Surface conditions of three types of commercial high purity alpha alumina powders produced by three different processes, in-situ chemical vapor deposition (A powders), hydrolysis of aluminum alkoxide (B powders), and a pioneer chemical vapor deposition (no longer in the market) (C powder) methods are evaluated by FT-IR (Fourier transform infrared) transmission and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. The spectroscopy results suggest that the surface characteristics of as-received high purity alpha alumina powders are not unique. In some of the B powders with small size, a mixture of aluminum trihydroxides like bands is observed. A specific band at 3472 cm\(^{-1}\) observed on the B and C powders does not belong to band spectra of the aluminum hydroxide references. Relating to the predicted band on infrared spectra of hydrated alpha alumina surface obtained from reported molecular dynamics calculation, this band may be associated with hydrogen bonded hydroxyl groups of a fully hydroxylated alpha alumina surface.

**Key-words:** High purity alpha alumina, Surface hydration, Transmission infrared spectroscopy, Diffuse reflectance infrared, Molecular dynamic simulation

1. Introduction

The surfaces of \(\alpha-Al_2O_3\) have played a key role in their performances in many technological applications such as a catalyst support, electronic packaging, and also in other fields where ceramic–metal bonding is used.

In the case of alumina powders, surface condition differences of the powders can influence their physical properties such as zeta potential,\(^4\) powder agglomeration\(^2\) and sintering behavior.\(^3\) Incorvati et al. have indicated that differences in surface chemistry can influence rheology of alumina slurries.\(^6\) The variation in the surface condition may yield different deflocculation responses in aqueous slurries when different lots of a particular Bayer-processed alumina are deflocculated using an ammonium polymethacrylate defloculant. The variable rheological behavior even can be extreme and may cause differences in slip-casting and spray-drying behaviors.\(^4\)

The surface condition differences may be found as effects of impurity of the powders as can be seen in the Bayer-process alumina. To remove the impurity effects, in this study, surfaces of high purity \(\alpha\)-alumina powders are evaluated. Surface of high purity \(\alpha\)-alumina powders may contain an aluminum hydroxide phase, which can also generate surface condition differences in the \(\alpha\)-alumina powders. The results are also examined in relation to the hydration predictions obtained from reported molecular dynamic simulations.

2. Experimental

Thirteen commercially available \(\alpha-Al_2O_3\) powders used for this study have specifications as shown in Table 1. Production method of “A” powders (AA-04, AA-07, and AA-05, Sumitomo Chemical Co., Ltd.) are different from “B” powders (AKP-30, AKP-50 and AKP-3000, Sumitomo Chemical Co., Ltd.). The former are produced by Bayer process and the later are produced by hydrolysis of aluminum alkoxide. The C powder was produced by a pioneer in-situ chemical deposition method that has been substituted by a new method, by which the A powders have been manufactured. Even though powders similar to powder C are no longer available, it is included in the present work because it was one of the powders investigated in the previous study.\(^5\) All powders have low impurity content. The values of impurity content are lower than the impurity in aluminum oxide produced with the Bayer process, which usually have high NaO impurity content. Table 1 summarizes the specifications of the powders used in this study. For comparison of the spectra, aluminum hydroxides of bayerite (\(\text{Al(OH)}_3\)) and gibbsite (Sumitomo Chem. Co., Ltd.) are also used as references in this study.

Samples for the transmission FT-IR measurements are prepared by self-supporting the powders in a stainless steel grid with hole opening of 0.20 mm and 0.22 mm in thickness. For inserting the powder into the grid holes, a uniaxial pressure of 60 MPa has been applied on the powder. The FT-IR transmission spectra with resolution of 4 cm\(^{-1}\) (number of scanning is 200) of all powders are obtained by using a Nicolet 410S spectrometer equipped with a DTGS
Surface Hydration States of High Purity $\alpha$-Al$_2$O$_3$ Powders

detector and OMNIC ver. 2.0 software for data processing.

Diffuse reflectance infrared fourier transform (DRIFT) spectra are obtained for the as-received powders using Shimadzu FT-IR 8000 spectrometer equipped with a Spectra-Tech diffused reflectance accessory and Shimadzu Hyper IR data processing software. To increase the spectrum signal from the alumina powder and to avoid influences of water absorbed on KBr, the investigated powder was placed in a micro sample holder without diluting in KBr. Each spectrum was scanned 200 times with resolution of 4 cm$^{-1}$. For measuring background signal, an aluminum mirror has been used as a reflector.

3. Results and discussion

Results of FT-IR transmission and DRIFT spectra measurements at 2700–4000 cm$^{-1}$ wavenumber range are shown in Figs. 1 through 5. The O–H stretching vibration bands observed in the spectra are reproducible with intensity much higher than the background signal.

For transmission spectra of powders A shown in Fig. 1, broad bands between 3000 cm$^{-1}$ and 3600 cm$^{-1}$ are seen in most of the powders A spectra. Some peculiar exceptions are found in powders A2b and A2c, which have smaller surface areas than the other A powders. The transmission spectra of those two powders do not have reproducibility, as well. However, the exceptions are not observed in their diffuse reflectance (DRIFT) spectra shown in Fig. 2. For the opaque powders with large particle size (up to about 2–5 μm), Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique is more suitable. In the DRIFT spectra of the A powders broad peaks are observed with some distinctive maxims at approximately 3300 cm$^{-1}$, 3450 cm$^{-1}$ and 3690 cm$^{-1}$, clearly distinguished for example in the spectrum of the A1b powder. The broad peak at 3300 cm$^{-1}$ might be partially attributed to stretching vibrational modes of water molecules physisorbed on the alumina surface, the broad band centered at 3450 cm$^{-1}$ to hydrogen bonded

<table>
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<tr>
<th>Nomenclature</th>
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<th>Lot No.</th>
<th>Production Methods</th>
<th>Particle Size / μm</th>
<th>Specific Surface Area / m$^2$/g</th>
<th>Impurities / ppm</th>
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<td></td>
<td></td>
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Table 1. Specification of the Powders Provided by the Manufacturer

Fig. 1. Hydroxyl stretching absorption frequency region showing FT-IR transmission spectra of the $\alpha$-alumina powders produced by a new in-situ chemical vapor deposition process. The ordinate represents the absorbance in arbitrary unit. A broad band between 3000 cm$^{-1}$ and 3600 cm$^{-1}$ is observed. A small band at 3690 cm$^{-1}$ is also observed for some of the powders. The later band is interpreted as free OH.

Fig. 2. Hydroxyl stretching absorption frequency region for DRIFT spectra of the $\alpha$-alumina powders produced by a new in-situ chemical vapor deposition process. Broad bands with maximum at around 3300 cm$^{-1}$ and 3450 cm$^{-1}$ are observed together with the small 3690 cm$^{-1}$ free OH band. The broad bands are interpreted mainly as superposition of different hydrogen bonded structures.
surface hydroxyls modes, and the small 3690 cm⁻¹ peak to free hydroxyl groups.

Figure 3 shows the transmission infrared spectra for powders B in the same range of wavenumber as in Fig. 1 for powders A. In the case of powders B, since all of them have small enough particle size, spectra of the powder can be measured by both transmission and DRIFT method with no significant differences, as can be seen in Fig. 3 and Fig. 4.

For the C powder, shown in Fig. 5, the difference between transmission and DRIFT spectra might be again associated with its large particle size (Table 1). The free surface hydroxyl group mode at 3691 cm⁻¹, as discussed in the case of powders A, is also clearly observed in the spectra of the B powders. The broad 3300 cm⁻¹ and 3450 cm⁻¹ bands are clearly observed in the spectra of powders B1a, B1b and B3b, meanwhile the spectra of powders B2a, B2b, B3a and C present several defined small bands (Figs. 4 and 5). Using diffuse reflectance infrared spectroscopy similar bands were also detected on some as-received commercial α-alumina produced by the Bayer-process and all investigated powders after washing in distilled water. The distinctive features were assigned to gibbsite/bayerite like structures. Dyer and Hendra, investigated the hydration of high purity γ-alumina. The DRIFT and Raman spectra of the hydrated product presented distinctive bands and XRD data showed the formation of a phase containing not only γ-alumina, but also Al(OH)₃ in the bayerite polymorph. The formed Al(OH)₃ features disappeared after heating at 200°C. Since the spectra of the heated product did not show boehmite bands, the authors concluded that the dehydration product must be Al₂O₃ and not AlOOH. An alum-derived high purity α-alumina with submicrometer particle size was colloidally dispersed and classified in either low pH water or ethanol to remove agglomerates from the as received powder. It was concluded that in the case of the water slurry a small amount of transition alumina reacted with water at low pH releasing Al³⁺ ions that formed a complex amorphous aluminum hydroxyl gel. On drying the slurry, it was
postulated that the gel would form a hardened cementlike bonding responsible of the presence of hard agglomerates. The same study indicated that the difference in reactivity between α-alumina and the transition aluminas can be explained not only by the difference of free energy of formation but also by difference of particle size, the solubility of fine particles being greater than that of coarse particles. Referring to Schindler, who pointed out about the effect of particle size on phase stability in aqueous systems, the authors stated that Al₂O₃ particles would dissolve in water and precipitate as hydroxide, which is a thermodynamically more stable phase below a critical size.

A comparison of the spectral features observed for some of the B α-alumina powders, was made with the reported spectra of the Bayer-process α-alumina powders, two α-alumina specimens prepared by thermal treatment of pure transition aluminas in the form of infrared pellets and the hydrated γ-alumina. The comparison is shown in Fig. 6. It is observed that the position of the distinctive spectral features of the B₂a powder are similar to those of the Bayer process α-alumina and the hydrated γ-alumina, Figs. 6(a) and 6(b), respectively. In the case of the Bayer processed α-

Fig. 6. Comparison between the spectrum of one of the α-alumina powders produced by the hydrolysis of aluminum alkoxide process showing specific hydroxide like bands (B₂a) with the spectra of alumina powders reported in the literature. (a) a Bayer process α-alumina, (b) a hydrated high purity γ-alumina, (c) and (d) hydrated α-alumina specimens prepared by heating a γ-alumina pellet for 12 and 22 h, respectively. So far the position of the specific bands, closer spectral similarities are found with the spectra of the Bayer process α-alumina (a), followed by the hydrated γ-alumina (b), as also seen in the data of Table 3. The shape of the broad absorption is also similar to the hydrated α-alumina specimen prepared by longer heating time of γ-alumina (d).
alumina the features were attributed to a mixture of bayerite and gibbsite-like structures on the surface\(^5\)\(^,\)\(^11\) and to bayerite in the case of \(\gamma\)-alumina.\(^12\)

Table 2 summarizes the range of hydroxyl stretching frequencies reported in the literature for different gibbsite\(^14\)\(^-\)\(^23\) and bayerite\(^14\),\(^16\),\(^18\),\(^19\),\(^23\) samples; together with the transmission and DRIFT bands detected in this work for synthetic gibbsite and bayerite samples. It should be pointed out that the hydroxides used in this work are not pure. The data for nordstrandite\(^19\) are also included. Differences in peak positions are found depending on the sample origin as manifested in the wide wave number range registered for certain bands. The presence of small amounts of other polymorphs is also manifested in additional bands. Nevertheless, the main features of each polymorph are distinguishable and the main bands observed in the gibbsite and bayerite samples analyzed in this work fall within the range. DRIFT spectra of gibbsite (Sumitomo Chem. Co., Ltd.) and bayerite (Al(OH)\(_3\) Soekawa) samples are shown in Figs. 7 (a) and (b) together with the B2a powder spectrum. A specific prominent band around 3472 cm\(^{-1}\), characteristic of some B and the C \(\alpha\)-Al\(_2\)O\(_3\) powders, which is also present in the Bayer process \(\alpha\)-alumina and hydrated \(\gamma\)-alumina shown in Fig. 6, can not be included in any of the band ranges reported for well-crystallized polymorphs.

This prominent band was also present in the spectrum of a cascading travertine-like deposit over volcanic tuffs on Raoul Island in the South Pacific.\(^24\) The spectrum is shown in Fig. 7 (c). This formation was produced from episodic discharge of spent caustic aluminate solution from a hydrogen generator and identified as bayerite by laser Raman spectroscopy even though X-ray powder diffraction and infrared spectral studies failed to give confident identification.\(^24\) The IR spectral data of this sample is not included in the summary of Table 2, but in Table 3 together with the data of the hydrated \(\alpha\) and \(\gamma\)-aluminas. Similarity was also found with the spectrum of synthetic nordstrandite preparations that contained bayerite.\(^23\) The spectrum of these preparations together with the B2a powder spectrum is shown in Fig. 7 (d). Figure 7 as well as the data in Table 3 tend to indicate that the features observed as hydration products of some \(\alpha\)-alumina and \(\gamma\)-aluminas are similar among themselves and do not correspond to the spectra of the commonly identify as gibbsite, bayerite or nordstrandite structures. Especially the prominent band centered around 3470 cm\(^{-1}\). It should be pointed out that even though in the case of gibbsite the review includes some natural products, in the case of bayerite they are all artificial products.

On the other hand, it is interesting to note that the spectrum of the formation found in the Raoul Island, identified as bayerite only by its Raman spectra, resembles those of the hydrated aluminas, especially that of the \(\gamma\)-alumina (Table 3). Elderfield and Hem followed the development of crystalline structure in aluminum hydroxide polymorphs on
temperature MD simulations of the idealized model of hydroxides. In this regard, Hass et al.25) also applied room temp., which is similar to the known surfaces of aluminum oxides, that the Al(OH)₃ species can be removed completely leaving a less reactive surface that is completely OsH terminated. It may depend strongly on sample history.25) It is also possible that the heavily hydrated surface is clearly very complicated and that the Al(OH)₃ species associated with this band might be considered similar to those in the crystals grow. It is then possible to interpret the prominent 3472 cm⁻¹ band as a type of hydrogen bonded hydroxyls characteristic of the hydrated aluminas. Even though the structural species associated with this band might be considered similar in that specific nature is hard to visualize. In this regard the results of molecular dynamic simulations might bring some insight.

Hass et al.25) simulated the chemistry of water on Al terminated (0001) alumina surfaces with ab-initio molecular dynamics (MD). Their simulation results clearly established that, in the low coverage, H₂O dissociation is kinetically as well as thermodynamically favorable on defect free α-Al₂O₃ (0001) at room temperature. Simulations at higher H₂O coverage showed that at least in the very early stages of reaction with H₂O, the unimolecular dissociation dynamics does not appear to be strongly perturbed by the presence of additional adsorbed molecules. They concluded that for a coverage of 10 OH per square nanometer, complete hydroxylation of α-Al₂O₃ (0001) would result in one O_adsH (O_ads: water oxygen) on each surface Al and one O_H (O: surface oxygen) for every three surface O atoms. At OH coverage >10 OH per square nanometer, many of the surface Al-O bonds were highly strained or broken, making some second-layer Al more accessible to H₂O. Further MD simulations showed that an interesting rearrangement can occur. The interior O_adsH replaces its neighboring O_H, whereas the O_H tilts up and becomes singly coordinated to a surface Al, providing a mechanism for the interchange of O_ads and evidence for incipient Al(OH)₃ formation on the surface. The authors also stated that the ultimate structure of the species might be expected to be slightly different from those of gibbsite, bayerite, and norstrandite, and on the other hand, the peculiar band around 3470 cm⁻¹ coincides with the calculated vibrational spectra of in-plane hydrogen bonded O-H groups of a fully hydroxylated alumina surface in which every Al atom has been substituted by three H atoms. Besides, the other peak predicted for the surface OH at 3650 cm⁻¹ is close to the bayerite band at around 3650-3660 cm⁻¹ and 3470 cm⁻¹, with the 3470 cm⁻¹ peak corresponding to in-plane OH groups.

The results of our study as well as the results of Lee and Condarte,11) Incorvati et al.4) and Dyer and Hendra12) might be taken as a confirmation of the predictions made by Hass et al.25) in regard to the possible formation of Al(OH)₃ species by hydration of alumina surfaces, but the question still remaining is whether the Al(OH)₃ is part of the alumina surface or it has been completely removed from it. This question is very difficult to answer from the IR spectra presented so far because on one side the nature of the surface Al(OH)₃ species might be expected to be slightly different from those of gibbsite, bayerite and norstrandite, and on the other hand, the peculiar band around 3470 cm⁻¹ coincides with the calculated vibrational spectra of in-plane hydrogen bonded O-H groups of a fully hydroxylated alumina surface in which every Al atom has been substituted by three H atoms. Besides, the other peak predicted for the surface OH at 3650 cm⁻¹ is close to the bayerite band at around 3650-3660 cm⁻¹ and 3470 cm⁻¹, with the 3470 cm⁻¹ peak corresponding to in-plane OH groups. The results of our study as well as the results of Lee and Condarte,11) Incorvati et al.4) and Dyer and Hendra12) might be taken as a confirmation of the predictions made by Hass et al.25) in regard to the possible formation of Al(OH)₃ species by hydration of alumina surfaces, but the question still remaining is whether the Al(OH)₃ is part of the alumina surface or it has been completely removed from it. This question is very difficult to answer from the IR spectra presented so far because on one side the nature of the surface Al(OH)₃ species might be expected to be slightly different from those of gibbsite, bayerite and norstrandite, and on the other hand, the peculiar band around 3470 cm⁻¹ coincides with the calculated vibrational spectra of in-plane hydrogen bonded O-H groups of a fully hydroxylated alumina surface in which every Al atom has been substituted by three H atoms. Besides, the other peak predicted for the surface OH at 3650 cm⁻¹ is close to the bayerite band at around 3654-3660 cm⁻¹ and 3660 cm⁻¹ for norstrandite. It is interesting to note that the hydrated γ-alumina distinctive bands including the 3470 cm⁻¹ band are almost identical to the Rauol Al(OH)₃ formation and no gibbsite like bands are present, whereas in the different commercial α-alumina products the characteristic bands of both polymorphs are present in varying proportions. It is interesting to note that the α-alumina specimens prepared by the thermal treatment of transition aluminas in the form of pellets, do not show bayerite like features, nor the 3470 cm⁻¹ band. Some bands of the specimen of larger particle size, heated longer, are close to those of gibbsite (Table 3). The bands in the 3200–3650 cm⁻¹ region are assigned to different hydrogen bonded "polymers" of the same OH unit. They decrease steeply in intensity upon dehydration below 250°C, feeding the only free OH band at 3733 cm⁻¹.15)

4. Conclusions

Surface conditions of three types of commercial high puri-
ty alpha alumina powders produced from in-situ chemical vapor deposition (A and C powders) and hydrolysis of aluminum alkoxide (B powders) methods, are evaluated by FT-IR (Fourier Transform Infrared) transmission and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. The DRIFT method can evaluate the surface hydroxyl groups with less influence of particle size and proven to be a powerful tool in the understanding of the hydration level achieved by different α-alumina powders.

The results of the present study show that the surface state of high purity α-alumina powders can not be regarded as α-alumina, but a hydrated state, as predicted by molecular dynamic simulation\(^2\) and that the nature of this hydrate can not be considered universal among different α-aluminas, even produced by the same production method and under the same identification code (Figs. 1–4). Particle size and production lot appears to play a very important role in the state of the surface hydration. In some of the small size powders made by hydrolysis of aluminum alkoxide (B2a, B2b, and B3a powders), a mixture of aluminum trihydroxides like bands is observed in the as-received powders and not in the larger size ones (B1a and B1b). The time dependence may be the reason for the lack of trihydroxide bands in the B3b powder, which is newer than the B3a powder. Some of the bands in those spectra are close to Al(OH)\(_3\) polymorphs bands reported in the literature (Table 3). However, there is a specific band at around 3470 cm\(^{-1}\) that is not significantly found in spectra of synthetically produced aluminum hydroxide. This band is the most prominent in the spectrum of powder C, together with a broad absorption at around 3650 cm\(^{-1}\), which coincide with the bands predicted by molecular dynamic simulation for a completely hydroxylated α-alumina surface.

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References