

15.2-2 K EDGE X-RAY ABSORPTION SPECTROSCOPIC INVESTIGATIONS ON SELECTED IRON COMPOUNDS WITH SYNCHROTRON RADIATION. By G. Henkel, B. Krebs, H.-F. Nolting, P. Eggers, Institute of Inorganic Chemistry, University of Münster, D-4400 Münster; C. Hermes, R.F. Pettifer and D.L. Foulis, EMBO Outstation, DESY, D-2000 Hamburg, Federal Republic of Germany

As a part of our systematic X-ray absorption spectroscopic investigations on biologically relevant metal coordination centers and of appropriate model compounds, XANES spectra were measured on a number of structurally known iron compounds. The aim was to derive systematic trends in the model compounds between the spectral characteristics and properties related to bonding, structure and chemical behaviour.

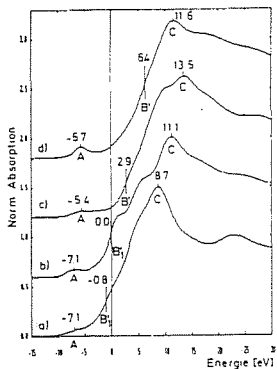


Fig. 1

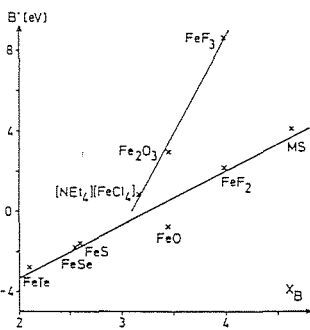


Fig. 2

The measurements were done at HASYLAB (DESY Hamburg) with the EMBL spectrometer (C. Hermes, E. Gilberg and M.H.J. Koch, Nucl. Instrum. Methods, 1984, 222, 207) and calibrated to absolute energy values. Fig. 1 shows, as examples, the K absorption edges of some simple iron(II) oxygen compounds (a: FeO, b:  $\text{FeCr}_2\text{O}_4$ , c:  $\text{Fe}_2\text{O}_3$ , d:  $\text{BaFeO}_4$ ; energy zero at 7120 eV). Similar results were obtained for chalcogenides and halides. The positions and relative intensities of the edge structures were correlated with chemical parameters (e.g. oxidation states and coordination symmetries of the iron atoms, electronic properties of the ligands) and with chemical shifts from XPS and Mössbauer measurements. Fig. 2 shows the correlations between the electronegativities  $X_B$  of the ligand atoms and the edge positions  $B'$  in the XANES spectra for a series of iron(II) and iron(III) compounds. Other relationships can be derived between the "coordination charge" of iron (J. Wong, F.W. Lytle, Phys. Rev. B, 1984, 30, 5596) and the edge width  $K_2$  in the spectra. The pre-edge structure which can be interpreted as a  $1s \rightarrow 3d$  transition was fitted with two Lorentz curves. The observed splitting of the d states follows the trend of the spectrochemical series. The evaluated edge structure results on the model compounds allow a transfer of the correlations to systems with unknown structures. Thus, structural informations can be derived on the active centers in metallo-enzymes and catalyst systems.

15.2-3 SYNCHROTRON STUDIES OF SOLID STATE TRANSFORMATIONS INVOLVING AMORPHOUS PHASES By J.B. Parise\*, A.W. Sleight, D.R. Corbin, H.S. Horowitz, M.A. Subramanian, E.I. Du Pont, CR&D, Wilmington, DE 19898, and T. Egami, W. Dmowski, University of Pennsylvania, Philadelphia, PA 19104, USA.

Heterogeneous catalysts, ceramics, and their precursors frequently give featureless wide angle x-ray diffraction patterns.

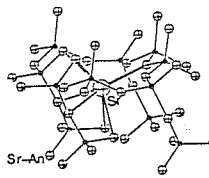
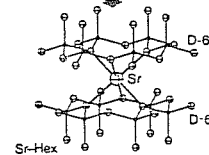
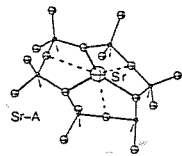


Figure 1

The National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL) has been used as an intense, tunable x-ray source to collect x-ray absorption spectra (EXAFS) and wide angle scattering data, for the calculation of the radial distribution function (RDF), in order to determine the short range structure in a variety of oxides.

Analysis of EXAFS at the Sr edge indicates retention of that ions coordination in a 6-ring of  $\text{SiO}_4$ - and  $\text{AlO}_4$ -tetrahedra when Sr-zeolite-A is decomposed at  $850^\circ\text{C}$  to form an amorphous material. Heating to higher temperatures converts this amorphous material to metastable Sr-hexacelsian and Sr-anorthite feldspar (Fig. 1). The mechanism involved is the condensation of 6-rings, retained in the initial decomposition, to form

sheets, followed by the formation of double 6-ring slabs (D-6) which sandwich  $\text{Sr}^{2+}$  in hexacelsian (Fig. 1).

The activated vanadium phosphate catalyst for selective oxidation of n-butane to maleic anhydride consists of a mixture of poorly crystallized  $(\text{VO})_2\text{P}_2\text{O}_7$  and amorphous material. Wide angle diffraction profiles of a crystalline sample of  $(\text{VO})_2\text{P}_2\text{O}_7$  as well as the activated catalyst were collected. The RDF for the amorphous material alone, obtained by Fourier transforming the difference between the structure factor for these two samples, was compared to distributions calculated from known structures of various pyrophosphates. Although, in agreement with recent work (Bergeret et al, Chem. Comm., 1986, 825), it appears the amorphous phase consists of corner linked  $\text{VO}_6$ -octahedra; the present data do not distinguish between several structures containing this grouping.

Other applications for the techniques have included the study of the growth of zeolite materials from gels and the role played by  $\text{ZrO}_2$  in nucleating cordierite glass ceramics.

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