Editor choice paper

In situ XAS study of the Mn(III)(salen)Br catalyzed synthesis of cyclic organic carbonates from epoxides and CO_2

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ABSTRACT

In situ X-ray absorption spectroscopy at the Mn K- and Br K-edge was employed to study the cycloaddition of carbon dioxide to propylene oxide and styrene oxide, catalyzed by Mn(III) salen bromide complexes. Three homogeneous complexes with varying salen ligand structure and one complex immobilized on silica were used and compared. Ex situ X-ray absorption spectroscopy showed that in all cases octahedral complexes in a distorted symmetry were present and that the bromide ligand was coordinated to the Mn central atom. Under reaction conditions the structure of the catalysts strongly changed. In order to investigate this change, a special spectroscopic batch reactor cell was designed that allowed continuous monitoring of catalyst structure under cycloaddition conditions directly at the synchrotron radiation source, i.e. while maintaining the demanding conditions of elevated pressure and temperature. Complementary XAS investigations on the two key elements of the catalyst, the manganese central atom and the bromide ligand, showed that the coordination sphere of the hexacoordinated manganese central atom changed due to the replacement of the bromo-ligand probably by an epoxide molecule under reaction conditions. This was the case for all three homogeneous catalysts with varying salen ligand structure as well as for the heterogeneous catalyst. In case of the heterogeneous catalyst bromide also went into the solution whereas most of the manganese remained on the solid support. The loss of the direct coordination of the bromine neighbors to the Mn central atom was also evidenced by EXAFS spectra, e.g. loss of Br backscattering in the Mn K-EXAFS spectra and the Mn-backscattering in the Br K-edge spectra. In the catalytic studies it was observed that propylene oxide usually reacted much faster than styrene oxide. This seems to be related to a faster coordination of propylene oxide to the Mn atom, which could be followed in a time-resolved manner at the Br K-edge. On the basis of the analysis of the XANES and EXAFS data together with observations from literature a reaction mechanism is proposed.

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1. Introduction

The use of CO_2 as an environmentally benign, safe, and cheap C_1 building block in synthetic chemistry has gained increasing attention in fine chemistry applications [1–3]. CO_2 can potentially substitute toxic and hazardous reactants, such as phosgene and carbon monoxide [4], and simultaneously serve as solvent with peculiar properties [5–7]. Among other applications, CO_2 is used in the synthesis of organic carbonates from epoxides, both polycarbonates and cyclic carbonates. Cyclic organic carbonates such as

propylene carbonate (4-methyl-[1,3]dioxolan-2-one) are applied in different areas, e.g. as polar and aprotic solvents for lithium batteries, resins, cleaning, and cosmetics, or as intermediate for polymer synthesis [8]. Among the various catalysts that have been developed for the synthesis of cyclic organic carbonates from CO_2 and epoxides, there are several homogeneous and heterogeneized salen (=bis(salicylidene)ethylenediamine) complexes, bearing Al, Co, Cr, Sn, Zn, and other metal centres [9–16]. Recently we reported that also salen complexes of Mn(III) are efficient catalysts for this reaction [17], only yielding cyclic carbonates as products (Scheme 1), and not also polymers, as it is the case for various other salen complexes [18,19].

In order to improve the performance of catalytic systems, it is essential to gain a mechanistic understanding of the catalysts behavior on a molecular level. This can be achieved by appropriate *in situ* spectroscopic experiments, which however turn out to be a demanding task for high pressure reactions such as the Mn(III) salen catalyzed cycloaddition of CO_2 to epoxides. Employing a suitable
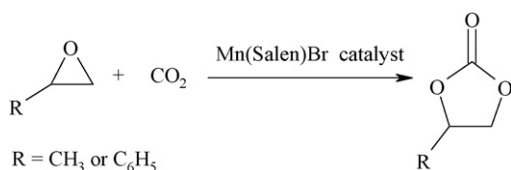
Scheme 1. Reaction scheme for the cycloaddition of carbon dioxide to propylene oxide and styrene oxide, yielding the corresponding cyclic carbonates.

experimental set up, X-ray absorption spectroscopy is a powerful tool for investigating this type of catalyst under reaction conditions. XANES and extended X-ray absorption fine structure (EXAFS) are able to provide detailed information on both key components of the catalyst, the Mn(III) centre of the complex, and the bromide ligand simultaneously, in both cases giving insight to the type of neighboring atoms, the distance (bond lengths) and for manganese the coordination geometry. Furthermore, XAS techniques do not require crystalline samples when probing solids, and they can be applied to liquids and solutions as well. X-ray absorption spectroscopy has been successfully employed in several similar studies, e.g. for the mechanistic investigation of Mn(salen)Br as epoxidation catalyst [20], the structural analysis of immobilized Mn(III) porphyrin systems [21,22], structural *in situ* studies on MnBr$_x$ in supercritical water [23], and for various biological and geological applications, e.g. [24,25].

The aim of this study was to investigate the behaviors of Mn(salen)Br and two homogeneous derivates of this catalyst under reaction conditions, as well as that of such a complex immobilized on silica, in the cycloaddition reaction of CO$_2$ to the model substrates styrene oxide and propylene oxide. For this reason, suitable spectroscopic batch reaction cells were employed. Based on the data obtained from the Mn K-edge and Br K-edge X-ray absorption spectroscopy experiments, a reasonable reaction mechanism could be proposed, adding further understanding to the results obtained previously on catalytic results, phase behavior, and IR-spectroscopy.

2. Experimental

2.1. Materials

The synthesis of the Mn(III)-complexes **1a**, **1b**, **1c**, and **2** as depicted in Scheme 2 as well as their structural analysis is described in [17]. The substrates propylene oxide (99%, Acros Organics), and styrene oxide (98%, Acros Organics), were used as received without further purification. Liquid carbon dioxide, supplied by Air Liquid at the synchrotron radiation beamline, was of purity 99.995%. Diethyl ether (99.8%, Fluka) and *tert*-butylbenzene (+98%,

Aldrich), employed for GC-analysis of the products, were also used as received.

### 2.2. X-ray absorption spectroscopy

The X-ray absorption experiments were performed at the beamline X1 at HASYLAB (Hamburg, Germany) and at the ANKA-XAS beamline (Karlsruhe, Germany). Due to different beamline characteristics, the former was mainly used for the Br K-edge experiments, whereas the latter was more optimized for Mn K-edge experiments at lower X-ray energy. All spectra were collected in transmission mode, using ionization chambers with the appropriate gas mixture fillings. The raw data were energy-calibrated, background-corrected, and normalized using WINXAS 3.1 software [26]. For the Mn K-edge measurements, manganese foil was used as reference. A platinum foil (Pt L$_{II}$-edge) was used for energy calibration at the Br K-edge. The $\chi(k)$ function was extracted from the EXAFS data, and a Fourier-transformation was performed on the k^3-weighted data in the interval $k = 3.0$–$12.5\,\text{Å}^{-1}$ for the Mn K-edge spectra. For the Br K-edge, the intervals are listed in Table 1. Data analysis in the R-space was performed using Br–Mn and Br–C shells calculated by FEFF 6.0 [27]. Only the first coordination shells were used for the fittings.

2.2.1. Ex situ XAS measurements

The catalysts **1a**, **1b**, **1c**, and **2** were measured as synthesized by pressing them into pellets (optimized to an edge jump $\mu d = 1.5$), embedded in a polyethylene matrix. Liquid 1-bromo-2-propanol was measured in a specially built transmission cell for liquids, bearing Kapton$^{\text{TM}}$-windows.

2.2.2. In situ XAS measurements

For the *in situ* experiments, a specially designed batch reactor for X-ray absorption spectroscopy was used, similar to the setup reported in ref. [28]. The stainless steel 10 mL-cell is equipped with two pairs of beryllium windows (5 mm × 1 mm) at different heights, allowing the investigation of a solid catalyst at the bottom of the cell through the lower windows, and the liquid phase 10 mm above through the upper windows. The cell has a much narrower diameter at the bottom, thus offering a very short path length for XAS measurements of solid catalysts at the bottom. These windows were only used when employing the immobilized catalyst **2**. For the homogeneous catalysts, only the upper windows with the longer path length were used at the Br K-edge, in order to gain better signal-to-noise ratio, also due to the dilution of the catalyst by epoxide and CO$_2$. The cell can withstand a pressure up to 250 bar and temperature up to 200 °C. Furthermore, the reactor is equipped with a magnetic stirrer, inlet and outlet valves, a burst plate (190 bar), and a thermocouple. For the *in situ* measurements
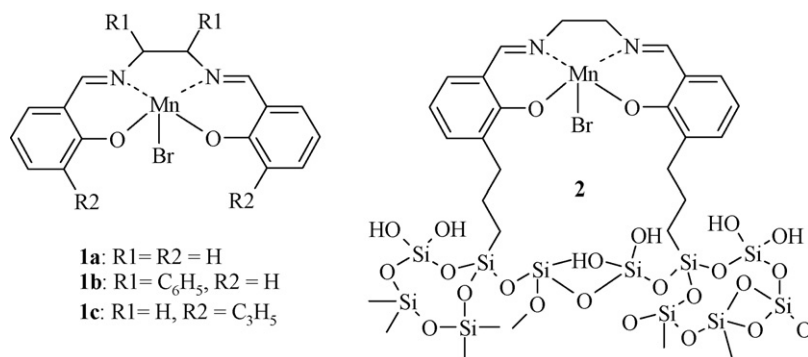
Scheme 2. Overview on the homogeneous and heterogenized manganese salen complexes used in this work. The nomenclature given is used throughout the paper.

Table 1
Structural parameters of the catalysts **1a** and **1b** determined from the *in situ* Br K-edge EXAFS spectra.

Catalyst	A–B[a]	r[b] [Å]	S_0^2[c]	N[d]	σ^2[e]	ΔE_0[f] [eV]	Residual[g]	k-range [Å⁻¹]
1a	Br–Mn	2.581	1.0	0.70	0.006	−4.51	3.86	2.5–12.0
As-synthesized	Br–C	–		–	–	–		
After addition of styrene oxide	Br–Mn	2.754	1.0	0.65	0.006	−3.93	4.19	2.5–12.0
	Br–C	–		–	–	–		
After addition of CO₂	Br–Mn	2.553	1.0	0.60	0.004	−7.25	5.08	2.5–12.0
	Br–C	–		–	–	–		
After reaction	Br–Mn	2.799	1.0	0.05	0.009	6.37	6.01	2.5–11.0
	Br–C	1.920		1.70	0.006	2.47		
1b	Br–Mn	2.548	1.0	1.01	0.007	3.72	3.36	2.5–14.0
As-synthesized	Br–C	–		–	–	–		
After addition of propylene oxide	Br–Mn	2.720	1.0	0.01	0.008	−0.40	2.60	2.5–13.0
	Br–C	1.951		1.12	0.004	3.52		
After reaction	Br–Mn	–	1.0	–	–	–	1.29	2.5–11.5
	Br–C	1.934		1.16	0.006	1.13		
1-Bromo-2-propanol	Br–C	1.957	1.0	1.01	0.003	6.83	6.18	2.5–14.0

[a] Absorber–Backscatterer pair.
[b] Distance.
[c] Amplitude reduction factor.
[d] Coordination number.
[e] Debye–Waller factor.
[f] Shift of the energy threshold.
[g] Residual indicates the quality of the fit (details, ref. [26]).

at the Mn K-edge, more modifications were necessary. At this low energy, the absorption of the surrounding air had to be taken into account and an aluminium box was built that surrounded the whole reactor, with a diameter of 20 cm, and with slits that were aligned with the windows of the reactor. A 30 cm tube along the direction of the beam was connected to that box on one side, leading directly to the ionization chamber. The metal box and the tube could be filled or flushed with helium, and the critical absorption of the X-rays by air therefore diminished.

For a typical experiment, a defined amount of solid catalyst (ca. 25 mg) was put into the reactor, either by pressing a pellet of the pure substance and putting it at the bottom (immobilized catalyst), or by dissolving it in 1 mL of liquid epoxide and pouring the solution inside (homogeneous catalysts). Then, 1–2 mL of epoxide was added to reach a total liquid volume of 2 mL, and the reactor was closed carefully. A first X-ray absorption spectrum (XAS) was taken at this stage. After that, ca. 1.5 g of liquid CO₂ was added, measured by a Rheonik mass flow controller and previously compressed by an attached compressor (PM-101, NWA). The reactor was then heated to 140 °C after recording another spectrum. Subsequent spectra were taken during heating and while remaining at the reaction temperature, which was maintained for 3–5 h. When the heating source was turned off, the reactor cooled down gradually and more spectra were recorded. The product mixture was measured a last time at room temperature after releasing the CO₂ pressure, and the product mixture was analysed by GC (see above).

Safety note: The experiments described in this paper involve the use of high pressure and require equipment with an appropriate pressure rating and safety mechanisms including burst plates, particularly if the experiment is performed at a synchrotron radiation source.

3. Results

3.1. Mn K-edge XANES

The XANES (X-ray absorption near edge structure) region of an XAS provides information on the first coordination shell of an absorbing atom, such as coordination geometry and oxidation state [29]. The X-ray absorption edge position thus indicates the charge of the excited atom, but this can be misleading, since it is also strongly affected by the coordination geometry [30]. More reliable information on the oxidation state and coordination geometry can be obtained from pre-edge features, which are sometimes observable some electron volt before the actual absorption edge and are caused by the transitions of electrons from the inner shells (here 1 s) to unoccupied states, such as 3d [30]. The strength of these pre-edge features strongly depends on the coordination symmetry around the excited atom [31]. Thus such features can provide valuable information about symmetry changes at for example the manganese central atom in salen complexes studied in this work.

The Mn K-edge XANES spectra of catalyst **1a** recorded during the cycloaddition of CO₂ to styrene oxide are depicted in Fig. 1. The changes in the absorption edge occurred already after addition of the epoxide, resulting in a decrease in the post-edge absorption at 6562 eV. Simultaneously, the absorption edge shifted a little towards lower energies, compared to the as-synthesized catalyst. This trend increased when CO₂ was added to the mixture. During heating to reaction temperature, the whole absorption edge shifted further down towards lower energies, while forming a more prominent white line. The post-edge absorption at 6562 eV decreased more. The XANES spectra remained in this form, and did not change anymore even after cooling down and releasing of the CO₂ pressure. The pre-edge feature observable as little peak at 6534 eV did not change drastically neither in shape nor in position during the whole *in situ* experiment.

Corresponding changes in the XANES spectra could be observed when catalyst **1c** was employed in the same reaction (Fig. 2). Similarly, the initial post-edge absorption at 6562 eV of the pure catalyst decreased gradually after addition of styrene oxide and CO₂, and the formation of a white line feature at 6541 eV were observed. The white line increased with reaction time, while the XANES after the edge jump showed the same ongoing decrease in absorption as in the first experiment. After 3 h at 140 °C the spectra remained constant, a longer reaction time of 5 h did not lead to further changes in the XANES spectra.

The covalently immobilized catalyst **2**, synthesized from catalyst **1c** as precursor, also showed a similar development in the Mn K-edge XANES (Fig. 2), with a slight shift of the edge jump towards lower energies upon addition of styrene oxide and CO₂, and the formation of a white line. In this case, however, the XANES of the as-synthesized catalyst already looked more like the catalyst after
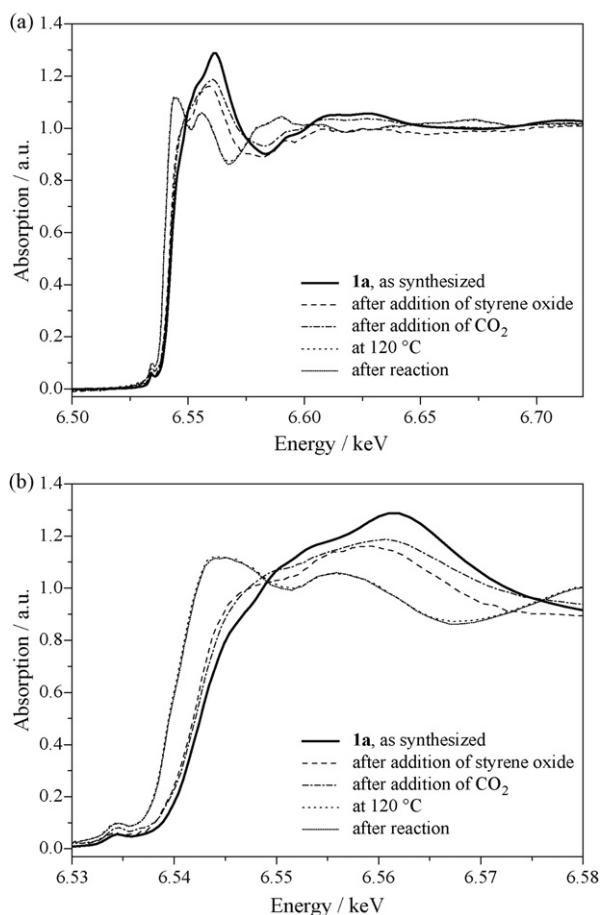
Fig. 1. *In situ* XANES spectra of catalyst **1a** at the Mn K-edge (a) and a more detailed view on the XANES region (b).

epoxide addition, compared to the previous experiments. Interestingly, the white line did not increase in intensity with the ongoing reaction, but decreased instead, after having shown a maximum when styrene oxide had been added. On the other hand, the pre-edge feature at 6534 eV did not change and showed a very similar behavior as in the experiments with the homogeneous catalysts.

3.2. Br K-edge XANES

In order to obtain complementary information about the behavior of the catalysts under reaction conditions, several *in situ* X-ray absorption experiments at the Br K-edge were performed. The XANES spectra obtained during the cycloaddition of CO_2 to styrene oxide, catalyzed by **1a**, are shown in Fig. 3. Changes in the spectra are mainly observable around the white line, which somewhat decreases continuously upon addition of styrene oxide and CO_2, and under reaction temperature. After the edge jump, some increase in absorption at 13,487 eV could also be observed. After reaction, the XANES spectra looked considerably different. The white line decreased drastically and the shape of the spectra after the edge jump showed a maximum in absorption at 13,480 eV.

Similar results were obtained with catalyst **1b** and propylene oxide as substrate (Fig. 3), also finding a decrease in the white line and an increase in absorption after the edge jump at 13,487 eV. There is however a remarkable difference. In this experiment, the XANES spectra changed already after addition of the epoxide in a way similar to the spectra of the previous experiment, but there only after a certain reaction time at 140 °C (Fig. 3). Obviously, the

Br-atom changes its coordination sphere much faster when using propylene oxide instead of styrene oxide. This agrees well with the fact, that styrene oxide shows a much longer initiation time than propylene oxide in the Mn(salen)Br-catalyzed reaction with CO_2, as reported in [17]. The spectra remained similar after the epoxide addition, with only minor differences.

The XANES spectra of the reaction with styrene oxide, catalyzed by the immobilized complex **2**, are depicted in Fig. 4. In this experiment, the two Be windows of the batch reactor were used alternately (as described in Section 2). The lower window was situated directly at the bottom of the reactor and allowed analysis of the solid catalyst during reaction. The liquid phase was monitored through the upper window. By turning the stirring off while the spectra were taken, formation of a suspension in front of the upper window could be minimized. The XANES spectra taken through the lower window (Fig. 4, top) show distinct changes after addition of styrene oxide, which become slightly more pronounced after CO_2-addition, as seen similarly in the previous experiments. Interesting in this case however is the observation that the spectra recorded at 140 °C and after the reaction resemble more the spectrum of the as-synthesized catalyst. The spectra recorded through the upper window (Fig. 4, bottom) also show drastic changes in the Br-coordination sphere during the reaction, the spectrum of the as-synthesized catalyst is included for comparison. The spectrum recorded after the addition of styrene oxide shows a striking post-edge absorption similar to the other spectra taken during reaction, but far more prominent. Directly after the edge jump, a shoulder is also observable. This spectrum is comparable to XANES spectra reported for Br–C bonds [32], thus indicating the formation of a Br–C bond in the liquid phase. The spectra taken at 140 °C and after reaction compare well to the spectra from the lower window. It seems that the shapes of the XANES spectra reflect different Br-coordination spheres present at the same time, but with changing ratios, depending on the actual conditions at a certain moment of the reaction. At the bottom of the reactor there is a fast change of the Br-coordination from Br–Mn to Br–C, resulting in the distinct change depicted in the top of Fig. 4. When the reaction proceeds, the Br–C species are gradually diffusing into the liquid phase on top, leaving behind some unreacted catalyst, and thus leading to X-ray absorptions that contain a higher fraction of Br–Mn contributions. At the upper window, there is initially only an absorption visible that indicates Br–C coordination, but later on changes towards a mixture of both Br–C and Br–Mn. This indicates that either parts of the immobilized complex are leached out of the support and dissolve in the liquid phase, or that fine catalyst particles are suspended in the liquid phase or deposited on the upper windows of the cell.

3.3. Mn K-edge EXAFS

EXAFS spectroscopy provides additional structural information from the post-edge part of the XAS spectra, especially on bond length, coordination number, and nature of scattering atoms around the absorbing center [33,34].

The Fourier-transformed k^3-weighted EXAFS spectra at the Mn K-edge are shown in Fig. 5, obtained from the experiments with catalysts **1a** and **1c**. In all cases, the main contribution stems from the N and O neighbors in the salen ligand. The strong chelating effect of this ligand prevents the Mn center from leaving the complex; therefore this contribution is the main feature in all the spectra. Unlike the Br K-edge EXAFS (vide infra), the *in situ* Mn K-edge EXAFS spectra were poorer in quality. This is due to the fact that the X-ray attenuation length decreases from the Br K-edge down to the Mn K-edge from 6 mm to less than 1 mm considering pure liquid carbon dioxide as solvent. Moreover, the extracted k-range
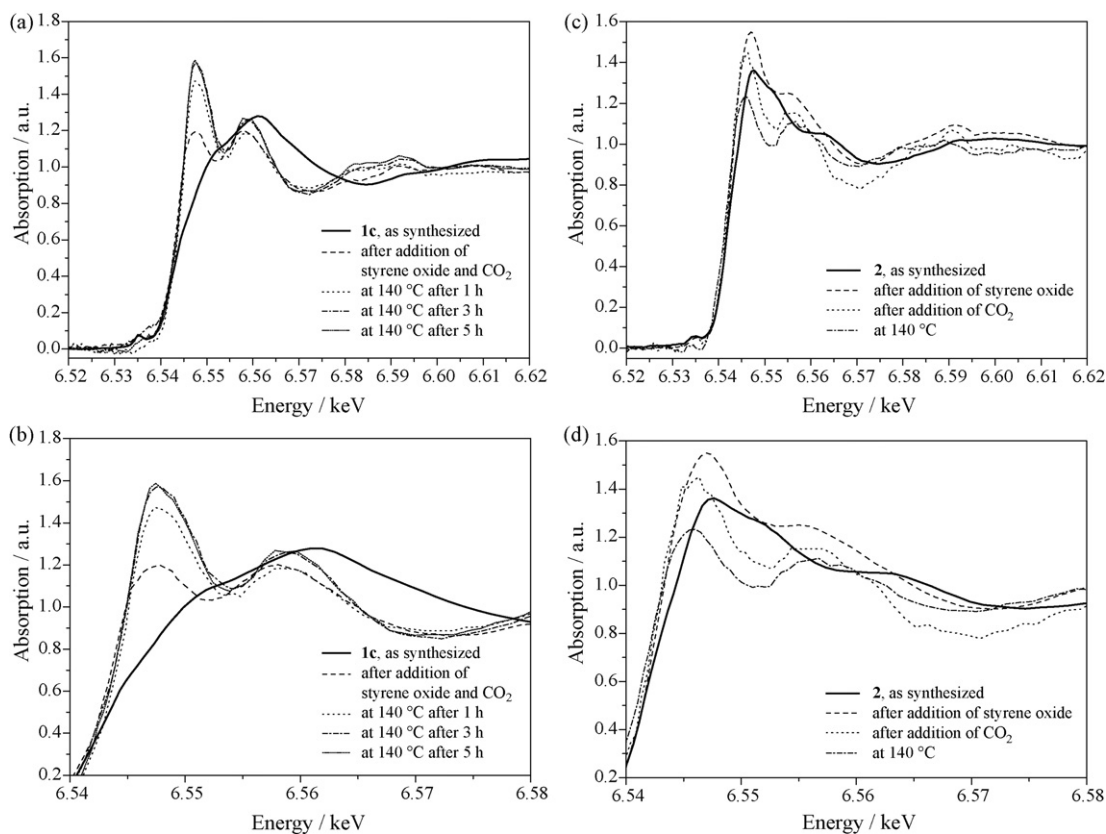
Fig. 2. *In situ* XANES spectra at the Mn K-edge of homogeneous catalyst **1c** (a), a detailed view on the edge region (b), and immobilized catalyst **2** (c), including a detailed view on the edge region (d). In both experiments, styrene oxide was used as substrate.
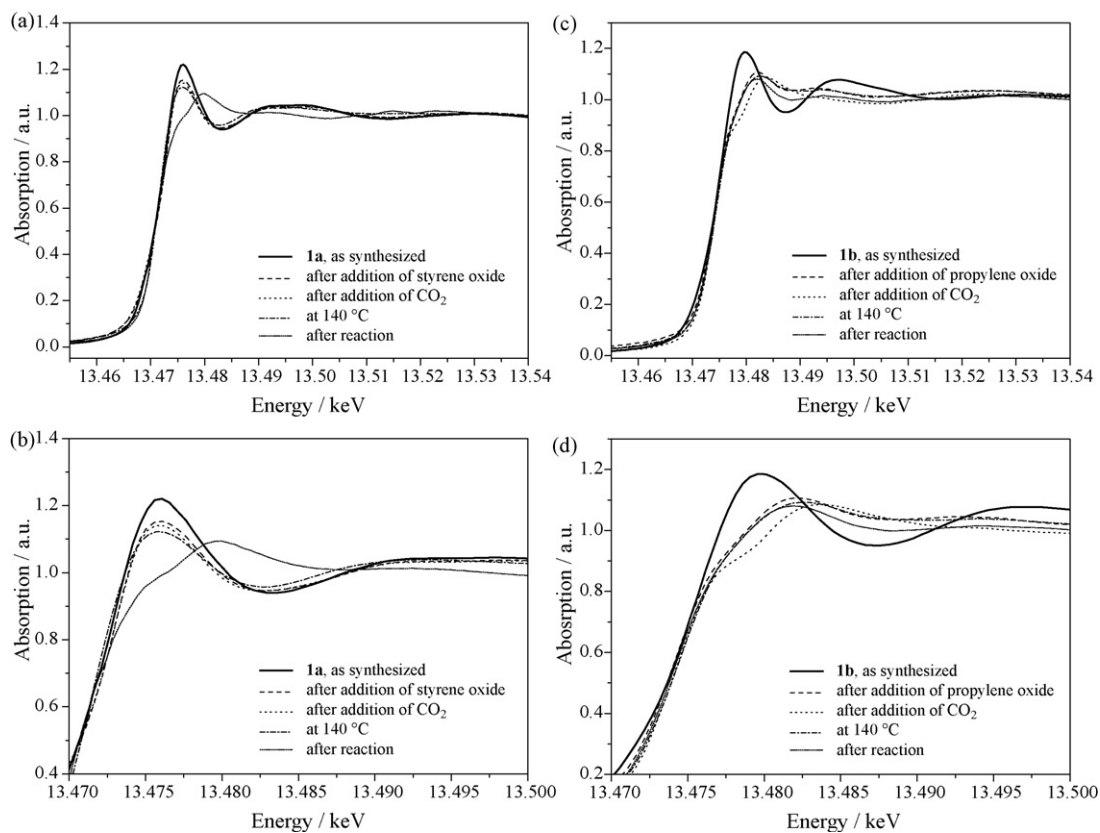

Fig. 3. *In situ* XANES spectra at the Br K-edge. (a) Catalyst **1a** with styrene oxide, (b) detailed view on the edge region. (c) Catalyst **1b** with propylene oxide, (d) detailed view on the edge region.
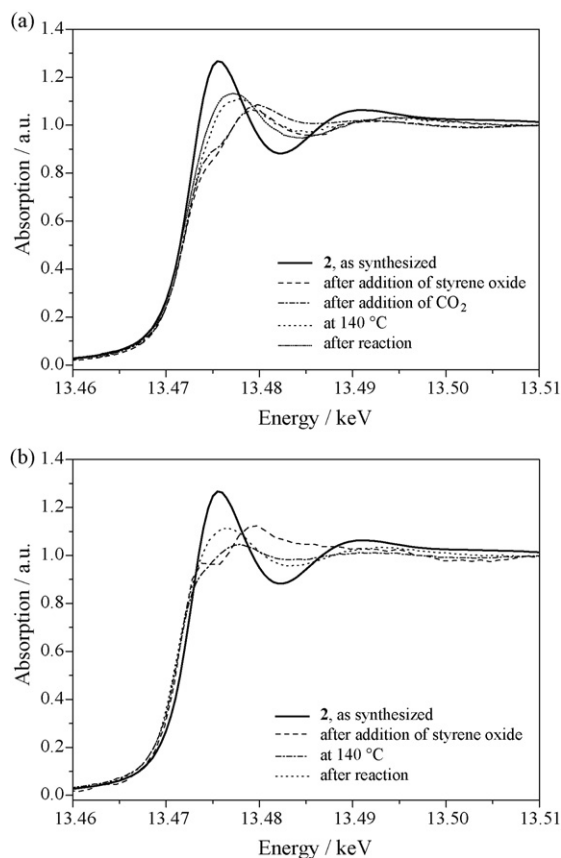
Fig. 4. *In situ* XANES spectra at the Br K-edge of immobilized catalyst **2**. A spectroscopic cell with two windows was used, one monitoring the solid catalyst at the bottom (a), the other monitoring the liquid phase on top (b).

Fig. 5. Fourier transformed *in situ* EXAFS spectra at the Mn K-edge. (a) Catalyst **1a** during the reaction cycle, (b) catalyst **1b**. In both cases, the contribution of the Br backscatterer at approximately 2.5 Å vanishes during reaction.

of 3–12 Å^{-1} allows only the fitting of maximal 2 shells [35] which gave not meaningful results since at least 2 oxygen shells and one bromine shell are present. As a qualitative comparison however, and as complementary information for the Br K-edge EXAFS, it provides additional information, especially when compared to published EXAFS studies on a similar Mn(III)-complex [20] and Mn(III)-porphyrin systems [21]. The peak at around 2.5 Å, visible in Fig. 5 in the as-synthesized catalyst spectrum, can be assigned to a bromine backscatterer, as reported in [20], where the peak vanished when two equivalents of an oxo-ligand was added to the complex, and bromide left the coordination sphere of Mn. Also in this present work, this peak at 2.5 Å decreases or vanishes upon addition of epoxide and further progress of the reaction, and it is thus strongly indicating that bromide is also leaving the complex in a very similar manner. The spectra depicted in Fig. 5 show a gradual decrease of this peak over the whole reaction. At the same time, the N/O-contribution of the salen ligand is shifted towards longer distances. This might be an indication that the Mn-center of the complex is being slightly moved out of the plane of the salen ligand, due to changing axial ligand coordination.

3.4. Br K-edge EXAFS

EXAFS analysis at the Br K-edge provides valuable information on the coordination sphere of the bromide during reaction, adding complementary information to the XAS data obtained at the Mn K-edge. Furthermore it generates more accurate data due to the higher absorption energy, which is less sensitive towards unwanted absorption by the oxygen-rich reaction medium.
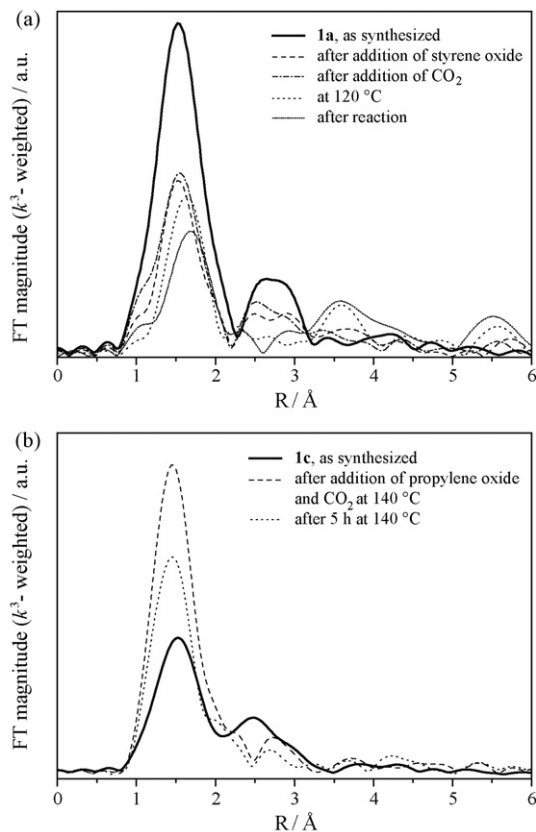
The EXAFS results of the *in situ* experiment with catalyst **1a** and styrene oxide are shown in Fig. 6. After addition of styrene oxide, the spectrum still widely resembled the spectrum of the unused catalyst. The strong signal at 2.6 Å is typical for the Br–Mn distance in such Mn(salen)Br-complexes [20], thus this indicates that bromide was still coordinated to the Mn center of the complex directly after addition of styrene oxide. Also after CO_2 was added, the signal at 2.6 Å was the most prominent one, but there occurred a change at shorter distances, shifting the signal at 1.2 Å towards larger distance values. When the reaction mixture reached 140 °C, the Br–Mn distance disappeared in the somewhat noisy spectrum, and only the increasing shorter distance between 1 and 2 Å was observable. At the end of the reaction, this signal was by far the most dominant, at a distance of 1.9 Å, corresponding well to typical Br–C distances in brominated hydrocarbons [32].

The Br K-edge EXAFS results of the *in situ* experiments with catalyst **1b** and propylene oxide are depicted in Fig. 6. As in the experiment with **1a**, the fresh catalyst **1b** showed a dominant signal at 2.6 Å, corresponding to the typical Br–Mn distance expected in this complex. Addition of propylene oxide at room temperature however led to a complete disappearance of this signal. This is in strong contrast to the experiment with styrene oxide and indicates that propylene oxide reacts much faster with the complex, or at least does not require high temperatures. Instantaneously a new signal at 1.9 Å became visible. This signal remained dominant through the whole reaction time and after reaction. For comparison, also 1-bromo-2-propanol dissolved in propylene oxide was measured in an additional experiment. This compound has a strong structural resemblance to the expected
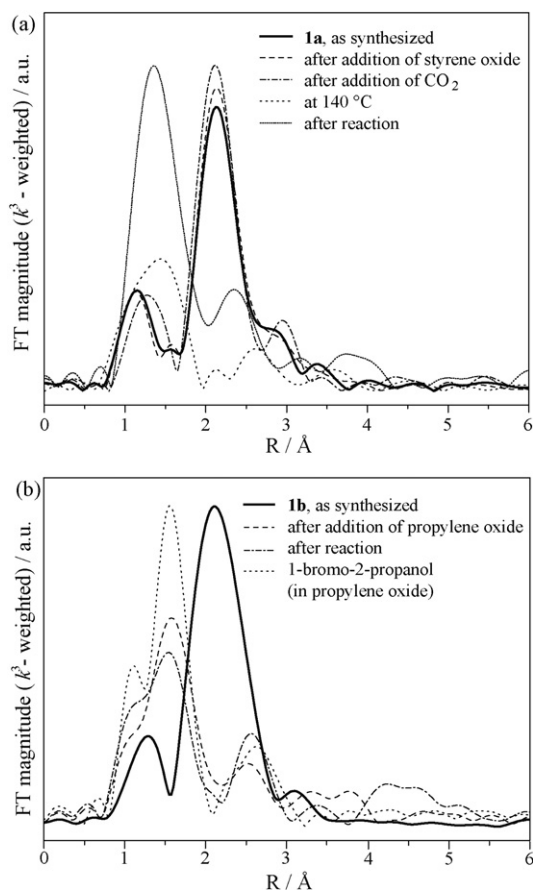
Fig. 6. Fourier transformed *in situ* EXAFS spectra at the Br K-edge. (a) Catalyst **1a** with styrene oxide, (b) catalyst **1b** with propylene oxide and 1-bromo-2-propanol for comparison. The Br–Mn distance at approximately 2.5 Å vanishes in both cases during reaction, but takes considerably longer in the case of styrene oxide.

intermediate in the assumed catalytic cycle (Scheme 3), where the bromide leaves the complex to perform a nucleophillic attack on the epoxide with subsequent ring-opening. The Fourier-transformed EXAFS spectrum of 1-bromo-2-propanol indeed showed a striking alikeness to the spectra obtained during and after reaction of this experiment, with a dominant signal at 1.9 Å for the Br–C distance.

4. Discussion

4.1. Mn K-edge XANES and EXAFS

The spectral information obtained by the *in situ* XANES measurements at the Mn K-edge for the catalysts **1a**, **1c**, and **2** provides important insight into the coordination geometry of the Mn(III) central atom of the catalysts. First of all, the pre-edge feature at 6534 eV did not change during reaction. This is clearly visible for catalyst **1a**, and substantiated also by the results of the other two catalysts. As reported in literature [20,36,37], this feature stems from an electron transition from the 1s core level to the empty 3d levels of Mn and is strongly affected by the coordination geometry of the complex, in this case clearly being a distorted octahedral or square pyramidal Mn(III) complex. Tetrahedral Mn(III) complexes or square pyramidal complexes with a higher oxidation state of Mn would exhibit a much more prominent pre-edge feature [20,23,38]. Mn(salen)Br and its derivates show a strong affinity to oxygen lig-

ands, which coordinate readily to the free coordination site trans to the halide ligand even during synthesis of the complexes, leading to water and other solvent molecules in the crystal lattice, as reported in several crystallographic publications [39–41]. The elemental analysis of the complexes used in this work also revealed such phenomena, depending on the synthetic route [17]. This facile coordination of an additional ligand is especially also true in solution, if the solvent has a coordinating oxygen atom, as it is the case for the epoxides used in this work. The observation of this persistent pre-edge feature and its negligible changes indicate therefore, that a distorted octahedral structure is most likely present during the whole catalytic cycle, regardless of whether the halide leaves the complex or not. This means that if the bromide leaves the coordination sphere of the manganese central atom, it has to be replaced immediately by another ligand, in this case an epoxide molecule. A bromide-free tetrahedral Mn(salen)$^+$ is obviously not present.

The observed formation of a white line and the changes after the absorption edge of the Mn K-edge XANES spectra of the catalysts **1a**, **1c** and **2** are more difficult to interpret. In all three experiments, the addition of styrene oxide and the subsequent addition of CO_2 led to an increasing white line, and simultaneously a decrease in the broad absorption maximum after the edge jump. This effect became more prominent with heating and progressing reaction time, thus supporting the assumption, that bromide is subsequently replaced by another ligand, most probably styrene oxide. This would certainly lead to changes in the edge- and post-edge structure, since the relatively heavy bromide is a much stronger backscatterer than oxygen-containing molecules. The white line was much more pronounced in the experiment with the allyl-substituted Mn(salen)Br **1c** than with standard Mn(salen)Br **1a**. This might be an indication that in the former case, the ligand might have different electronic properties due to the allylic substituent in ortho-position to the oxygen-atom on the aromatic ring of the ligand, or a different conformation due to steric effects of the substituent, leading to a slightly different coordination geometry and therefore slightly different electron scattering behavior. This remains, however, highly speculative. Accordingly, also the immobilized catalyst **2** showed such a distinct white line feature. This catalyst was synthesized from **1c** as homogeneous precursor [17].

The Fourier-transformed EXAFS spectra at the Mn K-edge have a certain limit in their interpretation, given the fact that the absorption of carbon dioxide is relatively high (cf. Section 3.2). Bertagnolli and coworkers reported a thorough EXAFS study on Mn(salen)Br in connection with its use as epoxidation catalyst [20]. Compared to their study, the bromide backscatterer was significantly less prominent in the present fresh catalyst, although elemental analysis confirmed a complete complexation of bromide in the catalyst sample [17]. This can be explained with the fact, that water molecules from the synthesis of the catalyst are coordinated to the manganese atom, forming a distorted octahedral structure rather than square pyramidal coordination geometry with five ligands [39,40]. Bertagnolli et al., who used a different synthetic route yielding the solvent-free crystalline catalyst, also lost considerable contribution from the bromine backscatterer when they added an equimolar amount of an oxygen-containing ligand, which formed octahedral coordination geometry. Only when two equivalents of the oxo-ligand were added, the bromide backscatterer contribution vanished completely. In our case, this also happened in both experiments while the reaction proceeded (Fig. 5), at the end of the reaction showing no more contribution at the Mn–Br distance of 2.5 Å. This might therefore be a reasonable indication that the bromide ligand leaves the complex during reaction.

L = epoxide or solvent from synthesis
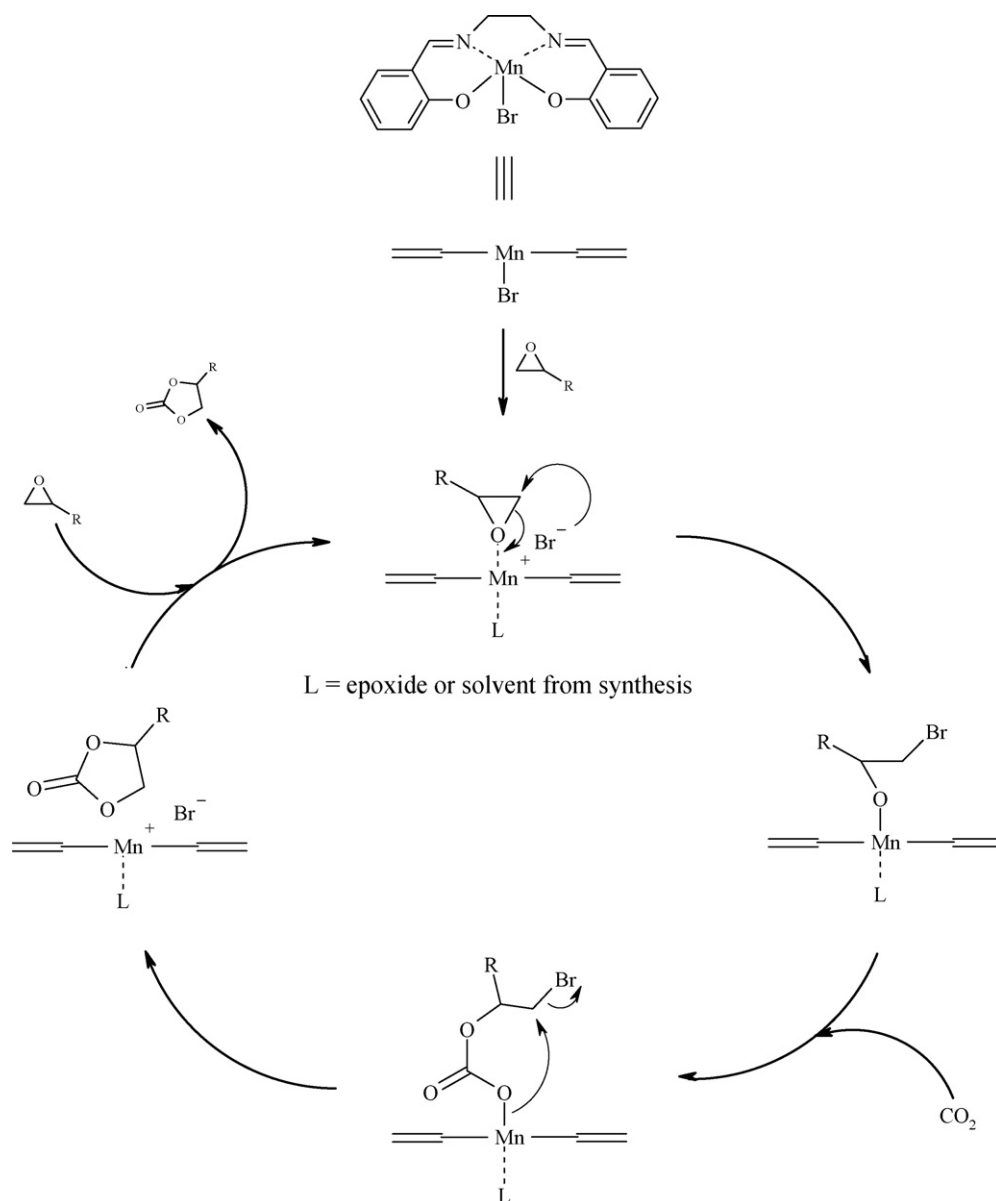
Scheme 3. Proposed mechanism of the catalytic cycle based on the data obtained by X-ray absorption spectroscopy. For the manganese salen complex, a simplified model (see top of the scheme) is used for clarity.

4.2. Br K-edge XANES and EXAFS

The *in situ* Br K-edge XANES spectra were generally of better quality than the spectra at the Mn K-edge, since the considerably higher edge energy of Br is less prone to absorption by surrounding media, such as CO_2-expanded liquid epoxide in this case. In general, it is reasonable to assume that different Br species are present at the same time, thus generating spectra, which cannot be directly related to those of pure substances. This is especially observable in the experiment with the immobilized catalyst **2** (Fig. 4), as mentioned in Section 3.2. In that case, the spectra taken at both window positions at the end of the reaction resemble the initial spectrum of the unused catalyst. This was not observed in the other experiments with the homogeneous catalysts. So it is more likely that considerable amounts of the immobilized catalyst remained idle in its as-synthesized state during the whole reaction, rather than the bromide would have been coordinated again to the manganese atom after reaction. The reason for this might be that during the

immobilization process a considerable amount of catalytic centres were created, which are not accessible due to steric hindrance. When the spectra after reaction at ambient pressure were measured, those species could have had a remarkable influence on the absorption spectra, perhaps due to deposition of catalyst material on the windows of the cell. The XANES spectra during reaction, which exhibit a shoulder on the absorption edge, have a strong resemblance to spectra of brominated aliphatic and aromatic compounds measured by Meyer-Klaucke and coworkers [42]. In the same publication, also NaBr was measured for comparison, which shows a very similar absorption spectrum to the as-synthesized catalysts used in this work. This supports the assumption, that indeed Br–C bonds are formed in a step of the catalytic cycle.

The observations made in the Fourier-transformed Br K-edge EXAFS spectra additionally support this hypothesis. The Mn–Br distance at 2.57 Å, typical for Mn(salen)Br complexes, vanished completely in both experiments during the reaction. Simultaneously, the signal at 1.9 Å, typical for Br–C distances, increased

while the reaction proceeded. Therefore, also these observations strongly indicate the formation of Br–C compounds on the expense of decreasing amounts of Br–Mn species. The Fourier-transformed k^3-weighted EXAFS spectrum of 1-bromo-2-propanol in propylene oxide, which strongly resembles those of the *in situ* experiments with catalyst **1b** and propylene oxide, furthermore supports the assumption that a brominated propanol-like intermediate is present during the catalytic cycle.

4.3. Mechanistic considerations

The observations and conclusions made from analysis of the XAS data together with other studies in literature allow proposing a catalytic cycle, which is shown in Scheme 3. An important observation, which is taken into consideration, is that the bromide ligand leaves the transition metal centre in a rather early stage. Several other publications on this reaction, but catalyzed by different transition metal salen complexes, report very similar catalytic cycles, but with the halide ligand (or an added nucleophile) remaining coordinated to the central atom during reaction [43,14,13,44,9]. To our knowledge, there is no other manganese salen system reported as catalyst in the cycloaddition of CO_2 to epoxides, but it appears that the mechanism is similar to the previously studied trivalent Al, Co, and Cr salen systems [19,45,46]. In a first step, when the complex is dissolved in liquid epoxide, at least one epoxide molecule is coordinated to the Mn central atom, leading to octahedral coordination geometry. This is supported by observations of the pre-edge feature of the Mn K-edge XANES. Apart from that, calculations on chromium salen complexes show that any free coordination site on a five-coordinate complex of that kind is rapidly occupied by an epoxide molecule, certainly in neat epoxide, as it is also the case in this present study [19]. This fact is further corroborated by several publications on manganese salen complexes, where often solvent molecules occupy the free position even in crystalline samples [39–41]. When propylene oxide is used as substrate, also the bromide ligand is quickly replaced by another epoxide molecule. In styrene oxide, this step takes longer or needs higher temperature. This assumption is supported by comparison of the Fourier-transformed *in situ* EXAFS experiments at the Br K-edge, which only show an instantaneous decrease in the signal at the Br–Mn distance in case of propylene oxide addition. The simultaneous or subsequent nucleophillic attack of bromide on the coordinatively activated epoxide molecule, yielding a brominated, manganese-bound intermediate, is supported by the observed formation of Br–C bonds and a striking alikeness of the corresponding EXAFS spectra to that of 1-bromo-2-propanol. In a following step, carbon dioxide is inserted, forming a coordinated carbonate species which still contains a C–Br bond. This CO_2-insertion is not observable by X-ray absorption spectroscopy, since the probe atoms Mn and Br do not change their coordination sphere. This insertion step is however very likely, as calculations (low energy barrier for those comparable systems) on chromium and aluminium salen complexes indicate [19]. Also several experimental works suggest this step (e.g. Refs. [13,14,47]). The following intramolecular attack of the manganese-bound oxygen atom onto the brominated carbon atom, resulting in the formation of the cyclic carbonate and bromide as leaving group, is referred to as "backbiting" mechanism [19,48]. This is in contrast to the chain-propagation step, desired in those cases for the production of copolymers. This intramolecular reaction step, forming the cyclic carbonate product, is favoured by high reaction temperatures as used in our experiments, as well as by other factors such as pressure, metal centre and nucleophile used, as thorough studies by Rieger and coworkers [19] indicate. In the case of Mn(salen)Br however, we previously reported catalytic results containing a wide range of parameter studies on temperature, CO_2-pressure and varying

nucleophiles, where never polymers were obtained as by-product [17]. These complexes might therefore exhibit an extraordinary selectivity towards the cyclic carbonate product, similar to Al, Fe or Zn salen complexes [19]. In a last step, the cyclic carbonate is replaced by another epoxide molecule and the catalytic cycle restarts. The bromide is in agreement with the X-ray absorption experiments not coordinating again to the manganese atom once it has left the complex. This also explains, why immobilized catalyst **2** shows a fast deactivation in repetitive use, but can be almost completely regenerated by addition of a bromide salt [17].

5. Conclusions

In situ XAS proved to be a well-suited technique for investigating the mechanism of the cycloaddition of carbon dioxide to epoxides catalyzed by manganese salen bromide complexes on a molecular level. Ex situ XAS measurements showed that the synthesized complexes exhibit a distorted octahedral coordination geometry with a bromide ligand coordinated to the Mn atom. The use of high pressure cells equipped with X-ray-transparent windows allowed monitoring the whole reaction directly at the synchrotron radiation source. Due to the much lower X-ray energy at the Mn K-edge, here, the signal-to-noise ratio was not sufficient for a complete EXAFS analysis, whereas it was well possible at the Br K-edge. Experiments both at the Mn K- and the Br K-edge provided complementary information on the behavior of both key components of the catalyst, the Mn(III) central atom and the bromide ligand, and revealed a persistent sixfold coordination geometry around the Mn atom, and an irreversible loss of the bromide ligand, which was replaced by an epoxide molecule and formed Br–C bonds during the reaction. Comparative experiments showed that propylene oxide replaces the bromide ligand much faster than styrene oxide. These observations added valuable insights to earlier catalytic studies and allowed proposing a consistent catalytic mechanism. *In situ* XAS thus proved to be a versatile spectroscopic tool for investigating both homogeneous and immobilized complexes even under demanding conditions regarding pressure, temperature and a dense reaction mixture consisting of CO_2-expanded liquid epoxide.

Acknowledgments

References

[1] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (2001) 953.
[2] A. Baiker, Appl. Organomet. Chem. 14 (2000) 751.
[3] A. Behr, Angew. Chem. Int. Ed. Engl. 27 (1988) 661.
[4] M. Aresta, E. Quaranta, ChemTech 27 (1997) 32.
[5] A. Baiker, Chem. Rev. 99 (1999) 453.
[6] J.D. Grunwaldt, R. Wandeler, A. Baiker, Catal. Rev. 45 (2003) 1.

[7] B. Subramaniam, C.J. Lyon, V. Arunajatesan, Appl. Catal. B: Environ. 37 (2002) 279.
[8] A.A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[9] M. Alvaro, C. Baleizao, E. Carbonell, M. El Ghoul, H. Garcia, B. Gigante, Tetrahedron 61 (2005) 12131.
[10] S.W. Chen, R.B. Kawthekar, G.J. Kim, Tetrahedron Lett. 48 (2007) 297.
[11] H.W. Jing, S.K. Edulji, J.M. Gibbs, C.L. Stern, H.Y. Zhou, S.T. Nguyen, Inorg. Chem. 43 (2004) 4315.
[12] X.B. Lu, Y.J. Zhang, B. Liang, X. Li, H. Wang, J. Mol. Catal. A: Chem. 210 (2004) 31.
[13] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.
[14] R.L. Paddock, S.T. Nguyen, Chem. Commun. (2004) 1622.
[15] M. Ramin, F. Jutz, J.D. Grunwaldt, A. Baiker, J. Mol. Catal. A: Chem. 242 (2005) 32.
[16] Y.M. Shen, W.L. Duan, M. Shi, Adv. Synth. Catal. 345 (2003) 337.
[17] F. Jutz, J.D. Grunwaldt, A. Baiker, J. Mol. Catal. A: Chem. 279 (2008) 94.
[18] D.J. Darensbourg, Chem. Rev. 107 (2007).
[19] G.A. Luinstra, G.R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, Chem. Eur. J. 11 (2005) 6298.
[20] M.P. Feth, C. Bolm, J.P. Hildebrand, M. Kohler, O. Beckmann, M. Bauer, R. Ramamonjisoa, H. Bertagnolli, Chem. Eur. J. 9 (2003) 1348.
[21] A.D.Q. Ferreira, F.S. Vinhado, Y. Iamamoto, J. Mol. Catal. A: Chem. 243 (2006) 111.
[22] A.L. Maclean, G.J. Foran, B.J. Kennedy, Inorg. Chim. Acta 268 (1998) 231.
[23] Y.S. Chen, J.L. Fulton, W. Partenheimer, J. Am. Chem. Soc. 127 (2005) 14085.
[24] H. Dau, P. Liebisch, M. Haumann, Anal. Bioanal. Chem. 376 (2003) 562.
[25] K.A. Evans, J. Mavrogenes, M. Newville, J. Synchrotron Radiat. 14 (2007) 219.
[26] T. Ressler, J. Synchrotron Radiat. 5 (1998) 118.
[27] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, Phys. Rev. B 52 (1995) 2995.
[28] J.D. Grunwaldt, M. Ramin, M. Rohr, A. Michailovski, G.R. Patzke, A. Baiker, Rev. Sci. Inst. 76 (2005).
[29] D.C. Koningsberger, R. Prins, X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES, Wiley, New York, 1988.
[30] A. Bianconi, Proceedings of an International Conference, Stanford, 1984.
[31] J. Wong, F.W. Lytle, R.P. Messmer, D.H. Maylotte, Phys. Rev. B 30 (1984) 5596.
[32] H. Bertagnolli, T. Engelhardt, B. Lengeler, Z. Phys. Chem. Neue Fol. 155 (1987) 79.
[33] K. Asakura, in: Y. Iwansawa (Ed.), X-ray Absorption Fine Structure for Catalysts and Surfaces, World Scientific, Singapore/New Jersey/London/Hong Kong, 1996, p. 33.
[34] D.C. Koningsberger, R. Prins, TRAC Trends Anal. Chem. 1 (1981) 16.
[35] Y. Iwansawa, X-ray Absorption Fine Structure for Catalysts and Surfaces, World Scientific, Singapore, 1996.
[36] F. Farges, Phys. Rev. B 71 (2005).
[37] J. Pellicer-Porres, A. Segura, J.F. Sanchez-Royo, J.A. Sans, J.P. Itie, A.M. Flank, P. Lagarde, A. Polian, Superlattice Microstruct. 42 (2007) 251.
[38] Y.S. Chen, J.L. Fulton, W. Partenheimer, J. Soln. Chem. 34 (2005) 993.
[39] C.P. Horwitz, Acta Crystallogr. C C51 (1995) 815.
[40] D. Martínez, M. Motevalli, M. Watkinson, Acta Crystallogr. C C58 (2002) m258.
[41] I.V. Korendovych, E.V. Rybak-Akimova, Acta Crystallogr. C C60 (2004) m82.
[42] M.C. Feiters, F.C. Kupper, W. Meyer-Klaucke, J. Synchrotron Radiat. 12 (2005) 85.
[43] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 45 (2004) 2023.
[44] R. Srivastava, T.H. Bennur, D. Srinivas, J. Mol. Catal. A: Chem. 226 (2005) 199.
[45] D.J. Darensbourg, R.M. Mackiewicz, J.L. Rodgers, C.C. Fang, D.R. Billodeaux, J.H. Reibenspies, Inorg. Chem. 43 (2004) 6024.
[46] X.B. Lu, Y. Wang, Angew. Chem. Int. Ed. 43 (2004) 3574.
[47] D.J. Darensbourg, J.C. Yarbrough, J. Am. Chem. Soc. 124 (2001) 6335.
[48] D.J. Darensbourg, R.M. Mackiewicz, D.R. Billodeaux, Organometallics 24 (2005) 144.