In-situ Probing of the Oxidation/Reduction Dynamics of Pure and contaminated Pt/Pd/Al_2O_3 DOC Catalysts by XAFS and flow reactor measurements

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Abstract: This work probes the reduction and CO-oxidation of fresh and contaminated Pt/Pd/Al_2O_3 diesel oxidation catalysts (DOC) using in-situ synchrotron methods in the form of XAFS and XANES, along with ex- situ STEM and EDS characterization of the elemental distribution on the support. These measurements are then correlated with light off curves to show that the contaminated samples (most pronounced in the case of Na) more easily reduce which has a positive correlation with lower light-off temperatures and association of the contaminant with the Pt as opposed to the support.

Keywords: Catalysis, DOC, in-situ

1. Introduction

Emission level goals for heavy duty vehicles are typically achieved by a combination of diesel oxidation catalysts (DOC), diesel particulate filters, selective catalytic reduction catalysts and ammonia slip catalysts. The DOC is often a Pt/Pd/Al_2O_3 catalyst placed first in the exhaust after-treatment system, and is of key importance for the overall effectiveness. This oxidation catalyst is heavily exposed to untreated exhaust, and thus particularly susceptible to chemical aging. In this work, we probe the effects of P, Na and K contaminations on the oxidation/reduction dynamics of the DOC catalyst using in-situ XAFS and supporting flow reactor and STEM studies.

2. Experimental

Catalysts were synthesized by two-step incipient wetness impregnation on γ-Al_2O_3 support, followed by drying at 110 °C and calcination for 4 hours at 500 °C. The target Pt loading was 0.9 wt-% and Pd 0.3 wt-%, one fresh sample was prepared along with three P, Na and K-contaminated with a target contaminant concentration of 1 wt-%. The samples were then probed by XAFS, XANES and STEM along with flow reactor measurements to provide light-off curves.

3. Results and discussion

Flow reactor and EXAFS data show a difference in reduction and oxidation dynamics for contaminated vs fresh samples. P, K and Na contaminated samples all show a faster and more complete reduction of the Pt-O bond (the Na case is illustrated in fig. 1), an effect that persists to some extent during reoxidation by CO in H_2O and O_2. Correlating this observation with the light-off curves for fresh and Na contaminated samples (fig 2) we can conclude that these dynamics can be used to explain the lower light-off temperature seen for the Na- contaminated samples in our flow reactor measurements. We further show using STEM studies that there is a preference for Na and P contaminants to associate with the Pt-particles as opposed to the alumina support which suggest a chemical or strong physical interaction between the two (Fig 3).

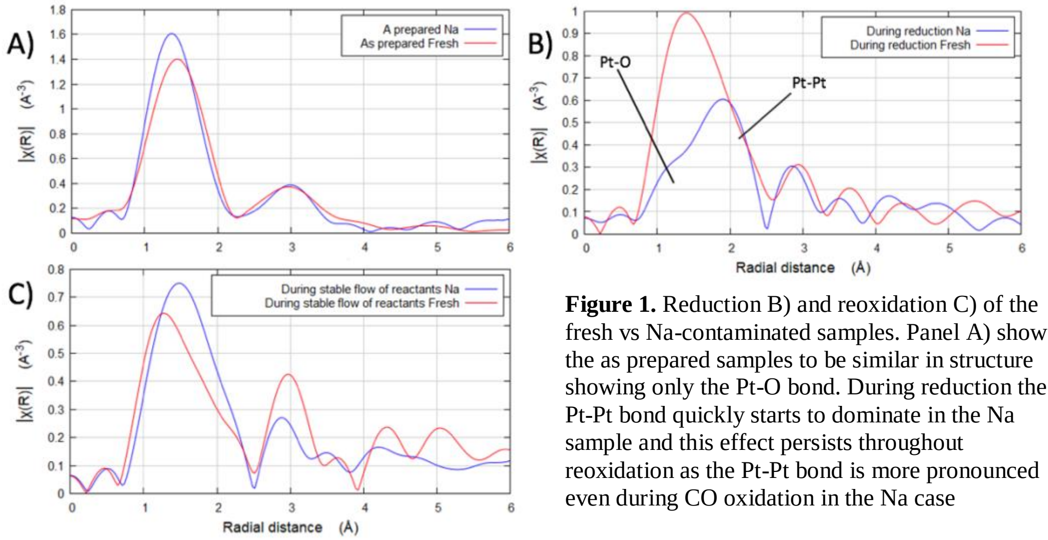

Figure 1. Reduction B) and reoxidation C) of the fresh vs Na-contaminated samples. Panel A) shows the as prepared samples to be similar in structure showing only the Pt-O bond. During reduction the Pt-Pt bond quickly starts to dominate in the Na sample and this effect persists throughout reoxidation as the Pt-Pt bond is more pronounced even during CO oxidation in the Na case

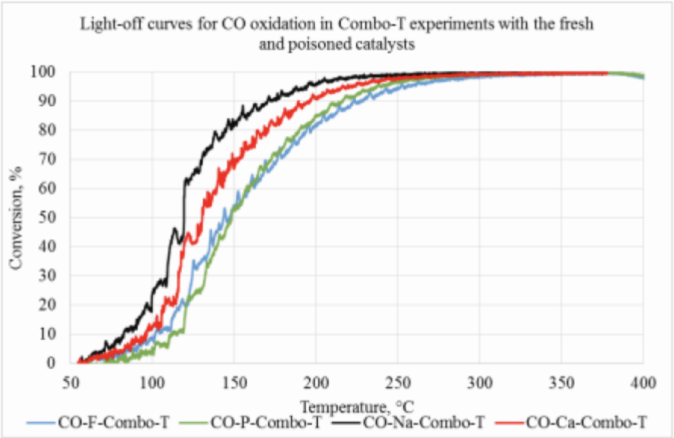

Figure 2. Light-off curves for CO-oxidation showing higher conversion for the Na-contaminated sample as a function of temperature

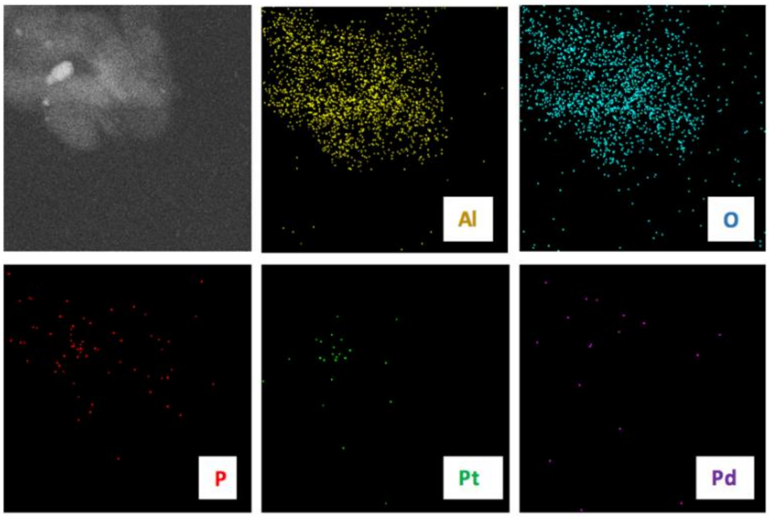

Figure 3. STEM and EDS data showing preferred association of the P with the Pt as opposed to the Al_2O_3 support

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4. Conclusions

A correlation between the reduction/oxidation dynamics as probed by XAFS and the light-off temperature has been found, indicating that Na, P and K-contaminated $Pt/Pd/Al_2O_3$ DOC catalysts are more susceptible to reduction of the Pt-O bond and that this effect can result in lower light-off temperatures. These trends hold true for P and K as well, to lesser degrees, and further synchrotron and flow reactor studies are currently underway to probe this effect.

References

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