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Solid-State ^{1}H NMR Studies of Aluminum Oxide Hydroxides and Hydroxides

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^{1}H CRAMPS (Combined Rotation and Multiple Pulse Spectroscopy) investigations have been used to identify the protons of Al−OH groups associated with low-surface-area aluminum oxide hydroxide and hydroxide materials. The ^{1}H CRAMPS spectrum of boehmite (γ-AlOOH) shows a single peak at 8.8 ppm due to protons associated with Al_2OH groups containing six-coordinate aluminum and three-coordinate oxygen, whereas the ^{1}H CRAMPS spectrum of diaspore (α-AlOOH) depicts a sharp peak at 10.8 ppm that is assigned to the protons associated with Al_3OH groups containing six-coordinate aluminum and four-coordinate oxygen. The ^{1}H CRAMPS spectra of aluminum hydroxides show three ^{1}H NMR peaks, in approximate 3:2:1 ratios, that are attributed to the protons associated with three different types of Al_2OH groups. In gibbsite (γ-$Al(OH)_3$), these ^{1}H NMR peaks appear at 5.8, 4.3, and 2.9 ppm and are assigned to protons (a) H(3), H(5), and H(6), (b) H(1) and H(4), and (c) H(2), respectively, on the basis of X-ray diffraction and neutron diffraction data. In bayerite (α-$Al(OH)_3$), these resonances are at 5.0, 4.3, and 2.9 ppm and are assigned to protons (a) H(1), H(2), and H(3), (b) H(4) and H(6), and (c) H(5), respectively. Dipolar dephasing experiments indicate that the protons associated with Al_2OH groups containing three-coordinate oxygens are involved in stronger ^{1}H−^{1}H dipolar interactions than the protons associated with the Al_3OH groups containing four-coordinate oxygens.

Introduction

Various aluminum oxide based materials of industrial importance include the anhydrous and hydrous aluminum oxides and hydroxides, and a wide range of calcined, aluminum oxides such as corundum or α-alumina (α-Al_2O_3), γ-alumina, and transitional aluminas.[1] The three hydroxides gibbsite, bayerite, and nordstrandite, have related crystal structures.[1−3] Gibbsite consists of double layers of a hexagonal close-packed array of hydroxyl ions; each aluminum is coordinated to six anions that form edge-shared octahedral $Al(OH)_6$ structural units. The double layers are stacked in the direction of the *c* axis with repeating A and B layers of the sequence ABBAABBA. The aluminum ions occupy only two-thirds of the available interstices in the oxide plane and are arranged in a pattern of hexagonal rings that surround the vacant sites. The stacking is deformed slightly in the direction of the *a* axis, giving a monoclinic lattice.[1] The crystal structure of bayerite is based on a double layer of closely packed hydroxyl ions, with two-thirds of the octahedral voids being filled by aluminums. The stacking arrangement is ABABAB, where the atoms of the third layer are placed above those of the first layer. The double layers are held together by hydrogen bonds between adjacent hydroxyl ions. The smallest O−O distance between two adjacent layers is larger in bayerite than in gibbsite.[2]

Aluminum oxide hydroxide [AlO(OH)] occurs in two distinct forms, boehmite and diaspore, that exist in a hexagonal close-packed arrangement of hydrogen-bonded oxides built up of edge-sharing $AlO_4(OH)_2$ or $AlO_3(OH)_3$ octahedral units.[4] Diaspore contains two types of Al−O bonding interactions: in the first type, the oxygen is approximately coplanar with the three surrounding aluminums at Al−O distances of 1.85 Å, whereas in the second type the oxygen forms a pyramid with the three adjacent aluminums at an Al−O distance of 1.98 Å. In boehmite, the Al^{3+} ion exists in a distorted, edge-sharing octahedral array of oxide ions that forms a double layer. The resulting double layers are connected by zigzag chains of hydrogen bonds.[5]

On the basis of infrared studies, Peri[6] postulated a surface model for γ-alumina that includes the five different surface hydroxyl sites as shown in Figure 1. This model was later refined by Knözinger and Ratnasamy[7] to include the (111) and (110) planes. This model provides a framework for discussing and describing the various proton, oxygen, and aluminum chemical environments associated with the various surface Al−OH sites. According to this model, aluminum hydroxides, oxide hydroxides, and transitional aluminas contain at least one of the five distinct hydroxyl sites. The type III site is the most

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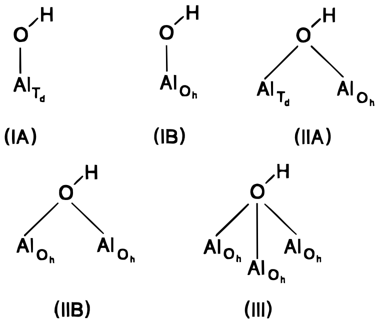

Figure 1. Types of surface hydroxyls, as proposed by Peri.[6]

acidic site, whereas the types IA and IB are the most basic. The relative contribution of specific crystal faces ultimately determines the occurrence and number of each OH group.[5]

Several solid-state NMR spectroscopic techniques have been succesfully used to obtain information related to both the structure and dynamics of the surface chemistry of aluminas.[8−13] Morris and Ellis[9] applied solid-state magic-angle spinning (MAS) ^{27}Al and cross-polarization (CP) MAS NMR to study the surface of α-alumina, γ-alumina, and several pretreated γ-aluminas. The MAS ^{27}Al spectra of γ-alumina showed single peaks that were assigned to structural tetrahedral and octahedral aluminum sites, respectively. The CP/MAS ^{27}Al spectra of α-alumina and boehmite (composed exclusively of octahedral sites) exhibited only a single peak associated with surface AlO_6 sites.

Huggins and Ellis[10] carried out variable-temperature solid-state MAS ^{27}Al NMR studies to examine the surface of α-Al_2O_3, γ-Al_2O_3, and several transitional aluminas. Two resonance peaks were observed in the ^{27}Al MAS spectra associated with surface octahedral and tetrahedral aluminum sites. These authors described the dynamics of the alumina surface using a model that involved several mechanisms of proton motion.[10]

Walter and Oldfield[4] used CP/MAS ^{17}O NMR to study structural surface sites in aluminum oxides and hydroxides and transitional aluminas. The MAS ^{17}O spectra of α-alumina showed only a single peak associated with structural Al_4O units, whereas ^{17}O-enriched crystalline boehmite showed two distinguishable peaks assigned to Al_4O and Al_2OH sites, respectively. The use of ^{1}H−^{17}O cross polarization permitted the selective enhancement of the weak Al_2OH signal. The MAS ^{17}O spectrum of ^{17}O-enriched bayerite showed only a single broad peak associated with Al_2OH sites. The presence of at least three crystallographically distinct oxygen sites made it difficult to obtain a well-defined CP/MAS ^{17}O NMR spectrum. The spectra of the transitional aluminas χ-Al_2O_3, η-Al_2O_3, γ-Al_2O_3, and θ-Al_2O_3 showed two overlapping peaks assigned to tetrahedral Al_4O sites containing four-coordinate oxygen and trigonal Al_3O units containing three-coordinate oxygen.

^{1}H NMR using the CRAMPS (combined rotational and multiple pulse spectroscopy) technique has been successfully used to examine the surface chemistry of silica/alumina materials. Bronnimann *et al.*[11] applied the ^{1}H CRAMPS technique to explore the surface moieties on silica−alumina catalysts. A sharp peak at 2.0 ppm was assigned to the protons associated with Si−OH moieties of either silica gel or silica-like regions, while two broad peaks centered at 3.1 and 4.8 ppm were assigned to protons of water molecules physisorbed onto silica gel or silica-like regions and to γ-alumina or alumina-like regions of silica−aluminas, respectively. An additional peak at 7 ppm was attributed to hydrated Brønsted sites, although Pfeifer assigned this peak to protons of residual NH_4^+ ion.[12] Bronnimann *et al.*[13] also utilized ^{1}H CRAMPS to examine the dehydration of the silica gel surfaces. The ^{1}H CRAMPS spectra of heated and evacuated silica gel samples showed two sharp peaks at 1.7 and 3.0 ppm, assigned to protons of "isolated" Si-OH groups and "physisorbed" water, respectively. In addition, a broad peak centered at 3.0 ppm was attributed to protons of hydrogen-bonded Si−OH groups.

Fitzgerald *et al.*[14] has recently utilized ^{1}H CRAMPS to identify and assign the protons for a high-surface-area pseudo-boehmite material following dehydration in the 110−1100 °C temperature range. Three distinguishable ^{1}H CRAMPS resonances were identified: a peak at 2.3 ppm assigned to protons of "isolated" (non-hydrogen-bonded) surface/internal AlOH groups, another peak at 8.2 ppm associated with the protons of highly coupled, "clustered" surface/internal Al_2OH groups, and a broad feature at 5.3 ppm attributed to the protons of "physisorbed" water. Removal of the physisorbed water peak (5.3 ppm) was demonstrated by *in vacuo* heating of the pseudo-boehmite materials at 110 °C. Dehydration experiments suggested that the Al_2OH groups condense at 300−350 °C, whereas the isolated AlOH groups required higher temperatures ($T >$ 350 °C) to condense. These authors proposed a model for the dehydration of pseudo-boehmite involving the condensation of these surface Al−OH groups, with the concomitant formation of Al−O−Al strained linkages in distorted six-coordinate or five-coordinate aluminum sites.

To date, ^{1}H CRAMPS techniques have been found to be a valuable NMR approach for elucidating the nature and population of the surface protons in silicas and aluminas.[12−14] The work reported herein summarizes ^{1}H CRAMPS investigations that were carried out to examine the nature of the proton population of the Al−OH groups that are associated with various low-surface-area aluminum oxide hydroxide and hydroxide materials.

Experimental Section

Commercially available gibbsite, prepared by precipitation from caustic Bayer liquor solutions, was used as received from Alcoa Technical Center (Alcoa Center, Pittsburgh, PA). Bayerite was prepared by precipitation from neutralized sodium aluminate solutions.[15] Boehmite was prepared quantitatively from the hydrothermal treatment of gibbsite by heating an aqueous slurry to boiling. Diaspore was prepared from high-pressure calcination of boehmite.[16] These samples contained additional phases as minor impurities.

^{1}H CRAMPS Experiments. For ^{1}H CRAMPS experiments, samples were placed into thick-walled 5 mm (OD) glass tubes (Wilmad PS241), evacuated at 6.5 mTorr for 24 h, and sealed off under vacuum. ^{1}H CRAMPS spectra were obtained at 360 MHz on a modified NT-360 spectrometer, using the BR-24 pulse sequence[17] and "home-built" probes. The 360 MHz CRAMPS spectra were obtained with $\tau \approx 3.1$ and 1.4 μs $\pi/2$ pulses at MAS speeds of 1.2−1.5 kHz. The BR-24 sequence was initiated with a preparation pulse and delay period τ, followed by 24 pulse−τ−pulse−2τ sequences. All spectra were

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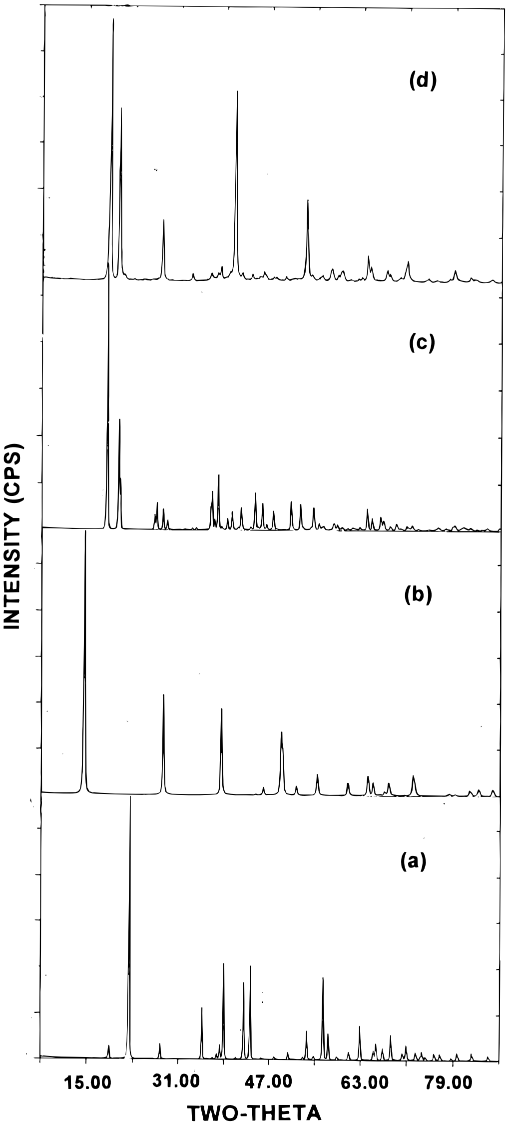

Figure 2. X-ray diffraction patterns for various aluminum oxide hydroxides and hydroxides: (a) diaspore; (b) boehmite; (c) gibbsite; (d) bayerite.

referenced to the chemical shift of tetrakis(trimethylsilyl)silane (TTMSS) at 0.38 ppm (with liquid tetramethylsilane at 0.00 ppm).

Powder X-ray Diffraction Analysis. Powder X-ray diffraction analysis was obtained using a Siemens Model D-500 diffractometer system using Cu Kα radiation. Figure 2 shows the powder X-ray diffraction patterns of the various oxide hydroxides and hydroxides (diaspore, boehmite, gibbsite, and bayerite) over the 2θ values from 7.00 to 87.00°. The various solids were found to contain very pure phases, with less than 1% impurities present.

Results and Discussion

Boehmite. Boehmite has been shown by single-crystal X-ray diffraction[18] and time-of-flight neutron diffraction[19] methods to have orthorhombic symmetry and to belong to the space group *Cmcm*. The dimensions of the boehmite unit cell are $a = 3.693$ Å, $b = 12.221$ Å, and $c = 2.865$ Å.[19] Boehmite consists of distorted AlO_6 octahedra that share 6 of their 12 edges asymmetrically with adjacent octahedra. The structure of boehmite contains equally distributed Al_2OH and Al_4O oxygen sites (see Figure S1, Supporting Information). The oxygen of the Al_2OH groups is coordinated to two hydrogens, while the second oxygen is involved in hydrogen bonding to the oxygen of the adjacent Al_2OH unit, as depicted in Figure 3a.[4]

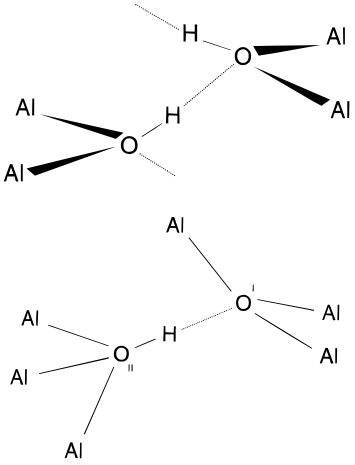

Figure 3. Distribution of hydrogen atoms in Al_2OH groups involved in hydrogen bonding in (a, top) boehmite and (b, bottom) diaspore.

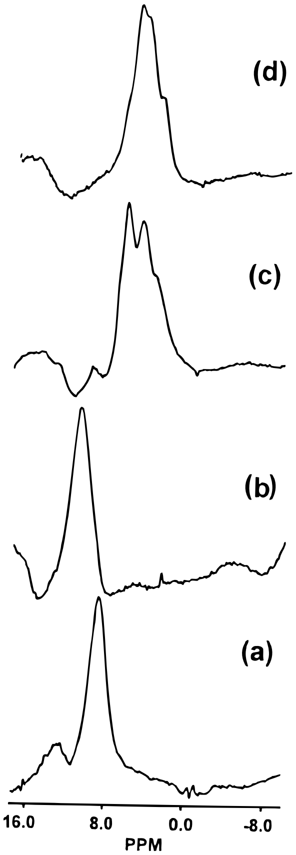

Figure 4. 360 MHz ^1H CRAMPS spectra for aluminum oxide hydroxide and hydroxide materials evacuated at 6.5 mTorr for 24 h: (a) boehmite; (b) diaspore; (c) gibbsite; (d) bayerite.

The ^1H CRAMPS spectrum of crystalline boehmite obtained at 360 MHz is shown in Figure 4a. This spectrum exhibits a single peak at 8.8 ppm assigned to the protons associated with six-coordinate aluminum Al_2OH sites, probably similar to the type IIB site of the surface model of γ-alumina proposed by Peri.[6] The results of a series of dipolar dephasing experiments for boehmite given in Figure 5a show that the protons associated with these Al_2OH sites dephase beyond observation after 20 μs dephasing periods. These dipolar dephasing results are very similar to those results obtained by Fitzgerald *et al.*[14] in ^1H CRAMPS studies of the Al_2OH sites found in a high-surface-

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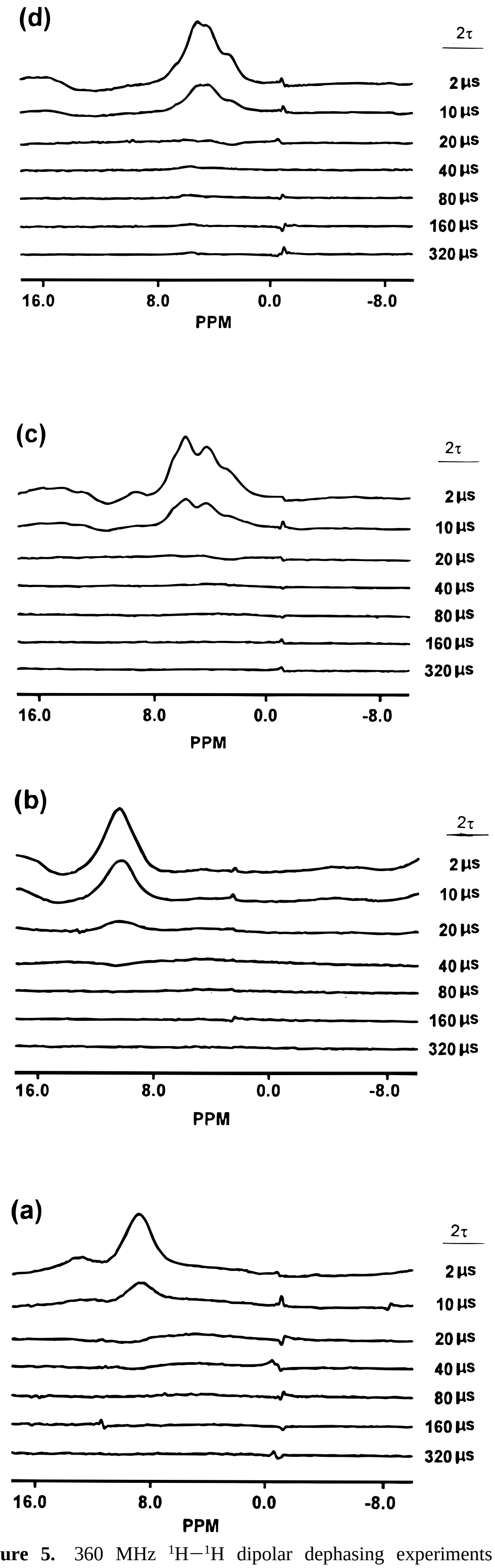

Figure 5. 360 MHz $^1H-^1H$ dipolar dephasing experiments for aluminum oxide hydroxide and hydroxide materials evacuated at 6.5 mTorr for 24 h: (a) boehmite; (b) diaspore; (c) gibbsite; (d) bayerite.

area pseudo-boehmite material. These high-surface-area pseudo-boehmite materials showed ^1H NMR resonances at 2.3 and 8.2 ppm that required dephasing periods of 20 and 80 μs, respectively, in order to eliminate the ^1H resonances. These two peaks were assigned to protons associated with octahedral surface/internal AlOH (2.3 ppm) and Al_2OH sites (8.2 ppm), respectively. The shorter dephasing period required for the complete elimination of the Al_2OH peak (8.2 ppm) suggested that protons associated with this species are involved in stronger $^1H-^1H$ dipolar coupling, due to hydrogen bonding.[15]

Diaspore. Diaspore shows orthorombic symmetry similar to boehmite with a space group of *Pbnm*.[20,21] The unit cell has the dimensions $a = 4.401$ Å, $b = 9.421$ Å and $c = 2.845$ Å.[21] Diaspore contains two types of oxygen atoms denoted O_I and O_{II} by Ewing.[20] The aluminum atoms are coordinated to three O_I and three O_{II} resulting in edge-sharing of the AlO_6 octahedra. The AlO_6 units form double strings extending in the *c*-direction, forming a three-dimensional network by sharing corner oxygens (see Figure S2, Supporting Information). The hydrogen atoms in diapore are exclusively covalently bonded to O_{II} oxygens and are hydrogen-bonded to O_I oxygens at an angle of 12.1° with respect to the $O_{II}-O_I$ direction, as shown in Figure 3b.

The ^1H CRAMPS spectrum obtained at 360 MHz for crystalline diaspore is shown in Figure 4b. This spectrum depicts a single peak centered at 10.8 ppm that is tentatively assigned to the protons associated with Al_3OH sites similar to type III hydroxyl groups for γ-alumina as proposed by Peri.[6] The inductive effect caused by the three second-nearest-neighbor aluminum ions causes the Al_3OH protons to be more acidic than the protons associated with the Al_2OH groups in boehmite; therefore, the lower shielding experienced by the Al_3OH protons leads to a lower field chemical shift. The 10.8 ppm peak assigned to the protons associated with Al_3OH sites in diaspore is observed to disappear after 40 μs of dephasing period (Figure 5b), indicating that these protons are involved in weaker $^1H-^1H$ dipolar couplings than the protons associated with the Al_2OH group protons of boehmite. The H···H distances in boehmite and diaspore are approximately 1.9 and 2.7 Å, respectively; therefore, it is expected that the protons in boehmite are coupled more strongly with each other than the corresponding hydrogen-bonded protons in diaspore.

Gibbsite. Saafeld and Wedde[22] have refined the gibbsite structure in the space group $P2_1/n$ of monoclinic symmetry. The gibbsite unit cell dimensions are $a = 8.684$ Å, $b = 5.078$ Å, and $c = 9.736$ Å, with a β angle of 95.54°.[22] In the ABABAB sequence of double layers in gibbsite, the OH^- ions of adjacent layers are located directly opposite to each other, with hydrogen bonding between the layers (see Figure S3, Supporting Information). Gibbsite is exclusively composed of Al_2OH octahedral sites similar to those of boehmite.

The ^1H CRAMPS NMR spectrum of gibbsite, shown in Figure 4c, depicts three distinguishable resonance peaks at 5.8, 4.3, and 2.9 ppm in an approximate 3:2:1 ratio, on the basis of deconvolution analysis. Six geometrically distinct protons have been reported to exist in gibbsite.[22,23] Three of these hydrogen atoms (H(1), H(2), and H(4)) are located within the oxide layers, forming intralayer hydrogen bonds, whereas the remaining three hydrogens (H(3), H(5), and H(6)) lie between the Al−OH layers, forming interlayer hydrogen bonds with hydroxyl groups of the adjacent layer. The average hydrogen-bond O−H···O distance of protons located between the layers is approximately 1.98 Å, whereas the corresponding average distance for hydrogen atoms situated within the layers is about 2.36 Å. Therefore, the ^1H

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CRAMPS peak at 5.8 ppm is assigned to the protons associated with the OH···O pairs O(6)H(6)···O(2), O(3)H(3)···O(4), and O(5)H(5)···O(1). The H(1) and H(4) hydrogens are horizontally oriented toward the same empty octahedral site, forming hydrogen bonds with oxygen O(6), as depicted in Figure S3, whereas the H(2) hydrogens are oriented toward an adjacent empty octahedral site and are hydrogen-bonded to oxygens O(3). On the basis of this difference in the structural environments of these three hydrogens (H(1), H(2), and H(4)) the ^{1}H peak at 2.9 ppm is tentatively assigned to hydrogen H(2), whereas the 4.3 ppm peak resonances are probably due to the hydrogens H(1) and H(4). These peak assignments would account for the 3:2:1 ratio observed for the peaks in the ^{1}H CRAMPS spectrum of gibbsite shown in Figure 4c. The Al_2OH protons associated with all three peaks are found to disappear at dephasing periods of 20 μs (Figure 5c), indicating that the ^{1}H−^{1}H dipolar coupling between the protons associated with the Al_2OH sites of gibbsite is very similar to the ^{1}H−^{1}H dipolar coupling of the protons in boehmite.

Bayerite. The crystal structure of bayerite shows monoclinic symmetry, with a space group of $P2_1/n$. The unit cell dimensions are $a = 5.062$ Å, $b = 8.672$ Å, and $c = 9.425$ Å, with a β angle of 90.26°.[24] The stacking of Al−OH octahedra layers is arranged in the sequence ABABABAB, with hydroxyl ions of the third layer lying in the depressions between OH positions of the second layer (see Figure S4, Supporting Information). Zigan *et al*.[24] determined that bayerite contains six symmetrically independent hydrogen atoms. The hydrogens H(1), H(2), and H(3) are located between adjacent Al−OH layers, forming hydrogen bonds between the layers, with an average hydrogen-bond OH···O distance of 1.99 Å. The hydrogens H(4), H(5), and H(6) are also involved in hydrogen bonding but within the same Al−OH layer, with an average hydrogen-bond distance of 2.3 Å.

The ^{1}H CRAMPS spectrum of bayerite shown in Figure 4d exhibits three peaks centered at 5.0, 4.3, and 2.9 ppm, in a 3:2:1 ratio, on the basis of deconvolution analysis. From the average hydrogen-bond distances listed above, the 5.0 ppm resonance peak is also tentatively assigned to the Al_2OH protons involved in the interlayer hydrogen bonding: O(1)H(1)···O(4), O(2)H(2)···O(6), and O(3)H(3)···O(5). The hydrogens H(4) and H(6) are oriented toward the same empty octahedral site, forming hydrogen bonds with oxygen O(2) of layer B, as depicted in Figure S4. The hydrogens H(5) are hydrogen-bonded to the oxygens O(1) and O(3) of an adjacent empty site in the same layer B. Hydrogens H(5) of layer A are also oriented toward the same empty octahedral site of layer B to which hydrogens H(4) and H(6) are oriented (see Figure S4). The dipolar dephasing results of Figure 5d indicate that all six types of protons in bayerite dephase at the dephasing period of 20 μs, suggesting that the ^{1}H−^{1}H dipolar interactions between these protons are very similar to the protons associated with the Al_2-OH groups in both boehmite and gibbsite.

Conclusion

Low-surface-area aluminum oxide hydroxides and hydroxides have been shown by ^{1}H CRAMPS to contain protons that are assigned to six-coordinate aluminum Al−OH structural sites on the basis of an analysis of X-ray and neutron diffraction data. The ^{1}H CRAMPS results indicate that the oxide hydroxides boehmite and diaspore are exclusively composed of three- and four-coordinate oxygen contained in Al_2OH and Al_3OH structural units, respectively. The protons associated with the Al_3-OH groups are more acidic than the Al_2OH group protons because of the inductive effect caused by the three second-nearest-neighbor six-coordinate aluminums in the Al_3OH sites. ^{1}H−^{1}H dipolar dephasing experiments have demonstrated that the protons associated with Al_2OH groups are involved in stronger ^{1}H−^{1}H dipolar interactions than those associated with the Al_3OH sites, as a direct consequence of the shorter H···H distances in boehmite. The ^{1}H CRAMPS spectra of the aluminum hydroxides gibbsite and bayerite show three distinguishable ^{1}H NMR peaks due to protons in an approximate 3:2:1 intensity ratio that are associated with Al_2OH groups containing six-coordinate aluminums. Assignment of these peaks has been made on the basis of (1) the distinction between protons involved in inter- and intralayer hydrogen bonding and (2) the orientation of protons involved in intralayer hydrogen bonding. ^{1}H−^{1}H dipolar dephasing results have indicated that the protons associated with the Al_2OH groups of the different forms of aluminum hydroxides are involved in ^{1}H−^{1}H dipolar interactions of a similar strength as the ^{1}H−^{1}H dipolar interactions of the protons in the Al_2OH groups in boehmite.

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Supporting Information Available: Figures depicting the distribution of hydrogen atoms using polyhedron models: S1a, AlO_6 polyhedra in boehmite; S1b, edge-sharing $AlO_4(OH)_2$ or $AlO_3(OH)_3$ octahedra in boehmite; S2a, AlO_6 polyhedra in diaspore; S2b, edge-sharing $AlO_4(OH)_2$ or $AlO_3(OH)_3$ octahedra in diaspore; S3a, $Al(OH)_6$ octahedra down the (001) face in gibbsite; S3b, labeling of hydrogen atoms in the "A" layer of gibbsite; S4a, $Al(OH)_6$ octahedra down the (001) face in bayerite; S4b, labeling of hydrogen atoms in the "A" and "B" layers of bayerite (8 pages). Ordering information is given on any current masthead page.

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