

# Thermal ageing phenomena and strategies towards reactivation of NO<sub>x</sub>- storage catalysts

M. Casapu<sup>a</sup>, J.-D. Grunwaldt<sup>a</sup>, M. Maciejewski<sup>a</sup>, A. Baiker<sup>a,\*</sup>, M. Wittrock<sup>b</sup>, U. Göbel<sup>b</sup>, and S. Eckhoff<sup>b</sup>

<sup>a</sup>Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zuerich, Switzerland

<sup>b</sup>Umicore AG & Co. KG, Rodenbacher Chaussee 4, D-63403 Hanau-Wolfgang, Germany

The thermal ageing and reactivation of Ba/CeO<sub>2</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> based NO<sub>x</sub>-storage/ reduction (NSR) catalysts was studied on model catalysts and catalyst systems at the engine. The mixed oxides BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub>, which lower the storage activity, are formed during ageing above 850 °C and 900 °C, respectively. Interestingly, the decomposition of BaCeO<sub>3</sub> in an atmosphere containing H<sub>2</sub>O/NO<sub>2</sub> leads again to NO<sub>x</sub>-storage active species, as evidenced by comparison of fresh, aged and reactivated Pt-Ba/CeO<sub>2</sub> based model catalysts. This can be technically exploited, particularly for the Ba/CeO<sub>2</sub> catalysts, as reactivation studies on thermally aged Ba/CeO<sub>2</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> based NSR catalysts on an engine bench showed. An on-board reactivation procedure is presented, that improved the performance of a thermally aged catalyst significantly.

**KEY WORDS:** NO<sub>x</sub> storage-reduction catalysts; ageing; reactivation; barium cerate; barium aluminate; motor bench test; pulse thermal analysis.

## 1. Introduction

Lean-burn engines with direct fuel injection have been introduced to improve fuel efficiency [1,2]. However, this mode of engine operation requires new catalyst concepts for NO<sub>x</sub>-reduction. Among them, the NO<sub>x</sub>-storage/reduction catalyst technology, which contains a noble metal in combination with alkaline earth metals (e.g. BaO) supported on metals oxides such as Al<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub>, is one of the most promising concepts [2,3]. Under operating conditions some deterioration may be observed due to poisoning by sulfur or thermal ageing. Thermal deterioration can be caused by particle growth of the precious metals [4–6] or by reaction of the NO<sub>x</sub>-storage component with the support or other washcoat components [7–9]. Recently, we have investigated the latter phenomenon in more detail and observed the formation of BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> in Pt/Ba/γ-Al<sub>2</sub>O<sub>3</sub> and Pt/Ba/CeO<sub>2</sub> model catalysts at elevated temperatures [10]. Interestingly, BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> are not stable in an atmosphere containing NO<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>.

In the present study, we extended these studies on model catalyst systems to develop possible strategies to reactivate thermally aged catalysts. Finally, the reactivation studies were applied to catalyst systems on an engine bench to prove the technical feasibility.

## 2. Experimental part

### 2.1. Basic studies on model catalysts

#### 2.1.1. Sample preparation

The Pt/Ba/γ-Al<sub>2</sub>O<sub>3</sub> and Pt/Ba/CeO<sub>2</sub> model catalysts were prepared by incipient wetness impregnation of commercial γ-alumina and ceria supports with aqueous solution of diammineplatinum (II) nitrite and barium acetate as described in a previous paper [10]. Aged catalysts were obtained by the calcination of the Pt/Ba/CeO<sub>2</sub> for 10 h at 1000 °C and Pt/Ba/γ-Al<sub>2</sub>O<sub>3</sub> at 1100 °C for 10 h in a furnace (Nabertherm).

#### 2.1.2. Catalysts reactivation

The aged model catalysts were reactivated in a continuous-flow fixed-bed reactor by the reaction with H<sub>2</sub>O and NO<sub>2</sub> at 400 °C for 6 h. The sample was heated for 30 min to the selected temperature in a continuous flow of He. During reaction the carrier gas (He) was first saturated with water at room temperature (ca. 3 vol.% H<sub>2</sub>O) and then mixed with 1 vol.% NO<sub>2</sub> in synthetic air. The total flow rate (controlled by mass flow controllers, Brooks model 5850E) was 50 ml/min: 25 ml/min of water saturated He and 25 ml/min of 1 vol.% NO<sub>2</sub> in synthetic air.

#### 2.1.3. NO<sub>x</sub>-storage tests

The tests were performed using ca. 70 mg sample at 300 °C with 1 ml NO and 1 ml O<sub>2</sub> pulses injected into the carrier gas stream (He) of 50 ml/min. Prior to the NO<sub>x</sub>-storage tests, the Ba(NO<sub>3</sub>)<sub>2</sub> formed during reactivation was decomposed by calcination in He with a heating rate of 10 K/min up to 500 °C.

\* To whom correspondence should be addressed.

E-mail: [baiker@chem.ethz.ch](mailto:baiker@chem.ethz.ch)

### 2.1.4. Characterization techniques

X-ray diffraction measurements were carried out on a Siemens D5000 powder X-ray diffractometer using Cu  $K_{\alpha}$  radiation in the step scanning mode between  $2\theta = 15$  and  $65^{\circ}$ , with a step size of  $0.01^{\circ}$  and 2 s per step.

Thermal Analysis (TA, PulseTA [11]) experiments were performed on a Netzsch STA 409 thermoanalyser equipped with a pulse device enabling injection of a certain amount of one or two pure gases or gaseous mixtures into the carrier gas stream flowing through the system. The flow rate was controlled by mass flow controllers (Brooks model 5850E). The outlet of the thermoanalyser was connected by a heated (ca.  $150^{\circ}\text{C}$ ) stainless steel capillary to a mass spectrometer (Pfeiffer Vacuum OmniStar).

## 2.2. Engine bench tests

### 2.2.1. Catalysts

Two types of  $\text{NO}_x$ -storage catalysts (Umicore) coated on ceramic honeycomb substrates were used for the engine bench evaluations: the Ba/CeO<sub>2</sub> based catalyst, with the barium containing species supported on zirconia stabilized ceria, and the Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst, prepared by supporting the barium containing species on  $\gamma$ -alumina. The preparation of the Ba/support materials was carried out as described above [10]. Both catalysts contain a total precious metal loading of 3.5 g/L (Pt, Pd, Rh) with the same precious metal ratio.

Before the catalysts were introduced into the exhaust systems (see below) they were aged in a furnace at  $950^{\circ}\text{C}$  for 12 h in air to ensure that the maximum amount of the Ba/CeO<sub>2</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> based  $\text{NO}_x$ -storage material was transformed into BaCeO<sub>3</sub> and BaAl<sub>2</sub>O<sub>4</sub>, respectively.

### 2.2.2. Engine bench and exhaust system

For catalyst evaluation and reactivation a 3.5L Mercedes-Benz V6, gasoline direct injection engine with spray guided combustion process was used [12, 13]. The exhaust system consists of two separate exhaust lines. Each line was equipped with a closed-coupled (cc)  $\text{NO}_x$ -storage catalyst and two under-floor (uf)  $\text{NO}_x$ -storage catalysts. Two exhaust systems were built up containing either the Ba/CeO<sub>2</sub> based catalysts or the Ba/Al<sub>2</sub>O<sub>3</sub> based catalysts.

### 2.2.3. Tests

Both catalyst systems were characterized at the engine bench using a  $\text{NO}_x$ -storage/reduction (NSR) test. In this test the lean operation time of the system was measured at seven different stationary operation points of the engine. The cc-catalyst inlet temperatures in these points ranged from  $250^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ . Lean/rich cycling was carried out at each operation point and the lean and rich phase was terminated by a  $\text{NO}_x$ -sensor positioned

downstream of the two under-floor  $\text{NO}_x$ -storage catalysts. Additionally, the stationary  $\text{NO}_x$ -storage capacity was measured at a cc-catalyst inlet temperature of  $250^{\circ}\text{C}$ . For this test the exhaust system was operated at rich conditions at  $\lambda = 0.9$  for 60 s before switching to constant lean conditions for 500 s. At the end, the stored  $\text{NO}_x$  mass in the whole exhaust system was calculated.

### 2.2.4. Catalysts reactivation

To reactivate the thermally aged catalysts the exhaust gas recirculation (EGR) of the engine was switched off to generate a high  $\text{NO}_x$  mass flow of about 1000 ppm at an air to fuel ratio of  $\lambda = 2$ . The cc-catalyst inlet temperature in this stationary operation point of the engine was adjusted to  $400^{\circ}\text{C}$  resulting in an average bed temperature of  $430^{\circ}\text{C}$ . The inlet temperature of the uf-catalyst was about  $350^{\circ}\text{C}$  with a catalyst bed temperature of about  $360^{\circ}\text{C}$ . After a reactivation period of 2 h, another characterization via NSR test was performed.

## 3. Results and discussion

### 3.1. Ageing and reactivation of Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-Ba/CeO<sub>2</sub> model catalysts

In a previous paper [10] the formation of barium aluminate and barium cerate at different temperatures in Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-Ba/CeO<sub>2</sub> based  $\text{NO}_x$ -storage/reduction catalysts was studied systematically by determination of the reaction progress using XRD, thermal analysis and X-ray absorption spectroscopy. Typical XRD patterns recorded after calcination at  $900^{\circ}\text{C}$  for different time periods are shown in figure 1. The peak areas of the reflections at  $2\theta = 28.3^{\circ}$  (BaAl<sub>2</sub>O<sub>4</sub>) and  $2\theta = 40.9$  and  $41.1^{\circ}$  (BaCeO<sub>3</sub>) were used for the

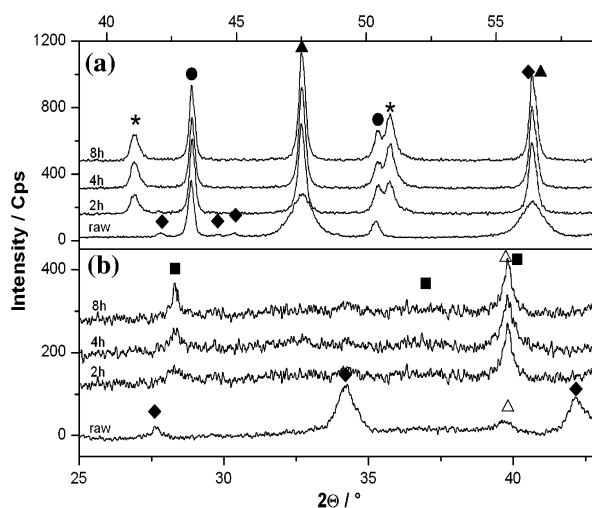


Figure 1. XRD patterns of as prepared samples and those calcined in air at  $900^{\circ}\text{C}$  for 2, 4 and 8 h. (a) Pt/Ba/CeO<sub>2</sub>, (b) Pt/Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; (\*) BaCeO<sub>3</sub>; (■) BaAl<sub>2</sub>O<sub>4</sub>; (◆) BaCO<sub>3</sub>; (●) CeO<sub>2</sub>; (△) Al<sub>2</sub>O<sub>3</sub>; (●) Cu.

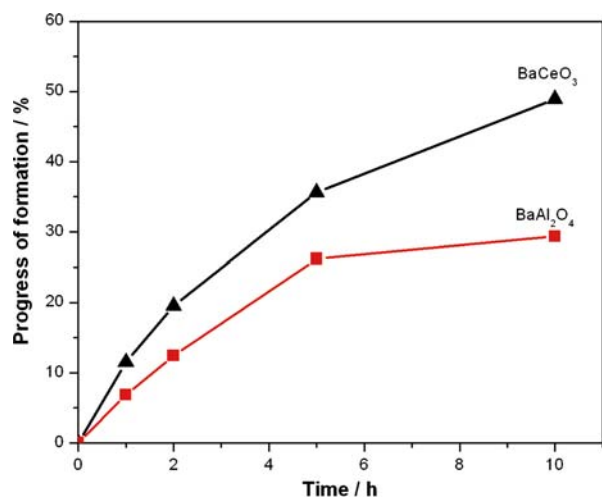


Figure 2. Progress of BaCeO<sub>3</sub> and BaAl<sub>2</sub>O<sub>4</sub> formation at 900 °C as a function of calcination time.

quantification of the amount of BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> phases formed, respectively. The intensities were standardized by comparison with the intensity of Cu (111) at  $2\theta = 43.17^\circ$ . The formation of BaCeO<sub>3</sub> was found to be faster than that of BaAl<sub>2</sub>O<sub>4</sub> (figure 2). The XRD patterns of BaCeO<sub>3</sub> were already observed at 800 °C, whereas the BaAl<sub>2</sub>O<sub>4</sub> reflexes were only found above 850 °C. These results are further supported by recent results by Kim *et al.* [14].

In a next step, the stability of the formed mixed oxides in the atmospheres containing (i) NO<sub>2</sub> and H<sub>2</sub>O and (ii) CO<sub>2</sub> was investigated. We observed that BaCeO<sub>3</sub> was decomposed by reaction with gaseous H<sub>2</sub>O at elevated temperature. The reaction was accelerated in the presence of NO<sub>2</sub> and the formation of the Ba(NO<sub>3</sub>)<sub>2</sub> was detected by XRD, supported by additional thermoanalytical studies. Figure 3 depicts the progress of BaCeO<sub>3</sub> and BaAl<sub>2</sub>O<sub>4</sub> decomposition by reaction with H<sub>2</sub>O and

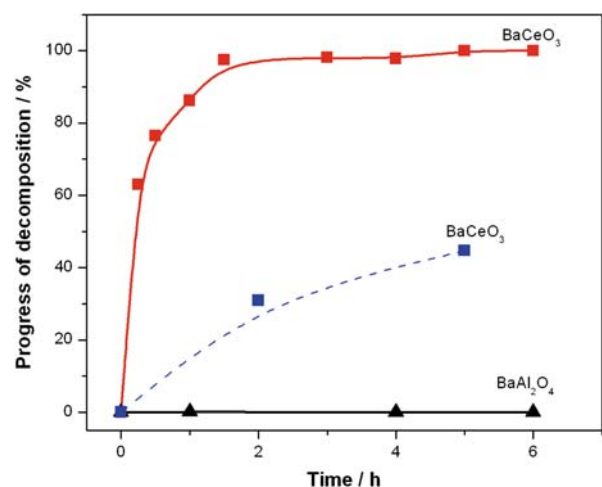


Figure 3. Progress of BaCeO<sub>3</sub> and BaAl<sub>2</sub>O<sub>4</sub> decomposition at 300 °C by the reaction with H<sub>2</sub>O and NO<sub>2</sub> (—) or H<sub>2</sub>O only (---); calculated from XRD measurements.

NO<sub>2</sub> at 300 °C. A maximum rate of barium cerate decomposition was observed at 400 °C. BaAl<sub>2</sub>O<sub>4</sub> built up in the aged Pt-Ba/Al<sub>2</sub>O<sub>3</sub> material could also be decomposed in a H<sub>2</sub>O/NO<sub>2</sub> atmosphere, but in contrast to BaCeO<sub>3</sub>, only at low temperatures, below 100 °C, where barium aluminate hydrates were formed.

Since the formation of BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> phases in thermally aged catalysts can significantly decrease the NSR activity, the observed instability of the undesired mixed oxides in water, NO<sub>x</sub> and carbon dioxide containing atmospheres could be exploited for reactivation of NSR catalysts. In order to check the influence of the reactivation process of barium-ceria based catalysts on the NO<sub>x</sub>-storage process we compared the NO<sub>x</sub>-storage capacity of fresh, aged and reactivated catalysts using thermogravimetric measurements. The practical importance of the reactivation was additionally investigated for Ba/CeO<sub>2</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst systems using engine bench tests.

### 3.2. NO<sub>x</sub>-storage experiments performed on fresh, aged and reactivated model catalysts

Under normal driving conditions the operating temperature of the NO<sub>x</sub>-storage catalyst is in the range of 250 °C to 450 °C. Since in this temperature range only BaCeO<sub>3</sub> can be decomposed by reaction with H<sub>2</sub>O and NO<sub>2</sub> the NO<sub>x</sub>-storage behavior was studied only for barium-ceria based catalyst. Pt/Ba/CeO<sub>2</sub> in fresh, aged and reactivated state was used for this study.

The interaction of NO<sub>x</sub> with the catalysts was investigated by the PulseTA method [11]. Alternated cycles of 1 mL NO and 1 mL O<sub>2</sub> pulses (2 pulses of NO and 3 pulses of oxygen within 1 min) were injected into the He carrier gas each 15 min. Figure 4 depicts the mass changes of the samples (TG signals) recorded during NO<sub>x</sub>-storage on fresh Pt/Ba/CeO<sub>2</sub>, calcined at 1000 °C

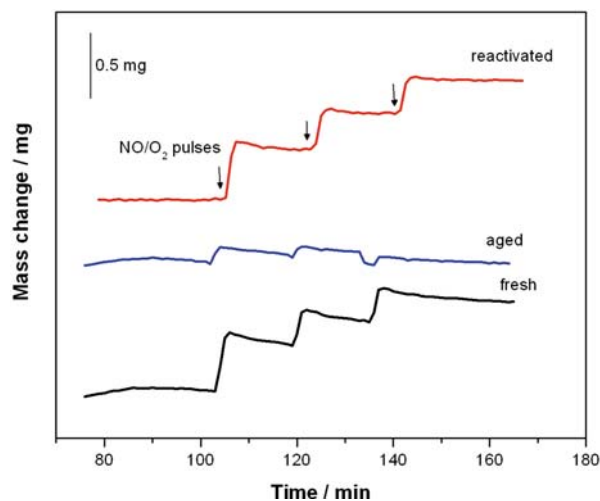


Figure 4. The change of the mass (TG signals) due to NO<sub>x</sub>-storage at 300 °C on fresh, aged and reactivated Pt/Ba/CeO<sub>2</sub> catalyst (sample mass ca. 70 mg). During each pulse 3 mL of O<sub>2</sub> and 2 mL of NO were injected.

for 10 h and for the reactivated sample exposed at 400 °C for 6 h to H<sub>2</sub>O/NO<sub>2</sub> atmosphere. The observed mass changes are the sum of two effects: Ba(NO<sub>3</sub>)<sub>2</sub> formation and BaCO<sub>3</sub> decomposition. The presented results evidence that the storage capacity of the reactivated sample is similar compared with the fresh catalyst. In the aged material Ba is mainly present as BaCeO<sub>3</sub>, which seems to be completely inactive in the NO<sub>x</sub>-storage process. After reactivation followed by the decomposition of formed Ba(NO<sub>3</sub>)<sub>2</sub> the sample contains BaO being active for NO<sub>x</sub>-storage. Thus a thermally aged NO<sub>x</sub>-storage catalyst, which partially transformed into undesired mixed oxides by reaction of barium oxide with its support during the ageing process, can be reactivated in the presence of NO<sub>x</sub> and water.

### 3.3. Reactivation of catalyst systems at the engine

Obviously, the ageing behavior of the NO<sub>x</sub>-storage material found in the model catalyst systems should have a strong influence on both the choice of the NO<sub>x</sub>-storage material in commercial catalyst systems and on the application of the corresponding catalyst. Whereas the formation of BaAl<sub>2</sub>O<sub>4</sub> in a Ba/Al<sub>2</sub>O<sub>3</sub> based NO<sub>x</sub>-storage material starts at 850 °C and seems to be an irreversible process under typical vehicle application conditions, the formation of BaCeO<sub>3</sub> starts at about 800 °C, but is reversible under certain vehicle operation conditions. Hence, a NO<sub>x</sub>-storage catalyst based on Ba/Al<sub>2</sub>O<sub>3</sub> storage material should be used, when BaAl<sub>2</sub>O<sub>4</sub> formation can be prevented, e.g. by keeping the temperature below 800 °C. If higher temperatures are not avoidable, it seems to be favorable to use a Ba/CeO<sub>2</sub>-based NO<sub>x</sub>-storage catalyst. The catalyst would lose NO<sub>x</sub>-storage performance by thermal ageing due to BaCeO<sub>3</sub> formation, but it should be possible to reactivate it under certain engine operation conditions.

In order to prove this hypothesis engine bench tests with Ba/CeO<sub>2</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst systems were carried out. All catalysts were thermally aged at 950 °C in air, prior to mounting them into the exhaust system. In a NO<sub>x</sub>-storage/reduction test the lean operation time of the systems was determined as a function of the closed-coupled catalyst inlet temperature. After the NSR characterization a reactivation step was established. Therefore, the exhaust gas recirculation (EGR) was switched off at an inlet temperature of 400 °C to generate a high NO<sub>x</sub> mass flow of 1000 ppm at an air to fuel ratio of  $\lambda = 2$ . After reactivation for 2 h another characterization via the NSR test was performed.

Figure 5 shows the results for the Ba/CeO<sub>2</sub> and the Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst systems. As expected, a significant improvement of the lean operation time could be observed for the Ba/CeO<sub>2</sub> based system, while almost no reactivation was observed with the Ba/Al<sub>2</sub>O<sub>3</sub> based system. Since the lean operation time is directly related to the NO<sub>x</sub>-storage capacity of the catalysts it is evident

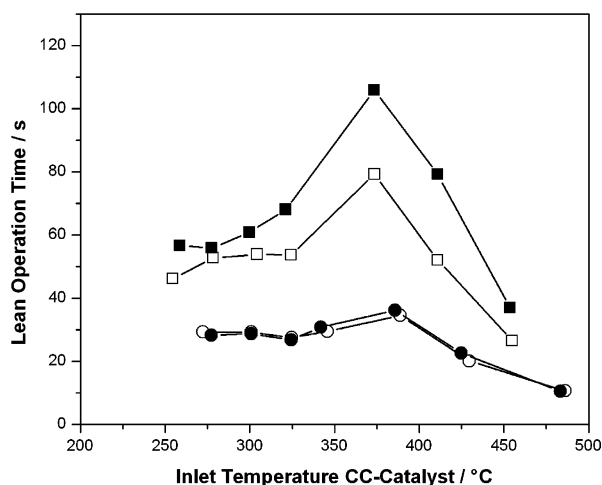


Figure 5. Lean operation time during 7 operation points of the engine, measured at temperatures between 250 °C and 500 °C; Ba/CeO<sub>2</sub> based catalyst before (□) and after (■) reactivation and Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst before (○) and after (●) reactivation; the reactivation time was 2 h at  $\lambda = 2$ .

that a significant part of the BaCeO<sub>3</sub> phase was decomposed during the described reactivation procedure, whereas BaAl<sub>2</sub>O<sub>4</sub> was stable. This is well in line with the results of the basic studies described above.

Figure 6 depicts the conversion of hydrocarbons before and after the reactivation treatment. The hydrocarbon (HC) conversion of the Ba/CeO<sub>2</sub> system could be improved due to the fact that with the decomposition of the BaCeO<sub>3</sub> also the oxygen storage material CeO<sub>2</sub> was reactivated. In case of the Ba/Al<sub>2</sub>O<sub>3</sub> based system the HC-conversion performance is rather constant before and after reactivation.

In order to get more information on the NO<sub>x</sub>-storage performance at low temperatures the stationary NO<sub>x</sub>-storage capacity at 250 °C cc-catalyst inlet temperature

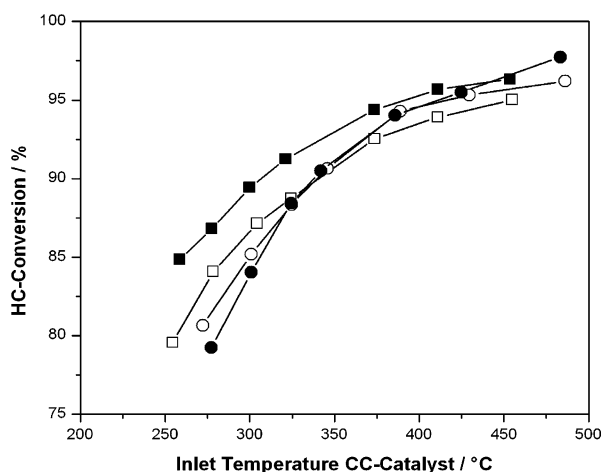


Figure 6. HC-conversion during 7 operation points of the engine; Ba/CeO<sub>2</sub> based catalyst before (□) and after (■) reactivation and Ba/Al<sub>2</sub>O<sub>3</sub> based catalyst before (○) and after (●) reactivation at the engine for 2 h at  $\lambda = 2$ .

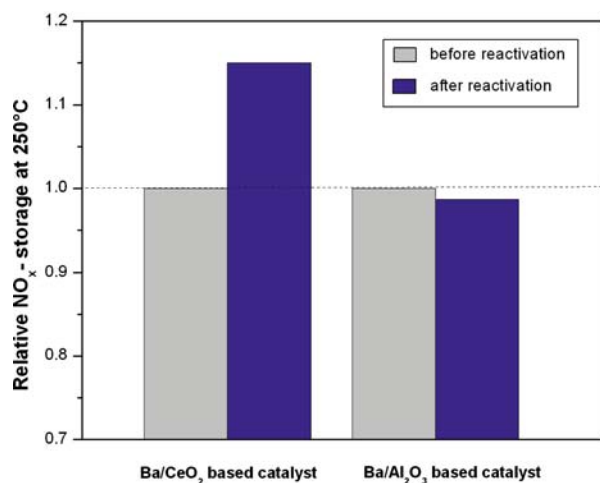


Figure 7. Relative stationary NO<sub>x</sub>-storage capacity at 250 °C before and after reactivation at the engine for 2 h at  $\lambda = 2$ .

was determined at the engine. Figure 7 shows the relative improvement of the NO<sub>x</sub>-storage capacity at 250 °C after the reactivation treatment. It is obvious that, in line with the previous results, the NO<sub>x</sub>-storage capacity of the thermally aged catalyst was improved under the chosen reactivation conditions in case of the Ba/CeO<sub>2</sub> based system, whereas no improvement was observed for the Ba/Al<sub>2</sub>O<sub>3</sub> based system.

#### 4. Conclusions

Thermal ageing of Pt/Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt/Ba/CeO<sub>2</sub> model catalysts leads to a formation of BaAl<sub>2</sub>O<sub>4</sub> and BaCeO<sub>3</sub> above 850 °C and 800 °C, respectively. The thermal deactivation of the Pt/Ba/CeO<sub>2</sub> model catalyst, resulting in BaCeO<sub>3</sub> formation, was found to lead to a loss of its NO<sub>x</sub>-storage capacity. The aged model catalyst could be reactivated by decomposition of BaCeO<sub>3</sub> in the presence of H<sub>2</sub>O, NO<sub>2</sub> and CO<sub>2</sub>. The reactivated catalyst exhibited the same storage capacity as the fresh material. For barium-ceria based commercial catalysts,

this finding from the basic studies could be technically exploited. Measurements at a gasoline direct injection engine with a spray-guided combustion process showed that a reactivation of a thermally aged Ba/CeO<sub>2</sub> based NO<sub>x</sub>-storage catalyst is generally possible under applicable conditions. Thus a systematic application of suitable conditions for an on-board reactivation is realistic without additional costs and helps to prolong the lifetime of commercially available NO<sub>x</sub>-storage catalysts.

#### References

- [1] R.M. Heck and R.J. Farrauto, *Catalytic Air Pollution Control*, (Van Nostrand Reinhold, New York, 1995).
- [2] K.-H. Glück, U. Göbel, H. Hahn, J. Höhne, R. Krebs, T. Kreuzer and E. Pott, *MTZ* 61 (2000) 6.
- [3] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi and K. Kasahara, *Catal. Today* 27 (1996) 63.
- [4] D. Uy, A. O'Neill, J. Li and W. Watkins, *Catal. Lett.* 95 (2004) 191.
- [5] G.W.J. Graham, H.-W. Jen, W.S. Chun, H.P. Sun, X.Q. Pan and R.W. McCabe, *Catal. Lett.* 93 (2004) 129.
- [6] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier and J.E. Parks, *Catal. Rev. Sci. Eng.* 46 (2004) 163.
- [7] N. Fekete, R. Kemmler, D. Voigtländer, B. Krutzsch, E. Zimmer, G. Wenniger, W. Strehlau, J.A.A.v.d. Tillaart, J. Leyrer, E.S. Lox and W. Müller, *SAE Tech. Paper* 970746 (1997).
- [8] S. Elbouazzaoui, X. Courtois, P. Marecot and D. Duprez, *Topics Catal.* 30–31 (2004) 493.
- [9] B.-H. Jang, T.-H. Yeon, H.-S. Han, Y.-K. Park and J.-E. Yie, *Catal. Lett.* 77 (2001) 21.
- [10] M. Casapu, J.-D. Grunwaldt, M. Maciejewski, M. Wittrock, U. Göbel and A. Baiker, *Appl. Catal. B* 63 (2006) 232.
- [11] M. Maciejewski, C.A. Müller, R. Tschan, W.D. Emmerich and A. Baiker, *Thermochim. Acta* 295 (1997) 167.
- [12] A. Waltner, P. Lückert, U. Schaupp, E. Rau and R. Kemmler, R. Weller, *27th International Vienna Motor Symposium*, Volume 2 (2006) 24–43.
- [13] S. Philipp, S. Eckhoff, S. Bremm, W. Müller, C. Schön, C. Brinkmeier and G. Vent, 3rd Emission Control Conference, Dresden, 2006.
- [14] D.H. Kim, Y.-H. Chin, J.H. Kwak, J. Szanyi and C.H.F. Peden, *Catal. Lett.* 105 (2005) 259.