On using spatially resolved techniques for the investigation of the H_2 effect on the CO oxidation over monolithic catalysts

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Introduction

The promotional effect of H_2 on the CO oxidation continues to be an intriguing subject for the scientific community and evaluating its effect during *operando* can help in optimizing the overall efficiency of a catalytic converter since it is considered to be a clean fuel and already present in the exhaust gas of diesel engines. However, common '*end-pipe*' analyses cannot provide information on aspects such as reaction pathways, intermediates and hydrodynamic parameters within monolith channels.

In the present work, SpaciMS was used to investigate the oxidation of CO in the absence and presence of small amounts of H_2 on a vehicle aged Pd/Al_2O_3 washcoated monolith. The resultant gas concentration profiles have been compared with a kinetic model which uses a dual global kinetics/micro-kinetics approach.

Materials and Methods

SpaciMS technique[1] was used to examine the promoting effect of small concentrations of H_2 on the light-off of CO on a Pd/Al_2O_3 washcoated monolith. By translating the spatially distributed capillaries and thermocouples from inlet to outlet of the catalyst using an automated scanning system, the influence of hydrogen on the CO oxidation across the monolith was assessed. The feed composition was kept constant (1% CO, 5% O_2 excess and 0.3%H_2 when added) and steady-state experiments were performed at temperatures bellow and above the light-off point.

Results and Discussion

SpaciMS measurements emphasized the promoting impact of hydrogen on the CO oxidation at various reaction temperatures. The use of a spatially resolved technique to study the real catalytic systems under operation helped in identifying and solving short comings in the model (*eg.* assessing the best approach for calculating Sherwood number to have a highly accurate kinetic model). The microkinetic model has simulated the concentration at set positions along the length of the catalyst corresponding to the positions set during the experiment and a very good correlation was observed with the experimental results, as emphasized in **Figure 1**. At fixed reaction temperature and constant gas compositions, the addition of H_2 caused a displacement of the reaction front from the last quarter of the converter (**Figure 1a**) to its first mm (**Figure 1b**). This promoting effect was also identified in the reaction exotherms. Thus, as shown in **Figure 2**, with H_2 in the feed, the 17 ^oC exotherm was observed within the first 10 mm of the monolith (**Figure 2b**), while in the absence of hydrogen, the centreline temperature was located in the second half of the catalyst (**Figure 2a**).

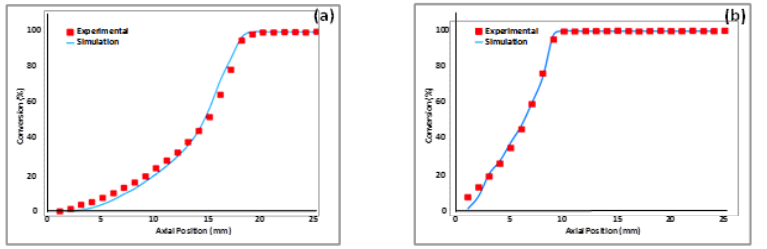

Figure 1. Experimental and simulated CO conversion profile over a Pd/Al_2O_3 washcoated monolith: (a) in the absence of H_2 and (b) with 0.3% H_2 in the feed.

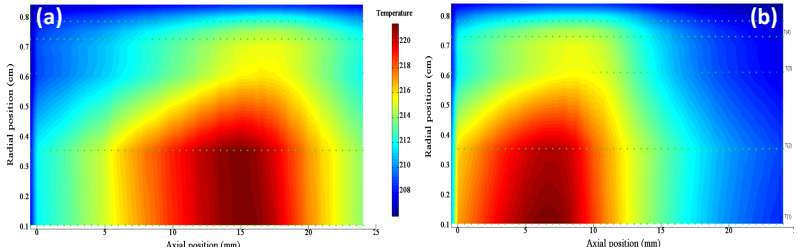

Figure 2. Spatially resolved temperature profiles of the CO oxidation over a Pd/Al_2O_3 washcoated monolith: (a) without H_2 and (b) with H_2.

The impact of hydrogen addition was higher at lower temperatures and on partially deactivated cores. Along with the promoting effect that hydrogen has for the CO conversion, an interesting observation was that it hinders the formation of kinetic oscillations[1]. Furthermore, the spatially resolved profiles also indicated that the formation of water occurs faster than that of CO_2 and this can be a good indication of a possible thermal effect played by hydrogen addition to the feed. However, this cannot fully explain the profiles observed at various conditions, in the absence and presence of hydrogen, therefore, a chemical effect is also considered.

Significance

The SpaciMS measurements unravelled the dramatic impact which small quantities of hydrogen have on the conversion of CO within a real catalytic converter by displacing the reaction front from the last quarter of the monolith upstream, to its first mm. The data was used to improve and validate a kinetic model based on a dual global kinetics/micro-kinetics approach. Having a tool such as a kinetic model can greatly help with the development of catalyst through bridging the gap between experimental tests whether between different reactors or between reactor and vehicle data.

References

1. Sá, J.; Fernandes, D. L. A.; Aiouache, F.; Goguet, A.; Hardacre, C.; Lundie, D.;, Naeem, W.; Partridge, W. P.; Stere, C. *Analyst* **2010**, *135,* 2260.