



	<b>Experiment title:</b> In-situ powder diffraction studies of catalysts under realistic working conditions	<b>Experiment number:</b> 01-02-764
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**Report:**

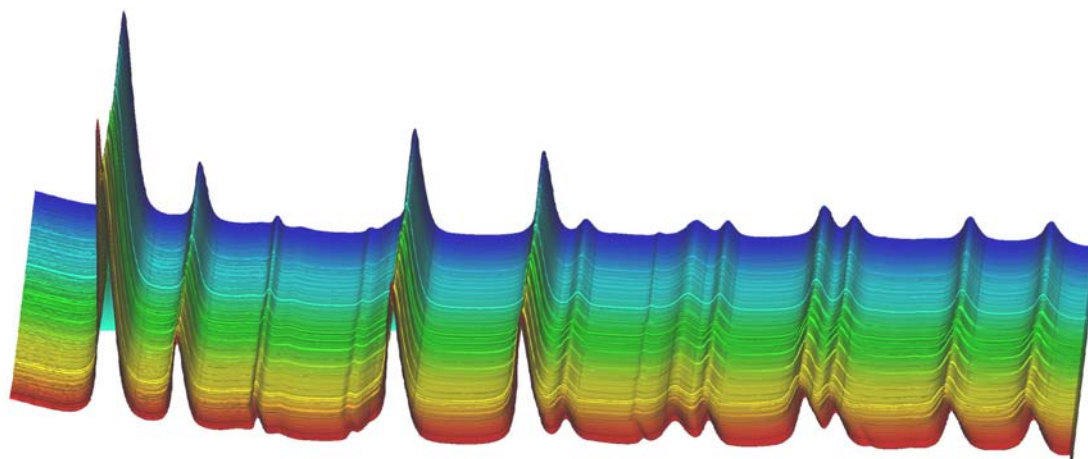
**In situ synchrotron powder diffraction study of the activation of 0.5%Au/35%CeO<sub>2</sub>/γAl<sub>2</sub>O<sub>3</sub> catalyst for anaerobic partial oxidation of methane**

The cerium oxide based material investigated in this experiment is used as low temperature (600 °C) catalyst for the anaerobic catalytic partial oxidation of methane to synthesis gas (CO+H<sub>2</sub>). The low temperature activity of the material is dependent on an activation step where the catalyst is exposed to discrete pulses of CH<sub>4</sub> followed by a corresponding number of O<sub>2</sub> pulses at 800 °C.

The goal of the present experiment was to investigate the possible structural changes connected with the activation process of the catalyst.

Formation of new phases, structural modifications of the Au and/or of the CeO<sub>2</sub> after the high temperature exposure to CH<sub>4</sub> was investigated.

The catalyst in form of powder was placed in a 0.5mm quartz capillary micro reaction cell.



**Figure 1.** 3D representation of the integrated diffraction patterns

One end of the capillary was mounted on a goniometer head in a Swagelok fitting and connected to the gas inlet from the gas mixing setup. The other end of the capillary was connected to a mass spectrometer for gas composition analysis.

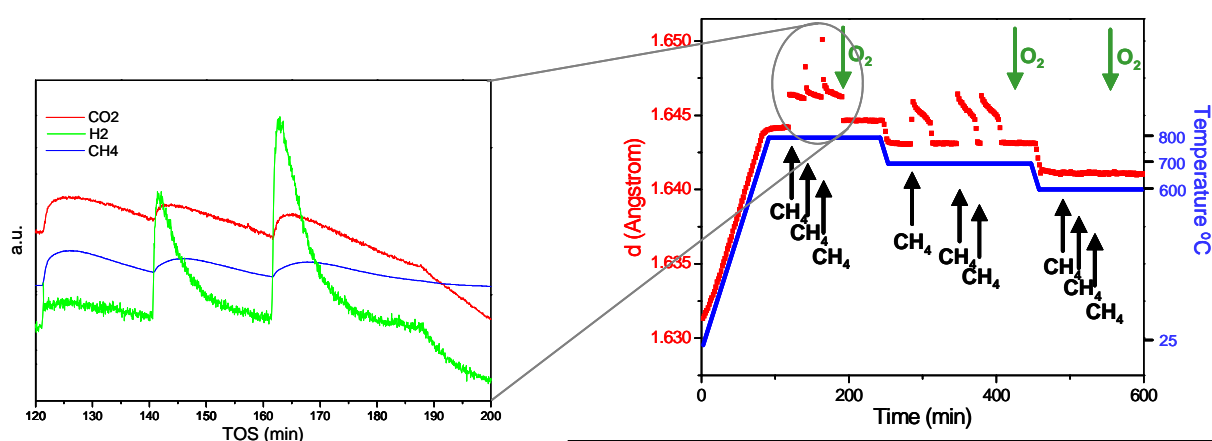
The sample was heated to 800 °C to simulate the activation step (3 discrete pulses of CH<sub>4</sub> followed by 30 minutes in O<sub>2</sub> atmosphere). Then the CH<sub>4</sub>/O<sub>2</sub> cycle was repeated at 700 °C and 600 °C. Diffractograms were recorded at intervals of 107 seconds using an imaging plate system (MAR345) with 20 seconds exposure.

No major structural changes occurred during the activation step at 800 °C or during the reaction with CH<sub>4</sub>/O<sub>2</sub> at 700 °C as shown in Fig.1.

The products of the reaction between CH<sub>4</sub> and CeO<sub>2</sub> were registered from the mass spectrometer, in fig.2. A typical pattern for 3 CH<sub>4</sub> pulses is presented. The gas flow through the capillary was not high enough to avoid back-mixing of gasses in the line connecting the capillary outlet to the MS, which generated very broad peaks.

In Figure 3 the variation in the unit cell parameter for cerium oxide (represented by the *d*-spacing of the 311 reflection) is shown. Reduction of ceria upon exposure to the CH<sub>4</sub>-pulses is observed as an increase in the unit cell volume in the experiments at 800 and 700°C. At 800°C there is a clear difference between the first and the subsequent methane pulses. At the first pulse, reduction is observed as an increase in the unit cell parameter to a constant level. At the subsequent pulses the unit cell parameter increases very fast to a high value and then decreases towards the value obtained in the first pulse. When correlating the X-ray data with the mass spectrometer data, a corresponding behaviour is observed. The first methane pulse is not associated with any increase in the hydrogen signal, whereas the subsequent two pulses give an increase in the hydrogen signal. Upon exposure to oxygen, the cerium oxide is re-oxidized.

At 600°C no change in the unit cell parameter is observed, indicating that no reaction takes place involving the bulk oxygen in cerium oxide. No reaction between CH<sub>4</sub> and the bulk oxygen of CeO<sub>2</sub> could be registered at 600 °C although the usual temperature for the reaction, as performed in our catalytic test setup, is 600 °C.



**Figure 2.** Mass Spectrometer signal for a set of three CH<sub>4</sub> pulses

**Figure 3.** Variation of the *d*-spacing for the 311 reflection of CeO<sub>2</sub> with temperature and atmosphere