In situ XAS and XRD investigations during reactivation of ceria based NO_x storage reduction catalysts

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Lean-burn engines with direct fuel injection have been recently introduced in car industry to decrease fuel consumption [1]. However, the well-known three-way catalyst cannot be used for efficient NO_x-removal due to an excess of air. Therefore new catalyst concepts for NO_x-removal have been developed. Among them, the NO_x-storage-reduction (NSR) catalyst system is well established [2]. Under operating conditions some deterioration is usually observed because of poisoning by sulfur and thermal deterioration leading to formation of mixed oxides such as aluminates, cerates, and zirconates through reactions of the NO_x storage component material with the support material or other washcoat compounds [3]. Recently, we have found that the $BaCeO_3$ formed in a thermally aged Pt-Ba-CeO_2 catalyst can be decomposed under certain process conditions, e.g. in the presence of NO_2, H_2O and CO_2 [4]. In order to further understand this reactivation process, both information on amorphous (short-range order) and crystalline (long range order) species are required. A combination of XAS and XRD is therefore required, which was built at beamline X1. Here we describe briefly the experimental setup used and report on some of the data recorded.

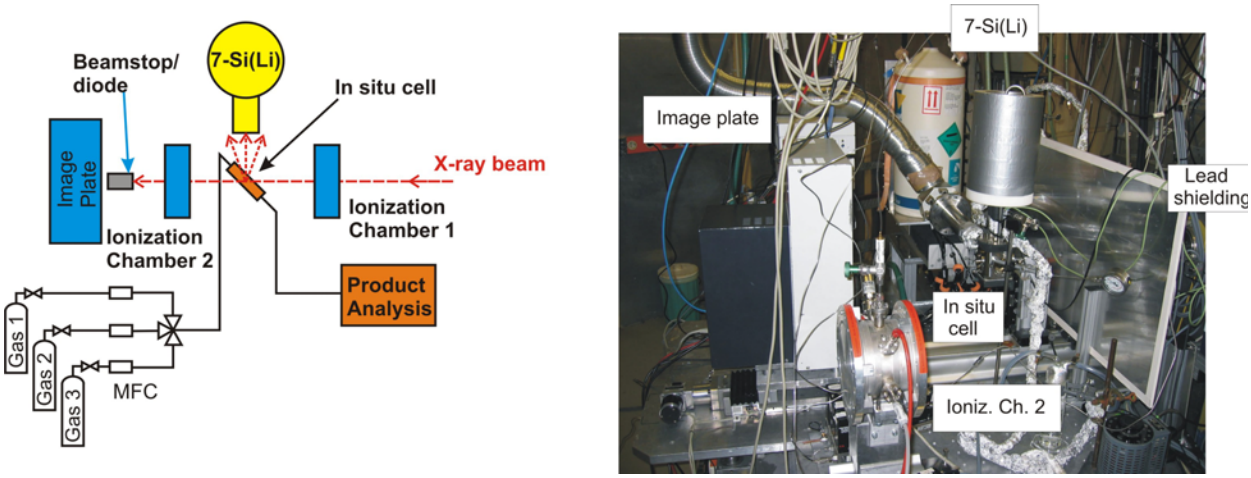

Fig. 1: Experimental setup for combined EXAFS/ XRD measurements.

The combination of XAS and XRD is not new and has been applied previously at beamline X1 [5,6]. The setup is based on the system, assembled by J. Wienold [6]. In Fig. 1, the experimental setup is shown schematically, it had has been built up in 2005 and was improved during a beamtime in 2006. The XRD patterns were taken using a MAR345 area detector (impage plate). As *in situ* cell either a capiallary or, as depicted here a heat-/colleable cell with Kapton-windows was used. In this case also fluorescence EXAFS data could be recorded by tilting the sample holder to a 45° position and using a 7-element Si(Li)-detector (Gresham). Transmission EXAFS data were taken in two different ways: Either by installing a second ionization chamber between the sample and the beamstop or by using a pin-diode with appropriate shielding in front of the beamstop. The latter arrangement allowed us that both EXAFS and XRD measurements could be taken in parallel. Nevertheless, it has to be noted that the image plate had to be read out after illumination so that placing the ionization chamber into the beam was not time limiting.

Figure 2 shows spectra taken on an aged 0.75%Pt-16%Ba-CeO_2 sample that contained significant amounts of $BaCeO_3$. The spectrum at the Pt L_3-edge was taken in fluorescence mode, at the Ba K-edge the pin diode was applied and the XRD patterns were taken below the Ba K-edge at 0.332 Å (37.4 keV).

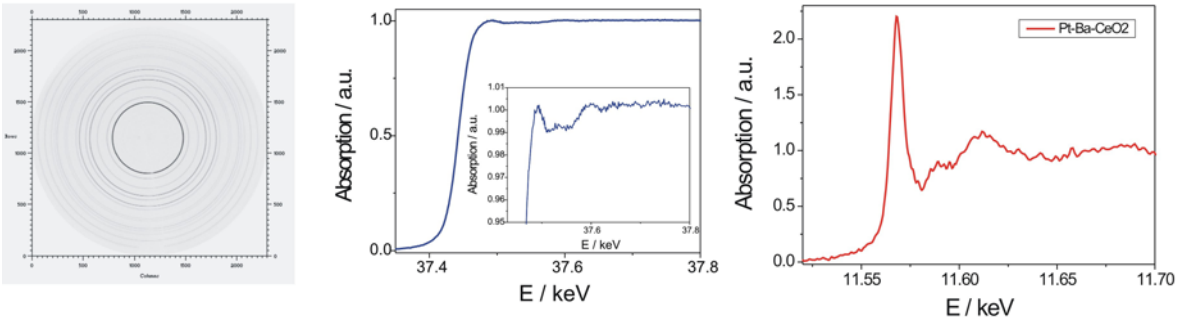

Fig. 2: XRD patterns, transmission EXAFS spectrum at the Ba K-edge and fluorescence EXAFS spectrum at the Pt L_3-edge of 0.75%Pt-16%Ba-CeO_2 (calcined for 10 h at 1000 °C).

The XRD patterns were extracted using the software FIT2D. The distance to the detector and the angle were calibrated using an LaB_6-standard. XRD-patterns taken during the decomposition of $BaCeO_3$ in H_2O/NO_2 atmosphere are shown in Fig. 3. The data support our previous observation that $BaCeO_3$ can be decomposed and it is thus an interesting option to reactivate aged NSR-catalysts. Obviously, the transformation occurs during a time interval of less than 2 h between 1:40 and 3:20 h. $BaCeO_3$ is directly transformed to $Ba(NO_3)_2$. In parallel *in situ* EXAFS data were recorded, which need to be further substantiated, and indicate that a transition of X-ray amorphous phases may occur first.

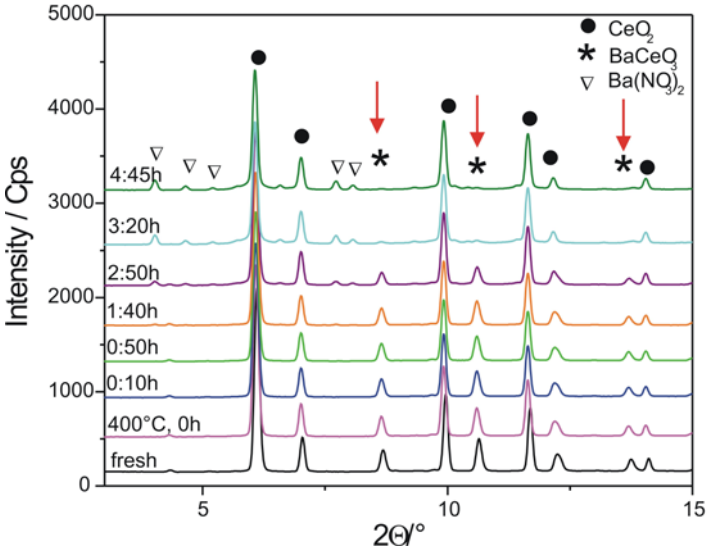

Fig. 3: *In situ* XRD to monitor the progress of $BaCeO_3$ transformation in 0.5%NO_2 -1.5%H_2O-10%O_2/He.

The X-ray patterns could be taken within a few minutes, but EXAFS scans required at least 30 min. For this purpose the setup seems to be appropriate. However, for dynamic structural changes with good time resolution (in the minute scale) further improvements are needed, since the "read-out time" and the "erase time" are limiting. Moreover, the image plate can be advantageously used for hard X-rays (< 1.2 Å). Another advantage of the use of an area detector is that the sample only needs to be aligned to the beam but not to the detector. Therefore the use of a pin diode in front of the beamstop is required to accelerate data acquisition. In view of a long-term strategy to build up combined EXAFS/XRD experiments at HASYLAB, either the use of a CCD detector or of an INEL- /microstrip-detector should be targeted.

We thank Carsten Baehtz, Jens Homeyer, Matthias Herrmann, and Julia Wienold for their support.

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