

# Al K-edge XANES study for the quantification of aluminium coordinations in alumina

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**Curve fitting analysis of Al K-edge XANES is employed as a novel characterization method for the quantitative estimation of tetrahedral and octahedral Al in various aluminas.**

Transition aluminas, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, formed by partial dehydration of aluminium hydrates have been of catalytic importance.<sup>1</sup> It is well established that the catalytic property of aluminas depends strongly on their local structure.<sup>1</sup> However, because of their poor crystallinity, accurate structures of the transition aluminas are not known except for  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, in which Al atoms are equally distributed between tetrahedral and octahedral sites of the spinel.<sup>2,27</sup> Al MAS NMR can be used to distinguish several Al atoms with different local structures, and quantification of Al coordination has been successful for crystalline materials.<sup>3</sup> However, for amorphous alumina, its application to quantitative structural analysis is difficult owing to a large quadrupolar interaction.<sup>4</sup> A conventional tool for determining Al distribution in catalytic alumina is desirable. X-Ray absorption spectroscopy (EXAFS/XANES) is another method for investigating local structure.<sup>5–8</sup> In general, EXAFS is popular for quantitative structural analysis, while XANES is less so. Considering the fact that XANES can potentially reflect the local site symmetry around X-ray absorbing atoms, and that the intensity of XANES spectra is higher than EXAFS oscillations, it can be a valuable tool for quantitative analysis if a proper method of analysis is established. Recently, we have succeeded in using Ga K-edge XANES analysis for the quantification of tetrahedral/octahedral Ga atoms in gallium oxides.<sup>7,8</sup> In this study, Al K-edge XANES analysis is applied for the quantitative determination of tetrahedral and octahedral Al atoms in transition aluminas.

Mordenite-type aluminosilicate (JRC-Z-HM15,<sup>9</sup> SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 15) containing Al atoms in the zeolite framework was supplied from the Catalysis Society of Japan.  $\theta$ -Al<sub>2</sub>O<sub>3</sub> was prepared by calcining  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-4<sup>10</sup> supplied from the Catalysis Society of Japan) at 1273 K for 12 h. Boehmite ( $\gamma$ -AlO<sub>2</sub>H) was prepared by hydrolysis of aluminium(III) triisopropoxide, followed by drying at 393 K for 12 h. A series of aluminas with various phases were prepared by calcining

boehmite in air at various temperatures (673–1773 K) for 2 h. The crystal phases of these samples were confirmed by X-ray diffraction and are given in Table 1. The diffraction pattern of the alumina sample calcined at 1773 K corresponds to that of pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum).

Al K-edge X-ray absorption spectra were measured on BL-7A at UVSOR with a ring energy of 750 MeV and a stored current of 70–220 mA in a mode of total electron yields. An YB<sub>66</sub> double crystal monochromator was used, and the absolute energy scale was calibrated to a negative glitch due to the Y L<sub>3</sub> peak of YB<sub>66</sub> at 2080.0 eV.<sup>11</sup> The monochromator scanning step width was 0.01°, which corresponds to ca. 0.3 eV at 1560 eV.

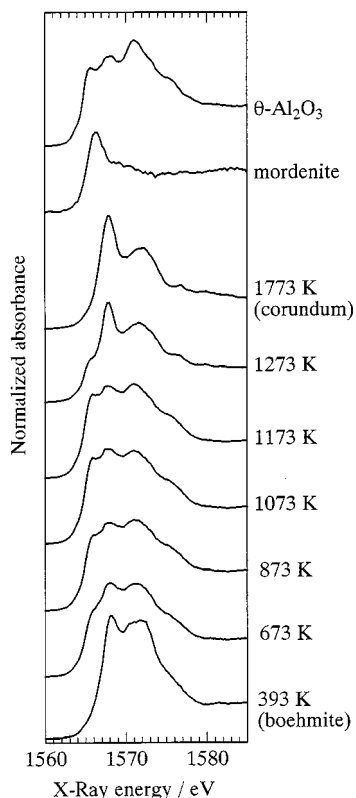
Fig. 1 shows the normalised Al K-edge XANES spectra of alumina samples together with those of model compounds containing AlO<sub>4</sub> tetrahedra (mordenite) and AlO<sub>6</sub> octahedra (corundum and boehmite). It is known in the literature that a clear distinction can be made between the XANES spectra of AlO<sub>4</sub> and AlO<sub>6</sub>; a white line peak at 1566 eV is characteristic of AlO<sub>4</sub> compounds, while peaks at 1568 and 1572 eV are characteristic of AlO<sub>6</sub> compounds.<sup>12,13</sup> In this study, it was confirmed that a single peak at 1566 eV due to AlO<sub>4</sub> appeared in the spectrum of mordenite, while a peak at 1568 eV and a broad peak at ca. 1571–1572 eV due to AlO<sub>6</sub> appeared in the spectra of corundum and boehmite. In addition, the edge positions of AlO<sub>6</sub> compounds were ca. 2 eV higher than those of AlO<sub>4</sub> compounds. For the transition alumina samples calcined in the temperature range 673–1273 K and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, XANES spectra exhibited three distinguishable peaks due to AlO<sub>4</sub> (1566 eV) and AlO<sub>6</sub> (1568 and 1572 eV). Clearly, the relative intensity of the 1566 and 1568 eV peaks differs from sample to sample. This observation is similar to that observed in our previous study of Ga K-edge XANES, where the relative intensity of white line peaks due to GaO<sub>4</sub> and GaO<sub>6</sub> varied with Ga distribution in the samples.

To estimate the ratio of Al atoms in tetrahedral and octahedral sites in transition aluminas, curve fitting analysis of XANES spectra<sup>6</sup> was carried out. Fig. 2 shows the deconvoluted spectrum of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> as an example. Following the method in

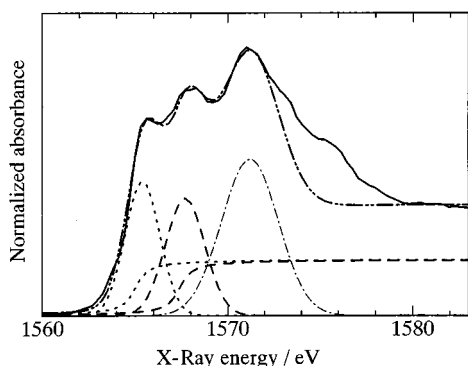
**Table 1** Parameters of deconvoluted peaks in XANES spectra of aluminium oxide

Sample (calcn. temp./K)	Crystal phase	AlO <sub>4</sub> tetrahedra/eV		AlO <sub>6</sub> octahedra/eV		Third peak/eV		AlO <sub>4</sub> :AlO <sub>6</sub> ratio <sup>b</sup>
		Position	Area	Position	Area	Position	Area	
$\theta$ -Al <sub>2</sub> O <sub>3</sub>	$\theta$	1565.4	2.6	1567.7	2.6	1571.2	5.0	50:50
393	boehmite	1565.5	0.6	1567.8	3.5	1571.4	15.6	15:85
673	boehmite (+ $\gamma$ )	1565.5	2.1	1567.6	3.4	1571.3	7.2	38:62
873	$\gamma$	1565.6	2.2	1567.5	2.9	1571.3	6.3	43:57
1073	$\gamma$	1565.6	3.3	1567.6	3.8	1571.3	8.3	47:53
1173	$\gamma$	1565.5	3.2	1567.5	3.9	1571.3	8.2	45:55
1273	$\alpha$ + $\theta$	1565.5	1.5	1567.7	4.0	1571.5	6.5	27:73
1773	$\alpha$ (corundum)	1565.5	0.5	1567.7	5.3	1571.8	5.7	9:91

<sup>a</sup> Calcination temperature. <sup>b</sup> Ratio of the area of AlO<sub>4</sub> peak:AlO<sub>6</sub> peak. The analytical error is estimated to be  $\pm 4\%$ .

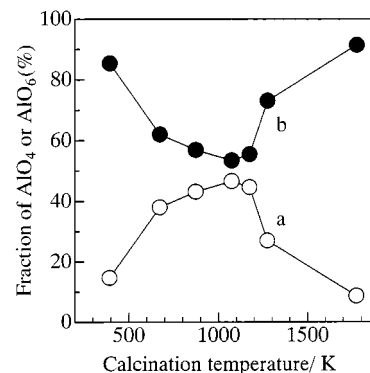


**Fig. 1** Al K-edge XANES spectra of alumina samples calcined at various temperatures and of reference compounds.



**Fig. 2** Al K-edge XANES spectrum of  $\theta$ - $\text{Al}_2\text{O}_3$  (—) and the simulated spectrum (---), which is composed of two sets of Gaussian and one arctangent function (dotted and broken) and a Gaussian function (— · —).

our previous study,<sup>7,8</sup> the analysis was performed on the assumption that absorptions due to  $\text{AlO}_4$  (1566 eV) and  $\text{AlO}_6$  (1568 eV) are expressed by a set of Gaussian and arctangent functions. As for the third peak (at 1572 eV), it is likely, from a comparison of the spectra of  $\text{AlO}_6$  compounds (corundum and boehmite) that the relative intensity of the 1568 eV peak to the 1571–1572 eV peak is not constant. Considering the suggestion that this peak can include multiple scattering contributions,<sup>14</sup> it was not employed for the quantitative analysis in this study, and was tentatively expressed by a Gaussian function. Thus, the best parameters, *i.e.*, the exact peak energy, and the peak area of each Gaussian were determined so as to simulate the original spectra in the range 1560–1572 eV and are listed in Table 1. The positions of the first and the second Gaussian peaks were centered at  $1565.5 \pm 0.1$  and  $1567.7 \pm 0.2$  eV, which were almost identical to those of  $\text{AlO}_4$  and  $\text{AlO}_6$  model compounds, respectively, within experimental error. For  $\theta$ - $\text{Al}_2\text{O}_3$ , the ratio of the areas of the 1566 and 1568 eV peaks was determined to be 50:50 with an analytical error of  $\pm 4\%$ . This value is in good agreement with that derived from X-ray diffraction analysis,<sup>2</sup> which suggests that the ratio of  $\text{AlO}_4$  to  $\text{AlO}_6$  in the samples can



**Fig. 3** Fraction of  $\text{AlO}_4$  tetrahedra (a) and  $\text{AlO}_6$  octahedra (b) in alumina samples as a function of calcination temperature.

be estimated quantitatively from the ratio of each Gaussian peak area.

The percentage of  $\text{AlO}_4$  and  $\text{AlO}_6$  was estimated by using the above method for a series of aluminas and is plotted as a function of calcination temperature (Fig. 3). The results show that the ratio of  $\text{AlO}_4$  to  $\text{AlO}_6$  is a function of the calcination temperature. For aluminium hydrate (boehmite), as expected,  $\text{AlO}_6$  octahedra are predominant. As the calcination temperature is increased to 1073 K, the fraction of  $\text{AlO}_4$  increases to a value of 47%, and then decreases at higher calcination temperatures. For the sample calcined at 1773 K, which is classified as  $\alpha$ - $\text{Al}_2\text{O}_3$  (corundum),  $\text{AlO}_6$  octahedra are again predominant. Thus, it is shown that XANES analysis is helpful for a better understanding of the effect of calcination conditions on the Al cation distribution in transition aluminas.

In conclusion, curve fitting analysis of Al K-edge XANES is shown to be a novel characterisation method for the quantitative estimation of Al coordination states (tetrahedra and octahedra) in alumina samples. This method will now be used for quantitative estimation of Al coordination states in unknown aluminium oxides.

## Notes and references

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