Low-temperature performance enhancement by periodic operation of three-way catalysts for controlling emissions of hybrid electric vehicles

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Highlights

- Comprehensive study investigating reaction condition, control variable and catalyst configuration
- Cost-efficient emission control method to decrease cold start emissions
- Periodic operation improves C_3H_8 and NO conversion by 80 % and N_2 selectivity at 250 °C

1. Introduction

Compared to conventional internal combustion engines (ICE), hybrid electric vehicles (HEVs) consume up to 49% less fuel under urban driving conditions and can therefore significantly reduce CO_2 emissions [1]. However, as a result of frequent engine starts and stops, the exhaust gas temperature is lower for HEVs, which results in a decrease of carbon monoxide (CO), nitrogen oxide (NOx), and unburned hydrocarbons (HC) conversion at the three-way catalyst (TWC) used for exhaust gas aftertreatment. In addition, the unselective reduction of NO in the TWC leads to the formation of the potent greenhouse gas nitrous oxide (N_2O) and ammonia (NH_3), which is detrimental to both human health and the ecosystem. In order to increase the pollutant conversion at the TWC, future ICEs could alternate between a rich and lean mixture instead of controlling the exhaust gas composition stoichiometrically. This method of catalyst operation, so-called dithering, can increase the low-temperature pollutant conversion and thus improve the cold-start performance of the catalyst [2]. The reason for the increase in the reaction rate could not be conclusively clarified in the literature. It is assumed that under steady-state conditions the excess of adsorbed reactants impedes efficient usage of the catalyst surface. The periodic operation removes the strongly adsorbed species from the catalyst on a regular basis, which allows the catalyst to be used more efficiently. In order to better understand the phenomena occurring under dithering conditions, a comprehensive parametric study of the influence of the reaction conditions temperature and GHSV, the variables of periodic operation frequency, amplitude, split cycle and mean lambda, as well as the oxygen storage capacity on the periodic operation of TWC was carried out.

2. Methods

A monolithic sample (400 cpsi, 3 cm length, 1.6 cm diameter) was prepared by dip-coating of 2 wt% Pd/Al_2O_3 catalyst powder (target loading 100 g/l) and tested under dynamic conditions in a laboratory catalyst testing bench using synthetic exhaust gas.

3. Results and discussion

Figure 1 shows the average conversion of the pollutants CO, NO, C_3H_6, and C_3H_8 as well as the selectivity of the products of NO reduction, namely N_2O, NH_3, and N_2, at different frequencies and temperatures at $GHSV = 75\,000\ h^{-1}$ and amplitude $A = 0.04$ of the air-fuel equivalence ratio (AFR) λ. In a temperature interval of 150 – 350°C, periodic operation enables higher pollutant conversion compared to stoichiometric steady-state operation ($f \rightarrow \infty$). For instance, an increase of 80 % in the conversion of NO and C_3H_8 at a temperature of 250 °C and a frequency of 1.2 Hz can be observed. Increasing the temperature leads to a shift of the optimal frequency to higher values until steady-state operation becomes the most efficient method of pollutant conversion. Although N_2 selectivity can be increased by up to 30 % under optimal fluctuating conditions, the optimal frequency of pollutant conversion does not

necessarily correspond to that of minimal NH_3 or N_2O formation. Considering previous research [3,4] and our own data, we explain the improvement in pollutant conversion by a temperature-dependent induction time for CO desorption after a rich-lean switch, which corresponds to the minimum time period that is needed for rate enhancement under periodic operation. As the desorption rate of CO increases with increasing temperature, induction time gets reduced and therefore higher frequencies are necessary to generate free surface sites for subsequent pollutant adsorption, maintaining the optimal reactant composition on the catalytic surface. The addition of ceria (CeO_2) increases the oxygen storage capacity of the catalyst and causes a shift of the optimum frequency to lower values. We attribute this shift to a slower transition from lean to rich steady-state due to adsorbate exchange between the support material and the noble metal.

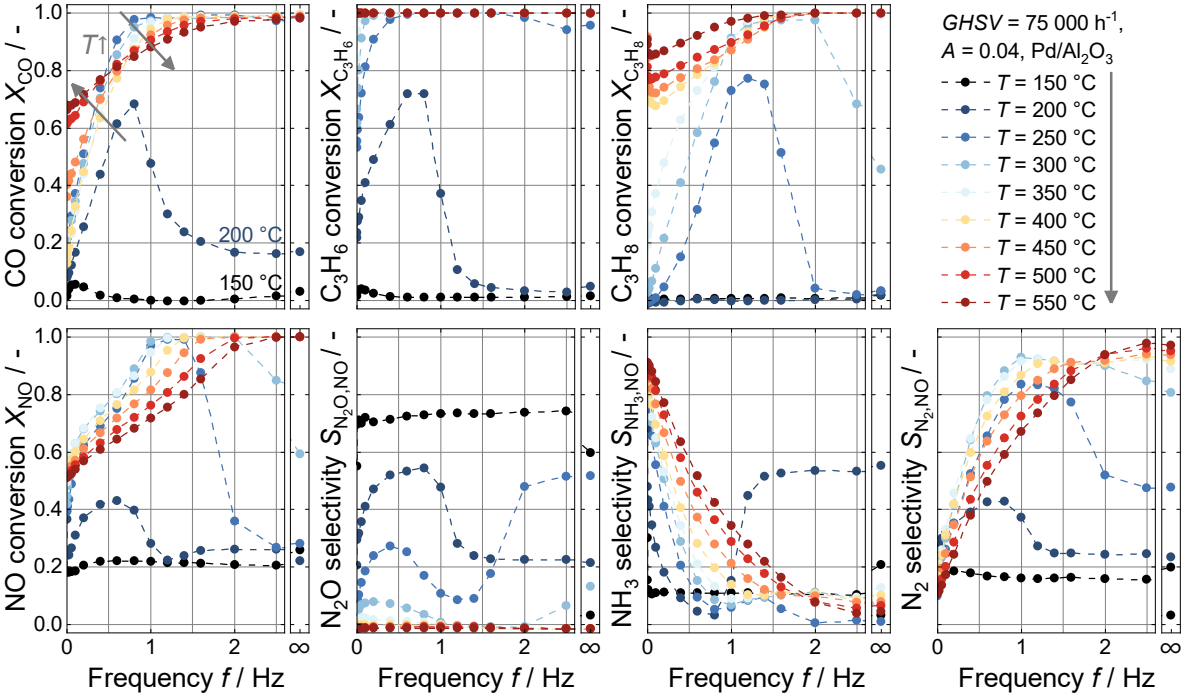

Figure 1. Average conversion of pollutants and selectivity of NO products at different frequencies and temperatures at constant *GHSV* = 75 000 h^{-1} and *A* = 0.04 (Gas composition: 13 % H_2O, 10 % CO, 1330 ppm NO, 360 ppm C_3H_6, 180 ppm C_3H_8 and either 0.9 % O_2, 800 ppm CO, 270 ppm H_2 (lean feed) or 1200 ppm O_2, 1.5 % CO, 0.5 % H_2 (rich feed).

4. Conclusions

By enhancing pollutant conversion at low and medium temperatures, periodic operation of TWCs can be used to reduce cold-start emissions from gasoline engines and hereby allows to meet more stringent emission limits in the future. Since dithering neither affects existing engine settings or operation conditions nor requires a complex feedback system, it is a cost-effective emission reduction strategy.

References

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Keywords

Dithering; oxygen storage capacity; palladium; periodic operation; three-way catalyst