	Time-resolved XAS study of Pd-TWC under real, operation conditions	Experiment number: ME-1292
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Report:

Alumina-supported Pd catalysts promoted with Ce-Zr mixed oxides (CZ component) are widely employed as three-way catalysts (TWCs) for the control of toxic emissions in the exhaust of petrol-fuelled automobiles. Analysis of the noble metal interactions with the CZ promoter and the carrier during “real” operation conditions is necessary to understand the physical basis of the catalytic behavior of TWCs. This goal requires the analysis of all components of TWCs subjected to rapid changes (1-3 Hz) of the exhaust gas mixture, which may have stoichiometric (equal molar ratio of reducing and oxidant molecules; $\lambda = 1$), oxidizing ($\lambda > 1$), and reducing ($\lambda < 1$) nature, and using working temperatures [1]. Here we compare several catalysts which correspond to Pd-based TWCs promoted with 10 and 33 wt. % of Ce-Zr (Pd1ZCA, Pd3ZCA), supported on Ce-Zr (PdZC) and a reference system supported on alumina (PdA).

XAFS experiments were carried at the beam line ID24 with a Si(311) monochromator in Laue-configuration and using a CCD detector. A plug-flow reactor were used to subject the samples to an atmosphere containing 0.1 % C₃H₆ + 0.1 % NO + 1 % CO (Ar balance) and variable quantities of oxygen in

order to go from oxidizing to reducing conditions and vice versa in a step change. Results at the Pd K-edge were taken with a typical temporal resolution of 50 ms and lasted several seconds. When departing from a reducing condition, the oxidation kinetics of the noble metal is very slow and can be studied by conventional methods [1]. This is not the case of the reduction process occurring when going from an oxidizing atmosphere ($\lambda = 1.02$) to a reducing one ($\lambda = 0.98$). In this case, the analysis of Pd K-edge XANES spectra (Factor Analysis) shows Pd^{2+} as the dominant species at the starting point and a $\text{Pd}^{2+} \rightarrow \text{Pd}^0$ transformation which takes longer to be completed as the Ce-Zr quantity of the catalyst increases; the delay in reaching the $\text{Pd}(0)$ state is more marked for PdCZ, evidencing a higher buffering capacity for the latter sample, which displays a significant capacity to stabilize the oxidized state (Fig. 1).

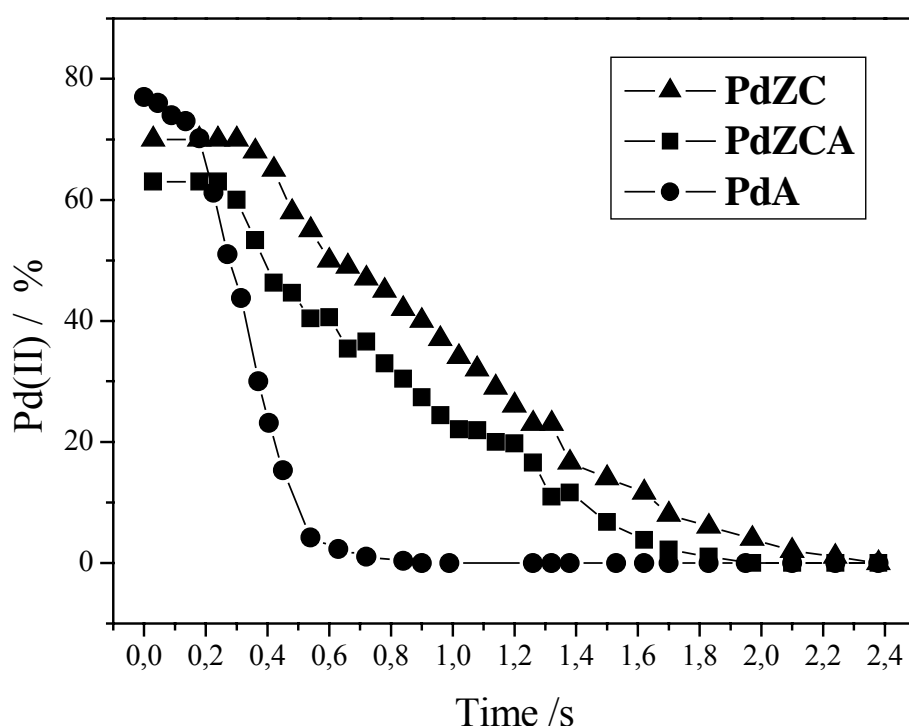


Fig. 1. Fraction of Pd as Pd^{2+} (from K-edge XANES).

Evolution of outlet gas concentrations during this experiment was measured simultaneously by using Mass Spectrometry. Comparison with XAS results indicates that the Pd oxidized state favors the elimination of hydrocarbons while the reduced state works better in the CO and NO elimination reactions.

1.- J.A. Botas et al., *Appl. Catal. B* **32**, 243 (2001); J.D. Grunwaldt et al., *PCCP* **5**, 1481 (2003).

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