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Thermal ageing phenomena and strategies towards reactivation of NO_x- storage catalysts

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The thermal ageing and reactivation of Ba/CeO₂ and Ba/Al₂O₃ based NO_x-storage/ reduction (NSR) catalysts was studied on model catalysts and catalyst systems at the engine. The mixed oxides BaAl₂O₄ and BaCeO₃, which lower the storage activity, are formed during ageing above 850 °C and 900 °C, respectively. Interestingly, the decomposition of BaCeO₃ in an atmosphere containing H₂O/NO₂ leads again to NO_x-storage active species, as evidenced by comparison of fresh, aged and reactivated Pt-Ba/CeO₂ based model catalysts. This can be technically exploited, particularly for the Ba/CeO₂ catalysts, as reactivation studies on thermally aged Ba/CeO₂ and Ba/Al₂O₃ 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_x 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_x-reduction. Among them, the NO_x-storage/reduction catalyst technology, which contains a noble metal in combination with alkaline earth metals (e.g. BaO) supported on metals oxides such as Al₂O₃ or CeO₂, 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_x-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 BaAl₂O₄ and BaCeO₃ in Pt/Ba/γ-Al₂O₃ and Pt/Ba/CeO₂ model catalysts at elevated temperatures [10]. Interestingly, BaAl₂O₄ and BaCeO₃ are not stable in an atmosphere containing NO₂, H₂O and CO₂.

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-Al₂O₃ and Pt/Ba/CeO₂ 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/CeO₂ for 10 h at 1000 °C and Pt/Ba/γ-Al₂O₃ 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 H₂O and NO₂ 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.% H₂O) and then mixed with 1 vol.% NO₂ 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.% NO₂ in synthetic air.

2.1.3. NO_x-storage tests

The tests were performed using ca. 70 mg sample at 300 °C with 1 ml NO and 1 ml O₂ pulses injected into the carrier gas stream (He) of 50 ml/min. Prior to the NO_x-storage tests, the Ba(NO₃)₂ formed during reactivation was decomposed by calcination in He with a heating rate of 10 K/min up to 500 °C.

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2.1.4. Characterization techniques

X-ray diffraction measurements were carried out on a Siemens D5000 powder X-ray diffractometer using Cu K_{α} radiation in the step scanning mode between $2\theta = 15$ and 65° , with a step size of 0.01° 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°C) stainless steel capillary to a mass spectrometer (Pfeiffer Vacuum OmniStar).

2.2. Engine bench tests

2.2.1. Catalysts

Two types of NO_x -storage catalysts (Umicore) coated on ceramic honeycomb substrates were used for the engine bench evaluations: the Ba/CeO₂ based catalyst, with the barium containing species supported on zirconia stabilized ceria, and the Ba/Al₂O₃ based catalyst, prepared by supporting the barium containing species on γ -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°C for 12 h in air to ensure that the maximum amount of the Ba/CeO₂ and Ba/Al₂O₃ based NO_x -storage material was transformed into BaCeO₃ and BaAl₂O₄, 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) NO_x -storage catalyst and two under-floor (uf) NO_x -storage catalysts. Two exhaust systems were built up containing either the Ba/CeO₂ based catalysts or the Ba/Al₂O₃ based catalysts.

2.2.3. Tests

Both catalyst systems were characterized at the engine bench using a 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°C to 500°C . Lean/rich cycling was carried out at each operation point and the lean and rich phase was terminated by a NO_x -sensor positioned

downstream of the two under-floor NO_x -storage catalysts. Additionally, the stationary NO_x -storage capacity was measured at a cc-catalyst inlet temperature of 250°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 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 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°C resulting in an average bed temperature of 430°C . The inlet temperature of the uf-catalyst was about 350°C with a catalyst bed temperature of about 360°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/Al₂O₃ and Pt-Ba/CeO₂ model catalysts

In a previous paper [10] the formation of barium aluminate and barium cerate at different temperatures in Pt-Ba/Al₂O₃ and Pt-Ba/CeO₂ based 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°C for different time periods are shown in figure 1. The peak areas of the reflections at $2\theta = 28.3^{\circ}$ (BaAl₂O₄) and $2\theta = 40.9$ and 41.1° (BaCeO₃) were used for the

Figure 1. XRD patterns of as prepared samples and those calcined in air at 900°C for 2, 4 and 8 h. (a) Pt/Ba/CeO₂, (b) Pt/Ba/ γ -Al₂O₃; (♦) BaCeO₃; (■) BaAl₂O₄; (▲) CeO₂; (△) γ -Al₂O₃; (●) Cu.

Figure 2. Progress of BaCeO₃ and BaAl₂O₄ formation at 900 °C as a function of calcination time.

quantification of the amount of BaAl₂O₄ and BaCeO₃ phases formed, respectively. The intensities were standardized by comparison with the intensity of Cu (111) at $2\theta = 43.17^\circ$. The formation of BaCeO₃ was found to be faster than that of BaAl₂O₄ (figure 2). The XRD patterns of BaCeO₃ were already observed at 800 °C, whereas the BaAl₂O₄ 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) NO₂ and H₂O and (ii) CO₂ was investigated. We observed that BaCeO₃ was decomposed by reaction with gaseous H₂O at elevated temperature. The reaction was accelerated in the presence of NO₂ and the formation of the Ba(NO₃)₂ was detected by XRD, supported by additional thermoanalytical studies. Figure 3 depicts the progress of BaCeO₃ and BaAl₂O₄ decomposition by reaction with H₂O and

Figure 3. Progress of BaCeO₃ and BaAl₂O₄ decomposition at 300 °C by the reaction with H₂O and NO₂ (—) or H₂O only (---); calculated from XRD measurements.

NO₂ at 300 °C. A maximum rate of barium cerate decomposition was observed at 400 °C. BaAl₂O₄ built up in the aged Pt-Ba/Al₂O₃ material could also be decomposed in a H₂O/NO₂ atmosphere, but in contrast to BaCeO₃, only at low temperatures, below 100 °C, where barium aluminate hydrates were formed.

Since the formation of BaAl₂O₄ and BaCeO₃ phases in thermally aged catalysts can significantly decrease the NSR activity, the observed instability of the undesired mixed oxides in water, NO_x 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_x-storage process we compared the NO_x-storage capacity of fresh, aged and reactivated catalysts using thermogravimetric measurements. The practical importance of the reactivation was additionally investigated for Ba/CeO₂ and Ba/Al₂O₃ based catalyst systems using engine bench tests.

3.2. NO_x-storage experiments performed on fresh, aged and reactivated model catalysts

Under normal driving conditions the operating temperature of the NO_x-storage catalyst is in the range of 250 °C to 450 °C. Since in this temperature range only BaCeO₃ can be decomposed by reaction with H₂O and NO₂ the NO_x-storage behavior was studied only for barium-ceria based catalyst. Pt/Ba/CeO₂ in fresh, aged and reactivated state was used for this study.

The interaction of NO_x with the catalysts was investigated by the PulseTA method [11]. Alternated cycles of 1 mL NO and 1 mL O₂ 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_x-storage on fresh Pt/Ba/CeO₂, calcined at 1000 °C

Figure 4. The change of the mass (TG signals) due to NO_x-storage at 300 °C on fresh, aged and reactivated Pt/Ba/CeO₂ catalyst (sample mass ca. 70 mg). During each pulse 3 mL of O₂ and 2 mL of NO were injected.

for 10 h and for the reactivated sample exposed at 400 °C for 6 h to H₂O/NO₂ atmosphere. The observed mass changes are the sum of two effects: Ba(NO₃)₂ formation and BaCO₃ 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 BaCeO₃, which seems to be completely inactive in the NO_x-storage process. After reactivation followed by the decomposition of formed Ba(NO₃)₂ the sample contains BaO being active for NO_x-storage. Thus a thermally aged NO_x-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_x and water.

3.3. Reactivation of catalyst systems at the engine

Obviously, the ageing behavior of the NO_x-storage material found in the model catalyst systems should have a strong influence on both the choice of the NO_x-storage material in commercial catalyst systems and on the application of the corresponding catalyst. Whereas the formation of BaAl₂O₄ in a Ba/Al₂O₃ based NO_x-storage material starts at 850 °C and seems to be an irreversible process under typical vehicle application conditions, the formation of BaCeO₃ starts at about 800 °C, but is reversible under certain vehicle operation conditions. Hence, a NO_x-storage catalyst based on Ba/Al₂O₃ storage material should be used, when BaAl₂O₄ 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/CeO₂-based NO_x-storage catalyst. The catalyst would lose NO_x-storage performance by thermal ageing due to BaCeO₃ 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/CeO₂ and Ba/Al₂O₃ 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_x-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_x 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/CeO₂ and the Ba/Al₂O₃ based catalyst systems. As expected, a significant improvement of the lean operation time could be observed for the Ba/CeO₂ based system, while almost no reactivation was observed with the Ba/Al₂O₃ based system. Since the lean operation time is directly related to the NO_x-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/CeO₂ based catalyst before (□) and after (■) reactivation and Ba/Al₂O₃ based catalyst before (○) and after (●) reactivation; the reactivation time was 2 h at $\lambda = 2$.

that a significant part of the BaCeO₃ phase was decomposed during the described reactivation procedure, whereas BaAl₂O₄ 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/CeO₂ system could be improved due to the fact that with the decomposition of the BaCeO₃ also the oxygen storage material CeO₂ was reactivated. In case of the Ba/Al₂O₃ based system the HC-conversion performance is rather constant before and after reactivation.

In order to get more information on the NO_x-storage performance at low temperatures the stationary NO_x-storage capacity at 250 °C cc-catalyst inlet temperature

Figure 6. HC-conversion during 7 operation points of the engine; Ba/CeO₂ based catalyst before (□) and after (■) reactivation and Ba/Al₂O₃ based catalyst before (○) and after (●) reactivation at the engine for 2 h at $\lambda = 2$.

Figure 7. Relative stationary NO_x-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_x-storage capacity at 250 °C after the reactivation treatment. It is obvious that, in line with the previous results, the NO_x-storage capacity of the thermally aged catalyst was improved under the chosen reactivation conditions in case of the Ba/CeO₂ based system, whereas no improvement was observed for the Ba/Al₂O₃ based system.

4. Conclusions

Thermal ageing of Pt/Ba/ γ -Al₂O₃ and Pt/Ba/CeO₂ model catalysts leads to a formation of BaAl₂O₄ and BaCeO₃ above 850 °C and 800 °C, respectively. The thermal deactivation of the Pt/Ba/CeO₂ model catalyst, resulting in BaCeO₃ formation, was found to lead to a loss of its NO_x-storage capacity. The aged model catalyst could be reactivated by decomposition of BaCeO₃ in the presence of H₂O, NO₂ and CO₂. 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/CeO₂ based NO_x-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_x-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.