

Unique Structural Properties of the Mg–Al Hydrotalcite Solid Base Catalyst: An In Situ Study Using Mg and Al K-Edge XAFS during Calcination and Rehydration**

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Abstract: The changes in the layered structure of Mg–Al hydrotalcite (Mg/Al = 2) during heat treatment have been investigated by using in situ XAFS simultaneously at the Mg and Al K-edges. The development of unique in situ instrumentation allowed the coordination environments at both the Mg and Al centers to be monitored as a function of the temperature and heat treatment. The results of this study show that the hydrotalcite structure is highly flexible, and should lead to the further development of hydrotalcites as new solid basic catalysts. Moreover, the Mg and Al cations in the cation layers show different behavior as a function of temperature. The coordination of some octahe-

dral Al ions decreases already at a temperature of 425 K, whereas the coordination about Mg does not show any modification at this temperature. However, hydrotalcite treated at 425 K, followed by cooling down to room temperature resulted in a complete reversal to the original octahedral Al coordination. It is proposed that Al–OH bond breakage occurs at ≈ 425 K, without the evolution of H₂O. This bond is restored after cooling to room temperature. The actual dehydroxylation of hydrotalcite

commences between 425 and 475 K, as indicated by a change in coordination of both the Mg and Al centers. This is accompanied by the evolution of H₂O molecules and the changes are hence irreversible without the presence of excess water. Heat treatment at 725 K leads to the development of an MgO-like phase (octahedral Mg) and a mixed octahedral/tetrahedral Al phase. A subsequent rehydration at room temperature entirely restores the original coordination about the Al and Mg centers of hydrotalcite to a distance of 15 Å, to which XAFS spectroscopy is sensitive.

Keywords: EXAFS spectroscopy • heterogeneous catalysis • hydrotalcite • solid bases

Introduction

Hydrotalcites (HTs) and structures derived therefrom have many applications that are related to their structural properties.^[1] Recently, modified HTs have proven to be active in the coupling of various ketones and aldehydes in base-catalyzed aldol condensation reactions,^[2,3] such as the condensation of citral and acetone to yield pseudoionone, which is an industrially important intermediary for the production of vitamin A. Usage of a solid base catalyst instead of the currently applied homogeneous alkaline bases makes reuse of the catalyst possible, leading to a reduction of waste streams. Furthermore, modified HTs display high activity already at

low temperatures. These properties make HT-like compounds promising catalysts for commercial use.

The structure and the related activity of HT-like compounds are strongly related to the applied heat treatment.^[3,4] A calcination step at high temperature (723–773 K) followed by a rehydration step at room temperature yields a highly active catalyst for the catalytic reactions mentioned above. An understanding of the processes leading to an active catalyst, demands detailed knowledge of the structural changes in HT during heat treatment.

Hydrotalcite, [Mg₆Al₂(OH)₁₆](CO₃)·4H₂O, is a layered double hydroxide (LDH). LDH structures are related to that of brucite, Mg(OH)₂, in which the Mg cations occupy the centers of hydroxy octahedra. These octahedra are joined along their edges, forming a layered structure, composing hexagonal platelets.^[1] In hydrotalcite some of the Mg²⁺ ions are replaced by Al³⁺ ions, inducing a net positive charge in the cation layers. Charge-balancing anions (usually CO₃²⁻) and water molecules are present in the interlayers.

X-ray diffraction (XRD), ²⁷Al MAS NMR, IR, thermal gravimetric analysis (TGA), and CO₂ temperature program-

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[**] XAFS = X-ray absorption fine structure.

med desorption (TPD) are often used techniques to determine the structure of HTs. It is well documented that for HTs, physisorbed and interstitial water is removed at temperatures above approximately 325 K and 460 K, respectively. At higher temperatures the HT undergoes dehydroxylation and decarboxylation, giving rise to H₂O and CO₂ evolution. XRD indicates the formation of an MgO-like phase at temperatures above 725 K,^[5] and in addition, at those temperatures, an amorphous Al₂O₃ phase is formed. Above about 1100 K the normal spinel MgAl₂O₄ appears.^[6]

²⁷Al MAS NMR spectroscopy^[7, 8] shows that the coordination of Al is lowered from octahedral to tetrahedral after calcination above 500 K. This process already commences at relative low temperatures. Rehydration of the calcined product at room temperature results in a restoration of the original structure, which is both shown with XRD and ²⁷Al MAS NMR spectroscopy. XRD indicates a return of the platelike structure and the NMR spectrum indicates the reappearance of octahedrally coordinated Al centers. This so-called memory effect is lost after calcination above 773 K, due to the formation of the stable spinel MgAl₂O₄.^[1] A calcination–rehydration cycle yields a modified HT with mainly OH[−] ions as charge-balancing anions. Repeated calcination–rehydration cycles result in the segregation of Al from the cation layer and in the formation of spinel MgAl₂O₄.^[9] Until now, little is known about the changes in the coordination at the Mg centers during heat treatment and subsequent rehydration. One ²⁵Mg MAS NMR study on hydrothermalite calcined to various temperatures shows the formation of a poorly crystalline MgO phase after calcination above 675 K.^[7]

To be able to understand and therefore to optimize the activation process, in situ characterization is a necessity. Recent instrumental development^[10, 11] has enabled in situ measurements by X-ray absorption fine structure spectroscopy (XAFS) at the Mg and Al K-edges. XAFS at the Al and Mg K-edges provides electronic and geometric information about these elements. The different coordinations at Mg and Al can clearly be distinguished by the appearance of characteristic features in the near-edge spectra.^[12] HT-like compounds have been studied by using XAFS spectroscopy, however, application of in situ studies was until now restricted to heavy elements.^[13]

In this study, structural information of both Mg and Al is obtained by measuring the Mg and Al K-edges under in situ (at elevated temperature) and ex situ (at room temperature after previous treatment in the laboratory) conditions. It will be shown that large differences exist between the results obtained by in situ and ex situ studies of the samples. Changes in coordination due to calcination and rehydration of hydrothermalite with Mg/Al = 2 will be discussed. Unique information can be obtained since the coordinations of the Al and Mg centers are determined in the same in situ experiment.

Results

Mg reference compounds

Figure 1 shows the Mg K-edge spectra of the reference materials having different Mg coordinations. The spectrum of MgAl₂O₄ was digitized from reference [14]. The position of

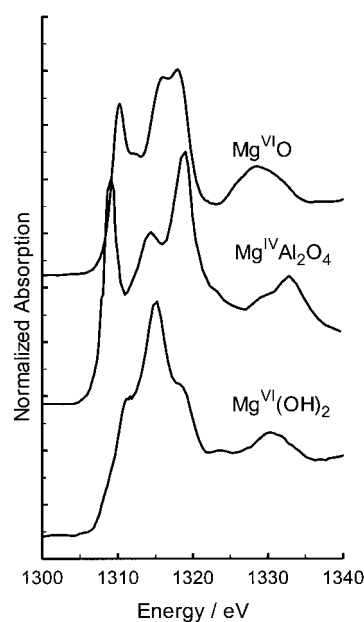


Figure 1. Mg K-edge spectra of reference compounds having tetrahedrally and octahedrally coordinated Mg centers.

the absorption edge in the spectrum of tetrahedral Mg in MgAl₂O₄ is lower in energy than the absorption edge in the spectrum of octahedral Mg. In the spectrum of Mg(OH)₂, a slowly rising edge is visible. However, the first maximum appears at approximately the same energy as the first maximum in the spectrum of MgO. These reference compounds show Mg K-edge spectra that are very similar to earlier reported data.^[14]

Al reference compounds

The Al K-edge spectra of reference compounds containing tetrahedral and octahedral Al, respectively, are presented in Figures 2a and 2b, respectively. These spectra and the

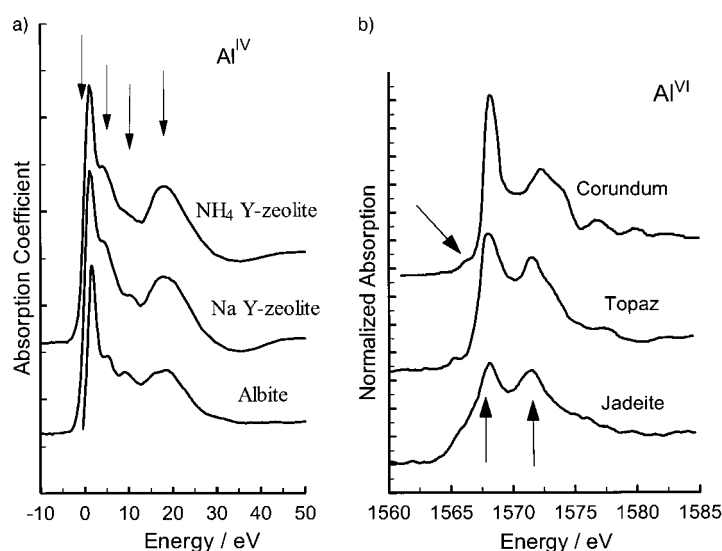


Figure 2. Al K-edge spectra of reference compounds having tetrahedrally (a) and octahedrally (b) coordinated aluminum centers.

relationship between the characteristic features (indicated by arrows) in the spectra and the structure of the samples have been discussed extensively elsewhere.^[12, 15, 16, 17, 18] It was concluded that the characteristic features in the near-edge spectra are indicative of different Al coordinations in the compounds.^[12] Criteria that can be used, are: 1) energy position of the edge, 2) intensity in the near-edge region, 3) shape of the whiteline, and 4) peaks at specific energy, including pre-edges. These different characteristic features are evident in Figures 2a and 2b. In general, an octahedral compound shows two resonances above the absorption edge at 1568 and 1572 eV, whereas a tetrahedral compound shows a single sharp rising edge at 1566 eV. Moreover, the near-edge in a spectrum of an octahedral compound has higher intensity than the near-edge for a tetrahedral compound. A broad peak at 20 eV above the absorption edge is visible in Al K-edge spectra of tetrahedral compounds. It is emphasized here that the near-edge region (0–15 eV above the edge) in the Al K-edge spectra is determined by long-range multiple scattering.^[19] Thus, the fine structure and peaks that appear in the spectra in this energy range are determined by ordering of the structure in the range 0–15 Å around the absorber.

As-synthesized hydrotalcite

Figure 3 shows the Mg and Al K-edge near-edge spectra of the as-synthesized hydrotalcite (HTa.s.). The energy scales of these spectra are aligned on the first maximum in the spectra,

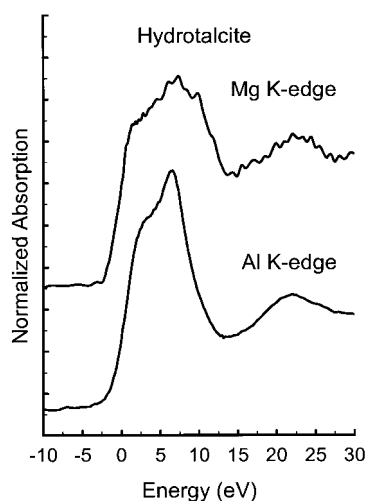


Figure 3. Mg and Al K-edge spectra of as-synthesized hydrotalcite (Mg/Al = 2:1).

and are set to 0 eV. The spectrum taken at the Mg K-edge is shifted by 1308 eV, and that taken at the Al K-edge by 1565 eV.

The Al K-edge spectrum is characteristic of a spectrum of octahedrally coordinated Al centers: It shows a split whiteline with resonances at 1568 and 1572 eV, indicated by arrows in Figure 2b. The spectrum is identical to an Al K-edge spectrum of HT reported in the literature.^[20] No intensity at 1566 eV, characteristic of tetrahedral Al centers is found.

The Mg K-edge spectrum of HTa.s. is very similar to its Al K-edge spectrum, although the peaks are less distinct and broadened and a surplus in intensity at about 10 eV above the absorption edge is visible. The spectrum is different from the spectrum of brucite Mg(OH)₂ (Figure 1), indicating that Mg in HT has a somewhat different octahedral structure.

Ex situ treated hydrotalcite

Figure 4 shows the room temperature Mg K-edge spectra of the ex-situ treated hydrotalcite (HTex'*T*'; where '*T*' = maximum calcination temperature) samples. The spectrum of

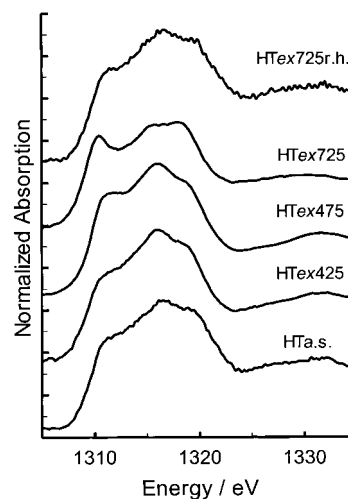


Figure 4. Mg K-edges of ex situ heat-treated hydrotalcite, showing a gradual change in the spectra after treatment above 475 K. A restoration of the structure is visible for a rehydrated sample that had previously been heated to 725 K (HTex725r.h.).

HTex425, is identical to the spectrum of HTa.s. After heating the hydrotalcite above 475 K, changes in the spectra appear: an increase in the intensity at about 1310 eV is observed. The absorption edge of the spectrum of HTex725 is shifted to lower energy and a clear decrease in intensity in the range 5 to about 15 eV above the edge is visible. Moreover, the peak at about 1330 eV occurs at a different energy than samples that are treated at lower temperature, indicating a change in Mg coordination. The spectrum of HTex725 resembles the spectrum of MgO (see Figure 1); however, the peaks are less distinct and less fine structure is visible in the spectrum of HTex725. The spectrum of the calcined and subsequent rehydrated HT (HTex725r.h.; Figure 4) is identical to the spectrum of the starting material, HTa.s., showing a complete and quantitative reversal of Mg coordination after rehydration.

The Al K-edge spectra of the HTex'*T*' samples are given in Figures 5a and 5b. The spectrum of HTex425 does not differ from the spectrum of HTa.s. A detailed comparison of the spectrum of HTex475 and HTex425 is given in Figure 5b. The spectrum of HTex475 shows a decrease in intensity of the octahedral peaks and an increase in intensity is visible at 1566 eV, showing a decrease in octahedral content, while tetrahedral Al centers appear. This is continued progressively at higher temperatures, as clearly visible in the spectrum of HTex725. The difference between the spectrum of HTa.s. and HTex725 is highlighted in Figure 6 by subtracting the spec-

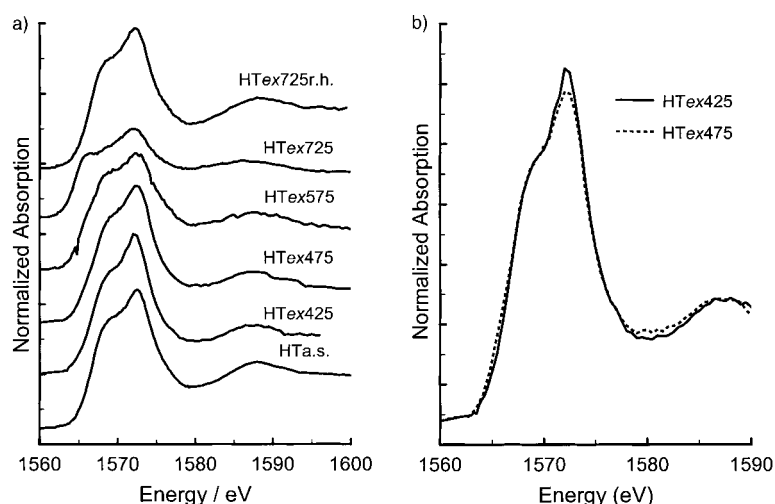


Figure 5. a) Al K-edges of ex situ heat-treated hydrotalcite, showing a gradual change in the spectra after treatment above 475 K. b) Al K-edge of HTex425 and HTex475.

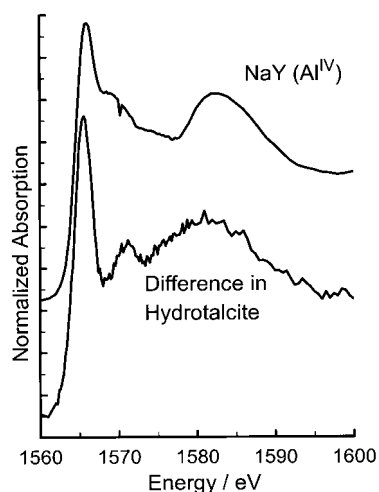


Figure 6. Contribution of tetrahedral Al sites isolated from HTex725 compared to a tetrahedral Al reference compound (NaY zeolite).

trum of HTa.s. from that of HTex725 while applying a normalization factor. In this manner the octahedral contribution to the spectrum of HTex725 can be removed leaving the contribution of the changed Al coordination in the spectrum. The normalization factor is varied until the difference spectrum did not contain any non-realistic negative contributions below the absorption edge.^[12] This difference spectrum is compared to a reference compound of tetrahedral Al (such as zeolite NaY^[12]). This spectrum reveals all the characteristic features of tetrahedral Al centers: A sharp absorption edge at 1566 eV, two features at 5–10 eV above the absorption edge, and a broad peak at about 20 eV. The spectra differ at 3–7 eV above the absorption edge, which may be due to a somewhat different octahedral coordination in the calcined HT, in comparison to the parent hydrotalcite, HTa.s.

High temperature treated hydrotalcite

Figure 7 shows the Mg K-edge spectra of hydrotalcite that are measured during treatment at high temperature HT'*T*' (where

'*T*' is the temperature at which the sample was measured). In the Mg K-edge spectra, no changes can be observed between HTa.s. and HT425 within the noise-level. An increase in intensity just on the absorption edge is visible in the spectra recorded for HT475.

Figure 8 shows the corresponding Al K-edge spectra which clearly show the differences between the spectrum for HT425 and that for HTa.s. The changes consist of a decrease in intensity of the two peaks at 1568 and 1572 eV, and an edge shift towards lower energy.

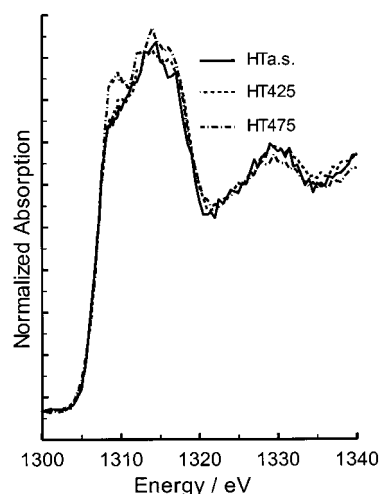


Figure 7. In situ measured Mg K-edge spectra of hydrotalcite indicating a change in Mg coordination at temperatures above 475 K.

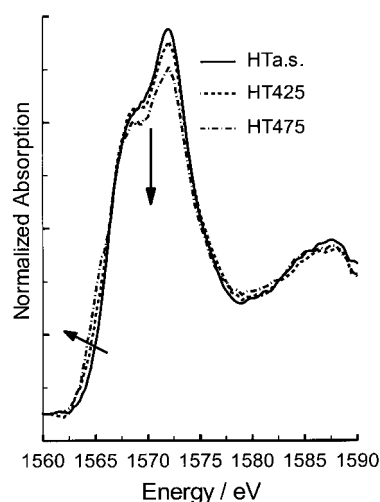


Figure 8. In situ measured Al K-edge spectra of hydrotalcite showing the appearance of less coordinated Al sites already at 425 K.

Moreover, a small increase in intensity at about 20 eV above the absorption edge appears, which is indicative of an increase in the tetrahedral Al content.^[12] The differences in the spectrum taken at 475 K are more distinct.

EXAFS analysis

The Fourier transforms after background subtraction and normalization of the Al K-edge spectra of HTa.s. and HTex725 are given in Figure 9. Both the magnitude and the

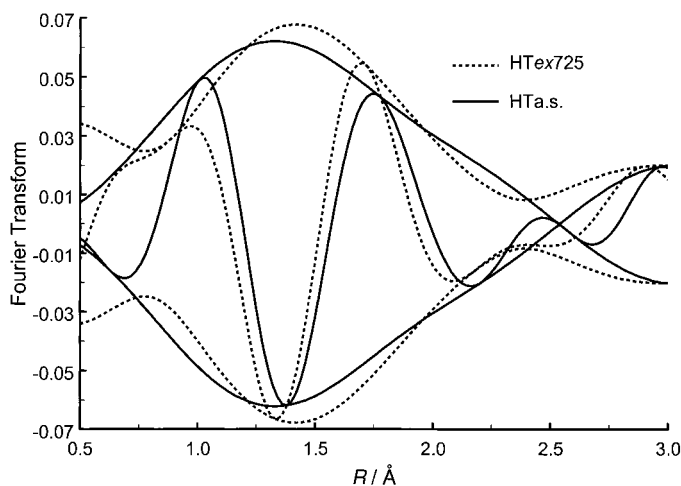


Figure 9. Fourier transform (k^1 , $\Delta k = 2.7-8 \text{ \AA}$) of the Al K-edge EXAFS of HTex725 and HTa.s. indicating differences in Al–O bond length and in coordination number by differences in node positions of the imaginary part and in absolute intensity.

node positions of the imaginary part are different, indicating differences in Al–O bond length and coordination number between HTa.s. and HTex725. R space fits of the spectra are given in Figure 10 (HTa.s.) and 11 (HTex725). The fit param-

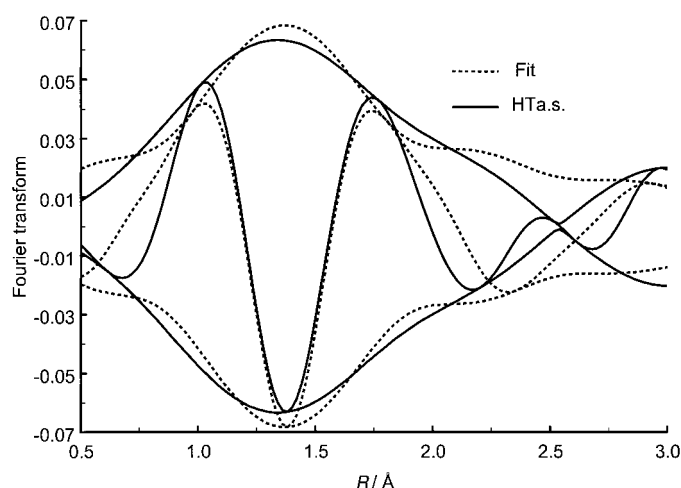


Figure 10. Fourier transform (k^1 , $\Delta k = 2.7-8 \text{ \AA}$) of the Al K-edge EXAFS of HTa.s. and the best fit obtained.

eters are given in Table 1. The spectrum of HTa.s. was fitted using one shell of oxygen neighbors, and a reasonable agreement of intensity and especially node position is

Table 1. Al–O fitted coordination parameters.^[a]

	N	Parameters		ΔE_0 [eV]
		$\Delta\sigma^2$ [\AA^2]	R [\AA]	
HTa.s.	6	0.0002	1.82	3.17
HTex450 oct	4.9	-0.064	1.86	-5.49
tet	0.7	0.01	1.56	-8.55

[a] Fitted in R space, $1 < R < 2$, $2.7 < k < 8$, k^1 -weighted.

obtained. An Al–O bond lengths of 1.83 and 1.86 \AA in HT are normal for octahedrally coordinated Al centers (compare the Al–O bond lengths in corundum which has three Al–O_a bonds of 1.86 \AA and three Al–O_b bonds of 1.97 \AA ^[21]).

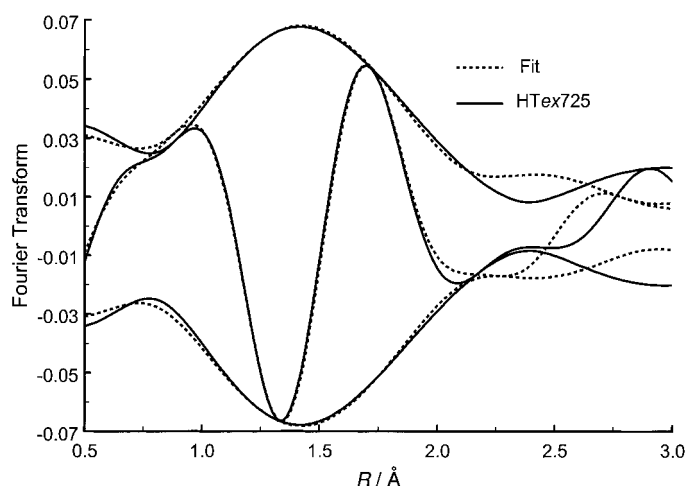


Figure 11. Fourier transform (k^1 , $\Delta k = 2.7-8 \text{ \AA}$) of the Al K-edge EXAFS of HTex725 and the best fit obtained.

The near-edge spectrum of HTex725 (Figure 5 a) indicated the presence of both tetrahedrally and octahedrally coordinated Al centers. Therefore, a two-shell fit was performed on the normalized EXAFS of HTex725, one comprising the tetrahedrally coordinated Al centers and one the octahedrally coordinated Al centers. The resulting fit was within the noise-level (Figure 11). In order to verify the effect of fitting a second shell to the spectrum of HTa.s., a two-shell fit was performed also for this spectrum; however, this did not lead to a better fit.

The coordination numbers (N) given in Table 1 are fractional, since in XAS spectroscopy a sum of all contributing atoms is measured. The shell with the shorter Al–O bond length represents the tetrahedrally coordinated content, and the longer bond length denotes the octahedrally coordinated content.

Discussion

Mg and Al coordinations in the HT structure

Figure 3 shows that in as-synthesized hydrotalcite, the edges in the respective Al and Mg K-edge spectra have similar characteristics, which is expected for two neighboring elements in the Periodic Table occupying identical cation positions. Both spectra show two peaks just above the

absorption edge that are more pronounced in the spectrum recorded at the Al K-edge. These peaks are broader in the Mg spectrum, which also has significant intensity at about 10 eV above the edge. In the HT structure, Al always has six Mg atoms at next-nearest-neighbor positions (connected through OH groups), whereas Mg has both Al and Mg at these positions.^[1] This more variable coordination around the Mg cations could result in less distinct peaks in the near-edge in Mg K-edge spectra. The broadening of the peaks in the Mg spectra could indicate that Mg has—on average—a more distorted environment than Al in terms of its first few coordination spheres within one cation layer: An X-ray absorption spectrum is an average of all the atoms contained in the sample. The near-edge in the spectra is determined by long-range scattering, and it is thus sensitive to ordering up to about 15 Å around the absorber (being either Mg or Al).^[19]

The broad peak at about 25 eV above the absorption edge is visible at both edges, which again is evidence for Mg and Al occupying identical cation positions. The Mg K-edge spectrum of brucite ($\text{Mg}^{\text{VI}}(\text{OH})_2$; Figure 1) shows sharper resonances and more fine structure than the spectrum of HTa.s. This is also evidence of less structured Mg coordination in HT than in brucite in the 0–15 Å range around the Mg atoms in both these structures. This local disorder is also observed in the XRD pattern of HT. In XRD spectra of HT, the in-plane reflections are relatively broad^[1, 2, 3] showing disorder at a somewhat longer range.

Changing Mg and Al coordinations as a function of temperature

HTex'T' samples: The Al and Mg coordinations change strongly as a function of the temperature of calcination. The edge in the Mg K-edge spectra (Figure 4) shifts to somewhat lower energy, and the intensity in the near-edge decreases. The Mg K-edge spectrum of HT calcined at 725 K, strongly resembles the spectrum of $\text{Mg}^{\text{VI}}\text{O}$ (Figure 1), indicating an MgO-like phase is formed during calcination at 725 K. In this structure the Mg center becomes octahedrally coordinated as in the rock salt structure. The rehydration at room temperature completely restores the original spectrum (Figure 4), indicating the Mg coordination is identical to that of Mg in as-synthesized HT, HTa.s., that is distorted octahedral.

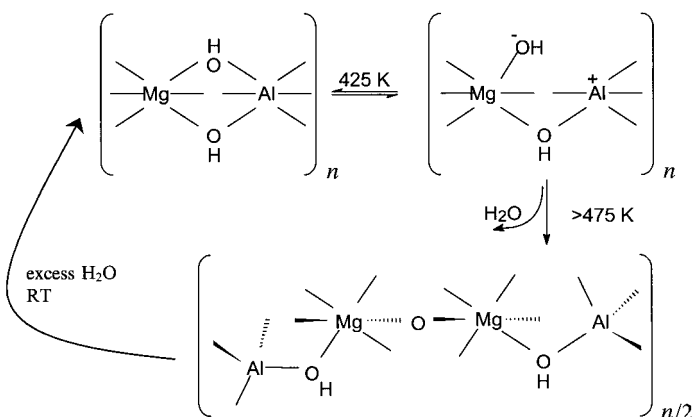
The Al K-edge spectra show a progressive decrease in intensity of the characteristic peaks for octahedral coordination at 1568 and 1572 eV, and an increase in intensity at 1566 eV (Figures 5a and 5b) after calcination above 475 K. Figure 6 shows the difference spectrum obtained from the subtracting the spectrum of HTa.s. from that of HTex725. This difference spectrum shows large similarities with the spectrum of NaY, which can be considered as a typical spectrum of tetrahedrally coordinated Al. This provides direct evidence for the presence of tetrahedrally coordinated Al centers after calcination of HT. The Al coordination can be quantitatively reversed to its original coordination after rehydration (HTex725r.h.). No indications exist of other modes of coordination (Mg or Al) in the rehydrated HT (HTex725r.h.) other than those already present in the as-synthesized HT.

HT'T' samples: Figures 7 and 8 show the Mg and Al K-edge spectra, respectively, measured in situ at room temperature, 425, and 475 K. At 425 K, the Al coordination already begins to change, which was not observed for the pretreated (at 425 K) calcined sample (HTex425) measured at room temperature. The Mg coordinations in HT'T' samples start changing at a temperature of 475 K, very similar to the case for HTex'T' samples. This is the temperature of the pretreated samples at which also the Al spectra showed changes (HTex475, Figures 5a and 5b). Apparently, the changes in Al coordination induced by calcination at 425 K (HT425) are fully reversed upon cooling down the sample to room temperature. Only when the Mg coordination is changed (which occurs above 475 K), the changes in the Al coordination are no longer reversible. This information is only available through performing XAFS experiments during the heat treatment. The consequences of this observation are discussed in the next section.

Discussion of the structure of HT

Activation of hydrotalcite is performed by calcination up to 725 K and followed by a rehydration step. The charge-balancing CO_3^{2-} ions are (largely) replaced by OH^- ions. After this calcination–rehydration cycle no new Mg and Al coordination modes are observed by Mg and Al K-edge XAFS; the Mg and Al coordinations are completely restored to the original octahedral hydrotalcite structure. During heat treatment, however, the Al and Mg coordinations alter. The in situ and ex situ experiments show clear differences, indicating the importance of using a true in situ technique.

Although some controversy exists concerning the temperatures at which changes in the HT structure occur, there is a common consensus that first adsorbed and interstitial H_2O is removed from the interlayer; second, dehydroxylation at the cation layers occurs, creating less coordinated Al centers.²⁷ Al MAS NMR spectroscopy recorded at elevated temperatures indicate that this process occurs already at temperatures above 375 K.^[7] Here it is shown more specifically that the coordination of Al is lowered at a temperature of 425 K. However, these changes are reversible after cooling down the sample to room temperature. As shown in Scheme 1 at 425 K,



Scheme 1. Processes occurring during heat treatment of hydrotalcite.

a few Al–OH bonds are broken, which lowers the Al coordination. However, this occurs without dehydroxylation at the cation layers. Most likely these are Al–OH–Mg groups that are positioned near the edges of the cation layers or in the top or bottom layer in the stacked cation layer arrangement.

The processes proposed in Scheme 1 are a working hypothesis. The structure as drawn in Scheme 1 at a temperature of 475 K could be stabilized by anions and water molecules in the interlayer through a delocalization of charge. It has been proposed^[22] that diffusion of protons and the reaction with hydroxyl ions to form water are the initial steps in the thermal decomposition of gibbsite, whose structure resembles that of hydrotalcite. Gibbsite also has a layered structure of octahedrally coordinated aluminum hydroxides. In hydrotalcites, a proton of a nearby hydroxide could diffuse to an Al–OH group at 475 K, yielding a water molecule. This water molecule coordinates less strongly to the aluminum center, hence the aluminum coordination is lowered. The relatively low temperature prevents this water molecule from completely losing contact with the aluminum center, and the structural change is fully reversed after cooling down the sample to room temperature.

At temperatures above 475 K, the actual dehydroxylation process commences and a change of both the Mg and Al coordination is expected, exactly as observed. These dehydroxylation processes are no longer reversible as indicated in Scheme 1. At 475 K, the Mg–OH bonds start breaking and the coordination at the Mg centers is altered by the formation of new Mg–O–Mg bonds. This process is accompanied by the evolution of H₂O from the sample. At this temperature, the formation of a rocksalt MgO-like phase starts occurring (Mg has an octahedral coordination in MgO). Once this phase has formed, the changes to the structure are no longer reversible after the sample has been cooled down. However, the addition of an excess of water (during rehydration at room temperature) fully reverses the changes in the coordinations, even after the hydrotalcite has been calcined to 725 K. X-ray diffraction reveals a change in the 003 and 006 reflections at about 455 K,^[3, 6, 23] showing a decrease in interlayer distance. This was attributed to a loss of interstitial H₂O. However, as shown in this study, at 425 K the Al coordination is already changing, and at 475 K also the Mg coordination. Thus at 425 K, some Al–OH bond-breaking occurs, and above 475 K, dehydroxylation is already occurring. It is therefore concluded that changes to the structure at these low temperatures take place in the interlayers as well as inside the Mg–Al hydroxide layers, the latter probably near the external surface of the cation layers.

At higher temperatures decarboxylation occurs, which is accompanied by the formation of an MgO phase. It has been proposed that dehydroxylation first occurs within one layer, and that only after removal of carboxyl ions a dehydroxylation between two consecutive layers may occur.^[24] This last process is accompanied by a loss of the lamellar arrangement of the layers leading to drastic changes in the XRD pattern. The temperature at which this process occurs starts at 525 K and continues up to 800 K. The structures formed after calcination at these temperatures still exhibit the so-called memory effect,^[1] although the restoration of the HT layered

structure is much slower for the samples calcined at the higher temperatures. The decarboxylation results in an MgO-like phase and a mixed tetrahedral–octahedral Al₂O₃ phase, which is confirmed in this study. The EXAFS of the HTex725 sample could be fitted taking two Al–O shells into account (Table 1). This shows the presence of both tetrahedrally and octahedrally coordinated aluminum centers with a short and a long Al–O bond length, respectively. However, a comparison of the Mg K-edge spectra of HTex725 (Figure 4) with those of MgO (Figure 1) reveals that the latter shows much more fine structure, indicating larger ordering and a more crystalline phase. The MgO-like phase formed after heating the HT at 725 K can be completely reversed into a HT structure, restoring the layered structure completely on the length-scale of the XAS, that is about 15 Å around the absorber atom. This implies that separation of a Mg and an Al phase does not occur and, hence large crystalline Mg oxide or Al oxide phases are not expected.

Conclusion

Mg and Al K-edge spectroscopy is a unique tool for monitoring the changes in Al and Mg coordinations as a function of (calcination) temperature in HT-like compounds. The in situ and ex situ experiments show clear differences. This proves the importance of application of true in situ techniques when structural changes during the activation of a catalyst are investigated.

The structure of HT is very flexible. The Al and Mg coordinations can change depending on the conditions. At 425 K, the coordination of some of the octahedrally coordinated Al centers becomes less through a reversible Al–OH bond breakage. At temperatures higher than 475 K, dehydroxylation of the Mg and Al cations in the cation layer occurs. This is a continuous process at increasing temperatures. The Mg coordination starts changing at temperatures above 475 K and formation of an MgO-like phase occurs. XAFS analysis indicates a MgO-like structure after calcination at 725 K and the presence of a mixed tetrahedral–octahedral Al phase. The HT layered structure is completely restored after rehydration at room temperature and within the length-scale of XAS (ca. 15 Å) the obtained structures are identical to the as-synthesized material.

Experimental Section

Sample preparation

An aqueous solution (45 mL) of Mg(NO₃)₂·6H₂O (0.1 mol, P.A. Acros) and Al(NO₃)₃·9H₂O (0.05 mol, Z.A. Merck) was added in one portion to a second solution (70 mL) containing NaOH (0.35 mol) and Na₂CO₃ (0.09 mol) at 333 K. The mixture was maintained at this temperature for 24 h under vigorous stirring, after which the white precipitate was filtered off and washed several times. The HT was dried for 24 h at 393 K. This is denoted as the as-synthesized HT (HTa.s.). ICP analysis revealed a Mg/Al ratio of 2. MgO was obtained by heating (MgCO₃)₄·Mg(OH)₂·5H₂O (Sigma) under a flow of dry nitrogen to above 825 K. The sample was cooled down under a flow of nitrogen to prevent the formation of hydroxides. Mg(OH)₂ was prepared by dispersing MgO into decarbonated

water. These compounds were checked for crystallinity and structure by XRD.

MgO has a rock salt crystal structure in which the Mg is octahedrally coordinated. MgAl₂O₄ is a normal spinel structure, in which Mg occupies tetrahedral sites and Al octahedral sites in close-packed oxygen layers. Mg(OH)₂ has the brucite structure, in which magnesium hydroxide octahedrons link to form infinite sheets. Hence, in MgO and Mg(OH)₂, Mg is octahedrally coordinated, whereas in the normal spinel, MgAl₂O₄, it is tetrahedrally coordinated.

Sample treatments

HTex'T' samples: Before measurement, the hydrotalcite was calcined to various temperatures in the laboratory under a nitrogen flow at heating rates of 10 K min⁻¹. These samples are called HTex'T', where 'T' represents the maximum calcination temperature. For example, HTex475 is HTa.s. heated in nitrogen at 10 K min⁻¹ to 475 K and maintained at that temperature for 8 h. The nitrogen flow was maintained during cooling down of the sample and the samples were stored under nitrogen. A batch of the sample calcined at 725 K (HTex725) was rehydrated at 303 K by use of a water-saturated nitrogen flow of 100 mL min⁻¹ for at least 6 h. This sample is referred to as HTex725r.h. XRD and N₂ and CO₂ sorption experiments on some of these samples have been published elsewhere.^[3] The HTex'T' samples were measured at room temperature.

HT'T' samples: HTa.s. was measured in situ at the Mg and Al K-edges. Heating rate was 10 K min⁻¹ under a flow of dry helium. These samples are called HT'T', where 'T' represents the temperature at which the measurement took place, hence HT425 is measured at 425 K under a flow of dry helium.

XAFS measurements

XAFS measurements were performed at beamline 3.4 at the SRS, Daresbury (UK). The in situ low-energy X-ray absorption fine structure (ILEXAFS) set-up^[10, 11] were used. Both electron yield (measuring drain current) and fluorescence yield (using a gas proportional counter) were used as detection of the XAS signal, yielding very similar results. The intensity of the initial X-ray beam is determined by measuring the drain current of either a Au or a Cu mesh with a thickness of less than 3 μm.

YB₆₆ crystals were used as monochromator crystals, allowing the measurement of both the Al K-edge near edge and the EXAFS. Using these crystals, the energy range at the Mg K-edge is limited to the near edge, due to higher order effects. Higher harmonics were removed by detuning the crystals (rocking of the Bragg peak) so the intensity was reduced to about 50% of the maximum intensity.

XANES analysis: The electron yield spectra were pre-edge and background subtracted and normalized after averaging three scans. The normalization was performed by dividing the pre-edge subtracted spectrum by the intensity of the post-edge background at 50 eV above the edge. As the energy range above the Mg K edge is limited, due to the used monochromator YB₆₆ crystals, the spectra were post-edge, background fitted over the maximum data range available (ca. 60 eV above the edge).

EXAFS analysis: The fluorescence data (average of three scans) were used to generate the EXAFS function. The background was subtracted using cubic spline routines.^[25, 26] Reference phase shifts and back-scatterings amplitude functions of the Al–O absorber back-scatterer pair were determined for α-AlPO₄ (The procedure followed has been described in detail elsewhere).^[28] The spectra were fitted in R space, from 1 < R < 2 Å after Fourier transform of 2 < k < 8. k⁰, k¹, and k³ weighting of the spectra was performed and the best fit was obtained in all dimensions.

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