Tetrahedral Aluminum Ions on High Purity Sub-Micron α -Alumina Powder Surfaces

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高純度サブミクロンαアルミナ表面上の4配位アルミニウムイオン

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The surface of six different grades of commercial sub-micron high purity α -Al₂O₃ powders produced by two different processes, in-situ chemical vapor deposition ("A" powders), and hydrolysis of aluminum alkoxide ("B" powders) methods, were evaluated by temperature programmed desorption mass spectrometry (TPDMS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Desorption of CO₂ molecules was detected for all the powders, but the quantity was greater for the "B" powders than the "A" powders. The maximum of the CO₂ desorption peak was in the range of 230–270°C for all powders. The desorbed CO₂ peak was considered to evolve from adsorbed CO₂ molecules forming hydrogen carbonyl groups through interaction with the Al^{IV}-OH groups on the α -Al₂O₃ surfaces. The DRIFT spectra of the powders heated at 700°C under vacuum confirmed a larger population of Al^{IV}-OH groups on the surface of α -Al₂O₃ powders and the effect of the type of manufacturing process on their proportion. [Received January 27, 2006; Accepted March 16, 2006]

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1. Introduction

The surface of materials is the key role in many technological processes and, therefore, the knowledge of the chemical composition of the first atomic layer becomes critical for the understanding of surface and interface phenomena.¹⁾ The dispersion of powders in a given solvent requires the knowledge of powder surface charge properties which control the adsorption of additives and attraction/repulsion forces. The superficial charge behavior is thought to be influenced by the ratio between acidic and basic groups.²⁾ For sub-micron-size powders, all these dispersion phenomena become even more crucial and strongly depend on the type and route of synthesis.

The surface of high purity α -Al₂O₃ powders may contain an aluminum hydroxide phase, which can also generate surface condition differences in the α -alumina powders.³⁾⁻⁵⁾ Diffuse reflectance infrared Fourier Transform (DRIFT) spectroscopy can be used for the qualitative characterization of weak-ly adsorbed molecules such as water, and hydroxyls on powder surfaces.⁶⁾ Furthermore, the DRIFT method can evaluate the surface hydroxyl groups with less influence of particle size and has proven to be a powerful tool in the understanding of the hydration level achieved by different α -Al₂O₃ powders.^{4),6)} Raharjo et al. have reported that the surface states of the same high purity α -Al₂O₃ powders investigated in the present study are not as α -Al₂O₃ but a hydrated state, and that the nature of this hydrate cannot be considered universal among different

 α -Al₂O₃ powder, 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.⁴⁾

Previously, we examined the surface of three different grades of commercial high-purity α -Al₂O₃ powders produced by hydrolysis of aluminum alkoxide, which differ each other in SSA are evaluated by temperature programmed desorption mass spectrometry (TPDMS) and DRIFT spectroscopy.⁵⁾ This work presented that 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 α -Al₂O₃ powders investigated is demonstrated.⁵⁾

The fundamental question on how powder surfaces are contaminated by atmospheric water, oxygen or carbon dioxide becomes of tremendous interest for sub-micron high purity α -Al₂O₃ powders.

In this study, by combining TPDMS and DRIFT spectroscopy techniques, it was possible to detect differences in the amount of surface tetrahedral aluminum ions of sub-micron high purity α -Al₂O₃ powders produced by different methods. We investigated the interaction between surface hydroxyl groups and CO₂ adsorbed molecules on sub micron high purity α -Al₂O₃ powders by combining TPDMS and DRIFT spectroscopy.

Experimental

Six commercially available α -Al₂O₃ powders used for this study have specifications as shown in **Table 1**. Production methods of "A" powders [A1 (SSA; 2.54 m²/g), A2 (SSA;

2.1 Materials

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Nomen- clature	Grades (Lot. No.)	Production Method	Particle Size/µm	Impurities				
			(Specific Surface Area/m ² g ⁻¹)	Si / ppm	Fe / ppm	Na / ppm	Mg/ ppm	Cu / ppm
A1	AA-07 (YE 6204)	In situ chemical vapor deposition	0.74 (2.54)	4	≤2	≤5	N.A.	N.A.
A2	AA-05 (YF 6601)		0.58 (3.10)	5	26	≤5	N.A.	N.A.
A3	AA-04 (YD 6701)		0.47 (4.23)	6	3	≤5	N.A.	N.A.
B1	AKP-3000 (MR 7Y11)	Hydrolysis of aluminum 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	13	9	2	2	<1

 Table 1. Production Method and Specifications of the Powders

3.10 m²/g) and A3 (SSA; 4.02 m²/g), Sumitomo Chemical Co., Ltd.] are different from "B" powders [B1 (SSA; 4.59 m²/g), B2 (SSA; 9.55 m²/g) and B3 (SSA; 10.07 m²/g), Sumitomo Chemical Co., Ltd.]. The formers are produced by in-situ chemical vapor deposition and the later are produced by hydrolysis of aluminum alkoxide. All powders have low impurity content. The values of impurity content are lower than the impurity in aluminum oxide produced by the Bayer process, which usually have high a NaO impurity content.

2.2 TPDMS procedures

About 30 mg of the 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 ultra-high 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 powders surface, were measured by a quadruple mass spectrometer (QMS). Temperature and QMS signals were recorded. Details of the TPDMS set up have been reported elsewhere.^{7),8)}

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),

$$r_{\rm d}(t) = \frac{S}{AkT} P(t) \tag{1}$$

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.⁹⁾ Thus, the total number of desorbed molecules is normalized by unit surface area, N, and obtained by integrating the desorption rate and time as;

$$N = \int_{\min}^{\max} r_{\rm d}(t) \, \mathrm{d}t = \frac{S}{AkT} \int_{\min}^{\max} P(t) \, \mathrm{d}t \tag{2}$$

The desorption rate and total number of desorbed molecules for CO_2 is calculated from their cracking patterns¹⁰⁾ and relative sensitivity of the mass spectrometer.¹¹⁾

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 #0030-0XX) and data processing software (Shimadzu Corp., Hyper IR) with 4 cm⁻¹ of resolution and 256 scanning times. The samples and background 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



Fig. 1. Surface area normalized CO₂ TPDMS spectra of α -Al₂O₃ powders "A1, A2 and A3," and "B1, B2 and B3," showing the maximum of the CO₂ desorption peak in the range of 230–270°C, but the variation of quantities of desorbed CO₂ molecules per unit.

avoid influences of water absorbed on KBr, each investigated powder was placed in a micro sample holder without diluting in KBr. To investigate strongly bonded surface groups, all powders were in-situ heated in a vacuum chamber (ST Japan, STJ-0123) with a vacuum system equipped with a turbo molecular pump and sorption pump. All powders were heated up to 700°C with a heating rate of 20 K/min at 5.3×10^{-3} Pa, and the DRIFT spectra were recorded at this temperature and vacuum conditions.

3. Results and discussion

The partial pressure of desorbed CO_2 (m/e: 12, 28 and 44) is measured. CO_2 TPDMS spectra of α -Al₂O₃ powders produced by in-situ chemical vapor deposition (A powders), and hydrolysis of aluminum alkoxide (B powders), are shown in **Fig. 1**.

In Fig. 1, the TPDMS CO_2 spectra of all "A" and "B" powders show the maximum of the CO_2 desorption peak in the range 230–270°C, but the quantities of desorbed CO_2 molecules per unit surface vary among the powders. In the case of the "A" powders the quantities are very low, however the "B" powders show much larger quantities of CO_2 desorbed molecules.

CO₂ molecules may adsorb to the high purity α -Al₂O₃ powder surface by hydrogen bonding with hydroxyl groups. Baraton et al.¹⁾ have reported that CO₂ molecules adsorb on a powder surface by hydrogen bonding with a hydroxyl group coordinated on a tetrahedral aluminum ion forming a hydrogen carbonyl group and without dissociation on hydroxyl groups coordinated on octahedral aluminum ions as shown bellow.

$$\begin{array}{ccc} OH & & O - \overrightarrow{C} - O^{\circ} H^{\circ} \\ I \\ AI \\ T \end{array} + O = C = O \longrightarrow AI \\ H \end{array}$$
(3)

0

$$\begin{array}{c} \mathsf{OH} & \mathsf{OH} \cdots \mathsf{O=C=O} \\ \mathsf{AI} & + & \mathsf{O=C=O} & \longrightarrow & \begin{array}{c} \mathsf{AI} \\ \mathsf{AI} \\ \mathsf{I} \\ \end{array} \end{array} \tag{4}$$

Moreover, under vacuum condition they indicated that the former combination desorbs at 200°C and the latter is removed at room temperature. In this study, since our TPDMS equipment is UHV type, the non dissociated hydrogen bonded



Fig. 2. DRIFT spectra of the heated at 700°C all "A" and "B" powders in the hydroxyl stretching absorption frequency region, showing the presence of Al^{IV}-OH as well as Al^{IV}-OH bands, and demonstrating that "B" powders show larger Al^{IV}-OH intensity peaks than the "A" powders.



Fig. 3. Comparison of Al^{IV} -OH population from DRIFT and CO_2 desorption from TPMDS showing good quantitative agreement.

 CO_2 molecules desorb by evacuation, thus, these molecules do not contribute to the TPDMS spectrum. Since, the main desorption temperatures (230–270°C) in the TPDMS spectra are close to the reported temperature of reported IR results,¹²) the main desorption peak in the TPDMS CO_2 spectrum is considered to be a desorption peak resulting from a hydrogen carbonyl group.

Figure 2 shows the DRIFT spectra of all "A" and "B" powders heated at 700°C in the hydroxyl stretching absorption frequency region. At this temperature, absorption bands at $3557-3600 \text{ cm}^{-1}$ corresponding to hydrogen bonded hydroxyls¹³) that could not achieve complete elimination are still observed, and bands at $3698-3711 \text{ cm}^{-1}$ and $3770-3800 \text{ cm}^{-1}$, respectively, ascribable to terminal hydroxyls coordinated to octahedral and tetrahedral aluminum ions,¹⁴⁾⁻¹⁶⁾ are clearly observed.

Figure 3 shows a comparison of the total amount of CO_2 desorbed molecules per unit surface area, from the spectra given in Fig. 1 and the Al^{IV}–OH peak intensity normalized by specific surface area, from the DRIFT spectra given in Fig. 2. There is good agreement between the DRIFT and TPDMS results indicating that the population of surface Al^{IV} ions is larger for the powders produced by the hydrolysis of aluminum alkoxide than for the powders produced by in-situ chemical vapor deposition.

From the results, it is concluded that on the surface of commercial high purity α -Al₂O₃ powders a complex hydrated layer exists by interaction between surface hydroxyl groups and CO₂ adsorbed molecules, unlike commonly accepted stable α -Al₂O₃ structure.

4. Conclusions

CO₂ molecules was detected for all the powders but the quantity is larger for the powders produced by hydrolysis of aluminum alkoxide ("B" powders) than for the ones produced by in-situ chemical vapor deposition ("A" powders). The maximum of the CO_2 desorption peak is in the range 230-270°C for all powders. The desorbed CO₂ peak is considered to evolve from adsorbed CO₂ molecules forming hydrogen carbonyl groups by interaction with Al^{IV}-OH groups on the α -Al₂O₃ surfaces. The DRIFT spectra of the powders heated at 700°C under vacuum conditions confirmed a larger population of Al^{IV}-OH groups on the surface of the "B" powders. The results confirm the existence of a complex hydrated layer on the surface of commercial high purity α -Al₂O₃ powders resulting from the interaction of the surface with atmospheric water and CO₂, unlike a commonly accepted stable α -Al₂O₃ structure. Further more, in the present study the presence and quality of $\mathrm{Al}^{\mathrm{IV}}$ on the surface of α -Al₂O₃ powders and the effect of type of manufacturing process on their proportion is demonstrated.

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