Increasing the performance of Pd/Al₂O₃ and Pd/CeO₂ catalysts for total methane oxidation by pre-reduction

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Pd-based catalysts, commonly supported on materials like alumina or ceria, are still the most efficient catalysts to oxidize the strong greenhouse gas methane in the low temperature regime typical for lean burn gas engines (approx. 400°C – 450°C). On the other hand, long-term applications still remain a challenge, since in the presence of water vapor or sulfur a strong deactivation is observed. The active phase is assumed to be PdO and it is claimed that methane oxidation on PdO follows a Mars-van-Krevelen mechanism. Water formed during both the combustion of methane in the engine and the catalytic after-treatment reaction is believed to induce the formation of inactive Pd(OH)ₓ species on the catalyst’s surface. A pre-treatment (i.e., pre-reduction) of Pd-based catalysts was shown to have a positive effect on catalytic activity and stability. However, neither the origin of the deactivation nor the exact effect of the pre-treatment have been completely elucidated yet.

To understand the activity increase observed after reduction prior to the activity tests, we used operando X-ray absorption spectroscopy (XAS) to follow the variations of oxidation state during dynamic operation. Both Pd/Al₂O₃ and Pd/CeO₂ were investigated, in order to evaluate the impact of the different oxygen mobility of the supports.

Pre-reduction of Pd/Al₂O₃ and Pd/CeO₂ catalysts shifted the light-off curve towards lower temperatures. This effect was also observed under model or simulated exhaust gas mixtures. Operando XAS revealed a completely reduced catalyst after the pre-treatment. In reaction mixture, with increasing temperature, continuous oxidation occurs, starting with surface oxidation and finally resulting in bulk PdO above 350°C, irrespective of the catalyst formulation. Although also phenomena such as particle morphology variations or surface roughening can contribute to performance enhancement, our operando XAS investigations uncovered that the freshly formed PdO phase, less deactivated by water, is the main reason for the increase of methane oxidation activity at low temperatures.

Figure 1. a) Activity data of a Pd/Al₂O₃ catalyst without (black lines) or with (red lines) pre-reduction; Dry and wet conditions are compared (solid and dashed lines respectively); b) Oxidation state evolution as obtained from XANES of the same catalyst during light-off after pre-reduction and corresponding activity data; c) Possible evolution of the structure of a Pd nanoparticle during re-oxidation (simplified scheme)