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Interaction of Water with the Surface of Calcite

Tetsuo Morimoto,* Jiro Kishi,[†] Osamu Okada, and Toshie Kadota
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700
[†] *Research Center for Industry in Okayama Prefecture, Ifuku-cho, Okayama 700*

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The interaction of water with the surface of ground calcite was investigated by measuring the water adsorption isotherm and the amount of thermally desorbed molecules *in vacuo*. The results showed that the surface of ground calcite has chemisorbed water at room temperature which can be completely desorbed by evacuation up to 600 °C, and on which water can be physisorbed in a H_2O:OH ratio between 1:2 and 1:1, depending on the conditions of the pretreatment. The isosteric heat of the physisorption of water on the hydroxyls showed that the activity of the adsorption sites for water is reduced by treating the sample at higher temperatures or by washing with water. Moreover, it was found that the surface of the calcite sample starts to release CO_2 molecules by heat treatment at relatively low temperatures below 300 °C *in vacuo*, and that the amount of CO_2 increases exponentially with an increase in the temperature.

It has previously been shown that metal oxide, when preserved in the atmosphere, chemisorbs water to form surface hydroxyls, on which water is further physisorbed, resulting in the alteration of the surface properties.[1–4] The studies of surface properties, especially those of the interaction with water, of inorganic materials provide important information concerning their technical use. We ourselves have reported that $BaSO_4$ only physisorbs, but does not chemisorb, water.[5] Calcite is one of the most important natural resources used as pulverized filler materials. Gammage and Gregg[6] have reported the effect of grinding Iceland Spar on its adsorbability for water. Recently, Goujon and Mutaftschiev[7] have investigated the dependence of the surface properties of ground calcite upon the calcination temperature by means of pH-measurements, heat of immersion, and mass spectrometry, and have concluded that about 30% of the surface carbonate ions are decomposed by calcination up to 450 °C. Hackerman and Hall[8] measured the water adsorption isotherm on calcite, but did not evaluate the effect of the calcination temperature on the adsorbability of water. The purpose of the present work is to study the interaction of water with the calcite surface in various stages of heat treatment, especially the existence and behavior of surface hydroxyls, by measuring the adsorption isotherms of water and the amounts of thermally desorbed water and CO_2.

Experimental

Natural calcite, from the Niimi district in Okayama Prefecture, was ground by using an impact pulverizer; a portion of the finest grade was then collected. The main impurities involved in the original material were SiO_2 0.06, Fe_2O_3 0.07, Al_2O_3 0.04, MgO 0.016, and P 0.01%. Part of the powdered sample was washed with water until the electric conductivity of the supernatant liquid became constant. X-Ray analysis showed the sample to be of the calcite type and not to contain aragonite. Electron-microscopic observation, using a scanning electron microscope (Hitachi S310), of the washed and unwashed samples did not show any characteristic difference between them and any evidence of sharp cleavage along the rhombohedral faces.

A sample of the 12—15 m^2 surface area was first pretreated at 150, 300, or 500 °C for 4 h in a vacuum of 1×10^{-3} Pa, followed by measurement of the water-adsorption isotherm in a volumetric adsorption apparatus equipped with an oil manometer. After measuring the first adsorption isotherm at 25 °C, the sample was exposed to saturated water vapor for 12 h at 25 °C to ensure surface hydration, evacuated at 1×10^{-3} Pa for 4 h at the same temperature to remove physisorbed water, and subjected to the measurement of the second adsorption isotherm of water at the same temperature as before. For the determination of the isosteric heat of adsorption, the second adsorption isotherms were also measured at 15 and 20 °C. The adsorption equilibrium of water was established within a short time, *i.e.*, within 10—20 min, for the whole measurement. The surface area was obtained by means of the BET N_2-adsorption.

The surface water content was determined by the successive ignition-loss method.[9] As it was found from mass analysis that the gas evolved during the course of this measurement is composed of H_2O and/or CO_2, the mixed gas was analysed by separating it into individual components in the following way. The sample treated at room temperature *in vacuo* was heated at 100 °C for 4 h, and the gas expelled was once trapped in a vessel cooled at −196 °C; its amount was determined volumetrically after evaporation at room temperature. Next, the gas was condensed at the temperature of a solid CO_2–ethanol mixture and outgassed to remove the CO_2 thoroughly; then the remaining condensed gas was determined volumetrically after reevaporation as before. The same procedure was repeated after every treatment of the same sample at increasingly elevated temperatures.

Results and Discussion

Figure 1 shows the surface water content and the amount of CO_2 on $CaCO_3$, which were obtained by the successive ignition-loss method. Assuming a water molecule to come from two hydroxyls through the condensation dehydration at higher temperatures, the water content is expressed by the number of OH groups per nm^2 remaining on the surface after the treatment at the temperature indicated, while the amount of CO_2 is the number of total CO_2 molecules evolved when the sample is heated up to the temperature. As is shown in Fig. 1, the surface water content decreases exponentially with a rise in the temperature of the treatment, and vanishes at 600 °C; the absolute values at relatively lower temperatures are comparable to those of metal oxides, but decrease more rapidly

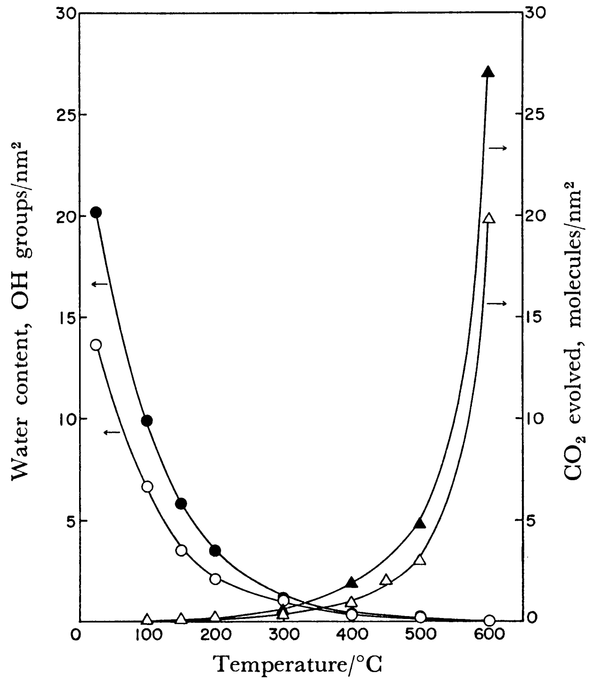

Fig. 1. Surface water content and the amount of evolved CO_2 on calcite as a function of evacuation temperature.

○△, Washed sample; ●▲, unwashed sample.

with a rise in the temperature compared to the cases of metal oxides.[1-4] It should be noticed that the evolution of CO_2 *in vacuo* starts at a very low temperature and increases exponentially with a rise in the temperature up to 600 °C; this result is entirely different from that found by Goujon and Mutaftschiev,[7] *i.e.*, that a constant amount of about 30% of CO_3^{2-} ions on the ground calcite surface was decomposed by outgassing the sample up to 420 °C.

The cleavage of the calcite crystal is known to be perfect on the $(10\bar{1}1)$ plane.[10] Assuming the actual surface of powdered calcite to be composed of this plane, the surface density of each of the Ca^{2+} and CO_3^{2-} ions can be computed to be 4.97 ions/nm². The surface water content of the washed calcite sample, after outgassing at room temperature, was found to be larger than the surface density of the Ca^{2+} ions. However, part of the surface water content survives even after the evacuation at 300 or 400 °C, which leads us to the conclusion that there is a great possibility of the chemisorption of water on the calcite surface.

In the present procedure for measuring water content, a part of the surface CO_3^{2-} ions are dissociated to evolve CO_2 molecules, as is shown in Fig. 1; the amount of CO_2 evolved when the sample is heated at 500 °C *in vacuo* is nearly equal to the number of CO_3^{2-} ions on the crystal surface, as calculated above. Admittedly, the chemisorbed water should have CO_3^{2-} ions beneath it, as is evident from the fact that it is

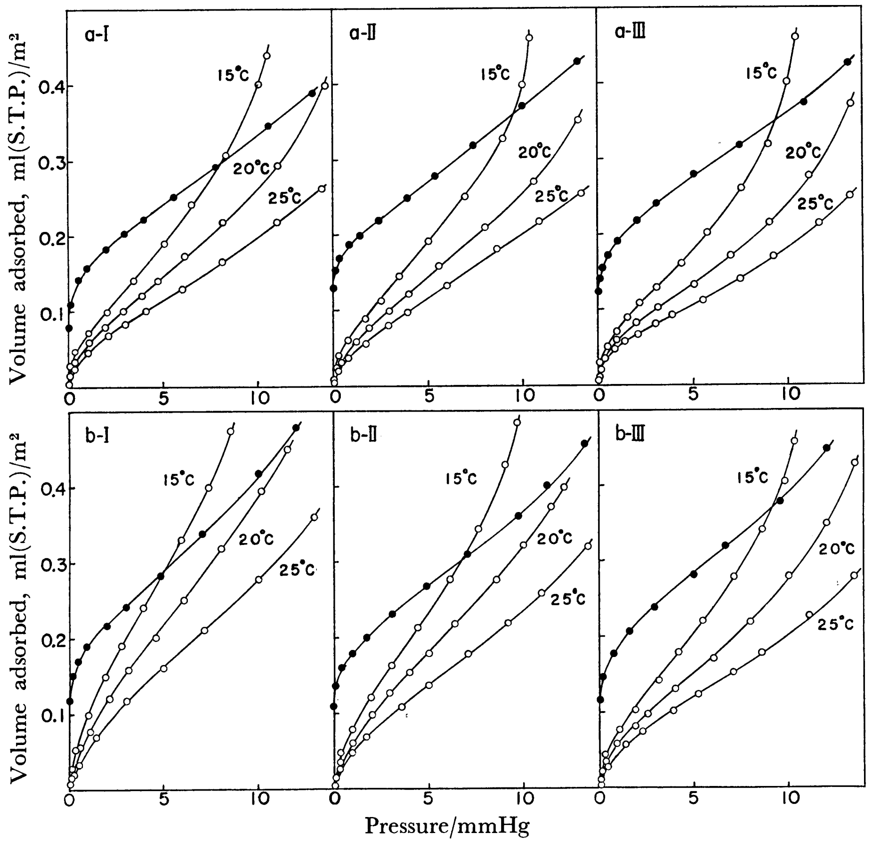

Fig. 2. Adsorption isotherms of water on (a) washed and (b) unwashed calcite treated at various temperatures: I, 150 °C; II, 300 °C; III, 500 °C.

●, First adsorption at 25 °C; ○, second adsorption.

Table 1. Relation between the amounts of physisorbed and chemisorbed water on the $CaCO_3$ surface (25 °C)

Sample	Pretreatment temperature (°C)	Specific surface area (m^2/g)	V_m (ml/m^2)	V_p (H_2O's/nm^2)	V_c (OH's/nm^2)	V_h (OH's/nm^2)	V_c+V_h (OH's/nm^2)	$V_p/(V_c+V_h)$
Washed	150	6.91	0.219	3.98	3.82	3.43	7.25	0.549
	300	6.80	0.236	3.93	4.83	1.17	6.00	0.655
	500	5.70	0.238	3.66	5.48	0.19	5.67	0.646
Unwashed	150	7.72	0.257	5.46	2.90	5.95	8.85	0.617
	300	7.67	0.242	4.65	3.72	1.33	5.05	0.921
	500	5.96	0.247	4.12	5.01	0.14	5.15	0.800

depleted at 500 °C, at which temperature the monolayer of CO_3^{2-} is decomposed completely. This circumstance may be one of the reasons why the desorbability of chemisorbed water from calcite is greater than that from metal oxides.

It is interesting to note that the calcite surface which has never experienced washing with water has a larger amount of chemisorbed water than the sample which was washed. This makes it possible to infer that water can be chemisorbed on the active sites like surface defects as soon as they are formed by grinding the sample in air and that they can be removed by washing the sample with water.

Figure 2 illustrates the adsorption isotherms of water on calcite powders pretreated *in vacuo* at 150, 300, and 500 °C. The adsorption isotherms obtained are all Type II isotherms, according to Brunauer's classification. In addition, the amount of adsorbed water for the first adsorption, measured just after the pretreatment at a higher temperature, is larger than that for the second adsorption obtained after evacuating the sample at room temperature after the first adsorption measurement has been completed; the two isotherms are parallel to each other. The water adsorption isotherm measured by Gammage and Gregg on a precipitated calcite sample is similar to the first adsorption isotherm in the present samples.[6] The parallelism between the first and second adsorption isotherms in the present study is quite similar to the cases of water adsorption on metal oxides.[1,2,11] On the basis of previous discussions concerning the parallelism of the first and second isotherms for most metal oxides,[1,2] we can conclude that the chemisorpion of water occurs on the surface of calcite, the difference between the two isotherms being the amount of chemisorbed water.

Table 1 gives the numerical data analysed from both water adsorption isotherms and water contents on calcite samples. The specific surface area of the samples was measured before the first and second water adsorption measurements, and the two values thus obtained were found to be equal to each other within an experimental error of ±1.5%. V_m and V_p are the monolayer capacities obtained by applying the BET equation to the first and second adsorption isotherms respectively, the latter involving only the amount of physisorbed water and being expressed by the number of water molecules per nm^2. V_m contains both physisorbed and chemisorbed water, expressed as the gaseous volume adsorbed on a unit of the surface area. The amount of chemisorbed water V_c, can, therfore, be obtained by subtracting V_p from V_m after changing the unit of V_m to the number of molecules of H_2O per nm^2; the difference (V_m-V_p) is then expressed as the number of OH groups per nm^2 by assuming a water molecule to be chemisorbed dissociatively on calcite to form two hydroxyls, as in the case of metal oxides. Another quantity of chemisorbed water is the water content, V_h, remaining on the surface after pretreatment at indicated temperatures, as obtained from Fig. 1.

It may be seen from Table 1 that the total amount of chemisorbed water falls within the range of 5 to 9 OH's/nm^2, regardless of whether the sample was washed with water or not. This indicates that the surface state of calcite is almost the same after the water adsorption measurement. These values are likely if we consider that a considerable portion of the surface CO_3^{2-} ions have been converted to OH^- ions.

From the above considerations, we may conclude that the real surface of calcite contains chemisorbed water molecules, irrespective of whether the sample was washed with water or not. Here, we may reasonably expect that the surface of calcite has been hydrolysed when washed with water,[7] which results in the formation of a hydroxylated surface according to this reaction:

$$CaCO_3 + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2CO_3 \qquad (1)$$

If the outermost monolayer of the calcite surface is altered to a hydroxide layer by this reaction during the course of washing, the resulting sample should release a maximum amount of water molecules or 4.97 H_2O/nm^2 upon heating *in vacuo*; reversely, the dehydrated surface can chemisorb the same number of water molecules. The experimental values, *i.e.*, 5—9 OH's/nm^2, of the total amount of chemisorbed water, V_c+V_h, are within this limit.

The evolution of CO_2 from the calcite surface takes place (Fig. 1) through the following reaction upon heat treatment *in vacuo*:

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (2)$$

The CaO layer thus formed will chemisorb water molecules during the adsorption process according to this reaction:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \qquad (3)$$

Here also, surface hydroxyls are produced and will behave similarly to those formed by the hydrolysis of the calcite surface, as has been described above.

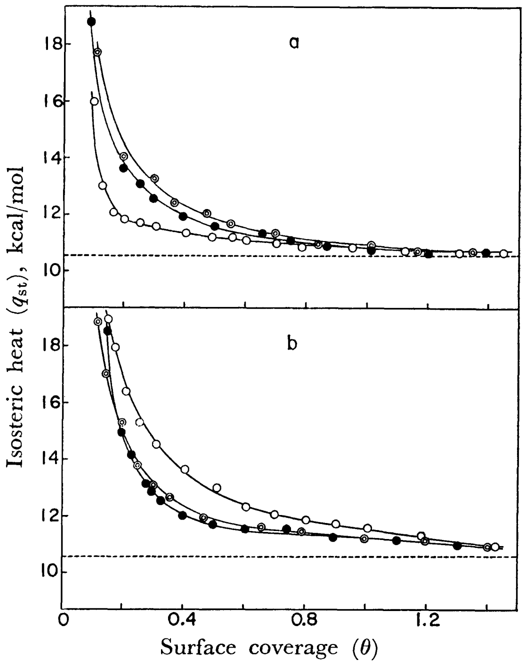

Fig. 3. Isosteric heat of adsorption of water on (a) washed and (b) unwashed calcite.
○, 150 °C; ●, 300 °C; ◎, 500 °C. Broken line represents the heat of liquefaction of water.

Indeed, it is interesting to realize that the total number of chemisorbed water molecules is 5—9 OH's/nm^2, despite the fact that at least two layers of CaO should be formed on the 500 °C-treated samples due to the decarbonation of $CaCO_3$ and the dehydration of $Ca(OH)_2$. In other words, only the outermost layer of the two CaO layers is considered to be partially hydroxylated during the water-adsorption process.

As may be seen from Table 1, the ratio, $V_p/(V_c+V_h)$, of the number of physisorbed water molecules in the first monolayer to that of the underlying hydroxyls is between 1:2 and 1:1. This indicates that a water molecule is physisorbed on one hydroxyl group or on two hydroxyls.

The isosteric heat of the physical adsorption of water, q_{st}, on the fully hydroxylated surface of calcite can be obtained by applying the Clausius-Clapeyron equation to the water-adsorption data in Fig. 2; it is illustrated in Fig. 3. The q_{st} value reveals a decreasing curve with an increase in the coverage of water, θ, and approaches the heat of the liquefaction of water at $\theta=1$, which indicates a characteristic surface heterogeneity in the samples used. Hackerman and Hall reported the q_{st}-curve of water on the 100 °C-treated powdered calcite, which is similar to that obtained on the washed and 150 °C-treated sample in the present study; it is not clear, however, whether their measurement was carried out on a fully hydroxylated surface.[8)] With the washed sample in the present study, treatment at 300 or 500 °C gives higher q_{st} values than that at 150 °C, whereas with the unwashed sample the 150 °C-treatment provides the highest value among the three treatments; the q_{st} curves of the 300 °C- and 500 °C-treated samples are similar to each other regardless of whether the sample is washed or unwashed. If the sample is unwashed, the surface will involve a variety of active sites, such as corners, edges, and other kinds of surface defects, and washing will remove some of these stronger adsorption sites; a partial removal of active sites will more or less also take place when the sample is subjected to heat treatment at higher temperatures. Thus, both the washing and the heating of the original sample may produce a similar surface activity. Finally, the washed and 150 °C-treated sample seems to give too small activity for water adsorption. This may be due to the fact that the fully washed surface of calcite could have lost active sites through dissolution and hydrolysis, resulting in the establishment of a less active surface; however, the succeeding treatment at higher temperatures (300 or 500 °C) produces more active surfaces.

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