



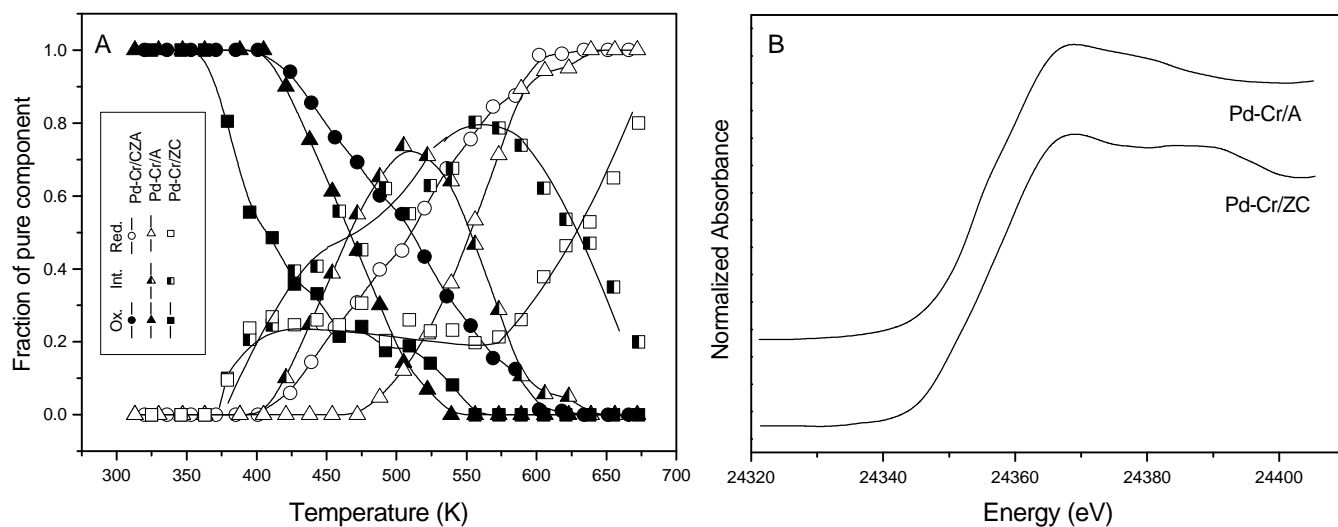
	<b>Experiment title:</b> In-situ XAFS of supported Pd-(Cr,Ni) catalysts for pollution abatement in automobile exhausts	<b>Experiment number:</b> CH-1185
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 5.09.2001 to: 10.09.2001	<b>Date of report:</b> 22.07.2002  <i>Received at ESRF:</i>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. G. Subias	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Dr. M. Fernández-García Dr. A. Martínez-Arias Ms. A. Iglesias-Juez Instituto de Catálisis (CSIC) Campus Cantoblanco, 28049-Madrid Spain		

### Report:

The behavior of Pd under gas mixtures simulating the exhaust pipe conditions of a gasoline vehicle was studied in a series of bimetallic catalysts containing 1.0 wt% of Pd in combination with a second metal (Cr and Ni, with a 1.0 wt% loading) and corresponding monometallic Pd references. These active components are supported in a mixed (10 wt%) CeZrO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> (CZA) material and the Al<sub>2</sub>O<sub>3</sub> (A), CeZrO<sub>4</sub> (CZ) parent supports. XANES was used to analyze the interaction between active metals, the active metal and the support and the influence of these parameters in catalytic behavior.

XANES experiments were carried out at the Pd K-edge using the step-up of beam line BM29 with a Si(311) monochromator, and a home-made treatment cell to perform experiments with controlled temperature and gas atmosphere and calibrating the energy scale by measuring simultaneously a Pd foil. In Fig. 1 is presented a quantitative analysis (using factor analysis) of the evolution of the Pd component in Pd-Cr catalysts during a light-off experiment under a simulated exhaust gas mixture. A strong effect of the nature of the support is evidence in the behavior of Pd. The initial, oxidized species has a local structure very similar to PdO (result not shown) and evolves through an intermediate in the case of A- and CZ-supported systems but

not for the CZA specimen (Fig. 1A). This clearly suggests that the complex CZA support inhibits, to a large extent, the interaction between both active metals. On the other hand, the intermediate significantly decreases the range of existence of the oxidized Pd species and has a very different nature in the A- and CZ- cases. In the first system, the analysis of the Pd XANES shape and edge position (together with the analysis of the Cr K-edge) indicates the formation of the Pd(I)-Cr(III) mixed oxide (Fig. 1B). For the CZ-supported specimen, the XANES shape is associated with the formation of a Pd-Cr alloy (Fig. 1B). At higher temperatures, both intermediates are unstable and evolve yielding monometallic, zero-valent Pd(0) particles. In the case of the Pd-Cr alloy, disruption of the heterometallic bond is likely related to the existence of a miscibility gap at the bulk phase at working temperatures (below 873 K). Metallic Pd(0) particles also correspond to the final Pd-containing species detected in the CZA case but, again, notable differences are encountered among samples in the temperature of appearance of such final, zero-valent species (Fig. 1A). Additionally, it can be observed that Pd coexists with the Pd-Cr alloy in the Pd-Cr/CZ sample at temperatures between 375 and 673 K.



**Fig. 1.** (A) Concentration profiles of Pd-containing species in Pd-Cr catalysts during a light-off, temperature reaction run. (B) Intermediate species detected in the experiment.

The marked influence of the support nature on Pd oxidation state and phase distribution allows to interpret the effect of Cr in Pd performance during elimination of pollutants in exhaust vent ports. Comparing with catalytic results, it can be shown that the formation of the Pd(I)-Cr(III) mixed oxide or Pd-Cr alloy intermediates favorably influences oxidation reactions (like CO oxidation) while has a different impact in the reduction of NO. In the latter reaction, the mixed oxide produces adverse effects in the light-off temperature while the alloy formation and/or coexistence with Pd at low temperatures enhances NO conversion levels. Therefore, the XAFS results presented give evidence of the importance to finely tune the interaction between Pd and Cr during the preparation steps in order to get the adequate Pd state/distribution (in the real, complex CZA-supported catalysts) and to maximize catalytic performance.

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