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THERMAL ANALYSIS OF BASIC MAGNESIUM CARBONATE CONTAINING DIFFERENT ALKALI METAL CARBONATES

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ABSTRACT

Thermal decomposition of basic magnesium carbonate impregnated with alkali metal (Li, Na, K, Rb and Cs) carbonate, in the preparation of alkali metal-doped MgO catalysts, has been investigated by TG, DTG and DTA techniques in the temperature range 30–1200 ° C. The exothermic DTA peak observed for the basic magnesium carbonate around 490 ° C is found to be absent from the samples containing alkali metal carbonates, except for the sample with $Na/Mg = 0.02$. The solid products (i.e. alkali metal-doped MgO) of decomposition at different temperatures have been characterized for its alkali metal content, crystalline phases, surface area and surface basicity. The thermal decomposition of basic magnesium carbonate and properties of solid products of the decomposition are found to be strongly influenced by the addition of alkali metal carbonate to the magnesium carbonate, depending on the type of alkali metal and its concentration. The addition of alkali metal carbonate has resulted in a large decrease in the surface area, but an increase in the density of surface basic sites, of MgO obtained in the decomposition.

INTRODUCTION

The alkali metal-doped MgO catalysts Li–MgO [1–6], Na–MgO [4–9], Rb–MgO [6–9] and Cs–MgO [6] are used in oxidative coupling of methane to C_2-hydrocarbons, which is a newly emerging process of great commercial importance. Catalysts showing high activity and selectivity in the above process can be prepared by thermal decomposition of basic magnesium carbonate mixed with alkali metal carbonate at a desired concentration [6]. It is, therefore, interesting to investigate the thermal decomposition of basic magnesium carbonate containing alkali metal by TG, DTG and DTA techniques.

Thermal analysis of magnesium carbonate has been thoroughly investigated earlier [10–14]. However, no information is available on the thermal decomposition of basic magnesium carbonate containing alkali metal

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carbonates. The present investigation was therefore undertaken to study the influence of alkali metal (Li, Na, K, Rb and Cs) carbonates on the thermal analysis and properties of solid products (i.e. alkali metal-doped MgO) of the thermal decomposition.

EXPERIMENTAL

Basic magnesium carbonate

Basic magnesium carbonate was prepared by precipitating it from an aqueous solution of magnesium nitrate (1 mol dm^{-3}) with an aqueous solution of sodium carbonate (1 mol dm^{-3}) at room temperature (30 °C) and at $pH = 9.0 \pm 0.2$, ageing the precipitate for 30 min, washing it thoroughly with deionized distilled water until free from sodium, filtering, drying at 80 °C in a vacuum oven for 8 h, and crushing to 120–200 mesh size particles.

The composition of the basic magnesium carbonate was $1.0MgO \cdot 0.77CO_2 \cdot 0.84H_2O$. The composition was obtained from the knowledge of weight loss and the amount of CO_2 evolved when the basic magnesium carbonate was heated from 30–1200 °C in a flow of moisture-free nitrogen. The crystalline phases observed in the basic magnesium carbonate sample were hydromagnesite (i.e. $5MgO \cdot 4CO_2 \cdot 5H_2O$) as a major phase and $MgCO_3 \cdot 3H_2O$ and $Mg(OH)_2$ as minor phases.

Basic magnesium carbonate containing alkali metal carbonates

The basic magnesium carbonate was impregnated with different alkali metal carbonates by adding an aqueous solution containing the desired amount of alkali metal carbonate to the powdered magnesium carbonate, mixing thoroughly and drying the resulting thick paste in an air oven at 120 °C for 4 h. The dried solid was crushed to 120–200 mesh size particles and stored in a desiccator.

TG, DTG and DTA

The thermal analysis (TG, DTG and DTA) results were obtained using an automatic Netzsch STA 409 model (Netzsch Geratebau GmbH) simultaneous thermal analysis apparatus under the following experimental conditions. Sample holder, platinum; sample size, 30 mg; reference compound, α-alumina; atmosphere, static air; temperature range, 30–1200 °C, and heating rate, 10 °C min^{-1}.

Samples of the solid products of decomposition were prepared by heating the basic magnesium carbonate with and without alkali metal carbonate in a muffle furnace at different temperatures (600 °, 750 ° and 950 °C) in static air for 6 h.

The presence of various crystal phases in the solid products was studied using a PW/1730 X-ray generator with Ni-filtered Cu Kα radiation and a scintillation counter. The specific surface area of the solid products was determined by a single-point BET method by measuring the adsorption of nitrogen at liquid nitrogen temperature and at a nitrogen concentration of 30 mol% (balance helium) using a Monosorb Surface Area Analyser (Quanta Chrome Corp., U.S.A.) based on a dynamic adsorption/desorption technique. The basicity of the solid products was determined by measuring the chemisorption of CO_2 at 50 °C using the method [15] based on thermal desorption of CO_2 (chemisorbed at 50 °C) from 50–900 °C and measuring the desorbed CO_2 by gravimetric analysis.

RESULTS AND DISCUSSION

The basic magnesium carbonate (composition $5MgO \cdot 3.85CO_2 \cdot 4.2H_2O$) used in the present investigation is essentially hydromagnesite ($5MgO \cdot 4CO_2 \cdot 5H_2O$) containing small amounts of $Mg(OH)_2$ and nesquehonite ($MgCO_3 \cdot 3H_2O$).

Thermal analysis

The TG, DTG and DTA curves for decomposition of the basic magnesium carbonate with or without lithium carbonate at different Li/Mg ratios are shown in Fig. 1. Figure 2 shows the influence of the addition of sodium carbonate to the basic magnesium carbonate at different Na/Mg

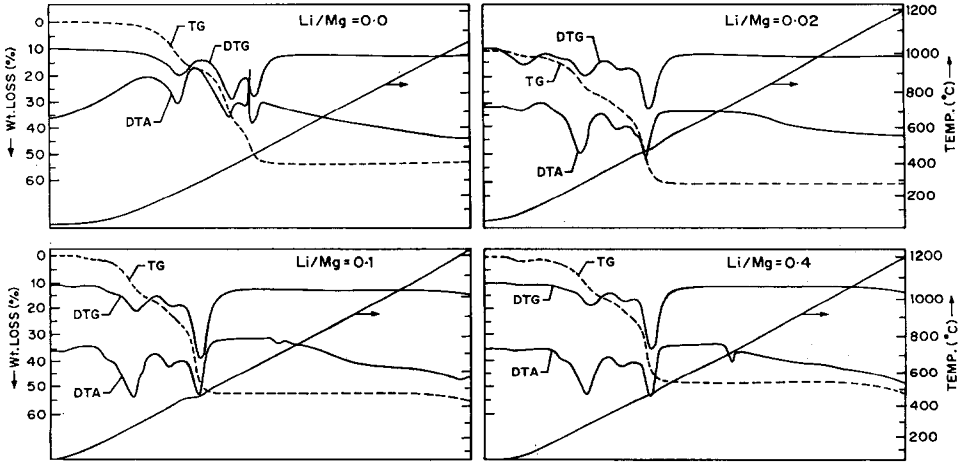

Fig. 1. TG, DTG and DTA curves for thermal decomposition of basic magnesium carbonate containing Li_2CO_3 at different Li/Mg ratios.

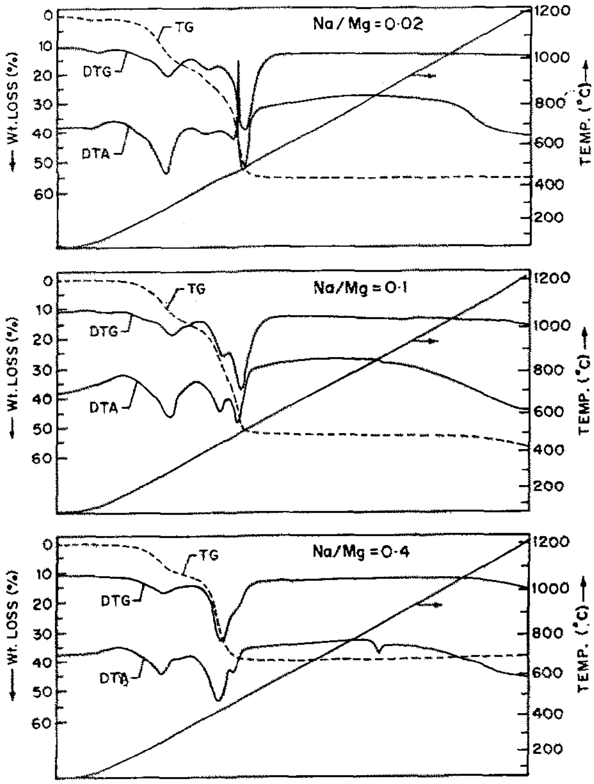

Fig. 2. TG, DTG and DTA curves for thermal decomposition of basic magnesium carbonate containing Na_2CO_3 at different Na/Mg ratios.

ratios on the thermal analysis. In Fig. 3, the TG, DTG and DTA curves for thermal decomposition of the basic magnesium carbonate containing K_2CO_3, Rb_2CO_3 and Cs_2CO_3 (alkali metal/Mg = 0.1) are presented. Data on the DTA and DTG peak temperatures and TGA for the basic magnesium carbonate containing the different alkali metal carbonates are given in Tables 1 and 2, respectively.

From the results (Figs. 1–3 and Tables 1–3) the following important observations could be made.

For the basic magnesium carbonate without alkali metal carbonate and for that containing Na_2CO_3 at Na/Mg = 0.02, an exothermic DTA peak at 490° and 467°C, respectively, is observed, whereas for all other cases, no exothermic peak is observed, An exothermic DTA peak has been observed earlier in the thermal decomposition of magnesium hydroxide around 450°C [16], magnesium carbonate around 465°C [17] and hydromagnesite around 500°C [13,14]. The exothermic peak results probably from evolution of heat due to removal of internal crystal defects in the metastable oxide lattice in the process of crystallization [17]. It is interesting to note that the addition

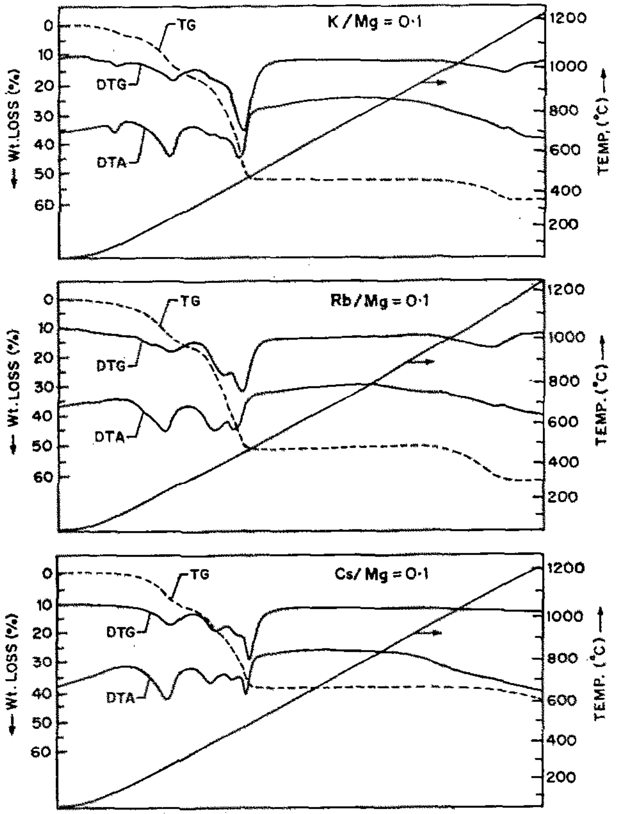

Fig. 3. TG, DTG and DTA curves for thermal decomposition of basic magnesium carbonate containing K_2CO_3, Rb_2CO_3 and Cs_2CO_3 (alkali metal/Mg ratio = 0.1).

of alkali metal carbonate (except Na_2CO_3 at Na/Mg = 0.02) eliminates the exothermic peak.

The DTA and DTG peaks observed near or below 100 °C are due to the desorption of physically adsorbed water. The DTG and highly endothermic DTA peaks observed between 200 and 500 °C are due to dehydration and decarbonation of the basic magnesium carbonate. The DTA and DTG data between 200 °C and 500 °C (Figs. 1–3 and Table 1) show that the thermal decomposition of basic magnesium carbonate is strongly influenced by the addition of alkali metal carbonates.

The small endothermic DTA peaks for the samples with Li/Mg = 0.1, Li/Mg = 0.4, Na/Mg = 0.1, Na/Mg = 0.4, K/Mg = 0.1 and Rb/Mg = 0.1 at 705°, 703°, 839°, 833°, 881° and 847 °C, respectively, for which there are no corresponding DTG-peaks is due to melting of the alkali metal carbonate added to the sample (melting points of Li_2CO_3, Na_2CO_3, K_2CO_3 and Rb_2CO_3 are 720°, 850°, 901° and 837 °C, respectively).

The DTA and DTG peaks observed above 1100 °C for the samples with

TABLE 1

DTA and DTG data for basic magnesium carbonate containing different alkali metal carbonates at different alkali metal/Mg ratios

Peak temperature (°C)									
DTA	DTG	DTA	DTG	DTA	DTG	DTA	DTG	DTA	DTG
Without alkali metal		Li/Mg = 0.10		Na/Mg = 0.02		Na/Mg = 0.40		Rb/Mg = 0.10	
262	273	56	85	55	62	63	78	269	281
423	439	275	285	274	285	252	269	404	420
490 [a]	–	388	404	392	402	419	424	460	471
495	500	456	460	467 [a]	–	450	466	841	–
–	–	705	–	475	480	833	–	1106	1108
–	–	> 1200	> 1200	–	–	> 1200	> 1200	–	–
Li/Mg = 0.02		Li/Mg = 0.40		Na/Mg = 0.10		K/Mg = 0.10		Cs/Mg = 0.10	
64	86	49	64	275	280	98	105	275	280
292	297	270	285	404	409	264	269	397	409
404	412	388	398	456	466	455	466	456	461
487	492	465	471	839	–	881	–	486	491
–	–	703	–	> 1200	> 1200	1137	1140	> 1200	> 1200
–	–	> 1200	> 1200	–	–	–	–	–	–

[a] Exothermic peak; all others endothermic.

TABLE 2

TGA data for basic magnesium carbonate containing different alkali metal carbonates at different alkali metal/Mg ratios

Alkali metal/ Mg ratio	Weight loss (%)						
	Desorption of physically adsorbed water	Dehydration and decarbonation				Evaporation of alkali metal compound	Total
		I	II	III	IV		
Without alkali metal	–	18.7	24.0	11.0	–	–	53.7
Li/Mg = 0.02	2.7	15.5	9.0	23.2	–	–	50.4
Li/Mg = 0.10	1.3	17.0	8.7	25.7	–	2.0 (1055–1200 ° C) [a]	54.7
Li/Mg = 0.4	1.3	15.4	7.0	25.0	–	7.0 (905–1200 ° C)	55.7
Na/Mg = 0.02	1.2	16.1	7.1	29.9	–	–	54.3
Na/Mg = 0.10	–	17.3	13.7	21.3	–	2.8 (1060–1200 ° C)	55.1
Na/Mg = 0.4	1.0	11.7	28.0	–	–	6.0 (1015–1200 ° C)	46.7
K/Mg = 0.1	3.6	14.3	34.7	–	–	6.3 (970–1150 ° C)	58.9
Rb/Mg = 0.1	–	15.6	20.0	13.7	–	13.0 (905–1150 ° C)	62.3
Cs/Mg = 0.1	–	12.3	10.0	6.0	10.6	2.1 (1040–1200 ° C)	41.0

[a] Values given in parentheses indicate the temperature range over which the evaporation of alkali metal compound occurred.

TABLE 3

Properties of solid products obtained from the decomposition (at different temperatures) of basic magnesium carbonate containing different alkali metal carbonates

Alkali metal/Mg ratio in sample used in decomposition	Surface area (m^2 g^{-1})			Alkali metal/Mg ratio × 10^2			Basicity (μmol m^{-2}) (Decomposition temperature 950 °C)
	600 °C	750 °C	950 °C	600 °C	750 °C	950 °C	
Without alkali metal	75.1	56.6	17.8	0.0	0.0	0.0	12.3
Li/Mg = 0.02	35.2	9.9	8.3	0.6	0.4	0.2	–
Li/Mg = 0.1	27.1	5.4	1.2	3.1	1.8	0.7	78.6
Li/Mg = 0.4	11.2	2.6	0.5	12.0	6.3	2.1	250.1
Na/Mg = 0.02	71.4	31.2	17.5	1.5	1.2	0.8	–
Na/Mg = 0.1	65.7	25.0	3.1	3.9	2.8	1.2	46.6
Na/Mg = 0.4	47.4	20.9	0.8	36.0	29.0	25.8	177.7
K/Mg = 0.1	59.8	31.0	16.2	0.7	0.5	0.12	9.6
Rb/Mg = 0.1	33.2	20.1	14.0	3.6	3.0	0.25	29.1
Cs/Mg = 0.1	72.3	35.0	5.9	2.2	1.9	1.2	21.8

alkali metal/Mg ratio $\geqslant 0.1$ is due to evaporation of the alkali metal compound.

It is interesting to note that the dehydration and decarbonation of the basic magnesium carbonate without alkali metal and with Li/Mg = 0.02–0.4, Na/Mg = 0.02 and 0.1 and Rb/Mg = 0.1 occur in three stages, whereas those for the samples with Na/Mg = 0.4 and K/Mg = 0.1 occur in only two stages. The dehydration and decarbonation of the sample with Cs/Mg = 0.1, however, take place in four stages (Table 2).

The evaporation of alkali metal compound from samples with Li/Mg = 0.1, Li/Mg = 0.4, Na/Mg = 0.1, Na/Mg = 0.4, K/Mg = 0.1, Rb/Mg = 0.1 and Cs/Mg = 0.1 starts from 1055°, 905°, 1060°, 1015°, 970°, 905° and 1040°C, respectively. However, a complete evaporation of alkali metal compound upto 1200°C occurs only for the samples containing K_2CO_3 and Rb_2CO_3.

Solid products of decomposition

The solid products of decomposition of basic magnesium carbonate with and without different alkali metal carbonates at 600°, 750° and 950°C (in static air for 6 h) have been characterized for their surface area, alkali metal content, basicity and crystalline phases.

The surface area of the solid products obtained in the decomposition are given in Table 3. The results show that the surface area of solid products is decreased by the addition of alkali metal carbonates. It decreases as the alkali metal/Mg ratio in the sample increases and also with the decomposition temperature. This leads to the conclusion that the growth of MgO crystals (or sintering of MgO) is promoted by the presence of alkali metal carbonate. The promoting action of the different alkali metal carbonates is in the following order:

At 600 ° C: $Li_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Cs_2CO_3$

At 750 ° C: $Li_2CO_3 > Rb_2CO_3 > Na_2CO_3 > K_2CO_3 \geqslant Cs_2CO_3$

At 950 ° C: $Li_2CO_3 > Na_2CO_3 > Cs_2CO_3 > Rb_2CO_3 > K_2CO_3$

The above observations indicate that the reduction in the surface area depends on both the alkali metal carbonate added and the decomposition temperature.

The data on alkali metal contents (alkali metal/Mg ratio) of the solid products are included in Table 3. Results show that the loss of alkali metal due to evaporation depends on both the alkali metal and the decomposition temperature. The loss of alkali metal carbonate in the decomposition is in the following order:

At 600 ° C: $K_2CO_3 > Cs_2CO_3 > Li_2CO_3 > Rb_2CO_3 > Na_2CO_3$

At 750 ° C: $K_2CO_3 > Li_2CO_3 \geqslant Cs_2CO_3 > Na_2CO_3 > Rb_2CO_3$

At 950 ° C: $K_2CO_3 > Rb_2CO_3 > Li_2CO_3 > Na_2CO_3 \simeq Cs_2CO_3$

The crystalline phases observed by X-ray diffraction (XRD) in the solid products of the decomposition at 750 ° and 950 ° C are presented in Table 4.

The XRD peaks (at $2\theta = 43°$, 63° and 110°) for the solid products

TABLE 4

Crystalline phases present in the solid products of the decomposition at 750 ° C and 950 ° C

Alkali metal/Mg ratio in the sample used for the decomposition	Crystalline phases	
	750 ° C	950 ° C
Without alkali metal	MgO	MgO
Li/Mg = 0.1	MgO	MgO
Li/Mg = 0.4	MgO (major) Li_2CO_3 (minor)	MgO
Na/Mg = 0.1	MgO (major) Na_2CO_3 (minor)	MgO –
Na/Mg = 0.4	MgO (major) Na_2CO_3 (minor)	MgO (major) Na_2CO_3 (minor)
K/Mg = 0.1	MgO (major) K_2CO_3 (traces)	MgO –
Rb/Mg = 0.1	MgO (major) Rb oxide (minor)	MgO (major) Rb oxide (traces)
Cs/Mg = 0.1	MgO (major) Cs oxide (minor)	MgO (major) Cs oxide (traces)

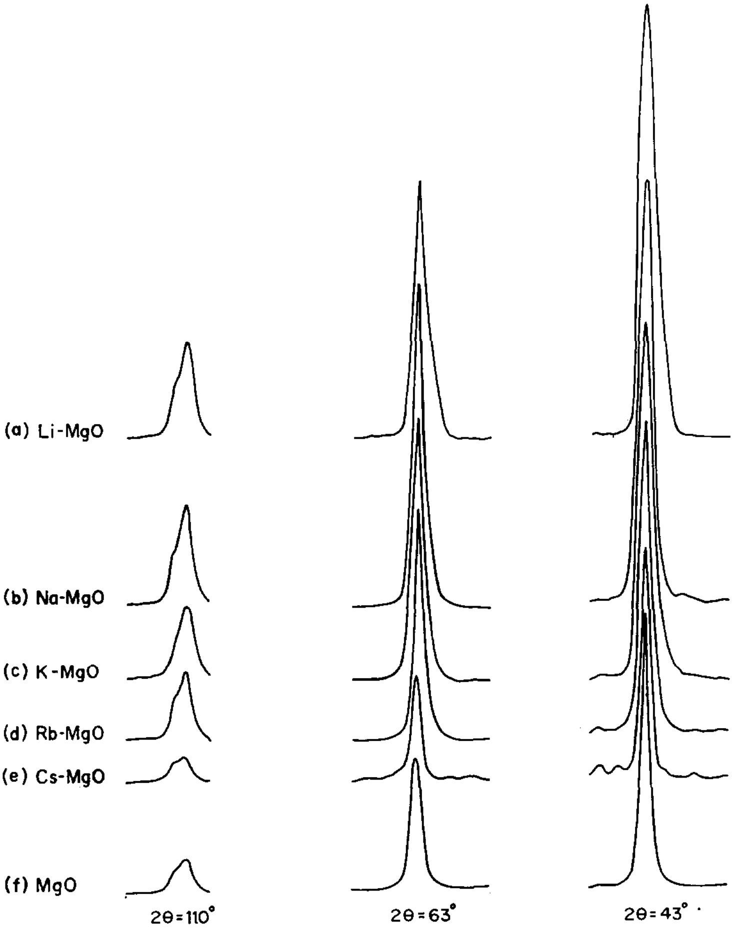

Fig. 4. XRD peaks at $2\theta = 43°$, 63° and 110° for alkali metal containing MgO obtained by the decomposition at 750 °C.

obtained at 750 ° and 950 °C are shown in Figs. 4 and 5, respectively. It is interesting to note from Fig. 4 that the XRD peaks for the solid products obtained by the decomposition in presence of different alkali metal carbonates (alkali metal/Mg ratio = 0.1) at 750 °C are broader than those for the solid product obtained at 750 ° C in absence of alkali metal carbonate. On the contrary, when the decomposition temperature is increased to 950 °C, the XRD peaks for the solid products containing alkali metal become narrower than for the solid product without alkali metal.

Generally, XRD peak broadening occurs because of a decrease in the crystal size and consequently an increase in the surface area and vice versa. In the present case, since the addition of alkali metal causes a decrease in the surface area, the peak broadening for solid products obtained at 750 °C is expected to be due mostly to distortion of the crystal lattice following incorporation of alkali metal cations. The alkali metal cations, except Li^+,

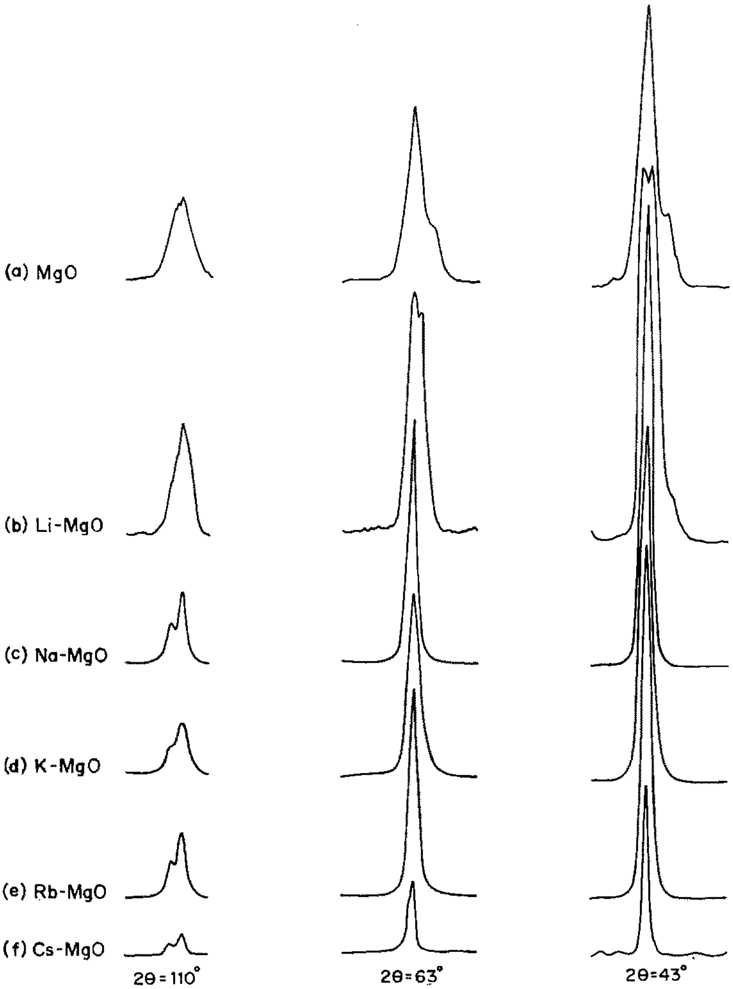

Fig. 5. XRD peaks at $2\theta = 43°$, $63°$ and $110°$C for alkali metal containing MgO obtained by the decomposition at 950°C.

are larger than Mg^{2+} (radii of Mg^{2+}, Li^+, Na^+, K^+, Rb^+ and Cs^+ are 0.66, 0.60, 0.95, 1.33, 1.48 and 1.69 Å, respectively). Hence, the doping of MgO with alkali metal is expected to result in distortion of its crystal lattice. In the case of Rb-promoted MgO, XRD peak broadening due to crystal distortion has been observed earlier by Iwamatsu and co-workers [9]. The narrowing of XRD peaks observed for the solid products obtained at 950°C in the presence of different alkali metal carbonates (Fig. 5) is expected to be attributable mostly to a large decrease in the surface area and consequently increase in the crystal size accompanied by annihilation of the crystal defects at the higher temperature (950°C).

Results on the surface basicity (measured in terms of the amount of CO_2 chemisorbed per unit surface at 50°C) of the solid products (obtained at

950 °C) are included in Table 3. The surface density of basic sites (μmol m^{-2}) is increased due to the addition of different alkali metal carbonates (except K_2CO_3), depending upon the alkali metal carbonate added and its concentration. The surface density of basic sites of the solid products with or without different alkali metals is in the order: Li–MgO > Na–MgO > Rb–MgO > Cs–MgO > MgO > K–MgO.

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