The location of europium in Eu^{3+}-exchanged zeolite-Y as determined by extended X-ray absorption fine structure (EXAFS) investigations at 77 K

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Eu L$_3$-edge EXAFS has been used to investigate the location of Eu^{3+} cations in an Eu^{3+}-exchanged zeolite-Y, with a framework Si/Al molar ratio of 13.5 ± 2.0, as a function of heat treatment up to 200 °C. All of the EXAFS data were recorded from samples cooled to 77 K following ion-exchange and heat treatment. The interpretation of the EXAFS data, in conjunction with a geometrical modelling approach, for the sample subject only to ion-exchange at 60 °C is consistent with hydrated Eu^{3+} cations being directly bound to framework oxygen atoms (O4) of free six-membered rings that border the supercages of the zeolite-Y structure. The hydrated Eu^{3+} cations are displaced from the high-symmetry SII sites. The coordination environment of the Eu^{3+} cation in the sample heated to 100 °C is similar to that in the as-exchanged sample. Heating of the Eu^{3+}-exchanged zeolite-Y at 200 °C results in migration of the Eu^{3+} cations into the sodalite cages where, as partially hydrated species, they are coordinated to three framework oxygen atoms in such a way as to be displaced from SI′ sites.

Introduction

Modified forms of zeolite-Y have been used for many years as hydrocarbon cracking catalysts in the petroleum-refining industry.[1–3] Two important types of modification have been the introduction of rare earth cations and the removal of aluminium from the zeolite framework by a chemical, or thermal, dealumination process.[4] In general, these modifications, either by themselves or in combination, enhance the hydrothermal stability and catalytic attributes of the zeolite-Y.

A wide variety of experimental and computer modelling techniques have been used to investigate the properties of modified zeolite-Y materials. In particular, attention has focussed on investigating changes in the state and location of rare earth cations within the zeolite-Y framework as a function of heat treatment.[5–10] These studies have mostly used non-dealuminated materials. It is generally acknowledged that increasing the temperature results in migration of the hydrated rare earth cation from a location within the supercage of the hydrated zeolite-Y into the sodalite cage; this process is accompanied by a partial loss of the hydration shell. A view of part of the framework structure of zeolite-Y, including the labelling convention[11] for high-symmetry, extra-framework cation sites is shown in Fig. 1.

In this work we use Eu L$_3$-edge EXAFS to investigate the location of Eu^{3+} cations in a dealuminated, Eu^{3+}-exchanged zeolite-Y as a function of relatively mild heat treatment (up to 200 °C) in air. All of the EXAFS data were recorded for samples cooled to 77 K following ion-exchange and heat treatment. A particular quality of EXAFS that is important in the present work, apart from its element specificity, is its ability to directly probe local structure without the need for site symmetry restrictions as is often a requirement in the analysis of conventional diffraction data.
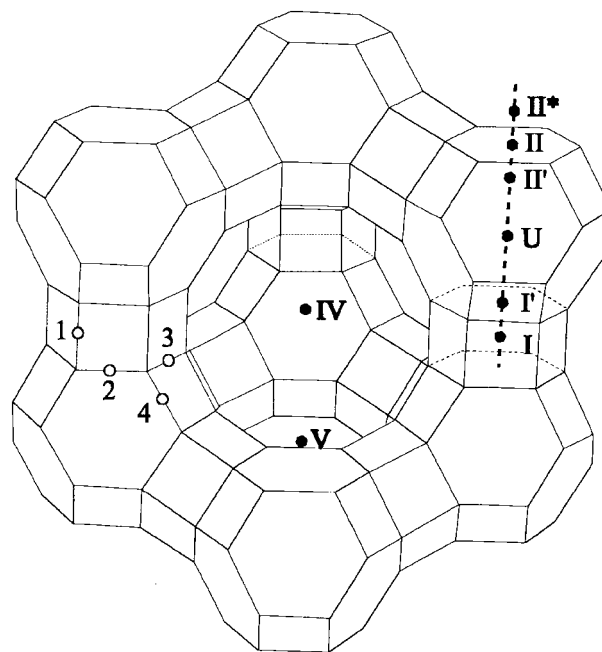

Fig. 1 A view of part of the framework structure of zeolite-Y. Each line intersection is occupied by a T atom (T = Si or Al). The four crystallographic oxygen atom positions within the framework are labelled O1 to O4. Generally accepted nomenclature is used to label other extra-framework sites: U and IV label sites at the centres of sodalite (or β-) cages and supercages, respectively; V labels a site at the centre of a 12-ring window and sites along the threefold [111] axis are labelled I through to II*.

Experimental

A commercial, dealuminated, ammonium-exchanged zeolite-Y was obtained from Zeolyst International (sample type CBV 712) with minimal Na^+ content (0.03% by mass) and a bulk Si/Al molar ratio of 5.73. The ^{29}Si MAS NMR spectrum recorded at 79.5 MHz using a JEOL EX-400 spectrometer and 5 mm DOTY MAS probe showed the framework value of the Si/Al molar ratio to be 13.5 ± 2.0 which lies at the limit of reliability of the standard technique for determining framework Si/Al molar ratios from ^{29}Si MAS NMR spectra.[12] The X-ray powder diffraction pattern (recorded with a Siemens D5000 diffractometer in reflection mode using Cu-K$_\alpha$ radiation) showed the presence of a highly crystalline zeolite-Y phase with a unit cell parameter of 24.35 Å which is typical for a dealuminated zeolite-Y.[13]

The Eu^{3+}-exchanged zeolite-Y was prepared by adding the commercial zeolite-Y to a 0.02 mol dm^{-3} aqueous solution of $Eu(NO_3)_3 \cdot 6H_2O$ followed by continuous stirring at 60 °C and pH 3 over a period of 24 hours. The product was removed by centrifugation, washed with deionised water (60 °C, pH 3), filtered and dried in air at 60 °C (3 h). The ^{29}Si MAS NMR spectrum for the Eu^{3+}-exchanged zeolite-Y was identical to that of the starting material. The europium content was determined by ICP-AES to be $1.96 \pm 0.13\%$ (by mass). It is reasonable to assume that all of the europium is associated with crystalline zeolite-Y since, throughout this work, no evidence was found for any association between amorphous material present in the zeolite and hydrated Eu^{3+} cations. On this basis, and assuming the MAS NMR value of the Si/Al molar ratio, the composition of the hydrated, crystalline, Eu^{3+}-exchanged zeolite-Y was calculated to be $Eu_{1.9}(NH_4)_{7.3}Al_{13}Si_{179}O_{384} \cdot n$-$H_2O$. There are less than 0.02 Na^+ cations per unit cell and the amount of Eu^{3+} exchange compared to the maximum capacity is approximately 45%.

The Eu^{3+}-exchanged zeolite-Y was divided into three samples. One of these, which we shall refer to as the hydrated sample, was stored in contact with air. The other two samples were individually heated at 5 °C min^{-1} to 100 °C and 200 °C, respectively, and held for a period of 60 minutes at these temperatures. Each was then stored in a sealed container.

The Eu L$_3$-edge EXAFS measurements were performed on Station 7.1 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, UK, with an average current of 200 mA at 2 GeV. The order-sorting, double Si(111) crystal monochromator was detuned to 90% of the maximum intensity to remove the harmonic. The data were collected at 77 K in fluorescence mode using a vertical, platinum-coated, collimating mirror. Energy resolution was estimated to be ca. 3 eV at the Eu L$_3$-edge. The samples were prepared by grinding to a fine powder using an agate mortar and pestle and then formed into pellets. No detectable rehydration of the samples heated at 100 °C and 200 °C took place during the short period of sample preparation and placing the samples in the cryostat. The SRS programs EXCALIB and EXBACK were used in the usual manner for calibration and background subtraction of the raw data. EXAFS data analyses were carried out using the program EXCURV98.[14] Phase shifts were obtained within this program using *ab initio* calculations based on the Hedin-Lundqvist/von Barth scheme.

Results and discussion

Europium L$_3$-edge EXAFS data recorded at 77 K and their corresponding Fourier transforms are shown in Fig. 2 for (a) hydrated, Eu^{3+}-exchanged zeolite-Y, (b) hydrated, Eu^{3+}-exchanged zeolite-Y heated at 100 °C and (c) hydrated, Eu^{3+}-exchanged zeolite-Y heated at 200 °C. In each case dashed lines indicate the best fit to the data for radial distances up to ca. 4.1 Å using the parameters collected in Table 1.

No evidence was found for any further atomic shells in the Fourier transforms in Figs. 2(a) and (b). It should be noted that it was not possible in the EXAFS analyses to distinguish between backscattering from silicon and aluminium atoms. A single shell involving these atoms is therefore denoted as Si(Al), although given the high framework Si/Al molar ratio it is unlikely that any shell would contain more than one Al atom. The values of $2\sigma^2$ in Table 1 are reasonable and are probably determined by static, rather than thermal, disorder since all of the experiments were carried out at 77 K. The goodness of fit, R, was found to be 14.8%, 13.0% and 22.3% for the data in Figs. 2(a), (b) and (c), respectively.

Qualitative features

A dominant feature in the Fourier transform of the hydrated, Eu^{3+}-exchanged zeolite-Y (Fig. 2(a)) is the peak corresponding to a shell of oxygen atoms with coordination number 8.6 and a europium–oxygen distance equal to 2.43 Å. These values are very similar to those obtained from X-ray scattering studies of aqueous Eu^{3+} solutions at room temperature.[15] They are also consistent with other EXAFS investigations of Eu^{3+}-exchanged zeolite-Y, although carried out at room temperature and using zeolite-Y starting materials with framework Si/Al molar ratios close to 2.5.[16,17] It is thus reasonable to infer that the primary coordination of the Eu^{3+} cation in the present ion-exchanged, dealuminated zeolite-Y is not significantly affected by reducing the temperature to 77 K. Furthermore, as might be expected, this coordination is not influenced by the framework Si/Al molar ratio.

The samples heated at 100 °C and 200 °C (Figs. 2(b) and (c), respectively) also have dominant peaks in their Fourier transforms that correspond to a coordination shell of oxygen atoms around the Eu^{3+} cation. Although it is difficult to determine coordination numbers to a high degree of accuracy in EXAFS data analysis, the change from 8.1 at 100 °C to 6.0 at 200 °C is sufficiently large to indicate that a significant change has occurred in the immediate local environment of the Eu^{3+} cation on heating to 200 °C. This is consistent with the generally held view that hydrated cations migrate, by a process involving both dehydroxylation and dehydration, from locations in the supercages of zeolite-Y to those in the sodalite cages as a function of heat treatment.[9,10] In the case of La^{3+} and Ce^{3+} cations, detailed studies by Lee and Rees[6,18] have shown that these cations have locations which are particularly sensitive to heat treatment in the temperature range between 80 °C and 160 °C. The present results indicate that this sensitivity may start at a higher temperature (>100 °C) in the case of Eu^{3+} cations as has also been found[19] recently in time-resolved Eu-luminescence studies. It should be noted that the zeolite-Y used in the luminescent studies had a Si/Al molar ratio close to 2.4 and so, compared with the present work, it appears that this ratio has little influence on the temperature range over which the migration of the hydrated Eu^{3+} cations occurs.

Hydrated, Eu^{3+}-exchanged zeolite-Y

An outer shell corresponding to a europium–silicon (or aluminium) distance of 3.43 Å is present in the Fourier transform (Fig. 2(a)) of the EXAFS data recorded from this sample (see Table 1). This indicates that at least a proportion of the hydrated Eu^{3+} cations are located in close proximity to the zeolite framework structure. More specifically, on the basis of simple geometrical considerations, this relatively short distance can only be accounted for if one, or more, of the oxygen atoms observed at the distance of 2.43 Å (which EXAFS cannot distinguish as belonging to water or the zeolite framework) belongs to the zeolite framework rather than the coordinated water molecules. Although the modelling was based on the
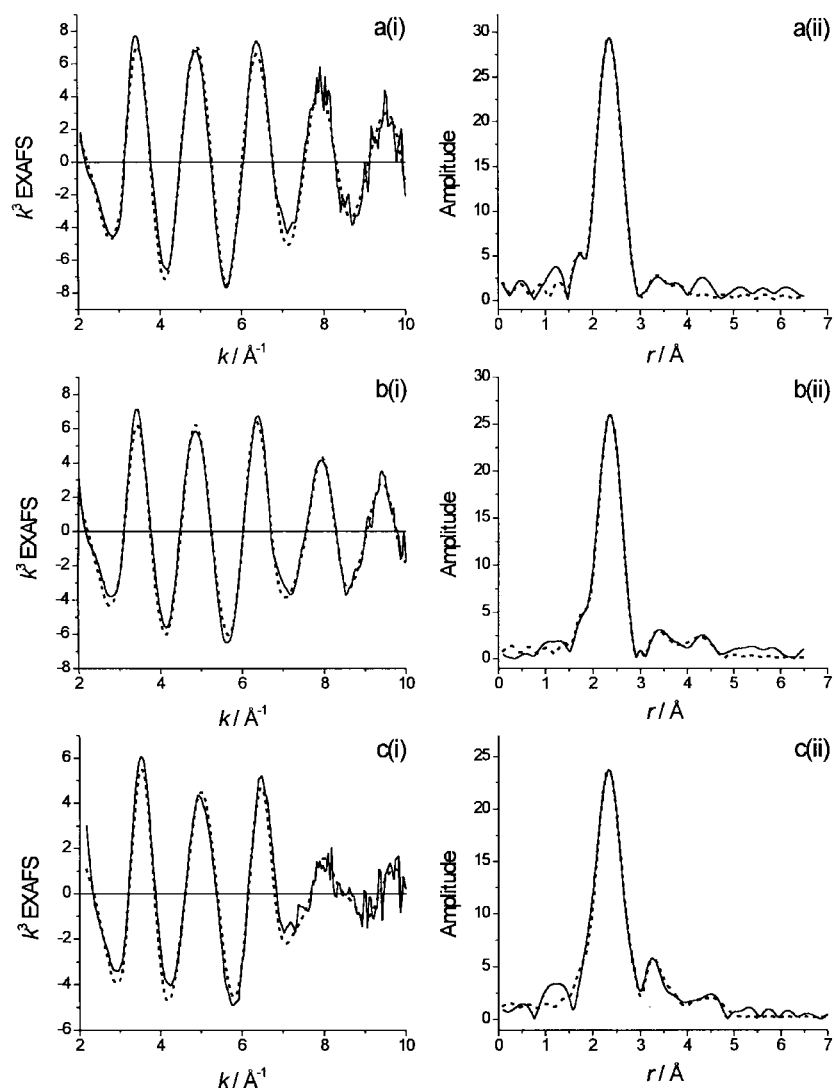
Fig. 2 k^3-Weighted europium L_3-edge EXAFS (i) and the corresponding Fourier transform (ii) recorded at 77 K from (a) hydrated, Eu^{3+}-exchanged zeolite-Y, (b) hydrated, Eu^{3+}-exchanged zeolite-Y heated at 100 °C and (c) hydrated, Eu^{3+}-exchanged zeolite-Y heated at 200 °C. The experimental data are indicated by the solid lines.

Eu^{3+} cation having ninefold coordination with the water molecules arranged in the same tricapped prismatic manner as found in the hydrates of the lanthanide trifluoromethanesulfonates,[20] a similar conclusion was reached by allowing variation in the arrangement of the ninefold coordination geometry, or by reducing the coordination to eightfold as found for some europium compounds.[21]

Detailed X-ray powder diffraction studies of a hydrated, La^{3+}-exchanged zeolite-Y (Si/Al = 2.34) at room temperature have been interpreted in terms of a model in which the La^{3+} cations are restricted to SII and SV sites in the supercages (see

Fig. 1).[9] Rietveld structure refinement could not provide an unambiguous assignment of the La^{3+} cations to these sites. In the case of the La^{3+} cations at the SII sites the refinement suggested that these cations would be coordinated to three oxygen (O2) atoms at a distance of 2.41 Å and to six silicon atoms at a distance of 3.29 Å. If Eu^{3+} cations were also located at SII sites then it might be expected that the local coordination would be comparable to that for the La^{3+} cations. However, the Eu L_3-edge EXAFS results recorded in this work show that this is not the case since, although the lanthanum–O(2) distance compares well with the EXAFS europium–oxygen distance of

Table 1 Final fitted parameters obtained from europium L_3-edge EXAFS data recorded at 77 K for Eu^{3+}-exchanged zeolite-Y samples

Sample	Atom type	Coordination number	Interatomic distance/Å ($\pm 1\%$)	$2\sigma^2/Å^2$ ($\pm 10\%$)
Hydrated, Eu^{3+}-exchanged	O	8.6	2.43	0.010
	O	1.9	3.01	0.007
	O	5.1	3.34	0.005
	Si(Al)	2.7	3.43	0.006
Hydrated, Eu^{3+}-exchanged (heated at 100 °C)	O	8.1	2.43	0.012
	O	1.3	2.96	0.016
	O	3.8	3.29	0.009
	Si(Al)	2.9	3.37	0.009
Hydrated, Eu^{3+}-exchanged (heated at 200 °C)	O	6.0	2.39	0.019
	Si(Al)	1.4	2.82	0.018
	O	2.5	3.37	0.014
	Si(Al)	0.9	3.81	0.010

2.43 Å, there is no evidence in the EXAFS study, *cf.* Table 1, of a Si(Al) shell with a high coordination number at 3.29 Å. This is an important result. It demonstrates that those Eu^{3+} cations in close proximity to the zeolite framework are not restricted, as has been generally assumed for rare-earth cations,[11] to only high-symmetry sites determined by the framework structure of zeolite-Y. Although the EXAFS measurements do not rule out the presence of Eu^{3+} cations at SV sites, it is not possible to quantify the relative proportion at these sites.

In order to model the location of the Eu^{3+} cations coordinated to the framework structure we have used a commercial crystal-drawing package[22] to visualise the structure of zeolite-Y. The approach was then twofold: (i) to determine the form of shells of atoms surrounding a bare Eu^{3+} cation as a function of its position and (ii) to compare these model shells with experiment. Overall, we find that a likely position for a Eu^{3+} cation, taking into account the bulk of its hydration shell, is determined by bonding to a framework oxygen O(4). This bonding would also be favoured[11] by the presence of an aluminium atom bonded to O(4) but such detail is not available from the EXAFS measurements. In physical terms the result is not unrealistic since the framework oxygen O(4) then acts as an anchor about which the hydrated Eu^{3+} cation can pivot in the supercage. We detail our analysis with the help of Fig. 3 which shows, in projection, the silicon (aluminium) framework of a free six-membered ring (sometimes denoted as RII[8]) that is not shared with a hexagonal prism and so borders a supercage.

The Eu^{3+} cation is bonded to a framework oxygen atom and the direction of this bond with respect to the plane of the six-membered ring is defined by the angle, α. In the case that the framework oxygen is of type O(4) then the calculated distances for the shells of atoms surrounding the Eu^{3+} cation as a function of angle α are summarised in Table 2; for convenience the shells are simply sorted into progressive bands each of width equal to 0.2 Å. The angular range is limited by the condition that no shell occurs at less than 2.5 Å. The distances between the Eu^{3+} cation and the two silicon (aluminium) atoms directly attached to oxygen O(4) were both fixed at the value found in the EXAFS study, that is 3.34 Å, *cf.* Table 1. This fixed geometry has the consequence that the europium–oxygen distance, which depends on the angle α, will always be greater than the experimental value of 2.43 Å; for example, the calculated distance lies between 2.45 Å and 2.85 Å for α in the range 25° to 180°. However, this does not invalidate the model since it is reasonable to expect[8] that some relaxation of the oxygen framework structure will occur in the vicinity of the Eu^{3+} cation. For comparison, Table 2 also includes a set of similar atom shell calculations for a bare Eu^{3+} cation directly bonded to framework oxygen O(2).

One of the simplest atom shell structures in Table 2, in particular with no contributions in the range 3.5 Å to 4.1 Å, is that for the Eu^{3+} cation directly bonded to oxygen O(4) and with angle α within the range 110° to 150°. This structure, in comparison with other possibilities, agrees reasonably well with the EXAFS data although the shell of oxygen atoms at 3.34 Å in the experimental data is not accounted for (see below). The modelling evidence is clearly not unequivocal but, nonetheless, it does suggest a reasonable alternative location to the SII site
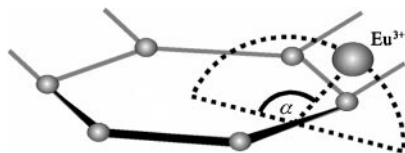

Fig. 3 The silicon (aluminium) framework of a free six-membered ring that borders a supercage in the zeolite-Y structure. The bridging O2 and O4 oxygen atoms are not shown. The Eu^{3+} cation is in a plane perpendicular to that of the six-membered ring and is located within the supercage: further details are given in the text.

for the hydrated Eu^{3+} cation; essentially this site is displaced sideways, towards the centre of the supercage, from the SII site. It is worth noting that the comparison between modelling and experiment may be helped by the fact that the EXAFS measurements were carried out at 77 K. This low temperature will favour low, or minimum, energy configurations of the corresponding room temperature state and, hence, restrict any distribution in the Eu^{3+} cation sites.

As already mentioned, the shell of oxygen atoms at 3.34 Å (see Table 1) could not be accounted for in our modelling. This shell is also present in the samples heated at 100 °C and 200 °C with a marked reduction in coordination number for the sample heated at the higher temperature. It is possible that the presence of this shell may be associated with oxygen atoms, primarily from water molecules, in the second coordination shell of the Eu^{3+} cation. Recent work[23,24] has shown that secondary hydration shell structures can be observed for hexa-coordinated metal ions in solution although multiple-scattering phenomena have to be taken into account in any quantitative analysis. For these highly symmetrical aqua-ions the solution structure is usually such that the distance between the ion and the oxygen atoms of the second shell is about twice the value corresponding to that of the first shell. However, this relationship may be more complex for the hydrated Eu^{3+} cation, particularly in the zeolite-Y structure. The influence of multiple-scattering phenomena may also influence the EXAFS measurements in a complex manner and represents an area which needs further investigation.

Hydrated, Eu^{3+}-exchanged zeolite-Y heated at 100 °C

The Fourier transform of the EXAFS data for this sample (Fig. 2(b)) is similar to that for the non-heated sample, *cf.* the fitting parameters summarised in Table 1. There is a general trend for the values of $2\sigma^2$ to increase and this may be associated with an irreversible increase in thermal disorder on heating which is then reflected in static disorder at 77 K. Overall, however, there is no evidence for any major changes in the local coordination environment of the Eu^{3+} cations. In a simple model, it is interesting to view these hydrated cations as gaining increased motional energy, whilst maintaining their direct bonding to oxygen O(4) atoms of the zeolite framework, as the temperature is raised. The energy barrier to migration into the sodalite cages, however, is too large for any significant population of Eu^{3+} cations to be established in these cages at 100 °C. The contributions to the energy barrier are no doubt complex since both dehydroxyla-tion and dehydration are involved in the migration process.

Hydrated, Eu^{3+}-exchanged zeolite-Y heated at 200 °C

It is generally proposed that rare earth cations are located at sites SI′ within the sodalite cages of zeolite-Y.[11] The high symmetry of the SI′ sites results in direct coordination to three framework O(3) oxygen atoms (Fig. 1). At a greater distance there are then three framework O(2) oxygen atoms followed by a shell of six silicon atoms. Klein, Fuess and Hunger[9] in their X-ray powder diffraction investigation of hydrated, La^{3+}-exchanged zeolite-Y (Si/Al = 2.34) heated to 200 °C found the $La^{3+}\cdots Si$ distance to be 3.36 Å. It is clear that the present EXAFS data (Fig. 2(c) and Table 1) do not support such a highly symmetrical local environment for the Eu^{3+} cation. Again using an approach based on the visualisation of the structure of zeolite-Y, a possible model for the location of Eu^{3+} cations, consistent with the EXAFS data, can be determined as shown in Fig. 4. In this model, the Eu^{3+} cation is displaced from the SI′ site so that there is direct coordination to two framework oxygen O(3) atoms and one oxygen O(2) atom. Selected structural information for this model is given in Table 3. This information is calculated

Table 2 Summary of the calculated distances for shells of atoms surrounding a bare Eu^{3+} cation directly bound to framework oxygen atoms of types O(4) and O(2)

	Atom type[b]							
	Shell distance[c]/Å							
Angle α[a]	2.5–2.7	2.7–2.9	2.9–3.1	3.1–3.3	3.3–3.5	3.5–3.7	3.7–3.9	3.9–4.1
Oxygen O(4)								
25°	O(×2)	O(×2)	O(×2)		Si(×4)	Si(×2)		
50°		O(×1)	O(×2)		Si(×2)		O(×3)	O(×2), Si(×2)
80°	O(×1)				O(×1), Si(×2)	O(×1)	O(×2)	
110°	O(×1)		O(×2)		Si(×2)			
150°	O(×1)		O(×2)		Si(×2)			
160°		O(×1)	O(×2)		Si(×2)			O(×1)
180°		O(×1)		O(×2)	O(×1), Si(×2)		O(×4), Si(×2)	
Oxygen O(2)								
25°	O(×3)	O(×1)	O(×2)		Si(×6)			
50°	O(×1)		O(×2)	O(×2)	Si(×2)		O(×1), Si(×2)	
70°		O(×1)			O(×2), Si(×2)	O(×2)		
90°		O(×1)	O(×2)		Si(×2)	O(×2)		Si(×2)
110°	O(×2)			O(×4), Si(×2)	Si(×2)			
120°	O(×2), Si(×2)	O(×3)		O(×1)	Si(×2)	Si(×2)	O(×1)	O(×2)

[a]The model on which these calculations are based is discussed in the text and summarised in Fig. 3. [b]Values in brackets indicate the number of atoms in a given shell; for convenience atoms of type Si(Al) are simply represented as Si. [c]Calculations are based on the unit cell constant determined for the commercial zeolite-Y at room temperature (24.35 Å). The effect of ion-exchange and reduction in temperature to 77 K will only have a marginal effect on the calculations.
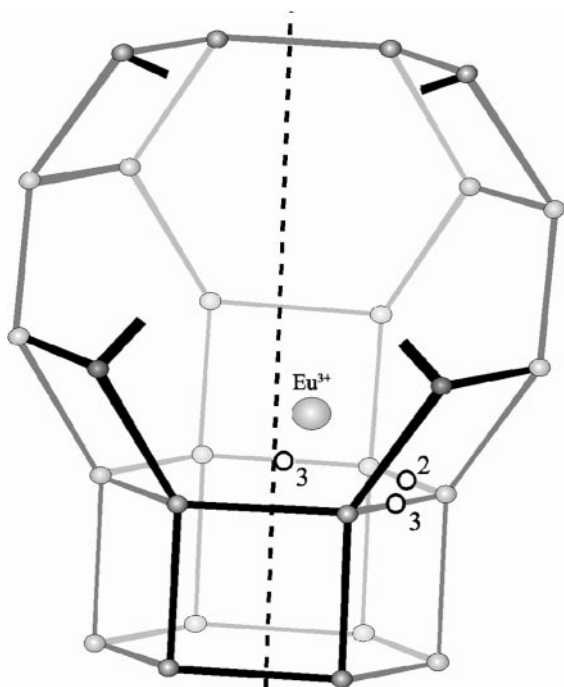

Fig. 4 Part of the framework structure of zeolite-Y showing a possible location for the Eu^{3+} cation in a sodalite cage. The threefold [111] axis is shown by a dashed line and the positions of the three directly-coordinating framework oxygen atoms are labelled.

assuming no relaxation of the zeolite framework within the vicinity of the Eu^{3+} cation; any such relaxation would be expected to allow all three framework oxygen atoms to have equal distances from the Eu^{3+} cation. Although not shown in the model the local coordination environment of the Eu^{3+} cation is completed by three directly-coordinated water molecules.

Conclusions

In this EXAFS study we have been able to monitor the local environment of Eu^{3+} cations in a dealuminated sample of zeolite-Y. In qualitative terms our results are consistent with

Table 3 Structural information related to the location of the Eu^{3+} cation in the sodalite cage according to the model in Fig. 4

Atom type	Distance[a] from Eu^{3+}/Å
O(3)	2.35 (×2)
O(2)	2.40 (×1)
Si(Al)	2.92 (×2)
Si(Al)	3.51 (×1)

[a]Values in brackets indicate the number of atoms at the given inter-atomic distance.

the generally accepted view that rare earth cations migrate from locations within the supercages of zeolite-Y to those in the sodalite cages under relatively mild heat treatment. At a more detailed structural level our results demonstrate the sensitivity of EXAFS, particularly for samples investigated at 77 K, as a probe of local environment. Furthermore, the analysis of the EXAFS data could be carried out without the need to incorporate any symmetry restrictions as, for example, is usually required in the Rietveld refinement and simulation of conventional powder diffraction patterns to obtain structural information. The use of geometrical modelling based on computer-simulated structures of zeolite-Y played an important role in the interpretation of the EXAFS data. We suggest that such an approach would be useful for other complex structural problems.

Acknowledgements

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