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Catalysis Today 39 (1998) 293–300

CATALYSIS TODAY

Combined (Q)EXAFS/XRD: Technique and applications

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Abstract

The advantages of the combined (Q)EXAFS/XRD technique are discussed with focus on recent studies where the technique has given additional insight into catalyst properties. XRD and also more recently EXAFS have become routine techniques in catalysis research. However, by use of a combination of the two methods both the long and the short range ordered structures can be probed enabling a much better description of many catalysts. Of vital importance is also the possibility to perform the studies in situ, revealing structural information directly related to the active state of the catalyst. Time dependent changes of both the crystalline and the amorphous phases in catalysts can be followed by using a technique which combines EXAFS in the quick scanning mode (QEXAFS) and XRD using a position sensitive detector. © 1998 Elsevier Science B.V.

Keywords: EXAFS; QEXAFS; XRD; Methanol; Cu; Molecular dynamics simulations

1. Introduction

Structural information about a catalyst is most often obtained from the use of X-ray diffraction (XRD) but in recent years, it has been realized that techniques based on X-ray absorption spectroscopy, such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), may provide important additional possibilities for catalyst characterization. For example, many catalyst systems which cannot be structurally characterized by XRD due to the presence of microcrystalline structures or amorphous phases are conveniently studied by EXAFS. XRD and EXAFS can be regarded as complimentary techniques since XRD probes structures with long-range order whereas EXAFS is sensitive mainly to the local surroundings of the atoms in a material. Thus, a combination of the two techniques offers new possibilities for obtaining a more complete structural description of complex materials such as catalysts [1–3].

One of the important advantages of both X-ray absorption and XRD techniques is the possibility to perform the studies, while the catalyst is in its working environment. This is important since such in situ studies assure that the structural information is directly related to the active state of the catalyst. Thus, direct correlations can be established between the structural and chemical features and the performance of the catalyst under different process conditions.

Previously, XRD and EXAFS were seldom used to study time dependent changes, mainly due to the lack of appropriate experimental equipment. However, with the recent progress in detectors, computers, and in situ cells such studies can now be carried out in a dynamical fashion and, in fact, it is often necessary to include such insight in order to arrive at a more detailed description and understanding of

PII S0920-5861(97)00115-6

the catalyst structure and the catalytic reactions. In order to follow time dependent changes of both the crystalline and the amorphous phases in catalysts, a technique which combines XRD and EXAFS in the quick scanning mode (QEXAFS) has been developed.

In the following, the technique on which the combined (Q)EXAFS/XRD method is based will be described and its potential in catalyst research will be demonstrated via some selected examples.

2. Combined (Q)EXAFS/XRD techniques

2.1. *In situ cells*

Materials containing mainly light elements are relatively transparent to high energy X-rays and that allows the construction of XRD and EXAFS in situ cells having windows of such material. In order to ensure that the obtained structural information is representative of the active state of the catalyst it is of utmost importance that the pretreatment of the catalyst samples and the following catalysis are carried out under conditions closely related to those in normal catalytic test reactors. However, a situation like that encountered in actual catalytic reactors where the entire gas is flowing through the catalyst bed is non-trivial to obtain in in situ cells where one also has to consider the requirements of the technique used (e.g. thickness of the sample; size, thickness, and maximum temperature of the windows).

These difficulties can of course be overcome to a large extent by adopting in the in situ cell the same geometry as that used in a tubular plug-flow reactor. Due to the requirement of an optimum X-ray absorption length caused by the catalyst sample and by other components (windows, air path, etc.) in the beam, the use of capillary tubes as combined in situ cells and catalytic reactors has been found to be appropriate [4]. This approach is illustrated in Fig. 1. The powdered catalyst sample is placed in a geometry similar to a normal catalyst fixed-bed and during the experiment, gases will pass through the bed such that unwanted gradients can be minimized. Depending on the construction material of the capillary, temperatures above 1000 K and pressures above 100 atm can be achieved. The heating/cooling is conveniently done indirectly and temperature uniformity is then typically better than 1 K [4]. The low mass and heat capacity allows quite rapid transients to be followed. The catalytic activities obtained in the in situ cell are similar to those measured in separate ideal plug-flow reactors [4] and this important feature makes it possible to make meaningful relationships between structural and catalytic information. The above in situ cell allows both XRD [4] and EXAFS experiments [5,6] to be carried out.

2.2. *Combined EXAFS/XRD*

For chemically stable systems where no time resolution is needed, it has been shown [7] that high quality spectra can be obtained by combining normal EXAFS with XRD simply by recording the two data

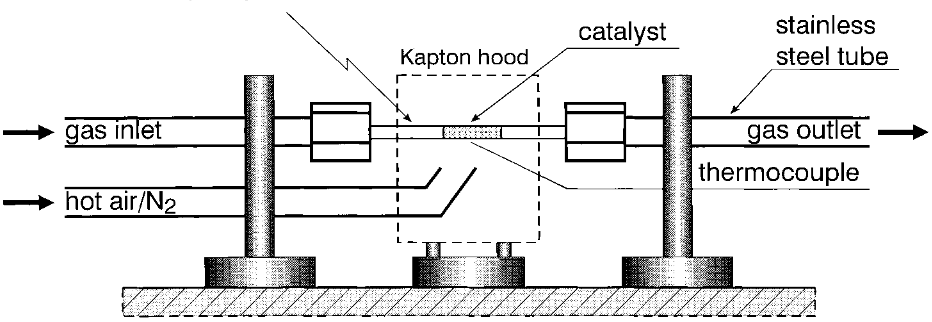

Fig. 1. Schematic drawing of the combined catalytic reactor and in situ cell used in the combined (Q)EXAFS/XRD studies. The quartz capillary tube has typically an outer diameter of 0.5 mm and a thickness of 10 μm (adapted from [4]).

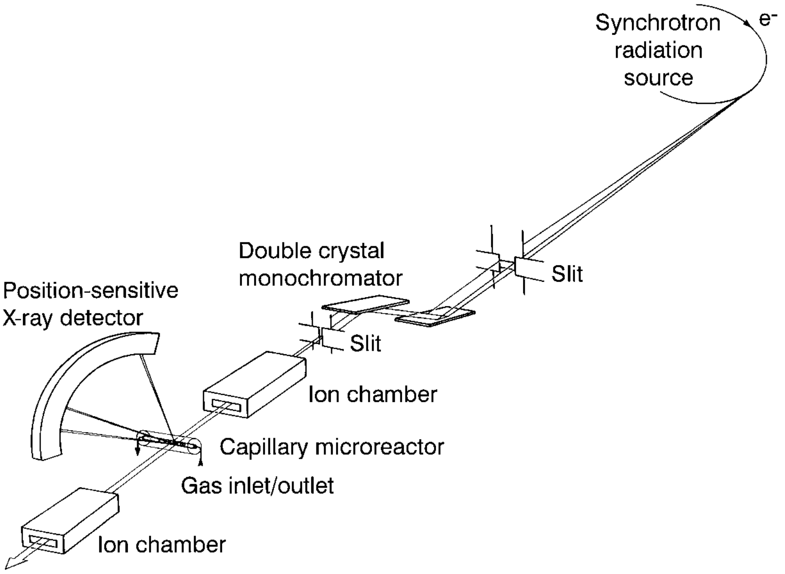

Fig. 2. Outline of the beamline with the experimental equipment for combined (Q)EXAFS/XRD in situ studies (adapted from [5]).

sets sequentially for the catalyst sample in the same set-up. In this approach (Fig. 2), a diffractometer was mounted between the first and the second ionization chamber in a standard EXAFS spectrometer set-up and the EXAFS is then recorded by step-scanning the monochromator through the energy region of interest [5]. The XRD pattern can be acquired at the most convenient wavelength, typically at the start of the EXAFS scan, i.e. at an energy below the absorption edge in order to minimize absorption and to avoid a high background due to the fluorescence radiation. This set-up provides EXAFS and XRD data on the *same* sample. By employing the above catalytic reaction cell, in situ studies are also possible. This approach has the great advantage that it is relatively straightforward to implement at existing EXAFS spectrometers.

2.3. Combined QEXAFS/XRD

The experimental set-up for combined QEXAFS/XRD is essentially identical to the above description of combined EXAFS/XRD but makes use of the fact that the time needed to record an EXAFS spectrum can be significantly reduced by moving the monochromator in a continuous manner instead of moving it in discrete steps [8,9]. The reasoning behind this is that when utilizing the high intensity synchrotron radiation it is not counting statistics which determines the time needed to collect a spectrum. A large fraction of the time between each step is spent on accelerating and decelerating the monochromator turntable and on waiting for the mechanical vibrations in the whole monochromator system to be subdued. Another limiting factor is the dead-time introduced by the data acquisition system. These computer dead-time problems can be minimized by either optimizing the computer input routines [10] or by utilizing a multichannel analyzer the content of which is stored in the computer only after each complete scan [11]. By use of the high brilliance X-ray radiation from an undulator on a third generation synchrotron facility such as ESRF, scan times of the order 1–2 s for a full spectrum (i.e. covering about 1000 eV) can now be obtained with the QEXAFS technique [11]. The minimum time needed to record an X-ray diffractogram depends on properties such as the source brilliance, the crystallinity of the sample, and the sensitivity of the detector. However, for typical catalyst powder samples and a conventional position sensitive detector covering a large Bragg angle (Fig. 2), it is difficult to reduce the collection time to much less than 1 s. Thus for the combined QEXAFS/XRD technique, a set of absorption and diffraction data can in principle be recorded in a few seconds.

Thomas and coworkers [12] have shown that time resolved data can also be obtained using EXAFS in the energy dispersive mode (DEXAFS) in combination with XRD. However, with powdered catalyst materials, it is in general quite difficult to obtain DEXAFS spectra of sufficient quality to extract meaningful quantitative information [3]. Nevertheless, the studies may provide important qualitative information about catalyst dynamics [12,13].

3. Application of combined (Q)EXAFS/XRD

The combined XRD/EXAFS technique has been essential in confirming a new EXAFS analysis procedure based on the molecular dynamics simulations for obtaining an improved estimation of the structural parameters of small metallic particles [6,14,15].

Particles smaller than about 10 nm have a large fraction of the atoms located at the surface and accordingly their radial pair distribution function will show a reduction in the coordination numbers compared to the bulk values. Provided the pair distribution has a Gaussian shape, EXAFS is a convenient technique to estimate such coordination numbers and especially for particles below 2–3 nm, this technique is rather unique. Various models have been proposed (see e.g. [16–18]) to relate coordination numbers to metal particle sizes but in none of these models, deviations from Gaussian-like pair distributions have been considered.

Molecular dynamics simulations carried out for Cu and Pt particles with sizes up to 7 nm in diameter have shown [6,14,15] that the surface atoms move in a much more anharmonic potential than the bulk atoms. Since the fraction of surface atoms increases with decreasing particle size, the pair distribution functions become increasingly asymmetric when going to smaller particles. These non-Gaussian pair distribution functions exhibit broad tails at the low k-part of the EXAFS spectrum. This part of an experimental spectrum is usually omitted in the data analysis since it is complicated by multiple scattering, insufficient removal of the atomic absorption, lifetime broadening of the excited state, etc. If the standard EXAFS formalism (see e.g. [19]) is used to curve-fit EXAFS "spectra" derived from the simulated pair distribution functions (excluding the small k-part), the errors introduced by not having access to this information have been estimated. Since the particle size is calculated from the coordination numbers, particle sizes deviating significantly from the real value may result from such analyses. Fig. 3(a) and (b) show the relations between the apparent coordination numbers determined from the above EXAFS analysis and the true coordination numbers calculated from the structures generated by the molecular dynamics simulations. The relations will depend on the nature of the metal and results for Cu and Pt are shown at different temperatures. It is evident that the coordination numbers determined by use of the standard EXAFS ana-

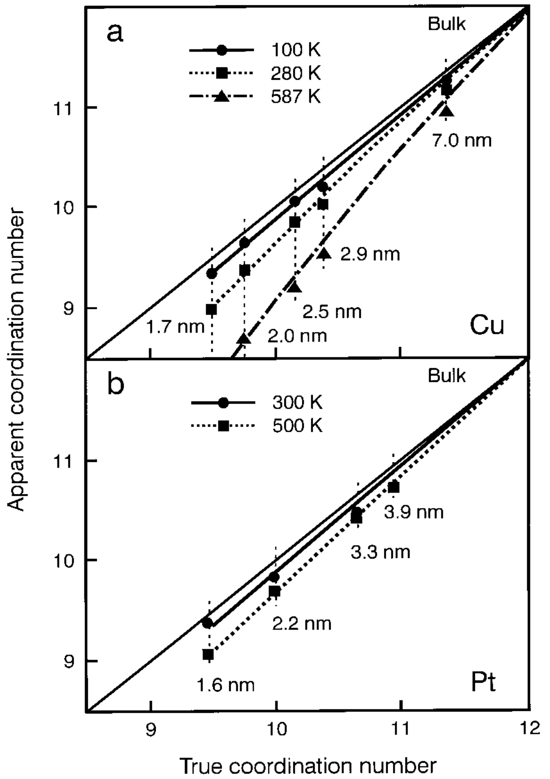

Fig. 3. Relation between the apparent first shell coordination number determined from the standard EXAFS analysis and the true coordination number derived from the structures obtained from molecular dynamics simulations: (a) Cu particles; (b) Pt particles. In the analysis (k^1-weighting and curve fitting from 3 to 20 $\mathrm{\AA}^{-1}$), the Debye–Waller factor was allowed to vary relative to the bulk value (adapted from [15]).

lysis technique are significantly smaller than the true values. The error in the coordination number is seen to become larger with decreasing particle size and with increasing temperatures. This is due to the fact that the anharmonicity of the motion of the metal atoms becomes increasingly important in the small particles and at high temperatures. Many catalysts consist of small particles and in order to understand the catalyst properties, it is often essential to carry out the studies at high temperatures. This procedure may thus aid the interpretation of such results.

Combined EXAFS/XRD studies [20] have also been used to study the gas phase induced wetting/non-wetting phenomena of metallic Cu particles on ZnO during catalysis. Fig. 4(a) shows the Fourier transformed EXAFS spectra above the Cu K-edge of a Cu/ZnO catalyst. The spectra, which show the typical features of relatively small metallic Cu particles, were obtained in situ during synthesis conditions at ambient pressure and in the gas mixtures indicated in the figures. The changes in the Cu–Cu coordination number upon changing the oxidation potential of the synthesis gas (Fig. 4(b)) were interpreted in terms of a change in the particle dispersion due to a wetting/non-wetting phenomenon of the small Cu particles on the ZnO support. An increase in the oxidation potential (wet conditions) gives rise to non-wetting, i.e. the Cu particles become more spherical giving relatively high coordination numbers. The subsequent decrease in the oxidation potential (dry conditions) results in wetting of the support, i.e. the Cu particles obtain a more disc-like shape resulting in relative low coordination numbers, i.e. relatively many low coordinated surface atoms. Due to the small size of the Cu crystallites, the simultaneously recorded XRD diffractograms did not provide unambiguous support for this interpretation. On the other hand, a very simple explanation for the observed results could be provided based on a calculation of the relative surface and interface free energies of a particle. The description of the change in particle morphology is based on the Wulff constructed particles [20]. This gives the surface area and distribution of surface planes for a particle for different contact surface free energies between particle and support. The change in contact surface free energy is related to the changes in the number of oxygen vacancies at the interface between the Cu particle and the ZnO support [21].

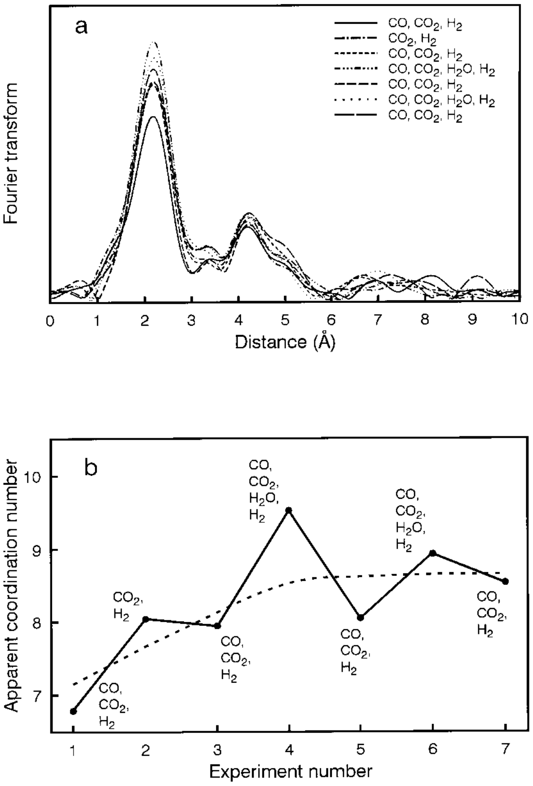

Fig. 4. (a) Fourier transforms of the EXAFS in situ spectra above the Cu K-edge for a Cu/ZnO catalyst under the influence of the changing gaseous environments. Typical gas composition is 5% CO, 5% CO_2, 90% H_2. H_2O is added in a concentration of about 3%. (b) Variation in the apparent Cu–Cu coordination number with changes in the gaseous environment (adapted from [20]).

The kinetic implications of the dynamical changes in catalyst morphology during methanol synthesis are dramatic. Fig. 5(a) shows the agreement between the predictions from a static microkinetic model and the measured rates of methanol synthesis over a Cu/ZnO/Al_2O_3 [21]. It is seen that in general the microkinetic model is able to explain the magnitude of the rate quite well, but the data are grouped into two families. The two families of points in Fig. 5(a) are characterized by having different reduction potentials and it is likely that the difficulty in obtaining agreement using the static model is due to the fact that the assumption of constant number of active sites is not valid. Thus, a dynamic microkinetic model of the methanol synthesis was developed by describing the changes in particle shape, i.e. surface area, with the changes in

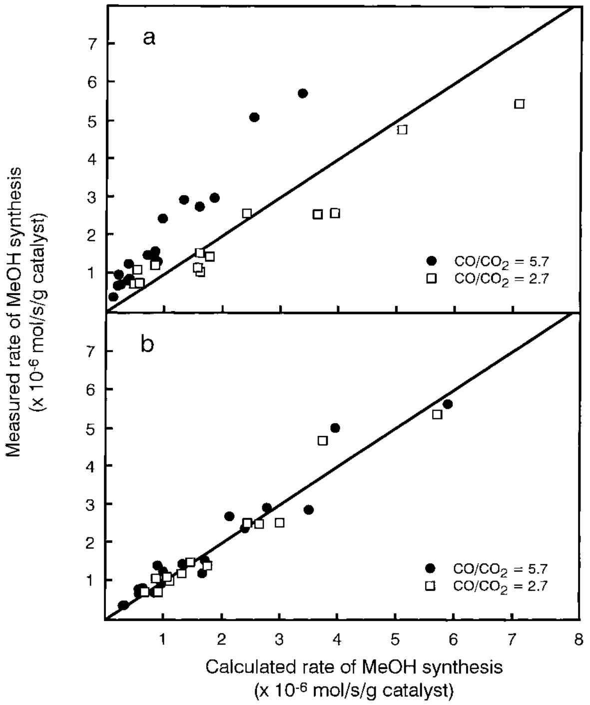

Fig. 5. (a) Comparison of the calculated rate with the measured rate of methanol synthesis over a $Cu/ZnO/Al_2O_3$ catalyst. The calculated rate is obtained from a static microkinetic model. (b) The corresponding comparison using a dynamic microkinetic model (adapted from [21]).

the gaseous environment having taken into account that the rate of methanol synthesis is different over the three low index facets [21]. The result of using this dynamic microkinetic model is shown in Fig. 5(b). It is seen that the separation of the data into two groups is no longer present and a much better description of the data is obtained.

The combined QEXAFS/XRD method may become an important technique for on-line, time resolved studies of catalysts. The method has been used, e.g., to study the solid state transformations taking place during activation (reduction) of a $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst [5]. A plot of the raw QEXAFS data recorded in situ during reduction is shown in Fig. 6(a). It is seen that the reduction of the copper oxide phase takes place within an extremely narrow temperature range. The spectra typical of CuO are observed to change within a few degrees Kelvin into spectra typical of metallic Cu. The

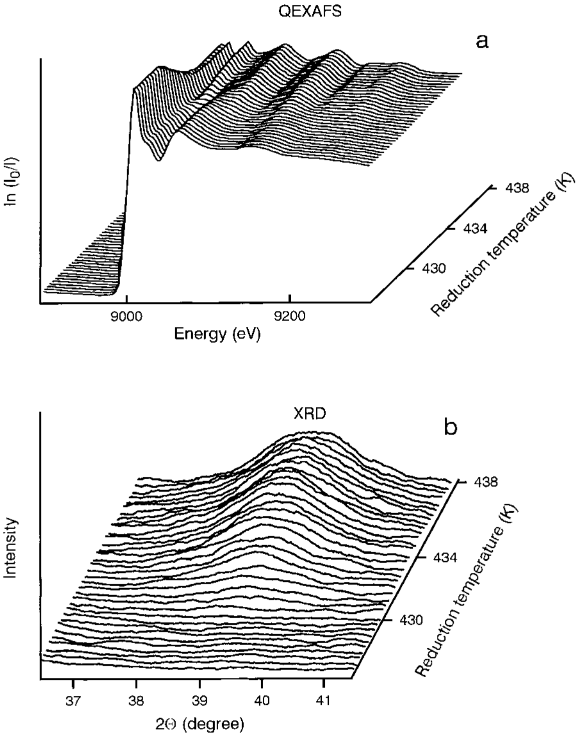

Fig. 6. (a) Raw QEXAFS data near the Cu K-edge obtained in situ during reduction of a $Cu/ZnO/Al_2O_3$ catalyst. The recording time for each spectrum was 120 s. (b) In situ XRD diffractograms of the Cu(1 1 1) line recorded simultaneously with the QEXAFS data in (a). The recording time for each difractogram was 90 s (adapted from [5]).

changes in the QEXAFS occurring during reduction are best illustrated by plotting the intensity of a specific feature (9040 eV) in the absorption spectra as a function of the reduction temperature (Fig. 7). In Fig. 6(b), the simultaneously recorded XRD diagrams are shown for the 2Θ angular region where the Cu(1 1 1) peak appears. The integrated intensity of this peak as a function of the reduction temperature is also shown in Fig. 7. A comparison of the intensity curves for XRD and QEXAFS reveals that QEXAFS detects Cu metal at a slightly lower temperature than does the XRD. This indicates that very small Cu clusters are formed initially. They can be observed by EXAFS but they are still too small to be observed with XRD (i.e. the clusters appear X-ray amorphous). The fact that the intensity of the curves for both QEXAFS and XRD changes smoothly from one level

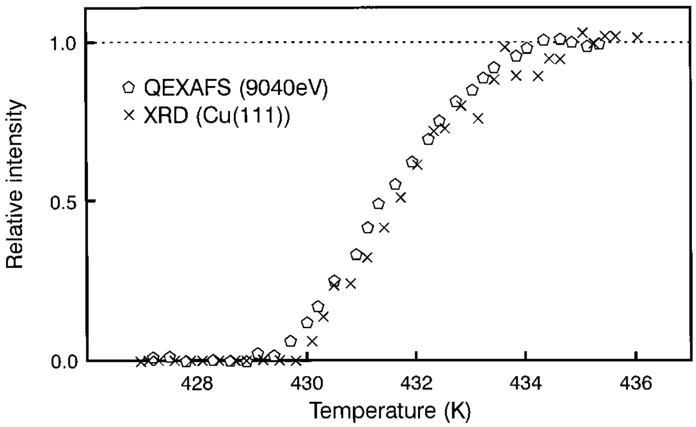

Fig. 7. Changes in the X-ray absorption feature at 9040 eV (scaled to coincide with the XRD data at low and high temperatures) and in the integrated intensity of the Cu(1 1 1) line during reduction of the Cu/ZnO/Al_2O_3 catalyst (adapted from [5]).

to another without any additional features could indicate that the reduction of CuO to metallic Cu does not involve the presence of an intermediate phase such as Cu_2O. However, QEXAFS studies with better time resolution strongly suggest that the reduction of CuO in the catalysts indeed proceeds via Cu_2O [11].

4. Conclusion

The time resolution of the combined QEXAFS/XRD technique may be improved in different ways. For XRD the time for collecting a diffractogram can in a simple way be significantly reduced by adopting new types of detectors such as image plates, CCD cameras, etc. For QEXAFS the time resolution is presently determined by the capabilities of the stepping motors and the mechanical stability of the monochromators which put strict limits on how fast one can repeatedly accelerate and decelerate the monochromator turntable between the QEXAFS scans. Instead of moving the whole turntable to position the monochromator crystals, tilt tables actuated by piezoelectric crystals may be used [22]. Since piezoelectric crystals can operate at extremely high frequencies, it is possible with this piezo-EXAFS technique to reach a data acquisition time of the order of microseconds for a spectrum. Although there are still problems to be solved regarding the well-known hysteresis effects in the piezos, their dynamically range, rapid data storage, etc., the technique has already proven its potential in ultra-fast studies of time dependent phenomena in catalysts [22,23].

The much shorter collection times possible with the combined QEXAFS/XRD technique mean that many dynamical phenomena can now be studied, and one does not have to worry about problems in connection with sample changes during the measurement.

Acknowledgements

The author is grateful to HASYLAB (Hamburg, Germany) for offering beam time for the (Q)EXAFS/XRD experiments. The Danish Natural Science Research Council is gratefully acknowledged for financial support through DANSYNC.

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