

Influence of remote control in Pt/Ba/Al₂O₃ NO_x storage-reduction catalysts

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NO_x storage-reduction (NSR) is applied for exhaust gas treatment of lean fuel engines [1]. The proximity between Pt and BaO in Pt/Ba/Al₂O₃ NSR catalysts has been found to affect the storage-reduction behavior due to its effect on the spillover of NO_x species [2]. Here we applied flame synthesis to control the location of the deposition of platinum either on the alumina support or on the Ba storage component. A two-nozzle system was used previously for the one-step synthesis of highly active Pt/Ba/Al₂O₃ catalysts [3, 4]

This setup allowed preferential deposition of Pt either on alumina or on the storage component BaCO₃. Different Pt sites were elucidated electron microscopy techniques. NSR behavior of these catalysts as well as of sequential setups of catalytic beds was investigated in a microreactor by switching between lean and rich conditions.

Our studies on the effect of the preferential deposition of platinum on the alumina support or Ba storage component corroborate that the remote control of the different constituents is a crucial factor for high performance of NSR catalysts. Especially for the regeneration of the catalyst powder with close proximity of Pt to Ba showed improved activity and time stability. Flame synthesis based on a two-nozzle system was shown to be a suitable tool for controlling the proximity of storage and reduction components in NSR catalysts.

Reference

- [1] Epling, W.S., Campbell, L.E., Yezerets, A., Currier, N.W., and Parks, J.E., Overview of the fundamental reactions and degradation mechanisms of NO_x storage/reduction catalysts. *Catal. Rev.-Sci. & Eng.*, 46 (2004), 163-245.
- [2] Cant, N.W., Liu, I.O.Y., and Patterson, M.J., The effect of proximity between Pt and BaO on uptake, release, and reduction of NO_x on storage catalysts. *J. Catal.*, 243 (2006), 309-317.
- [3] Strobel, R., Madler, L., Piacentini, M., Maciejewski, M., Baiker, A., and Pratsinis, S.E., Two-nozzle flame synthesis of Pt/Ba/Al₂O₃ for NO_x storage. *Chem.Mater.*, 18 (2006), 2532-2537.
- [4] Piacentini, M., Strobel, R., Maciejewski, M., Pratsinis, S.E., and Baiker, A., Flame-made Pt-Ba/Al₂O₃ catalysts: Structural properties and behavior in lean-NO_x storage-reduction., *J. Catal.*, 243 (2006), 43-56.

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Objective

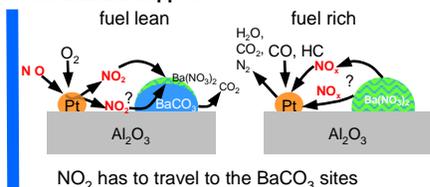
Pt/Ba/Al₂O₃ catalyst are used for abatement of combustion generated NO_x from lean burn engines operating at conditions conventional three way (TWC) catalysts are inefficient.

Lean NO_x trap (LNT) or NO_x storage reduction (NSR) catalysts store effluent NO_x under lean conditions and regenerate during a short fuel rich period.[1] Catalyst powders were made using a flame process allowing scaleable and continuous synthesis of a variety of nano-particles. The two nozzle flame spray pyrolysis (FSP) setup allows controlling particle mixing at the nano level in multicomponent systems [2] as well as a preferential deposition of Pt on support or storage compound controlling the precursor composition and geometry of the setup.

motivation

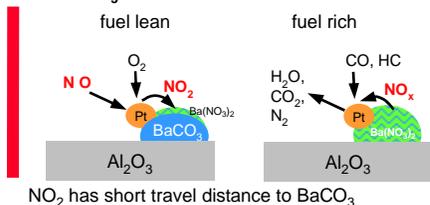
The distance of Pt to the storage sites of Ba plays an important role in NSR catalysis as this distance has to be overcome by NO₂. [3] Furthermore the support of Pt influences its catalytic activity:

Pt on alumina support



Pt on alumina is well known for good conversion of NO to NO₂ being transported over the gas or the surface to the Ba sites. During fuel rich regeneration once more NO₂ has to diffuse back to the Pt sites.

Pt on BaCO₃

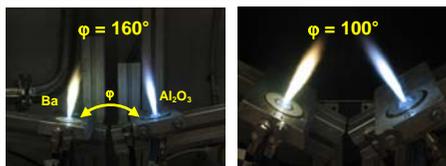


In this case Pt is right on top of the BaCO₃ and NO₂ formation near to the Ba sites. Storage and especially reduction are facilitated due to the short transport distance. BaCO₃ on the other hand is a dynamic support as it is transforming its crystal structure and composition e.g. to Ba(NO₃)₂ and back to BaCO₃. During these transformations active Pt sites could lose contact to the Ba support or be covered into a Ba layer. In this study, however, no such effect was observed.

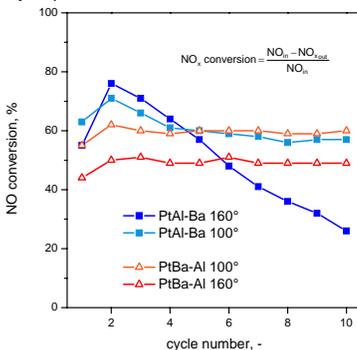
Acknowledgements

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Preferential deposition of Pt

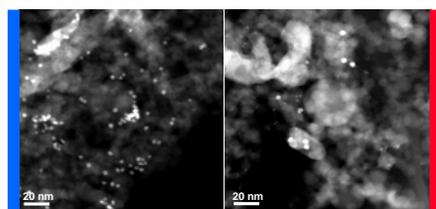


In 2 FSP setup BaCO₃ and Al₂O₃ are produced in separated flames from individual precursors. Preferential deposition of Pt on Al₂O₃ or BaCO₃ can be achieved by adding Pt only to one of the precursors and choosing high $\varphi = 160^\circ$. For high angles Pt particles form before intermixing of the Al₂O₃ and BaCO₃ particles streams and therefore only deposit on of them

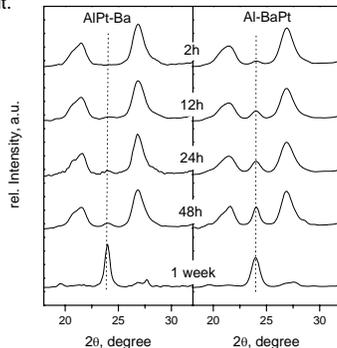


For $\varphi = 100^\circ$ the meeting distance is too short and Pt will deposit on the Ba and on Al independent of the initial precursor mixture.

characterization



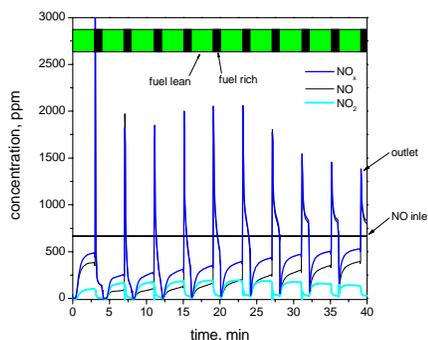
STEM of Pt/Ba/Al₂O₃ with Pt preferential on alumina (left) and Pt preferential on BaCO₃ (right). Not exactly all Pt particles are on its preferential site, however a general tendency can be made out.



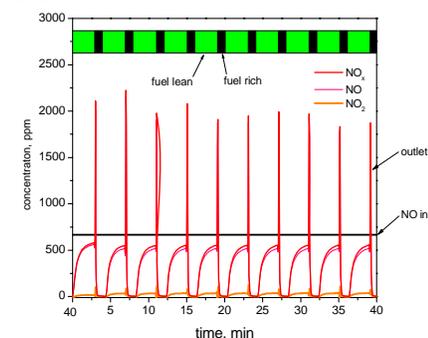
Flame made BaCO₃ is known to transform from monoclinic to the more stable orthorhombic structure.[2] The presence of Pt accelerates this transformation, probably due to crystal defects introduced by Pt that will promote the change in BaCO₃ crystal structure.

NO storage/reduction

For a constant NO inlet of 666 ppm the storage and reduction behavior was investigated at 300°C for Pt/Ba/Al₂O₃ catalyst with Pt preferentially located on Ba (blue) or for Pt located on Al₂O₃ (red):



Pt close to Al shows higher NO oxidation rate and better overall storage of the inlet NO compared to Pt on Ba. However reduction activity is lower and thus not all Ba(NO₃)₂ can be regenerated into BaCO₃. At the same time a steady deactivation of the catalyst was observed: During fuel lean phases more NO and NO₂ are emitted, and also during lean phases less NO₂ was formed with time.



Pt on top of BaCO₃ shows better reduction and regeneration behavior. The low NO oxidation rates during lean conditions is probably limiting the storage process.

Conclusions

2 nozzle FSP is a suitable method to deposit Pt preferentially on storage (BaCO₃) or on the support (Al₂O₃) material.

Pt on alumina showed higher activity for NO oxidation and overall Ba(NO₃)₂ formation and is the material of choice for NO storage, although deactivation with time of the Pt activity was observed.

Pt with direct contact to the Ba-species assisted regeneration of Ba during fuel lean conditions and therefore showed longer NSR activity and no decrease of the activity was observed during several reduction/regeneration cycles.

References

- [1] W. S. Epling *et al.*, Catal. Rev.-Sci. & Eng., 46 (2004), 163.
- [2] R. Strobel *et al.*, Chem. Mater. 18 (2006) 2532.
- [3] N. W. Cant *et al.*, J. Catal. 243 (2006) 309.