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	Experiment title: Time-resolved study of the structural dynamics of the La-Co-Cu-O oxide using high energy X-ray diffraction	**Experiment number**: MA-3131
Beamline: ID15	**Date of experiment**: from: 1.12.2016 to: 05.12.2016	**Date of report**: 3.3.2017 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. Marco Di Michiel	

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Report:

Set up of the home equipment (gas manifold, cell, mass spectrometer, gas lines, switch valves; Figure 1) and alignment of the beamline lasted 1 day. The experimental setup is esentially identical to that used previously in various beamtimes (for example see beamtime MA-3145 and report).

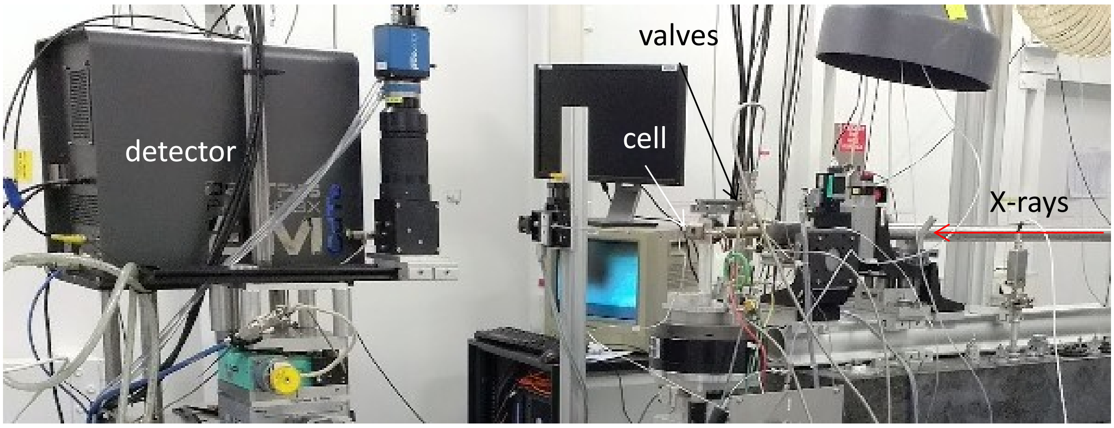

Figure 1. Experimental setup at ID15. The new Pilatus detector is on the left hand side.

The aim of the experiment was to analyze potential three-way catalysts (TWC) based on perovskite-type oxides substituted with Cu under the pulsed experimental conditions that are typical of their operation. The possibile structural changes occurring during reaction were followed using hihg energy X-ray diffraction (HEXRD). We have used the new Pilatus detector available at ID15 that allowed to follow in a time-resolved manner these structural changes over short pulses of reactants (20-30 s). HEXRD data where collected continuously (0.5 s/pattern; Q= 0-12 Å^{-1}; 74.9 keV) while the samples were heated to 450°C and then cooled

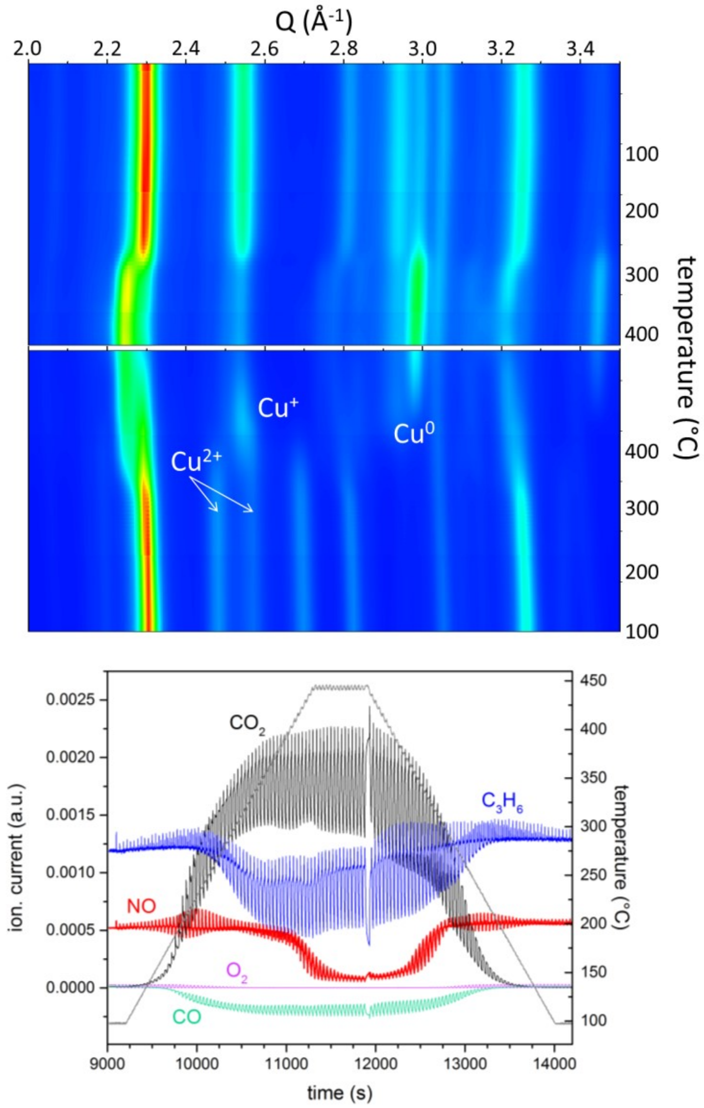

Figure 2. 2D visualization of the operando time-resolved HEXRD patterns obtained while heating/cooling CuO/$La_{0.5}Sr_{0.5}CoO_3$ in 0.7 vol% CO, 0.15 vol% NO, 0.16 vol% C_3H_6 and oscillating O_2 conventration (1-0.7 vol%) between 100 and 450°C. The bottom panle is the representation of the reactants and product gas evolution measured using a MS.

in the reaction feed consisting of 0.7 vol% CO, 0.15 vol% NO, 0.16 vol% C_3H_6 and oscillating O_2 concentration values (1-0.7 vol%, 30 s) after treatment at 400°C in 5 vol% O_2 for 30 min. A dedicated homemade flow reactor cell equipped with two graphite windows and allowing fast switching was used throughout. The exhaust of the cell was monitored online using a mass spectrometer (MS).

XRD shows that 20 wt% $Cu^{II}O/La_{0.5}Sr_{0.5}CoO_3$ initially comprises of $Cu^{II}O$ deposited on $La_{0.5}Sr_{0.5}CoO_3$. In the temperature programmed ramp in the continuous feed simulating stoichiometric conditions no substantial NO reduction activity was observed. Only CO could be converted to some extent. The operando XRD data did not show any substantial structural change under these conditions. In marked contrast, the temperature ramp under oscillating feed simulatinge short shifts to rich conditions exhibited variations of both catalytic activity and catalyst structure (Figure 2). Beside full CO conversion, the mean NO conversion attained close to 90% in the heating segment. In the cooling segment, NO reduction extended down to ca. 300°C.

The hysteresis of NO conversion was provided by structural changes. XRD demonstrated that the doublet of $Cu^{II}O$ disappeared in favor of $Cu^{I}O$ above 340°C, which further reduced to metallic Cu at ca. 440°C that persisted in the plateau of maximum NO conversion. In the cooling segment, where NO reduction activity persisted for longer time, Cu^0 oxidized to $Cu^{I}O$ but reoxidation to $Cu^{II}O$ was not observed until 100°C. During the transformation of the Cu component, $La_{0.5}Sr_{0.5}CoO_3$ also displayed reduction. First, the intense reflection at 2.3 $Å^{-1}$ shifted to lower angles due to loss of O and lattice expansion. At ca. 350°C the perovskite phase changed into a parent oxygen deficient brownmillerite phase simultaneous to the $Cu^{II}O \rightarrow Cu^{I}O$ transformation. The $La_{0.5}Sr_{0.5}CoO_3$ phase was restored in the cooling segment below 300°C.

An identical experiment on a 6 wt% CuO/La_2O_3 catalyst showed no $Cu^{II}O$ reduction and poor activity suggesting that the combination of $Cu^{II}O$ and the perovskite is essential for the observed changes. Moreover, this also indicates that the reversible reduction of the perovskite phase is needed to induce catalytic activity. Additionally, an experiment on $Cu^{II}O/La_{0.5}Sr_{0.5}CoO_3$ in absence of C_3H_6 clearly demonstrated that C_3H_6 reforming to produce H_2 is the reaction pathway responsible for NO reduction under the oscillating feed.

Extensive data evaluation of both HEXRD and MS datasets is on-going. Dr. M. Di Michiel and the team of ID15 are greatly acknowledged for their support during the allocated beamtime.