Operando X-ray absorption spectroscopy for understanding the origin of phosphorous induced chemical aging of Pd-based three-way catalysts

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Introduction and Objectives

Three-way catalysts (TWC) play an important role in the abatement of hazardous exhaust emissions from spark ignition engines to meet the regulations [1-3]. Although they have proven efficient for this application, new fuel concepts like compressed natural gas (CNG) consisting of mainly methane and new EURO VI legislations post new challenges. One of them is chemical aging caused namely by phosphorous (P) originating from engine oil additives such as zinc dialkyldithiophosphate (ZDDP) which reacts with washcoat and catalyst composition. Commonly observed P compounds are $AlPO_4$ and $CePO_4$ [2-4]. However, the effect of P is not completely understood, especially on noble metals. Therefore, better understanding of the influence of P on TWC may provide a way forward to mitigate P influence on the catalyst efficiency. In this work, model TWC powders namely Pd/Al_2O_3 and $Pd/Al_2O_3/CeZrO_2$ were subjected to P aging (1.8 or 7.5 wt.% P poisoned and aged at 700°C for 5h) followed by detailed operando spectroscopic and activity studies.

Results and Discussion

The physisorption data show that both the surface area and pore volume of the catalysts decrease for P aged catalysts as compared to the fresh ones, indicating the presence of P on the surface and within the pores of the supports. Solid state Al^{27} and P^{31} MAS NMR spectra suggest the formation (even at 1.8 wt.% P) of $AlPO_4$ and $CePO_4$ like species in the catalysts [4]. The P species mitigate the oxidation and reduction efficiency of the catalysts as evident form the activity data obtained under simulated $\lambda = 1$ conditions. The origin of the decreased catalyst efficiency is explored by operando XANES and DRIFTS during the reaction. As an example, operando XANES during methane oxidation are shown in Fig.1. By comparison of the conversion profiles over the fresh and P aged catalysts it is evident that the former is more active than the latter. On the fresh catalyst the conversion starts at around 300°C and completes at around 370°C, while it starts only at 400°C and complete conversion attains only at around 850°C on the P aged one.

During cooling from 850°C, the drop in the conversion is observed on both the catalysts but to different extents and at different temperatures. On the fresh catalyst the maximum loss in the conversion is 20% at 550°C, while it is 90% at 650°C on the aged one.

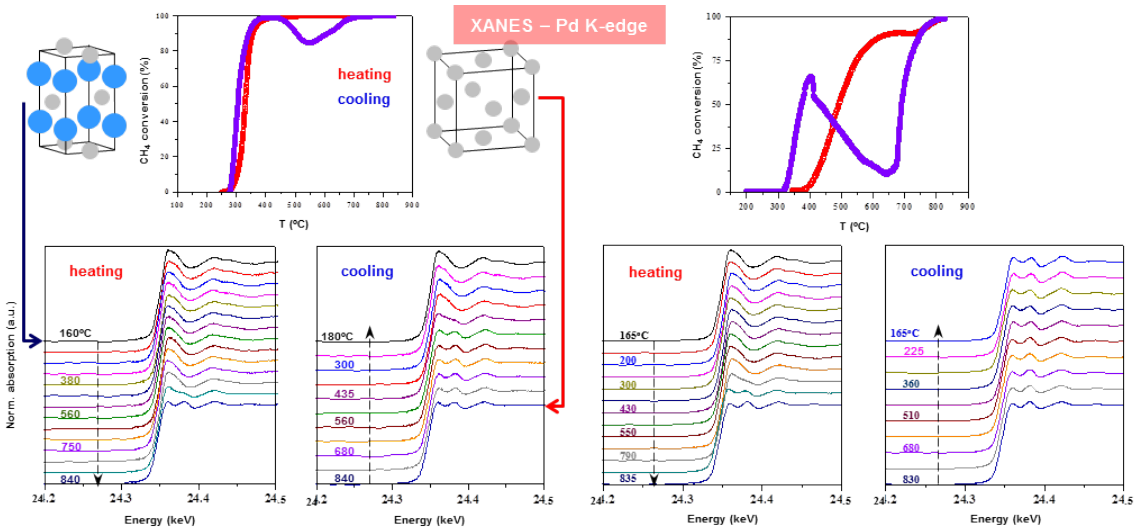

Fig. 1 Conversion of methane profile (heating and cooling) over fresh Pd/Al_2O_3 (left) and 7.5wt%P/ Pd/Al_2O_3 obtained by mass spectrometry simultaneously with the operando XANES. Conditions: catalyst mass 800 mg; 1 vol % CH_4 and 4 vol % O_2 in He; total flow 800 ml min^{-1}; heating rate 5 K min^{-1}.

From the corresponding XANES spectra, it is evident that while heating Pd is in an oxidized state up to 800°C and above this temperature it is reduced on both the catalysts. However, during cooling, the reduced Pd reoxidizes (<435°C) only in the fresh catalyst. This indicates that P alters the redox properties of PdO_x species in the catalysts, which is in line with the H_2-TPR followed by XANES data that show the decreased reducibility of PdO_x species in the catalysts [4]. By correlating the activity and spectroscopic data, it emerges that Pd oxide plays an important role in the methane oxidation at low temperatures (< 675 °C) and at high temperatures metallic Pd can also catalyse the reaction as evident from the drop in the methane conversion and from the corresponding XANES spectra. In conclusion, chemical aging caused by P diminishes both the reduction and oxidation efficiency of the catalysts by altering the redox properties of PdO_x species.

References

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