

# Monitoring of Fast Transformations in Solid-state Chemistry and Heterogeneous Catalysis by QEXAFS in the Second Scale

B. Griesebock,<sup>1</sup> D. Lützenkirchen-Hecht,<sup>1</sup> J.-D. Grunwaldt,<sup>2</sup> M. Richwin,<sup>1</sup> A. Baiker,<sup>2</sup> R. Frahm<sup>1</sup>

<sup>1</sup>Institut für Materialwissenschaften und Fachbereich Physik, Bergische Universität Wuppertal, Wuppertal, Germany

<sup>2</sup>Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, Zürich, Switzerland

## Introduction

A number of solid-solid transformations, such as decomposition reactions or the reduction/oxidation of heterogeneous catalysts, occur relatively fast (i.e., within less than a minute). Time-resolved investigations are thus important in order to gain insight into the mechanisms of such solid-solid transformations (e.g., during changes of temperature or gas atmosphere). Since intermediate phases are usually present in an amorphous form, x-ray anomalous near-edge structure (XANES) or extended x-ray anomalous fine structure (EXAFS) experiments seem to be appropriate methods. In a previous *in situ* study [1], x-ray absorption near-edge spectra were taken in the subsecond scale by using the piezo-quick scanning EXAFS (piezo-QEXAFS) technique. In many cases, full EXAFS spectra are needed for a proper interpretation. Hence, the monochromator needs to be moved over a larger angular range. For this purpose, we developed new crystal-driving mechanics that make use of a tilt table that is moved by an excenter disc [2]. The description of this new monochromator will be the subject of a forthcoming publication [3]. Here we report on time-resolved investigations of decomposition reactions of cobalt oxalate at the Co K edge in different gas atmospheres.

## Methods and Materials

The polychromatic radiation from the x-ray source was monochromatized by using a Si(111) channel-cut crystal, that was indirectly cooled via a hollow copper block and liquid nitrogen in a closed cycle [2]. The cooler with the crystal was mounted on a tilt table with two solid-state hinges that was driven by an excenter disc. This excenter disc is directly mounted on the shaft of a dc motor, the turning speed of which is controlled by a computer and can be varied from about 0.1 to 40 Hz [2, 3]. Different excenter discs with different asymmetries enable the angular range of the tilt table to be modified from about 0.05° to about 1.52°. When a Si(111) crystal is used in the vicinity of, for example, the Cu K edge (8980 eV), these values correspond to an available energy range for the EXAFS experiments from about 100 eV to more than 2500 eV. The EXAFS data were obtained in transmission geometry. N<sub>2</sub>-filled ionization chambers were used as detectors for the intensity of the incoming and the transmitted radiation. A slit system in front of the first ionization chamber was used for the horizontal and

vertical definition of the beam, which was typically (0.3 mm)<sup>2</sup>. The current signals from the ionization chambers were converted and amplified by Keithley 428 current-to-voltage amplifiers. Their output signals were directly sampled by a fast analog-to-digital (A/D) converter (four channels with up to 200 kHz simultaneously) and stored on a personal computer. Further details of this setup are given elsewhere [2, 3].

The *in situ* cell for the experiments (design similar to that used in Refs. 4 and 5) consists of a quartz glass capillary tube, with a 0.5-mm diameter and 10- $\mu$ m wall thickness, that was loaded with the samples of interest (i.e., Co-oxalate-dihydrate in the present case, diluted with alumina). Different premixed gases from a gas manifold could pass through the capillary reactor cell with a typical gas flow of about 5 mL/min. Heating of the *in situ* cell microreactor up to 600°C was performed by passing a defined flow of hot N<sub>2</sub> gas beside the capillary encapsulated in a shield of Kapton<sup>®</sup> foil (compare with description in Ref. 4).

## Results and Discussion

Because of their relatively low decomposition temperatures, transition metal oxalates are of high interest as, for example, precursors for the preparation of fine metal or oxide powders of the respective element, as well as for the synthesis of catalyst materials. Furthermore, their thermal decomposition has model character for solid-solid transformations in general [6, 7]. Co-oxalate is of special interest because of its use in preparing catalysts for the Fischer-Tropsch synthesis. We investigated the thermal decomposition of Co-oxalate-dihydrate (CoC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) in different gas mixtures *in situ* at the Co K edge (7709 eV). Figure 1a shows the room-temperature spectrum of a Co-oxalate-dihydrate sample and a Co-metal reference, simultaneously measured within about 250 ms (2-Hz oscillation frequency, 10-kHz sampling rate). In addition, the different EXAFS structures above the edge (in particular, the small edge shift between both materials) are evident — one of the big advantages of the setup used. Because of the use of a reference foil, even small edge shifts were monitored very sensitively. Figure 1b depicts EXAFS spectra measured *in situ* in the vicinity of the Co K edge during the thermal decomposition of Co-oxalate-dihydrate in a mixture of Ar + 4% H<sub>2</sub> in the course of a temperature ramp (10 K/min) from 35°C to

about 530°C. More than 9000 spectra were measured for each single experiment.

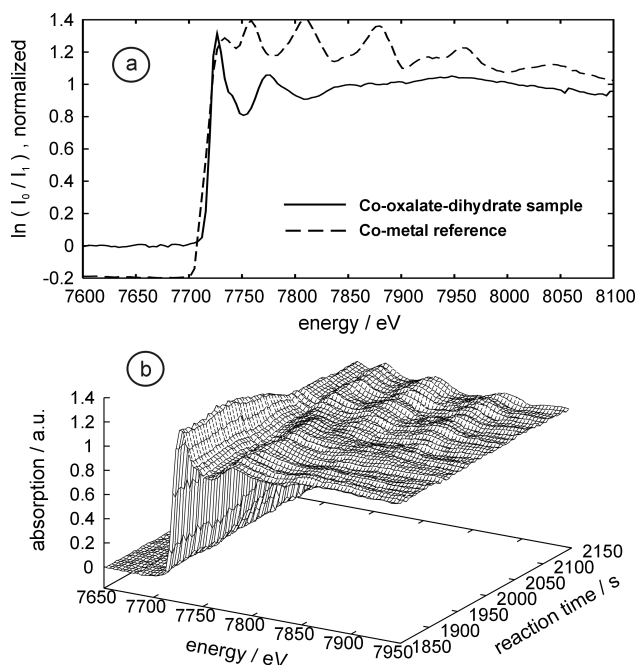
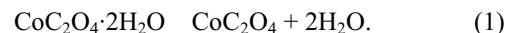


FIG. 1. (a) Co K-edge EXAFS spectrum of  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  measured *in situ* within 250 ms before the initiation of a decomposition reaction together with the Co-metal reference measured simultaneously. (b) *In situ* Co K-edge absorption spectra measured during the thermal decomposition of  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{Ar} + 4\% \text{H}_2$ . Each spectrum was measured within 250 ms. The displayed spectra belong to the temperature region between about 340 and 400°C.

Obviously, both the structures at the edge and above the edge change dramatically at a reaction time of around 2000 seconds: while the white line intensity at the edge decreases significantly, the absorption maximum at about 7770 eV shifts to a lower value of about 7750 eV, and further structures appear at around 7900 eV. In addition to making a determination of accurate values for the edge energy position as a function of the reaction time (and temperature), a principal component analysis [8] was performed by using the software package R [9] in order to identify the numbers and types of the contributing phases. We found only two contributing principal components during decomposition between 330 and 395°C, which could be identified as the Co-oxalate and Co-metal (i.e., the Co(II)oxalate is directly transformed to metallic Co). More detailed results are compiled in Fig. 2. Between about 150 and 175°C, a slight decrease of the absorption edge position to smaller energies by about 0.4 eV was observed. In agreement with previously published data [7], this decrease can be understood in terms of the

dehydration of the oxalate-hydrate according to the reaction



The small edge shift indicates that the oxalate-hydrate has a slightly increased valency compared to pure  $\text{CoC}_2\text{O}_4$ . In addition, the z-score of Co metal, which is related to the Co-metal concentration in the sample, shows a slight increase accordingly. It should be noted that the z-score is, in general, not simply proportional to the concentration; the latter has to be determined from the z-score by means of a target transformation [8, 10-12]. However, this is a nontrivial task because of the large number of spectra involved in the current experiment. Nevertheless, by comparison with the z-score of the reference compounds ( $\text{CoC}_2\text{O}_4$  and Co metal), we can conclude that a negative z-score of the metal corresponds to a high concentration of  $\text{CoC}_2\text{O}_4$  and that positive values belong to a high metal concentration [2].

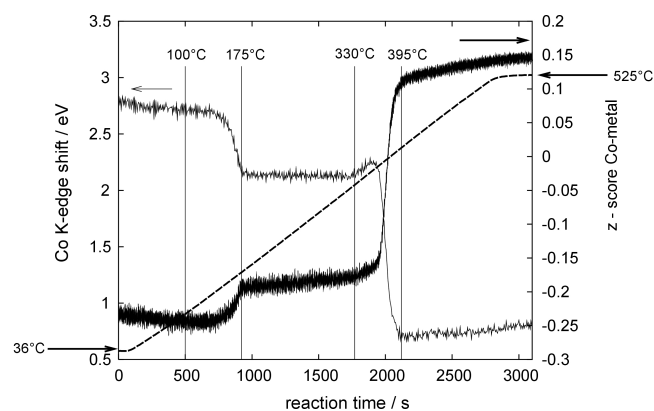
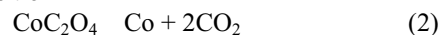


FIG. 2. EXAFS data analysis for the *in situ* decomposition reaction of Co-oxalate-dihydrate in  $\text{Ar} + 4\% \text{H}_2$ . The dashed line shows the temperature as a function of time. The regular line belongs to the observed edge shift of the Co K edge during the experiment (left ordinate), and the bold line corresponds to the principal component of Co metal (z-score, right ordinate). Negative and positive values of the z-score belong to small and high Co-metal concentrations, respectively.

A further increase of the temperature to about 340°C results in a steep decrease of the Co K-edge position by about 2.5 eV within a time frame of less than 100 seconds. At the same time, the Co-metal z-score increases from about -0.2 to 0.15 in parallel. Thus, it is very likely that the decomposition



occurs in this temperature interval. Apart from this spontaneous decomposition reaction, hydrogen can also directly reduce the Co(II). For comparison, the z-score of metallic Co is 0.16; therefore, we can conclude that the decomposition of the oxalate results in more than just Co metal (i.e., a small fraction Co-O species remains within the sample).

For comparison, decomposition experiments were also performed in pure Ar atmospheres [2]. These experiments show that course of the reaction is sensitive to the composition of the gas atmosphere, in agreement with recent studies [7]. Our experiments show that the separation of the crystal water according to Eq. (1) occurs for a broader temperature interval compared with the interval for experiments in an Ar hydrogen-containing atmosphere (i.e., it starts at a lower temperature of about 100°C and is finished at a slightly elevated temperature of about 195°C, as can be seen in Fig. 3).

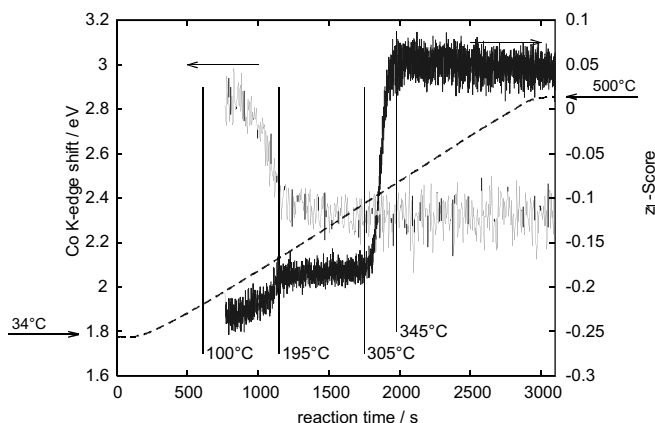


FIG. 3. Analysis of the *in situ* EXAFS data obtained during the decomposition of Co-oxalate-dihydrate in pure Ar. The dashed line shows the temperature as a function of time. The regular line belongs to the observed edge shift of the Co K edge during the experiment (left ordinate), and the bold line corresponds to the principal component of Co metal (z-score, right ordinate).

The decomposition of the formed oxalate starts at about 300°C and is finished at about 345°C, as evidenced by the temperature dependency of both the Co K-edge position and the z-score. Thus also the decomposition of the oxalate occurs at a lower temperature in a pure Ar atmosphere than in the H<sub>2</sub>-containing Ar atmosphere. However, a closer inspection shows that the shift in the Co K-edge position as well as the change in the z-score are smaller in pure Ar than in the decomposition experiment in Ar + H<sub>2</sub>. While the edge shift observed for the decomposition in Ar + H<sub>2</sub> was about 2 eV, it was only about 0.5 eV in pure Ar. The corresponding changes for the z-score were about 0.3 and 0.4 for the decomposition without and with H<sub>2</sub>, respectively. Both observations suggest that the decomposition was not complete in pure Ar. This finding agrees quantitatively with the results of the principal component analysis, which suggest the presence of three contributing species: CoC<sub>2</sub>O<sub>4</sub>, CoO, and metallic Co [2]. Our experiments suggest that CoO and

Co metal exist in equal amounts, as also observed by Malecka et al. [7]. In contrast, Maciejewski et al. found only 13% of CoO in samples that were subjected to a decomposition in pure He [7]. These differences can be explained by the fact that the residual oxygen in the Ar may play an important role in oxidizing Co during the decomposition process. The results indicate that not all Co oxalate is completely decomposed according to Eq. (2) and that some Co oxide forms directly. The application of a target transformation is very desirable, especially for this experiment, to determine accurate values for the respective concentrations; see, for example, Refs. 11 and 12.

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