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DeNO$_x$ removal techniques for automotive applications – A review

David Maizak[a], Tabbi Wilberforce[b,*], A.G. Olabi[b,c]

[a] Institute of Engineering and Energy Technologies, University of the West of Scotland, Paisley, UK
[b] Mechanical Engineering and Design, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, UK
[c] Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah, United Arab Emirates

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ABSTRACT

A sector that contributes immensely to global warming due to the release of harmful gases into the atmosphere annually is the automotive industry. This has led to several optimization of diesel engines from their initial inert system with lower power density to fast running types with higher power densities. Despite these modifications coupled with the introduction of Diesel Oxidation Catalyst (DOC) and Diesel Particulate Filter (DPF), there are still environmental concerns that need to be critically analyzed. The current types of diesel engines have challenges pertaining to NOx reduction due to their lean operations. These limitations further led to the technological evolution of Selective Catalytic Reduction and NOx storage catalysts (NSC). This investigation therefore explored the current state of Selective Catalytic Reduction (SCR) and NOx storage catalyst (NSC). The effect of temperature and uniform distribution of ammonia associated to these technologies were critically reviewed. Factors impeding the integration of these technologies in the automotive industry were also discussed Possible solutions to mitigate these challenges were proposed. From the review gathered, there is still the need for further research activities in this field in terms of optimization to enhance the overall performance of diesel engine cars with lower toxic emission.

1. Introduction

Fossil product demand keep increasing despite efforts made by the research computing in developing alternative sources of energy generation. Several factors can be attributed to the high demand of fossil products (Ijaodola et al., 2019). Notable among them are increase in population and technological advancement. The high reliance on fossil products comes with some consequences (Khatib et al., 2019; Ogungbemi et al., 2019; Wilberforce et al., 2019d; Olabi et al., 2020d). The first of these challenges has to do with climate change as the burning of these fossil products lead to emissions of toxic substances into the atmosphere (Wilberforce et al., 2016, 2018, 2017b, 2017a, 2019c, 2019b, 2019g, 2019a; Ijaodola et al., 2018; Baroutaji et al., 2019). Again, the prices of these fossil products are also unstable coupled (Wilberforce et al., 2017a, 2017b, 2017c, 2017d, 2019f, 2019e; Wilberforce and Olabi, 2020b, 2020a). Fossil reserves are also gradually becoming depleted hence the urgent need to find ways of addressing this challenging subject (Olabi et al., 2020b, 2020c, 2020a, 2021; Abdelkareem et al., 2020; Elsaid et al., 2020; Khatib et al., 2020). The world in general has come up with several agreement like the Paris and Kyoto agreement to check the total emissions into the atmosphere annually (Ogungbemi et al., 2020b, 2020a; Abdelkareem et al., 2021; Rabaia et al., 2021) One sector that has significantly failed to meet this task is the automotive industry. This can be attributed to the high demand of vehicles in recent times compared to a decade ago. Vehicle today are significant for mobility and luxury. There are many types of vehicles manufactured yearly (Olabi et al., 2020d). From electric to diesel engine vehicles, these automotive machines are designed in tandem to strict regulations and policies. The diesel engine is mostly preferred by many due to its high fuel economy but it is also one of the largest sources of pollutants into the atmosphere. Carbon dioxide, carbon monoxide, nitric oxide etc. are some of these pollutants generated as a result of using these diesel engine vehicles. This review therefore presents techniques to reduce these toxic emissions and highlights the future of these sectors.

1.1. *Selective Catalytic Reduction (SCR) with NH$_3$*

Since the1970s, a technique has been used in stationary application in power plants to reduce nitric oxides (Olabi et al., 2020d). This technique is called Selective Catalytic Reduction (SCR). It was first applied in heavy duty applications in the automotive industry in 2004. Today, all newly released heavy-duty vehicles are equipped with an SCR system. With the introduction of the Euro6 standard, Original Equipment Manufacturer (OEMs) started to equipped passenger cars with the SCR system as well.

Principle of operation: The SCR technique uses ammonia to convert nitric oxides to molecular nitrogen, because it offers the possibility to

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[*] Corresponding author.
E-mail address: awotwet@aston.ac.uk (T. Wilberforce).

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Table 1
Matrix of properties of different coatings for SCR applications.

	Vanadium-based	Iron-based	Copper-based	MMO-based
Performance at low temperature	+	-	++	0
Performance at high temperature	0	++	+	-
High temp durability	-	+	++	0
Performance with low NO_2	0	-	++	+
Performance with high NO_2	-	++	0	+
NH_3 storage ability	-	++	0	+
Selectivity (N_2O)	++	-	0	+
Sulfur tolerance	++	+	-	0
SCR cost	++	+	0	-

++, very good; +, good; 0, average; -, poor; –, very poor.

achieve high conversion rates in temperature and flow velocity fields of a current diesel engine (Olabi et al., 2020d).

For this reason, there were several different approaches developed for the usage of ammonia. The final decision by the OEMs was made in favor of the usage of urea ($CO(NH_2)_2$) diluted in a water solution. It is not toxic in this form, and it is produced worldwide on a large scale (Halonen et al., 2017), which makes it widely available and affordable.

The trade name for the urea-water solution is AdBlue in Europe and DEF (Diesel Exhaust Fluid) in the US. Since the urea content of AdBlue and DEF is predefined, it will be referred to as UWS (urea-water solution). In the automotive industry, urea with a concentration of 32.5 wt% is typically used. This concentration was chosen because it is the concentration with the lowest crystallization point of −11 °C even though higher concentrations of up to 50 wt% could be achieved. Detailed properties of urea are published by Halonen et al. (2017). Regarding the evaporation, the various solutions only slightly differ in terms of the boiling point. Industry technical information leaflets that were found state the boiling point to be 100 °C (AdBlue2008), whereas the findings of van Vuuren and Sayar (2012) based on technical information of indicate a boiling point of 104 °C.

In regards to the suitability of UWS for current catalysts, Yim et al. (2004) and Yang et al. (2015) found that the zeolite catalyst exhibits good catalytic performance and supports the decomposition of urea (HNCO to NH_3), which increases with increasing temperature and exceeds 80% at 250 °C and can even reach 100%.

These metals would lead to decreased efficiency of the catalyst. However, the SCR process involves the injection of the urea-water solution (UWS), which undergoes a decomposition process, releasing the ammonia as detailed below. Recent SCR systems have a mixer between the injector and the catalyst, which generates turbulences to distribute the ammonia uniformly and breaks the droplets up into finer ones easier to distribute and easier to heat up.

Catalyst: Two groups of base metal SCR catalysts—vanadium and zeolite-based—have recently been of great interest for use in the automotive field. For passenger car applications, zeolite-based catalysts are predominantly used. These consist of crystalline microporous alumina silicates with an Al_2O_3 wash coat and with a copper or iron coating. While iron-zeolites show a high temperature performance of between 350 °C and 600 °C (Heck et al., 1994; Yim et al., 2004). Copper-zeolites exhibit higher activity at low temperatures of between 150 °C and 450 °C (Cheng et al., 2016). Table 1 shows different coatings in terms of their pros and cons.

As explained in Olabi et al. (2020d), the trend is moving towards lowering fuel consumption, which is directly linked to lower exhaust gas temperatures. Therefore, especially copper is currently favored by the automotive industry since cu-based SCR catalysts exhibit higher activity at lower temperatures (Kim et al., 2012).

As shown by Ma et al. (2013), modern coatings achieve NO_X conversion rates of approximately 65% at temperatures as low as low as 140 °C and conversion rates of almost 90% at 165 °C, if when the NO_2/NO_X ratio is 50%. Moreover, as shown by Holderbaum (2009), manufacturing catalysts with microporous structures assists the SCR process at low temperatures, aiding in NO_X conversion for a short time where the UWS injection is partly suspended at cold start and low load conditions. This can be attributed to the ammonia storage effect of the catalyst, which provides ammonia in a temperature range where the UWS injection is not possible due to the effects explained above. As described by Kamasamudram et al. (2010), a copper-based catalyst offers the capability to store about 0.5 g/L of ammonia at exhaust gas temperatures below 150 °C. As found by Colombo et al. (2010) even at exhaust gas temperature of around 180 °C, this can provide a 30% conversion rate of both NO_X and ammonia. In this way, the NH_3 storage effect of the catalyst contributes significantly to DeNOxification at low exhaust gas temperatures.

However, since the stored ammonia is limited, the provision of UWS by injection needs to provide new ammonia as soon as possible. A comparison of the efficiency as a function of the O_2 and NO/NO_2 ratio for an exhaust gas temperature of 200 °C (left) and 300 °C (right) of the aforementioned catalyst coating as shown in Fig. 1.

However, a new trend is shown by Sultana et al. (2013). The studies revealed the advantages of combined Fe and Cu zeolite SCRs in sequential bricks, mixed wash coats in one layer and dual layer catalysts with both coatings have the advantages of increased high and low temperature activity. One challenge is that zeolite-based catalysts may be prone to stability problems when exposed to high temperatures in the presence of water vapor. When exposed to temperatures above 600 °C in a high water content process stream, zeolites tend to deactivate. Due to the necessity to regenerate the DPF, these high temperatures are reached frequently. A theoretic way to reduce the frequency of DPF regeneration could be the increase of NO_X generation by combustion. This would first lower the soot generation, thereby reducing the regeneration rate, and secondly increase the Continuously Regenerating Technology (CRT) effect, which would also reduce the necessity to regenerate.

Chemical reactions: As explained above, NH_3 is injected into the exhaust line as urea dissolved in water. The process to generate involves at least eight preceding steps before reducers ammonia can be generated from UWS as shown below in Fig. 2 (Koebel and Strutz, 2003).

The diagram above details the energy required for the eight preceding steps of the generation of reducers ammonia from UWS. As can be deduced by this diagram, the thermal decomposition of urea depends greatly on a comparatively high amount of heat. As stated by Koebel and Strutz (2003) and detailed above in the present studies, one of the main challenges is that the residence time of the urea droplets upstream of the catalyst is insufficient. However, the main reactions according to their relevance are explained below. As can be seen in the diagram above, the first reaction is the evaporation of the water according to reaction scheme as shown in Eq. (1)

$$CO(NH_2)_{2(aq)} \rightarrow 0.126\ CO(NH_2)_{2(m)} + 0.874\ H_{2(g)} \tag{1}$$

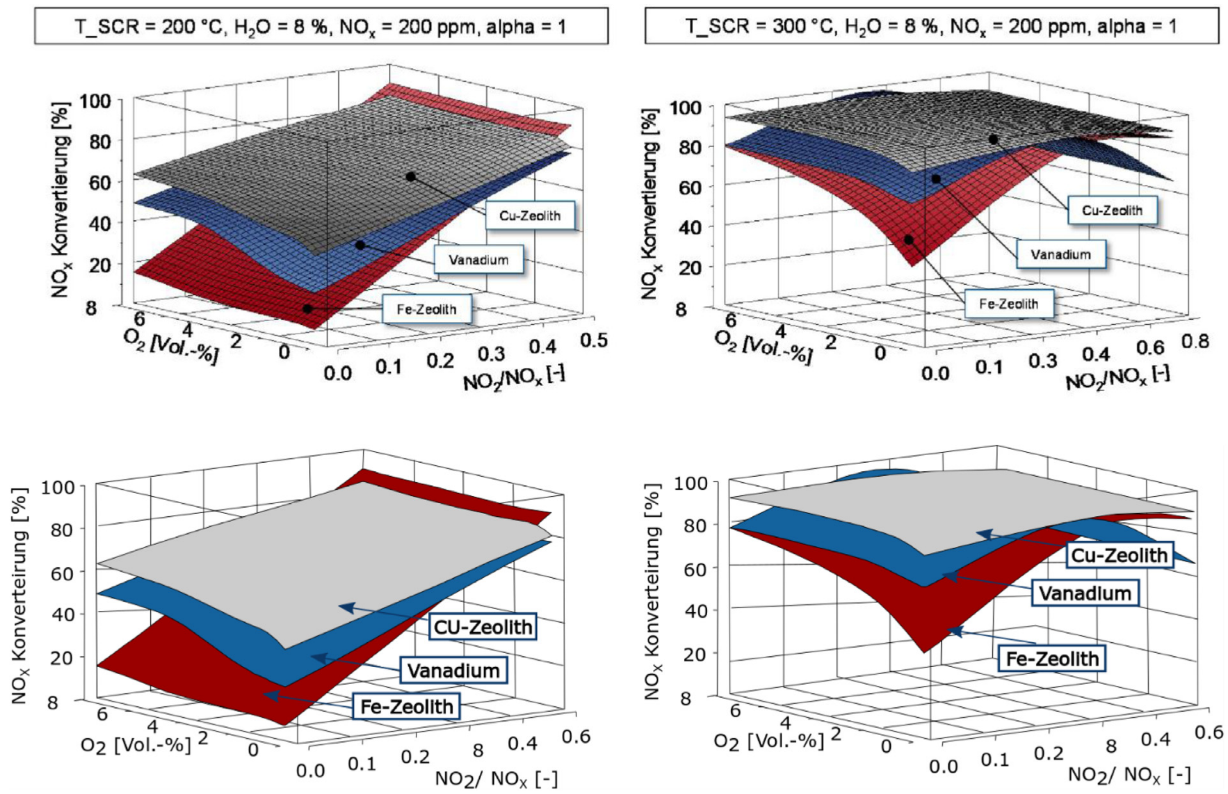

Fig. 1. Trade-off between brake-specific NO_X and soot emissions in different test modes at EOP 1750 rpm and 4.5 bar bemp (Zamboni and Capobianco, 2012).

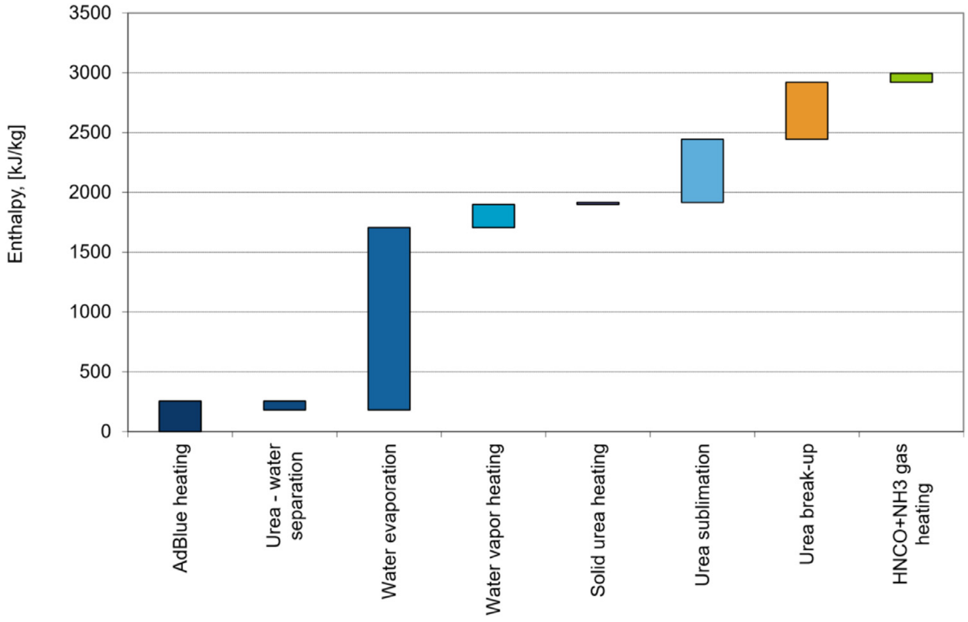

Fig. 2. Energies required to convert UWS into reducers NH_3 (Koebel and Strutz, 2003).

which is ideally followed by the decomposition in a two-step process, explained by several authors, such as Koebel et al. (2000) and Fang and DaCosta (2003). In the first step, the urea break ups in a reaction called thermolysis, forming ammonia and isocyanic acid (HCNO) as shown in Eq. (2).

$$CO(NH_2)_2 \rightarrow NH_3 + HCNO \tag{2}$$

The first step of thermolysis is the primarily temperature-driven decomposition of urea. The reaction speed can be defined with the Arrhenius equation with the frequency factor of A=0.42 and activation energy E_a=69,000 J/mol (Fang and DaCosta, 2003).

$$k = D*A*e^{\frac{E_a}{R*T}} \tag{3}$$

As found by Birkhold et al. (2006), the solid urea melts, evaporates and dissociates into ammonia and isocyanic acid at temperatures of more than approximately 133 °C (Schaber et al., 2004). It is worth mentioning that, as indicate by Koebel and Strutz (2003), the thermal decomposition of urea upstream of the catalyst might remain low even if temperatures are actually high enough to promote the reaction. From investigations in literature, the main challenge is the insufficient heat

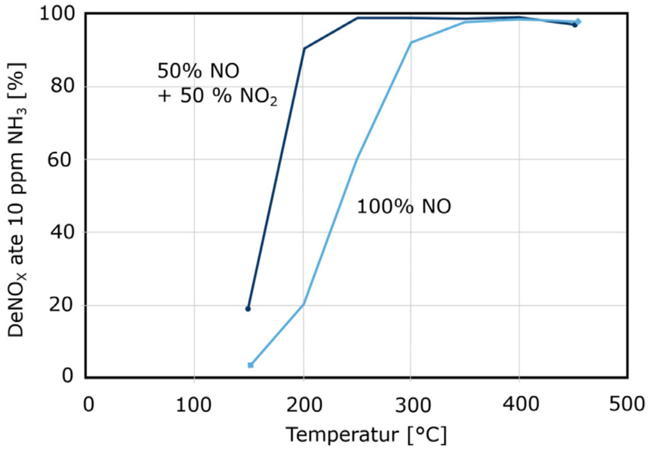

Fig. 3. DeNO$_X$ at 10 ppm NH$_3$ slip for standard SCR and fast SCR as a function of temperature. GHSV = 52,000 h^{-1}, base feed with 1000 ppm NO$_X$, NH$_3$ varied (Koebel et al., 2002).

transfer from the exhaust gas to the UWS droplets to evaporate urea and initiate thermolysis within the short timeframe the urea has before reaching the catalyst. The result is the reaction shown below. A hydrolysis in which the HCNO reacts with water and produces an additional NH$_3$ molecule, which is adversely affected by the preceding thermolysis of urea and the availability of HNCO.

$$HCNO + H_2O \rightarrow NH_3 + CO_2 \tag{4}$$

A way to enhance the process is proposed by Jeong et al. (2005), who found that droplets should be finely atomized to raise the rate of evaporation and therefore the DeNO$_X$ efficiency. Moreover, as found by Yim et al. (2004), hydrolysis would commence only slowly within the gas flow due to isocyanic acid being quite stable in the humid gas phase at temperatures below 400 °C (Piazzesi et al., 2006).

$$CO\,(NH_2)_2 \rightarrow 2NH_2 + CO \tag{5}$$

This thermal decomposition is confirmed by the proven formation of CO during SCR processes with urea (Held et al., 1990; Hug et al., 1993). The NH$_2$ radical can then react with NO as follows in Eq. (6).

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{6}$$

However, previously generated ammonia reaches the catalyst in an ideal process. The reaction pathways are shown below according to Nova and Tronconi (2014). According to Cho (1994), Eq. (7) represents the dominant reaction mechanism, since NO is the dominant NO$_X$ species in exhaust gas. Thus, this reaction is called the 'standard SCR reaction':

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{7}$$

NO$_2$ has also always been present in the exhaust gas in addition to NO since the introduction of the DOC hence the reaction according to Eq. (8) is also pertinent.

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \tag{8}$$

This reaction, with a stoichiometry of NO$_2$/NO of ideally one, is called "fast SCR reaction" and is the preferred reaction since it is very fast (Schaber et al., 2004). Ciardelli et al. (2007) indicates a factor of ten in comparison to the standard reaction. A second key point is that this reaction takes place at a low temperature, as stated by Gieshoff et al. (2001) and Koebel et al. (2002).

Therefore, this reaction is the dominant one at exhaust gas temperatures below 200 °C and necessary to achieve sufficient conversion rates. This behavior is shown in the Fig. 3 where the ordinate is the temperature and the abscissa is the denitrification efficiency. On the other hand, a reduction with if NO$_2$ exceed 50% of mole share is less favorable, once the temperature rises, as it is shown in Eq. (9) below.

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{9}$$

This is because it is much slower than the standard SCR reaction (Koebel et al., 2001) and is therefore called "slow SCR reaction". In addition, this reaction consumes more NH$_3$ and consequently increases the UWS consumption. An extensive overview of different NO/NO$_2$ ratios and their influence on DeNO$_X$ efficiency and the by-products generated is given by Ciardelli et al. (2007).

As suggested by Fang and DaCosta (2003), reactions displayed below in reaction schemes in Eqs. (10) and (11) may play an important role based on engine test results.

$$2(NH_2)_2CO + 6NO \rightarrow 5N_2 + 4H_2O + 2CO_2 \tag{10}$$

$$4HCNO + 6NO \rightarrow 5N_2 + 2H_2O + 4CO_2 \tag{11}$$

Two more reactions, Eqs. (12) and (13) were observed following the formation of N$_2$ [37].

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \tag{12}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{13}$$

Since oxygen is always present in exhaust gas it can interact with NH$_3$ in a desirable reaction, forming N$_2$ according to the reaction scheme in Eq. (14).

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{14}$$

On the contrary, there are also unwanted reactions because they, in the best case, only unproductively consume ammonia as described by reaction in Eq. (15).

$$4NH_3 + 3O_2 \rightarrow 4N + 6H_2O \tag{15}$$

Or, in the worst case, they can form secondary emissions such as nitrous oxide (N$_2$O) as presented in Eq. (16) and other toxic emissions.

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \tag{16}$$

Especially when the NO$_2$ content exceeds the stoichiometry of one, forming N$_2$O, as was stated by Madia et al. (2002) and shown in the reaction schemes in Eqs. (17) and (18).

$$8N_2O + 6NH_3 \rightarrow 7N_2O + 9H_2O \tag{17}$$

$$4N_2O + 4NH_3 + O_2 \rightarrow 4N_2O + 6H_2O \tag{18}$$

An overview of unwanted products as a function of temperature is given below in the Fig. 4.

It became apparent, not only the formation of the desired N$_2$ but also the formation of unwanted by-products depends greatly on temperature. Another point to consider was described by Willi et al. (1996) and Huang et al. (2002).

Some of the wanted reactions are inhibited by H$_2$O, which is always present in the exhaust gas. Furthermore, in conjunction with ammonia and NO$_2$, it can produce ammonium nitrate (NH$_4$NO$_3$) depicted in Eq. (19). Ammonium nitrate can build solid deposits in the pores of the catalyst, leading to its temporary deactivation [41].

$$2NH_3 + 2NO_2 + 2H_2O \rightarrow NH_4NO_3 + NH_4NO_2 \tag{19}$$

Additional undesired emissions can occur, for example NH$_3$ combining with the SO$_3$ formed by the upstream DOC to form ammonia sulfates, such as (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$, which deposits on and fouls the catalyst, as well as piping and equipment.

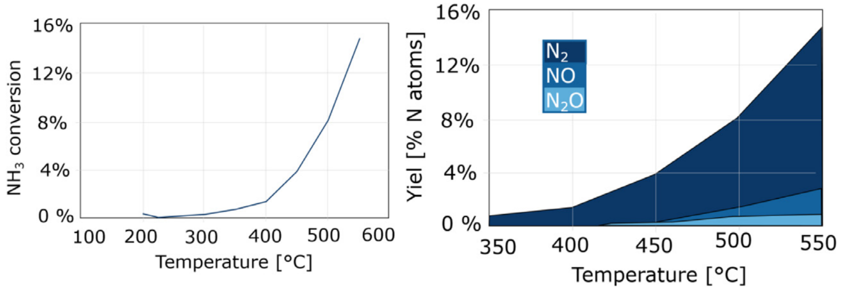

Fig. 4. NH_3 oxidation behavior (left) and its associated yield (right). Data collected with a fresh catalyst sample operated at a GHSV of 90,000 h^{-1} and a feed of 300 ppm NH_3, 10% O_2, 5% CO_2, 5% H_2O (Chen, 2014).

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \qquad (20)$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \qquad (21)$$

At low exhaust temperatures, generally below 250 °C, the fouling by ammonium sulfate may lead to a deactivation of the SCR catalyst (Wijayanti et al., 2015). Since modern diesel cars have a DOC installed upstream of the SCR catalyst, it is exposed to a mixture of SO_2 and SO_3. As shown by Cheng et al. (2009), sulfur poisoning has an impact, especially in the presence of oxygen and water, leading to severe ageing of the catalyst.

Regeneration: Although the deactivation of SCR catalysts due to sulfur poisoning does not have a grave influence on the permanent activity, it directly affects the overall SCR performance. Copper-based catalysts are highly prone, especially at low temperatures under 300 °C, as found by Cheng et al. (2009). If sulfur poisoning occurs, catalyst activity can be restored after exposing the catalyst to temperatures over 650 °C (Cheng et al., 2009). These temperatures can be reached in diesel engines at high load conditions or during the DPF regeneration (Jangjou et al., 2016). Another approach for regeneration was found by Kumar et al. (2016). He showed that enriching the exhaust gas with hydrocarbons, affects lower temperature demand. This leads to a reduced thermal ageing of system components and to a substantial reduction of the fuel penalty.

System layout: In recent applications there are two dominant systems: the under floor system and the close coupled system. This nomenclature describes the arrangement of the catalysts in the exhaust gas aftertreatment system. In addition to the catalysts, there are several other components, as shown in Fig. 5 below.

The tank consists of several components such as the pumps, the sensors to detect the filling level and in some cases the quality of the UWS, and a heating device to thaw the UWS at cold temperatures. Injectors are used to supply the UWS into the exhaust line. All recent systems have a static mixer installed between the injector and catalyst to enhance the uniform mixing of the ammonia with the exhaust gas. One challenge of the SCR process is that it requires precise control of the ammonia injection rate. If the injection is too small, the NO_X reduction cannot be fully completed. If the injection rate is too high, it can cause an undesirable ammonia slip into the environment and solid deposits on the exhaust line. The ratio of NH_3/NO_X for series production cars is between 0.9 and 1 (Olabi et al., 2020d).

These components are the same for both the under floor system and the close-coupled system, which differ only in the position of the SCR catalyst. In recent configurations, both systems include a DOC at the turbocharger outlet and a DPF installed close behind it and sometimes even in the same canning. For close- coupled systems, the DPF substrate is often used in conjunction with a SCR coating. The Diesel Particulate filter with SCR coating (SDPF) is the potential future method to enhance the functionality at low load points without the use of costly precious metals.

The intention is to bring the SCR catalyst close to the engine (heat source) and thus enable a faster light off. The system can be installed near the engine, which benefits exhaust gas with elevated temperature by avoiding heat loss. However, demand of good amount of NO_2 is needed for both DPF regeneration and NO_X conversion in the SCR. Furthermore, as shown by Tronconi et al. (2015), the integrated SCR and DPF efficiency is affected by increasing the soot load. This problem is obscured by an increased DPF regeneration frequency, but that eventually negatively affects the fuel consumption and CO_2 balance (Majewski, 2005).

In addition, the thermal load due to the high temperature during the regeneration process might accelerate the ageing of the SDPF and thus reduce its efficiency. Further the negative aspects of backpressure that influences in the increased fuel consumption needed to be accounted. This backpressure depends on the amount of coating materials in the SDPF in comparison to a conventional DPF or cDPF (coated Diesel Particulate Filter) (Nova et al., 2008).

Nevertheless, the mixing sections between the UWS injection and catalyst are also smaller. Consequently, evaporation, decomposition, uniform mixing, and distribution of UWS with the exhaust gas on the catalyst surface become more difficult (Dolanc et al., 2016). A new trend might solve these problems by using two SCR systems, called twin dosing. One installed close-coupled and the other in the under – floor.

Performance and challenges: At low exhaust gas temperatures at the SCR inlet, generally < 200 °C (Peter Lanzerath, 2011), the use of SCR technology is limited by:

- Slow and/or incomplete evaporation/decomposition of UWS into ammonia
- Low SCR reaction
- Formation of solid deposits
- Poor ammonia distribution.

The performance of the SCR system can be narrowed down to four essential factors: The thermodynamic conditions (temperature, space velocity), the accurate amount of ammonia and its uniform supply to the catalyst, the composition of the exhaust gas (presence or absence of species), and the character of the catalyst, especially its coating. Within this factorization the temperature and space velocity play a key role in the preparation of ammonia and its subsequent reaction over the catalyst. The temperature is important in terms of the energy supply for the involved reaction, whereas the flow velocity influences the time available for the reaction to take place. An overview of the conversion efficiency as a function of temperature and space velocity is given in Fig. 6.

Fig. 6 demonstrates that low exhaust gas temperatures have a grave influence on the conversion efficiency, as well as the space velocity. It must be taken into account that many more influencing factors, such as the NO_2/NO and the water content in the exhaust gas, can support or reduce the conversion efficiency, especially at low temperatures. However, the conversion efficiency is high within the temperature window of a common diesel engine.

Another important point that can influence the efficiency is the uniform distribution of the ammonia over the catalyst. The poorer the Uniformity Index (UI), the poorer the conversion efficiency. It is customary for the preparation of the injected UWS solution to combine very fine droplet sizes and a large spray cone to guarantee a good distribution of droplets over the entire mixing section. On the contrary, a poor dis-

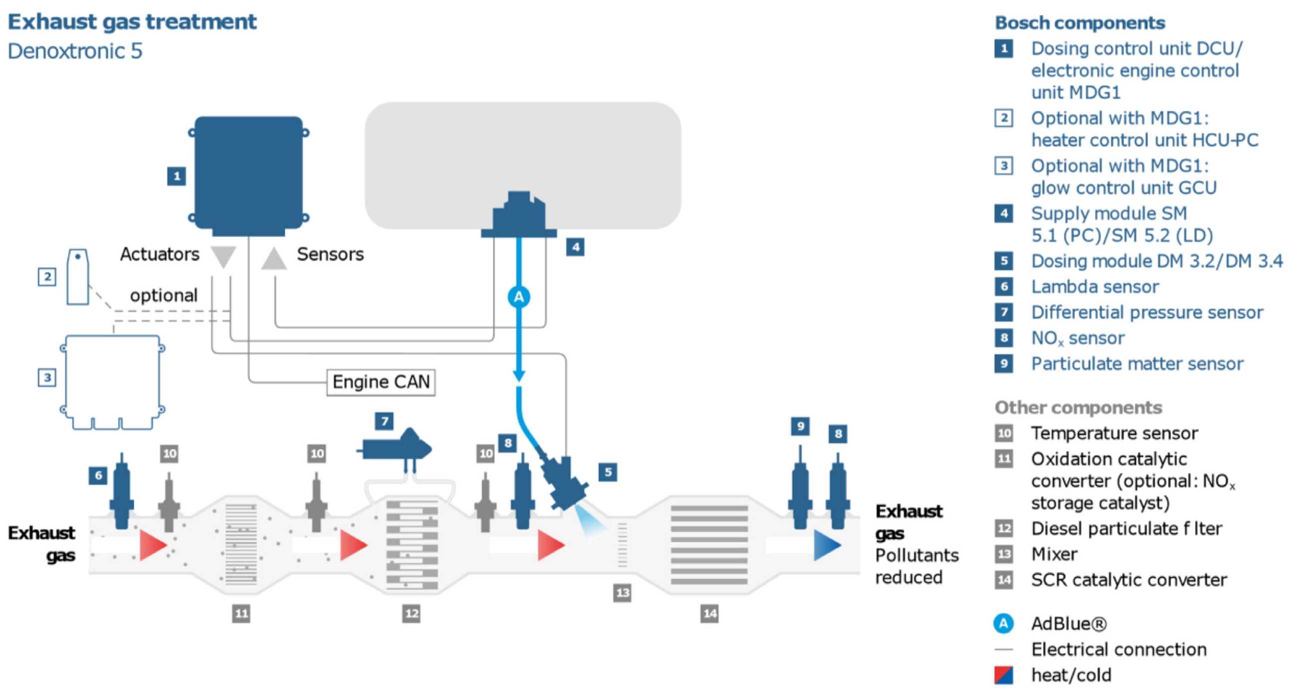

Fig. 5. Exhaust gas after-treatment system layout (Gmbh, 2013).

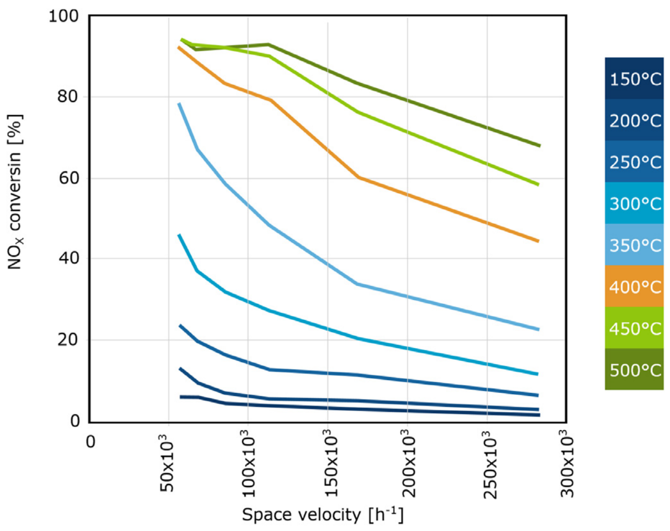

Fig. 6. Steady state NO_X conversions obtained during the standard SCR reaction studied on the commercial Fe-zeolite catalyst as a function of space velocity (Metkar et al., 2012).

tribution can result in a NH_3 breakthrough called ammonia slip in areas with a local oversupply of ammonia. As previously mentioned, the storage of ammonia in the SCR is temperature dependent. With quickly rising temperatures, the ammonia storage capacity in the SCR is over filled and starts to slip out of the Catalyst (Holderbaum, 2009). Another side effect of a non-uniform distribution or of a local over supply is the previously mentioned generation of solid deposits, especially at low exhaust line temperatures where the decomposition process is slow (Sluder et al., 2004; Xu et al., 2007). Therefore, the dosing strategy must be well adapted to avoid low conversion rates and also prevent the risk of ammonia slip.

A challenge comes with the cross sensitivity of NO_X sensors to NH_3 (Aliramezani et al., 2016). Accordingly, NH_3 slip would be interpreted as NO_X by the sensor, leading to an increased dosing, which would increase the NH_3 slip. This harmful release of ammonia gas can be contained by placing an anti-slip catalyst (ASC) or a precious metal coating at the end of the SCR, as described above. With this advanced technique, secondary CO emissions from the DPF regeneration process are also contained but eventually generate additional NO_X downstream of the SCR. This results in a negative impact of overall NO_X conversion efficiency, increased package complexity, and additional costs. In addition, an NO_X model is applied in the Engine Control Unit (ECU) of modern diesel engines to continuously validate the dosing strategy and prevent overdosing.

The current challenges of SCR-only are the consumption of large quantities of UWS at high mass flow NO_X rates, leading to the necessity of an additional UWS tank with negative impacts on the package, costs and vehicle weight. On the other hand, the SCR technique allows the engine to function independently from the exhaust gas aftertreatment, delivering an optimal thermal dynamic range with respect to fuel and power. Simultaneously, SCR has high potential to reduce high mass flow NO_X to a fare >95% (Mackensen, 2012) at temperatures above light-off. Hence, it is a favored technique for large engine segment vehicles and OEMs for controlling NO_X emissions into the atmosphere.

1.2. NO_X storage catalyst (NSC)

The concept of the NSC technique was introduced by Toyota laboratories (Takahashia et al., 1996; Matsumoto, 1996) and patented in 1995 by Takeshima et al. (1998). The NO_X storage catalyst (NSC) technique involves absorption and desorption, either to convert nitric oxide to nitrogen molecules by continuous shifting of lean-burn to rich-burn combustion and vice versa, or by re-releasing NO_X and converting it in reduction systems such as the SCR installed downstream. (Majewski, 2005) clarifies that different authors use different terms for active NO_X adsorbers, such as:

- NO_X storage catalyst (NSC)
- Lean NO_X trap (LNT)
- NO_X adsorber catalyst (NAC)
- DeNO_X trap (DNT)
- NO_X storage/reduction catalyst (NSR)

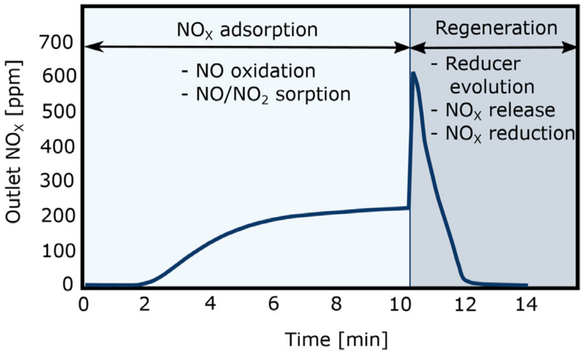

Fig. 7. NO$_X$ release profile in NO$_X$ adsorber (Epling et al., 2004).

and for passive applications, the

- Passive NO$_X$ Adsorber (PNA).

Operating principle: For the operating principle, it must be differentiated between the active system (NSC) and the passive system (PNA). Both catalyst types store nitric oxides (adsorb) under lean exhaust gas conditions (with the air/fuel ratio $\lambda > 1$). Once the active catalyst attains its threshold storage capacity, the desorption process is initiated by shifting to the rich-burn mode (with the air/fuel ratio $\lambda < 1$), converting NO$_X$ to N_2 due to the occurrence of HC, CO and H_2 in a conventional three-way process (Takeshima et al, 1998). A schematic overview is given in Fig. 7 above.

The passive adsorber only includes the adsorption, no conversion. Its desorption is triggered by the exhaust gas temperatures, releasing again the adsorbed nitric oxides. As a consequence, the application strategy is different to the active catalyst, which can be run as a stand-alone system. The PNA is supposed to adsorb the nitric oxides in modes where no denitrification can take place, and release them once the downstream DeNO$_X$ catalyst has reached its light-off, without switching to a rich mode (Theis and Lambert, 2015).

Catalysts: Both catalysts are made of a ceramic substrate and wash coated. The active catalyst is manufactured by coating three metal components: An oxidation component to generate NO_2 during the lean state (I), an absorption component to store the nitric oxides during the lean state (II), a reduction component to generate N_2 during the regeneration state (III) (Liu and Gao, 2011).

- Alkaline earth, primarily Ba-based absorbers
- Combined Ba + alkali metal (K, Na, etc.) adsorbers.

As Dou and Balland (2004) reported, Ba + alkali metal shows a higher DeNO$_X$ potential at higher temperatures (350 °C to 600 °C) and a superior sulfur resistance. The disadvantages are lower DeNO$_X$ efficiencies at low temperatures, in comparison to Ba-based adsorbers. Hence the adsorbers for passenger and light-duty vehicles prefer Ba-based catalysts. Many diesel NO$_X$ absorbers also include ceria in the catalyst wash coat to store oxygen in the lean-burn mode and release it in rich conditions (Epling et al., 2004). A broad overview of advantages and disadvantages of barium or other alkaline – earth metals is given in Shi et al. (2012) and Ji et al. (2008).

Since passive adsorbers do not involve an active regeneration strategy, it is mandatory for them to have both a high adsorbing capacity and being adapted to decomposable under lean conditions. Passive adsorbers commonly consist of materials such as alumina and ceria to store NO$_X$ and avoid the use of barium or other alkaline-earth metals, as these materials form more stable nitrates that require high temperatures or a rich exhaust gas environment for regenerating (Ji et al., 2015). To promote nitrite formation, it was shown by Melville (2012) that both adsorption and desorption of NO$_X$ in Pd-based systems involves primarily nitric oxide, especially at lower temperatures when practically all NO$_X$ is desorbed from the PNA in the form of NO. As Theis and Lambert (2015) elucidated, because of the want to oxidize NO to NO_2, active catalysts generally do not provide high NO$_X$ storage efficiency at temperatures below 150 °C.

However, for active applications, it is desired to form stable nitrates instead of nitrites compounds, releasing the nitric oxides on demand. As clarified by Epling et al. (2004), most NO$_X$ trapping materials can adsorb NO_2 more effectively in comparison to NO. Therefore, the first step is to oxidize the NO to NO_2 via a noble metal such as palladium (Pd) or platinum (Pt), with platinum currently being the primary choice for active adsorbers and palladium for passive adsorbers (Wang et al., 2013). An overview of the advantages and disadvantages of platinum and palladium coatings is giving by Salasc et al. (2002).

To form nitrogen molecules during the rich phase, rhodium has shown the highest reduction activity of Pt, Pd and Rh, according to Ohtsuka and Tabata (2001) and Roy and Baiker (2009). A detailed overview of the effect of different Rh loadings is given by Wang et al. (2013). Most recent series production vehicles and most studies in the literature deal with the Pt and Ba supported on-Al_2O_3 wash coat on a cordierite substrate, commonly designated as Pt/Ba/Al_2O_3. Therefore, all explanations that follow refer to Pt/BaO/Al_2O_3 catalysts. An overview of the basic working principle, including the lean NO$_X$ storage and the rich reduction phase is given in Fig. 8 below.

Storage, Lean-burn operation and generation phase: As explain above, the NO$_X$ in exhaust gases exits the engine mainly as NO. Due to the fact that most NO$_X$ trapping materials can adsorb NO_2 more effectively, the NO is converted as shown in Eq. (22), via oxygen and a noble metal coating such as Pt or Pd to form NO_2.

$$2NO + O_2 \rightarrow 2NO_2 \tag{22}$$

Storage, Lean-burn operation and adsorption phase: During the lean state, the storage material (i.e. BaO) is a carbonate which reacts with the NO_2 to form nitrates. The reaction is depicted in Eqs. (23)–(25) (Roy and Baiker, 2009).

$$BaO + NO_2 \rightarrow BaO - NO_2 \tag{23}$$

$$BaO - NO_2 \rightarrow BaO_2 + NO \tag{24}$$

$$BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2 \tag{25}$$

Rich-burn operation, release phase: Once the storage capacity reaches its threshold, the engine mode switches to rich-burn combustion, reducing the oxygen content in the exhaust gas and increasing the content of hydrocarbons, carbon monoxide and hydrogen. The different species show advantages and disadvantages regarding the regeneration and conversion efficiency. Abdulhamid et al. (2004) showed that H_2 and CO display a high reduction rate at 350 °C compared to C_3H_6. In contrast to C_3H_6, H_2 shows an increased capability to reduce stored NO$_X$ at 250 °C, while CO shows a high reduction rate at the beginning of the reduction period.

Rich-burn operation, regeneration phase: During the reduction phase, the nitric oxides are desorbed by the decay of the barium nitrate, again forming barium carbonate. The desorbed nitric oxides are reduced under the influence of H_2 as captured in Eqs. (26)–(28) and HC over the noble metal, especially rhodium (Rh), forming elementary N_2.

$$Ba(NO_3)_2 + 5H_2 \leftrightarrow N_2 + 5H_2O + BaO \tag{26}$$

$$Ba(NO_3)_2 + 5CO \leftrightarrow N_2 + 5CO_2 + BaO \tag{27}$$

$$9Ba(NO_3)_2 + 5C_3H_6 \leftrightarrow 9N_2 + 15CO_2 + 9BaO \tag{28}$$

Here again, in addition to the desired product, there are also some unwanted products depending for example on the reducer species and their concentrations, the temperature, and the residence time Pihl et al.,

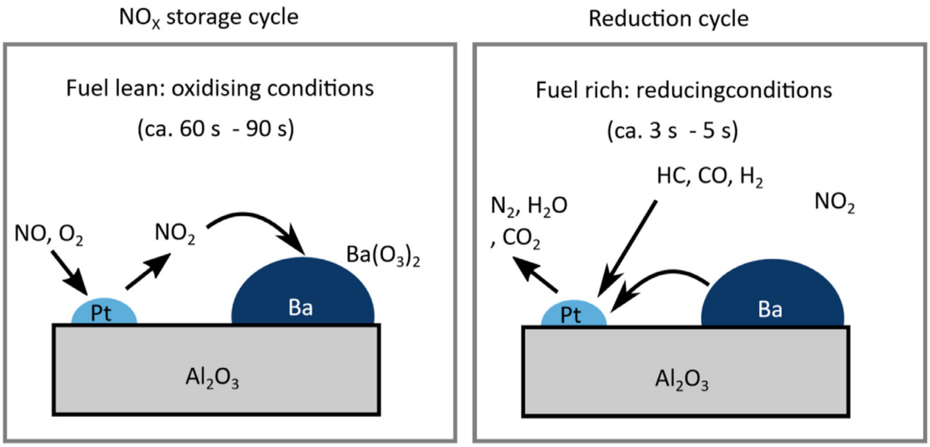

Fig. 8. Mechanism of adsorption during lean-burn (left) and regeneration during rich-burn phase (right) (Epling et al., 2004).

2006). Some of these unwanted rations are displayed below in Eqs. (29)–((31).

$$Ba(NO_3)_2 + 3H_2 \leftrightarrow 2NO + 3H_2O + BaO \tag{29}$$

$$Ba(NO_3)_2 + 4H_2 \leftrightarrow N_2O + 4H_2O + BaO \tag{30}$$

$$Ba(NO_3)_2 + 8H_2 \leftrightarrow 2NH_3 + 5H_2O + BaO \tag{31}$$

As aforementioned, these unwanted exhaust gas components have a toxic effect on humans and are dangerous to the environment. Thus, to limit them to a certain amount, an additional catalyst should be implemented. Furthermore, some adsorbers also have undesired reactivity in regards to sulfur compounds derived from diesel fuel and engine lubricating oil. Sulfur reactions are basically equivalent to the reactions of NO_X according to Majewski (2005) and represented in Eqs. (32) and (33).

$$SO_2 + {}^1\!/_2O_2 \leftrightarrow SO_3 \tag{32}$$

$$BaO + SO_3 \leftrightarrow BaSO_4 \tag{33}$$

In the first step, sulfur undergoes oxidation from sulfur dioxide to sulfur trioxide. Then, the SO_3 reacts with the barium to form barium sulfate. The adsorption of sulfur is preferential to the adsorption of NO_X, according to Majewski (2005). As a result, the catalyst performance is gradually decreased due to the saturation of the available Ba. Sulfur poisoning is reversible (or partially reversible) and site activity can be restored by a desulphation process involving the decomposition of the sulfate species.

Regeneration: To maintain the functionality of the adsorber, the regeneration of nitric compounds and sulfur compounds is mandatory. The NO_X regeneration is to be triggered once the catalyst attains its threshold storage capacity. The regeneration can be triggered two ways. The first is via increased temperature. In lean exhaust conditions, NO_X is released from barium sites at temperatures more than 450 °C. The second and preferred way is to shift the exhaust gas environment to rich, because regeneration occurs at much lower temperatures under rich exhaust gas conditions, converting NO_X to N_2 in a conventional three-way process due to the occurrence of HC, CO and H_2 (Mackensen, 2012).

For state-of-the-art systems, barium-based NSC the NO_X conversion temperature window usually ranges between 150°–500 °C. The conversion efficiency decreases towards both flanks of this window, according to Serrano et al. (2013). NO_X adsorbers can fully regenerate at 250 °C. However, a partial regeneration can be achieved at temperatures as low as 150 °C provided the air-to-fuel ratio is maintained at $\lambda < 1$, according to Ekkehard Pott (1998). Therefore, as previously mentioned, the operation of recent adsorber systems involves continuous cycling through lean and rich fuel conditions. The duration of the regeneration ranges from less than one to several seconds. Storage periods of 1 min–2 min, followed by rich spikes of 3 s–5 s, are typically used in real systems (Roy and Baiker, 2009). A schematic is illustrated in Fig. 9 below.

As aforementioned, in addition to the normal regeneration, the regeneration for sulfur compounds becomes mandatory due to the poisoning effect, leading to a lowering of the adsorption capacity. Even in the European and the US markets, where the sulfur content in fuel and engine oil is quite low, regeneration is mandatory.

As found by Amberntsson et al. (2002), the degree of deactivation of the NO_X storage capacity was proportional to the amount of sulfur it is exposed to. Since BaSO4 is thermodynamically very stable in comparison to other (desired) Ba species, the desulphation of the catalyst requires very high temperatures >1000 °C under lean conditions, as shown by Lide (2007). Similar to the regeneration of nitrate species, the desulphation of adsorbers can be performed at lower temperature (600 °C–750 °C) applying a rich exhaust gas. In contrast to NO_X regeneration, shows that a desulphation by lean/rich cycling seems to be necessary due to the occurrence of high amounts of H_2S that are formed under constant rich conditions, even though constant rich desulphations are often found to be more effective from the standpoint of the overall sulfur removal rate. As reported by Majewski (2015) in theory, after the desulphation of NO_X adsorbers, they should regain their full adsorption capacity. In practice, a permanent and irreversible poisoning of some barium sites has been reported.

However, morphologically different forms of stored sulfur have different impacts on the NO_X adsorber performance (Yezerets et al., 2003). Surface sulfates, which can be removed at relatively low temperatures, have the most impact on the NO_X storage capacity. Bulk sulfates, which require higher desulphation temperatures which may exceed 1000 °C, have disproportionately less impact on NO_X performance. As reported by Theis and Lambert (2015), exposure to high temperatures during repeated desulphation is the main cause of a permanent lessoning of the NOX adsorber performance. This is caused by thermal degradation of the wash coat and catalyst materials. Hence, the desulphation strategy is a critical function in the NO_X adsorber design. If sulfates are left in the catalyst washcoat, the NO_X conversion efficiency is compromised. Frequent desulphation, on the other hand, may involve significant fuel economy penalties and accelerated thermal deterioration of the catalyst.

System layout: The system layout differs between a passive and an active system. As described above, the passive system depends on an additional catalyst installed downstream. The PNA is therefore always installed closely coupled to the engine to have its light-off as quickly as possible to adsorb the nitric oxides while the downstream catalyst is not viable. Likewise, the common NSC is positioned close-coupled to the engine as well, in order to gain the same fast light-off.

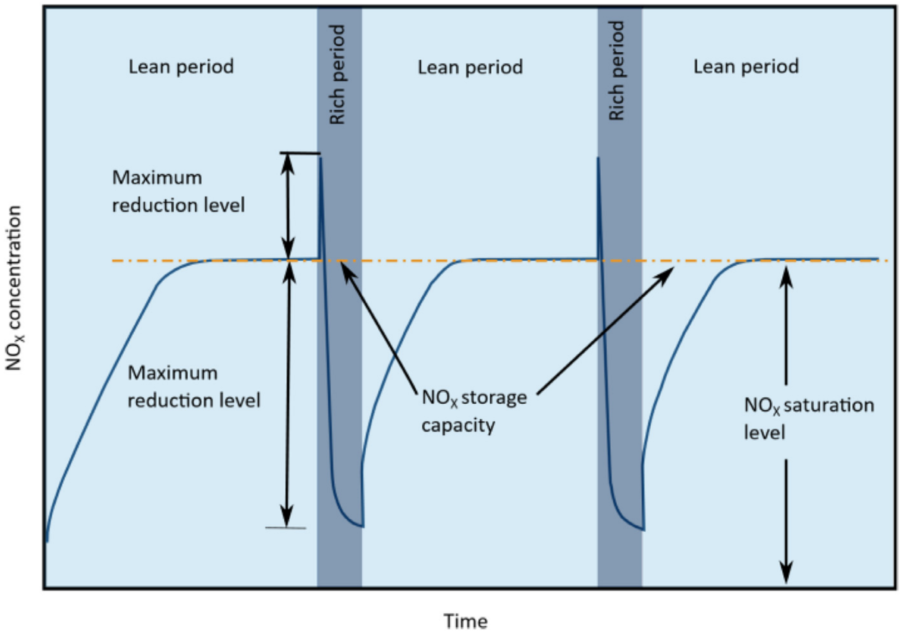

Fig. 9. NO_X storage and reduction illustrative sketch of lean and rich driving cycles (Epling et al., 2004).

While the passive adsorbers release the adsorbed nitric oxides within the normal exhaust gas temperature range, the active adsorbers depend on a rich air-to-fuel mixture for regeneration. Because the regeneration (or desulphation) of active adsorbers requires not only the presence of reductants but also the absence of oxygen, in contrast to the particulate filter regeneration where high oxygen concentrations do not interfere with the respective processes.

Two techniques have established themselves to provide the reducing agents to the exhaust gas, as shown by Majewski (2015):

- In-cylinder enrichment
- Exhaust gas enrichment.

In-cylinder enrichment can indeed be achieved by a delayed extended main injection or a post injection (Parks et al., 2008). Some of the challenges are strongly increased soot formation or increased wear of the engine due to oil dilution through spray/wall wetting. Thus, many strategies applied in series production use intake air throttling and exhaust gas recirculation (EGR) additionally in order to lower the oxygen content in the exhaust gas if the hardware is available, whereby the EGR rates, commonly 15–20% during lean operation, are increased to 30–35% during rich excursions (Majewski, 2015). A further challenge is the necessity to intervene in combustion to influence engine efficiency. However, in-cylinder enrichment is the state of the art technique to generate reducers for the regeneration.

Exhaust gas enrichment provides the reducing agents via exhaust line injection without intervening in the combustion. It can be implemented with an additional injector installed in the exhaust line upstream of the catalyst. The fuel evaporates from the heat of the exhaust gas and is decomposed into reductants, including shorter chain hydrocarbons and hydrogen. In 2011, Toyota published that it is possible to overcome the temperature limitation using the so called di-air system by operating the conventional NSC system with short timed diesel injections into the exhaust line upstream of the NSC.

Performance and challenges: The performance of an adsorber system can be narrowed down to four essential factors: the thermodynamic conditions (temperature, space velocity), the composition of the exhaust gas (presence or absence of species), the character of the catalyst, especially its coating, and, for active regenerations, the accurate amount of reductants and their uniform supply to the catalyst. The activity of active NO_X adsorbers covers a temperature range from about 150 °C to 450 °C, whereas the maximum performance typically lies at a temperature of about 350 °C. As explain above, the lower temperature performance limit is set by as low kinetics for the oxidation of NO to NO_2, while nitrate decomposition and the NO/NO_2 equilibrium limit the NO_X conversion at high temperatures.

The various challenges of NSC are briefly elaborated below. The figure below shows the temperature and the mass flow rate of the NO_X storage catalyst operation range. Increasing the exhaust mass flow rate reduces the reaction time to oxidize the NO_X to NO_2, which is required for the adsorption process. Furthermore, a lower temperature limits the NO_X oxidation process. At higher temperatures, the stored nitrate is thermodynamically unstable; furthermore, it undergoes thermal decomposition even at lean conditions, leading to reduced absorption efficiency (Mackensen, 2012). Therefore, it is necessary to undergo detailed calibration for the efficient regeneration process at optimum balance range between 250 °C and 350 °C and at low mass flow rates. This limits the entire map range usage.

As stated in Nova and Tronconi (2014), higher fuel consumption is one of the major challenges. Post cylinder injection affects oil dilution caused by wall wetting needs to be accounted (Majewski, 2005). Furthermore, HC slippage must be controlled significantly by high calibration effort. Undesirable secondary emissions like ammonia, nitrous oxide (N_2O) and hydrogen sulfide (H2S) should also be accounted for in order to retain its efficiency (Majewski, 2015). As already explained, subsequent sulfur present in the fuel and lubricants is oxidized to sulfur oxides in the combustion process and reacts with an absorbent (e.g. BaO) to form thermodynamically-favored sulfate, consequently obstructing the NO_X absorption and this eventually altering the catalyst operation. The current limits lead the NSC application to low sulfur containing fuels and engine oils otherwise obligates to a high frequency regeneration at elevated temperatures.

The application of NSC in heavy-duty vehicles at high exhaust mass flow rate is not feasible due to the necessity of a large CAT produced with precious metals that adversely increase costs. Thus, current NSC applications are limited to the small car segments, according to, due to their low exhaust mass flow rate, reduced costs, and package feasibility (no additional tank required).

Perhaps the di-air system is feasible to maintain under operation conditions as they occur for larger vehicle classes. They show that it is possible to achieve NO_X reduction efficiencies of more than 70% at catalyst temperatures up to 700 °C with additional fuel expenditure of as little as 2% compared to the respective lean operation mode.

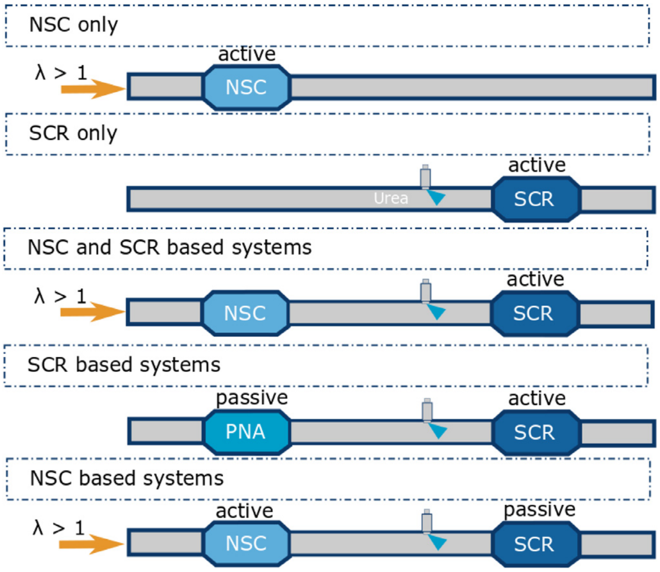

Fig. 10. Schematic overview of general layout concepts for NSC, SCR and combined systems.

1.3. *Possible system layout to overcome the specific challenges of SCR/NSC only systems*

As mentioned in Olabi et al. (2020d) the widely spread application fields, from Microcar to the full-size SUV and from urban driving to highway driving, and the requirement to adhere to the global exhaust emission standards eventually generate a large system layout matrix whereas OEMs are continuously striving to synergizes the exhaust gas system layouts of different vehicles and markets to a common platform to reduce the cost. As described above, currently the two technologies SCR and NSC have successful proved to meet the EURO-6-NO_X limits and further revealed its higher potential towards achieving future emission regulations. It became apparent that both technologies have their own significant potentials and challenges. The SCR can provide high DeNoOx efficiencies over nearly the entire engine load point map only suffering from low efficiency at low exhaust gas temperatures. The NSC is so to speak the opposite, providing its peak efficiency at low exhaust gas temperatures while providing a poor efficiency at high exhaust gas temperatures. Because of these different efficiencies in different engine load point areas OEM strive to combine both techniques to provide maximum DeNOx efficiency over the entire engine load point map. Some examples of possible combined system layouts are giving below in Fig. 10.

NSC + SCR based systems: The most attractive potential technique to contain NO_X at both cold and hot engine conditions is the usage of active NSC and SCR/SDPF together in the exhaust after treatment system combining both advantages and hence maximize the efficiency.

Fig. 11 depicts the NOx conversion rate based on different layouts in the exhaust aftertreatment. The orange curve denotes the NO_X rate without exhaust aftertreatment system. It is evident that the NOx conversion rate by the NSC+SCR (green curve) is higher in comparison to SCR-Only (blue curve) systems.

As described above, at cold start or low load cycles where low temperature prevails, SCR is partly suspended due to the insufficient UWS decomposition and formation of solid deposits in the exhaust pipe. Hence an additional active NSC placed upstream of the SCR catalyst, acts as an active component at low temperature to adsorb and convert NO_X to a harmless gas. When temperature and mass flow rise beyond the NSC optimum working range, the $DeNO_X$ can be performed by an active SCR catalyst located downstream of the NSC hence the system layout provides the maximum DeNOx efficiency in the entire engine load point map.

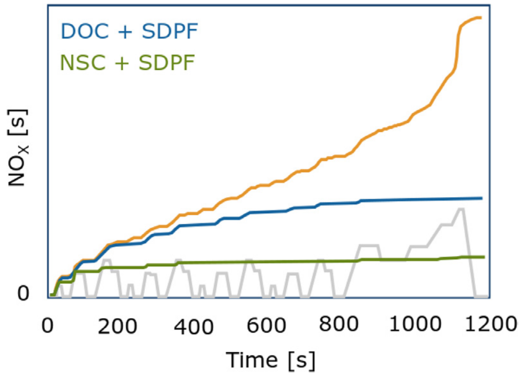

Fig. 11. Comparison between DOC – SDPF and NSC – SCRF efficiency based on (Yang et al., 2015).

The challenge arises when a high NOx load impacts on the NSC at cold start where NO_X brims over its threshold storing capacity resulting in a NOX slip. This slip cannot be contained by the SCR due to cold exhaust condition. Hence, it is evident to have a detailed calibrated storage/regeneration model and strategy for efficient NOx conversion. In order to maintain NSC storage under threshold level at cold condition, a frequent regeneration is imperative with compromising increased CO2 emissions, fuel consumption as well as secondary emissions like HC, CO and H2S due to the periodic shifting to rich engine operation. These H2S emission during the NSC regeneration can be controlled by the usage of a Cu based SCR catalyst downstream of the NSC. Moreover obligation for a huge package space is evident with this layout with increase in cost. However, despite having above challenges, it quotes positively with the reduction of UWS consumption rate at the SCR system. Currently this layout is limited to a large vehicle segments and needed further intensive research and development for wide series utilization for all segments.

SCR based systems: The above NSC +SCR layout has an extensive cost due to a usage of precious metals in the NSC. The usage of new technique such as PNA+SCR layout in the exhaust system surmounts this cost challenge by non-utilization of precious metals in Passive-NO_X-Absorber (PNA). PNA stores NOx under cold condition and low load and released to SCR once its operational exhaust temperature is attained. The regeneration of the PNA is similar to that of NSC by shifting to a rich combustion state where it traces same advantages and disadvantages as mentioned above. However, this technique also needed to perform active regeneration of the PNA in order to maintain the NOx load at below its threshold levels for an effective operation in the cold start. This results in the necessity to solve complex logic control algorithms and calibration efforts in real vehicle. An additional challenge comes with a non-existent capability of the PNA to generate NO_2 which is quite significant for both NO_X and soot reduction. A possible solution to this challenge is the usage of cDPF that is positioned downstream of the PNA and upstream of the SCR.

Currently PNA functionality is limited to low initial NOx load, NO_X mass flows and space velocities and simultaneously its non-capability towards NO_X reduction makes its stand-alone variant layout impossible.

NSC based systems: The NSC + SCR system surmounts the challenge of ammonia release during regeneration phase of NSC only. The active NSC placed upstream to the passive SCR oxidize NO_X and stored it as NO_2. Once its storage threshold is attained, it is regenerated by shifting to rich combustion state where it converts NO_2 to N_2 but simultaneously form ammonia gas. This harmful ammonia gas is forced to inhibit its releases to the atmosphere by placing Passive SCR downstream of the NSC. The SCR stores this ammonia gas and converts the slipped NOx from the NSC to harmless nitrogen molecules.

The frequent shifting from lean to rich mixture leads to negative impact in fuel consumption and release of excess CO_2 to the atmosphere. The possible solution to this challenge is to store SCR with sufficient ammonia gas during regeneration phase of NSC. Later, once the NSC reaches its threshold limit at the lean mixture condition, NOx slippage takes place where it is reduced by stored ammonia gas in the SCR to a harmless gas. This strategy enables the extended lean phase operation in the NSC and therefore reduces the fuel consumption. Simultaneously it avoids the need for an additional reductant (UWS) and supply hardwares for the SCR operation. As a result this technique assists in saving cost and good packaging feasibility. However, this technique needs complex monitoring of ammonia level at the SCR and NOx slippage level from the NSC. It is also bounded to have a detailed calibration effort in shifting frequency from lean to rich state and vice versa.

Conclusion

This investigation explored the main and mostly used approaches in the elimination of toxic nitric oxides emissions produced from the automotive industry. Selective Catalytic Reduction (SCR) was thoroughly described as it has been and still is the main and most efficient method to reduce NOx in mobile applications. The ambitious limits of the Euro 6 standard, encouraged original equipment manufacturers to equip passenger vehicles with this efficient and reliable technology. This technology leads to the production of nitrogen from nitric oxide hence highly recommended, but the process requires the usage of ammonia. Ammonia is naturally not environmentally friendly due to its toxicity. Temperature, amount of ammonia, coating of catalysts were observed to be key factors that affected the performance of SCR. Other factors discussed to have effect on SCR is the uniform distribution of the ammonia. Poor ammonia distribution led to ammonia slip. There is also generation of solid deposits in the event that the ammonia is not distributed properly. Another challenge relating to SCR are the consumption of large UWS at high mass flow NO_X rates.

Another technique that was also discussed and recommended is NO_X storage catalysts (NSC). The approach involves the application of absorption and desorption in the conversion of nitric oxide to nitrogen molecules. Despite these success achieved in the last few decades, there is still the need for more improvements in terms of optimization of the techniques discussed.

However, as described in Olabi et al. (2020d) the exhaust gas emission limits will be tightened. Also it can be expected that the engines will become more efficient resulting in lower exhaust gas temperature which than again will challenge the denoxiation which is highly dependent on the exhaust gas temperature. As shown in this paper, both described techniques have the advantages and disadvantages, which are in different areas of the engine load point map. As described above, some OEMs are going for recombining both technologies to an exhaust gas aftertreatment system capable to provide a maximum DeNOx efficiency in the entire engine load point map.

Declaration of Competing Interest

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

References

Abdelkareem, M.A, et al., 2020. Transition metal carbides and nitrides as oxygen reduction reaction catalyst or catalyst support in proton exchange membrane fuel cells (PEMFCs). Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2020.08.250.

Abdelkareem, M.A, et al., 2021. Environmental aspects of fuel cells: a review. Sci. Total Environ. doi:10.1016/j.scitotenv.2020.141803.

Abdulhamid, H., Fridell, E., Skoglundh, M., 2004. Influence of the type of reducing agent (H_2, CO, C_3H_6 and C_3H_8) on the reduction of stored NOX in a Pt/BaO/Al_2O_3 model catalyst. In: Topics in Catalysis. Springer, Netherlands, pp. 161–168. doi:10.1023/b:toca.0000029745.87107.b8.

Aliramezani, M., Koch, C.R., Hayes, R.E., 2016. Estimating tailpipe NOx concentration using a dynamic NOx/ammonia cross sensitivity model coupled to a three state control oriented SCR model. IFAC-PapersOnLine 49 (11), 8–13. doi:10.1016/j.ifacol.2016.08.002, Elsevier B.V..

Amberntsson, A, et al., 2002. Investigations of sulphur deactivation of NOx storage catalysts: influence of sulphur carrier and exposure conditions. Catal. Today 279–286. doi:10.1016/S0920-5861(02)00011-1.

Baroutaji, A, et al., 2019. Comprehensive investigation on hydrogen and fuel cell technology in the aviation and aerospace sectors. Renew. Sustain. Energy Reviews doi:10.1016/j.rser.2019.02.022.

Birkhold, F. et al. (2006) ‘Analysis of the Injection of Urea-Water-Solution for Automotive SCR DeNOx-Systems: Modeling of Two-Phase Flow and Spray/Wall-Interaction’, in *SAE Technical Papers*. doi: 10.4271/2006-01-0643.

Chen, H.-Y. (2014) ‘Cu/Zeolite SCR Catalysts for Automotive Diesel NOx Emission Control’, in, pp. 123–147. doi: 10.1007/978-1-4899-8071-7_5.

Cheng, Q, et al., 2016. FEM simulation and performance analysis of a novel heated tip SIDI injector. Int. J. Heat Fluid Flow doi:10.1016/j.ijheatfluidflow.2016.03.001.

Cheng, Y, et al., 2009. Sulfur tolerance and DeSOx studies on diesel SCR catalysts. SAE Int. J. Fuels Lubr. 1 (1), 471–476. doi:10.4271/2008-01-1023.

Ciardelli, C, et al., 2007. Reactivity of NO/NO_2-NH_3 SCR system for diesel exhaust aftertreatment: identification of the reaction network as a function of temperature and NO_2 feed content. Appl. Catal. B: Environ. 70 (1–4), 80–90. doi:10.1016/j.apcatb.2005.10.041, Elsevier.

Colombo, M., Nova, I., Tronconi, E., 2010. A comparative study of the NH_3-SCR reactions over a Cu-zeolite and a Fe-zeolite catalyst. Catal. Today doi:10.1016/j.cattod.2010.01.010.

Dou, D., Balland, J., 2004. Impact of Alkali Metals on the Performance and Mechanical Properties of NOx Adsorber Catalyst. SAE International Available at: https://www.jstor.org/stable/pdf/44734520.pdf .

Dolanc, G, et al., 2016. Control of autothermal reforming reactor of diesel fuel. J. Power Sour. 313, 223–232. doi:10.1016/j.jpowsour.2016.02.073, Elsevier B.V..

Ekkehard Pott (1998) *EP0891806A3 – Process and apparatus for regenerating a sulphur-trap – Google Patents*. Available at: https://patents.google.com/patent/EP0891806A3/en (Accessed: 9 November 2020).

Elsaid, K, et al., 2020. Environmental impact of desalination technologies: a review. Sci. Total Environ. doi:10.1016/j.scitotenv.2020.141528.

Epling, W.S, et al., 2004. Overview of the fundamental reactions and degradation mechanisms of NOx storage/reduction catalysts. Catal. Rev. – Sci. Eng. 163–245. doi:10.1081/CR-200031932.

Fang, H.L., DaCosta, H.F.M., 2003. Urea thermolysis and NOx reduction with and without SCR catalysts. Appl. Catal. B: Environ. doi:10.1016/S0926-3373(03)00177-2.

Gieshoff, J. et al. (2001) ‘Advanced Urea SCR Catalysts for Automotive Applications’, in *SAE Technical Papers*. doi: 10.4271/2001-01-0514.

Gmbh, R. B. (2013) *Diesel Systems Denoxtronic 6-5 – Urea Dosing System for SCR Systems*, Robert Bosch GmbH Diesel Systems Postfach.

Halonen, S, et al., 2017. Urea-water-solution properties: density, viscosity, and surface tension in an under-saturated solution. Emiss. Control Sci. Technol. doi:10.1007/s40825-016-0051-1.

Heck, R.M., Chen, J.M., Speronello, B.K., 1994. Operating characteristics and commercial operating experience with high temperature SCR NOx catalyst. Environ. Progress doi:10.1002/ep.670130410.

Held, W. et al. (1990) ‘Catalytic NOx Reduction in Net Oxidizing Exhaust Gas’, in *SAE Technical Papers*. doi: 10.4271/900496.

Holderbaum, B., 2009. Dosierstrategie für ein SCR-System zur NOx-Reduktion im Diesel-PKW – Technische Informationsbibliothek (TIB) Ph.D. Thesis.

Huang, Z., Zhu, Z., Liu, Z., 2002. Combined effect of H_2O and SO_2 on V2O5/AC catalysts for NO reduction with ammonia at lower temperatures. Appl. Catal. B: Environ. 39 (4), 361–368. doi:10.1016/S0926-3373(02)00122-4, Elsevier.

Hug, H. T., Mayer, A. and Hartenstein, A. (1993) ‘Off-Highway Exhaust Gas After-Treatment: Combining Urea-SCR, Oxidation Catalysis and Traps’, in *SAE Technical Papers*. doi: 10.4271/930363.

Ijaodola, O, et al., 2018. Evaluating the effect of metal bipolar plate coating on the performance of proton exchange membrane fuel cells. Energies doi:10.3390/en11113203.

Ijaodola, O.S, et al., 2019. Energy efficiency improvements by investigating the water flooding management on proton exchange membrane fuel cell (PEMFC). Energy doi:10.1016/j.energy.2019.04.074.

Jangjou, Y, et al., 2016. SO_2 poisoning of the NH_3-SCR reaction over Cu-SAPO-34: effect of ammonium sulfate versus Other S-containing species. ACS Catal. 6 (10), 6612–6622. doi:10.1021/acscatal.6b01656, American Chemical Society.

Jeong, S. J. et al. (2005) ‘Simulation on the Optimum Shape and Location of Urea Injector for Urea-SCR System of Heavy-Duty Diesel Engine to Prevent NH3 Slip’, in *SAE Technical Papers*. doi: 10.4271/2005-01-3886.

Ji, Y, et al., 2008. Influence of ceria on the NOx storage/reduction behavior of lean NOx trap catalysts. Catal. Today 136 (1–2), 146–155. doi:10.1016/j.cattod.2007.11.059, Elsevier.

Ji, Y., Bai, S., Crocker, M., 2015. Al_2O_3-based passive NOx adsorbers for low temperature applications. Appl. Catal. B: Environ. 170–171, 283–292. doi:10.1016/j.apcatb.2015.01.025, Elsevier.

Kamasamudram, K, et al., 2010. Overview of the practically important behaviors of zeolite-based urea-SCR catalysts, using compact experimental protocol. Catal. Today doi:10.1016/j.cattod.2010.03.055.

Khatib, F.N, et al., 2019. Material degradation of components in polymer electrolyte membrane (PEM) electrolytic cell and mitigation mechanisms: a review. Renew. Sustain. Energy Rev. doi:10.1016/j.rser.2019.05.007.

Khatib, F.N, et al., 2020. A comparison on the dynamical performance of a proton exchange membrane fuel cell (PEMFC) with traditional serpentine and an open pore cellular foam material flow channel. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2020.08.199.

Kim, Y.J, et al., 2012. Mn-Fe/ZSM5 as a low-temperature SCR catalyst to remove NOx from diesel engine exhaust. Appl. Catal. B: Environ. 126, 9–21. doi:10.1016/j.apcatb.2012.06.010, Elsevier.

Koebel, M., Elsener, M., Kleemann, M., 2000. Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines. Catal. Today doi:10.1016/S0920-5861(00)00299-6.

Koebel, M., Elsener, M. and Madia, G. (2001) 'Recent Advances in the Development of Urea-SCR for Automotive Applications', in *SAE Technical Papers*. doi: 10.4271/2001-01-3625.

Koebel, M., Madia, G., Elsener, M., 2002. Selective catalytic reduction of NO and NO$_2$ at low temperatures. Catal. Today doi:10.1016/S0920-5861(02)00006-8.

Koebel, M., Strutz, E.O., 2003. Thermal and hydrolytic decomposition of urea for automotive selective catalytic reduction systems: thermochemical and practical aspects. Ind. Eng. Chem. Res. doi:10.1021/ie020950o.

Kumar, A, et al., 2016. Chemical deSOx: an effective way to recover Cu-zeolite SCR catalysts from sulfur poisoning. Catal. Today doi:10.1016/j.cattod.2016.01.033.

Lide, D., 2007. CRC Handbook of Chemistry and Physics, 87th Ed Editor-in-Chief: David R. Lide (National Institute of Standards and Technology). CRC Press/Taylor and Francis Group, Boca Raton, FL, p. 2608. doi:10.1021/ja069813z 2006$139.95. ISBN 0-8493-0487-3.'*Journal of the American Chemical Society*. American Chemical Society (ACS), 129(3), pp. 724–724. doi:.

Liu, G., Gao, P.X., 2011. A review of NOx storage/reduction catalysts: mechanism, materials and degradation studies. Catal. Sci. Technol. 552–568. doi:10.1039/c1cy00007a, The Royal Society of Chemistry.

Ma, L, et al., 2013. Characterization of commercial Cu-SSZ-13 and Cu-SAPO-34 catalysts with hydrothermal treatment for NH$_3$-SCR of NOx in diesel exhaust. Chem. Eng. J. 225, 323–330. doi:10.1016/j.cej.2013.03.078, Elsevier.

Mackensen, A. (2012) *NO X-Minimierung durch Einsatz passiver NO X-Adsorber Dissertation*.

Madia, G, et al., 2002. Side reactions in the selective catalytic reduction of NOx with various NO$_2$ fractions. Ind. Eng. Chem. Res. doi:10.1021/ie020054c.

Majewski, W. A. (2005) 'Diesel Filter Regeneration', DieselNet Technology Guide.

Majewski, W. A. (2015) *NOx Adsorbers*. Available at: https://dieselnet.com/tech/cat_nox-trap.php (Accessed: 9 November 2020).

Matsumoto, S., 1996. DeNOx catalyst for automotive lean-burn engine. Catal. Today 29 (1–4), 43–45. doi:10.1016/0920-5861(95)00259-6, Elsevier BV.

Melville, J. E. et al. (2012) *Thermally regenerable nitric oxide adsorbent*.

Metkar, P.S., Balakotaiah, V., Harold, M.P., 2012. Experimental and kinetic modeling study of NO oxidation: comparison of Fe and Cu-zeolite catalysts. Catal. Today doi:10.1016/j.cattod.2011.11.032.

Nova, I., Lietti, L., Forzatti, P., 2008. Mechanistic aspects of the reduction of stored NOx over Pt-Ba/Al2O3 lean NOx trap systems. Catal. Today 136 (1–2), 128–135. doi:10.1016/j.cattod.2008.01.006, Elsevier.

Nova, I., Tronconi, E. (Eds.), 2014. Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts. Springer, New York, NYNew York (Fundamental and Applied Catalysis) doi:10.1007/978-1-4899-8071-7.

Ogungbemi, E, et al., 2019. Fuel cell membranes – pros and cons. Energy doi:10.1016/j.energy.2019.01.034.

Ogungbemi, E., Wilberforce, T., Ijaodola, O., Thompson, J., Olabi, A.G., 2020. Review of operating condition, design parameters and material properties for proton exchange membrane fuel cells. Int. J. Energy Res. doi:10.1002/er.5810.

Ogungbemi, E., Wilberforce, T., Ijaodola, O., Thompson, J., Olabi, A.G., 2020. Selection of proton exchange membrane fuel cell for transportation. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2020.06.147.

Ohtsuka, H., Tabata, T., 2001. Roles of palladium and platinum in the selective catalytic reduction of nitrogen oxides by methane on palladium-platinum-loaded sulfated zirconia. Appl. Catal. B: Environ. 29 (3), 177–183. doi:10.1016/S0926-3373(00)00201-0, Elsevier.

Olabi, A.G, et al., 2020. Critical review of energy storage systems. Energy doi:10.1016/j.energy.2020.118987.

Olabi, A.G., Wilberforce, T., Sayed, E.T., Elsaid, K., Abdelkareem, M.A., 2020. Prospects of fuel cell combined heat and power systems. Energies doi:10.3390/en13164104.

Olabi, A.G., Wilberforce, T., Sayed, E.T., Elsaid, K., Rezk, H., et al., 2020. Recent progress of graphene based nanomaterials in bioelectrochemical systems. Sci. Total Environ. doi:10.1016/j.scitotenv.2020.141225.

Olabi, A.G., Maizak, D., Wilberforce, T., 2020. Review of the regulations and techniques to eliminate toxic emissions from diesel engine cars. Sci. Total Environ. doi:10.1016/j.scitotenv.2020.141249.

Olabi, A.G., Wilberforce, T., Abdelkareem, M.A., 2021. Fuel cell application in the automotive industry and future perspective. Energy doi:10.1016/j.energy.2020.118955.

Parks, J, et al., 2008. Characterization of Lean NOx Trap Catalysts With in-Cylinder Regeneration Strategies. SAE International *SAE Technical Papers* doi:10.4271/2008-01-0448.

Peter Lanzerath (2011) Alterungsmechanismen von Abgaskatalysatoren für Nutzfahrzeug-Dieselmotoren. Available at: https://core.ac.uk/download/pdf/11681262.pdf (Accessed: 9 November 2020).

Piazzesi, G, et al., 2006. Adsorption and hydrolysis of isocyanic acid on TiO$_2$. Appl. Catal. B: Environ. doi:10.1016/j.apcatb.2005.12.018.

Pihl, J.A, et al., 2006. Product Selectivity During Regeneration of Lean NOx Trap Catalysts. SAE International *SAE Technical Papers* doi:10.4271/2006-01-3441.

Rabaia, M.K.H, et al., 2021. Environmental impacts of solar energy systems: a review. Sci. Total Environ. doi:10.1016/j.scitotenv.2020.141989.

Roy, S., Baiker, A., 2009. NOx storage-reduction catalysis: from mechanism and materials properties to storage-reduction performance. Chem. Rev. 109 (9), 4054–4091. doi:10.1021/cr800496f, American Chemical Society.

Salasc, S., Skoglundh, M., Fridell, E., 2002. A comparison between Pt and Pd in NOx storage catalysts. Appl. Catal. B: Environ. 36 (2), 145–160. doi:10.1016/S0926-3373(01)00300-9, Elsevier.

Schaber, P.M, et al., 2004. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. Thermochim. Acta doi:10.1016/j.tca.2004.05.018.

Serrano, D., Obiols, J. and Lecointe, B. (2013) 'Optimization of Dual Fuel Diesel-Methane Operation on a Production Passenger Car Engine – Thermodynamic Analysis', in *SAE Technical Papers*. doi: 10.4271/2013-01-2505.

Shi, C, et al., 2012. NOx storage and reduction properties of model ceria-based lean NOx trap catalysts. Appl. Catal. B: Environ. 119–120, 183–196. doi:10.1016/j.apcatb.2012.02.028, Elsevier.

Sluder, S. et al. (2004) Oak Ridge National Laboratory Urea Decomposition and SCR Performance at Low Temperature.

Cho, S.M., 1994. Properly apply selective catalytic reduction for NOx removal. Chem. Eng. Progr. 90 (1), 39–45. American Institute of Chemical Engineers (AIChE)Available at: https://www.cheric.org/research/tech/periodicals/view.php?seq=49722 . (Accessed: 8 November 2020).

Sultana, A, et al., 2013. Tuning the NOx conversion of Cu-Fe/ZSM-5 catalyst in NH$_3$-SCR. Catal. Commun. 41, 21–25. doi:10.1016/j.catcom.2013.06.028, Elsevier.

Takahashia, N, et al., 1996. The new concept 3-way catalyst for automotive lean-burn engine: NOx storage and reduction catalyst. Catal. Today 27 (1–2), 63–69. doi:10.1016/0920-5861(95)00173-5, Elsevier.

Takeshima, S. (1998) Exhaust Gas Purification Device for an Internal Combustion Engine.

Theis, J.R., Lambert, C.K., 2015. An assessment of low temperature NOx adsorbers for cold-start NOx control on diesel engines. Catal. Today 258, 367–377. doi:10.1016/j.cattod.2015.01.031, Elsevier.

Tronconi, E, et al., 2015. Interaction of NOx reduction and soot oxidation in a DPF with Cu-zeolite SCR coating. Emiss. Control Sci. Technol. doi:10.1007/s40825-015-0014-y.

van Vuuren, N. and Sayar, H. (2012) 'High Speed Video Measurements of a Heated Tip Urea Injector Spray', in *SAE Technical Papers*. doi: 10.4271/2012-01-1747.

Wang, J, et al., 2013. The study on the capacity of NOx storage-reduction catalyst for lean-burn engine. In: Lecture Notes in Electrical Engineering. Springer, Berlin, Heidelberg, pp. 599–608. doi:10.1007/978-3-642-33841-0_46.

Wijayanti, K, et al., 2015. Impact of sulfur oxide on NH$_3$-SCR over Cu-SAPO-34. Appl. Catal. B: Environ. 166–167, 568–579. doi:10.1016/j.apcatb.2014.11.043, Elsevier.

Wilberforce, T, et al., 2016. Advances in stationary and portable fuel cell applications. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2016.02.057.

Wilberforce, T., Makky, A.Al, et al., 2017. Computational fluid dynamic simulation and modelling (CFX) of flow plate in PEM fuel cell using aluminum open cellular foam material. In: Proceedings of the 2017 IEEE Texas Power and Energy Conference, TPEC 2017 doi:10.1109/TPEC.2017.7868285.

Wilberforce, T., El-Hassan, Z., Khatib, F.N., Al Makky, A., Mooney, J., et al., 2017. Development of Bi-polar plate design of PEM fuel cell using CFD techniques. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2017.08.093.

Wilberforce, T., El-Hassan, Z., Khatib, F.N., Al Makky, A., Baroutaji, A., et al., 2017a. Developments of electric cars and fuel cell hydrogen electric cars. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2017.07.054.

Wilberforce, T., El-Hassan, Z., Khatib, F.N., Al Makky, A., Baroutaji, A., et al., 2017b. Modelling and simulation of proton exchange membrane fuel cell with serpentine bipolar plate using MATLAB. Int. J. Hydrog. Energy doi:10.1016/j.ijhydene.2017.06.091.

Wilberforce, T, et al., 2018. Effect of bipolar plate materials on performance of fuel cells. Reference Module in Materials Science and Materials Engineering doi:10.1016/b978-0-12-803581-8.11272-x.

Wilberforce, T., El Hassan, Z., Ogungbemi, E., et al., 2019. A comprehensive study of the effect of bipolar plate (BP) geometry design on the performance of proton exchange membrane (PEM) fuel cells. Renew. Sustain. Energy Rev. doi:10.1016/j.rser.2019.04.081.

Wilberforce, T., Ijaodola, O., Khatib, F.N., et al., 2019. Effect of humidification of reactive gases on the performance of a proton exchange membrane fuel cell. Sci. Total Environ. doi:10.1016/j.scitotenv.2019.06.397.

Wilberforce, T., Khatib, F.N., Ijaodola, O.S., et al., 2019. Numerical modelling and CFD simulation of a polymer electrolyte membrane (PEM) fuel cell flow channel using an open pore cellular foam material. Sci. Total Environ. doi:10.1016/j.scitotenv.2019.03.430.

Wilberforce, T., Baroutaji, Ahmad, et al., 2019. Outlook of carbon capture technology and challenges. Sci. Total Environ. doi:10.1016/j.scitotenv.2018.11.424.

Wilberforce, T., El Hassan, Zaki, Durrant, A., et al., 2019. Overview of ocean power technology. Energy doi:10.1016/j.energy.2019.03.068.

Wilberforce, T., Baroutaji, A., et al., 2019. Prospects and challenges of concentrated solar photovoltaics and enhanced geothermal energy technologies. Sci. Total Environ. doi:10.1016/j.scitotenv.2018.12.257.

Wilberforce, T., Ijaodola, O., Ogungbemi, E., et al., 2019. Technical evaluation of proton exchange membrane (PEM) fuel cell performance – a review of the effects of bipolar plates coating. Renew. Sustain. Energy Rev. doi:10.1016/j.rser.2019.109286.

Wilberforce, T., Olabi, A.G., 2020a. Design of experiment (DOE) analysis of 5-cell stack fuel cell using three bipolar plate geometry designs. Sustainability doi:10.3390/su12114488.

Wilberforce, T., Olabi, A.G., 2020b. Performance prediction of proton exchange membrane fuel cells (PEMFC) using adaptive neuro inference system (ANFIS). Sustainability doi:10.3390/su12124952.

Willi, R, et al., 1996. Selective reduction of NO by NH3 over vanadia-based commercial catalyst: parametric sensitivity and kinetic modelling. Chem. Eng. Sci. doi:10.1016/0009-2509(96)00171-6.

Xu, L, et al., 2007. Laboratory and Engine Study of Urea-Related Deposits in Diesel Urea-SCR After-Treatment Systems. SAE International *SAE Technical Papers* doi:10.4271/2007-01-1582.

Yang, L, et al., 2015. NOx Control Technologies for Euro 6 Diesel Passenger Cars: Market Penetration and Experimental Performance Assessment (White Paper). International Council on Clean Transportation, Washington.

Yezerets, A., Currier, N.W., Eadler, H.A., 2003. Experimental Determination of the Kinetics of Diesel Soot Oxidation by O_2 – Modeling Consequences. SAE International *SAE Technical Papers* doi:10.4271/2003-01-0833.

Yim, S.D, et al., 2004. Decomposition of urea into NH3 for the SCR process. Ind. Eng. Chem. Res. doi:10.1021/ie034052j.

Zamboni, G., Capobianco, M., 2012. Experimental study on the effects of HP and LP EGR in an automotive turbocharged diesel engine. Appl. Energy doi:10.1016/j.apenergy.2012.01.046.