iridium. Indeed, Ir was found less active than Pt and Pd in the NO/H₂ reaction, but DFT predicted higher catalytic activity than Pt and Pd preferentially on (211) facet.

Presently, the lack of precise insights on reaction mechanisms for the NO/H₂ reaction is an obstacle in the development of novel practical approaches to increase intrinsic activity and stability at high temperature of PGMs. A broad number of catalytic formulations has been explored leading to different single and/or dual-sites reaction mechanisms. Their prevalence can be determined by the operating conditions, i.e. temperature and NO/H₂ ratio, as well as many parameters characterizing the PGM–support interface, the oxidation state of PGM, the redox and

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**Fig. 15** Pt/Ba/Al₂O₃ catalyst: NOx conversion at 400 °C under cycling lean (60 s, 500 ppm NO, 10% H₂O, 10% CO₂) condition, NOx conversion (%) (gray column) and into NH₃ (black column) and related data. Influence of H₂ concentration in the rich pulses (1–6%). This figure has been adapted/reproduced from ref. 149 with permission from Elsevier, copyright 2011.
2.5. Combined technologies to improve the global catalytic efficiency

Different approaches have been already examined concerning the combination of catalysis with electrochemical assistance. As a matter of fact, non-faradaic electrochemical promotion of catalysis (NEMCA) can be a suitable strategy to control the surface composition of heterogeneous catalysts working under transient conditions, especially during lean/rich switches. Plasma assisted technology has been also extensively studied, particularly for the atmospheric pollutant removal. Such hybrid technologies could meet some recommendations related to the reduction of critical materials and/or to activate atmospheric pollutants at lower temperature. In practice, contrasted observations were reported. For plasma catalysis, lab-scale experiments did not lead to a mature technology for further extrapolation at industrial scale. Some controversies regarding the main parameters controlling their efficacy, i.e. input energy for plasma discharges and/or catalysts compositions, still remain unclear. The formation of secondary pollutants such ozone can be promoted and must be avoided. The generation of \( \text{OH} \) radicals is also a critical point increasing the concentration of \( \text{NO}_2 \) and nitrates which deactivate the catalysts. Nonetheless, some improvements seem to be noticeable showing that the formation of poisonous by-products, i.e. \( \text{O}_3 \) and \( \text{NO}_x \), can be controlled by lowering the input power.

More recently, the induction heating has been profitably used. In principle such a method could be suited to activate refractory molecules at low temperature. In practice this method earlier described consists in transferring energy produced from radiofrequency directly to materials exhibiting magnetic properties through an absorption process at an appropriate frequency characteristic of the material. The main advantage provided by this technique is to avoid a temperature gradient. Consequently, the energy needed to activate the reaction is directly supplied then reducing the heat dissipation. Such a concept could be profitably used during the laps of time corresponding to the start up when the three-way catalyst has not reached its optimal operating temperature. Presently, most of papers report studies of methane reforming which is a reaction of interest in the post combustion catalysis. Interesting observations pointing out that the temperature obtained at the surface through induction heating depends on the surface properties, i.e. metal loading and particle size distribution. Based on this, such a relationship would offer some prospects to optimize the global efficiency of such systems by controlling properly the growth of the surface thanks to appropriate preparation methods.

2.6. Towards the development of PGM free catalytic after-treatment systems: dream or reality?

The reduction of critical materials with respect to economic importance or supply risk has been put forward by the European Community. Among them, PGMs and rare earths are extensively used in the post combustion catalysis and represent important targets for which a minimization in their utilization is strongly recommended, particularly in postcombustion catalysis. As a matter of fact, continuous efforts regarding the reduction of the PGM loading has been illustrated in this review article consisting in the addition of promoters such as base transition metal oxides. Among these, \( \text{CoO}_x \), \( \text{MoO}_x \) have been extensively used. Thanks to their interaction with PGM, geometric or electronic effects can be promoted that improve the PGM dispersion and modify their adsorptive properties. Support effects have also been extensively examined to stabilize highly-dispersed nano-sized PGM particles and/or control their oxidation state.

Technical advances to improve the efficiency of catalytic after-treatment systems face to significant issues. Indeed, reduction and oxidation reactions should occur simultaneously in a narrow range of temperature. Such conditions can be only fulfilled for three-way catalysts. For lean-burn applications, CO and HCs are readily oxidized on DOC and will be no longer available to reduce \( \text{NO}_x \) into \( \text{N}_2 \). As previously explained, a sequential reduction process of \( \text{NO}_x \) reduction must be set up. An interesting study has been earlier reported for LNT coupled to SCR catalyst systems for
the treatment of diesel emissions. The authors have compared the performance of LNT containing low and high PGM contents combined or not with SCR system. The question is not directly related to the extrapolation of these configurations to H₂-fuelled engines but more to the opportunity to reduce the use of PGM in LNT without altering significantly the efficiency. As illustrated in Fig. 16, no drastic change in the catalytic behaviour is noticeable with low or high PGM loadings for the LNT systems. This seems an interesting observation for further scale-up utilization.

A scenario already explored at the lab-scale but never developed due to persistent kinetic limitations is the catalytic NO decomposition. As a matter of fact, NO decomposition is the simplest reaction that can be envisioned leading to the release of N₂ and O₂ reaction products. In the absence of a reducing agent, already consumed in large excess of oxygen, this reaction is feasible and corresponds to the most cost-efficient catalytic NOx abatement process without the need for a reducing agent. However, some challenges remain associated to a strong kinetic limitation due to an oxygen-inhibiting effect. As the consequence, high temperatures are usually needed to desorbed oxygen. In the absence of a reducing agent, a complete NO conversion over Ru, Pt, Pd and Rh can be observed above 800 °C. However, among the different PGM, iridium appeared as the most competitive as NO is removed more readily than CO which means that NO decomposition is morefavoured on iridium compared to other PGMs. Subsequent doping with gold shows that the method employed for gold incorporation can lead to various geometrical or electronic effects with an electron transfer from Ir to Au. Interestingly, these authors found that geometric effects outweigh electronic effects, suggesting that the CO/NO and CO/O₂ reactions are structure-sensitive. Such structure-sensitivity was also observed on Pd/α-Al₂O₃. Both, the turnover number and the apparent activation energy measured for the NO decomposition and the NO reduction by CO on Pd/α-Al₂O₃ depends on the Pd particle size, smaller particles being more active. For small particles, a strong Pd-support interaction would lead to the growth of a preferential surface presumably ascribed to the (111) facet. Pisanu et al. also showed that small particles can accommodate a greater amount of oxygen compared to large Pd particles. But this factual observation was not related to a weaker inhibiting effect of oxygen.

A recent study reports the performance of Pt single atoms deposited on a carbon support. The development of supported catalysts for which the active phase is atomically dispersed is cost-efficient. By this way, we can rationalize the amount of active phase in order to reduce this one still maintaining high catalytic performance. However, this approach is suitable if single atoms remain stable at the surface and do not coalesce to form large aggregates in the course of the reaction. As illustrated in Fig. 17, the temperature of the pre-reductive thermal treatment prior to the reaction is a crucial parameter. On sample pre-reduced at 250 °C, NO decomposes at low temperature on single atoms of Pt/C. On the other hand, the single atoms sinter into large particles when the reduction was carried out at 500 °C (see Fig. 17(A) and (B)). Therefore, the decomposition of NO is strongly delayed above 400 °C. It was also found that single Pt atoms are remarkably stable in lean conditions which make them suitable in lean and wet conditions. Nonetheless, the most critical parameter ascribed to oxygen-inhibiting seems to be strongly attenuated when Pt is atomically dispersed. On the contrary, this detrimental O₂-inhibiting effect is restored on sintered Pt particles even though the particle size remains lower than 10 nm.

In fact, the decomposition of NO was more extensively investigated on single and mixed metal oxides. As a matter of fact, it was expected that these variety of materials would be less sensitive to O₂-inhibiting effect even though they are intrinsically much less active than PGMs. Unfortunately, the presence of gaseous oxygen induces in most cases side detrimental effects. For instance, Co–Mg–Mn–Al mixed oxides containing Co³⁺ and Mn⁵⁺ in an appropriate octahedral coordination oxidizes NO to NO₂ leading to unreactive surface nitrates species. Similarly, on doped-spinel K–Zn₁₋ₓCoₓO₄ catalysts supported on α-Al₂O₃, Grzybek found a strong inhibiting effect due to the
accumulation of nitrates which decompose above 550 °C. While lab- and pilot-scale experiments revealed a comparable contamination, structural changes also occur in this latter case showing that the (100) surface is less sensitive to contamination than the (111) surface. All these observations emphasize the fact that an extra reducing agent would be still needed to suppress the deleterious effects due to nitrate accumulation blocking the active sites.

3. Conclusion and outlooks

This review focused on the adaptation of existing catalytic after-treatment processes in case of the substitution of liquid fuels by gaseous fuels. A particular attention was paid to methane and hydrogen. Presently, such resources are not fully green but their homogeneous combustion leads to lower atmospheric emissions, especially particulate emissions which seriously complicate the existing architecture of end-of-pipe technologies for the diesel exhaust. Hence, in case of low detection limit complying with the regulation then the implementation of filter particulates could be no longer needed.

In the particular case of methane, different richnesses can be considered. For the three-way catalysis, palladium is the benchmark to remove methane. The Rh addition is needed to comply with the NOx emission level. The main targets are related to: (i) improved resistance to deactivation at high temperature and improved tolerance to poisoning effects at low temperature, typically during the cold start engine, and – (ii) the suppression of ammonia formation in slightly rich conditions. This latter case represents a gran challenge because this supposes the suppression of H2 production from the steam reforming reaction. Based on this, new opportunities appear related to the set up a passive ammonia-SCR system downstream the TWC. Indeed, the stored ammonia during the rich cycle would react with unreduced NOx on the TWC in lean switching. For lean-burn applications, the oxidation reactions are strongly favoured. Hence, an extra reducing agent is principle needed to reduce NOx. A simple architecture would consist in coupling DOC with urea-SCR system. The advantage of this latter system is related to the absence of PGM in its chemical composition. However, the complex optimization to avoid ammonia leakage can be considered as a serious obstacle. LNT system can be an alternative but similarly to TWC, PGMs are extensively used. Certain advantages could be obtained by coupling LNT with SCR in terms of gain in efficiency but also in a more rational use of precious metals making it possible to envisage a reduction in their load in LNT systems.

H2-powered engines could be the best option but a serious drawback is associated to the production of green hydrogen to have a significant impact on the carbon footprint. Ammonia and methanol can be also produced from hydrogen and used as alternative fuels. Hence, H2, NH3, or bi-fuel H2–NH3 powered engines can be envisioned. It appears that this type of motorization complies more for the decarbonization of the marine industry but also leads to high concentrations of NOx in the exhaust. The problematic linked to the sulphur tolerance would be no longer prevalent except in case of potential pollution due to lubricant. On this basis a simple catalytic-after treatment could be envisioned for H2-fuelled engines breaking with existing technologies. Indeed, the simplest one is associated to the catalytic decomposition of NOx. This reaction suffers from significant kinetic limitations. However, the sharp inhibiting effect of oxygen can be strongly attenuated over noble metals when they are quasi atomically dispersed. The gran challenge is related to their stability especially in rich conditions. Obviously, this constraint restricts their application to lean-conditions. However, this approach undoubtedly goes to a better rationalization in the use of PGMs. In case of ammonia-fuelled engines the classical ammonia-SCR seems to be the best available technology.

Finally, the complete replacement of PGMs for the depollution of light-duty vehicles irrespective of the richness will not comply to a more severity of the regulations in the next Euro 7 regulations. An important target lies the development of catalytic device working at low temperature. Obviously, this scenario could be more profitable for H2-fueled engines than CH4-engine regarding the high energy demand to activate methane.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Y. Zheng and A. Decoster collected and selected the literature data. V. Parvulescu participated in the writing the draft, reading and polishing the final version. Pascal Granger conducted the writing of the review and finalized the final version. Prior to submission, all the authors approved the submitted version.

Conflicts of interest

There are no conflicts to declare.

Notes and references

94 L. Wei, H. Zhang, C. Sun and F. Yan, ISA Trans., 2022, 126, 679.
100 M. Sunil Kumar, M. S. Alphin, S. Manigandan, S. Vignesh, S. Vigneshwaran and T. Subash, Fuel, 2023, 344, 128125.


