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Thermoanalytical characterization of powder samples
I. Wet pretreated samples[1]

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Abstract

Routine wet pretreatment of a powder sample causes a drastic change in the thermoanalytical results. The pretreatment may alter the crystallographic or molecular structure, but more distinguished change occurs in the powder characteristics. Thus, consistent thermoanalytical results can be obtained by subjecting the powder sample to wet pretreatment for classification.

Keywords: TA; Wet pretreatment; Powder samples

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1. Introduction

Thermoanalytical results have long been discussed mainly in relation to crystallographic or molecular structures and the chemical composition of the substance under consideration. In the case of TA of solid samples, however, a sample is often size reduced into a powder. Because a 5-mg portion of a powder sample mounted on a pan 5 mm in diameter contains about 10^6 to 10^8 particles, the sample behavior must be discussed taking the powder characteristics into consideration. In previous papers [1–4] concerning dolomite decomposition, it has been found that the reaction is greatly influenced by the powder characteristics, and in particular, that TA results are closely related to the particle size distribution of the powder expressed by a power function $P(x) \propto x^n$ (where x is the scaled particle size, and n is the power depending on the material). This signifies that the power n can be utilized as a material constant [2]. Theoretically, the

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powder particles obtained by mechanical size reduction are statistically self-similar, and this is also supported by the well known energy law of comminution [5]. The product obtained by mechanical size reduction yields not only a self-similar particle size distribution, but also a self-similar surface, i.e. a fractal surface. The surface of a particle can thus be expressed qualitatively using the fractal dimension. A reaction on a solid particle is believed to proceed depending on the surface morphology or the geometry. This signifies that the rate of reaction of a single particle can be expressed as a function of surface fractal dimension. The reaction functions based on the fractal surface and fractal morphology were also derived theoretically [6].

We report here a case in which the thermoanalytical result of a powder sample is greatly influenced by wet sample preparation. The temperature for the initiation of a reaction was greatly influenced (as much as 60°) by a routine wet pretreatment that had been widely used for separating dolomite from calcite [7]. The same discussion as that made on ground powder samples is valid in this case. More specifically, calcian dolomite samples accompanying calcite as accessory mineral are treated with dilute acetic acid solution according to a well known method of sample preparation. The change in structure as well as in chemical composition is discussed in relation to the thermoanalytical results. The results are compared with those obtained on an acid-treated stoichiometric dolomite with high crystallinity.

2. Experimental

2.1. Calcian dolomite

Calcian dolomite samples (K-12 to K-16) from Kuzuu, Tochigi Pref., Japan, accompanying calcite as accessory mineral were used. The chemical composition in mol% of the samples was determined by electron probe microanalysis (EPMA) using a JEOL JXA-733 analyzer operating under routine conditions (accelerating voltage 15 kV, sample current 1.05×10^{-3} mA, beam diameter 30 μm on MgO, counting time 10 s, take-off angle 40°). Samples fractions were mounted in an epoxy resin. Corrections were made using Bence and Albee's method.

The starting bulk material was size-reduced and classified using a Tyler sieve to obtain particles 44 μm or less in size. The five powder samples thus obtained were subjected to the well-known routine treatment for removing calcite from dolomite using a dilute aqueous 2 wt.% acetic acid solution. The powder samples were each immersed into the dilute acetic acid solution, which was stirred and further subjected to ultrasonic treatment for a duration of 15 min once a day. The samples were taken out of the solution every day, and dried for phase identification using XRD. This was repeated until no X-ray peaks attributed to calcite became discernible. Thus were obtained acid-treated calcite-free samples AK-12 to AK-16.

Lattice parameters were determined by the XRD method using the internal standard method (silicon powder, SRM 640 supplied by NIST). The XRD runs were made on a Rigaku Geigerflex RAD AB system operating with graphite-monochromatized CuKα radiation under routine conditions for the determination of precise lattice parameters

(40 kV/20 mA, preset time 4 s, step width 0.004°, slits 1° DS/0.3 mm RS/1° SS). IR analysis was carried out by the KBr method using 1.5–3.0 mg samples and 210 mg KBr powder consisting of particles 34 μm or less in size. The spectrograms were obtained by using a KBr disk method. A 1.5–3.0 g portion of each of the powder samples passed through a 400 mesh sieve was mixed with 210 mg of fine KBr powder. A Hitachi 260-50 IR spectrophotometer was run under normal scanning conditions (parameter mode 2, gain 2.4, slit normal, and scanning speed 26 min for the whole scanning range) for qualitative analysis over a wavenumber range of 4000–250 cm^{-1}.

Simultaneous TG-DTA analysis was performed using 5 mg of sample and reference (α-Al_2O_3) charged in a platinum sample pan mounted on a top-load-type sample holder of a Rigaku Thermoflex simultaneous TG-DTA apparatus. The temperature was detected with a Pt–Pt13%Rh thermocouple fixed in a position near the sample pan. The programmed heating rate was 10°C min^{-1}. The TG-DTA curves were recorded at a TG sensitivity of 5 mg, a DTA sensitivity of ±50 μV and a chart speed of 5 mm min^{-1}. The gas flow was upward from the bottom inlet. The thermal decomposition process was investigated under a flow of gaseous CO_2 at a rate of 100 ml min^{-1}.

2.2. Highly crystalline dolomite with stoichiometric composition

For comparison, a Korean dolomite sample having high crystallinity and containing 50.20 mol% Ca and 49.80 mol% Mg (determined by wet chemical analysis) was treated with a dilute aqueous 2 wt% acetic acid solution. Because the sample does not accom-

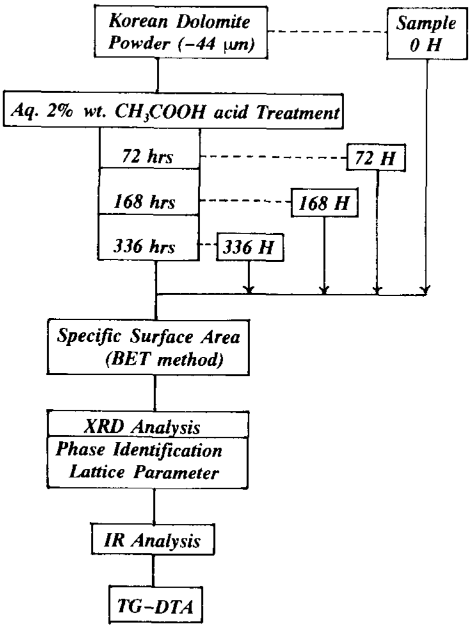

Fig. 1. Experimental procedure for Korean dolomite.

Table 1

Chemical composition of Kuzuu dolomite samples (by EPMA)

Sample nos.	Content (mol %)			
	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$
K-12	54.30	45.75	–	0.02
K-13	54.96	44.54	–	0.50
K-14	54.80	44.57	0.15	0.48
K-15	61.49	37.91	0.09	0.51
K-16	56.60	42.88	0.05	0.47

pany any calcite, the duration of treatment was varied to see the influence of acid treatment on the crystallinity (structural ordering) of dolomite. The experimental procedure is shown in Fig. 1. The bulk sample was ground and classified in the same manner as in the calcian dolomite samples to obtain particles 44 μm or less in size as the starting powder sample. (Untreated sample; sometimes denoted as "sample 0H"). The duration of acid treatment was varied in a range from 3 days to 2 weeks to obtain samples 72H (3 days), 168H (1 week), and 336H (2 weeks).

XRD, IR, and TG-DTA analyses were performed in the same manner as those described for the calcian dolomite samples. In addition to these analyses, the measurement of a specific surface area was performed by the Brunauer–Emmett–Teller (BET) method using a Digisorb 2600 surface-area, pore-volume analyzer (Micromeritics Instrument Corporation) with argon as the adsorption gas.

3. Results and discussion

3.1. Calcian dolomite

The results obtained by chemical analysis are given in Table 1. It can be seen that all the samples are high in calcium containing more than about 55 mol% $CaCO_3$.

By comparing the lattice parameters for the calcian dolomite samples K-12 to K-15

Table 2a

Hexagonal unit cell dimension of dolomite samples (untreated)

Sample nos.	Å		
	a_0	c_0	c_0/a_0
K-12	4.803_6	16.00_4	3.332
K-13	4.801_6	16.07_3	3.348
K-14	4.807_5	15.99_6	3.327
K-15	4.806_9	16.00_9	3.331
K-16	4.805_3	16.00_5	3.331

Table 2b

Hexagonal unit cell dimension of dolomite samples (acetic acid treated)

Sample nos.	Å		
	a_0	c_0	c_0/a_0
AK-12	4.816_2	16.04_1	3.331
AK-13	4.815_7	16.05_0	3.333
AK-14	4.816_8	16.03_2	3.328
AK-15	4.815_4	16.05_6	3.334
AK-16	4.815_7	16.03_8	3.331
Lake Arthur (Reeder, 1983)	4.8069_2	16.0034_6	3.3292
Eugui (24°C) (Reeder, 1986)	4.8069_9	16.002_1	3.3290
Eugui (200°C) (Reeder, 1986)	4.8104_9	16.055_1	3.3376

with those for the acid-treated samples AK-12 to AK-16 given in Tables 2a,b, respectively, the acid-treated samples were found to be slightly elongated (about 0.3%) along the a- and c-crystallographic axes. Lattice parameters reported by Reeder [8] for a Lake Arthur dolomite are given for comparison. Reeder and Markgraf [9] reports the lattice expansion of dolomite with increasing temperature; the lattice parameters for the starting Eugui (Spain) dolomite at 24°C (a_0 4.8069_9 Å and c_0 16.002_1 Å) are well comparable to those of the Lake Arthur dolomite. However, the crystallographic lattice is found to be elongated to $a_0 = 4.8104_9$ Å and $c_0 = 16.055_1$ Å at 200°C. The degree of structural disordering of the acid treated dolomite can be therefore estimated as comparable to the dolomite at 200°C.

Referring to Table 3, the degree of short-range ordering around the carbonate group (CO_3^{2-}) using the results obtained by IR analysis [10], the acid-treated samples seem to have the higher degree of crystallinity as judged from the IR intensity ratio. The result suggests an ordered arrangement of Ca and Mg around the carbonate group.

Referring to Fig. 2, the TG-DTA curves for the acid-treated samples greatly differ from those of the starting dolomite samples. The first endothermic peak corresponding to the decomposition reaction accompanies the evolution of gaseous CO_2, and is expressed by the following equation (1):

Table 3

Intensity ratio I_{730}/I_{880} of dolomite samples obtained from infrared absorption spectra

Sample nos.	I_{730}/I_{880}	Sample nos.	I_{730}/I_{880}
K-12	0.629	AK-12	1.056
K-13	0.955	AK-13	1.400
K-14	0.591	AK-14	1.286
K-15	1.000	AK-15	1.500
K-16	1.000	AK-16	1.167

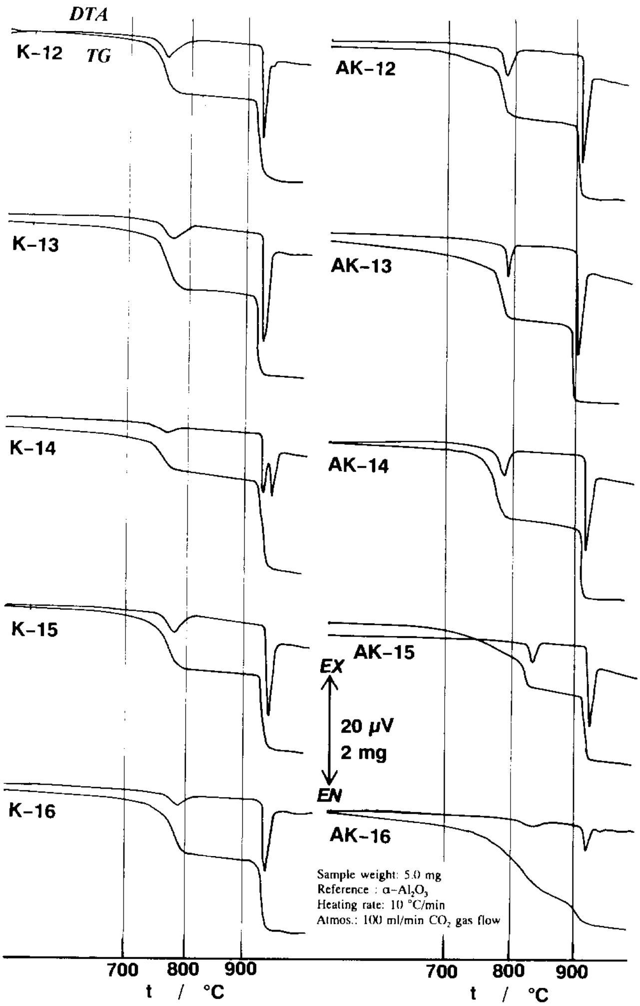

Fig. 2. TG-DTA curves for untreated and acid-treated calcian dolomites.

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

The reaction for acid-treated samples is found to occur at higher temperatures compared with that for the non-treated samples. The temperature is shifted at least 20° compared with that of the initial samples. In extreme cases (K-15 and K-16), the T_e (extrapolated onset) read from the DTA peaks is found to shift for 60°. It can be read also from the TG curves that the reaction corresponding to the first step occurs more swiftly for the acid-treated samples, as observed from the reaction that is completed in a narrower tempera-

Table 4

Hexagonal unit cell dimension of dolomite samples (untreated and acetic acid treated)

Sample nos.	Å		
	a_0	c_0	c_0/a_0
Untreated	4.809_7	16.01_9	3.331
72H	4.807_5	16.01_1	3.330
168H	4.807_8	16.01_2	3.330
336 H	4.808_7	16.01_4	3.330
Lake Arthur (Reeder, 1983)	4.8069_2	16.0034_6	3.329

ture range. This signifies that the initiation of the reaction is suppressed in the lower temperature region, but that the reaction proceeds smoothly once the reaction is initiated. A reaction process of this type is very similar to the case of a dolomite sample P-0 from the Philippines as described previously [11]. This sample is characterized in that it has a symmetrical particle size distribution with a large population of fine particles below 1 μm, and it undergoes an abrupt reaction at higher temperatures. The TA results above may be influenced by the structural distortion or by the change in the powder characteristics such as particle size distribution that is induced by acetic acid treatment. To make this point clear, the Korean dolomite described above was subjected to acetic acid treatment to see the change with increasing duration of treatment.

3.2. *Korean dolomite*

The precise lattice parameters obtained in the same manner as that for the calcian dolomite are listed in Table 4. It can be seen that practically no change is observed with increasing duration of acid treatment. Concerning the change in degree of ordering as evaluated by IR analysis (Table 5), slight decrease in ordering is observed with increasing time period of acid treatment. This result is in conflict with the result obtained for calcian dolomite. Presumably, calcium atoms that are present in excess in the dolomite structure of calcian dolomite dissolve by acid treatment to realize a more ordered arrangement of Ca and Mg atoms in calcian dolomite.

The most distinguished change is again observed in TG-DTA curves. Fig. 3 shows the TG curves for the starting and acid-treated dolomite samples. It can be seen clearly that

Table 5

Intensity ratio I_{730}/I_{880} of dolomite samples obtained from infrared absorption spectra

Untreated	Sample nos.		
	72H	168H	336H
0.833	0.849	0.713	0.600

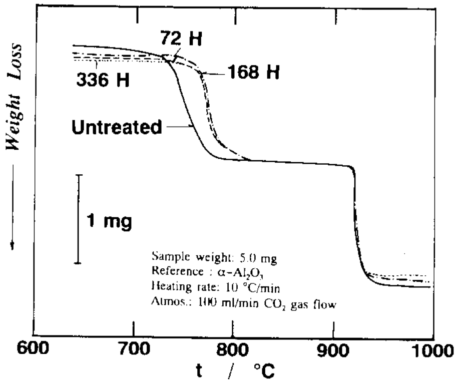

Fig. 3. TG curves for acid-treated Korean dolomites.

the first endothermic reaction expressed by Eq. (1) for samples 72H, 168H, and 336H occurs in the higher temperature range compared with that for the initial sample 0H, and that the reaction proceeds swiftly after it is initiated. This phenomenon again is very similar to the case reported previously for the sedimentary sample P-0 consisting of particles distributed in a narrow particle size range. The second endothermic reaction corresponding to the decomposition of calcite is not influenced by the acid treatment. This also suggests that the basic structure remains without being considerably disturbed by the acid treatment. It should be noted, however, that there is no considerable difference between the TA results of the acid-treated samples. In other words, consistent and reproducible thermograms are obtained for acid-treated samples regardless of the duration of treatment.

As described in the foregoing, the TA results of a powder sample are greatly influenced by an acid treatment, even though a dilute solution is used. In particular, a considerable shift in temperature T_i (initial temperature of reaction as read from TG curves) of 50° for the structurally stable Korean dolomite cannot be attributed to structural distortion. Short-range disordering may occur on the dolomite structure, however, this is in conflict with the previously established relation between the temperature of decomposition and the degree of ordering evaluated by the IR method. More specifically, according to previous reports [10,12], the reaction temperature read by TA lowers with decreasing degree of ordering obtained by the IR absorption intensity ratio. Moreover, the shift in the decomposition temperature for 20–60° is too drastic for a structural fluctuation or distortion. Conclusively, another reason for the shift in the decomposition temperature to the higher side must be considered.

Table 6 shows the change in specific surface area of Korean dolomite. It can be seen that the initial specific surface area is halved after treatment for 72 h. The decrease in surface area signifies a decrease in reaction sites. The highly crystalline Korean dolomite being homogeneous, fine particles dissolve more quickly in the acid solution. Thus, the fine particles which serve as the catalysts and play an important role in the initial stage of the reaction are lost by the acid treatment. The decrease in the specific surface area may be interpreted as the consumption of fine particles which function as a "detonator". The

Table 6

Specific surface area (BET) of dolomite samples untreated and acetic acid-treated ($m^2\ g^{-1}$)

Untreated	Sample nos.		
	72H	168H	336H
7.05	3.51	1.60	1.84

sample resulting from the acid treatment is equivalent to consisting of particles narrowly distributed in a larger particle size region, similar to sample P-0 described in the previous report [11], and hence yields an endothermic peak in the higher temperature side.

4. Conclusion

Routine wet pretreatment of a powder sample may offer a drastic change in TA results. The pretreatment may alter the crystallographic or molecular structure, but more distinguished changes occur on the powder characteristics.

As stated in previous papers of the present authors, TA is an effective method for evaluating powder characteristics [2]. TA results are more influenced by the powder characteristics than by a change in structural or chemical fluctuation of about 5%. Consistent and reproducible TA results were obtained by using a powder with a self-similar particle size distribution [3]. We propose here another method for obtaining reproducible TA results by wet-treating the powder sample.

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References

[1] M. Ochiai, R. Ozao, Y. Yamazaki, R. Otsuka and A. Holz, Proc. Inst. Stat. Math., 38 (1990) 257.
[2] M. Ochiai and R. Ozao, Thermochim. Acta, 198 (1992) 279.
[3] R. Ozao and M. Ochiai, Thermochim. Acta, 198 (1992) 289.
[4] R. Ozao and M. Ochiai, Thermochim. Acta, 208 (1992) 161.
[5] M. Ochiai and R. Ozao, Bull. Ceram. Soc. Jpn., 26 (1991) 1181; M. Ochiai and R. Ozao, J. Therm. Anal., 38 (1992) 1901.
[6] R. Ozao and M. Ochiai, Thermochim. Acta, 220 (1993) 191.
[7) For example, J.R. Goldsmith and D.L. Graf, J. Geol., 66 (1958) 678.
[8] R.J. Reeder, in R.J. Reeder (Ed.), Carbonates: Mineralogy and Chemistry, Mineral. Soc. Am., 11, 1983, p. 18.
[9] R.J. Reeder and S.A. Markgraf, Am. Mineral., 71 (1986) 795.
[10] R. Ozao, J. Arai and R. Otsuka, Gypsum and Lime, 201 (1986) 79 (in Japanese).
[11] R. Ozao and M. Ochiai, A. Yamazaki and R. Otsuka, Thermochim. Acta, 183 (1991) 183.
[12] H. Schneider, Mineral. Mag., 40 (1976) 579.