Solubility of BaSO₄ Powders in Water Containing a Strong Acidic Ion Exchange Resin

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強酸性イオン交換樹脂を含む懸濁水中への BaSO₄ 粉体の溶解性

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In our previous study, it was found that BaSO₄ powders, a sparingly soluble salt, was able to dissolve in water suspended with a strong acidic ion exchange resin (abbreviated as H-R). This paper presents a method to elucidate the surface activity of BaSO₄ powders which are heat-treated up to 800°C. Some factors responsible for the dissolution tendency of BaSO₄, such as H-R/H₂O ratio, soaking temperature and the amount of H-R were examined to determine the optimum condition. The average particle diameter was compared with an electron microscope. A remarkable change in solubility was observed for the BaSO₄ powders calcined at 450°-500°C without any significant change in particle size. Calcination at higher temperatures resulted in a slight increase in solubility in spite of the enhanced grain growth.

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1. Introduction

It is generally known that activity of powders depends on many factors such as particle size, shape, size distribution, lattice distortion and imperfections. These factors more or less dominate chemical and physical phenomena in relation to powders, including decomposition, vaporization, sintering, reactivity with other substances, peptization and so on¹⁾⁻³⁾.

Therefore, it is of great importance to estimate activity of powders by a reliable method in order to handle or utilize powders effectively.

Up to the present time, the proposed methods include estimation through specific surface area, catalytic activity, lattice distortion and solubility, among which measurement of solubility is considered one of the most simple and practical method. It is easy to examine the relationship between solubility and activity for inorganic powders with an adequate solubility while it is usually difficult to collect reliable data on sparingly soluble ones.

The authors have found that BaSO₄ powders with poor solubility could be dissolved readily into water in the presence of H-form ion exchange resin (H-R) when we tried to determine the exact composition of δ -BaCO₃⁴⁾. This technique can be applied to estimate activity of sparingly soluble

powders by means of solubility measurement. This dissolution procedure is more favorable than that using mineral acids because it can reduce chance of contamination. Consequently, this method may be utilized for chemical analysis of solids with poor solubility. For example, 200 mg CaSO₄ powders or 100 mg SrSO₄ powders can be easily dissolved in 20 ml H₂O dispersed with 2 g H-R.

This study is concerned with an estimation of activity of calcined BaSO₄ powders, which is reported to exhibit solubility as low as 10×10^{-6} mol·dm⁻³ at 25°C⁵⁾. After fundamental experiment was conducted to obtain more reliable data, the solubility of BaSO₄ powders in the presence of H-R as a function of calcination temperature was determined and employed as a simple indication to estimate activity of BaSO₄ powders.

2. Experimental procedure

Solubility measurement was carried out for about 100 mg BaSO₄ powders (Merck Co., Ltd.) with diameter ranging from 0.1 to 0.3 μ m after they were dried at 110°C for 2 or 3 days. Before H-R (Dow Chemical Co., Ltd., Dowex 50 W-X 4, 200-400 mesh) was used for dissolution, it was washed repeatedly with distilled water. The amount of released SO₄²⁻ caused by cation ex-

change between H^+ and Ba^{2+} was determined with a calibration curve in the concentration range from 5 to 30 ppm using K_2SO_4 (Merck Co., Ltd.) solution as a standard.

The ion chromatography (Dionex Co., Ltd., Ion Chromatography 10) equipped with an anion fiber suppressor at the suppressor column, was operated in the sensitive range of $30\ \mu S$ using a mixture of 3 mM $NaHCO_3$ and 2.4 mM Na_2CO_3 as an eluent and 0.025 N H_2SO_4 as a regeneration agent. The electrical conductivity and pH were measured with an electrical conductivity meter (Toa Electronic Co., Ltd., CM-5 B, cell constant 1.03) and a pH meter (Toa Electronic Co., Ltd., IM-78), respectively, using ultra pure water (Organo Co., Ltd.) as a solvent.

The morphology of the $BaSO_4$ powders was examined by scanning electron microscopy (SEM; JEOL Co., Ltd., JCSA-733) and transmission electron microscopy (TEM; JEOL Co., Ltd., JEM-1200 EX).

After overlapping of the particles in the TEM image was eliminated, the average particle size was calculated from the number and area of the particles in the modified TEM image, which were determined with an image analyzer (Nihon Regulator Co., Ltd., LUZEX 500). In this procedure, it is assumed that the presumed particles would be spherical and possess the same area as the actual ones.

3. Results and discussion

3.1 Dissolution of $BaSO_4$ powders in the presence of H-R

3.1.1 Effect of H-R on solubility of $BaSO_4$ powders

Although solubility of $BaSO_4$ in H_2O is negligibly small, it can be increased drastically by the presence of H-R⁴⁾. Figure 1 shows a comparison of solubility for 100 mg $BaSO_4$ powders soaked in 20 ml H_2O (A), where 3 ml of 1 N HCl (B), 1.0 g H-R (C) and 3.0 g H-R (D) were added, respectively.

The amount of dissolved SO_4^{2-} was as small as 0.5 mg for H_2O and slightly increased to 1.9 mg by adding HCl (B), while it was remarkably increased with the mass of H-R up to 19.4 mg (C) and 28.5 mg (D). The significant difference indicates that the solubility of $BaSO_4$ can be increased by the presence of H-R. The mechanism of promoted dissolution is thought to be

Fig. 1. Ion chromatograms indicating the effect of H-R on the dissolution of $BaSO_4$ powders in H_2O .

A; 100 mg $BaSO_4$ +20 ml H_2O

B; 100 mg $BaSO_4$ +20 ml H_2O +3 ml 1 N HCl

C; 100 mg $BaSO_4$ +20 ml H_2O +1 g H-R

D; 100 mg $BaSO_4$ +20 ml H_2O +3 g H-R

much different from the general dissolution mechanism of soluble materials and explained as follows.

The dissolution equilibrium of $BaSO_4$ at a constant temperature is given by the reaction (1).

If H-R is added to this system, the ion exchange reaction will take place, which is given by the reaction (2),

leading to increase in solubility of $BaSO_4$ in which $Ba-R_2$ denotes exchanged product on the resin.

The ion exchange capacity of H-R for Ba^{2+} has been reported to be about 30 mg per 1 g H-R⁴⁾.

3.1.2 Effect of dispersion concentration of H-R on solubility

100 mg $BaSO_4$ powders and 4.0 g H-R were added to graded amounts of H_2O ranging from 20 to 200 ml. After the suspensions were kept for 10 min, they were filtered without any washing, and analyzed. As shown in Fig. 2, the solubility tends to decrease with the amounts of coexisted H_2O contrary to the general dissolution trend of ionic crystal powders.

The dependence of the solubility on dispersion concentration of H-R indicates that the solubility is controlled by transportation process of Ba ion toward the surface of H-R.

Fig. 2. Solubility of BaSO₄ vs. amount of H₂O in a suspension with 4 g H-R.

In order to dissolve BaSO₄ effectively, a suspension of H-R with small amount of water is favorable to increase the interaction between Ba²⁺ and H-R.

3.1.3 Effect of temperature on solubility

A series of suspensions containing 50 ml H₂O and 1.0 g H-R were kept at a fixed temperature ranging from room temperature to 80°C, then, 100 mg BaSO₄ powders were added and stirred for 3 min. Immediately after stirring, the suspensions were filtered and cooled down to room temperature and the solubility was determined for each filtrate. As shown in Fig. 3, the amount of dissolved SO₄²⁻ increases monotonously with an increase of soaking temperature. The tendency is some orders of magnitude more than the solubility of BaSO₄ in H₂O viz. 0.22×10^{-3} and 0.39×10^{-3} g/100 g-H₂O at 25° and 100°C, respectively⁶⁾.

The result suggests that the mobility of Ba²⁺ in H₂O is accelerated with temperature.

3.1.4 Effect of H₂O amount during filtration on solubility

As to the dissolution procedure described in 3.1.1 and 3.1.2, no washing of undissolved BaSO₄ and H-R during filtration was carried out.

However, washing is usually essential procedure for filtration. If H-R coexist with BaSO₄ powders during washing, it is expected that the cation exchange reaction follows the onset of the dissolution of BaSO₄.

Fig. 3. Dependence of solubility of BaSO₄ on the soaking temperature.

Therefore, the dependence of the amount of dissolved BaSO₄ on washing was examined. After 20 ml H₂O and 100 mg BaSO₄ powders were added to 4.0 g H-R, the solutions were stirred for 5 min and filtered.

The resultant residue was washed with H₂O, the amount of which ranged from 40 to 300 ml, subsequently the summation of dissolved SO₄²⁻ in the filtrate and washings was determined. The relationship between these two amounts is shown in Fig. 4. The dissolved amount of SO₄²⁻ increases nearly in proportion with the amount of washings, indicating that dissolution of BaSO₄ can take place during washing of the residue.

Therefore, it is essential to compare the dissolution data in the presence of H-R under the condition that the solutions are filtered without washing or that they are filtered with a constant amount of washing.

3.1.5 Dissolution behavior of BaSO₄ with the amount of H-R

The solubility of BaSO₄, pH and electrical conductivity were measured for the suspension prepared as follows. After 100 mg BaSO₄ was put into 50 ml H₂O and H-R, the amount of which ranged from 0.5 to 10.0 g, was added to the

Fig. 4. Effect of washings on the dissolution of BaSO₄.

Fig. 5. Dissolution behavior of BaSO₄ with the amount of H-R.

resultant suspension, it was kept for 10 min, filtered without washing and analyzed. The solubility, pH and the specific conductivity as a function of the H-R amount are shown in Fig. 5.

With an increase in the H-R amount, the solubility and the conductivity increased whereas the pH decreased. Analogous results were obtained for anhydrous CaSO_4 and SrSO_4 powders. Furthermore, the specific conductivity was nearly in proportion to the dissolved SO_4^{2-} amount. The decrease in the pH is thought to be due to formation of H^+ caused by the ion exchange reaction between Ba^{2+} and H^+ (H-R) represented by the reaction (2). On the other hand, the amount of the dissolved SO_4^{2-} was not in proportion to that of H-R, indicating the decrease in the exchange capacity due to some kinetic factors.

Consequently, the dissolution procedure of BaSO_4 in the presence of H-R can be understood by dividing it into a few stages, namely, the dissolution of BaSO_4 in H_2O , the migration of Ba^{2+} to the surface of H-R and the ion exchange of Ba^{2+} for H^+ in H-R. As a whole, the dissolution rate exhibits considerable dependence on the dissolution condition.

3.2 Temperature dependence of activity of the calcined BaSO_4 powders

As the solubility of the powders depends on the dissolution condition and the ion exchange reaction undergoes the reverse reaction in the concentration range above ca. 0.02 N H_2SO_4 , small

Fig. 6. solubility of BaSO_4 vs. calcining condition showing the deactivation of the powder surface.

A; Effect of heating time at each temperature.

B; Effect of heating temperature treated for 10 min.

amounts of the BaSO_4 powders was used so that the concentration of H^+ would not exceed the above level. The solubility of the BaSO_4 powders was examined under the conditions described as follows. About 100 mg BaSO_4 powders calcined at various temperatures were weighed accurately and put into 25 ml H_2O together with 4.0 g H-R, then stirred for 3 min and filtered while the residue was washed with 300 ml H_2O , followed by adjustment to 500 ml in a volumetric flask. Subsequently, the amount of the dissolved SO_4^{2-} in the resultant solution was determined. The solubility dependence on the calcination temperature is shown in Fig. 6. Even at the temperature as low as 380°C, the solubility gradually decreased with the period of calcination. As the temperature was raised, the solubility decreased sharply with calcination time while it again turned to decrease

Fig. 7. TEM of BaSO_4 calcined at each temperature for 10 min.

A; 400°C, B; 500°C, C; 600°C (Bar: 200 nm)

Fig. 8. Relationship between mean grain size and solubility of BaSO_4 calcined at each temperature for 10 min.

gradually in higher calcination temperature region. The change is marked in the temperature range from 400° to 500°C having the most remarkable one around 450°C. The TEM microphotographs corresponding to the powders calcined at 400°, 500° and 600°C are exhibited in Fig. 7. Significant change in size and shape can be found for the powders calcined at 500° and 600°C.

From the observation by SEM, the particles became more or less round and underwent necking partly. Those calcined at 600°C began to sinter and exhibited remarkable grain growth.

Comparing the change in the morphology with that in the solubility, it is found that the solubility had changed markedly before significant alternation in the particle size and shape took place. The relationship between the solubility and the mean particle size for the powders calcined at each temperature for 10 min is shown in Fig. 8. In the low temperature region (400°–500°C), the solubility changed sharply while the particle size changed slightly. On the contrary, in the high temperature region, the particle size changed markedly while the solubility changed a little.

Consequently, the decrease in the solubility of BaSO_4 in the presence of H-R is thought to be associated with the commencement substantial migration to the particle surface in the pre-sintering stage.

It is not clear, at the moment, whether the solubility dominating factor is the morphology change or relaxation of the lattice imperfections introduced during the powder preparation. Although more precise data should be accumu-

lated to clarify the mechanism, it is inferred that both factors would contribute to a certain extent to decrease the solubility.

As this technique is considered applicable to most of sparingly soluble solids, it would be an effective method to estimate activity or to relate the solubility with other properties regarding the solids with poor solubility.

4. Summary and conclusion

As to the sparingly soluble BaSO_4 powders, the solubility in the presence of H-R was determined and its temperature dependence for the powders calcined under various conditions was examined. The latter was employed as a simple indication to estimate the activity of the calcined powders.

The solubility was drastically promoted by the coexistence of H-R, the degree of which depended sensitively on the dissolution conditions owing to complexity of the dissolution mechanism.

In the low calcination temperatures, the solubility of the BaSO_4 powders decreased gradually with the period of calcination, whereas it decreased sharply in the intermediate temperature region and again turned to decrease gradually with the time in the higher temperature region.

From the observation of the calcined powders in combination with the solubility data, it is inferred that the significant activity decrease in the intermediate temperature region would be caused by the change in morphology or relaxation of the lattice imperfection.

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