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X-ray absorption spectroscopy of transition aluminas

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The X-ray absorption spectroscopy of a series of transition aluminas derived from pseudoboehmite (α-alumina monohydrate) by calcination at 350, 400, 538, 750, 1000 and 1200 °C were examined at the Al edge. The transitions from ordered to disordered structure and eventually back to the ordered corundum structure are easily observed in both the XANES spectrum and EXAFS. The near-edge spectrum consists of 5 peaks, three of which are reasonably constant in intensity throughout the transitions. The first two peaks are attributed to the white lines of tetrahedral and octahedral Al. The tetrahedral Al white line coincides with an additional pre-edge peak, which makes accurate estimation of the tetrahedral content difficult; NMR is more accurate. Other peaks are ascribable to multiple scattering among the Al metal lattice and other structures. The EXAFS show that, with increasing calcination temperature, the Al coordination number decreases and disorder increases, as expected from the known structure changes. With the formation of α-alumina at 1000 and 1200 °C, the coordination number abruptly increases, as expected. This data will be of value in examining alumina structures in supported catalysts.

Keywords: transition aluminas, XANES, EXAFS

Introduction

Transition aluminas are high surface area materials formed by high temperature calcination of alumina hydrates(see, for example, Wefers, 1987). Specifically, γ-Al_2O_3, formed by calcination of synthetic α-alumina monohydrate (pseudoboehmite), is ubiquitous as a support for catalysts and sorbents. In this study, pseudoboehmite calcined at different temperatures up to 1200 °C have been examined by means of X-ray absorption spectroscopy (XAS) at the Al edge. Such information will be of value in characterizing alumina supports in catalysts with other active components.

A variety of Al containing materials have been examined by XAS at the Al edge: oxides(McKeown, *et al.*, 1985; Ildefonse *et al.*, 1994), glasses and clays(Ildefonse *et al.*, 1994), phosphates(Daviero, *et al.*, 1993), feldspars and garnets(Wu, *et al.*, 1996 and 1997) and Y zeolites (Dooryhee, *et al.*, 1990; Koningsberger&Miller, 1994). EXAFS has been generally limited to 6k above the Al edge because silica monochromators can only be used below the Si edge at 1832 eV (although the recent implementation of the YB_{66} monochromator at SSRL will extend that range, see Wong, *et al.* 1990). The near edge spectra (XANES) of the octahedral Al oxides is quite detailed and has been the source of most of the theoretical analyses on Al materials, particularly the recent study of Cabaret, *et al.*(1996) on corundum and other octahedral and tetrahedral Al oxides and silicates.

Experimental

The transition aluminas were prepared by calcination of pseudoboehmite for 3 hours in air at 350, 400, 538, 750, 1000 and 1200 °C. Sample properties are shown in Table 1:

Table 1 Alumina Properties.

Calcination Temperature, °C	Surface Area, m2/g	%T (^{27}Al NMR)	XRD Phase
α-Monohydrate	-	0	boehmite
350	-	5	
400	157	25	Boehmite/γ
538	151	36	γ
750	122	37	γ/δ
1000	-	34	
1200	<5	0	α

Al-K XAS were collected at the SA32 station at the LURE-SUPERACO facility in Orsay, France. The ring operated at 800 MeV and between 200 and 400 mA. The monochromator used two α-quartz crystals cut along (1010). Samples were mounted directly on a copper plate from suspensions in acetone. Total electron yield spectroscopy was performed under a vacuum of 10^{-5} torr using the drain current measurement and an incident angle of 45° between the beam and sample surface. Resolution was .2 ev. An Al foil was used for calibration of the edge at 1559 eV. XANES scans were collected between 1550 and 1600 eV with steps of 0.3 eV; EXAFS was collected up to about 1820 eV with 1 eV steps.

The WinXAS program (Ressler,1998) was used to reduce the data and extract the EXAFS function. Spectra were normalized by dividing by the height of the absorption edge. Background subtraction was done by the cubic spline method. Standard Fourier transforms were calculated with a window between nodes at 3-3.5 and ~7k with k^1 weighting.

The XANES were deconvoluted with the software program Peakfit 4. The data was extracted from the background-subtracted and normalized data. Gaussian line shapes were found to be the most successful. An arctangent function was used to simulate the edge jump itself.

The ^{27}Al MAS NMR spectra were obtained at 11.7T on a Bruker AM-500 spectrometer at 130.32 MHz with 4.5 - 5.0 kHz spinning speed, 1 μs excitation pulses, and a 0.1 s recycle time. The ^{27}Al chemical shifts were referenced to $Al(H_2O)_6$ at $\delta = 0.0$ ppm. The magic angle was accurately adjusted prior to data acquisition using KBr. Relative O_h and T_d Al contents were determined directly from the integration of the ^{27}Al MAS NMR spectra. Standards were used to ensure complete quantification of the Al.

Results and Discussion

XANES

The XANES results are shown in Figure 1. Ildefonse, *et al.* (1994) assigned the designations of A-D to the 4 peaks of the corundum spectrum (corresponding to the 1200 °C material in Figure 2); in the other intermediates in this study, the C peak appears to consist of two peaks, which are designated here as C1 and C2. Deconvolution of the spectra gave excellent fits with the five peaks A-D.The peak locations given in Table 2. Relative areas are shown in Figure 2. Within the error of the measurements and deconvolutions, the positions of all the peaks remain relatively constant at 1566, 1568, 1570-1571, 1572-1573 and 1575-1576 eV. The visible changes in the spectra are due to changes in intensity, mainly in A and C2.

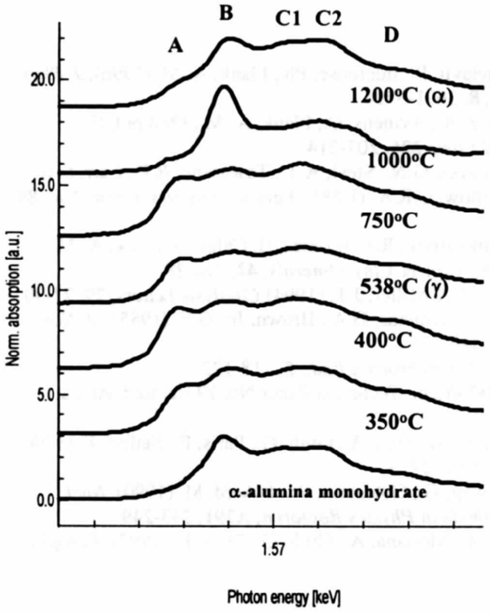

Figure 1 XANES spectra of Transition Aluminas

Table 2 Peak Positions in eV

Compound	A	B	C1	C2	D
α-Monohydrate	1566.2	1567.8	1570.2	1572.4	1574.8
350 C	1565.9	1567.9	1570.4	1572.6	1575.1
400 C	1565.9	1567.9	1570.6	1572.8	1575.6
538 C (γ)	1565.6	1567.7	1570.6	1572.7	1575.4
750 C	1565.8	1567.9	1570.9	1573.1	1575.6
1000 C	1565.6	1568.0	1571.0	1573.1	1575.6
1200 C (α)	1565.9	1567.7	1570.0	1572.7	1574.5

It is known (McKeown, *et al.*, 1985) that the edge for tetrahedral Al is 2 eV lower than that of octahedral Al. In the intermediates, peaks A and B correspond to the white lines for tetrahedral and octahedral Al, respectively. Clearly tetrahedral Al is being formed up to 538 °C, as evidenced by the increased intensity of peak A; the amount then changes only slightly until formation of α-alumina (corundum) at 1200 °C. ^{27}Al MAS NMR verifies the growth of tetrahedral Al, but neither the starting α-alumina monohydrate nor the final high temperature product α-alumina contain any tetrahedral Al.

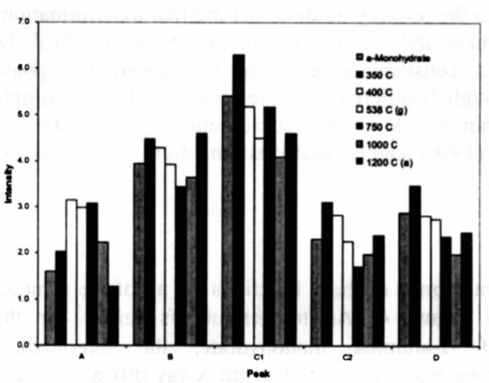

Figure 2 Peak Intensities

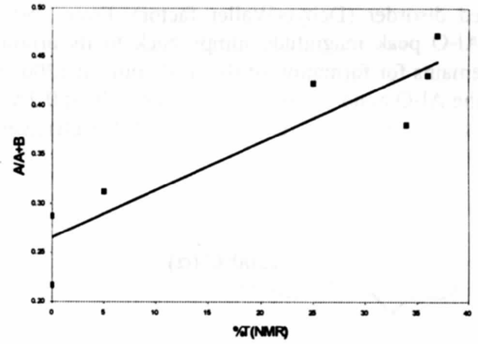

Figure 3 Relative Intensity of Peak A

A plot of A/A+B vs. %T (NMR) shows (Figure 3) an intercept of ~0.25, indicating that peak A, in addition to including intensity from the tetrahedral edge, also includes a contribution from octahedral structures. So the ratio A/A+B cannot be used to forecast tetrahedral contents, at least in this system.

The A peak for corundum had been recently identified as being due to medium range multiple scattering, as it does not appear in the calculated spectra until cluster sizes are greater than 13 Å (Cabaret, *et al.* 1996). The Al lattice structures in these intermediates is very similar to Al metal and changes little metal, suggesting this sublattice as the origin for this MS peak.

The sharpness of the B peak in the monohydrate and corundum has been attributed to presence of only one Al crystallographic site in these materials (Wefers, 1987;Ildefonse, *et al.*, 1994;Cabaret, *et al.*, 1996); the broadening of B with increasing calcination temperature corresponds to formation of additional octahedral sites in the more disordered intermediates.

C1, C2 and D have also been attributed to medium range multiple scattering interactions (Cabaret, *et al.* 1996). Peak C1 is relatively broader (~4 eV halfwidth) than the other peaks and its intensity remains relatively constant over all the transformations so it may also be due to multiple scattering between Al atoms, intensity changes only being due to interfering oxygen atoms in the disordered structures. Peak C2, the intensity of which changes more dramatically than C2, may be due to Al-O multiple scattering, since the primary mode of the thermal transformations involve movement and disorder of the oxygen atoms. Peak D, which remains constant in intensity throughout the phase transitions through disordered structures could be due to multiple scattering within the Al-O first coordination sphere, although Cabaret, *et al.* (1996) suggest that it is a medium range multiple scattering peak.

EXAFS

The Fourier transforms of the χ functions for all of the samples are shown in Figure 4. As temperature is raised for the calcination of α-alumina monohydrate, the intermediate structures become more disordered (from X-ray diffraction) and correspondingly less dense. The highest surface area is that of γ-Al_2O_3, formed at 538 °C. Further increase in temperature results in loss of surface area and increased density.

The EXAFS is qualitatively consistent with this picture: The Al-O peak decreases in intensity due to loss of coordination number and/or increased disorder (Debye-Waller factor). From 750 to 1000 °C, the Al-O peak magnitude jumps back to its original intensity and remains for formation of the α-alumina at 1200 °C. Up to 538 °C, the Al-O bond distance decreases by about 0.2Å as tetrahedral Al is formed, then increases again with the increasing formation of octahedral Al.

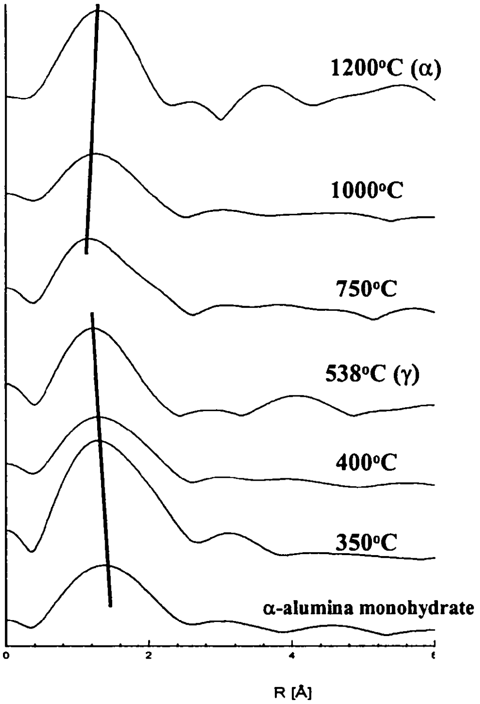

Figure 4 Fourier Transforms of Transition Aluminas

Conclusion

The XAS for transition aluminas formed by calcination of pseudoboehmite at temperatures up to 1200 °C are consistent with the known structural changes, in which high surface area intermediates containing tetrahedral Al are formed, and then ultimately convert to denser phases. This information should be useful for investigations of changes in alumina supports in the presence of active components in catalysts and sorbents.

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