Determination of redox-activ Centers in CGO Materials used in DeNO\textsubscript{x}/Flue Gas Purification Processes by insitu-XANES Spectroscopy

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Electrochemical flue gas purification is a method to clean different flue gasses for e.g. nitrogen oxides (NO\textsubscript{x}) (= DeNO\textsubscript{x} process), soot and hydrocarbons. Ce\textsubscript{0.9}Pr\textsubscript{0.1}O\textsubscript{2} (CPO10) and Ce\textsubscript{0.8}Pr\textsubscript{0.2}O\textsubscript{2} (CPO20) are possible candidates which can be used to purify flue gasses, in particular diesel exhaust gasses. To optimize the degree of efficiency (e.g. by varying the composition or the reaction temperature), it is important to understand the redox mechanisms in these systems. XANES (X-ray Absorption Near Edge Structure) spectroscopy can give information about the change of the oxidation states during different exposures to Air or NO, which helps to understand the redox process and to determine the active redox centers in the tested materials. In CGO the Ce as well as the Pr cations could be involved in the observed reaction with NO gas. Therefore, insitu-Xanes measurements in different atmospheres and at different temperatures were performed to investigate the oxidation states of Ce and Pr in the CGO.

![Figure 1: Overview measurement of CGO10 at room temperature.](image)

A homemade flow cell was used for the in situ measurements. CGO/BN pellets were placed in a holder inside a glass tube with Kapton windows for the x-ray beam. The glass tube was placed inside a tubular furnace, which allowed the temperature to be controlled, and the sample could be heated up to 500 °C. The atmosphere in the glass tube could be changed between air and 1 % NO in Ar. As shown in the overview measurement of the CGO10 sample in figure 1, the Pr L\textsubscript{III} and Ce L\textsubscript{III} edges can be recorded simultaneously.

Heating from room temperature to 500 °C in air had no effect on the oxidation state of neither the Ce nor the Pr in CPO10 and CPO20. No change in the oxidation state for the Ce was observed when varying the atmosphere between air and 1 % NO in Ar at 400 °C and 500 °C (figure 2). Likewise the Pr L\textsubscript{III} edge did not shift, when changing the atmosphere at 400 °C. But at 500 °C the Pr L\textsubscript{III} edge was shifted slightly to lower energies for both CPO10 and CPO20 (figure 2). This indicates that some of the praseodymium ions were reduced in the 1 % NO in Ar gas, changing their valence from +4 to +3. Based on these results, it can be assumed that CGO is redox stable in
air up to 500 °C. In 1 % NO at 500 °C a shift at Pr L_{III} edge indicates an oxidation of the NO gas and that the Pr ion is the active redox center in this process. Cycling experiments, in which the atmosphere was varied forward and backward between the two gases, showed that the process is reversible.

![XANES spectra of Ce L_{III} and Pr L_{III} edge at 500 °C in different atmospheres](image)

Figure 2: XANES spectra of the Ce L_{III} and the Pr L_{III} edge at 500 °C in different atmospheres