ESRF	**Experiment title:** EXAFS for the characterization of heterogenized metal complexes with application in carbon dioxide fixation	**Experiment number**: 01-01-601
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Shifts:	**Local contact(s)**: Dr. W. van Beek, Dr. H. Emmerich	

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Report:

Introduction

Anchoring of homogeneous catalysts to an inorganic support is a well-known approach [1] to gain heterogeneous catalysts which offer a number of opportunities: this approach combines the engineering advantages of heterogeneous catalysts, such as ruggedness and ease of recovery, with the advantageous features of homogeneous catalysts, including well-defined structures with high activity and/or selectivity. One of the important areas in heterogeneous catalysis, where we have applied and utilized this route, is the use of carbon dioxide as a C_1 feedstock for the manufacture of valuable chemicals and fuels as alternative to the predominant use of carbon monoxide or phosgene [2-4]. Zinc complexes with pyridine and bromide ligands are reported to be good catalysts for the carbon dioxide fixation in propylene oxide [5-8]. The organic ligand has to be modified for the anchoring on silica, and for monitoring a possible change at the metal center. All intermediate compounds (1 – 4, fig. 1) were tested catalytically and characterized by EXAFS. Accurate characterization of the catalytic centers is needed, also in order to draw conclusions on structure-activity relationships. EXAFS measurements provide information concerning the elemental neighborhood of the metal center (including the bond length between the metal centre and the ligand and the coordination number). Such information is required for our catalysts to obtain a feedback to the applied synthesis route and the observed catalytic activities.

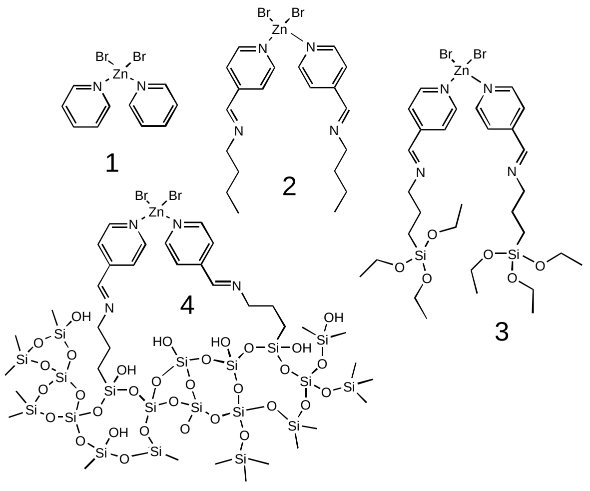

Fig. 1. Series of complexes.

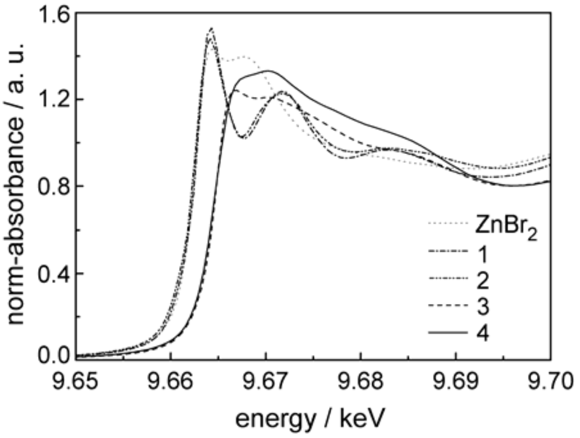

Fig. 2. XANES at the Zn K-edge.

Experimental

For the experiment, the samples were diluted with BN and pressed as pellet (13 mm diameter). Typically the spectra were taken in transmission in the step scanning mode (energy range: 9.5 to 10.6 keV).

Results

The Fourier transformed k^1-weighted EXAFS spectra at the Zn K-edge of the zinc pyridine bromide catalyst gave quantitative information on the N and Br neighbors for the free and immobilized complexes. The spectra were fitted with calculated data for zinc bromide and zinc carbonate, in both cases only the first sphere was used. Note that it is not possible to differentiate between N and O neighbors in these measurements. The Zn K-edge XANES spectra in fig. 2 show a shift in the edge energy according to the different structures. The absorption edge of complexes 3 and 4 were shifted to higher energies and the acquired coordination numbers from the Fourier transformed EXAFS spectra of the N/O neighbors were increased. This could be explained by coordination of the zinc atom with oxygen atoms from the ethoxy groups of complex 3. Comparable results are found for the immobilized catalyst 4. The relatively high coordination number for N and O could also be explained by ethoxy groups, but it is furthermore possible that oxygen from silanol groups of the silica

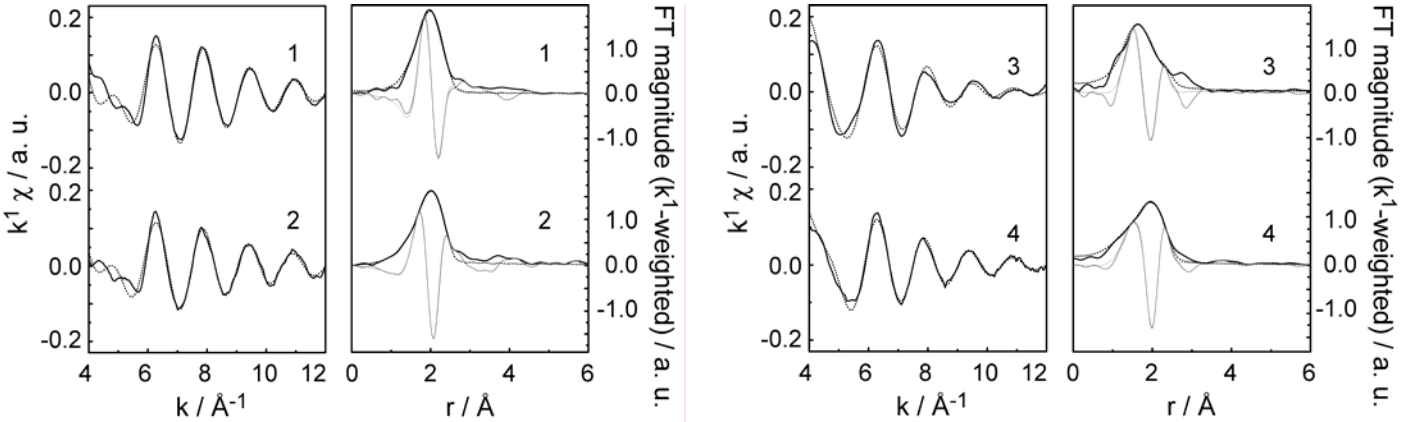

Fig. 3 and 4. Experimental and calculated k^1 χ functions and their Fourier transforms (Zn K-edge). Experimental data is designated by solid lines, calculated by dotted lines. Grey lines in the right part of each figure are the imaginary part of the Fourier transform. The numbers are corresponding to the catalysts shown in fig. 1.

surface were coordinating the zinc center. Catalytic measurements show that these higher coordinated species are less active. Hence, the additional coordination of substrate ligands to the zinc center seems to hamper the catalytic activity in particular for catalysts 3.

Conclusions

EXAFS measurements showed the successful immobilization of complex 3 on a silica surface and that a higher coordination number of the center atom decreases the catalytic activity.

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Reference

(1) M.H. Valkenberg, W.F. Holderich, Catal. Rev. Sci. Eng. 44 (2002) 321-74.

(2) A. Baiker, Appl. Organom. Chem. 14 (2000) 751-62.

(3) W. Leitner, Appl. Organom. Chem. 14 (2000) 809-14.

(4) X.D. Xu, J.A. Moulijn, Energy & Fuels 10 (1996) 305-25.

(5) D.J. Darensbourg, S.J. Lewis, J.L. Rodgers, J.C. Yarbrough, Inorg. Chem. 42 (2003) 581-89.

(6) H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem., International Edition 39 (2000) 4096-98.

(7) H.S. Kim, J.J. Kim, H.N. Kwon, M.J. Chung, B.G. Lee, H.G. Jang, J. Catal. 205 (2002) 226-29.

(8) H.S. Kim, J.J. Kim, S.D. Lee, M.S. Lah, D. Moon, H.G. Jang, Chem. Eur. J. 9 (2003) 678-86.