Catalytic performances of a meso-structured $MgAl_2O_4$ supported catalyst: comparison with a commercial DOC.

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Introduction

Today's challenge for automotive exhaust gas control technologies is not only to meet the regulations for pollutant emissions, but also to achieve high catalytic performances and sustainability using a Platinum Group Metal (PGM) content as low as possible. One of the major issues is to optimize Metal-Support Interactions (MSIs)[1] in order to promote both a high dispersion and a strong anchorage of the metallic active phase(s) upon ageing.

Therefore, a catalytic support should be constituted by nano-sized crystallites and should exhibit a high specific surface area with tailored host sites[2]. The present study is dealing with a meso-structured, ultra-divided $MgAl_2O_4$ Magnesium Aluminate Spinel (MAS) support synthesized via an aqueous sol-gel route. It appears to be a suitable host for catalytically active phase(s), due to its low acidity and good thermal stability. The Diesel Oxidation Catalysts (DOCs) are currently bimetallic ones, using Pt-Pd. Such catalysts present a higher long-term efficiency than the respective monometallic ones in promoting carbon monoxide (CO) and hydrocarbons (HC) oxidation.

Materials and Methods

Each of our catalysts was prepared with a formulation allowing a direct comparison of performances with a commercial DOC that was a mixture of La-doped γ-Al_2O_3 and zeolite supports with a 2.5 wt. % Pt-Pd (3:2 weight) content. For our catalysts, $Pt(NO_3)_2$ and $Pd(NO_3)_2$ aqueous solutions were used for wet impregnation of a spray-dried ultra-divided $MgAl_2O_4$ powder,[2] synthesized via an aqueous sol-gel route. The impregnated powders were ball-milled with zeolite to form slurries into which a monolithic honeycomb substrate was dipped in order to reach PGM content of $90g/ft^3$. We aim to compare three catalytic compositions. The commercial DOC, our catalyst for which Pt and Pd species were simultaneously impregnated (so-called co-impregnated), and a catalyst prepared the same way as the co-impregnated one but containing only Pt as an active phase.

The catalytic performances were evaluated in a reactor under a continuous flow with a GHSV of 55 000h^{-1}. HC, CO and nitrogen oxides (NOx) were fed in the proportions of 430, 1500 and 100 ppm respectively. The temperature was gradually raised from room temperature to 450°C. The fresh catalysts, not reduced, were first hydrothermally aged at 650°C for 2h under 70%N_2-20%O_2-10%H_2O vol. and then at 750°C for 5h. ΔT_1 and ΔT_2 are the differences between the Light-Off temperatures at fresh state and after the 650°C-ageing, and between the 650°C-ageing and the 750°C-ageing, respectively.

Results and Discussion

The Light-Off Temperatures corresponding to a 50% CO conversion rate ($T_{50}CO$) and a 80% HC conversion rate ($T_{80}HC$) over fresh and aged catalysts were compared to those of a commercial DOC, as shown in Figure 1. At fresh state, the $T_{50}CO$ of the two catalysts were slightly higher than that of the DOC. The $\Delta_1 T_{50}CO$ and $\Delta_2 T_{50}CO$ indicated that our catalysts behave the same way as the DOC under hydrothermal atmosphere. For HC conversion, our co-impregnated catalyst showed the same behavior as the DOC, unlike the monometallic Pt-based catalyst. This last one was more impacted by the second ageing at 750°C due to the absence of palladium. These results can be explained by the MSIs generated by the impregnation, the active species obtained and the support tailored microstructure.
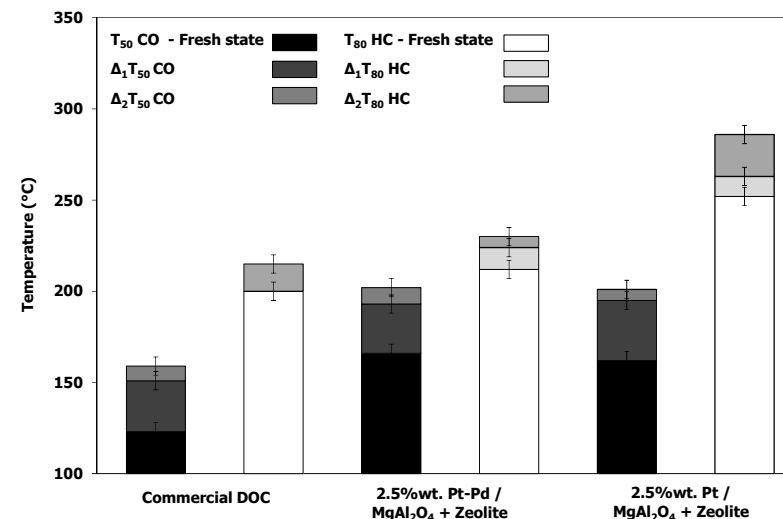

Figure 1 : The T_{50} for CO conversion, T_{80} for HC conversion and ΔT_1 and ΔT_2 over fresh and aged catalysts.

Conclusions

The $MgAl_2O_4$ support allows a good chemical anchorage of the active phase at fresh state. Under hydrothermal ageing, the $MgAl_2O_4$-supported catalysts activity depends on its mesostructure that limits the active phase coalescence by mechanical anchorage. The main deactivation sources are the solid solutions formation and the inhibition of the active sites by steam. A further study will deal with the optimization of the impregnation method in order to obtain more relevant morphologies for active Pt and Pd species, while preventing them from diffusing into the oxide support. Therefore we expect to reach catalytic performances equivalent or superior to those of the DOC with a lower PGM content.

References

1. Liu, J. J. *ChemCatChem*, **2011**, vol. 3, pp. 934-948.
2. Air Liquide patent FR1060629, 16/12/10.