ESRF	**Experiment title:** In-situ XAFS of supported Silver catalysts for pollution abatment in automobile exhausts	**Experiment number**: CH-969
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Names and affiliations of applicants (* indicates experimentalists):

Dr. J.C. Conesa

Dr. M. Fernández-García (*)

Dr. Martínez-Arias (*)

Mrs. A. Iglesias-Juez (*)

Instituto de Catálisis (CSIC)

Campus Cantoblanco, 28049-Madrid, Spain

Report:

Diesel or lean-burn engines operates with oxygen-rich air/fuel mixtures in order to reach maximum fuel efficiency. In this condition, the actual technology for abatement of dangerous pollutants emitted by motor engines, particularly NOx (nitrogen oxides), does not work correctly. The alumina-supported silver system is one of the most promising catalysts tested up to date. This material shows a catalytic activity strongly dependent on silver loading, displaying maximum activity for intermediate loading (between 2-3 wt. %), a fact that has been grounded on the existence of metallic silver for higher loadings at reaction conditions which, in turn, favors the burning of hydrocarbons with oxygen and not with NOx. In this study a careful preparation method of the Ag/Al_2O_3 catalyst was used in order to maximize the quantity of silver active species and then facilitate the analysis of its electronic/geometric characteristics and behavior under reaction conditions.

XAFS experiments were carried out at the Ag K-edge using the set-up of beam line BM29 with a Si(111) monochromator, a home-made treatment cell to perform experiments under controlled temperature and atmosphere and calibrating the energy scale by measuring simultaneously a Ag foil (XANES study). Two

catalysts, displaying very high activity in the selective reduction of NO_x with hydrocarbons and containing, respectively, 1.5 and 4.5 wt. % of Ag, were analyzed. Fig. 1A shows the XANES spectra of these samples in their calcined, initial state and some reference material having linear (Ag_2O, α-$AgAlO_2$) or tetrahedral (β-$AgAlO_2$) local geometry for the first silver coordination shell. Although some differences are encountered in the region of ca. 25525 eV, a remarkable similarity can be observed between both Ag/Al_2O_3 specimens and the β-$AgAlO_2$ XANES reference spectrum; this clearly indicates that silver active species have a strong contact with the support, stabilizing in this way dispersed entities having silver cations in tetrahedral local geometry. EXAFS was used (Fig. 1B) to proof that these tetrahedral silver clusters are stable under reaction conditions, being practically unaltered when subjected to a gas mixture simulating the exhaust gas up to temperatures of 823 K.

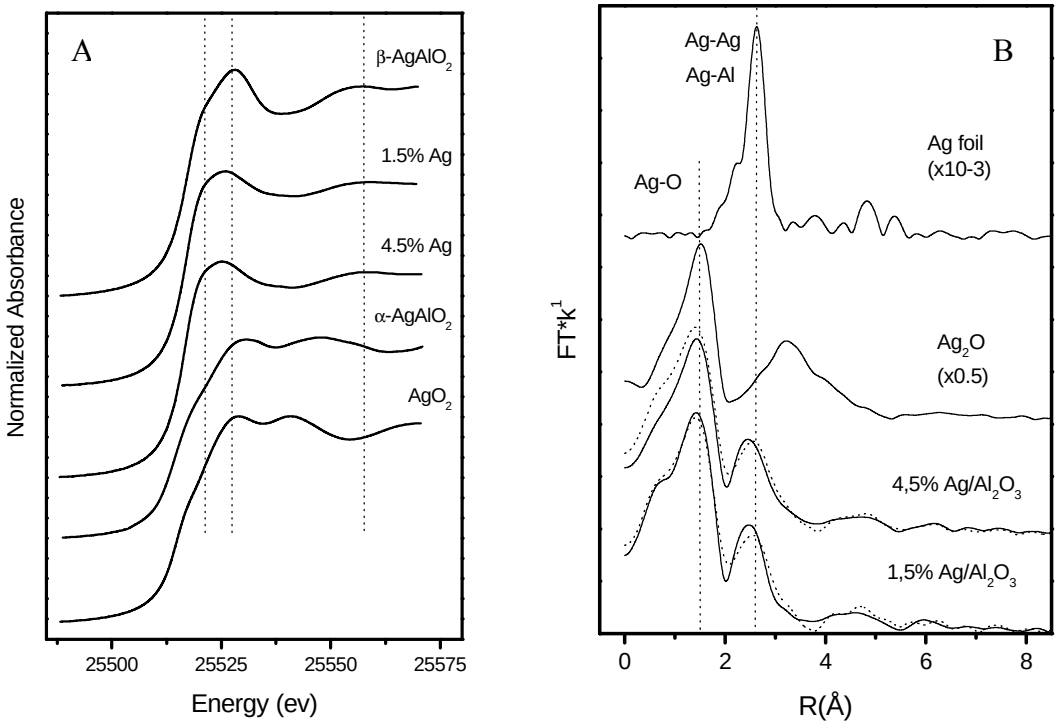

Fig. 1. (A) XANES and (B) EXAFS spectra of Ag/Al_2O_3 catalysts and reference materials. Full lines; calcined samples; dashed lines; samples after reaction.

Differences between the catalytic activity of the two catalysts analyzed should be then grounded on relative variations of the interaction of reactants with the active phase and not on silver phase nature or distribution. In our case, the 4.5 Ag system displays a lower light-off temperature for NO conversion. Mechanistic studies and thermo-programmed reaction runs (followed by XANES –result not shown) in presence of the hydrocarbon suggest that the ease with which the reductant extracts oxygen from the silver-containing active phase and produce a partially oxidized organic compound can be the key parameter to optimize the catalytic behavior of the system.

Assistance of BM29 staff during this experiment is gratefully acknowledged.