CH_4 oxidation on a Pd-only three-way catalyst under fluctuating rich/lean conditions

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The current technology for the control of the exhaust gas of natural gas fueled passenger vehicles (NGV) is based on three-way catalysts (TWC) that are set to operate around stoichiometry (λ= 1) [1]. TWC contain predominantly palladium as the active phase because this metal is the most efficient for C-H activation of methane (CH_4), the major component of natural gas. Targeted catalyst development, which appears to lag behind that of TWC for gasoline applications, would be helpful to improve the performance of present catalysts and control strategies of stoichiometric engines, but the understanding of the chemistry of TWC for NGV is still limited. Here, we show the effect of rich/lean operation on CH_4 conversion.

A honeycomb Pd-only TWC subjected to linear temperature ramps in the presence of CO, NO, CH_4 and water displayed very poor CH_4 oxidation activity in a continuous feed corresponding to λ= 1. Both CH_4 and NO conversions reached high levels (>90%) when the catalyst was subjected to an oscillating rich/lean feed that is more representative of TWC operation. CO was fully removed in the whole temperature range showing that CO oxidation occurs constantly and irrespective of the presence of CH_4. In a second series of experiments, the catalyst was tested at 425°C while decreasing the mean O_2 concentration in the feed stepwise from 7000 ppm to 0 ppm. Contrary to the typical behavior of a TWC, CH_4 oxidation and NO reduction did not occur at λ = 1 but CH_4 removal was more efficient under rich of stoichiometry [2]. CH_4 oxidation initiated only when CO was removed completely confirming the inhibition of CH_4 oxidation by CO [3]. When these experiments were conducted under oscillating rich/lean feeds the O_2 concentration for maximum CH_4 conversion moved towards the λ= 1 value and the window of CH_4 oxidation broadened. The need to periodically switch the feed to reducing conditions to enhance CH_4 removal confirms that steam reforming is a preferred route for CH_4 oxidation and NO reduction occurs predominantly by H_2.

Hence, significant improvement of CH_4 abatement can be achieved on TWC under realistic periodic conditions compared to steady state conditions. This observation points to the need to study such catalysts under relevant operation conditions. The results suggest that the CH_4 abatement potential and the operation window of the TWC can be improved upon adequate control strategies, thus potentially contributing to further develop targeted after-treatment technologies for NGV.

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