Forced dynamic reactor operation for boosting the activity and selectivity of Pd-based ammonia oxidation catalysts

Camilo CÁRDENAS[1], Thomas HÄBER[2], Olaf DEUTSCHMANN[1,2], Patrick LOTT[*1]
[1]Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry,
Engesserstr. 20, 76131, Karlsruhe, Germany.
[2]Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT),
Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany.
**patrick.lott@kit.edu*

Significance and Relevance

That ammonia (NH_3), which is considered a valuable C-free energy carrier, may be emitted both during direct combustion and during decomposition calls for technical solutions, i.e., selective oxidation catalysts, that selectively convert NH_3 into elemental nitrogen (N_2). This study provides spatiotemporal insights obtained during forced dynamic reactor operation of Pd-based NH_3 oxidation catalysts operated in lean conditions: Dynamic operation, i.e., introduction of rich pulses, enhances both the activity and selectivity of the Pd-based catalysts and induces gradients along the catalyst samples. The combination of noble metal-based catalysts with Fe- and Cu-zeolites further enhances the selectivity.

Preferred and 2nd choice for the topic: (1) Automotive and stationary emission control *(2)* Air cleaning and combustion.
Preferred presentation: Oral preferred.

Introduction and Motivations

Among the energy carriers that are considered feasible for large-scale decarbonization of the global energy system, ammonia (NH_3) is one of the most popular ones. In contrast to sustainable hydrogen (H_2), e.g. produced by electrolysis or pyrolysis of methane, whose transport and storage are considered challenging, the production, handling, and distribution of NH_3 can rely on established infrastructure. In addition, NH_3 has been suggested as a potent H_2 carrier, which can be decomposed into its elements or which can directly be converted into energy during combustion processes. That small amounts of NH_3 are emitted in both cases[1,2] calls for technical solutions capable of abating NH_3 emissions into the atmosphere. In this respect, the selective catalytic oxidation of ammonia (NH_3-SCO) is a viable approach to convert undesired NH_3 slippage into N_2; in fact, this technology is widely exploited already nowadays in automotive catalysis for ammonia slip catalysts (ASC).[3] While such NH_3-SCO catalysts commonly contain a noble metal, particularly platinum (Pt), which acts as oxidation functionality, also non-noble metal elements may be added as well since they have been demonstrated to exhibit great potential in suppressing the formation of undesired nitrous oxide (N_2O) as a byproduct on the one hand and to reduce the risk of NH_3 overoxidation to form nitric oxide (NO) on the other hand.[4]

While its lower activity impeded the widespread application of palladium (Pd) in NH_3-SCO catalysts, the present study demonstrates how forced dynamic reactor operation enables exploiting the unique Pd-PdO redox properties[5] for boosting the activity and selectivity of Pd-based ammonia oxidation catalysts.

Materials and Methods

After preparation of Pt- and Pd-based powder catalysts by means of incipient wetness impregnation, the materials were washcoated onto plates and monolithic substrates, respectively. Kinetic catalyst tests were conducted in lab-scale setups equipped with an FTIR spectrometer and a mass spectrometer for end-of-pipe gas analysis. In addition, spatially resolved measurements were possible: An optically accessible reactor geometry enabled obtaining spatially resolved information on selected gas phase species by applying laser-based analysis,[6] and the capillary-based spatial profiling (SpaciPro) technique implemented in a plug-flow reactor provided insights into the monolithic samples regarding temperature and species concentrations, even in more complex and realistic gas mixtures.[7]

Results and Discussion

While in light-off tests Pt-based NH_3 oxidation catalysts barely benefit from forced dynamic operation, i.e., introduction of short reducing pulses (SRP; O_2 supply cut off for 10 s) during otherwise lean operation (60 s), the conversion of NH_3 increased significantly over Pd-based samples and dynamic operation even allowed Pd-based catalysts to outperform their Pt-based counterparts. Also, the selectivity to the desired reaction product nitrogen (N_2) is enhanced substantially and although the N_2O level increases, the Pd-based catalyst in dynamic operation still outperforms the Pt-based reference catalyst. NO formation was found to an only minor extent.

The spatially resolved conversion data obtained by means of spatial profiling (SpaciPro) at T_{50} and T_{97}, i.e., the temperature of 50% and 97% NH_3 conversion, respectively, underscore the superiority of Pd/Al_2O_3 in dynamic operation compared to static operation. For instance, dynamic operation reduces T_{50} by 41°C in dry conditions (Fig. 1a) and by 53°C in humid conditions (Fig. 1b). The data obtained at T_{97} point to a pronounced shift of the reaction zone towards the inlet of the monolithic catalyst sample, both in dry (Fig. 1c) and humid (Fig. 1d) conditions. The addition of non-noble metal-based materials, namely copper- and iron-loaded zeolites, to noble metal-based ammonia oxidation catalysts can further enhance the selectivity to the desired product N_2, while suppressing NO and N_2O formation. The spatially resolved species concentration profiles suggest that double-layer washcoating is superior over zone-coating, which is assumed to originate from an intrinsic suppression of intermediate and byproduct formation along the entire length of the catalyst. Herewith, the results provide valuable guidance in designing material combinations that ensure highly efficient emission abatement.

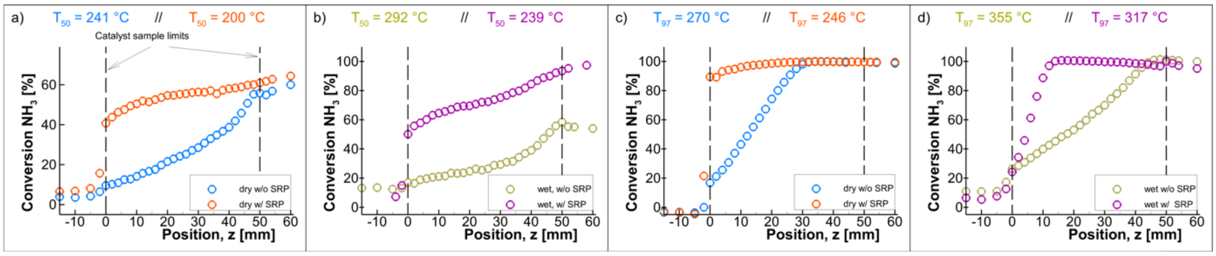

Figure 1 Spatially resolved activity data obtained for a monolithic Pd/Al_2O_3 catalyst sample in static ("w/o SRP") and dynamic SRP operation ("w/ SRP"). Gas mixture: 1000 ppm NH_3, 10 vol.% O_2 (0 vol.% for 10 s during SRP, every 60 s), 0% H_2O ("dry") or 10% H_2O ("wet"), bal. N_2.

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