

Preferential Oxidation of Carbon Monoxide from Cold Start under a Simulated Exhaust Gas Stream on a Crushed Pd/Al₂O₃ monolith.

Jacqueline Brown¹, Robbie Burch¹, Chris Hardacre^{1*}, John Breen¹, Roy Douglas¹, Richard J. Blint²

¹*CenTACat and School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, UK*

²*GM Corp, R&D Ctr, Chem & Environm Sci Lab, Warren, MI 48090 USA*

*c.hardacre@qub.ac.uk

Introduction

The largest proportion of pollutants - CO, hydrocarbons (HC), and NO_x, emitted from vehicles are given off in the cold start period, due to the fact that the catalytic converter used to control vehicle emission is relatively inactive at low temperatures under exhaust gas flow. While much work has been carried out investigating CO oxidation on Pd/Al₂O₃, the studies generally make use of a simplified exhaust gas, with only a few components found in a real engine exhaust gas present [1] and the laboratory experiments fail to accurately portray actual catalytic behavior in vehicles [2]. With this in mind, tests have been carried out on a real engine front brick under more realistic conditions than previously used to gain a better understanding of the effects of the different components that constitute a real engine exhaust.

Materials and Methods

Steady state experiments at temperatures ranging from 45 - 350°C were carried out on a 0.4 wt.% Pd/Al₂O₃ monolith, de-greened in nitrogen at 400°C for 8 hours. Kinetic testing was performed in a fixed bed tubular quartz reactor with a catalyst sample of 100 mg of the crushed monolith, mesh size 250-425 μm. The gas composition used consisted of 1% CO, 1% H₂, 500ppm NO, 450ppm HCs (145ppm C₃H₆, 83ppm iso-octane, 222ppm meta xylene), 10% CO₂, 10% H₂O and O₂ (in a 5% excess or 2.5% deficiency) balanced in Ar. Testing was carried out in both rich and lean gas mixtures where all components were present, and with one of the following removed; NO, or HCs, or CO₂, or H₂O. This experimental set was then repeated with the H₂ removed. Analysis was carried out using a Perkin Elmer Clarus 500 Gas Chromatograph, fitted with a Thermal Conductivity Detector and a Flame Ionization Detector, and a Signal NO_x analyzer Series 4000. In situ XRD and DRIFTS experiments have also been carried out.

Results and Discussion

Fig.1 shows the effect on the conversion of CO of the removal of various effect occurred when H₂ was removed from both the lean and rich mixes. In both cases the removal of H₂ retarded the light-off temperature by more than 100 °C. The removal of H₂O and H₂ from the lean mixture further delayed the light off temperature for the lean mix. The dramatic enhancing effect of hydrogen suggests that it may have a role in reducing less active surface palladium oxide to a more active metallic form, with a combination of hydrogen and H₂O resulting in the formation of a highly active catalytic surface. In contrast to H₂, the removal of the HCs and NO had negligible effect on CO conversion in lean gas mixtures. Surprisingly, Fig.1 also shows that CO₂ has a positive effect on the CO oxidation kinetics in the rich mixture.

The unusual effects of H₂ and CO₂ have been probed further using in situ XRD and DRIFTS. The results of these and other analyses will be used to generate a global understanding of the effects of the addition and removal of gaseous components on both the structure of the catalyst and nature of surface species under reaction conditions.

In summary, the studies carried out under cold start conditions show surprising results, where the components which would be expected to have a great effect on conversion, such as the HCs, show no real change in conversion, while apparently less important components, H₂O and CO₂, cause greater changes in performance.

Significance

This investigation into the behavior of emission control catalysts gives an insight into how a real catalytic converter performs using a monolith supported catalyst. The information obtained provides valuable input data to the complex catalytic modeling currently being undertaken to understand and predict catalyst performance under cold start conditions.

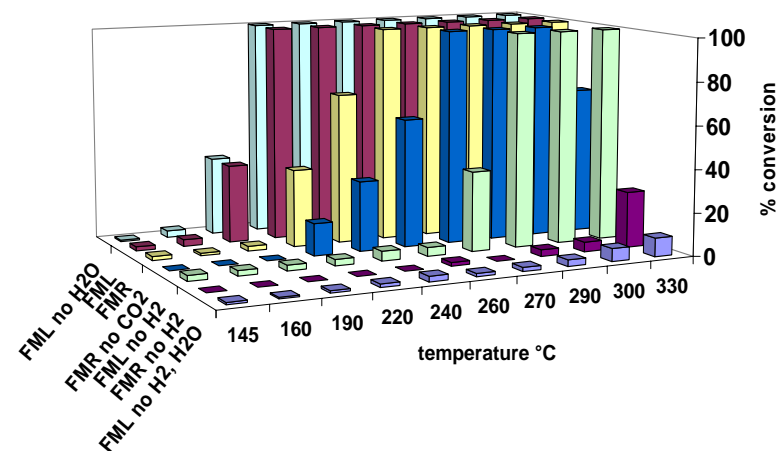


Figure 1. Comparison of the conversion of CO as a function of temperature in lean or rich conditions in the full gas mix (indicated as FML and FMR respectively) and in the full gas mix with the H₂ removed, the H₂O removed, the CO₂ removed or the H₂ and H₂O removed.

References

1. L. Olsson, B. Andersson, *Topics in Catalysis*, 28 (2004) 89
2. B.K. Cho, *Ind. Eng. Chem. Res.* 27 (1988) 30