Investigation of different catalysts for partial oxidation with X-ray absorption spectroscopy

J. Wienold[1], O. Timpe, D. Niemeyer

Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany
[1]HASYLAB at DESY, Notkestr. 85,22607 Hamburg, Germany

Abstract A series of oxides in the systems Mo/O, Mo/Cr/O, Mo/Mn/O and Mo/Fe/O, prepared from acidic aqueous solutions, were tested for their catalytic potential in the partial oxidation of propene and propan and characterized with various techniques. The process of preparation and the structural characterizations indicate the importance of the structural arrangements even on the level of the precursor materials.

Introduction The oxidation of saturated hydrocarbons, as ethane or propane, is very attractive due to the low costs compared to the related olefins. On the other hand, the reactivity is low and up to now, most processes for direct conversion of alkenes suffer from poor yields. Heterogeneous catalysts used for the partial oxidation of hydrocarbons predominantly consist of molybdenum oxides. In general these materials are mixed oxides, with Molybdenum being the major component [1].

Experimental The samples were prepared starting from a solution of the (metastable) free acid H_2MoO_4. To this solution, adequate amounts of the nitrates of Cr(III), Fe(III) or Mn(II), dissolved in nitric acid, were added. The Iron provokes spontaneous precipitation so far as molybdenum is still in

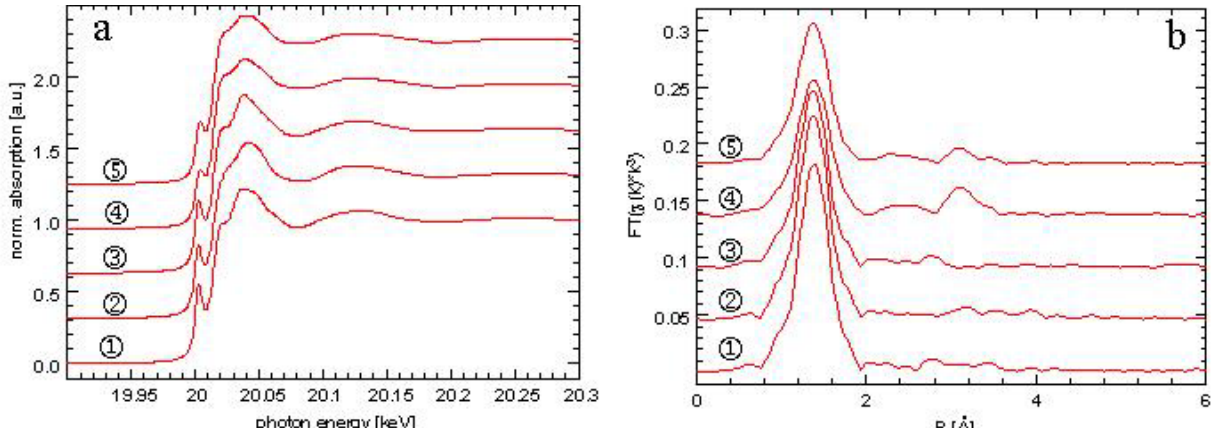

Figure 1 a) XANES of 1: Na_2MoO_4 (reference); 2: 44% Mn; 3: 81% Cr; 4: 45 % Cr; 5: 72% Cr.

b) associated RDFs

large excess. The Cr and Mn containing solutions needed to be partially neutralized with ammonia to get a gelly precipitate. The samples were tested by TPRS in the oxidation of propene. X-ray absorption spectra of the oxides were taken at beam line X1 (HASYLAB) at the Molybdenum, Manganese and Chromium K-edge. Measurements at the Iron K-edge are outstanding. The oxides were pressed in pellets with a diameter of 13 mm and with polyethylene as carrier material. Sample loading were adjusted to $\mu_T d = 2.6$ with respect to the different edge energies. Spectra were taken in transmission mode. Data reduction and analysis were carried out with the software WinXAS [2] following standard procedures. Simulations were calculated, applying phases and amplitudes generated by the ab initio multiple scattering code FEFF7 [3], on the base of single crystal data.

Results and Discussion Selected XANES and FT(χ(k)*k^3) of different samples and of a reference, Na_2MoO_4, are shown in figure 1a and b, respectively. All XANES show a distinct pre-edge peak, indicating a tetrahedral coordination of the molybdenum via oxygen. As a reference for tetrahedral coordination of the molybdenum via oxygen, Na_2MoO_4 was chosen. Its structure is build up from isolated. The pseudo radial distribution function (RDF), FT(χ(k)*k^3), reflect this structural

condition. Only one narrow shell around 1.8 Å can be estimated. Within the shown RDFs only two of the chromium containing samples show weak additional shells at higher distances. All RDF, in a range of 0.2 Å to 2.1 Å, can be simulated with Mo-O paths calculated on the base of single crystal data [4]. As an example the experimental RDF of chromium containing sample and the refined simulated RDF are shown. In table 1 the results and the refinement conditions are given. The results of the refinement and the good R-value, which both reflect that the experimental RDF is well described by the model, are an indication that the sample is build up by $[MoO_4]^{-2}$-tetrahedra. In comparison to the results of a refinement of the model at the data from the reference sample, only the Debye-Waller factor is smaller, which is an indication for higher disorder in the chromium-containing sample. There exist no long-range order, e.g. the sample is X-ray amorphous, for the given example. However, the EXAFS analysis shows an order on the short-range scale. Some of the prepared sample, which matches the structural model of isolated $[MoO_4]^{-2}$-tetrahedra, shows promising results in the catalytic test.

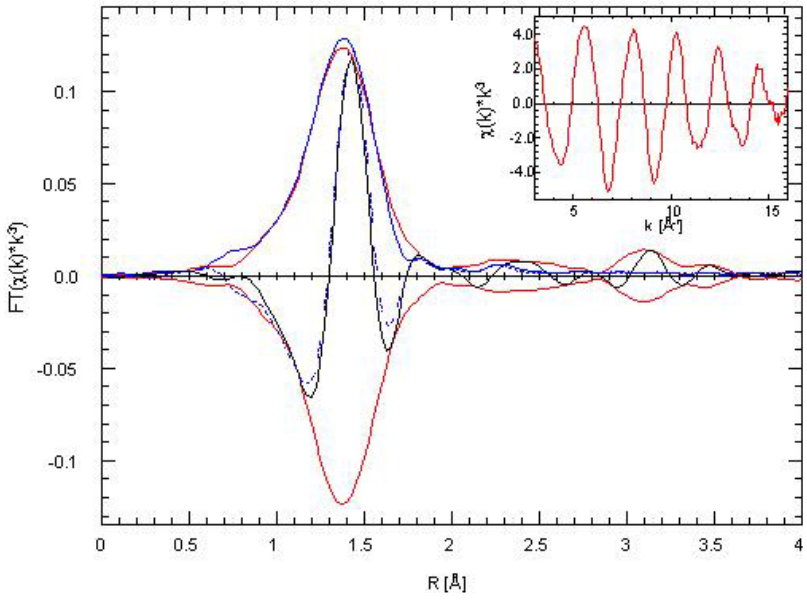

Figure 2 Experimental and refined simulated RDF of No. 4 in figure 1 (45% Cr); as inlet: the associated $\chi(k)*k^3$

Table 1 Results of the refinement of the model; (Refinement conditions: CN: fixed; S_0: fixed =1; E_0: one for all path; σ^2: one for all path) R = 7.4

Pair	CN	R(initial) / Å	R(fit) / Å	σ^2 / Å^{-2}	E_0 / eV	w(%)
Mo - O	2	1.742	1.767	0.00282	2.83	100
Mo - O	1	1.781	1.774	0.00286	2.83	49.39
Mo - O	1	1.785	1.851	0.00287	2.83	44.68

Conclusion The results of the EXAFS analysis confirm the influence of the preparation methods on the samples. It is clearly shown that it was possible to prepare samples with isolated $[MoO_4]^{-2}$-tetrahedra. This result and their catalytic activity, together with results from other methods confirm a proposed model for the understanding of Mo-oxide catalysts. Therein the genesis of active oxides starting from the aqueous solution is proposed. It comprise that the key processes, to get an active material, are the formation of molybdate oligomers in solution, their agglomeration and, predominantly, the stability of the resulting material under reaction conditions, e.g. the ability to transform into the infinite ordered structure of MoO_3 or other crystalline phases.

References

[1] Ruth, K., Journal of Catalysis 175: 16 (1998)

[2] T. Ressler, Journal of Synchrotron Radiation 5, 118 (1998)

[3] J.J. Rehr, C. H. Booth, F. Bridges, and S. I. Zabinsky, Physical Review B 49, 12347 (1994)

[4] ICSD 16154; structure of K_2MoO_4; it is assumed that the exchange of the kation wont add any effect to the Mo-O coordination.