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EXAFS study of highly dispersed Ru-oxide in Mo-oxide based catalyst matrices

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Ruthenium as heterogeneous catalyst for oxidation reactions has attracted much attention in the past. Namely the oxidation of CO on Ru and or Ru-oxide surfaces was subject of intense studies and the behaviour of the system often was taken as example for the so called pressure gap, as the latter seemed to be overcome in this case. The nature of the "active phase" on the surface of a bulky Ru metal was found in UHV surface sensitive studies to be RuO_2, formed under reaction conditions. However, the catalytic mechanism for the CO oxidation is still subject of debate and last results rather suggest, the existence of bulk deviating surface layers or the coexistence of different phases may be decisive for the outstanding activity of RuOx [1,2].

Mo based mixed oxide materials enriched by highly dispersed Ru-oxide were prepared. As precursor material the Ru(III) salts of hetero-poly-acids (HPA) was prepared, taking into account as benefit the limited thermal stability of HPA salts formed with small cations [3,4]. Such materials decompose at rather moderate temperature to generate corresponding oxide phases. In the present work we started our investigation with the Ru(III) salt of [PMo]. At around 423 K this compound transformed into ortho-MoO_3 (in air or in inert atmosphere as well) as the lone phase detectable by XRD. The Ru (8.3 atom % relative to Mo) remained completely dispersed since no Ru-containing phases or crystallites could be found by SEM/EDX nor XRD. Furthermore, this Ru-HPA can be added to establish Mo/V/Nb/Te catalyst precursors prior to calcinations procedures to generate the final catalyst containing the highly dispersed Ru-oxide. The formation of XRD amorphous nano-crystallized Ru and RuO_x-phases was ruled out probing the short range order applying Ru-K-edge EXAFS (extended X-ray absorption spectroscopy).

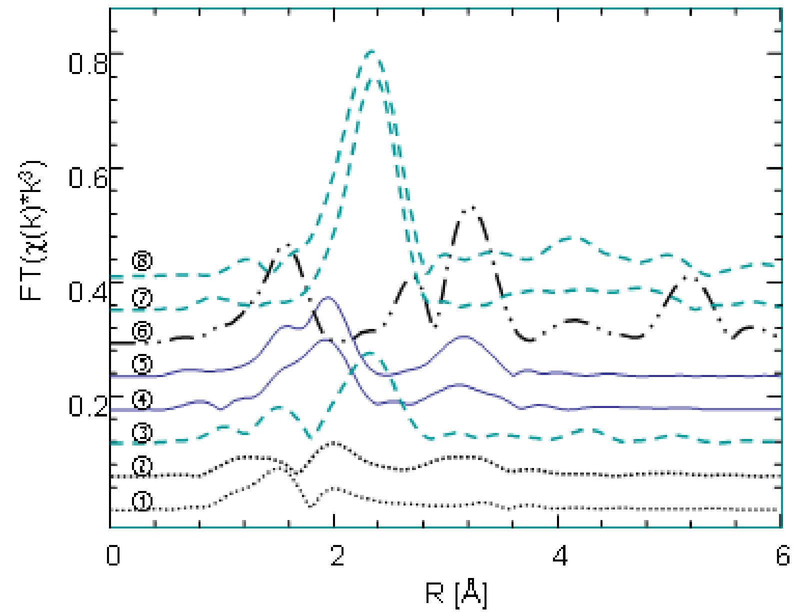

Figure 1) Fourier transformed χ(k)*k3 of the samples and references (Ru K-edge). ① 'Ru-HPA' decomposed in helium. ② 'Ru-HPA' decomposed in O_2. ③ 'Ru-HPA' on aerosil, decomposed in helium. ④ 'Ru-HPA' ⑤ $RuCl_3$ ⑥ RuO_2 ⑦ 'Ru-HPA on a Mo/V/Nb/Te catalyst precursor ⑧ Ru-foil

For the XAS (X-ray absorption spectroscopy) measurements the weight of the samples were adjusted to a μ_{td} of 2.6 mixed with polyethylene, grind and pressed in to pellets. The measurements were carried out at the Ru and Mo K-edge at the beam line X1 at HASYLAB using a Si (311) crystal pair. Inhibition of higher harmonics was performed by detuning of the first crystal and stabilization via a piezo crystal with feedback loop. An optical encoder (Heidenhain) at the goniometer axis of the monochromator provides a precise measurement of the energy. Fillings of the ionization chambers were adjusted to 10% for the first and 50% for the second and third. All measurements were carried out at room temperature and in air. As references $RuCl_3$ (ChemPur, precursor in the Ru-HPA preparation) RuO_2 and a Ru-foil were measured additionally.

Data analysis was performed with the software WinXAS 3.1 [5]. For energy calibration, the first inflection point on the edge of reference materials were set to tabulated values. Subtraction of the underground was done by fits of a polynomial of 1. order for the pre edge background and a 2. order polynomial for the post edge background. The spectra were normalized by the edge jump. Adjustments of μ_0 were carried out with spline functions. Adjustments of simulations to the original data were carried out using paths calculated with FEFF7 [6] on the basis of single crystal data.

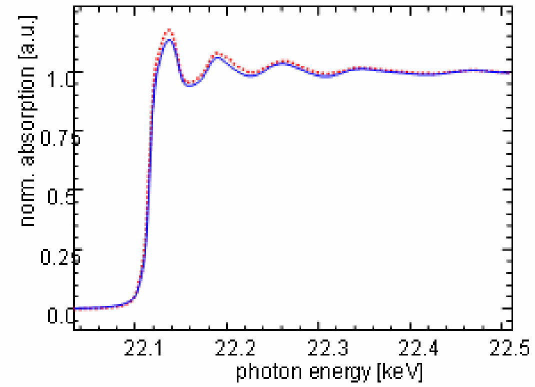

Figure 2) XANES of $RuCl_3$ (□) and ‚Ru-HPA' (—) at the Ru K-edge.

In figure 1 the Fourier transformed $\chi(k)*k^3$ of the samples together with the references are shown. From a qualitative look on the spectra and further analysis the following can be concluded. The two decomposition products of the 'Ru(III)-HPA' in air and in helium (number 1 and 2) show very small amplitudes and broad shells, indicating highly amorphous ruthenium species. The overall features of the spectra couldn't be compared to any of the references and are yet not further characterized. The decomposition product of the 'Ru(III)-HPA' on a Mo/V/Nb/Te catalyst precursor (number 7) can be directly compared to the foil (number 8). The ruthenium metal character is confirmed with a fit of the FEFF7 ruthenium metal simulation (after ICSD 76155) to the experimental data. Also the decomposition product of the 'Ru(III)-HPA' mixed with aerosil (number 3) shows metallic character together with a shell around 1.5 Å (not phase corrected!) indicating a partial oxidised state. Furthermore the shell around 2.3 Å (build from Ru-Ru paths) shows a smaller amplitude than those from the foil and the 'Ru(III)-HPA' on a Mo/V/Nb/Te catalyst precursor, and thus this sample shows a higher disorder of the metal part (σ^2(Ru-HPA on aerosil) = 0.01056 Å^2; σ^2(Ru-foil) = 0.004519 Å^2). A comparison of the 'Ru-HPA' spectra and the $RuCl_3$ reference reveals good accordance. This is even clearer in a comparison of the XANES as shown in figure 2. The identification of the $RuCl_3$ phase in the assumed 'Ru-HPA' is confirmed by a fit of a FEFF7 simulation (ICSD 20717) to the experimental data. This result is in contrast to the X-ray diffraction pattern of this sample which shows no $RuCl_3$ phase. Following this it can be assumed that the $RuCl_3$ is x-ray amorphous. The Mo K-edge spectra of the assumed 'Ru-HPA' confirms a Keggin structure for the Mo-O coordination.

Nevertheless that the presented results show that the assumed 'Ru-HPA' is a mixture of $RuCl_3$ and a heteropolyacid without or at least a low content of Ruthenium on a cation place in the HPA structure, they confirm the desired preparation effect. It is possible with the tested precursors and decomposition routes to produce (highly) amorphous dispersed types of ruthenium species on a molybdenum oxide matrix.

References

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