



Analysis of Pd-TWC Systems under Real Motor Operation Conditions

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ME-605

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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 three catalysts which correspond to Pd-based TWCs promoted with 10 wt. % of Ce-Zr (PdZCA), 10 wt. % of Ce (PdCA) and a reference system supported on alumina (PdA).

XAFS experiments were carried at the beam line ID24 with a Si(111) 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

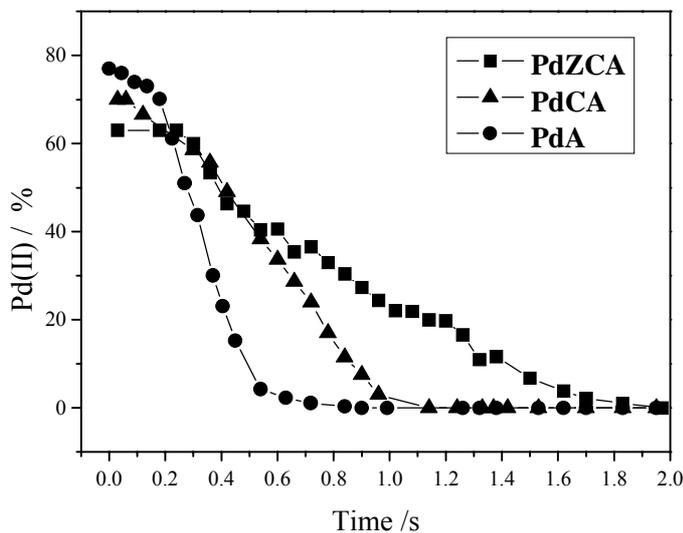


Fig. 1. Fraction of Pd as Pd²⁺ (from K-edge XANES).

order to go from oxidizing to reducing conditions and vice versa. Results at the Pd K-edge were taken with a typical temporal resolution of 50 ms. 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 ($\lambda = 1.01$) to a reducing one ($\lambda = 0.98$). In this case, the analysis of Pd K-edge XANES spectra

(Factor Analysis) shows Pd²⁺ as the dominant species at the starting point and a Pd²⁺ → Pd⁰ transformation which takes longer to be completed for the Ce-containing catalysts; the delay is more marked for PdCZA, evidencing for the latter a higher buffering capacity in spite of its smaller total amount of Ce (Fig. 1).

Evolution of outlet gas during this experiment was measured simultaneously by using Mass Spectrometry. Fig. 2 shows that switching from oxidizing to reducing conditions leads to fast suppression of NO while the appearance of excess reductant (CO; hydrocarbon conversion is always complete) is delayed. The delay is larger for the promoted catalysts, and, among these, for the (Ce,Zr) mixed oxide containing one. Therefore, the redox behavior of Pd is shown to be dependent on noble metal – promoter interactions.

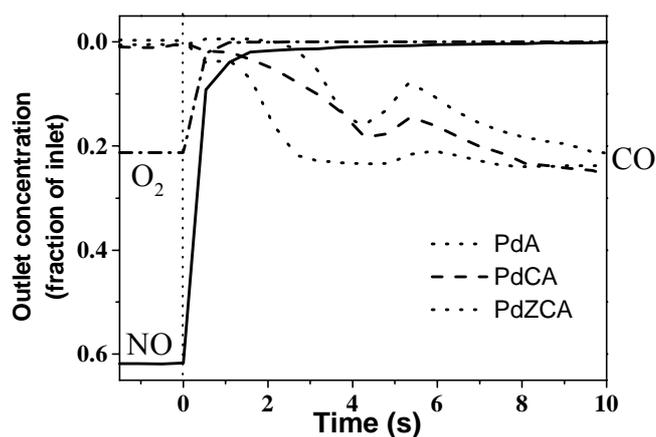


Fig. 2. Changes detected upon switching in gas composition (diluted CO+NO+C₃H₆+O₂) at t=0 from $\lambda=1.01$ to $\lambda=0.98$ for catalysts in *in situ* XANES reactor at 723 K.

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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