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Effect of Additives on Thermal Decomposition of Basic Magnesium Carbonate[1]

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The effect of eleven halides on the thermal decomposition of basic magnesium carbonate ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) has been studied by means of thermogravimetry (TG), differential thermal analysis (DTA) and gas chromatography. The size of crystallite of magnesium oxide prepared by heating the carbonate containing halide was determined by X-ray diffractometry, the oxides being studied by transmission electron microscopy. The thermal decomposition of basic magnesium carbonate was influenced by the addition of beryllium chloride tetrahydrate, magnesium chloride hexahydrate, calcium chloride hexahydrate and magnesium bromide hexahydrate. The DTA curve was changed with the amount of additive, *i.e.*, three endothermic peaks (at about 300, 430, and 530 °C) and an exothermic peak (at 490 °C) turned to only two endo-thermic peaks in the case where the molar ratio of an additive to the carbonate exceeded 0.005, the peak at higher temperature becoming sharp with shift toward lower temperature. The results of TG of basic magnesium carbonate corresponded to those of DTA. Gas chromatographic data showed that the composition of evolved gas varied with temperature. The activation energies of decarbonation and dehydration were obtained by gas chromatography by use of Freeman-Carroll's technique. Increase in the amount of additive caused a decrease in the activation energy of decarbonation, but not in that of dehydration except for magnesium bromide hexahydrate. The size of crystallite of magnesium oxide prepared by calcination at 600 °C for 2 hr, increased with the increase in the amount of additive.

The effect of impurities or additives on the thermal properties of compounds and the characteristics of materials produced by thermal decomposition have been extensively investigated.[2-4]

Basic magnesium carbonate shows the DTA curve as seen in Fig. 1c, which is similar to that given by Mackenzie.[5] We also reported that the DTA curve was influenced by the addition of magnesium chloride hexahydrate and environmental atmosphere.[6] Sawa reported that the addition of lithium fluoride also affected the shape of the curve.[7]

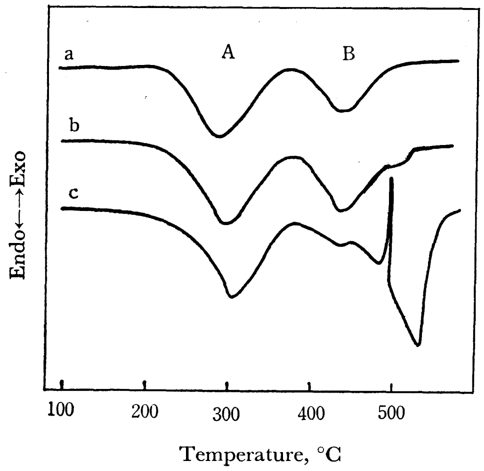

Fig. 1. DTA curves of basic magnesium carbonate Heating rate of a, b, and c was 1, 3, and 20 °C/min respectively. Sample weight was about 18 mg.

In this paper, the effect of halides (mainly chlorides) which affect the decomposition of magnesium hydroxide prepared from sea salt,[8] on the decomposition of basic magnesium carbonate was investigated by the measurement of DTA and TG curves, the calculation of apparent activation energy (referred to hereafter as "activation energy") of decarbonation and dehydration, and the determination of the size of crystallite of magnesium oxide prepared from basic magnesium carbonate.

Experimental

Materials. Basic magnesium carbonate (Earth Seiyaku Co., Ltd.) and additives of reagent grade were used. X-Ray diffractometry showed the structure of basic magnesium carbonate to be $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ although the composition is known to be either $5MgO \cdot 4CO_2 \cdot 5H_2O$ or $4MgO \cdot 3CO_2 \cdot 5H_2O$ according to the mode of preparation.

The following additives were used. Alkali metal chlorides (lithium chloride, sodium chloride, potassium chloride, and rubidium chloride) alkaline earth metal chlorides (beryllium chloride tetrahydrate, magensium chloride hexahydrate, strontium chloride hexahydrate, and barium chloride dihydrate), and magnesium halides (magnesium fluoride, magnesium bromide hexahydrate, and magnesium iodide).

Procedure. A given volume of methanolic solution of additive or a given weight of solid additive was mixed with a given weight of basic magnesium carbonate in an automatic mortar for a short time.

Simultaneous DTA–TG was performed with a Rigaku Denki Thermoflex 8002. DTA–TG runs were made at a

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[1] Studies on Technical Analytical Methods by Differential Scanning Calorimetry, Differential Thermal Analysis and Thermogravimetry, IV. Part III of this series: G. Hashizume and K. Amita, *Bunseki Kagaku*, **20**, 340 (1971).

[2] G. V. S. Rao, M. Natarajan, and C. N. R. Rao, *J. Amer. Ceram. Soc.*, **51**, 179 (1968).

[3] J. M. Schempf, F. E. Freeberg, and F. M. Angeloni, *Anal. Chem.*, **37**, 1704 (1965).

[4] G. Hashizume, Y. Arai, M. Ishino, and S. Takashima, *Reports of Industrial Research Institute, Hyogo Pref.*, 5 (1966); I. F. Guilliatt and N. H. Brett, *Trans. Brit. Ceram. Soc.*, **69**, 1 (1970).

[5] Ed. by R. C. Mckenzie, "Differential Thermal Analysis," Vol. 1, Academic Press (1970), p. 315.

[6] G. Hashizume and K. Amita, *Bunseki Kiki*, **8**, 388 (1970).

[7] H. Sawa and M. Oya, The 24th Annual Meeting of Chemical Society of Japan, Preprints page 970 (Apr. 1971).

[8] Unpublished.

heating rate of 3 °C/min under dry nitrogen flow of 100 ml/min, except for that of 20 °C/min in the measurement of a sample containing 1 mol% of an additive. The weight of sample was about 18 mg.

Gas evolved during the course of decomposition was measured with a gas chromatograph (Hitachi Ltd., Model 063) connected with DTA–TG apparatus equipped with an automatic gas sampler. A katharometer was used as a detector. The glass column was packed with Porapak-Q 80/100 (Water Associate Inc.). The column temperature was 110 °C. The time interval to collect a gas sample was 15 s.

The size of crystallite was determined by a Rigaku Denki Geigerflex X-ray diffractometer. Ni-filtered CuKα-radiation was used. The size of magnesium oxide samples was calculated from half width of diffraction peak by Sherrer's equation, taking that of magnesium oxide prepared by the combustion of magnesium metal as a standard.

Particle forms were observed with a transmission electron microscope (Japan Electron Optics Laboratory Co., Ltd., model JEM-T6S). A specimen was prepared by placing a sample on a collodion membrane, and carrying out vacuum-evaporation with carbon to prevent sintering of the sample by an electron beam. Samples used for X-ray diffractometry and transmission electron microscopy were prepared by calcination at 600 °C for 2 hr.

Results and Discussion

Effect of Additives on DTA Curve. The DTA curve of basic magnesium carbonate changes with environmental atmosphere[9] and heating rate. Four transitions were observed on the DTA curve at a heating rate of 20 °C/min (Fig. 1c): Endothermic peak (1) at about 300 °C due to dehydration, (2) at about 430 °C due to partial decarbonation, (3) at about 520 °C due to decarbonation, and an exothermic peak at 490 °C attributable either to crystallization of amorphous magnesium oxide or recombination of magnesium oxide with carbon dioxide evolved. When the heating rate decreased, the DTA curve showed two endothermic peaks (Fig. 1a).

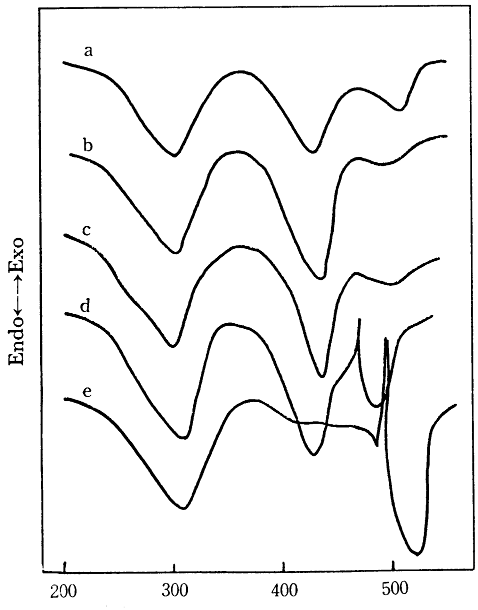

Fig. 2. Comparison of DTA curves of basic magnesium carbonate with those of additives.
a: $BeCl_2\cdot4H_2O$, b: $MgCl_2\cdot6H_2O$, c: $CaCl_2\cdot6H_2O$, d: $SrCl_2\cdot6H_2O$, e: $BaCl_2\cdot2H_2O$.

The DTA curves of the sample containing 1 mol% of alkali earth metal chlorides are given in Fig. 2. Decomposition was greatly influenced by the addition of beryllium chloride tetrahydrate, magnesium chloride hexahydrate, calcium chloride hexahydrate and magnesium bromide hexahydrate, but the effect of strontium chloride hexahydrate was small and no effects were observed by other additives.

We see that all the additives with considerable effect contain four or six molecules of water of crystallization which would cause the hydrolytic cleavage of hydrogen chloride from the halides at relatively low temperature, as suggested from the following reaction scheme.[10]

$$MgCl_2\cdot6H_2O \longrightarrow MgCl_2\cdot4H_2O + 2H_2O \quad 95\text{—}115^\circ C$$
$$MgCl_2\cdot4H_2O \longrightarrow MgCl_2\cdot2H_2O + 2H_2O \quad 135\text{—}180^\circ C$$
$$MgCl_2\cdot4H_2O \longrightarrow MgOHCl + HCl + 3H_2O$$
$$MgCl_2\cdot2H_2O \longrightarrow MgCl_2\cdot H_2O + H_2O \quad 185\text{—}230^\circ C$$
$$MgCl_2\cdot2H_2O \longrightarrow MgOHCl + HCl + H_2O$$
$$MgCl_2\cdot H_2O \longrightarrow MgCl_2\cdot H_2O \quad \text{over above } 230^\circ C$$
$$MgCl_2\cdot H_2O \longrightarrow MgOHCl + HCl$$
$$MgOHCl \longrightarrow MgO + HCl$$

Evolution of hydrogen chloride or hydrogen bromide was also detected from three other additives by gas chromatography. The temperature of liberation of hydrogen chloride was the same as or very close to that of decarbonation and dehydration of basic magnesium carbonate.

Effect of the Amount of Additive on DTA Curve. Concentrations of four additives greatly influenced DTA curves. The DTA curves for various concentrations of magnesium chloride hexahydrate are shown in Fig. 3. The other three additives also show similar tendency. With increase in the amount of additive endothermic peak A at a lower temperature shifted somewhat to a higher temperature and peak B at a higher temperature shifted considerably to a lower temperature. The change in the maximum temperature of peak B is illustrated in Fig. 4. Of the four additives, magnesium bromide showed the largest temperature shift (80°) to lower side.

Effect of Additive on the TG Curve. In Fig. 5 are shown the TG curves of the sample containing magnesium chloride hexahydrate in the region 300—500 °C, where decarbonation, partial dehydration from basic magnesium carbonate and decomposition of additive are known to occur. The other three additives also show a similar tendency. It is thus evident that the TG curve is also influenced by additive. It appears that the rate of decomposition increases with the increase in the amount of additive.

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[9] H. Hashimoto, T. Tomizawa, and M. Mitomo, *Kogyo Kagaku Zasshi*, **71**, 480 (1968); R. M. Dell and S. W. Weller, *Trans. Faraday Soc.*, **55**, 2203 (1959).

[10] "Jikken Kagaku Koza," ed. by Chemical Society of Japan, Vol. 9, Maruzen, Tokyo (1970), p. 143.

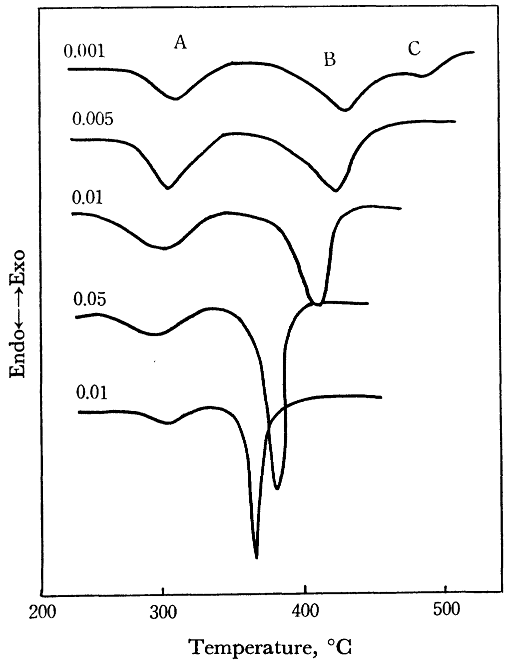

Fig. 3. DTA curves of $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$-$MgCl_2 \cdot 6H_2O$.
0.001—0.1: $[MgCl_2 \cdot 6H_2O]/[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]$

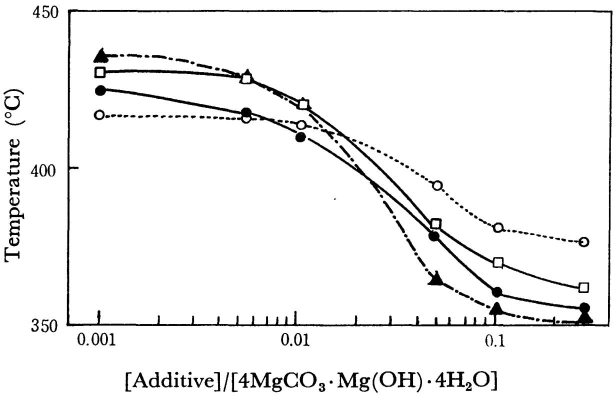

Fig. 4. Variation of the peak maximum temperature of decarbonation
○—○ $BeCl_2 \cdot 4H_2O$ ●—● $MgCl_2 \cdot 6H_2O$
□—□ $CaCl_2 \cdot 6H_2O$ ▲—▲ $MgBr_2 \cdot 6H_2O$

Effect of Additive on the Activation Energy. To evaluate the activation energy from the TG curve, we employed Freeman-Carroll's technique[11] and Coat's technique.[12] An abnormally high activation energy was obtained for decomposition of the sample containing additive at about 450 °C, although the decomposition occurred more abruptly and at a lower temperature than that for an additive-free sample. Reason why the above high value was obtained was considered as follows: Weight loss obtained by TG might be attributed to the decomposition of basic magnesium carbonate and additive. Not only the rate of decomposition but also the composition of the evolved gas varied with the amount of additive (Fig. 6).

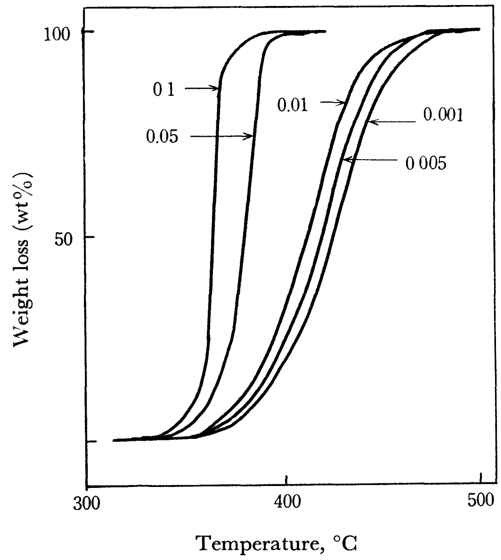

Fig. 5. Effect of magnesium chloride hexahydrate on TG curve of basic magnesium carbonate in the region of 300 to 500 °C.
0.001—0.1: $[MgCl_2 \cdot 6H_2O]/[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]$

We employed gas chromatography for the evaluation of activation energy using the Freeman-Carroll equation:

$$\frac{\frac{-E}{2.3R}\Delta\frac{1}{T}}{\Delta\log Wr} = -\mathrm{x} + \frac{\Delta\log\frac{dw}{dt}}{\Delta\log Wr}$$

where E, T, R, and x represent the activation energy, the absolute temperature at which gas is collected, the gas constant and the order of reaction with respect to the component, respectively, dw/dt being the rate of

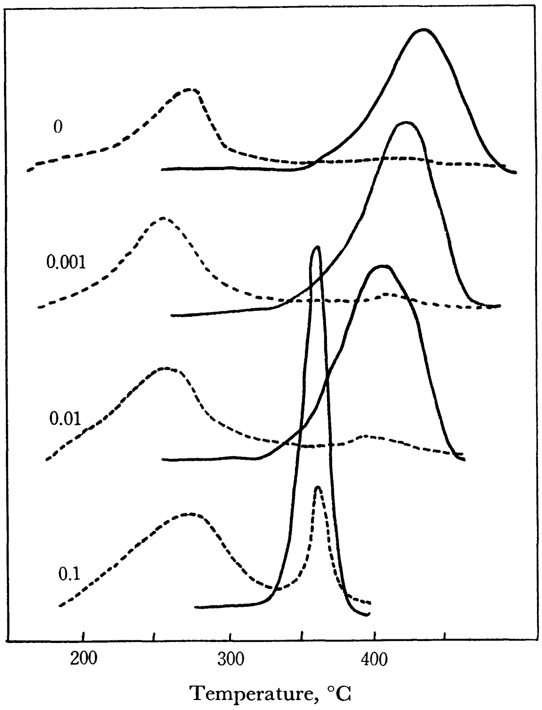

Fig. 6. Rate of dehydration and decarbonation
0—0.1: $[MgCl_2 \cdot 6H_2O]/[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]$
——: CO_2, ------: H_2O

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[11] E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
[12] A. W. Cats and J. P. Redfern, *Nature*, **201**, 68 (1964).

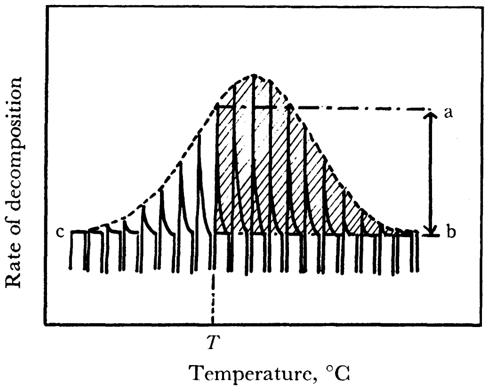

Fig. 7. Gas chromatogram obtained by thermal decomposition.

decomposition at T K, and Wr the difference between the weight loss at completion of reaction and total weight loss up to T K. Gas chromatograms obtained are shown in Fig. 7. The differential curve given by a dotted line (namely dw/dt *vs.* t) corresponds to the rate of decomposition. The length from (a) to (b) is the rate of decomposition reaction (dw/dt) at T K. The areas bound by a dotted line and basement (b—c) represent the total amount of water or carbon dioxide. Wr corresponds to the shaded part. Thus dw/dt and Wr can be determined directly from the curve (dotted line), and the activation energy could be readily calculated by plotting $(\Delta\log dw/dt)/\Delta\log Wr$ against $(T^{-1})/\Delta\log Wr$.

Validity of this gas chromatographic method is clear from the following evidences. Although basic magnesium carbonate evolved water vapor only in a very small amount in the range 350—500 °C, this does not seem to affect the evaluation of activation energy. Thus the values of $\Delta\log dw/dt$ and $\Delta\log Wr$ determined by gas chromatography for the additive-free sample seems to be the same as those by TG. The activation energies calculated from gas chromatogram agreed with the one from the TG curve, *viz.*, 47.7 and 47 kcal/mol.

The activation energies of decarbonation obtained by gas chromatography are shown in Fig. 8. The rate of decomposition was too large for the evaluation of activation energy for the sample containing an additive in a molar ratio greater than 0.05.

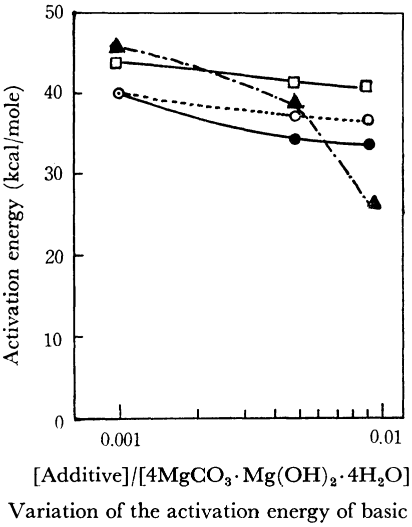

Fig. 8. Variation of the activation energy of basic magnesium carbonate with additives

○---○ $BeCl_2 \cdot 4H_2O$ ●—● $MgCl_2 \cdot 6H_2O$
□—□ $CaCl_2 \cdot 6H_2O$ ▲-·-▲ $MgBr_2 \cdot 6H_2O$

Although the effect of additive on dehydration at about 200 °C of basic magnesium carbonate is not clear since dehydration of the additive took place in a similar temperature range, the influence on the activation energy of dehydration would be neglected due to a very low concentration of additive. The activation energies of dehydration of the sample containing beryllium chloride tetrahydrate, magnesium chloride hexahydrate, calcium chloride hexahydrate, and additive-free were 13, 15, 23, and 25 kcal/mol, respectively. They were not affected by the amount of additive. On the other hand, the values for the sample containing magnesium bromide hexahydrate in the molar ratio range 0.001—0.01 varied from 25 to 15 kcal/mol.

The amount of magnesium bromide hexahydrate affects the activation energies of both decarbonation and dehydration remarkably. The effect might be mainly ascribed to hydrogen bromide generated in addition to the difference in the mode of decomposition of additive.

Effect of Additive on the Size of Crystallite of Magnesium Oxide. Sizes of the crystallite of magnesium oxide are shown in Fig. 9.

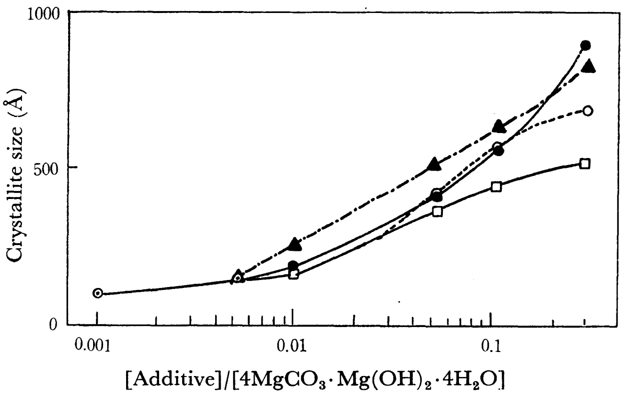

Fig. 9. Variation of the crystallite size of MgO with concentration of additives

○---○ $BeCl_2 \cdot 4H_2O$ ●—● $MgCl_2 \cdot 6H_2O$
□—□ $CaCl_2 \cdot 6H_2O$ ▲-·-▲ $MgCl_2 \cdot 6H_2O$

Transmission electron micrographs of basic magnesium carbonate and magnesium oxides are shown in Fig. 10. Magnesium oxide exists as an aggregate of small particles of the oxide. The shape of the aggregate is similar to that of basic magnesium carbonate, the particle size of magnesium oxide increasing with the increase of the amount of additive. The results obtained the micrographs (Fig. 10) are in line with those obtained with X-ray diffractometry. Since it is known that sintered magnesia of large size is prepared by heating magnesium oxide under a flow of hydrogen chloride,[13] it seems that the growth of crystal of magnesium oxide is influenced by hydrogen halide evolved

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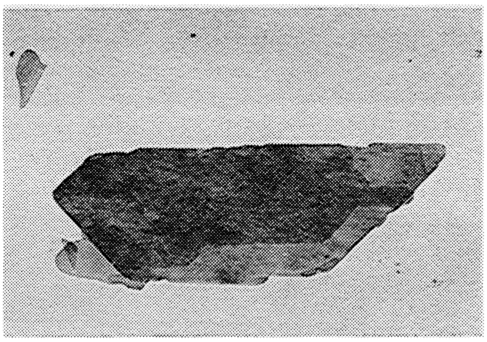
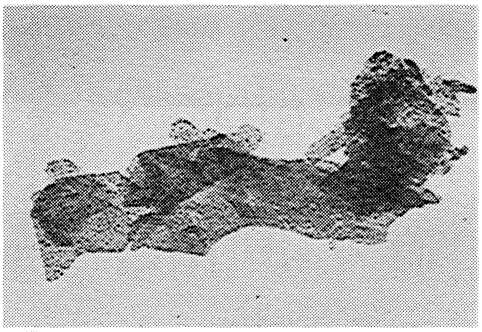
[13] T. Titani, "Muki Kagaku," Sangyo Tosho, Tokyo, (1959).



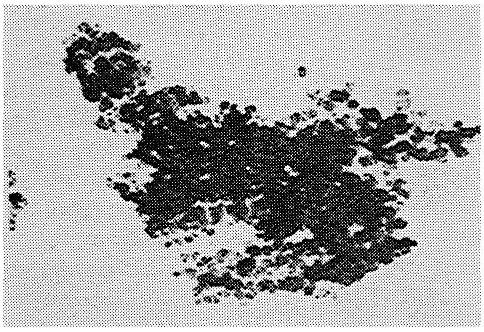
Basic magnesium carbonate

0

0.001



0.01



0.1

Fig. 10. Electron micrographs of basic magnesium carbonate and magnesium oxide.
0—0.1: $[MgCl_2 \cdot 6H_2O]/[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]$

by the decomposition of an additive.

It should be noted that thermal decomposition of basic magnesium carbonate and the size of the crystallite of magnesium oxide prepared from basic magnesium carbonate are influenced by hydrogen halide evolved from an additive.