Effect of biodiesel poisoning and hydrothermal ageing in different Pt:Pd ratio Diesel Oxidation Catalysts – an experimental and modelling study

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Heavy-duty vehicles have strict emissions limits that are tightening with each new regulation. Euro VI, the last emission legislation currently ongoing in Europe, specifies that the useful life of the catalysts has to exceed 7 years or 700 000 km [1]. During normal operation, catalysts are exposed to high temperatures and impurities coming from the combustible and oils, which can reduce its performance. In that scenario, the ability to design and predict the activity of the catalysts used becomes quite useful. Accordingly, we tested different Diesel Oxidation Catalysts (DOC), either fresh or hydrothermally aged and poisoned ones. Theoretical values for biodiesel poisoning were obtained from the exposure of a real heavy-duty catalyst with a biodiesel consumption of 35 L/km during 700,000 km [2]. Experimental data obtained from experiments performed with the fresh and aged DOC catalysts allowed to develop a macro kinetic model to predict DOC with different compositions. Five DOC catalysts with different Pt:Pd ratios and PGM content were prepared by incipient wetness impregnation of γ-Al_2O_3. The support was initially calcinated at 650 ºC for 5 hours under an air flow of 100 ml/min. Then, the support was consecutively impregnated with a Pt and Pd aqueous solution and calcined at the previous same conditions. Impurities were added to the impregnation solution. Ca, K, Na and P are typical impurities present in biodiesel and motor lubricants. In this study, their concentrations were considered to be 1.4% wt., 0.5% wt., 2% wt. and 7% wt., respectively. In order to reproduce the half-life, concentrations half of these quantities were also considered. Catalysts were poisoned with each of these impurities or all of them at the same time. The hydrothermal ageing (HTA) was done under 100 ml/min airflow containing 10 % H_2O at either 700 ºC for 16 h or 700 ºC for 96 h. Then, an additional HTA at 700 ºC for 16h was added for each sample after addition of impurities.

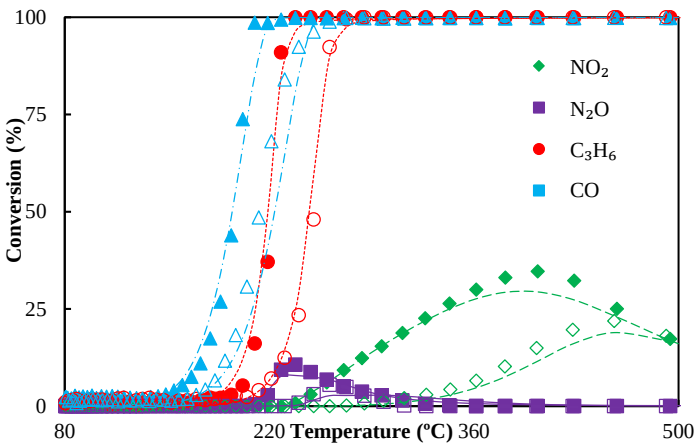

Figure 1: Experimental results of the CO, C_3H_6, NO-NO_2 and NO-N_2O conversion for the fresh (filled points) and fully poisoned (empty points) catalysts. Simulation results in the colored lines.

For establishing a full macro kinetical model of the fresh DOC, the oxidation of each single component and in combination with the rest of them was performed by considering different Pt:Pd ratios. The model was extrapolated to catalysts with different total PGM and Pt:Pd ratios. This model allowed to predict the effect of each individual poisoning and HTA. In addition, it was validated at different levels of poisoning and HTA. Once the model was able to predict the individual poisoning and HTA, it was used to compute the combined effect of the impurities all together along with HTA. It was found that the combined effect of all impurities was equivalent to that of the phosphorous alone. Different phosphates were detected by XRD. From the results derived from the model, it can be proposed that poisoning affects NO oxidation due to an interaction with the metal active sites that modifies the adsorption properties. On the other hand, the CO and C_3H_6 oxidation rate was negatively affected by pore blocking and no modification of the reaction tendencies was observed. The experimental and model results for the fresh and fully poisoned catalysts is shown in Figure 1.

[1] Adamowska, M., Lauga, V. and Da Costa, P., *Top. Catal.* 56 267–272 (2013).

[2] Anguita, P., García-Vargas, J.M., Gaillard, F., Iojoiu, E., Gil S. and Giroir-Fendler, A., *Chemical Engineering Journal*, 352, 333-342 (2018).