Selective aerobic oxidation of alcohols to the corresponding carbonyl compounds and carboxylic acids over hydroxyapatite-based materials is an attractive approach [1,2]. Two classes of these catalysts can be distinguished: supported metals such as Pd, Ru, or Au, and “ion-exchanged” materials, where transition metal ions are incorporated into the channel-like structure. Here we concentrated on the ion-exchanged Ru-hydroxyapatite (RuHAp), which were additionally modified by cobalt. Both the RuHAp and the Co-promoted RuHAp catalyst showed good performance (in particular high selectivity) in the selective oxidation of alcohols to the corresponding carbonyl compounds [2]. The structure of the active Ru-species is still under discussion, e.g. active RuCl$_2^+$ [3] and Ru$^{3+}$ hydroxospecies [2] have been speculated to be the active species. Since the material is X-ray amorphous, X-ray absorption spectroscopy is one of the few methods that can provide deeper insight into the structure and was thus applied in this study.

The studies were performed at beamline X1 and the oxidation of benzyl alcohol to benzaldehyde in toluene was chosen as model reaction over 0.5%Co-3.5%Ru-hydroxyapatite. The reaction mixture and pure toluene were stored in three glass bubble tanks, which allowed deoxygenation with Ar or saturation with oxygen. The liquids could be transferred by a pump (ISMATEC, REGLO 100) through the continuous-flow in situ reaction cell and then to a collector vessel (more details on the in situ setup can be found in refs. [4,5]). The experiments were performed in transmission geometry using a Si(311) double crystal for monochromatization of the beam at the Ru K-edge. Under stationary conditions EXAFS spectra were taken around the Ru K-edge in the step scanning mode between 21900 and 22800 eV. QEXAFS scans were recorded between 22100 and 22250 eV (Ru K-edge, typically 0.18s/eV). The raw data were energy-calibrated (RuCl$_3$ at 22120 eV), background corrected, and normalized using the WINXAS 3.0 software [6]. Fourier transformation for EXAFS data was applied to the k-weighted functions in the interval k = 3 – 13 Å$^{-1}$. Data fitting was performed in R-space using theoretical backscattering phases and amplitudes calculated with the ab initio multiple scattering code FEFF6.0 [7].

At first, ex situ XANES and EXAFS spectra were recorded to clarify the nature of the active Ru species (Fig. 1). XANES spectra of different Ru-exchanged catalysts were very similar. Some variation occurred compared to RuO$_2$ and Ru$_2$O$_3$/Al$_2$O$_3$, probably due to a different symmetry and thus different multiple scattering paths. More different are the Fourier transformed spectra of the Ru- and CoRu-hydroxyapatite samples compared to reference samples (RuCl$_3$, RuO$_2$ and Ru$_2$O$_3$/Al$_2$O$_3$) as well as model samples calculated by the FEFF code (Fig. 1). Obviously, no Ru-Ru contribution above 3 Å is observed, whereas Ru neighbours are clearly visible in RuO$_2$. Also Ru$_2$O$_3$/Al$_2$O$_3$ and Ru-chloride show some Ru-Ru contribution. Hence Ru seems to be well-dispersed on hydroxyapatite. This is also supported by fitting of the data. Scattering events occurring between 1.5 and 2.1 Å can be attributed to oxygen nearest neighbours. Only two oxygen nearest neighbours were fitted.

**Fig. 1:** Fourier transformed EXAFS data (k$^{-1}$-weighted χ(k)-function, 3 – 13 Å$^{-1}$) of RuO$_2$/Al$_2$O$_3$, RuO$_2$, RuCoHAp, and RuCl$_3$, and the calculated curve of a theoretical RuHAp structure (assuming a simple replacement of a fraction of Ca$^{2+}$ of HAp; cf. ref. [8]).
Note, however, that several species may be present on the surface, including Ru$^{3+}$ species bound to phosphate, calcium, and another Ru$^{3+}$ via oxygen nearest neighbours. The comparison to a model spectrum of Ru$^{2+}$ placed on a Ca$^{2+}$ site in calcium hydroxyapatite clearly showed that this situation is not found since Ru$^{3+}$ is much smaller than Ca$^{2+}$. In all cases, oxygen contributions at 1.88 – 1.90 Å and 1.99 – 2.01 Å were found with a higher coordination number for the oxygen backscattering at higher R-values. The first shell can be attributed to Ru-OH species while the other one can be connected to Ru-O-X (X=P, Ru, Ca) species. Note that in the Co-doped samples the coordination number of the oxygen shell at higher distance was higher (details, see ref. [8]). In no case Ru-Cl-species were found in the fits as reported previously by Yamaguchi et al. [3].

An important aspect is the structure of the catalyst under reaction conditions. Hence, we treated the catalyst in a plug-flow reactor first in toluene at 80 °C, added a toluenic benzyl alcohol solution (Ar-saturated) at 80 °C and finally changed to oxygen saturated benzyl alcohol solution. The changes observed in the XANES and EXAFS spectra are shown in Fig. 2. Minor changes were observed while treating the catalyst in toluene. However, continuous structural changes were found during the addition of benzyl alcohol. In contrast to Pd-based catalysts [4,5], the ruthenium species were not reduced to Ru$^0$ by benzyl alcohol under reducing conditions. However, significant changes of the near-edge structure are observed, that are maintained, even if the catalyst is subjected to oxygen-saturated benzyl alcohol in toluene. In the EXAFS spectra, the decrease of the shoulder at lower R-values indicates that the shorter Ru-O bond is exchanged by a longer Ru-O bond, e.g. by formation of an alkoxy species. In the presence of air, 9.0% conversion of benzyl alcohol was achieved after 70 min stabilization period and benzoaldehyde was the only product detected.

The study shows that the active site in RuHAp catalysts is probably a ruthenium hydroxo species and the in situ XAS study indicates the formation of a Ru-alcoholate species, which may undergo a β-hydride elimination to produce the carbonyl compound. This speculation is further supported by a kinetic analysis performed in our laboratory (cf. ref. [8]).

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References