



# On the Suitability of NO<sub>x</sub>-Storage-Catalysts for Hydrogen Internal Combustion Engines and a Radio Frequency-Based NO<sub>x</sub> Loading Monitoring

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## Abstract

Hydrogen combustion engines can contribute to CO<sub>2</sub>-free mobility. However, they produce NO<sub>x</sub> emissions, albeit only to an extremely small extent when operated very leanly. One approach to reduce these emissions even further is to use exhaust gas aftertreatment systems like NO<sub>x</sub> storage catalysts (NSC). So far, they have mainly been used in diesel or gasoline applications. This contribution shows that under conditions such as those prevailing in hydrogen engines, the NSC can achieve not only a higher storage capacity for nitrogen oxides (NO<sub>x</sub>) but also a higher conversion. To ensure permanently high conversion rates, the amount of stored NO<sub>x</sub> has to be monitored permanently to prevent NO<sub>x</sub> breakthroughs. Conventional NO<sub>x</sub> sensors may not be accurate enough due to the very low NO<sub>x</sub> emissions. The functionality of the radio frequency (RF) sensor, which enables a direct determination of the NO<sub>x</sub> loading, is demonstrated for operation under hydrogen conditions. Furthermore, the influence of rich exhaust gas on the RF signal, which is relevant for a correct NO<sub>x</sub> loading determination during regeneration, is analyzed.

**Keywords** NO<sub>x</sub> storage catalyst (NSC) · Hydrogen engine · Exhaust gas aftertreatment · Microwave cavity perturbation · RF-sensor

## 1 Introduction

Besides the ongoing tightening of exhaust emission limits, e.g. with regard to nitrogen oxides, the urgency to reduce global CO<sub>2</sub> emissions poses major challenges for the future usage of combustion engines. In 2010, the transport sector contributed a total of 14% to the global greenhouse gas emissions [1]. Primary contributors are road vehicles, which account for 72% of these emissions [2]. Thus, to achieve the desired CO<sub>2</sub> reduction targets, conventional combustion engine vehicles using non-renewable fossil fuels have to be replaced. Currently, this is mainly accomplished by battery

electric vehicles. Due to numerous challenges, such as short range along with long charging times, the establishment of the charging infrastructure or the impact of charging on the power grid, “clean” fuels can be an alternative [3–5].

“Clean” fuel refers to carbon-neutral fuels, that are produced using renewable energy. One example thereof is hydrogen (H<sub>2</sub>), which can be used in fuel cells, to generate electrical energy, or directly in internal combustion engines (ICE) [6–8]. Hydrogen fueled ICEs (H<sub>2</sub>-ICE) offer a number of advantages, such as lower required fuel purity or simpler manufacturing process [9]. Furthermore, nitrogen oxides (NO<sub>x</sub>) can be formed by the Zeldovich mechanism due to high combustion temperatures, albeit to a much lesser extent compared to conventional combustion engines when operated very leanly [9–12]. Therefore, to achieve a zero emission vehicle, an exhaust gas aftertreatment system is necessary for H<sub>2</sub>-ICEs [13, 14]. One option is the selective catalytic reduction (SCR), which is one of the major exhaust aftertreatment technologies in diesel applications [15]. These catalysts require a reductant in the form of ammonia (NH<sub>3</sub>) to convert nitrogen oxides. That must be provided separately, e.g. in form of an aqueous urea solution.

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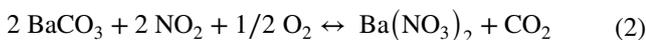
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To avoid this, some approaches utilize the already available hydrogen fuel as the reducing agent (H<sub>2</sub>-SCR). However, this goes along with significantly lower conversion rates than conventional SCR systems [13, 16–19].

An alternative solution for catalytic exhaust gas aftertreatment are NO<sub>x</sub> storage catalysts (NSC). They store nitrogen oxides under lean exhaust gas conditions and reduce them subsequently during a short rich phase [20]. In addition to the nitrogen oxide storage, NSCs usually contain ceria for oxygen storage [21]. In detail, NO in the exhaust must first be oxidized at catalytically active platinum sites (Eq. 1) [22].



Subsequently, it is stored as nitrate by converting the carbonates of the storage material while releasing CO<sub>2</sub> (e.g. Eq. 2 with a barium based storage material) [23].



Under rich conditions reducing exhaust components convert the stored NO<sub>x</sub> to harmless gases, like H<sub>2</sub>O and N<sub>2</sub>. Thereby, hydrogen is considered the most effective reducing agent [23, 24]. Consequently, the regeneration behavior of the NSC with a H<sub>2</sub>-ICE should not be worse or even better than with a diesel engine, regardless of the lower CO<sub>2</sub> concentration in the exhaust gas originating only from the intake air.

According to Eq. 2, CO<sub>2</sub> must be present to restore the carbonate state of the storage material during releasing nitrogen oxides. In a hydrogen engine, however, CO<sub>2</sub> is limited to the fraction already present in the intake air and, to a very small extent, to burnt engine oil [25]. Nevertheless, a release of nitrogen oxides is possible despite low CO<sub>2</sub> concentrations, whereby the storage material is then not present as a carbonate but as hydroxide [e.g. Ba(OH)<sub>2</sub>] or oxide (e.g. BaO) [26, 27]. Conversion to one of these compounds in an almost CO<sub>2</sub>-free atmosphere could even have a positive effect on the NO<sub>x</sub> storage capacity [27]. This paper will examine whether this effect can also be found in commercially available NSCs during exhaust gas conditions comparable to H<sub>2</sub>-ICEs. Furthermore, the conversion performance of an NSC under “hydrogen conditions” as well as its selectivity will also be analyzed and compared with those in a typical diesel engine application.

In addition, the engine operation regarding to air–fuel ratio has to be controlled depending on the NO<sub>x</sub> loading [28]. This is usually determined by cumulative balancing of NO<sub>x</sub> concentration signals from NO<sub>x</sub> sensors up- and downstream of the catalyst [29]. Due to up to two magnitudes lower concentrations in lean-operated hydrogen engines than in typical diesel engines, this is, however, strongly dependent on the accuracy of the sensors [10]. The accuracy of a typical NO<sub>x</sub> sensor is ± 10 ppm for NO < 100 ppm (± 10%

above 100 ppm) [30]. An alternative approach is the radio frequency (RF) based catalyst state diagnosis (RF-sensor). It determines the loading state directly by measuring the dielectric properties of the storage material [31, 32]. The functionality of the RF-sensor has already been demonstrated for NSCs with diesel engines [33, 34]. Additionally, this work will investigate whether monitoring of the NO<sub>x</sub> loading via the RF-sensor is still possible for the exhaust gas conditions of a hydrogen engine and how the RF-signal depends on the air–fuel ratio during regeneration.

## 2 RF Catalyst State Diagnosis

The RF-sensor can detect the state of a catalyst via the propagation behavior of electromagnetic waves within the catalyst. They depend on the dielectric properties of the catalyst [31, 35]. For this purpose, the RF-sensor excites standing electromagnetic waves (resonances) inside the metallic catalyst canning using two coupling elements in the form of coaxial probe antennas. These resonances can be evaluated with respect to characteristic parameters, like the resonant frequency  $f_{\text{res}}$  and the quality factor  $Q_0$ . Both parameters depend on the complex relative permittivity ( $\epsilon = \epsilon_1 - j\epsilon_2$ ). Based on the cavity perturbation method, an increase in material polarization  $\chi_e$  (resp. relative permittivity  $\epsilon_1$ ) results in a decrease of the resonant frequency (Eq. 3). The inverse quality factor  $Q_0^{-1}$ , on the other hand, is directly proportional to the dielectric losses  $\epsilon_2$  of the catalyst (Eq. 4) [35–37].

$$\Delta f_{\text{res}} \propto -\Delta\chi_e = -\Delta(\epsilon_1 - 1) \quad (3)$$

$$\Delta Q_0^{-1} \propto \Delta\epsilon_2 \quad (4)$$

However, the relationships described in Eqs. 3 and 4 apply only to small material samples compared to the resonant cavity (i.e., the canning). For larger samples, as a catalyst typically is, interference between the two resonant parameters may occur [37]. Nevertheless, it could have already been shown in [34], that these two effects allow a distinct evaluation of the storage components of an NSC. While oxygen storage mainly influences the quality factor, the amount of stored NO<sub>x</sub> affects mainly the resonant frequency.

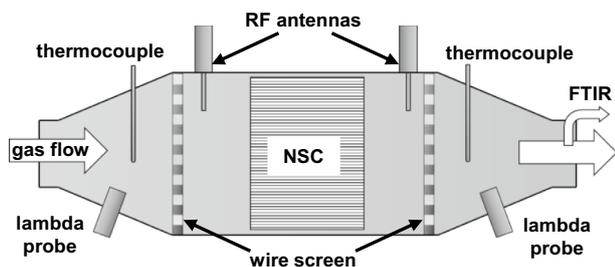
## 3 Experimental

In this work, a commercially available honeycomb NSC (kindly provided by Umicore) with a cell density of 400 cpsi and a precious metal content of 43 g/ft<sup>3</sup> platinum, 10 g/ft<sup>3</sup> palladium and 2 g/ft<sup>3</sup> rhodium was examined. Since all

measurements were performed on a gas test bench with a flow rate of 40 l/min, cores of 4.6 cm diameter and 2.54 cm length were cut from the NSC to obtain a space velocity of around 57,000 l/h, comparable to real engine conditions. The catalyst temperature was varied between 220 and 420 °C by adjusting the preheated gas mixture as well as an external heating of the canning to reduce heat losses. Gas temperature was measured using thermocouples up- and downstream of the catalyst. Their average is the catalyst temperature  $T_{\text{NSC}}$ . During lean gas conditions, the maximum temperature difference between both thermocouples was below 8 °C, and less than 1 °C under stationary rich conditions.

To determine the conversion characteristics of the NSC, a part of the downstream gas was analyzed by Fourier-transform infrared spectroscopy (FTIR). In addition, a broadband lambda probe was located up- and downstream, allowing for evaluation of the stored oxygen during regeneration. The lambda probe, however, is calibrated to typical diesel exhaust gas and therefore does not provide an accurate air–fuel ratio due to the rich-shift phenomena [38]. Nevertheless, it can be used to determine the point in time when the oxygen storage is completely emptied respectively filled. During all investigations, a vector network analyzer connected to both antennas was used to measure the complex scattering parameter  $S_{21}$  about every 0.6 s in the range from 3.55 to 3.70 GHz. From these data, the resonant frequency  $f_{\text{res}}$  and the quality factor  $Q_0$  of the  $\text{TE}_{113}$  resonant mode were determined as described in [39]. The measurement setup is shown schematically in Fig. 1.

All experiments used nitrogen with 8 vol% water as base gas. To set exhaust gas conditions similar to a  $\text{H}_2$ -ICE, 0.1%  $\text{CO}_2$  was added (“ $\text{H}_2$  conditions”). In order to compare the catalyst performance under these conditions with that of a diesel engine, the tests were also carried out with 7%  $\text{CO}_2$  (“diesel conditions”). Before each measurement, the NSC was preconditioned by several rich-lean changes. The rich phases were set for the “ $\text{H}_2$  conditions” by solely adding hydrogen to the base gas, while for the diesel conditions,



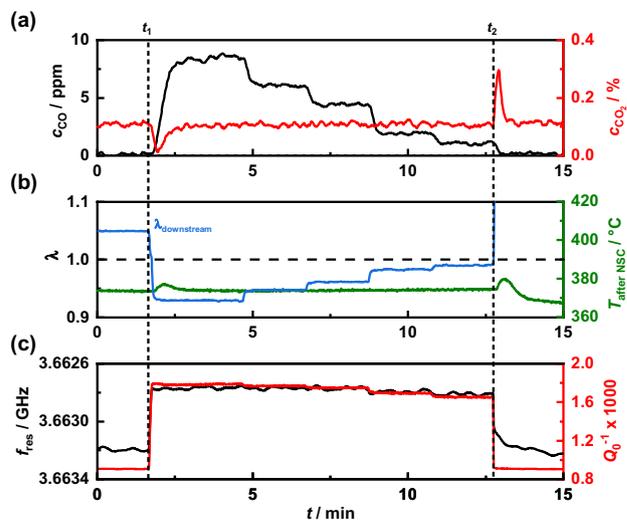
**Fig. 1** Schematic illustration of the experimental setup. In addition to the canning, the resonant cavity is further defined by wire screens up- and downstream of the catalyst to increase the signal quality of the RF-sensor

carbon monoxide was present as well. The lean phases were realized regardless of engine operation by adding oxygen.

## 4 Results and Discussion

### 4.1 Influence of Rich Gas Atmospheres on the RF-Sensor

First, the influence of rich exhaust gas, in particular regarding the radio frequency signal, was determined. This analysis was carried out exclusively for conditions occurring with a  $\text{H}_2$ -ICE (i.e., at 0.1%  $\text{CO}_2$ ). For this purpose, after a lean phase, rich conditions were set by adding 1%  $\text{H}_2$  to the then oxygen-free base gas. After reaching stabilized gas concentrations downstream of the NSC, the hydrogen concentration was reduced stepwise to 0.7%, 0.5%, 0.2% and 0.1% before returning to lean atmosphere. This measurement is shown in Fig. 2 exemplarily for a gas temperature of about 370 °C. Thereby, the downstream air–fuel ratio measured with the lambda probe ranges from 0.935 to 0.996 and decreases with the reduction of the supplied hydrogen. Depending on this, also carbon monoxide forms, which can be explained by the reverse water gas shift reaction [40]. Due to the small amounts of  $\text{CO}_2$  converted by this reaction, it has no measurable effect on  $\text{CO}_2$ . Significant changes, however, can be measured shortly after rich-lean changes. The short decrease in downstream  $\text{CO}_2$  concentration can be explained by its sorption into the NSC storage material. In turn, switching



**Fig. 2** Variation of hydrogen content under rich exhaust gas conditions at around 370 °C; **a** downstream concentration of CO (black) and  $\text{CO}_2$  (red) measured with FTIR; **b**  $\lambda$  (blue) and gas temperature (green) downstream of the NSC; **c** resonant frequency (black) and inverse quality factor (red). The switch to rich conditions ( $t_1$ ) as well as back to lean ( $t_2$ ) are marked with dashed lines (Color figure online)

back to lean leads to the release of CO<sub>2</sub> over a period of only 30 s.

The resonant parameters also indicate the rapid transformation of the catalyst material after switching between rich and lean. In rich, the inverse quality factor  $Q_0^{-1}$  increases significantly, indicating higher dielectric losses according to Eq. 4. These losses may occur, for instance, not only due to sorption of CO<sub>2</sub>, but also due to the oxidation state of the ceria [41]. Simultaneously, the resonant frequency  $f_{res}$  decreases. This can be explained by the higher permittivity in the oxidized state.

The differences in the resonant parameters compared between rich and lean was evaluated in a temperature range from 220 to 420 °C for each rich gas composition after reaching a steady state (Fig. 3). In case of the resonant frequency, it is noticeable that – independent of the air–fuel ratio—at low temperatures, a shift towards higher frequencies occurs, while above 300 °C the shift tends towards lower frequencies. A similar behavior was already observed in [34]. This could be an indication of the influence of different storage materials. An increase in resonant frequency should only be caused by a decrease in permittivity. However, it is known from [41] that the permittivity of ceria in the reduced state is always above the oxidized value. Thus, the increase in the resonant frequency is possibly due to a higher permittivity of the NO<sub>x</sub> storage material. However, since the exact material composition of the studied NSC is not known, a change in oxygen storage cannot be excluded as a possible reason for the increase in resonant frequency, especially since even at the lowest examined temperatures, storage of oxygen by the storage material could still be observed by the lambda probes during the rich-lean changes.

Regarding the quality factor, the signal difference to lean increases significantly with higher temperatures, but is still noticeable at the lowest observed temperature of 220 °C. Therefore, the temperature-dependent behavior is strongly similar to that of pure ceria in a TWC [41]. With variation of hydrogen concentration respectively the reduction of richness level, changes in the resonant parameters occur, albeit to a minor extent compared to the change from lean to rich. In general, a richer gas mixture leads to a stronger change

of the resonant parameters. A similar behavior has already been observed for TWCs and could be associated with the oxidation degree of ceria [42].

### 4.2 Storage and Regeneration Behavior

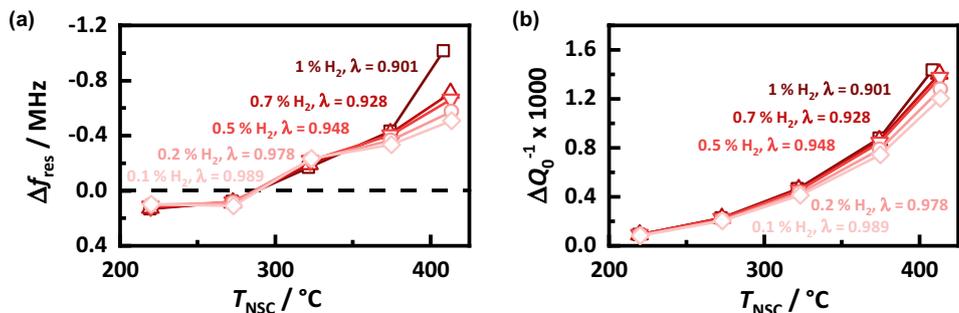
In this section, NO<sub>x</sub> sorption and the subsequent regeneration of the NSC will be examined. Thereby, conversion characteristics during a typical operation with a H<sub>2</sub>-ICE will be compared to those with a diesel engine. Regarding “H<sub>2</sub> conditions”, a lean gas mixture was set at the beginning of the experiment by adding 10% oxygen to the base gas (8% H<sub>2</sub>O and 0.1% CO<sub>2</sub> in nitrogen). Subsequently, 40 ppm NO were added and the empty NSC got loaded with NO<sub>x</sub> until a (almost) complete breakthrough of NO<sub>x</sub> was reached. Then, regeneration was initiated by switching to rich gas, which was achieved by adding 1% hydrogen to the base gas. In chosen “diesel operation conditions”, which refers to a base gas with 8% H<sub>2</sub>O and 7% CO<sub>2</sub>, NO<sub>x</sub> storage took place at a lower oxygen content of 1% but at significantly higher NO concentration of 500 ppm. Regeneration occurred without hydrogen only by adding 0.4% carbon monoxide. The gas concentrations during these tests are summarized in Table 1.

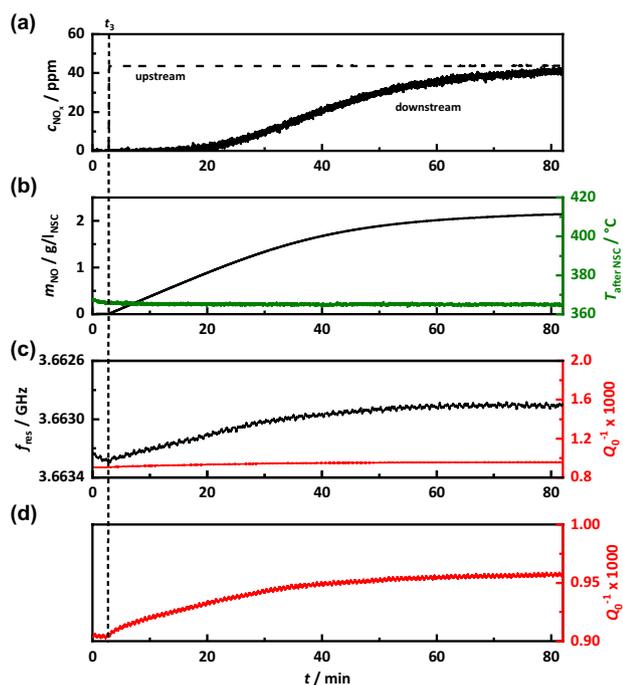
The NO<sub>x</sub> loading shown in Fig. 4 – just as the lambda variation in Fig. 2 – was carried out under “H<sub>2</sub> conditions” at a temperature of approx. 370 °C and lasted 80 min. Based on the measured NO<sub>x</sub> concentrations up- respectively downstream (Fig. 4a), the amount of stored NO  $m_{NO}$  could be determined for all storage experiments (Fig. 4b) by integration. The resonant parameters are shown in Fig. 4c) with the same scaling as for the air–fuel ratio variation in Fig. 2. Thereby it can be clearly seen that the dielectric losses, described by the inverse quality factor, are barely affected

**Table 1** Gas concentrations added to the base gas during the experiments to determine the storage and regeneration behavior of the NSC

	Lean operation	NO <sub>x</sub> loading	Rich operation
“H <sub>2</sub> ”	10% O <sub>2</sub>	40 ppm NO	1% H <sub>2</sub>
“Diesel”	1% O <sub>2</sub>	500 ppm NO	0.4% CO

**Fig. 3** Temperature-dependent shift of resonant frequency  $\Delta f_{res}$  (a) and inverse quality factor  $\Delta Q_0^{-1}$  (b) under different rich gas atmospheres compared to lean conditions



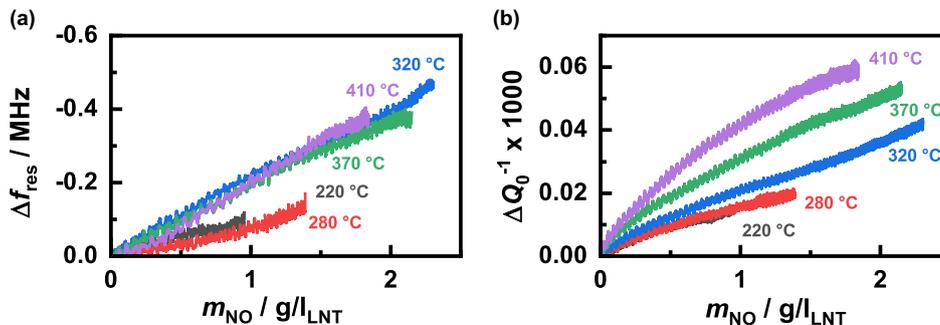


**Fig. 4**  $\text{NO}_x$  storage under “hydrogen conditions” at around 370 °C. Start of  $\text{NO}_x$  admixture at  $t_3$  is marked with a dotted line; **a** concentration of  $\text{NO}_x$  upstream (dashed line) and downstream of the catalyst; **b** calculated mass of  $\text{NO}$  stored in the NSC relative to its volume  $m_{\text{NO}}$  and gas temperature downstream the NSC (green); **c** resonant frequency (black) and invers quality factor (red) with the same axis scaling as in Fig. 2; **d** inverse quality factor (red) as in (c) but with different scaling (to highlight the small effect) (Color figure online)

by  $\text{NO}$ . Thus, a stored  $\text{NO}$  amount of 2  $\text{g/l}_{\text{NSC}}$  yielded an increase of  $Q_0^{-1}$  by 0.05, while switching to rich conditions resulted in a 16 times greater increase (cf. Figure 2c). Despite the only small signal change, the quality factor nevertheless resembles the stored  $\text{NO}$  (Fig. 4d). In case of the resonant frequency, in contrast, the effect is much more pronounced compared to rich-lean changes. In addition, the resonant frequency clearly resembles the storage signal  $m_{\text{NO}}$ .

Examining the resonance parameter shift as a function of the stored  $\text{NO}$  mass  $m_{\text{NO}}$  in Fig. 5 confirms the linear relationship regardless of the catalyst temperature. However,

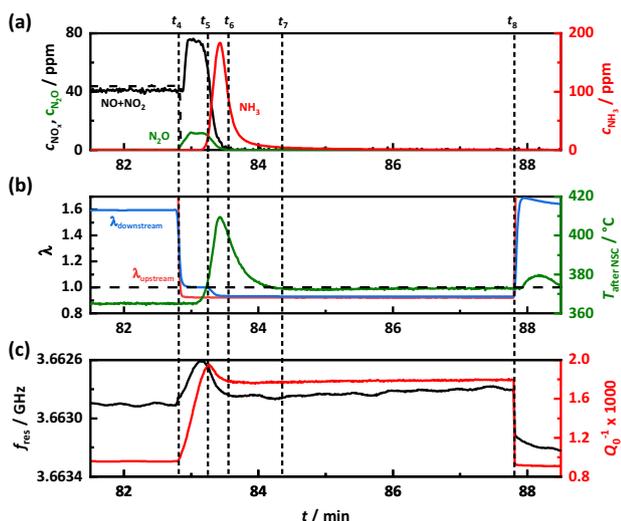
**Fig. 5** Shift of resonant frequency  $\Delta f_{\text{res}}$  (a) and inverse quality factor  $\Delta Q_0^{-1}$  (b) relative to the NSC under lean conditions depending on the amount of stored  $\text{NO}$  for different catalyst temperatures



the sensitivity of the RF signal varies with the temperature significantly. The response of resonant parameters to  $\text{NO}$  loading during “ $\text{H}_2$  conditions” is thus consistent with the findings in [34] and will therefore not be discussed further in this work.

The subsequent regeneration is considerably faster than the storage phase (Fig. 6). After just 1.5 min ( $t > t_7$ ) after starting regeneration at  $t_4$ , barely any undesired by-products resulting from  $\text{NO}_x$  conversion, such as nitrous oxide ( $\text{N}_2\text{O}$ ) or ammonia ( $\text{NH}_3$ ), can be detected downstream. Also, for  $t > t_7$ , the downstream temperature has dropped to a steady state value after a brief peak of 40 K due to the exothermic regeneration. Initiating regeneration ( $t_4$ ), the downstream air–fuel ratio does not immediately switch to rich in contrast to the value measured upstream, but remains at stoichiometric for about 30 s (until  $t_5$ ) due to the consumption of oxygen stored in the NSC. This is mirrored by the inverse quality factor  $Q_0^{-1}$  that increases almost linearly during this period indicating ceria reduction as known from [43]. Evaluation of still stored  $\text{NO}$  is more difficult. On one hand, unlike during the sorption process, it cannot be determined by balancing gas concentrations before and after the catalyst, since hydrogen used for regeneration cannot be measured by FTIR. On the other hand, evaluation of the resonant frequency also turns out to be more difficult, since different material effects are overlapping as a result of simultaneous  $\text{NO}_x$  and oxygen release. Furthermore, the resonant frequency is also more dependent on temperature changes than the quality factor, which can be seen, for example, in its increase after  $t_8$ . This is due to a temperature decrease of the catalyst casing as there is no longer an additional heat source due to the exothermic reactions during the regeneration phase. The subsequent thermal reduction in size leads to a decreased resonant cavity size and thus to an increase in the resonant frequency. Nevertheless, after reaching an almost constant resonant frequency signal from  $t_6$  onward, a completely emptied  $\text{NO}_x$  storage can be assumed, since at this point the oxygen storage is already completely reduced.

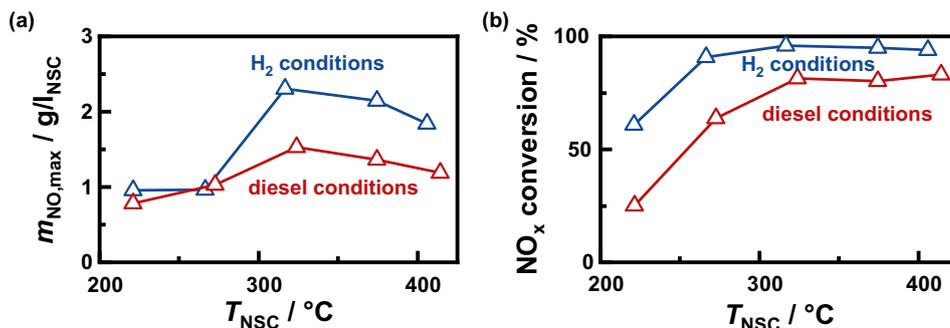
For easier comparison of the  $\text{NO}_x$  storage characteristics under different gas conditions simulating a hydrogen and diesel combustion engine, the stored  $\text{NO}$  shortly before



**Fig. 6** Regeneration under hydrogen conditions” at around 370 °C. Start of regeneration at  $t_4$ , end of stoichiometric conditions downstream at  $t_5$ , reaching a constant resonant frequency at  $t_6$ , reaching constant temperature at  $t_7$  and change back to lean conditions at  $t_8$  are marked with a dotted line; **a** concentration of NO upstream (dashed line) and NO+NO<sub>2</sub> (black) resp. N<sub>2</sub>O (green) downstream of the catalyst on the left y-axis and downstream NH<sub>3</sub> concentration (red) on the right y-axis; **b** measured  $\lambda$  downstream (blue) and upstream (red) of the catalyst as well as gas temperature (green) downstream the NSC. The upstream lambda signal during lean phases deviates significantly from the downstream signal with a value of approx. 3.4 and is therefore not visible in the graph, as the scaling was chosen with a focus on the breakthrough behavior of the oxygen storage during the regeneration; **c** resonant frequency (black) and invers quality factor (red) with equal axis scaling as in Fig. 4 (Color figure online)

regeneration  $m_{NO,max}$  (i.e., the maximum storable NO mass at the given gas conditions) was evaluated (Fig. 7a). At temperatures above 300 °C, approx. 50% more NO could be stored under the conditions prevailing at a H<sub>2</sub>-ICE. A reason therefore could be due to the high oxygen levels under hydrogen conditions [44, 45]. At lower temperatures, storage capacity drops to the same level for both operating modes of about 1 g/l<sub>NSC</sub>. However, even with this reduced storage ability, the NSC would still be able

**Fig. 7** **a** Maximum amount of NO stored in the catalyst relative to the catalyst volume; **b** proportion of previously stored NOx converted into non-harmful gases during regeneration



to buffer emissions of 40 ppm NO at a space velocity of 60,000 1/h over a period of 20 min.

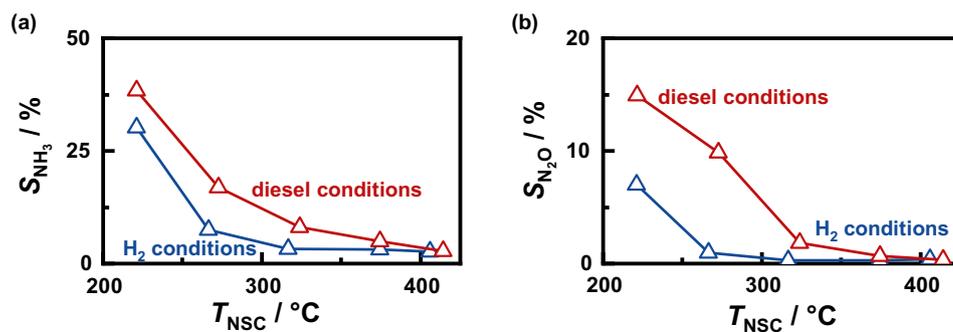
The NO<sub>x</sub> conversion rates shown in Fig. 7b are determined by integrating all downstream nitrogen containing species measured by FTIR (i.e., NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>). Thereby, for hydrogen conditions, a better catalyst performance is observed, regardless of its temperature. The conversion is always above 60% even at low temperatures and it increases up to over 95% for 320 °C. Under diesel conditions, a comparable temperature-dependent behavior occurs, but the conversion reaches only around 80%. At the lowest temperature of 220 °C, only a quarter of the stored NO can be converted. This may be due to using CO as the reductant, since its inferior regeneration behavior compared to hydrogen is already known in literature [24].

To evaluate the regeneration behavior not only the conversion is relevant, but also the amount of NO<sub>x</sub> converted into other harmful exhaust gases such as ammonia or nitrous oxide. The related selectivities shown in Fig. 8 are determined by the released amount of those gases relative to  $m_{NO,max}$ . Again, hydrogen conditions exhibit better catalyst performance due to the reduced formation of both NH<sub>3</sub> and N<sub>2</sub>O.

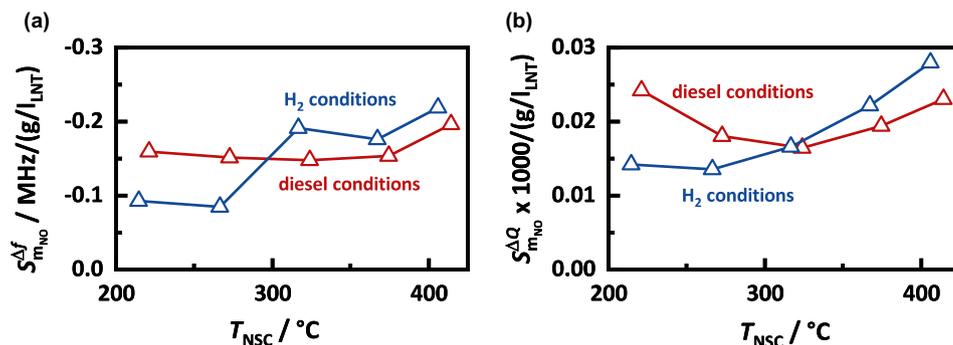
Along with the improved conversion behavior at higher temperatures, selectivity towards harmful gases also decreases. Above 300 °C, NH<sub>3</sub> selectivity is below 10% in diesel operation and 3.5% at hydrogen conditions. Moreover, these amounts of ammonia could be stored and converted by a small passive SCR catalyst downstream of the NSC, and could therefore be used to reduce not converted NO<sub>x</sub> even better [46]. Far more problematic is the formation of nitrous oxide with its strong greenhouse impact. Even under hydrogen conditions, where N<sub>2</sub>O selectivity is by far lower, up to 7% of the stored NO are still converted to nitrous oxide at the lowest tested temperature (220 °C). Nevertheless, N<sub>2</sub>O selectivity drops significantly with increasing temperature to less than 0.3% at 375 °C. Overall, to prevent emission of harmful exhaust gases, regeneration temperatures of above 300 °C are preferred.

Finally, Fig. 9 compares the sensitivity of the RF-sensor to NO storage for the two engine conditions. Under

**Fig. 8** Temperature-dependent selectivity of the NSC. Amount of  $\text{NH}_3$  (a) or  $\text{N}_2\text{O}$  (b) released during regeneration in relation to the previously stored amount of NO



**Fig. 9** Temperature-dependent shift of (a) the resonant frequency signal and (b) the quality factor relative to the stored NO



hydrogen conditions, a slightly higher sensitivity, both in terms of resonant frequency  $S_{\text{mNO}}^{\Delta f}$  and quality factor  $S_{\text{mNO}}^{\Delta Q}$ , can be observed at high temperatures. At temperatures below 300 °C, however, there is a clear drop in sensitivity at the resonant frequency for hydrogen conditions, which was already clearly noticeable in Fig. 5. Under diesel conditions, on the other hand, the  $S_{\text{mNO}}^{\Delta f}$  shows almost no temperature sensitivity. With respect to the quality factor signal, an increase in sensitivity at higher temperature is evident, whereas under diesel conditions the sensitivity increases again at low temperatures. The reasons for the differences between both engine conditions were not analyzed further. In general, it is evident that the RF-sensor can detect the loading state of an NSC when operated with a hydrogen engine with a similar sensitivity as in combination with a diesel engine.

## 5 Conclusion

Hydrogen combustion engines can contribute to achieve  $\text{CO}_2$ -neutral mobility. However, zero emission operation cannot be achieved without exhaust aftertreatment systems, as nitrogen oxides may be formed due to high temperatures during combustion. With a  $\text{NO}_x$  storage catalyst,  $\text{NO}_x$  emissions could be reduced without additional reducing agents such as urea solutions in SCR systems.

In this work, it has been shown that an NSC operated under conditions typical for a hydrogen engine performs better than under those corresponding to a diesel engine.

In addition to higher  $\text{NO}_x$  storage capacity and better conversion rate, the formation of harmful by-products during regeneration such as  $\text{NH}_3$  or  $\text{N}_2\text{O}$  was also reduced during hydrogen operation. In order to minimize these secondary emissions, NSCs should be preferably regenerated at temperatures not much lower than 300 °C. Nevertheless, the measurements also proved that, even at low exhaust gas temperatures of 200 °C, the storage capacity of NSCs is sufficient to buffer the very low  $\text{NO}_x$  emissions of a hydrogen ICE until regeneration at higher temperatures is possible.

To ensure emission-free operation, a permanent monitoring of the  $\text{NO}_x$  storage level is necessary to prevent breakthroughs of nitrogen oxides and to avoid too frequent regenerations. While previous work has already shown that the RF-sensor can be used to monitor the  $\text{NO}_x$  loading in diesel NSCs, this has now also been proven under the low  $\text{CO}_2$  concentrations present in hydrogen applications. Furthermore, under rich conditions, a dependence between the resonant parameter shift and the air–fuel ratio could be found, which could possibly correlate with the oxidation degree of the NSC. Compared to diesel conditions, the RF-sensor shows a similar sensitivity with respect to  $\text{NO}$  loading. Thus, when operating with a hydrogen engine, the RF-sensor allows for a precise determination of the  $\text{NO}_x$  storage, similar as previously shown in [34] for diesel applications. If the air–fuel ratio is known during rich operation, it is also possible with the RF-sensor to determine the  $\text{NO}_x$  and  $\text{O}_2$  storage during regeneration allowing a termination of the

regeneration before a breakthrough of reducing exhaust gas pollutants occur.

Since only loading with pure NO has been investigated so far, future work should also consider the influence of different NO/NO<sub>2</sub> mixtures. Furthermore, based on RF-sensor signals, a control system for ending regeneration automatically as soon as the NO<sub>x</sub> storage is emptied would be conceivable. The evaluation of a possible advantage of the RF-sensor regarding the achievable conversion rate compared to the current used integrative determination using NO<sub>x</sub> sensors should be carried out under realistic conditions on a transient test bench.

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