Article

Screening NO$_x$ Storage Performance—Demonstrating a High Throughput Approach for Evaluating Emission Control Catalysts under Transient Conditions

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Abstract: At hte the high throughput (HT) approach is applied in the field of environmental catalysis on a routine basis. Research programs for automotive applications require validated screening protocols for conditions relevant to engine exhaust as well as experimental measures to ensure quality control using statistical design of experiment. To illustrate the HT approach for a test protocol with dynamic feed switches in a 48-fold reactor, 15 model catalysts for lean NO$_x$ traps (LNT) were prepared and screened fresh and after 800 °C hydrothermal aging. In the fresh state, highest NO$_x$ efficiency was found at 350–450 °C. A ranking of BaO > SrO > CaO was found as the most active NO$_x$ storage components when used as dopants on alumina. 800 °C aging results in a severe performance loss. Using XRD and BET analysis, Pt sintering is identified as most likely cause. These findings agree well with results from conventional tests reported in the literature.

Keywords: high throughput screening; automotive catalysis; simulated exhaust; automated data processing; lean NO$_x$ trap

1. Introduction

To meet current and future emission targets, rather complex after-treatment systems consisting of several catalysts and filters are applied [1]. Each component has specific functionalities and depending on the field of application (e.g., light-duty vs. heavy duty or off-road equipment) it must be able to survive under application-specific aging conditions. When combining these varying technical requirements with overall cost constraints, there is an obvious need for advanced test technologies to support rapid improvement and optimization of existing commercial emission control catalysts. Increased screening capacity is also required for long-term R&D projects searching for future technologies. Using high-throughput (HT) approaches allows preparation as well as evaluation of large sample libraries. A typical scenario is the optimization of washcoat formulations by systematic variation of different parameters (e.g., catalyst support, PGM type, PGM loading, promoter type and quantity, preparation route, calcination temperature, binder, slurry pH, aging condition, etc.) based on statistical design of experiment methods [2,3]. During the last decades high-throughput methods have become an established tool for evaluation of heterogeneous catalysts for different chemical processes [4–23]. hte's approach to HT testing is based on a patent filed on March 3, 1998 which relates to parallel reactor systems for testing the activity measurement of solid catalysts simultaneously exposed to gaseous feed streams [24,25].

In the field of automotive catalysis, however, a relatively low number of studies report on the use of HT screening technologies and the conclusions based on these test results [26–35].

In addition to the reactor system, which includes a flexible process automation software at the core of the HT screening unit, several other challenges need to be addressed specifically in the field of automotive applications:

(1) Time resolved on-line analytics of all reactants and products, when using small catalyst amounts, i.e., limited gas flow and the increased impact of wall effects.
(2) Data acquisition, especially for test protocols involving fast feed switches in an automated mode of operation.
(3) Software solutions for robust data processing and a data reduction infra-structure.
(4) Besides the testing infrastructure, for a full assessment, new materials have to be evaluated after implementation in relevant washcoat formulations which are close to production and therefore usually proprietary. This requires development of a small-scale slurry processing workflow as well as aging procedures (high temperature aging, catalyst poisoning e.g., with sulfur).

Since 2000 hte has developed laboratory workflows to apply HT technology in the field of catalytic automotive exhaust after-treatment. The power of the rapid testing paradigm has been successfully demonstrated in several R&D programs exploring large formulation matrices. Results of some examples have been described in previous publications [26,27].

This work describes hte's HT screening approach with focus on test protocols involving transient conditions implemented by dynamic feed switches. Lean NO_x Trap (LNT) catalysts are an important emission control technology, especially for light passenger cars with small displacement Diesel engines having comparatively low exhaust temperatures. Since there is no known catalyst for direct NO_x decomposition (into N_2 and O_2) under lean conditions, LNTs must use a different strategy. NO_x is stored during an extended phase of lean operation (several minutes). Before the storage capacity is exhausted, a short rich pulse (3–10 s) is applied [1]. In this period, the amount of available reductants (CO, H_2, unburned HC) exceeds the residual oxygen and NO_x is reduced to N_2—clearing out the NO_x storage capacity for another lean cycle. LNT catalysts consist of a NO_x storage component as well as precious metal components (responsible NO_2 formation in the lean phase and for the rapid NO_x reduction during rich pulses). Both components/functionalities are closely linked since storage and release kinetics of one component need to match the activity of the other. Thus, screening NO_x storage and PGM functionality independently have limited prospect for success. Consequently, a test protocol with rapid feed switches has to be implemented in the HT screening equipment for rapid differentiation of NO_x storage material/PGM combinations under realistic conditions. In addition to a general description of the experimental setup used at hte for routine screening, some results from LNT testing are provided to exemplify the process automation, data acquisition and data reduction workflow.

2. Results

2.1. Description of the HT Platform

HT evaluation workflows for emission control catalyst screening at hte include sample preparation, aging (hydrothermal and sulfation), characterization, HT lab testing, data management and processing (cf. Figure 1). Main fields of application include:

- Fast primary screening of new materials
- Optimization of washcoat composition in large parameter spaces
- Accelerated catalyst evaluation for multiple applications by automated variation of test conditions (GHSV, T, feed composition, etc.).

Test units with 48 parallel reactors operated at hte have been described in detail in previous publications [33,34]. Generally, the units consist of a reactor block operated at isothermal conditions. The feed is evenly distributed over all positions to allow the catalysts to equilibrate. For catalytic measurement one position at a time is selected and put under active flow control. The exhaust from

the selected position is switched to a dedicated line for catalytic measurement. In typical stationary test protocols, the 48 positions are scanned sequentially, allowing ~3–5 min equilibration time + 30 s sampling time for each catalyst, for tests with feed switches the measurement times are usually longer because several cycles are required to allow the catalyst to stabilize. For test protocols like the LNT catalysts screening described here, measurement times > 10 min for each reactor position are needed. This makes it even more important, that all operations are fully automated to ensure 24/7 utilization of the test equipment.
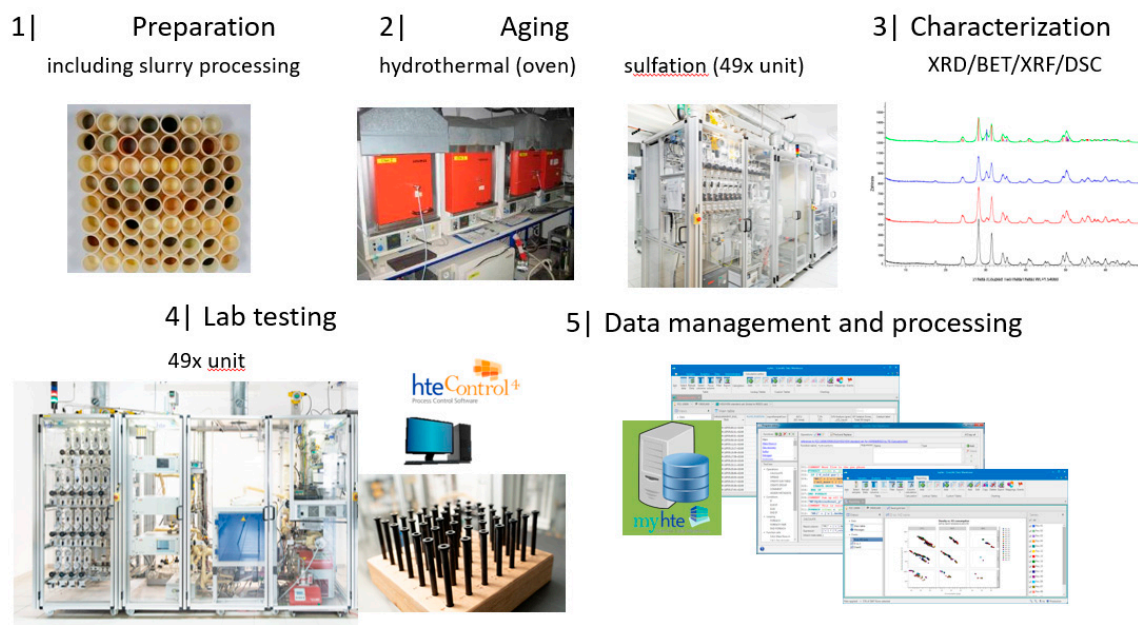

Figure 1. hte's platform for environmental catalysis R&D.

The key reactor features comprise:

- 48 catalytic reaction positions and 1 by-pass position for measurement of catalyst inlet gas composition (cf., Figure 2)
- Individual, removable reactors made from stainless steel (for up to 1 mL sample volume). This allows to decouple the time-consuming step of reactor filling from the operation of the test unit increasing utilization.
- T = 100–575 °C; atmospheric pressure; GHSV: 30,000–100,000 h^{-1} (See test procedure section of definition of GHSV in these powder tests)
- Dosing of gases (NO, NO_2, NH_3, N_2O, HC, CO, CO_2, O_2, N_2) and liquids (H_2O, HC) in relevant concentration ranges.
- Time resolved analytics of CO, CO_2, O_2, HC, H_2, NO, NO_2, N_2O and NH_3.
- Monitoring specific components by MS (mass spectrometer) (m/z 1-512).
- Rapid switching of feed gas composition with cycle frequencies up to 0.5 Hz (e.g., lean/rich cycles).
- Flexible process automation ("hteControl4" software) to run complex test protocols in unattended and safe 24/7 operation.
- Change between several operation modes without hardware reconfiguration (e.g., DOC, TWC, SCR, LNT)
- Integration into an automated data management system ("myhte" software) for automated reduction of primary data, allowing easy data export to more sophisticated data analysis solutions.
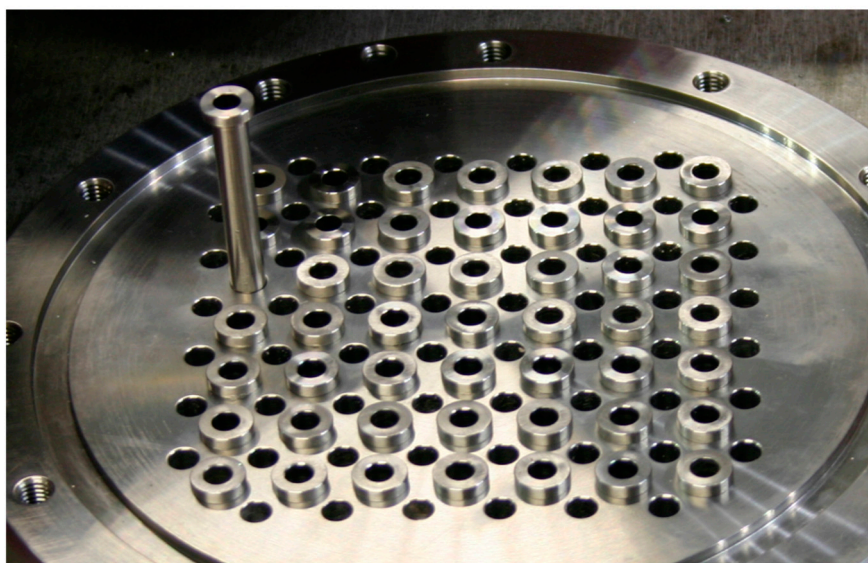
Figure 2. HT reactor block layout with 48 reaction and 1 by-pass positions, one reactor is lifted, others are completely inserted as in an experiment.

2.2. Screening Protocols

Testing protocols and on-line analytics are as close as possible to the conventional lab testing of automotive catalysts. Feed composition, space velocities and temperatures are adjusted to mimic the conditions in the exhaust after-treatment system for selected operating points within regulated driving cycles (e.g., different for light-duty and heavy-duty applications). Due to the high thermal mass of the 49-fold reactor block, in this setup only isothermal operation is possible. Instead of dynamic temperature ramps only stationary experiments with discrete temperature setpoints can be performed in the parallel testing units. At each setpoint, all positions are exposed to the same feed all the time, the measured channel is selected by down-stream multiport selection valves [34]. While the catalyst in a selected position is evaluated at a defined space velocity under active flow control, the remaining channels are exposed to a lower flow rate (~1/50–1/25 of the rate selected for the measured sample), at the same gas composition. This methodology has the advantage to keep all catalysts close to their steady state activity for each operating condition, thus allowing for a short equilibration time after a new position is selected and space velocity is increased to the target value. In general, an experiment in the parallel reactor system has the following test sequence, automated in the control software:

(1)   Set first experimental condition (temperature, feed gas composition)
(2)   Wait until the whole reactor is equilibrated
(3)   Switch to position 1.
(4)   Equilibrate in stationary feed or run dynamic feed switching program
(5)   Repeat steps 3 and 4 for all 48 reactor positions. Run duplicate tests on selected positions to obtain statistical data.
(6)   Set next experimental condition (e.g., higher temperature)
(7)   Continue with steps 2–6 until all conditions are evaluated for all 48 reactors.
(8)   This sequence has the advantage over many conventional experiments in that detector drifts in the analytical equipment can be decoupled from sample comparison by repeated measurement of inert and control samples within each plate.

The two groups of test protocols: (i) steady-state tests and (ii) dynamic tests with feed switches result in different levels of complexity in process control as well as in data management and data reduction. In all cases, continuous validation and adaption based on feedback from scale-up experiments on cores and full-size parts in associated laboratories is needed.

2.3. Catalyst Evaluation

2.3.1. Steady-State Tests

Most of the protocols described herein are related to catalyst technologies for emission control of Diesel engines, some are described in detail below:

- Diesel oxidation catalysts (DOC): New Diesel cars use a rather complex system arrangement including a particulate filter and components for reduction of NO_x emissions. An important catalytic functionality is the oxidation of CO and HC which often is included in a dedicated DOC located close to the engine. In systems containing a DOC in combination with a NO_x reduction component, the DOCs activity towards NO oxidation plays also an important role for the whole system and the temperature dependency of the NO_2/NO_x ratio is a critical characteristic in catalyst optimization. Typical DOC tests involve simulated "light-off" experiments in which steady-state catalyst activity is monitored at temperatures between 115 and 350 °C (typically screened in 10–12 levels) on fresh and oven aged samples. Since the sensitivity for sulfur poisoning is critical in a lean exhaust, usually tests for performance after exposure to SO_2 and thermal regeneration are already included in early screening stages. A typical feed gas simulating Diesel exhaust contains 500–3000 ppm CO, 80–500 ppm-C_1 HC (i.e methane, propene, octane, decane, toluene or mixtures with varying composition), 50–500 ppm NO, 5–10% O_2, 5–10% CO_2, 5–10% H_2O. The experiments are conducted with a total flow rate per reactor corresponding to a gas hourly space velocity (GHSV) of 45–80 Kh^{-1}.
- Selective catalytic reduction (SCR): Experiments on powder samples are performed with a simulated exhaust using NH_3 as the reductant. As the reaction rate at low temperatures is strongly affected by the NO_2/NO_x ratio, samples are tested without NO_2 ("standard SCR conditions") and with varying levels of the NO_2/NO_x ratio in a temperature window between 150–575 °C (screened in 5–10 levels) at GHSV of 30–90 Kh^{-1}. Typical feed compositions contain 50–1000 ppm NO, 50–300 ppm NO_2, 50–1000 ppm NH_3 5–10% O_2, 5–10% H_2O, optional: 5–10% CO_2, 50–500 ppm-C_1 HC (see DOC testing).
- NH_3 oxidation: To avoid slip of excessive NH_3 into the environment, an SCR aftertreatment system needs an additional important component. The NH_3-oxidation catalyst ensures removal of unconverted NH_3 and is located downstream of the SCR catalyst. Typical feed composition for evaluating this functionality: 50–1000 ppm NH_3 5–10% O_2, 5–10% H_2O, GHSV: 30–90 Kh^{-1}, temperatures are evaluated between 200–575 °C, (typically screened in 2–5 levels).

2.3.2. Dynamic Tests with Feed Switches

Such protocols (see Figure 3) are required for the evaluation of TWC (three-way catalyst) functionality for exhaust after-treatment in gasoline cars. Also, catalyst technologies for NO_x abatement have aspects that require dynamic testing. Two examples are lean NO_x traps, which work by repeated reductive regeneration, or measurement of the NH_3 storage capacity to characterize an important property or SCR catalysts:

- TWC (Three-way catalysis): For optimal catalytic performance, Gasoline engines are operated near an air:fuel ratio of 1. This is ensured by active engine management using λ sensors. However, in dynamic driving conditions deviations from the optimal value difficult to avoid and the catalyst should tolerate excursions from this optimal point. Therefore, tests with λ perturbations are crucial. Several protocols are used to evaluate the different functionalities of fresh and aged catalysts. Results of this test have been previously reported [33,34].

○ Light-off tests (i.e., multiple temperature set points) with average λ = 1 and high frequency (up to 0.5 Hz) λ perturbations.

○　λ-sweep tests (i.e., multiple λ set points) at different temperatures. These are performed similar to light-off tests with a high frequency λ-perturbation, but with different average λ-set-points. Typically, the conversion of different feed components is plotted as a function of λ at different temperatures.

○　OSC test (Oxygen Storage Capacity): specific test for the oxygen-storage function of the catalyst, responsible for its tolerance for short-term deviation from an optimal air:fuel ratio. The test involves feed switches between CO and O_2 in nitrogen and monitoring CO_2 generation from stored oxygen.

- Ammonia storage for SCR: Employed to measure the dynamic NH_3 storage capacity at constant temperature. By cyclic switching NH_3 supply on and off, the NH_3 breakthrough curve is recorded under reaction conditions.

- LNT (lean NO_x trap): This technology uses rich pulses to regenerate a NO_x storage material. A crucial aspect for lab testing of this functionality is the ability to generate reproducible rich pulses with well-defined rich λ and pulse width. Usually 3–7 pulses are applied to each catalyst. After each rich pulse the NO_x breakthrough curve is recorded for 2–10 min and integrated in several ways to calculate average NO_x conversion efficiency or average NO_x storage. In these tests it is important to compare NO_x storage in each individual rich/lean cycle and to monitor time on stream effects. The LNT test is usually run at several temperatures covering the typical operating window. A more detailed description of the LNT test conditions is given in the Materials and Methods section.
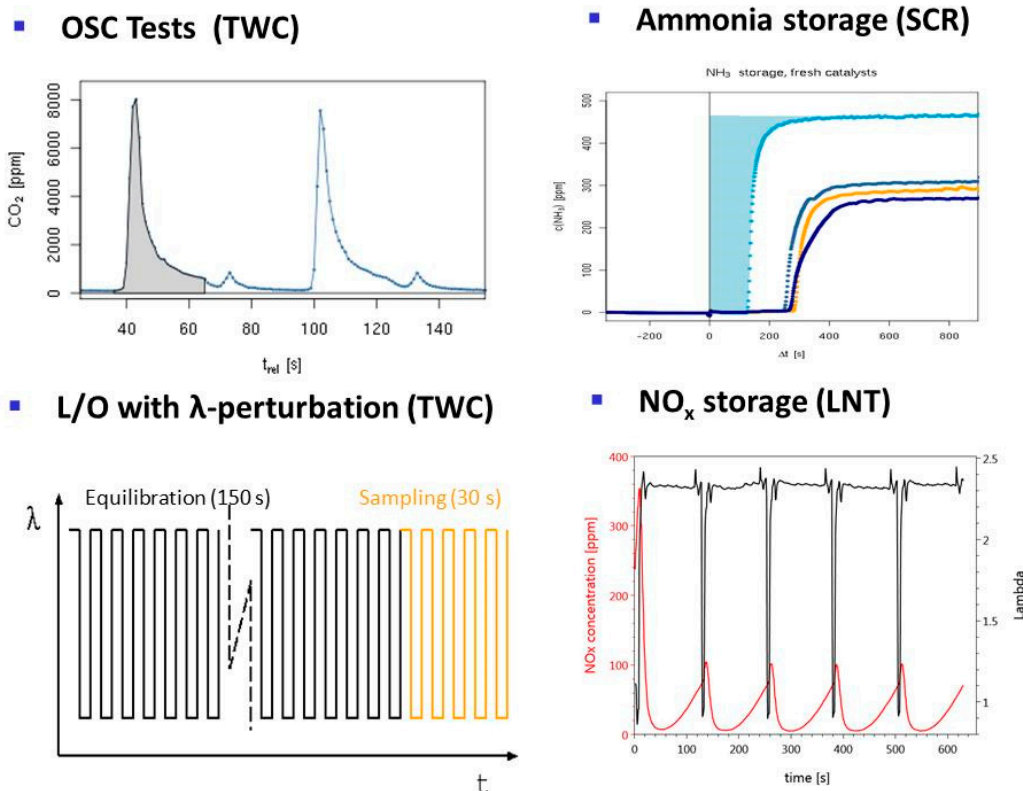

Figure 3. Examples for dynamic test protocols implemented on a 48-fold reactor system. *Top left:* OSC test, cycling O_2 and CO containing feed and monitoring CO_2 release in the absence of O_2 in the gas phase as a measure for the oxygen storage capacity at a given temperature. *Top right:* NH_3 storage test by cycling NH_3 and monitoring the NH_3 breakthrough under SCR reaction conditions (i.e., in the presence of NO, O_2, H_2O, optionally CO_2 and/or HC). *Bottom right:* LNT test with repeated rich regeneration cycles with defined λ. The NO_x concentration is monitored and analyzed. *Bottom left:* TWC testing in a feed with rapid λ oscillations with defined amplitude. After an equilibration time of 150–180 s, the traces from relevant gas analyzers are averaged for 30s.

2.4. Test Procedure

2.4.1. Catalyst Library Design and Preparation for Testing

For sample preparation, all conventional methods (e.g., impregnation, precipitation, ion-exchange etc.) are explored in small scale (3–5 g samples) including slurry processing methods such as pH adjustment and milling. Usually a DoE approach is used for the design of sample matrixes (cf. Figure 4) with relevant variables for PGM powders (support material, PGM type, PGM loading, promoters, preparation route, shaping procedure, calcination temperature, aging conditions). The type of DoE depends on the objective.
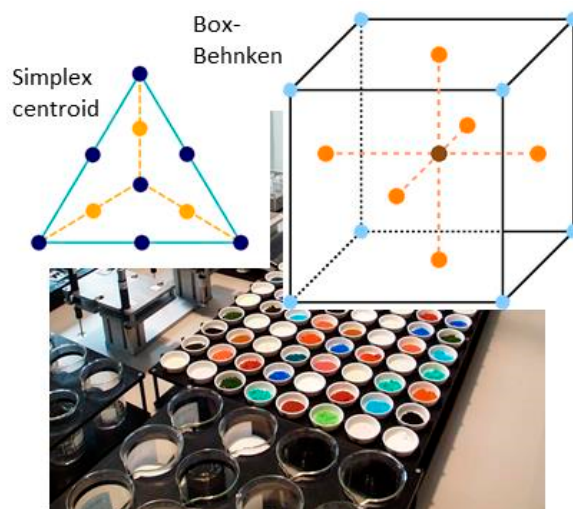

Figure 4. Examples for typical DoE layouts used for catalyst libraries. Simplex lattice designs are used for mixtures (the constraint that all components add to 100% must be met), response surface designs like Box-Behnken can be more suitable to optimize the content of dopants that make up only a small fraction of the catalyst.

In studies targeting optimization of washcoat compositions, the variables for slurry processing include slurry additives, binder, milling conditions and pH. To perform statistically robust experiments standard reference samples should be included in every run and preparation and testing of duplicate samples should be used to control the statistical error of the whole procedure (cf. Table 1 for the experimental design of the current study, a detailed description of the sample preparation is given in the Materials and Methods section).

To get an acceptable back-pressure in tests with comparatively high space velocity, powders need to be shaped for testing. A particle size fraction of 250–500 μm is a good compromise between back-pressure and simulating diffusion lengths found in coated catalysts. Typically, shaping is performed by formulating the active components into a slurry, milling to a $D_{50} < 15$ μm, drying under agitation and crushing/sieving after calcination. To simulate realistic washcoat loadings, most catalysts are tested as reactor loads with an active mass of 100–300 mg diluted to 1 mL bed volume using corundum (α-Al_2O_3) of same particle size fraction. The exact quantity of catalyst is selected to represent washcoat amount found in 1 mL of coated monolith catalyst. Testing coated samples in a high-throughput reactor involves careful crushing of the monolith catalysts and using a sieve fraction between 500 and 1000 μm and loading a mass that corresponds to 1mL of coated catalyst. Space velocities can then be calculated with reference to 1 mL of catalyst volume facilitating direct comparison with monolith core and full-size tests.

Table 1. Variation of the NO$_x$ storage component (NSC) in the case study matrix. The NSC amount is normalized to 20 wt% BaO, other elements partially or completely replace Ba on a molar basis. The DoE (a mixture design in each of the dopants) allows to resolve main effects of different alkaline earth elements as replacement for Ba as well as secondary effects such as concentration effects and Ba:M interaction effects. Cf. Materials and Methods section for a description of sample preparation.

Sample No.	BaO	SrO	CaO	MgO	ZnO	Comment
001	0	0	0	0	0	Base line
002	1	0	0	0	0	Main effect Ba
003	0	1	0	0	0	Main effect Sr
004	0	0	1	0	0	Main effect Ca
005	0	0	0	1	0	Main effect Mg
006	0	0	0	0	1	Main effect Zn
007	2/3	1/3	0	0	0	Interaction Ba:Sr +
008	1/3	2/3	0	0	0	Sr concentration
009	2/3	0	1/3	0	0	Interaction Ba:Ca +
010	1/3	0	2/3	0	0	Ca concentration
011	2/3	0	0	1/3	0	Interaction Ba:Mg +
012	1/3	0	0	2/3	0	Mg concentration
013	2/3	0	0	0	1/3	Interaction Ba:Zn +
014	1/3	0	0	0	2/3	Zn concentration
015	1	0	0	0	0	Repeat of 002

2.4.2. Hydrothermal Aging

Typically, catalysts are tested both fresh and after hydrothermal oven aging. Usually aged performance is more critical as it allows to predict catalyst performance over the full lifetime. To simulate realistic exhaust conditions during aging, an atmosphere containing 5–15% water is used. Aging temperatures and durations are set to simulate typical conditions and depend on the application. For Diesel exhaust, catalysts are kept for 5–24 h at temperature between 600 and 850 °C in water/air mixture, the higher temperature range is typical for systems with active particulate filter regeneration. In the case of gasoline exhaust for the TWC application, aging temperatures between 850 and 1150 °C are applied with duration of 5–24 h. To simulate the impact of changing oxidizing and reducing environment, "rich/lean" aging is performed with two gas feeds containing 10% water (4% H$_2$ in N$_2$ and air) that are switched every 10 min during aging. For quality assurance, furnaces are equipped with time resolved monitoring of temperature and steam dosing. A certain degree of automation ensures that samples are cooled to 300 °C in the presence of water and further to room temperature in air.

A critical aspect of HT testing is the requirement, that all 48 channels are equivalent with respect to temperature and flow rate. This assumption needs to be verified for every new test protocol. In the present study, three identical loads of each LNT catalyst were filled. Figure 5 shows the results of such an experiment. It illustrates the time dependencies of NO$_x$ at 450 °C for all fresh samples. On the one hand, the curves for three loads are rather close (i.e., good load-load reproducibility) on the other hand it reflects the typical behaviour for each catalyst composition. Largest differences between loads were found at low temperatures, where also a strong time on stream effect is observed by large cycle-cycle differences (this effect is shown in Figure 6b, at 250 °C for the fresh catalyst). This might be explained by the absence of the Rh component in these model catalysts which is typically included in real LNT formulations [36], which is essential for the effective reduction of the stored NO$_x$ especially at low temperatures. Consequently, the storage capacity is not fully cleared out and the effective capacity shows a slow cycle-cycle deterioration until a steady state is reached. Otherwise, load-load variations give no evidence for systematic errors like dosing stability or temperature distribution over the reactor block.
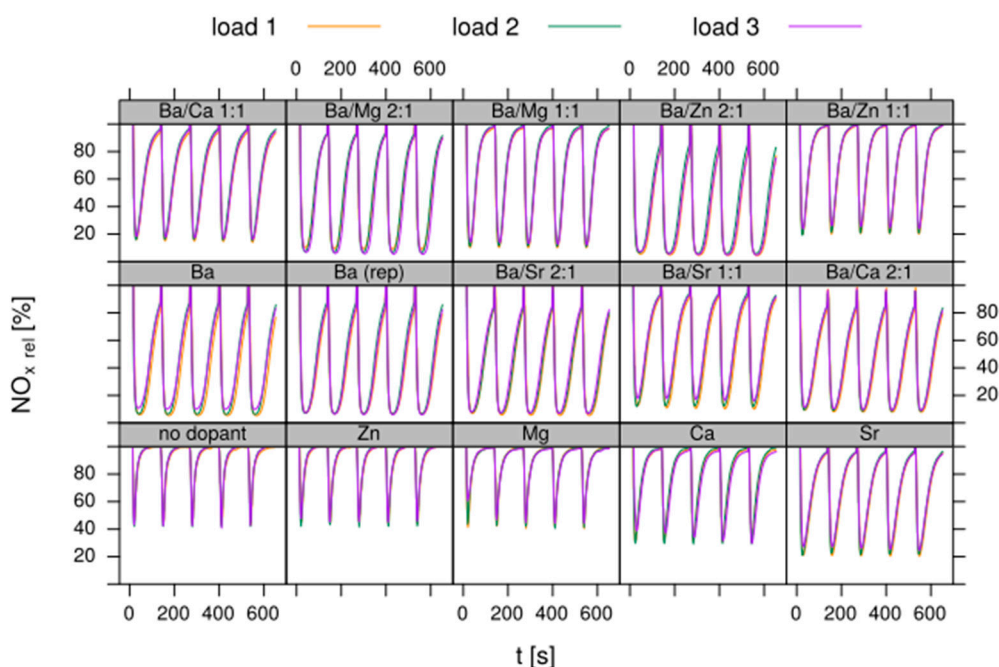
Figure 5. Time dependencies of NO$_x$ efficiencies at 450 °C for three loads of each fresh catalyst (cf. Table 1 for composition details).

Changes in the composition of NO$_x$ species vs. time in five rich/lean cycles for two catalysts (1%Pt/Al$_2$O$_3$ and 1%Pt/20%BaO-Al$_2$O$_3$) are shown in Figure 6. The results for fresh and 800 °C aged catalysts for all reaction temperatures are included. As can be seen from the NO$_x$ concentration curves in the lean phase, already a Pt/alumina sample without further dopants (cf. Figure 6a) reveals some storage performance but fresh performance is significantly improved by the presence of Ba especially at 350 °C (cf. Figure 6b). These results are in line with the optimum temperature window for NO$_x$ storage at 300–350 °C reported for a conventional LNT with barium as major NO$_x$ storage and aluminium oxide on a cordierite substrate [36].
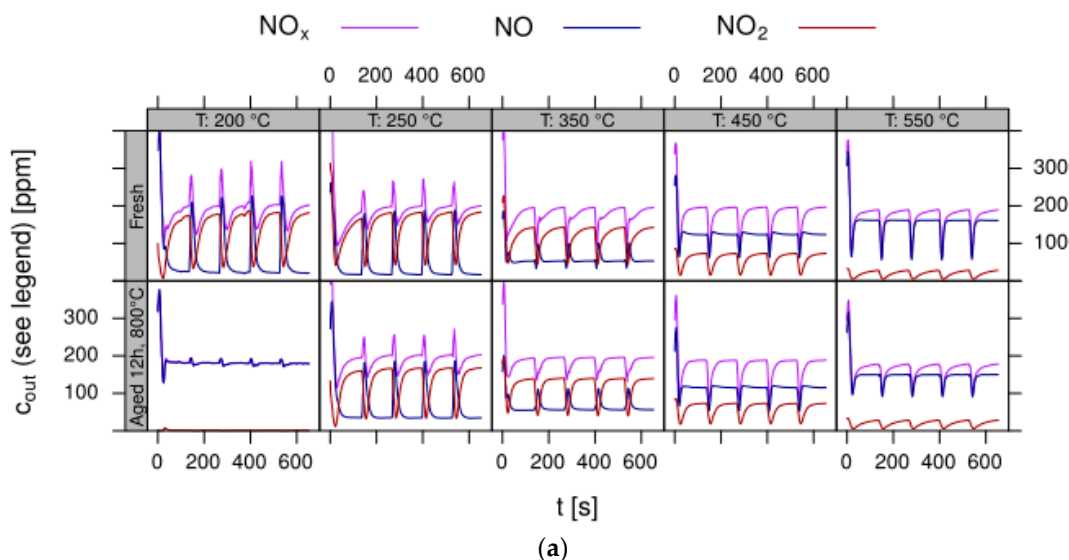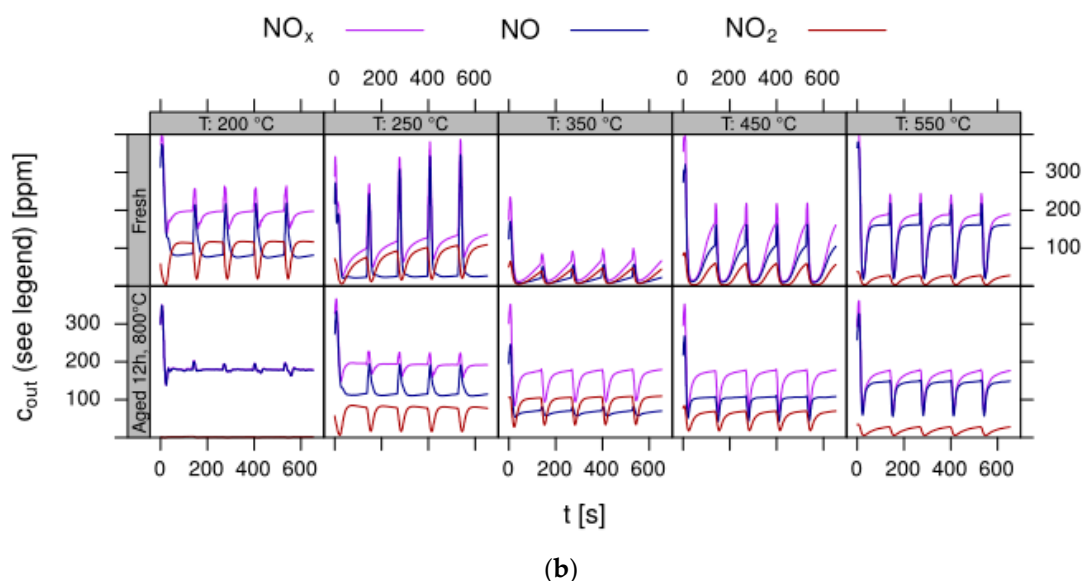

(**a**)

Figure 6. *Cont.*

Figure 6. Development of NO_x species during five rich/lean cycles at different temperatures for (**a**) 1%Pt/Al$_2$O$_3$ (sample 001) and (**b**) 1%Pt/20%BaO- Al$_2$O$_3$ (sample 002).

Aging at 800 °C has a significant negative impact on NO_x storage; both aged samples no longer show any activity at 200 °C and the performance of Pt/20%BaO-Al$_2$O$_3$ is not significantly better than that of 1%Pt/Al$_2$O$_3$. The detrimental effect of aging on model Pt/BaO/Al$_2$O$_3$ catalysts was also described elsewhere [37].

The essential Pt functionality is oxidation of NO to NO_2 which according to the simplified LNT mechanism [38] is then stored on the catalyst. The time dependency of the NO_2 concentration in the lean phase reflects the catalysts ability to form and store NO_2. Once the storage capacity is fully saturated the NO_2 concentration becomes constant over time as for example on fresh Pt/Ba-alumina at 200 °C and on both aged samples shown in Figure 6 at T = 250, 350 and 450 °C. In these cases, saturation is reached within less than two minutes of the lean operation. For the simple model system, there are also pronounced NO_x spikes during the rich phase due to incomplete reduction of the stored NO_x to N_2. This is most pronounced at lower temperatures of 200–250 °C. These results are in line with [36] which showed for lean NO_x trap technology that temperatures of at least 300 °C are favourable for complete regeneration as well as NO_x reduction.

In the present study, the lean phase of the last cycle is used as performance indicator for catalyst comparison (cf. Materials and Methods section and corresponding figures). The average NO_x efficiency within 2 min of this phase is automatically calculated for each measured sample. Results at different temperatures for fresh and aged samples are plotted as function of the Ba-content in Figure 7 (results for the three separate loads are shown).

A clear difference in the performance of different samples upon variation of the NSC composition is observed in the fresh state. After aging the NO_x efficiencies are rather low for all catalysts but the general trends are preserved. In all cases, replacing BaO by Sr, Ca, Mg and Zn oxides results in lower NO_x efficiencies under the test conditions applied. As long as only 1/3 of Ba is replaced by another alkaline earth metal, the detrimental effect is small, as soon as larger amounts are substituted the performance loss becomes substantial. The performance ranking of samples in which the NSC contains less than 1/3 BaO indicates that Sr > Ca are most active replacements for Ba while Zn and Mg are ineffective.
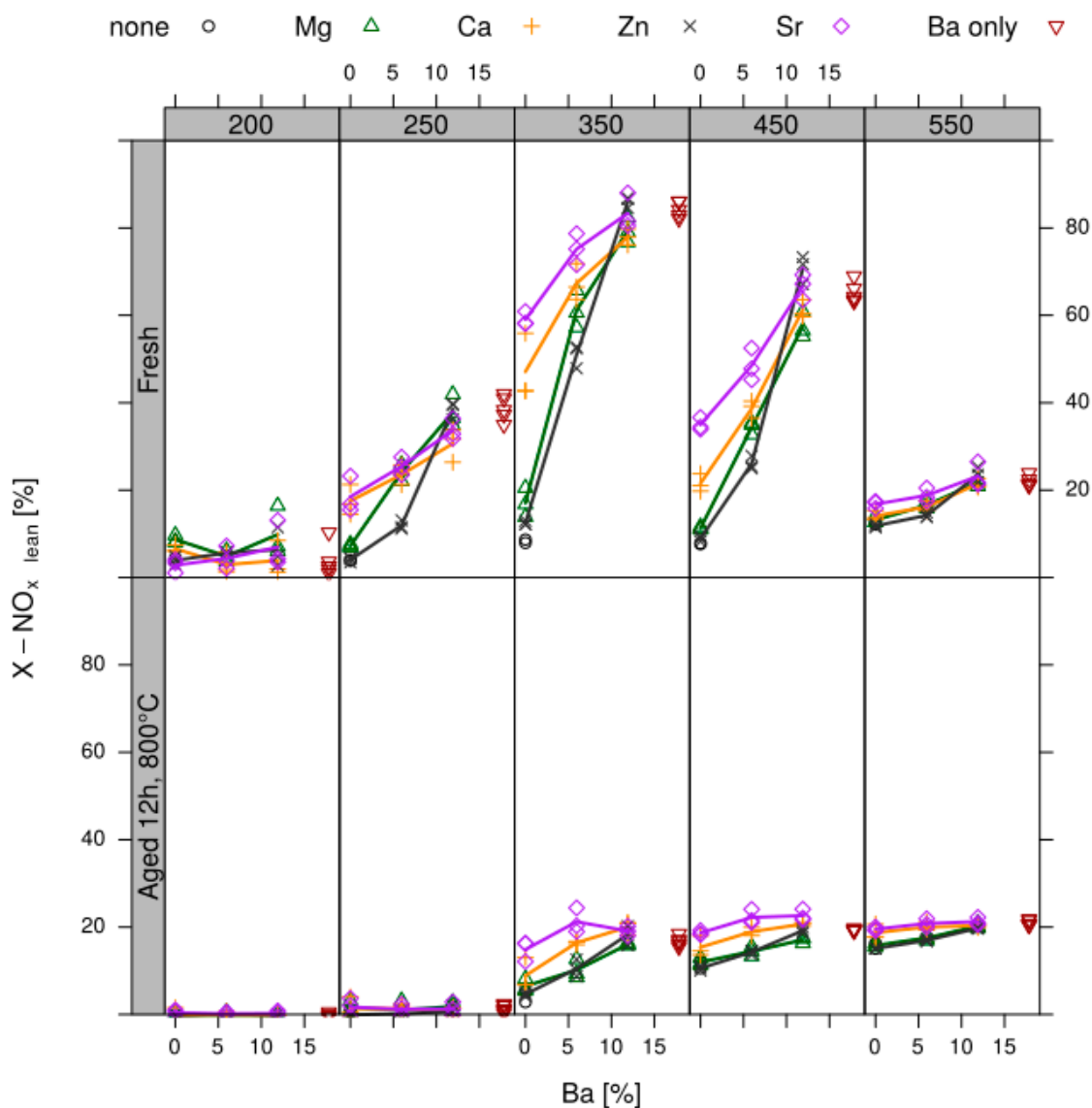
Figure 7. Correlation of NO_x efficiencies at different temperatures with Ba content, grouped by co-dopants (three loads of each composition are shown as separate points, lines are drawn through the averages of three loads with the intention to highlight trends), data points are calculated from the area highlighted in Figure 5. Detailed numerical values are given in Table 2.

Especially Mg on the alumina support results in a storage capacity which is indistinguishable from the undoped alumina (i.e., the baseline sample used in this study). The results also demonstrate that the ranking of dopants does not significantly change over the whole tested temperature range and no synergies (e.g., for extending the effective temperature window) between different dopants are found. Another finding from this study is that at 550 °C neither aging nor alkaline earth metal doping have strong impact on the performance, which is an indication that mainly the alumina support is acting as storage function.

Based on the lean efficiency data, the NO_x storage capacities are calculated and the average value from three loads for each catalyst are summarized in Table 3. Due to significant loss of NO_x storage capacities after hydrothermal aging at 800 °C BET and XRD characterization of selected catalysts were performed. Results on BET surface areas are summarised in Table 2. As to be expected, none of the samples showed a significantly decreasing BET surface area upon aging. Therefore, loss of surface area does not explain the nearly complete activity loss. However, in the XRD patterns a significant

increase in the intensity of Pt peaks is observed; an example for the effect of aging on XRD patterns is given in Figure 8. The Pt crystallite sizes in the aged catalysts estimated by the Scherrer equation are in the range of 50–60 nm. These values are close to results reported in [36] on a similar Pt/Ba/alumina model catalyst for 800 °C aging temperature. To minimize the effect of Pt sintering in the real catalyst, different dopants are used, which are missing in the simple model catalyst library.
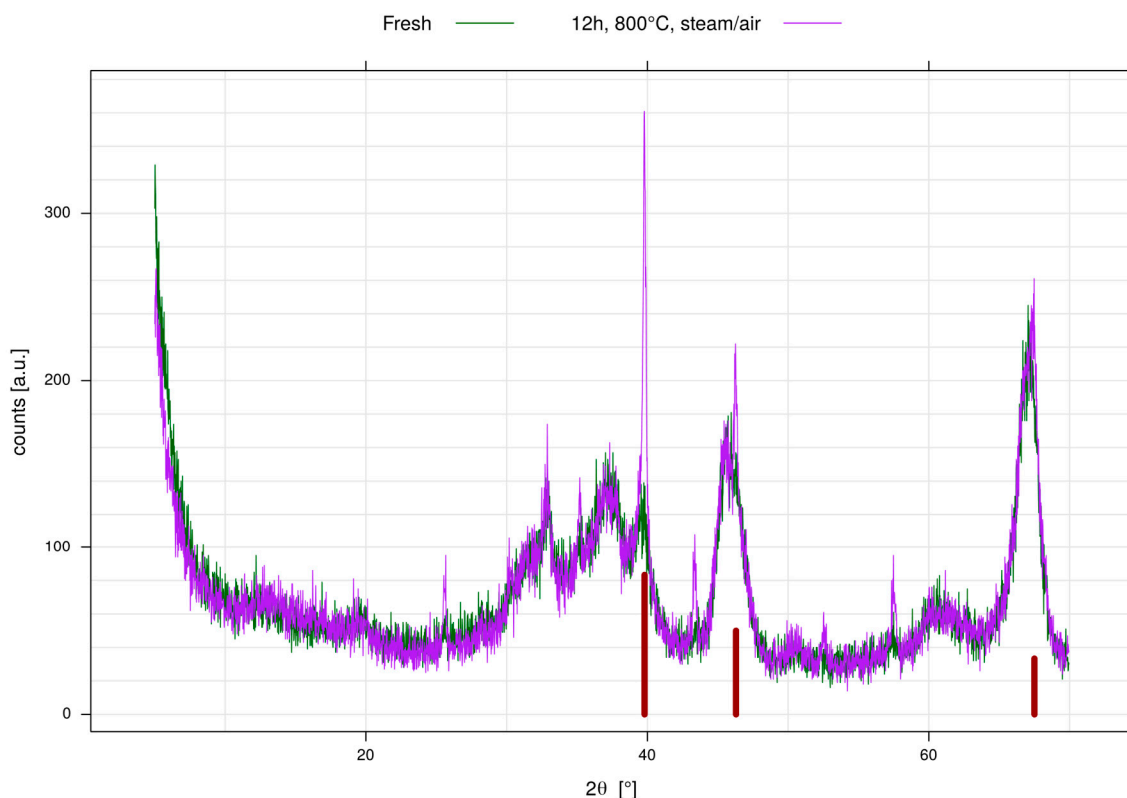

Figure 8. XRD pattern of fresh and aged 1%Pt/20%BaO-Al$_2$O$_3$ catalyst, red bars: powder diffraction pattern for cubic Pt (space group Fm-3m (225)), PDF 00-004-0802.

Table 2. BET surface areas for selected fresh and aged samples. All samples show a loss of surface area upon aging that is comparable to the alumina support without alkaline earth element doping.

Sample No.	Description	BET Fresh [m^2/g]	BET Aged [m^2/g]
001	SCFa140	136.7	114.2
002	BaO/SCFa140	115.5	96.9
003	SrO/SCFa140	129.2	98.4
004	CaO/SCFa140	123.1	110.5
005	MgO/SCFa140	132.9	115.4
006	ZnO/SCFa140	124.5	106.3

Table 3. Storage capacities for the last lean cycle in μmol(NO$_x$)/g sample at each tested temperature. For all samples, aging almost entirely suppresses low temperature storage. Assuming that the alkaline earth metal is fully utilized to form M(NO$_3$)$_2$ upon storage, and neglecting the capacity of the alumina support, a theoretical limit of ~2170 μmol(NO$_x$)/g catalyst can be expected.

Dopant	200 °C		250 °C		350 °C		450 °C		550 °C	
	Fresh	*Aged*	Fresh	*Aged*	Fresh	*Aged*	Fresh	*Aged*	Fresh	*Aged*
Ba	117	*5*	591	*47*	1528	*292*	1193	*346*	421	*381*
Ba/Ca 2:1	76	*0*	436	*31*	1452	*344*	1144	*380*	399	*377*
Ba/Ca 1:1	56	*6*	316	*39*	1310	*297*	758	*365*	312	*387*
Ca	101	*12*	290	*36*	940	*169*	436	*310*	279	*377*
Ba/Mg 2:1	161	*2*	631	*44*	1498	*292*	1081	*317*	406	*378*
Ba/Mg 1:1	75	*6*	371	*25*	1203	*194*	678	*281*	325	*340*
Mg	172	*5*	137	*20*	347	*132*	228	*245*	265	*324*
Ba/Sr 2:1	125	*8*	464	*43*	1537	*323*	1219	*405*	425	*387*
Ba/Sr 1:1	77	*6*	302	*39*	1399	*359*	909	*413*	344	*387*
Sr	53	*12*	260	*47*	1116	*265*	669	*352*	318	*370*
Ba/Zn 2:1	106	*2*	592	*28*	1590	*312*	1307	*346*	430	*361*
Ba/Zn 1:1	82	*0*	168	*6*	957	*193*	495	*270*	267	*319*
Zn	70	*0*	74	*0*	246	*91*	176	*206*	228	*296*
no dopant	88	*0*	82	*3*	211	*91*	174	*242*	254	*324*

3. Discussion

hte has been running parallel reactors for 19 years. During this time a large amount of operating experience has been acquired. In the field of environmental catalyst screening, the most important lesson learned is that realistic test conditions are required to generate relevant data. Oversimplified test conditions and sample preparation methodologies must be avoided. Typical examples are neglecting well-known inhibiting effects of steam and sulfur in the exhaust. This will then postpone the detection of problems to a later, more expensive screening stage. HT units are used for the fast primary screening of new materials under conditions close to the actual application. Even for screening large sample libraries in the initial stage, in most cases such studies take hydrothermal and S-aging into account to avoid costly false positives.

Another important aspect is close interaction with scale-up and engine testing. There is a constant pressure to simplify experiments to save time and/or costs, however, accepting any simplification requires frequent re-evaluation of the underlying assumptions. With every new finding, it has to be verified that an observed effect is real for the application. Environmental catalysis is a rather mature field and performance of state of the art catalysts is at a high level. Every new development needs to be benchmarked against relevant references under the same reaction conditions. Therefore, HT technology is often used for incremental improvements. Existing catalyst technologies are modified by small changes rather than a fully combinatorial screening using application detached, simplified conditions. If necessary, HT units need to be modified to be able run more relevant test conditions. This is facilitated by close integration of HT powder testing with scale-up experiments.

The sample throughput in environmental catalyst screening is still orders of magnitude smaller than what is considered "high throughput" in pharmaceutical or biochemical fields. Nevertheless, HT workflows can significantly increase the screening capacity of an environmental catalyst development lab using conventional testing. By applying proper statistical tools like DoE much larger parameter spaces can be screened in a more reliable way.

For efficient utilization of HT screening capacity, designed experiments, automated data processing and statistical methods for catalyst optimization are of high importance. In addition for fully automated test unit operation, also software for data reduction and data management are crucial to handle the large amount of data and drive a rational approach to catalyst development. Under this aspect, HT experimentation has matured beyond the level of pure primary material screening and has become a valuable enhancement to automotive catalyst development.

hte's technology platform enables fast material screening while providing for variation of catalyst properties such as preparation methodology and aging parameters. Analysis of HT data allows for differentiation of intrinsic differences between catalyst formulations and can be reliably used for the development of advanced emission control systems to meet ever stricter emission regulations.

4. Materials and Methods

For illustration of HT screening approach, a sample matrix consisting of 15 model catalysts was prepared and tested fresh and after hydrothermal aging using an LNT protocol.

- Design of sample matrix: The LNT model catalysts contained alumina as support material. This is loaded with a NO_x storage component (NSC) and Pt for NO oxidation. The variation parameter in the sample matrix for this case study was the NSC composition (cf. Table 1). Different alkaline earth oxides and ZnO as individual components as well as of BaO/MO combinations (M = Mg, Ca, Sr, Zn) with a gradual replacement of BaO by another oxide on a molar basis (BaO (2/3) + MO (1/3) and BaO (1/3) + MO (2/3)) were used as NSC. In addition to the NSC variation, a baseline sample w/o NSC, i.e., 1% Pt on alumina (sample 001) was prepared. This takes into account that also the alumina support has some NO_x storage capability. The references (sample 002 and 015 as repeat) contain 20 wt% BaO on alumina as NSC since Ba is typically used in state-of-the-art LNT formations. In all other samples the amount of NSC is normalized to 20 wt% on carrier BaO, other elements (Sr, Ca, Mg and Zn) replace Ba on a molar basis to get—at least in theory—an equivalent amount of active storage sites.
- Sample preparation: For sample preparation Puralox SCFa140 (Sasol, Brunsbüttel, Germany) was used as support. For each catalyst, 5 g alumina were impregnated with a solution of the corresponding alkaline earth metal nitrate using the incipient wetness technique. After careful mixing samples were dried at 100 °C and calcined for 2 h at 500 °C in air. The resulting powders were then impregnated with a solution of $Pt(NH_3)_4(NO_3)_2$ (CAS: 20634-12-2) using incipient wetness impregnation, dried and calcined for 1 h, 400 °C in air. As the alkaline earth metal content in each sample was normalized on a molar basis, the Pt content was set to 1 wt% based on the weight of the alumina carrier. For shaping, the calcined powders were set to slurry with D.I. water (~30 wt% solid content) and milled for 5 min at 500 rpm in a ball mill (using ZrO_2 beakers and milling balls). For pure alumina this procedure was verified to result in a particle size distribution with D_{50} < 15 μm. The slurry was then dried under stirring and calcined for 2 h at 500 °C in air. Afterwards the resulting cake was crushed and sieved to a particle size fraction of 250–500 μm used for testing. A fraction of these shaped particles was aged for 12 h at 800 °C in a muffle oven flowed through with a stream of 10% H_2O in air. Additional aliquots of selected catalysts were aged and submitted to XRD and BET analysis.
- Test procedure: For the catalytic test, sample amounts were adjusted to have the same amount of Pt in each reactor. This also ensures that, with exception of the baseline sample w/o NSC, the molar amount of the storage component is constant for the whole sample library. For the pure alumina reference, this corresponded to 200 mg diluted with corundum to simulate 1 mL coated catalyst with a washcoat loading of 3.3 g/in^3. To control time on stream effects and to achieve better statistical robustness, each catalyst was tested in 3 loads, filling one plate of fresh and one plate of aged catalysts in the 48 fold parallel screening unit. Splitting the samples in this way into two plates aims at achieving maximum resolution of the NSC effect among fresh and aged samples. In the experiment, each catalyst was tested for 5 lean/rich cycles at temperatures T = 550, 450, 350, 250, 200 °C. The total flow in the measured reactor is set to meet a GHSV of 60,000 h^{-1} based on 1 mL bed volume. A simulated Diesel exhaust gas was mixed using mass flow controllers. During the lean phase (2 min) the feed consisted of: 200 ppm NO, 1500 pm CO, 10% O_2, 6% H_2O, 6% CO_2, balance N_2. Using fast switching magnetic valves this feed is replaced by a rich gas for 10s with minimal perturbation of the flow. In the rich phase the O_2 concentration is reduced to 1% and λ is adjusted to λ = 0.95 by adding CO/H_2 in a ratio of 1:3 while the concentration of other gases

remains at their lean level. The gap between lean and rich flow rate is compensated by additional balance N_2 added to the rich stream.

- Data processing: Throughout each experiment, the process values from all sensors (temperature, flow, pressure, gas analysers) are recorded with a frequency of 1 Hz and automatically linked by the control software to the corresponding set-points for that condition, and most importantly to the reactor position that is being tested. An example of the typical LNT raw data output at one temperature for each position is shown in Figure 5. For the whole experiment on the complete LNT matrix in the current study, taking about 4 days on the test unit close to 300,000 data points are collected for each individual sensor. Obviously, raw data are not suitable for direct catalyst comparison and data reduction is required. This data reduction process is developed when a new test protocol is implemented and automated in the control software, which e.g., averages the concentration readings for several lean/rich cycles or over a predefined time interval within a lean rich cycle. Some examples on possible sampling time intervals in LNT tests are shown in Figure 6. For efficient screening, different evaluations should be easy to configure in the data management system. In the current study, the average NO_x efficiency in the lean phase of the last cycles has been used as performance indicator. The reduced data sets are then stored in a relational database system ("myhte" data warehouse) from which they can be retrieved for further processing (e.g., R, a language and environment for statistical computing was used for analysis in the current case) [39]. For results stored in the database it is possible to relate individual measurements, such as using the inlet concentration measured for the by-pass line to calculate conversion. For the LNT application, an important step is the calculation of the average NO_x efficiencies and product distribution (e.g., NO_2/NO_x ratio) within different time windows or after a certain time of the lean phase. The overall process of calculating relevant parameters for the LNT application has been implemented as an automated data processing workflow. Even for an experiment on 48 different samples (see Figures 9 and 10) evaluation is a routine task which requires only little human interaction. In hte's lab, similar workflows have been established for other test protocols, some of them, such as automated extraction of light-off temperatures have been described elsewhere [33,34].

- DoE evaluation: In most cases, experiments in HT screening involve catalyst libraries that are designed based on principles of statistical design of experiments (DoE) [2,3], rather than a collection of unrelated catalysts. The goal of a DoE is it identify cause-effect relationships between the parameters controlled in the experiment (such as composition, thermal activation, or other treatments like milling or binders) and the observed catalyst performance. If possible, samples of a library are prepared and aged together with a reference of known performance to avoid aliasing of effects by uncontrolled factors and errors. If libraries cannot be fit into a single plate, some care has to be taken to control statistical error by introducing proper blocking factors e.g., using split plot designs. Depending on the amount of prior knowledge, either DoEs for factor screening in an early stage (such as fractional factorial designs) or response surface design methodologies can be applied. In the current case a factor screening (impact of different elements as NSC) was attempted. By screening the concentration at three levels also secondary effects can be resolved by the DoE. As the capacity of the 48-fold parallel reactor naturally limits the number of samples, in the current case the variable "Aging" was used as a splitting factor because we were mainly interested in the effect of composition before and after aging. In less obvious cases, computer-generated optimal designs such as D-optimal designs are required to ensure that split-block design constraints do not introduce uncontrolled statistical bias. However, in the current case the hydrothermal aging had such a dramatic effect that this was not critical. As additional QC measure protect against creeping loss of precision, it is advisable to include at least one standard sample into every experimental plate to control effects caused by sensor aging or contamination of the equipment. Specifically, for parallel reactors it is critical to avoid that factors of the experimental design are aliased with respect to either reactor position or time on stream. If time on stream effects can be expected as in

the current case of storage catalysts, testing multiple loads of at least some samples helps to make experiments more robust.
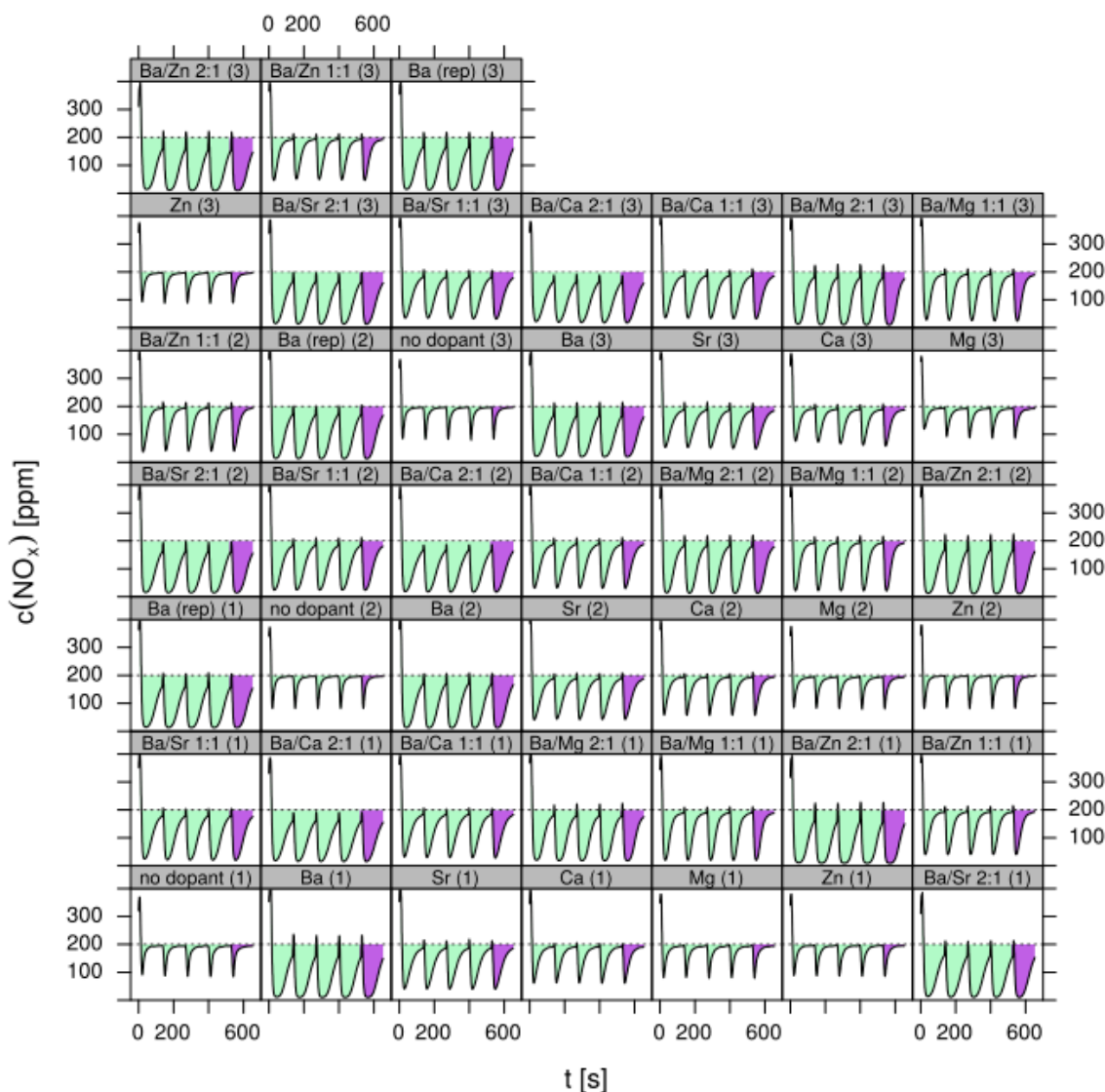

Figure 9. Overview of time resolved sensor readings for all test positions at one temperature from a typical LNT test including with rich/lean excursions. The positions are already labelled with the NSC component and the load number. The shaded area corresponds to the total NO_x efficiency, the part of data aggregated and used for sample ranking in this study is highlighted in purple.
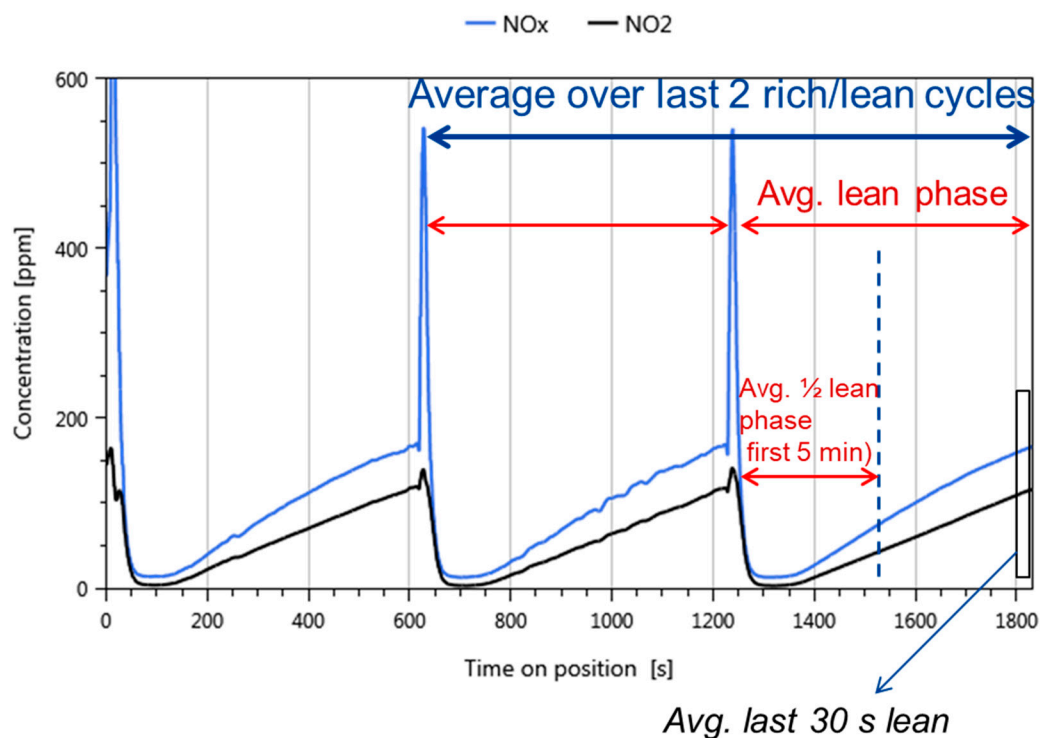
Figure 10. Examples of automated data reduction procedures. These performance indicators allow to do a direct catalyst ranking needed for DoE evaluation.

References

1. Heck, R.M.; Farrauto, R.J.; Gulati, S.T. *Catalytic Air Pollution Control, Commercial Technology*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2009; ISBN 978-0-470-27503-0.
2. Montgomery, D.C. *Design and Analysis of Experiments*, 8th ed.; John Wiley & Sons: Hoboken, NJ, USA, 2012; ISBN 1118146921.
3. Box, G.E.P.; Hunter, J.S.; Hunter, W.G. *Statistics for Experimenters: Design, Innovation, and Discovery*, 2nd ed.; Wiley: New York, NY, USA, 2005; ISBN 978-0-471-71813-0.
4. Senkan, S.M. High-throughput screening of solid-state catalyst libraries. *Nature* **1998**, *394*, 350–353. [CrossRef]
5. Rodemerck, U.; Wolf, D.; Buyevskaya, O.V.; Claus, P.; Senkan, S.; Baerns, M. High-throughput synthesis and screening of catalytic materials: Case study on the search for a low-temperature catalyst for the oxidation of low-concentration propane. *Chem. Eng. J.* **2001**, *82*, 3–11. [CrossRef]
6. Hendershot, R.J.; Lasko, S.S.; Fellmann, M.F.; Oskarsdottir, G.; Delgass, W.N.; Snively, C.M.; Lauterbach, J. A novel reactor system for high throughput catalyst testing under realistic conditions. *Appl. Catal. A Gen.* **2003**, *254*, 107–120. [CrossRef]
7. Lucas, M.; Claus, P. High throughput screening in monolith reactors for total oxidation reactions. *Appl. Catal. A Gen.* **2003**, *254*, 35–43. [CrossRef]
8. Mills, P.L.; Nicole, J.F. A novel reactor for high-throughput screening of gas-solid catalyzed reactions. *Chem. Eng. Sci.* **2004**, *59*, 5345–5354. [CrossRef]
9. Paul, J.S.; Jacobs, P.A.; Weiss, P.-A.W.; Maier, W.F. Combinatorial discovery of new catalysts for the selective oxidation of isobutene. *Appl. Catal. A Gen.* **2004**, *265*, 185–193. [CrossRef]

10. Hendershot, R.J.; Snively, C.M.; Lauterbach, J. High-Throughput Heterogeneous Catalytic Science. *Chem. Eur. J.* **2005**, *11*, 806–814. [CrossRef] [PubMed]

11. Zech, T.; Bohner, G.; Klein, J. High-throughput screening of supported catalysts in massively parallel single-bead microreactors: Workflow aspects related to reactor bonding and catalyst preparation. *Catal. Today* **2005**, *110*, 58–67. [CrossRef]

12. Brooks, C.; Cypes, S.; Grasselli, R.K.; Hagemeyer, A.; Hogan, Z.; Lesik, A.; Streukens, G.; Volpe, A.F., Jr.; Turner, H.W.; Weinberg, W.H.; et al. High throughput discovery of CO oxidation/VOC combustion and water-gas shift catalysts for industrial multi-component streams. *Top. Catal.* **2006**, *38*, 195–209. [CrossRef]

13. Farrusseng, D. High-throughput heterogeneous catalysis. *Surf. Sci. Rep.* **2008**, *63*, 487–513. [CrossRef]

14. Moehmel, S.; Steinfeldt, N.; Engelschalt, S.; Holena, M.; Kolf, S.; Baerns, M.; Dingerdissen, U.; Wolf, D.; Weber, R.; Bewersdorf, M. New catalytic materials for the high-temperature synthesis of hydrocyanic acid from methane and ammonia by high-throughput approach. *Appl. Catal. A Gen.* **2008**, *334*, 73–83. [CrossRef]

15. Turner, H.W.; Volpe, A.F., Jr.; Weinberg, W.H. High-throughput heterogeneous catalyst research. *Surf. Sci.* **2009**, *603*, 1763–1769. [CrossRef]

16. Gaudillere, C.; Vernoux, P.; Mirodatos, C.; Caboche, G.; Farrusseng, D. Screening of ceria-based catalysts for internal methane reforming in low temperature SOFC. *Catal. Today* **2010**, *157*, 263–269. [CrossRef]

17. Valtchev, M.; Hammes, M.; Richter, R.; Holtzen, H.; Stowe, K.; Maier, W.F. Corrosion-Resistant Parallel Fixed-Bed Reactors for High-Throughput Screening of New Deacon Reaction Catalysts. *Chem. Eng. Technol.* **2014**, *37*, 1251–1260. [CrossRef]

18. Hagemeyer, A.; Volpe, A.F. (Eds.) *Modern Applications of High Throughput R&D in Heterogeneous Catalysis*; Bentham Science Publishers: Sharjah, UAE, 2014; eISBN 978-1-60805-872-3, ISBN 978-1-60805-873-0. [CrossRef]

19. Zhu, H.B.; Laveille, P.; Rosenfeld, D.C.; Hedhili, M.N.; Basset, J.M. A high-throughput reactor system for optimization of Mo-V-Nb mixed oxide catalyst composition in ethane ODH. *Catal. Sci. Technol.* **2015**, *5*, 4164–4173. [CrossRef]

20. Luneau, M.; Schuurman, Y.; Meunier, F.C.; Mirodatos, C.; Guilhaume, N. High-throughput assessment of catalyst stability during autothermal reforming of model biogas. *Catal. Sci. Technol.* **2015**, *5*, 4390–4397. [CrossRef]

21. Luchters, N.T.J.; Fletcher, J.V.; Roberts, S.J.; Fletcher, J.C.Q. Variability of Data in High Throughput Experimentation for Catalyst Studies in Fuel Processing. *Bull. Chem. React. Eng. Catal.* **2017**, *12*, 106–112. [CrossRef]

22. Emmanuel, J.; Hayden, B.E.; Saleh-Subaie, J. The particle size dependence of CO oxidation on model planar titania supported gold catalysts measured by parallel thermographic imaging. *J. Catal.* **2019**, *369*, 175–180. [CrossRef]

23. Pfeifer, M.; Schwarz, T.; Stöwe, K. Quaternäre Metall/Metalloxid-Katalysatoren als Wandkatalysatoren in Mikroreaktoren für Power-to-Gas-Applikationen mittels kombinatorischer Hochdurchsatzmethoden. *Chem. Ing. Tech.* **2019**, *91*, 607–613. [CrossRef]

24. Brenner, A.; Schüth, F.; Schunk, S.A.; Stichert, W. Anordnung zum Testen der Katalytischen Aktivität von einem Reaktionsgas ausgesetzten Feststoffen. Patent DE 198 61 316 B4, 6 March 1998.

25. Haas, A.; Strehlau, W.; Brenner, A.; Koechel, O.; Friess, M.; Zech, T. Device and Method for Pressure and Flow Control in Parallel Reactors. U.S. Patent WO 2005063372 A2, 26 May 2009.

26. Strehlau, W.; Gerlach, O.; Maier, J.; Gabriel, T. Catalysts for the Simultaneous Removal of Carbon Monoxide and Hydrocarbons from Oxygen-Rich Exhaust Gases and Processes for the Manufacture Thereof. U.S. Patent WO 2005/102513 A1, 11 October 2007.

27. Strehlau, W.; Gerlach, O.; Maier, J.; Gabriel, T. Catalyst for the Treatment of Exhaust Gases and Processes for Producing the Same. U.S. Patent WO 2006/120013 A1, 18 September 2008.

28. Hendershot, R.J.; Rogers, W.B.; Snively, C.A.; Ogunnaike, B.A.; Lauterbach, J. Development and optimization of NO_x storage and reduction catalysts using statistically guided high-throughput experimentation. *Catal. Today* **2004**, *98*, 375–385. [CrossRef]

29. Hendershot, R.J.; Vijay, R.; Snively, C.M.; Lauterbach, J. High-throughput study of the performance of NO_x storage and reduction catalysts as a function of cycling conditions and catalyst composition. *Chem. Eng. Sci.* **2006**, *61*, 3907–3916. [CrossRef]

30. Iojoiu, E.E.; Bassou, B.; Guilhaume, N.; Farrusseng, D.; Desmartin-Chomel, A.; Lombaert, K.; Bianchi, D.; Mirodatos, C. High-throughput approach to the catalytic combustion of diesel soot. *Catal. Today* **2008**, *137*, 103–109. [CrossRef]

31. Kern, P.; Klimczak, M.; Heinzelmann, T.; Lucas, M.; Claus, P. High-throughput study of the effects of inorganic additives and poisons on NH_3-SCR catalysts. Part II: Fe–zeolite catalysts. *Appl. Catal. B Environ.* **2010**, *95*, 48–56. [CrossRef]

32. Gärtner, A.; Lenk, T.; Kiemel, R.; Casu, S.; Breuer, C.; Stöwe, K. High-Throughput Screening Approach to Identify New Catalysts for Total Oxidation of Methane from Gas Fueled Lean Burn Engines. *Top. Catal.* **2016**, *59*, 1071–1075. [CrossRef]

33. Sundermann, A.; Gerlach, O. High-Throughput Screening Technology for Automotive Applications. *Chem. Ing. Tech.* **2014**, *86*, 1941–1947. [CrossRef]

34. Sundermann, A.; Gerlach, O. High-Throughput Screening as a Supplemental Tool for the Development of Advanced Emission Control Catalysts: Methodological Approaches and Data Processing. *Catalysts* **2016**, *6*, 23. [CrossRef]

35. Kim, M.Y.; Park, J.J.; Lee, B.M.; Kang, H.; Song, J.; Na, S.; Han, H.S. *High Throughput Vehicle Test for Spatiotemporal Emissions Evaluation*; SAE Technical Paper 2018-01-0642; SAE International: Warrendale, PA, USA, 2018. [CrossRef]

36. Maurer, M.; Holler, P.; Zarl, S.; Fortner, T.; Eichlseder, H. *Investigations of Lean NO_x Trap (LNT) Regeneration Strategies for Diesel Engines*; SAE Technical Paper 2017-24-0124; SAE International: Warrendale, PA, USA, 2017. [CrossRef]

37. Kim, D.H.; Chun, Y.-H.; Muntean, G.G.; Yezeretz, A.; Currier, N.W.; Epling, W.S.; Chen, H.-Y.; Hess, H.; Peden, C.H.F. Relationship of Pt particle size to the NO_x storage performance of thermally aged $Pt/BaO/Al_2O_3$ lean NO_x trap catalysts. *Ind. Eng. Chem. Res.* **2006**, *45*, 8815–8821. [CrossRef]

38. Fridell, E.; Skoglundh, M.; Westerberg, B.; Johansson, S.; Smedler, G. NO_x Storage in Barium-Containing Catalysts. *J. Catal.* **1999**, *183*, 196–209. [CrossRef]

39. R Foundation for Statistical Computing, Vienna, Austria. Available online: http://www.R-project.org/ (accessed on 14 September 2019).