

## Structure and Oxidation State of Ce and Pd in Automotive Exhaust Catalysts

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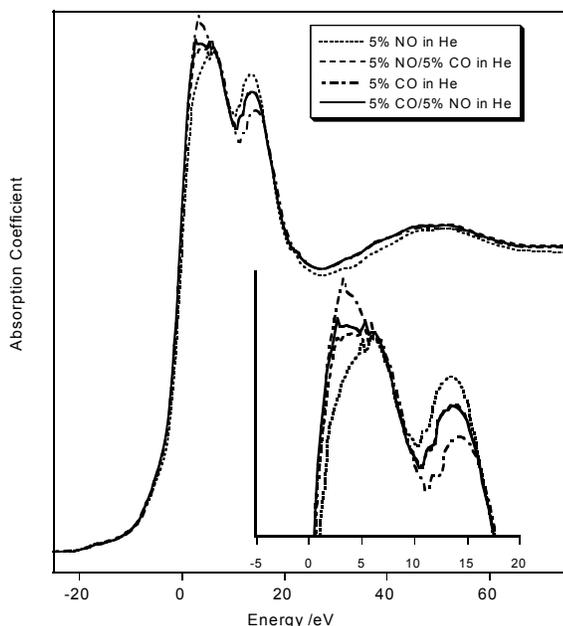
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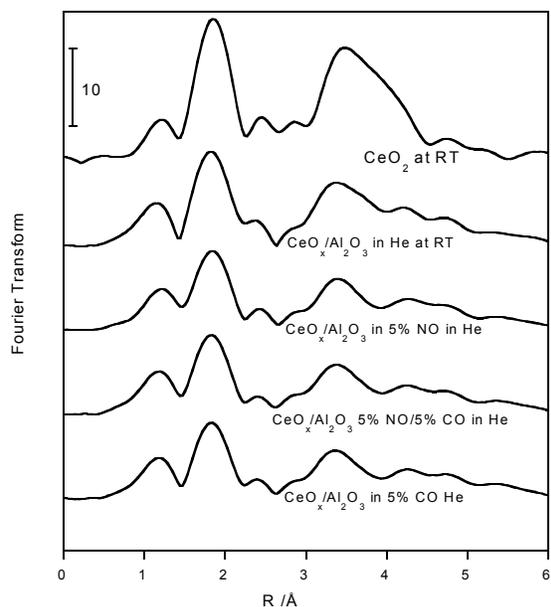
**Introduction:** Removal of NO from automobile emissions occurs over ceria (cerium oxide) promoted transition metals (typically Pt and Rh) in a catalytic converter. The newest generation of automobile exhaust catalysts incorporates Pd instead of Rh. In addition, current automobile engines cycle between oxidizing and reducing conditions to help minimize emissions. However, little is known about the electronic and structural state of the Pd and ceria under these varying conditions.

**Methods and Materials:** In situ x-ray absorption spectroscopy (XANES and EXAFS) at the Ce L<sub>III</sub> and Pd K edge was used to characterize the oxidation state and structural parameters of CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts during the reduction of NO by CO. The samples were exposed to oxidizing (5% NO in He), reducing (5% CO in He) and stoichiometric (5%NO/5%CO in He) gaseous environments.

**Results:** The Ce XANES for this sample are shown in Figure 1 as a function of atmosphere. The Ce L<sub>III</sub> edge structure indicated that one third of the cerium readily changed oxidation state between 3+ and 4+ upon exposure to various mixtures of NO and CO at 673 K. Additionally, the results obtained in stoichiometric NO+CO did not depend on the sample being previously exposed to oxidizing or reducing conditions. However, structural



**Figure 1.** Ce L<sub>III</sub> edge spectra for CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> at 673 K as a function of atmosphere.



**Figure 2.** Radial structure function for Ce L<sub>III</sub> EXAFS.

parameters derived from the EXAFS analysis indicated that cerium remained in the CeO<sub>2</sub> crystal structure regardless of the gaseous environment. The similarity of the EXAFS functions among the samples in various environments can be seen in the radial structure functions of Figure 2. Apparently, supported CeO<sub>2</sub> did not transform to Ce<sub>2</sub>O<sub>3</sub> upon partial reduction, but may instead form an oxygen deficient CeO<sub>2</sub> crystallite. As reported previously, the average oxidation state of Pd was also affected by gaseous environment with an average oxidation state between 0 and 2+ for a stoichiometric mixture of NO and CO. Exposure of Pd particles to NO resulted in the formation of a chemisorbed oxygen and/or a surface oxide layer which can be completely removed by exposure to CO at 573 K. Similar to the Ce results, Pd structural parameters derived from EXAFS analysis indicated no change in crystal structure.

**Conclusions:** In situ x-ray absorption spectroscopy has shown that cerium oxide readily changes oxidation state upon exposure to various mixtures of NO and CO. However, the ceria does not appear to transform out of the CeO<sub>2</sub> crystal structure. Gas composition also affected the average oxidation state of Pd but did not affect the Pd crystal structure.

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