

# Chapter 12

## X-Ray Absorption with Transmission X-Ray Microscopes

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### 12.1 Introduction

In this section we focus on the use of transmission X-ray microscopy (TXM) to measure the XAS spectra. In the last decade a range of soft X-ray and hard X-ray TXM microscopes have been developed, allowing the measurement of XAS spectra with 10–100 nm resolution. In the hard X-ray range the TXM experiments pose the same restrictions on in situ experiments as bulk XAS experiments, allowing experiments with capillaries to study catalysts under working conditions. In the soft X-ray range, dedicated transmission nanoreactors are needed. Considering catalysts the main result the in situ TXM experiments are the determination of nanometer range variations of catalysts under working conditions. An important property of X-rays is their short wavelength below 1 nm. This allows direct imaging of catalysts in scanning mode or full field mode. In contrast, visible light with an energy of 1 eV has a diffraction limited resolution of approximately 500 nm and VUV light with an energy of 10 eV has a diffraction limit of ~50 nm.

We will compare TXM microscopes in detail with transmission electron microscopes (TEM) that allow a similar combination with spectroscopy using electron energy loss spectroscopy (EELS). We will omit scanning probe near field microscopes as they are limited to surfaces and do not directly look at the interior of catalyst materials, including the non-exposed internal surfaces. Catalytic activity very often takes place within micro and/or mesoporous structures implying that not only the external surface of a catalyst is of importance. Examples include the active sites within zeolites and enzymes. The catalytic active sites in these systems cannot be studied with probes that only map the outside of the system. TEM and TXM

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detect a column of material through the system of study. As such they provide information on both the surface structure and the internal structure of a material.

## 12.2 Soft X-Ray TXM Microscopes

In a scanning TXM microscope, a synchrotron X-ray absorption beamline is used to illuminate a Fresnel zone plate. The zone plate characteristics determine the spot size to which the X-ray beam is focused, typically between 10 and 50 nm. The focal length is in the order of a few millimeters, which is a design limitation for in situ reactor cells. Full-field TXMs use two zone plates, allowing the synchronous detection of an image plane [1]. Soft X-ray TXM microscopes cover the energy range between 200 and 2000 eV. This includes the 1s core states or K edges of the elements from carbon (280 eV) to phosphorus (2150 eV) [2]. A range of soft ray TXM microscopes exist, including beamlines at NSLS Brookhaven [3]; BESSY Berlin [4]; SLS Villingen (Pollux) [5]; CLS Saskatoon [6], and ALS Berkeley [7, 8]. The soft X-ray range included C, N, O and also Mg, Al, Si, and P. The soft X-ray 2p core states ( $L_{2,3}$  edges) range from potassium (290 eV) to Sr (2000 eV). In particular the 3d transition metal ions are important for catalysis and are often studied, also because they provide very rich  $L_{2,3}$  edge spectral shapes. A range of other edges are available for heavier elements. Using the specific absorption of a core level one can obtain quantitative elemental maps in a TXM microscope, for example by determining the ratio between a recorded map just before and after the edge.

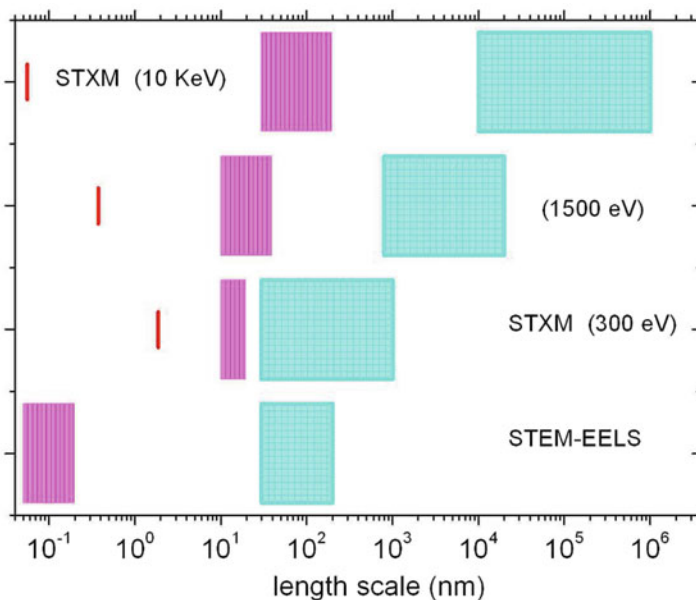
Soft X-ray K edges can be interpreted as mapping the empty states of the element under study. The variation in the empty states implies variation in the XAS spectral shape, which can be used for chemical contrast. The spectral shapes of carbon, nitrogen and oxygen containing systems reveal a large variation in spectral shapes and, as such, are ideal for chemical contrast [9]. The transition metal L edges cannot be interpreted with a density of states concept, as their spectral shape is dominated by multiplet effects induced by the core hole in the final state [10]. One observes a rich spectral fine structure allowing detailed chemical analysis. Transition metal L edges are split by the 2p spin-orbit coupling splits the L edge into its  $L_3$  and  $L_2$  components. Intra-atomic correlations (multiplet effects), crystal field effects and the effects of charge fluctuations dominate the spectral shape analysis [11]. Charge transfer multiplet analysis yields information on the metal valence, spin state, the site symmetry, and the crystal field strength [12, 13].

Soft X-rays have a strong interaction with matter. This implies that transmission experiments are only possible for solid samples of limited thickness. In addition, the transmission through gas atmospheres is also affected by significant soft X-ray absorption, limiting the X-ray path through the gas phase to several 100  $\mu\text{m}$ . The windows should ideally have thickness below 50 nm of a light material. The sample thickness for soft X-rays must ideally be in the (sub)micron range, dependent also

on concentration and elemental composition. Note that the experiments are transmission experiments implying that the edge energy and concentration of the probed element determines the ideal thickness of the sample.

Because of the X-ray transmission induced sample limitations, traditionally soft XAS spectra have been measured with electron yield detection or fluorescence yield (FY) detection. Yield methods use the core hole decay, which gives rise to electrons and X-rays escaping from the surface of the substrate. Detection of these decay products, allows the measurement of samples with arbitrary thickness. With total electron yield (TEY), one detects all electrons that emerge from the sample surface and due to the electron escape depth of a few nm this turns the TXM into a surface technique. For dilute systems, transmission might not yield a measurable signal and FY is an option. A complication is that the optical component of a TXM microscope is usually very close to the sample, which makes it difficult to use TEY and FY detectors. Soft X-ray TXM is ideally suited to study, in addition to the organic phase (by their C, N, O K edges) also the inorganic phase via their metal edges.

In Fig. 12.1 we compare the spatial resolution and the maximal sample thickness of a TXM experiment with transmission electron microscopy (TEM) combined with Electron Energy Loss Spectroscopy (EELS). TEM-EELS can be considered as



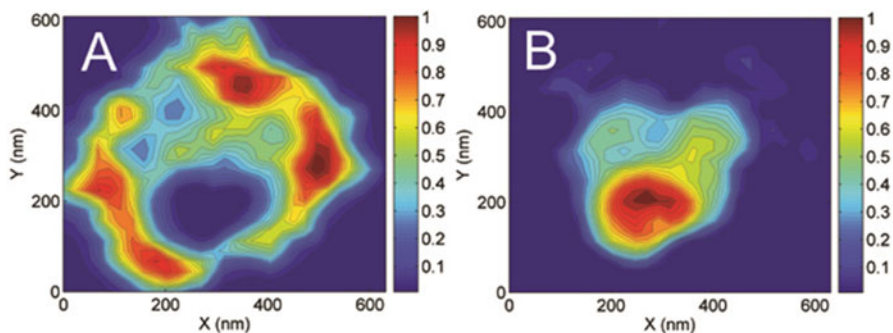
**Fig. 12.1** The range of experimental, spatial resolutions (*pink*) and maximal sample thicknesses (*blue*) are indicated on a logarithmic scale for, from *bottom to top*, TEM-EELS, TXM at 300 eV, TXM at 1.5 keV and TXM at 10 keV. The sample thicknesses is limited by attenuation but also by spectral deformations due to saturation effects. The *red vertical lines* indicate the diffraction limited resolution of the X-rays

the electron analogue of TXM-XAS. The data for TEM-EELS assumes a 100 keV electron beam. The resolution of TEM-EELS is between 0.1 and 0.5 nm, with some possible improvements to less than 0.1 nm [14–16]. The maximal sample thickness for chemical contrast imaging is dependent on the material. TXM experiments have resolution of approximately 10 nm [17], larger than the diffraction limited resolution. The maximal sample thickness of TXM is dependent on energy. In case of edge absorption in the soft X-ray range the sample thickness for which the signal is not distorted can be as low as 50 nm. This does not mean that thicker samples cannot be measured, but the signal will be distorted. For hard X-rays, for example at 10 keV one needs different, thicker, zone plates. Recently hard X-ray zone plates have also reached resolution of 10 nm. The reduced X-ray absorption strength and scattering of hard X-rays increase the possible sample thickness towards the mm range. Hard X-ray microscopy experiments in the micron range are very interesting for catalysis as the hard X-rays allow realistic catalytic conditions.

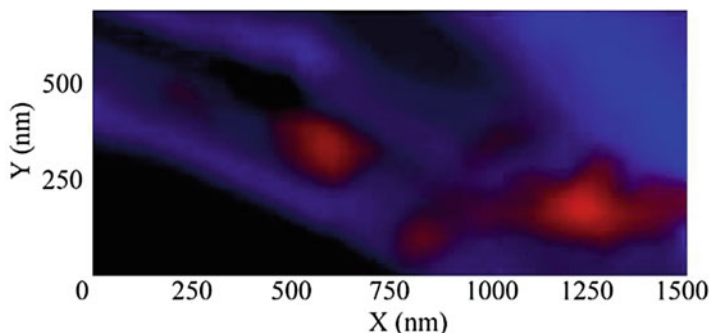
### 12.3 In Situ Soft X-Ray TXM of Catalytic Solids

The first in situ TXM-XAS experiments on a working catalyst have been published in 2008 by de Smit et al. [18]. They measured an iron-based Fischer–Tropsch catalyst under working conditions. The Fischer–Tropsch reaction enables the production of high-purity chemicals and transportation fuels from sources other than conventional crude oil, most notably natural gas, coal, and biomass.

Figure 12.2 shows an example of an  $\text{Fe}_2\text{O}_3$  nanoparticle that was reduced under 1 bar hydrogen pressure. After initial reduction on the outside the reduction is first complete in the interior of the nanoparticle. For the Fischer–Tropsch catalyst the Fe 2p XAS was used to map the iron valence and the oxygen K edge to distinguish between different oxygen-containing species ( $\text{SiO}_2$  and iron oxides; cf. Fig. 12.3). The carbon K edge was measured to image the type and location of carbon species



**Fig. 12.2** Elemental map of (a) iron-oxide and (b) iron metal in an  $\text{Fe}_2\text{O}_3$  nanoparticle after reduction at 250 °C, using the iron L edge STXM XAS spectra. The spatial variation of the reduction is shown



**Fig. 12.3** Elemental map of SiO<sub>2</sub> (*blue*) and Fe<sub>2</sub>O<sub>3</sub> (*red*) of an iron-based Fischer-Tropsch catalyst, using the oxygen K edge and iron L edge STXM XAS spectra

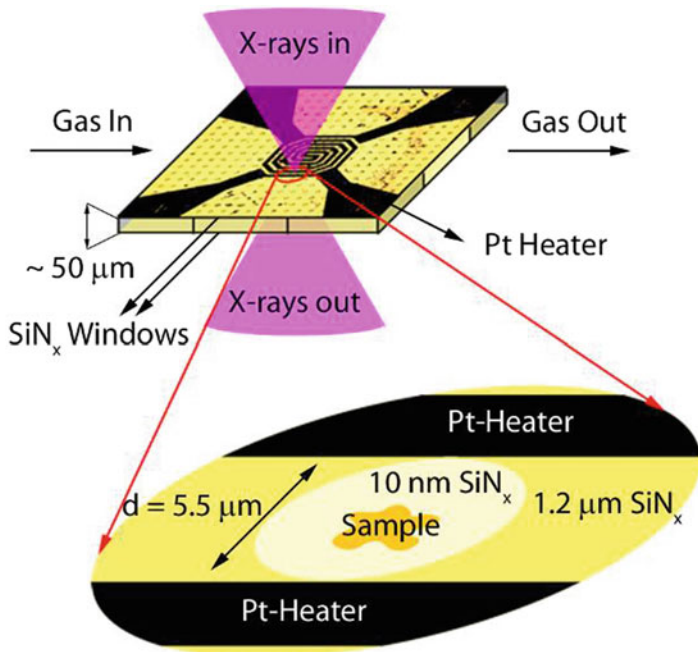
present in the catalyst during reaction. For further details, we refer to the original publications [19]. As such, this nanoscale chemical imaging technique provides insights into the local particle morphology and chemical reduction behavior of a complex Fischer-Tropsch catalyst system.

## 12.4 Nanoreactors

One common goal in the design of nanoreactors is the minimization of the path length that X-rays have to travel through the gas and/or liquid reactant phase. This will minimize X-ray attenuation and yield higher signal intensities. One possibility is to use nanoreactors that are designed for in situ TEM studies [20]. The current design of the cell allows for experiments up to  $\sim 2$  bar and 500 °C (Fig. 12.4).

## 12.5 Comparison of STXM-XAS with STEM-EELS

The main difference between STXM-XAS and STEM-EELS is the significantly stronger interaction with matter of electrons compared with X-rays [21]. Table 12.1 gives a brief overview and in the subsequent paragraphs we briefly discuss these aspects, including energy resolution, energy range, time resolution, spatial resolution, detection modes, detection limits, sample thickness, sample conditions, sample damage, and tomography options.



**Fig. 12.4** Sketch of the nanoreactor windows indicating the spiral heater and the  $\sim 5 \times 5 \mu\text{m}^2$  windows used to investigate the material of interest

**Table 12.1** Overview of the comparisons between STXM-XAS and STEM-EELS

	STXM-XAS	STEM-EELS
Spatial resolution	10 nm	0.1 nm
Energy resolution	0.2–0.6 eV	0.2 eV
Energy range	200–2500 eV	1–1500 eV
Data collection	Single energy	All energies
Detection modes	Transmission (T) Fluorescence Yield (FY) Electron Yield (EY)	Transmission (T)
Sample thickness	200–20,000 nm	<500 nm
Element sensitivity	1000 ppm (T) 10 ppm (FY)	1000 ppm (T)
In situ pressure	1 bar	Vacuum (1 bar in TEM)
Beam damage	High	Very high

### ***12.5.1 Spatial and Energy Resolution***

The spatial resolution can be below 0.1 nm for STEM-EELS microscopes [22, 23], which is a factor 100 better than the spatial resolution in STXM-XAS. The energy resolution of soft X-rays on a STXM beamline is typically  $E/\Delta E = 5000$  and implying better than 0.2 eV resolution at the carbon K edge. De facto this implies that for solids the experimental resolution is mainly determined by the lifetime broadening of the core holes. The energy resolution of EELS varies significantly from microscope to microscope. Most EELS-dedicated microscopes have a core level energy resolution of 0.2–0.5 eV.

### ***12.5.2 Detection Modes and Limits***

In STEM-EELS all core levels are measured simultaneously. In STXM-XAS, the X-ray energy is set to one particular value and only at that energy the X-ray absorption is measured. STXM-XAS can be measured with EY and turned into a surface probe, or it can be measured with FY for dilute species. STEM-EELS and STXM-XAS are transmission experiments and the required contrast for a core level signal implies that spectral shapes of dilute species cannot be measured. As a rule, concentrations above 5000 ppm are required for good spectra.

### ***12.5.3 In Situ Conditions and Sample Thickness***

Soft X-ray STXM can be measured up to 2 bar and up to 550 °C. Hard X-ray experiments can be performed under extreme conditions, including high-pressure diamond anvil cells. STEM-EELS requires a sample less than ~200 nm thin. STXM-XAS can handle samples with thicknesses up to 20  $\mu\text{m}$  at 1.5 keV and in the millimeter range for hard X-rays. The much thicker specimen that can be handled with STXM-XAS offers a wider and more flexible range of materials that can be studied, including objects such as intact biological cells.

### ***12.5.4 Sample Damage***

STEM-EELS requires a high radiation dose in comparison with normal TEM, which implies that sample damage is potentially high, including knock-on damage, carbon deposition, sputtering, and electrostatic charging. In STXM-XAS a highly focused X-ray beam is used, which, especially at resonance, generates large amount

of electrons, yielding damage from electrostatic charging and carbon deposition. Combining all beam damage effects and the required doses for imaging, as a rule it is found that STXM-XAS causes less damage than STEM-EELS [24, 25].

In conclusion, it can be stated that STEM-EELS offers better spatial resolution and the simultaneous detection of all core levels. STXM-XAS can handle large samples and a wider range of sample conditions including catalysis under working conditions.

## 12.6 Future Developments

The temperature and pressure range of STXM will increase to 1000 °C and 10 bar, thereby extending the range of feasible materials science and catalysis experiments. An important future development is the performance of in situ STXM tomographic experiments. STXM of ultra-dilute samples with concentrations down to 100 ppm are not straightforward in transmission mode, implying that fluorescence yield detection must be used. Such fluorescence yield based experiments would allow the mapping of impurities/promoters in heterogeneous catalyst and in materials science in general.

STXM will likely not reach the 0.1 nm spatial resolution as obtained by electron microscopy. STEM-EELS experiments on the other hand will be unfeasible for many samples and for many sample conditions.

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