CALORIMETRIC AND THERMOANALYTICAL ASSESSMENT OF MECHANICALLY ACTIVATED PbCO₃

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ABSTRACT

Excess enthalpy values, ΔH^*, were obtained through the change in the heats of dissolution into Na–EDTA (ΔH_L^*) as well as of decomposition to PbO (ΔH_D^*). They tallied fairly well with each other, although a slight systematic discrepancy depending on the conditions of vibro-milling was recognized. A good correlation between ΔH^* and the relative non-crystallinity was observed when the material was activated under the same conditions with a varying grinding time. Changes in the grinding conditions, such as in amplitude or atmosphere, brought about a considerable shift of the correlation between ΔH^* and the non-crystallinity. Thus, under the same degree of non-crystallinity, materials ground in cyclohexane stored a larger amount of energy than those ground in air. These differences in the correlation were discussed by referring the degree of dispersion, the distribution of active sites, and the effect of temperature.

INTRODUCTION

Calorimetric measurements seem to have been recognized as a standard method for the evaluation of the degree of mechanical activation [1]. However, there are no well-established standard procedures for obtaining the excess energy. In principle, any kind of heat of reaction at constant pressure can be utilized to obtain the excess enthalpy. The only necessary condition is that the final state of the reaction should be identical, irrespective of the state of activation of the specimen. Dissolution calorimetry has been hitherto preferentially used because the final dissolved state can be uniquely identified only by defining the concentration of the solution. However, there are many substances which can be dissolved only in very strong acids or at elevated temperatures, these situations being inappropriate for conventional calorimetry. Many of these difficulties could be avoided, however, if the calorimetry were substituted by a conventional thermal analysis method, such as DTA or DSC. There are many studies using the results of DTA or

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DSC to describe the extent of the preliminary mechanical treatments [2]. Only few comparative studies were reported, however, where the results of dissolution calorimetry and thermal analyses were compared. Schrader and Hoffmann [3] obtained the stored energy of vibro-milled $CaCO_3$ as the excess enthalpy from dissolution calorimetry. They revealed that $\Delta H^{\star}$ was approximately 12 times smaller than the difference in the heat of decomposition, $\Delta H_D^{\star}$. The latter value was obtained, however, from the variation of the dissociation pressure, and therefore could not serve as a direct measure of the mechanical activation.

In the present study, it was attempted to obtain the excess enthalpy of vibro-milled $PbCO_3$ from both the heats of dissolution and decomposition. After checking the energy state of the specimens at the end of the decomposition reaction by subsequent dissolution calorimetry, the correlation between these values was compared and discussed.

EXPERIMENTAL

Mechanical treatments

A 1.0-g sample of $PbCO_3$ (Merck, pro analysi) was vibro-milled in a cylindrical steel vessel with an inner diameter of 35 mm and a capacity of 50 cm^3 with 100 6-mm steel balls. The amplitude, α, of the up-and-down motion was varied from 10 to 50 mm. Grinding was carried out at constant ambient temperature, 30°C, in air or in 30 cm^3 cyclohexane. The frequency was kept constant at 12 Hz.

Energy measurements

Applied work done, W, was measured calorimetrically by assuming that most of the net applied energy was dissipated as heat [4]. The excess enthalpy, $\Delta H^{\star}$, was evaluated by two different methods: from the difference in the heats of dissolution or of decomposition between the activated and original materials. The heat of dissolution was obtained by measuring the heat evolved during the dissolution of a 40-mg specimen into 30 cm^3 0.1 N disodium ethylenediaminetetraacetate aqueous solution in a twin microcalorimeter (CM-204 D1, Rhesca, Japan). The difference in the heats of dissolution between activated and original materials is denoted as $\Delta H_L^{\star}$.

A differential scanning calorimeter (Thermoflex, Rigaku, Japan) was used to measure the heat of decomposition. The measurement was carried out by using a 40-mg specimen in an N_2 flow of 500 cm^3 min^{-1}. The specimen was heated at a constant rate, 10 K min^{-1}, to 923 K, where the decomposition was complete for every sample. The excess enthalpy, $\Delta H_D^{\star}$, was obtained from the difference in the heat of decomposition between the activated and original materials.

The specific surface area was measured by a conventional BET method with N_2 adsorption. The lattice distortion, η, and the crystallite size, D, were evaluated from the integral breadth by X-ray diffractometry following Hall's method [5]. A mean relative intensity ratio, I_r, from the diffraction peaks of $PbCO_3$, (110) (220) and (221), was also obtained by using CaF_2 as an internal standard.

RESULTS AND DISCUSSION

Excess enthalpy from heats of dissolution and decomposition

The excess enthalpy, $\Delta H_L^\star$, obtained from the heat of dissolution increased with the net work done, W, as shown in Fig. 1. As an overall correlation, a regression line was calculated on the semi-log plots between $\Delta H_L^\star$ and log W, i.e.

$$\Delta H_L^\star = 3.9 \log W - 8.0 \tag{1}$$

with a correlation factor, $r = 0.897$. However, the relationship between $\Delta H_L^\star$ and W seems to vary slightly depending on the amplitude as well as the environment of grinding. Compared at the same work done, $\Delta H_L^\star$ is larger with larger amplitude. This amplitude-dependency is more sensitive for those ground in air than those in cyclohexane.

The variation of another excess enthalpy, $\Delta H_D^\star$, obtained from the difference in the heat of decomposition, with W is shown in Fig. 2. The monotonical increase of $\Delta H_D^\star$ with increasing W as a whole, is similar to the
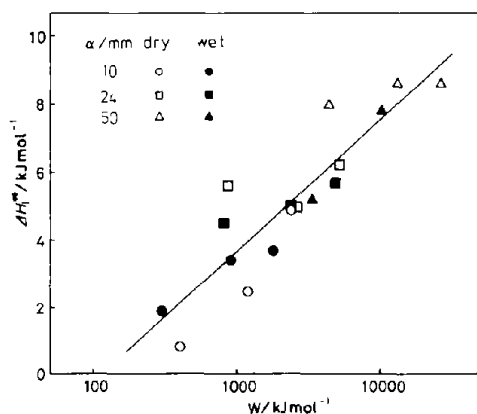

Fig. 1. Relationship between $\Delta H_L^\star$ and W. Open and filled symbols denote samples ground in air and in cyclohexane, respectively.

relationship between $\Delta H_L^\star$ and W, giving an overall correlation

$$\Delta H_D^\star = 3.0 \log W - 5.1 \tag{2}$$

with $r = 0.839$. A closer observation reveals, however, that $\Delta H_D^\star$ is less sensitive to the amplitude, environment and the net work done. In order for $\Delta H_D^\star$ to be significant at all, and worth comparing with $\Delta H_L^\star$, the final state of the decomposed products, PbO (massicot), should be energetically identical. The heat of dissolution of the decomposed product was therefore measured in the same manner as those for $PbCO_3$. Since the enthalpy of dissolution of PbO is approximately five times as large as that of $PbCO_3$, a correspondingly larger scattering was unavoidable. No systematic variation was detected, however, the average value being 93.3 ± 2.3 kJ mol^{-1}.

Correlation between $\Delta H_L^\star$ and $\Delta H_D^\star$

$\Delta H_L^\star$ and $\Delta H_D^\star$ tallied fairly well with each other, as shown in Fig. 3. A slight systematic discrepancy was to be noticed, however, depending on the condition of vibro-milling. With an amplitude of 10 mm, $\Delta H_D^\star$ was larger than $\Delta H_L^\star$, whereas with 50 mm, a deviation in the opposite direction occurred. Both excess enthalpies agreed well for the results with $\alpha = 24$ mm.

Relation between $\Delta H^\star$ and crystallographical changes

It is to be noted that the extent of the X-ray-amorphous portion or the degree of non-crystallinity, $1 - I_f$, increased with decreasing crystallite size, D, as shown in Fig. 4. No significant deviation due to the grinding condition, i.e., the amplitude and the environment, was observed. On the other hand, the correlation between η and $1 - I_f$ was a little ambiguous. This suggests that the loss of crystallinity is accompanied by a decrease in the coherent
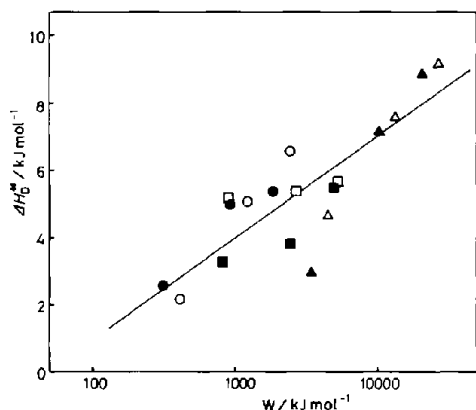

Fig. 2. Relationship between $\Delta H_D^\star$ and W. Symbols as Fig. 1.

units of lattice orientation, and is one of the most significant crystallographical changes which gives rise to the mechanical activation in the vibro-milled $PbCO_3$.

The relationship between the excess enthalpy and $1 - I_f$ again depends on whether the sample was ground in air or in cyclohexane, as shown in Fig. 5. Whereas the relation as a whole could be interpreted to be mutually proportional for those ground in cyclohexane, a significant decrease in the crystallinity does not bring about a large excess enthalpy, ΔH_L^*, in the case of dry-ground materials. The most remarkable contrast between dry- and wet-ground $PbCO_3$ was observed in the case of the smallest amplitude, and the difference decreased with increasing amplitude.
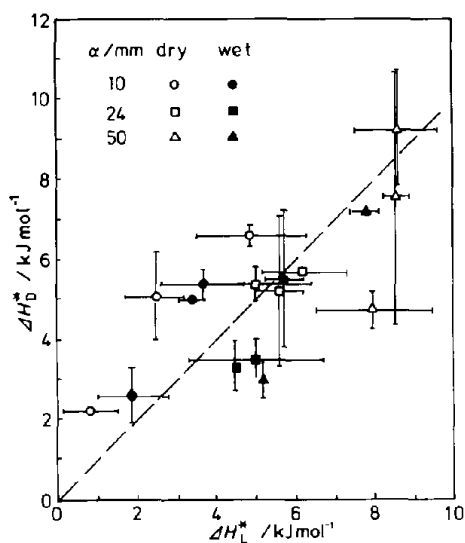

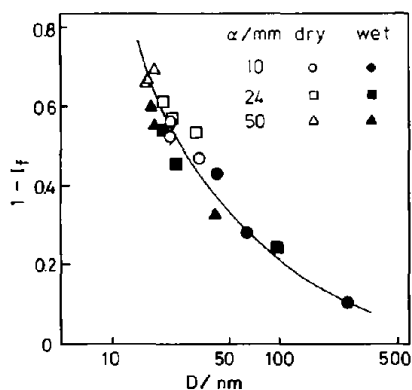Fig. 3. Relationship between ΔH_L^* and ΔH_D^*.

Fig. 4. Relationship between $1 - I_f$ and D. Symbols as Fig. 1.

The role of external surface

Variation of BET surface area, S, with applied work done is shown in Fig. 6 for the typical extremes, i.e., those ground in cyclohexane with $\alpha = 10$ mm and in air with $\alpha = 50$ mm. Whereas the former showed a normal increase in S with increasing work done, the surface area of the specimen ground in air with a larger amplitude decreased with increasing work done, indicating the formation of compact aggregates.

When the two excess enthalpies, $\Delta H_L^\star$ and $\Delta H_D^\star$, are plotted against S for these two series of samples, the correlation differs significantly from each other, as shown in Fig. 7. A positive correlation was observed between S and $\Delta H^\star$ for those ground with $\alpha = 10$ mm, the reverse being recognized for
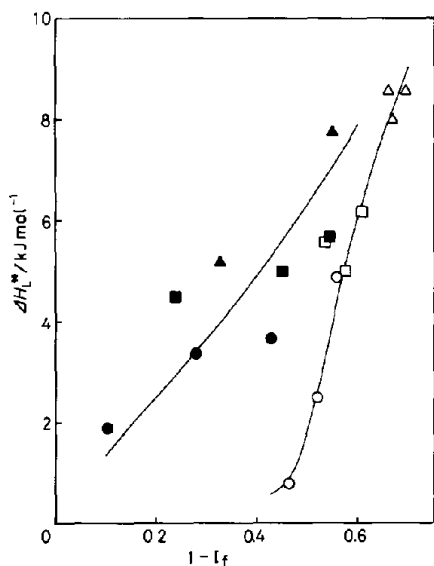
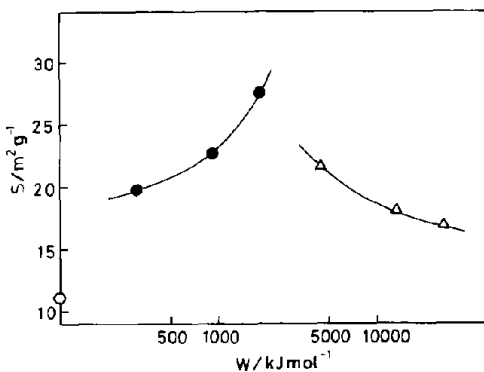Fig. 5. Relationship between $\Delta H_L^\star$ and $1 - I_f$. Symbols as Fig. 1.

Fig. 6. Relationship between S and W. Symbols as Fig. 1.

those ground with a larger amplitude. The relative sequence between $\Delta H_D^\star$ and $\Delta H_L^\star$ was also opposite between the two sets of samples.

It should therefore be noted that a simple positive correlation between surface area and the degree of mechanical activation cannot always be expected, particularly in cases where significant agglomeration takes place due to a severe mechanical treatment. The difference in the extent of the mechanical activation is more significant for $\Delta H_L^\star$ than for $\Delta H_D^\star$ when they are compared at the same BET surface area.

Other factors influencing the correlation between $\Delta H_L^\star$ and $\Delta H_D^\star$

When the same amount of net mechanical work done was applied to the material in a vibro-mill with different amplitudes, a difference in the distribution of activated spots could arise. A larger number of smaller impacts are applied to the material when ground with a smaller amplitude. This inevitably causes a concentration of active sites near the surface of the particle. Conversely, the mechanical effect could reach deeper into the interior of the particle when ground with a larger amplitude, the number of hits being smaller. This kind of difference in the distribution of active sites could affect the $\Delta H_L^\star$ and $\Delta H_D^\star$ values, since the very sluggish release of the stored energy, which cannot always by detected in the thermal analysis as a distinct peak, occurs differently depending on the distribution of the active centers.

Apart from the possible error due to the recovery as mentioned above, the fact that the excess enthalpy, $\Delta H_D^\star$, is obtained from the signals at elevated temperatures could cause more a fundamental deviation from $\Delta H_L^\star$, the latter being measured at room temperature. If the heat capacity, C_p, changed
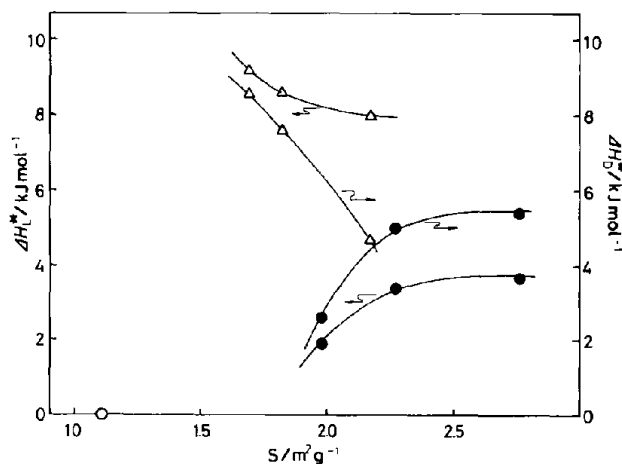

Fig. 7. Variation of $\Delta H_L^\star$ and $\Delta H_D^\star$ with S. Symbols as Fig. 1.

significantly due to mechanical activation, then the difference in C_p could influence the value of the excess enthalpy. According to Torkar [6], the difference in the heat capacity could be expressed as

$$C_p^\star - C_p = 2\beta T \tag{3}$$

where $C_p^\star$ is the heat capacity of the activated material at constant pressure, β is a constant and T is the temperature. By neglecting the entropy contribution, the change in the Gibbs free energy difference due to the change in temperature, ΔT, is proportional to $-\beta \Delta T^2$ [6]. Although little was reported on the heat capacity of activated materials, β was estimated as 6.1×10^{-4} for ZnO [7]. If the value of β for the present $PbCO_3$ is assumed to be similar in order of magnitude, the change in the C_p can safely be neglected in discussing the difference between $\Delta H_L^\star$ and $\Delta H_D^\star$.

Finally, it should be remembered that, although a significant difference in the heats of dissolution of decomposed PbO was not detected in the present study, it cannot be ignored that the difference in the degree of activation could remain, to some extent, in the decomposed PbO.

CONCLUDING REMARKS

Both the dissolution calorimetry and the thermal analysis of decomposition can be used for the evaluation of mechanical activation. The agreement between the values of excess enthalpy obtained from completely independent methods is fairly satisfactory when the errors involved in these measurements are taken into account. Nevertheless, care should be taken in judging the "real" extent of mechanical activation, since these two excess enthalpies involve different factors and are influenced differently by factors associated with the degree of dispersion as well as the distribution of the active sites.

A further study is necessary to elucidate the effect of the environment or atmosphere of grinding on the correlation between non-crystallinity and the excess enthalpy, although the surface recombination in the case of grinding in air could partly explain the lower value of $\Delta H^\star$, compared at the same degree of non-crystallinity.

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