Surface hydration states of commercial high purity $\alpha$-Al$_2$O$_3$ powders evaluated by temperature programmed desorption mass spectrometry and diffuse reflectance infrared Fourier transform spectroscopy

Takashi Shirai, Jin Wang Li, Koji Matsumaru, Chanel Ishizaki*, Kozo Ishizaki

Nagaoka Gijutsu-Kagaku Daigaku, Nagaoka University of Technology, Niigata 940-2188, Japan

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Abstract

The surface of three different grades of commercial high-purity $\alpha$-Al$_2$O$_3$ powders produced by hydrolysis of aluminum alkoxide, which differ each other in SSA are evaluated by temperature programmed desorption mass spectrometry (TPDMS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. For the DRIFT evaluation the powders were heated in situ under vacuum from 25 to 700 °C. The TPDMS spectra of desorbed H$_2$O were obtained by heating the samples under ultra high vacuum at a rate of 20 K min$^{-1}$ up to 1200 °C.

The presence of hydrogen bonded water molecules, amorphous Al(OH)$_3$ and AlOOH structures, as well as associated and isolated hydroxyl groups on the surface of all the $\alpha$-Al$_2$O$_3$ powders investigated is demonstrated. On the surface of one of the powders the presence of crystalline Al(OH)$_3$ structures, as evidenced by an additional sharp peak in the H$_2$O TPDMS spectrum, is confirmed.

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Keywords: High purity Al$_2$O$_3$; Surface; Temperature programmed desorption mass spectrometry (TPDMS); Diffuse reflectance infrared Fourier transform (DRIFT); Al(OH)$_3$; AlOOH; Hydroxyl

1. Introduction

As solutions of environmental problems, it is important to decrease energy consumption in light source devices. In the case of metal halide lamps, the luminescence tube is made from quartz. The materials (mercury, sodium and scandium) in the luminescence tube react with quartz at high temperature when lighting and the life of the lamp is inferior to the mercury-vapor lamp and the high-pressure sodium lamp. Translucent Al$_2$O$_3$ has advantage in heat resistance, improving various characteristics and longevity. Many articles have been reported on the production method of translucent Al$_2$O$_3$ ceramics since its first development by Coble [1–3]. The number of grain boundaries, the bulk density of the sintered body, the impurity and microscopic imperfections have been listed as factors that affect in-line transmittance [3].

High purity $\alpha$-Al$_2$O$_3$ is widely used and studied as electronic packaging, corrosion resistance ceramics and translucent ceramics. The surface condition differences of the powders can influence their physical properties such as zeta potential [4], powder agglomeration [5,6] and sintering behavior [7]. Ishizaki et al. concluded that the surface of the same B2, high-purity, sub-micron, $\alpha$-Al$_2$O$_3$ powder investigated in the present work followed the hydration pattern predicted by Hass et al. [8] with formation of surface Al(OH)$_3$ structures of adjacent particles creating crystalline structures similar to the aluminum trihydrate polymorphs and these structures to be responsible for hard agglomerate formation even in the as-received $\alpha$-Al$_2$O$_3$ powder [6]. Raharjo et al. have reported that the surface states of the same high purity $\alpha$-Al$_2$O$_3$ powders investigated in the present study are not as $\alpha$-Al$_2$O$_3$ but a hydrated state, and the nature of this hydrate cannot be considered universal among different $\alpha$-Al$_2$O$_3$, even if they are produced by the same production method and under the same identification
code. Hence, particle size and production lot appear to play an important role in the state of the surface hydration [9].

In this study, the surface hydration state of three different grades of commercial high-purity α-Al2O3 powders produced by hydrolysis of aluminum alkoxide, which differ each other in specific surface area (SSA), as previously investigated [6,9] are evaluated by temperature programmed desorption mass spectrometry (TPDMS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

2. Experimental

2.1. Materials

The three commercially available α-Al2O3 powders produced by hydrolysis of aluminum alkoxide used for this study have specifications as shown in Table 1. 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.

2.2. TPDMS procedures

Details of the TPDMS set up have been reported elsewhere [10,11]. Approximately 30 mg of powder sample was placed in a molybdenum container (3 mm in diameter, 10 mm in height). Each sample was initially placed in a pre-vacuum chamber under 10^{-4} Pa, transferred into an ultrahigh vacuum chamber under 10^{-7} Pa, and heated up to 1200 °C with a constant heating rate of 20 K min^{-1}. During the heating of sample powders, partial pressures of desorbed gases, which were generated by reactions and desorbed from the powder surfaces, were measured by a quadruple mass spectrometer (QMS). Temperature and QMS signals were recorded. Considering an ideal gas flow, the obtained partial pressure spectrum with respect to temperature is converted into desorption rate, \( r_d \), which is the number of desorbed molecules per unit surface area per unit time, using Eq. (1).

\[
r_d(t) = \frac{S}{AkT} P(t)
\]

where \( S \) is the pumping speed, \( A \) the surface area of the sample, \( k \) the Boltzmann constant, \( T \) the temperature in the vacuum chamber, \( P \) the partial pressure of the species in the chamber by desorption, and \( t \) is time [12].

Thus, the total number of desorbed molecules is normalized by unit surface area, \( N \), and obtained by integrating the desorption rate and time as:

\[
N = \int_{\text{min}}^{\text{max}} r_d(t)dt = \frac{S}{AkT} \int_{\text{min}}^{\text{max}} P(t)dt
\]

The desorption rate and total number of desorbed molecule for water (H2O) is calculated from their cracking patterns [13] and relative sensitivity of the mass spectrometer [14].

The obtained TPDMS spectra are separated to several peaks using a Jandel Peak Separation and analysis software.

2.3. DRIFT procedures

The DRIFT spectra of sample powders without dilution were recorded by using FTIR spectrometer (Shimadzu Corp., FTIR 8300) equipped with a triglycine sulfate (TGS) detector, DRIFT accessory (Spectra Tech, Inc., Model no. 0030-0XX) and data processing software (Shimadzu Corp., Hyper IR) with 4 cm^{-1} of resolution and 256 scanning times. The samples and backgrounds spectra were collected in power mode and stored as single beam spectra for further processing. 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. The DRIFT spectra of all powders were recorded under atmosphere and under 5.3×10^{-3} Pa of vacuum using a vacuum chamber (ST Japan, STJ-0123) with a vacuum system equipped with a turbo molecular pump and sorption pump. The samples were also heated in situ in a dome with BaF windows under vacuum condition up to 700 °C.

2.4. Hydrothermal treatment

In order to produce a hydrothermal reaction on the surface, the hydration process was conducted by placing B3 powder, without contact with water, in a modified pressure cooker heated inside an oven at 100 °C under water saturated pressure.

| Nomenclature | Grades (lot. no.) | Production method | Particle size/μm (specific surface area/m² g⁻¹) | Impurities |
|--------------|-------------------|------------------|-------------------------------------------|-----------|
|              |                   |                  |                                           | Si (ppm)  | Fe (ppm) | Na (ppm) | Mg (ppm) | Cu (ppm) |
| B1           | AKP-3000 (MR 7Y11) | Hydrolysis of aluminium alkoxide | 0.47 (4.59) | 3 | 7 | 4 | 1 | 1 |
| B2           | AKP-30 (HB 7712)  |                  | 0.28 (9.55) | 8 | 5 | 3 | 2 | 1 |
| B3           | AKP-50 (HD 8811)  |                  | 0.25 (10.07) | 13 | 9 | 2 | 2 | <1 |
3. Results and discussion

In a TPDMS experiment, a powder sample is kept in a container and heated at a fixed heating rate. As the temperature of the sample increases, adsorbed molecules on the surface may desorb, or surface groups decompose on the powder surfaces. A record of the concentration of the desorbed molecules from the powder surface may be referred to as a TPDMS spectrum. The spectrum generally consists of one or more peaks. The shape of the spectrum and position of the peak maxima on a temperature scale (temperature of active site) are related to the desorption process, and therefore provide information about the surface species. Raw powders which are produced by different manufacturing methods or different grades of powder, have different surface chemistry, and have also different bonding between their surface and adsorbed molecules [15,16]. The comparison of the bonding energies among several types of the powders reveals the difference of their surface chemistry. The difference appears as a change of active site temperatures on their TPDMS spectra as direct information about powder surface chemistry. In the case of \( \alpha \)-Al\(_2\)O\(_3\) powders kept in atmosphere with appreciable amounts of vapor, OH are the most probable species present on their surfaces.

The partial pressure of desorbed H\(_2\)O (mle: 2, 17 and 18) was measured. TPDMS H\(_2\)O spectra of \( \alpha \)-Al\(_2\)O\(_3\) powders produced by hydrolysis of aluminum alkoxide are shown in Fig. 1; meanwhile Fig. 2 shows the total amounts of H\(_2\)O desorption for each powder and Table 2 a summary of the peaks temperature. The TPDMS analysis is sensitive enough to detect minor differences and clearly shows that each powder produces different desorption patterns and quantity of desorbed H\(_2\)O under the same experimental conditions.

Fig. 3 shows common scale surface area normalized DRIFT spectra of the heated powders in the hydroxyl stretching absorption frequency region. The OH stretching vibration bands observed in the spectra are reproducible with intensity much higher than the background signal.

The broad band in the spectrum of the B1 powder at room temperature shows a clear maximum at around 3300 cm\(^{-1}\), assigned to the OH stretching vibration of hydrogen-bonded water molecules [17]. The same authors show that this band
disappeared when heating the sample up to 300 °C. In Fig. 3(a) we can see that this band progressively decreases and it is not observed in the spectrum after heating at 300 °C, therefore we assign the TPDMS H₂O desorption peak of powder B1 at 252 °C to hydrogen-bonded water molecules. This H₂O desorption peak is not observed in powders B2 and B3 in agreement with this assignment.

In the room temperature spectra of the B2 and B3 powders a maximum is visible at approximately 3475 cm⁻¹. This wave number is close to the one predicted for in plane hydrogen bonded OH groups of a fully hydroxylated alumina surface [8] indicating a higher hydration state for these powders, that is also in agreement with the amounts of desorbed H₂O obtained from the TPDMS measurements shown in Fig. 2. Several defined small bands are observed in the DRIFT spectra of powders B2 and B3, especially clear in the spectrum of powder B2. The distinctive sharp peaks observed in the spectrum of the B2 powder, have been previously assigned to a mixture of aluminum trihydroxide polymorphs bands, namely bayerite, gibbsite and norstran-dite [18]. Similar bands were also detected on some as received commercial α-Al₂O₃ produced by the Bayer process and all investigated powders after washing in distilled water, and these bands were also assigned to gibbsite/bayerite like structures [8,19].

The TPDMS results show that only B2 powder presents a sharp additional H₂O desorption peak (peak S), meanwhile, the other powders do not. For the identification of peak S, B3 powder, that shows similar TPDMS H₂O desorption behavior with B2 powder excluding peak S, was subjected to a hydrothermal treatment for a period of 50 h as described in Section 2. Fig. 4 shows the TPDMS H₂O spectra of as-received B3 powder and after thermally hydrated for 50 h. For the hydrated B3 powder, the additional peak (peak S) appears on the TPDMS H₂O spectrum, simultaneously, the peak B decreases and peak C increases.

XRD patterns of the as-received and hydrated B3 powder are shown in Fig. 5. In this figure, the aluminum trihydroxide peaks are detected in the hydrated B3 powder. On the other hand, almost no peaks of crystallized aluminum trihydroxide are detected in the XRD pattern of

| Peak | Peak temperature, T °C |
|------|------------------------|
|      | B1  | B2  | B3  |
| A    | 252 | ×   | ×   |
| B    | 325 | 324 | 316 |
| S    | ×   | 327 | ×   |
| C    | 394 | 410 | 415 |
| D    | 573 | 562 | 575 |
| E    | 705 | 704 | 697 |

Fig. 3. Hydroxyl stretching absorption frequency region showing common scale surface area normalized DRIFT spectra of the α-Al₂O₃ powders; (a) B1, (b) B2 and (c) B3 at different heating temperatures.

Table 2
The summary of peak temperatures on TPDMS H₂O spectra for each powder obtained from Fig. 1

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the as-received B3 powder. The hydration results are helpful in the assignment of peaks S and B on TPDMS H2O spectrum to the decomposition of crystalline and amorphous Al(OH)3 structures, respectively.

All powders show a peak (named as ‘peak C’) at around 400 °C on the TPDMS spectrum. This temperature corresponds to transformation of boehmite to transition alumina [20]. The peak C may be attributed to the decomposition of amorphous (AlOOH) structures. The IR spectrum of boehmite has a characteristic OH stretching band with two equally strong maxima at 3297 and 3090 cm⁻¹ according to Ryskin [21]. van der Marel and Beutelspacher, however, reported a very strong maximum at 3280–3287 cm⁻¹ [22]. Frost et al. undertook infrared emission spectroscopy study of the dehydroxylation of various boehmites at elevated temperatures [23]. They showed that the natural boehmite exhibits bands at 3451, 3291, 3090 and 2908 cm⁻¹. The variation in the band positions is attributed to variations in the boehmite structure. This structure consists of parallel sheets of octahedral with aluminum ions at centers of the octahedral. These octahedral are joined through hydrogen bonds between the hydroxyls of one sheet and the oxygen of the adjacent parallel sheet. The octahedral are joined in continuous chains. The DRIFT spectra of all the powders show a broad band at around 3300–3500 cm⁻¹ that decreases with increasing temperature and is not longer visible in the 500 °C spectra. From these results, the peak C observed in the TPDMS spectra is considered to be due to the water desorption from the hydroxyl groups of AlOOH structures, similar to boehmite.

As observed in Fig. 3, for all powders by increasing the heating temperature the bands corresponding to free and hydrogen bonded OH become visible. The assignments are based on several DRIFT studies performed by other researchers as follows. Morterra et al. assigned a very broad band, whose maximum is at 3418–3426 cm⁻¹ when treated as a symmetrical peak, to hydrogen bonded OH. These hydrogen bonded species are destroyed below 600 °C, but most resistant ones show a band centered at 3564–3571 cm⁻¹ [24]. Ballinger et al. have reported that as the temperature is increased, dehydroxylation occurs to produce H2O(g) as the lower frequency associated hydroxyl groups are initially removed. By 527 °C, all such groups have been removed from the surface. Further heating causes the removal of the isolated hydroxyl groups, and two new bands could be resolved at 3798 and 3711 cm⁻¹ after heating to 727 °C. AHPDMS 8C, no hydroxyl groups can be detected by infrared spectroscopy [25]. There are two high-frequency sharp bands, clearly ascribable to free surface hydroxyl groups, and a third band at 3691–3693 cm⁻¹ which is also assigned to a free or nearly free OH species in view of the high frequency, moderate width, thermal resistance and the presence of a free OH species at nearly the same frequency on all transition aluminas [24]. The TPDMS spectrum of all powders shows broad peaks (named as ‘peak D’ and ‘peak E’) at around 550–600 and 700–800 °C, respectively. Based on the DRIFT results the peak D of TPDMS spectra is assigned to the water desorption from the hydrogen bonded associated hydroxyl groups, and the peak E to the water desorption from the isolated free hydroxyl species on the surface.

The assignment of the observed peaks in the H2O TPDMS spectra could be successfully accomplished with the aid of the DRIFT results. A summary of the assignments is shown in Table 3.

Table 3
Assignment of the peaks observed in the TPDMS spectra

| Peak | Assignments | B1 | B2 | B3 |
|------|-------------|----|----|----|
| A    | H-bonded H2O | ○  | ×  | ×  |
| B    | Al(OH)3 amorph | ○  | ○  | ○  |
| S    | Al(OH)3 xtal  | ×  | ○  | ×  |
| C    | AlOOH       | ○  | ○  | ○  |
| D    | Associated OH| ○  | ○  | ○  |
| E    | Isolated OH | ○  | ○  | ○  |
4. Conclusions

The surface of three different grades of commercial high-purity $\alpha$-$\text{Al}_2\text{O}_3$ powders produced by hydrolysis of aluminum alkoxide, which differ each other in SSA, as previously investigated [6,9] are evaluated by TPDMS and in situ heating DRIFT spectroscopy.

The results of the present study show the presence of hydrogen bonded water molecules (peak A), amorphous Al(OH)$_3$ (peak B), amorphous AlOOH (peak C), associated hydroxyl groups (peak D) and isolated hydroxyl groups (peak E), on the surface of all the $\alpha$-$\text{Al}_2\text{O}_3$ powders investigated. On the surface of powder B2 the presence of crystalline Al(OH)$_3$ structures, as evidenced by the additional sharp peak S at around 330°C in the H$_2$O TPDMS spectrum, is confirmed.

The combination of the two techniques used in the present study proved to be useful in the elucidation of the surface states of different $\alpha$-$\text{Al}_2\text{O}_3$ powders and may be useful in the study of other powder surfaces.

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