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Activation of magnesium chloride by dry milling

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Extensive dry ball milling (up to 200 h in a vibratory mill) of the layer-lattice type $MgCl_2$ structure (used as olefin polymerization support) results in a moderate reduction in the mean particle size and a more pronounced decrease in crystallite size in directions parallel and transverse to the hexagonal crystal axis. The relative reductions in crystallite size are understood on the basis of sliding of the Cl–Mg–Cl double layers by the action of shear. The effect is accompanied by a change from cubic or hexagonal close packed layer structures to arrangements with lattice disorder. The effect can be reversed completely by annealing above about 250 °C.

1. Introduction

Magnesium chloride is an industrially important chemical with a major application as a component for olefin polymerization catalysts [1]. Although various crystal modifications of $MgCl_2$ have been reported [2, 3], invariably "active magnesium chloride" is required for use as a catalyst support, a product which embraces crystalline forms with lattice disorder. Active forms of $MgCl_2$ are usually taken to be those which are characterized by the fact that in the X-ray spectrum a halo appears with maximum intensity comprised between 0.256 nm and 0.295 nm [1].

Active $MgCl_2$ may be obtained by subjecting anhydrous $MgCl_2$ to shearing forces or by chemical synthesis along various low-temperature ($T \approx 100\,°C$) routes, such as Grignard and Wurtz reactions [4], i.e.

$$2\,RMgCl \rightleftharpoons R_2Mg + MgCl_2 \qquad (1)$$

$$2\,RCl + Mg \rightarrow RR + MgCl_2 \qquad (2)$$

$$RMgCl + HCl \rightarrow RH + MgCl_2 \qquad (3)$$

Other synthesis routes which may be envisaged are rapid crystallization of $MgCl_2$, in analogy to CdI_2 [5], or low-temperature dehydration of the hydrates, as in the case of $CdBr_2$ [6] and $NiBr_2$ [7]. Similarly, dealcoholation procedures of ethanol adducts, $MgCl_2{\cdot}n\mathrm{EtOH}$, have successfully been employed [8]. Obviously, the adsorptive and catalytic properties of these supports depend on a combination of factors – crystal structure, pore texture, surface structure – which are, in turn, determined by the features of the starting products (hydrates, alcoholates, etc.) and by the specific synthesis procedures used. We report here a quantitative study of the disordered product obtained by extensive grinding of $MgCl_2$ in an effort to correlate the extent of mechanical action with materials properties.

2. Experimental procedure

2.1. Sample preparation

High-purity anhydrous $MgCl_2$ was used throughout. Activation of α-$MgCl_2$ was carried out by ball milling with steel balls in a dry nitrogen atmosphere at room temperature. A conventional cylindrical mill (l = 10 cm, diameter = 5 cm) was used with 550 g 9.5 mm diameter stainless steel balls as the grinding medium and a charge of 10 g $MgCl_2$. The degree of activation was varied by the duration of milling (up to 200 h), which was performed at 125 r.p.m. For more intense milling, a 1 l vibratory mill (Vibratom, Siebtechnik Gmbh, Mülheim) was used. Samples of active material (60 g) were prepared at room temperature by grinding with 2.5 kg 16 mm diameter stainless steel balls for arbitrarily selected lengths of time up to 200 h.

2.2. Materials characterization

Surface areas and pore volumes were determined according to the BET method [9] by means of nitrogen adsorption at liquid-nitrogen temperature in a Sorptomatic Series 1800 instrument. The measurements were carried out after outgassing at 10^{-2} torr (1 torr = 133.322 Pa) for 2–4 h at room temperature. The average particle diameter was measured by sedimentation with a Micromeritics Sedigraph 5000 D particle size analyser (Micromeritics Instrument Corp., Norcross, Ga). Differential thermal analysis (DTA) was performed with a Mettler TA2 apparatus at a heating rate of 5 °C min^{-1}. Ultrasonic agitation was carried out in a Kerry instrument. Electron diffraction and TEM experiments (up to × 70 000) were carried out on a Philips EM-300 electron microscope. X-ray powder patterns were recorded with a Philips PW 1050/70 goniometer using CuK_α radiation. The samples were protected from moisture in the air by mixing with paraffin oil under dry nitrogen. (Paraffin

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oil shows up in the X-ray spectra as a broad band centred at 18° in 2θ.) During pattern collection, a dry-nitrogen flux was maintained over the sample. The Scherrer equation (with $K = 1.84$ for the $(1\,1\,0)$ plane and 0.89 for $(0\,0\,3)$ [10] was employed to connect measurements of the widths of interferences at points of half-maximum intensities with crystallite size. The $(0\,0\,3)$ and $(1\,1\,0)$ planes of α-$MgCl_2$ were found to be convenient for determining an average crystallite size dimension in the direction of the crystal c-axis and along the Cl–Mg–Cl layer plane, respectively. Particular attention was paid to the spectral range around the $(1\,0\,\bar{2} + 0\,0\,6)$ and $(1\,0\,4)$ reflections ($28° < 2\theta < 40°$) in order to correlate the modifications observed as a result of grinding and annealing of the samples with the disorder of the layer packing. Deconvolution of the experimental profiles was performed in terms of six gaussian functions, four being centred at the angular positions of the Bragg reflections of the cubic (α-form) and hexagonal (β-form) packing of the chlorine layers of $MgCl_2$ (allowing a numerical tolerance of $\pm 0.2°$), and two other gaussians being considered in a floating position to describe the scattering intensity arising from structural disorder of the layer packing. The latter two gaussians grow with the contemporary disappearance of the $(1\,0\,\bar{2})$ and $(1\,0\,4)$ reflections due to gliding of the anionic layers. The ratio of the areas of these two gaussians with respect to the total area of the diffraction pattern in the angular range of $28° < 2\theta < 40°$, I (disorder)/I (total), is taken as measure of the degree of disorder of the samples.

3. Results

Dry milling of $MgCl_2$ for varying lengths of time affects particle size, surface area, crystallite size and structure, as shown in Fig. 1 and Table I. A modest particle-size reduction takes place during the early stages (1 h) of grinding in a vibratory mill. Subsequently, even a small increase in particle size is observed. Surface-area measurements of samples ground in the vibratory mill indicate a steep increase with time of milling, especially during the first 3 h; the effect appears to be only slightly dependent on particle size.

Dry milling also causes drastic crystallographic changes in the layer-type structure of $MgCl_2$, as shown by the diffraction patterns of Fig. 1. As may be seen, milling for a few minutes in a vibratory mill does not modify the narrow and sharp X-ray pattern of α-$MgCl_2$. The initially observed differences in the relative intensities of the various diffraction peaks with respect to ASTM 25-1156 (Powder File Card) reflect preferred orientation phenomena of the crystallites (platelets) in the samples. At longer milling times, the diffraction lines become progressively broader and more diffuse, indicating that a significant reduction in crystallite size has occurred. Simultaneously, the appearance of broad haloes, shifted in position with respect to the sharp diffraction bands of the unmilled samples, suggests that structural changes have also occurred which are taken as indicative of the presence of disordered δ-$MgCl_2$. The essentially complete conversion of α-$MgCl_2$ into the δ-form, which is characterized by disordered chlorine stacking, is easily recognized after 96 h milling in a vibratory mill. Grinding times far in excess have no marked effect because there is no significant difference between the 96 and 200 h grinds. The same effect is more easily obtained by milling $MgCl_2$ in the presence of $TiCl_4$. On the other hand, grinding of α-$MgCl_2$ under milder conditions in an ordinary glass mill does not induce pronounced disorder even after 200 h (Fig. 2, Table II). The maximum degree of disorder reached corresponds to that induced in about 2–3 h in vibratory mill conditions.

As the disorder in the packing of the Cl–Mg–Cl layers increases, the $(1\,0\,\bar{2})$ reflection develops into a halo shifted towards higher 2θ values with the position of its maximum ranging from $30.5° < 2\theta < 31.3°$. Instead, the $(1\,0\,4)$ reflection develops into a halo shifted towards lower 2θ values with a maximum located

TABLE I Effect of milling of magnesium chloride in a vibratory mill

Milling time (h)	Crystallite size (nm)[a]		Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Phase distribution	I(disorder)/I(total)	Mean Stokes' diameter[b] (μm)
	D_{003}	D_{110}					
0.03	(60)	(55.5)	< 1	nil	α	–	25.78
0.08	(32)	43	2.3	0.010	α	0.14	20.20
0.25	37	30	10.9	0.030	α	–	13.30
0.50	23	32.5	12.1	0.043	α	0.28	11.33
1.0	27	30	29.3	0.093	α	0.27	9.62
3.0	16	29	50.1	0.132	$\alpha + \delta$	0.47	8.89
7.0	17	34	51.3	0.151	$\alpha + \delta$	–	9.50
16.0	14	31.5	58.6	0.170	$\alpha + \delta$	0.64	9.65
24.0	14	33	59.0	0.196	$\alpha + \delta$	0.64	11.43
96.0	11	27.5	68.4	0.170	δ	0.83	10.49
200.0	10.5	32.5	64.8	0.170	δ	0.84	10.73
200.0 + 8 h/200 °C[c]	13	37.5	22.9	0.162	δ	0.90	n.d.
200.0 + 8 h/300 °C[c]	17	39	19.1	0.156	$\alpha + \delta$	0.85	n.d.
200.0 + 8 h/350 °C[c]	25	51	7.1	0.060	$\alpha + \delta$	0.75	n.d.
200.0 + 8 h/400 °C[c]	(100)	150	4.0	0.029	$\alpha + \delta$	0.43	n.d.

[a] Values in brackets refer to oriented samples and are approximate only.

[b] Spherical equivalent diameter.

[c] Ground and annealed samples.

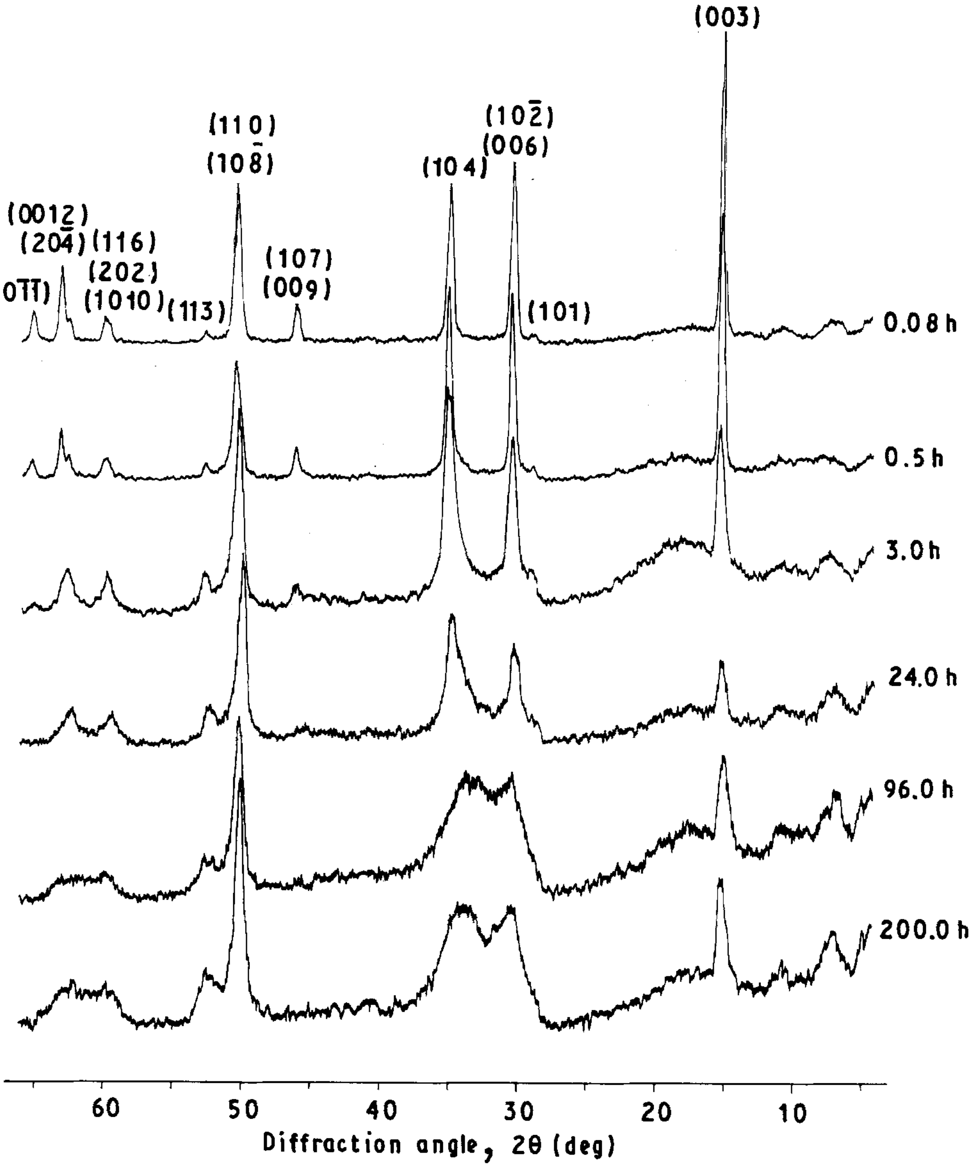

Figure 1 X-ray powder diffractions patterns (CuK_α radiation) of $MgCl_2$ produced by intense grinding of commercial-grade material in a vibratory mill.

between $33.5° < 2\theta < 34.5°$. The disorder affects all $(1\,0\,l)$ reflections and in particular also the $(1\,0\,\bar{8})$ reflection gives rise to a halo at higher angles (Fig. 1). However, we have limited our analysis to the angular range $28° < 2\theta < 40°$, where the effects of disorder are more pronounced.

Fig. 3 shows the resulting deconvolution of the X-ray spectrum of the 3 h milled sample, in which also the weak (1 0 3) reflection (cubic indexing) is present, which derives from fractions of material with hexagonal packing. The positions of the gaussians due to the disordered structure are probably slightly affected by the numerical tolerance of 0.2–0.3° adopted in the deconvolution procedure to allow for instrumental factors. The width and area of the gaussian derived from the (1 0 4) reflection are generally higher than those resulting from the $(1\,0\,\bar{2})$ reflection; this is in agreement with the relative intensities of the corresponding reflections of regular α-$MgCl_2$.

Due to the uncertainties in background removal, it is felt that only qualitative significance can be attributed to the parameter I(disorder)/I(total), which has been taken to express the amount of disordered material (δ-form) with respect to the α-form. Parameter values below 0.40 are considered to be indicative of almost regular α-$MgCl_2$ (cf. Fig. 2 and Table II); on the other hand, as above 0.85 the (1 0 4) reflection has completely disappeared, this value is taken to describe a completely disordered δ-form. As suggested by a weak endothermal effect, extending from 300–450 °C (DTA, $\Delta T = 5$ °C min^{-1}), the δ modification is readily converted into the c c p α-$MgCl_2$ form by annealing. Line broadening of milled powder (200 h in Vibratom) markedly decreases between 200 and 400 °C under isothermal conditions (Fig. 4). The structural changes due to annealing are associated with an increase in the average crystallite size, as measured by X-ray diffraction line broadening. BET specific surfaces of the powders decrease after annealing at 200–400 °C (Table I).

Similarly, a weak endothermal effect between 155 and 255 °C was observed by heating a sample of β-$MgCl_2$ [3] under the same conditions as above. Annealing at 400 °C for 8 h leads to almost complete

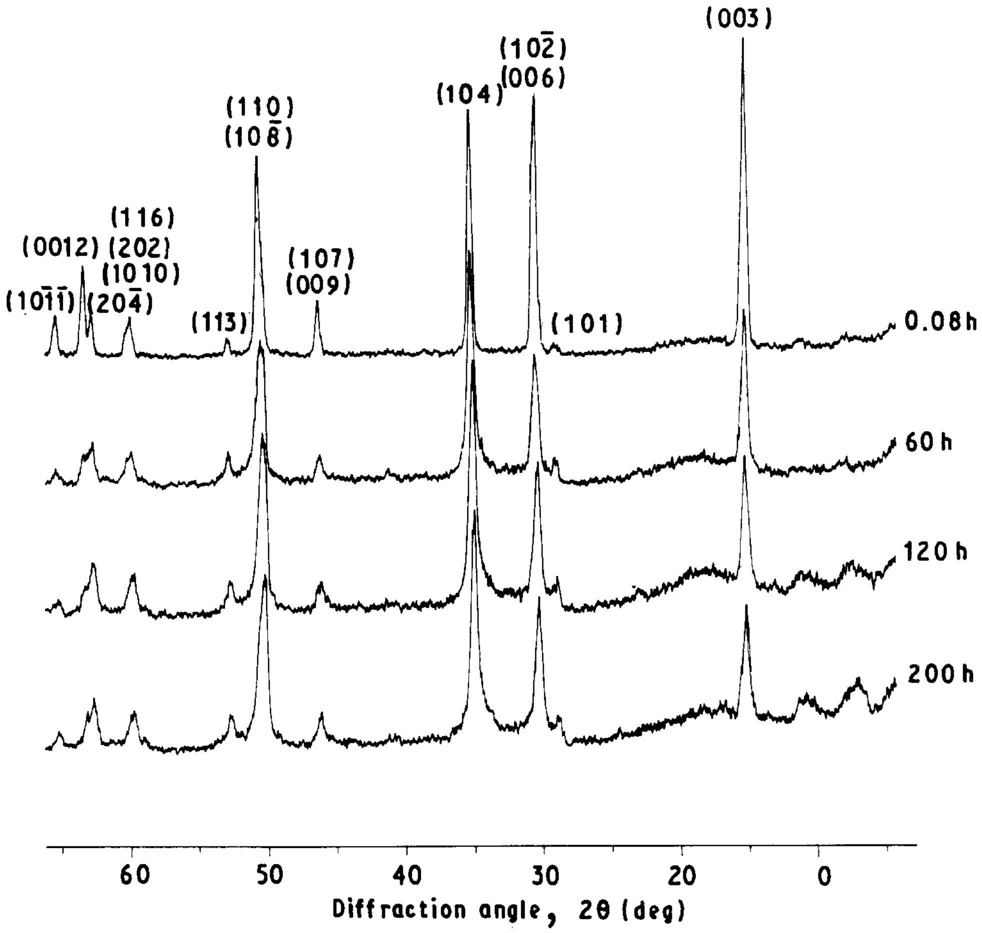

Figure 2 X-ray powder diffraction patterns (CuK_α radiation) of $MgCl_2$ produced by grinding of commercial-grade material in a glass mill.

TABLE II Effect of milling of magnesium chloride in a glass mill

Milling time (h)	Crystallite size (nm)[a]		Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Phase distribution	I(disorder) / I(total)	Mean Stokes' diameter[b] (μm)
	D_{003}	D_{110}					
0.08	(–)	(60)	< 1	nil	α	–	–
60.0	22	28.5	25.2	0.089	α	0.39	10.30
120.0	17.5	30	23.2	0.090	α	0.39	7.80
200.0	20	28.5	25.6	0.107	α	0.42	4.00

[a] Oriented sample.
[b] Area ratio.

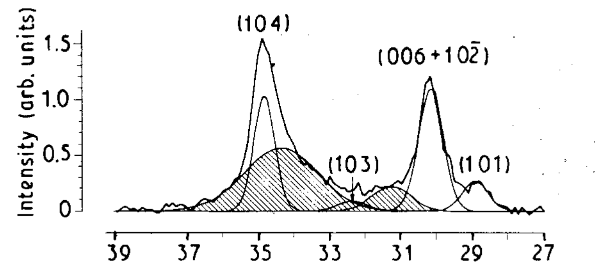

Figure 3 Deconvolution of the X-ray spectrum of a $MgCl_2$ sample obtained after 3 h in a vibratory mill.

conversion to α-$MgCl_2$. Grinding of β-$MgCl_2$ for 24 h in a vibratory mill induces disorder of a type similar to that found for α-$MgCl_2$.

4. Discussion

Dry grinding of the rather coarse original α-$MgCl_2$ leads to a modest particle-size reduction and a porous structure with great internal surface area, indicating aggregation of the crystallites.

As may be seen from Fig. 1, milling not only changes the particle size but also induces structural variations. The degree of distortion increases with higher milling times and can be as high as indicated by the broad, low-intensity patterns as produced by $MgCl_2$ ground for 200 h in a vibratory mill (Fig. 1). Apart from some minor effects, which are evinced by low and small-angle ($2\theta < 10°$) scattering with superlattice reflections at 1.241 and 0.823 nm (and occasionally at 0.977 nm), the nature of the high-angle effects in the X-ray spectra is essentially well understood as being a direct consequence of the layer-lattice structure of the material. It is well known that $MgCl_2$ exists in two polymorphic forms: α-$MgCl_2$ ($R\bar{3}m$, $a = b = 0.3632$ (4), $c = 1.7795$ (16) nm) [2] and β-$MgCl_2$ ($P\bar{3}m1$, $a = b = 0.3641$ (3), $c = 5.927$ (6) nm) [3]. The difference between these forms is confined to the stack-

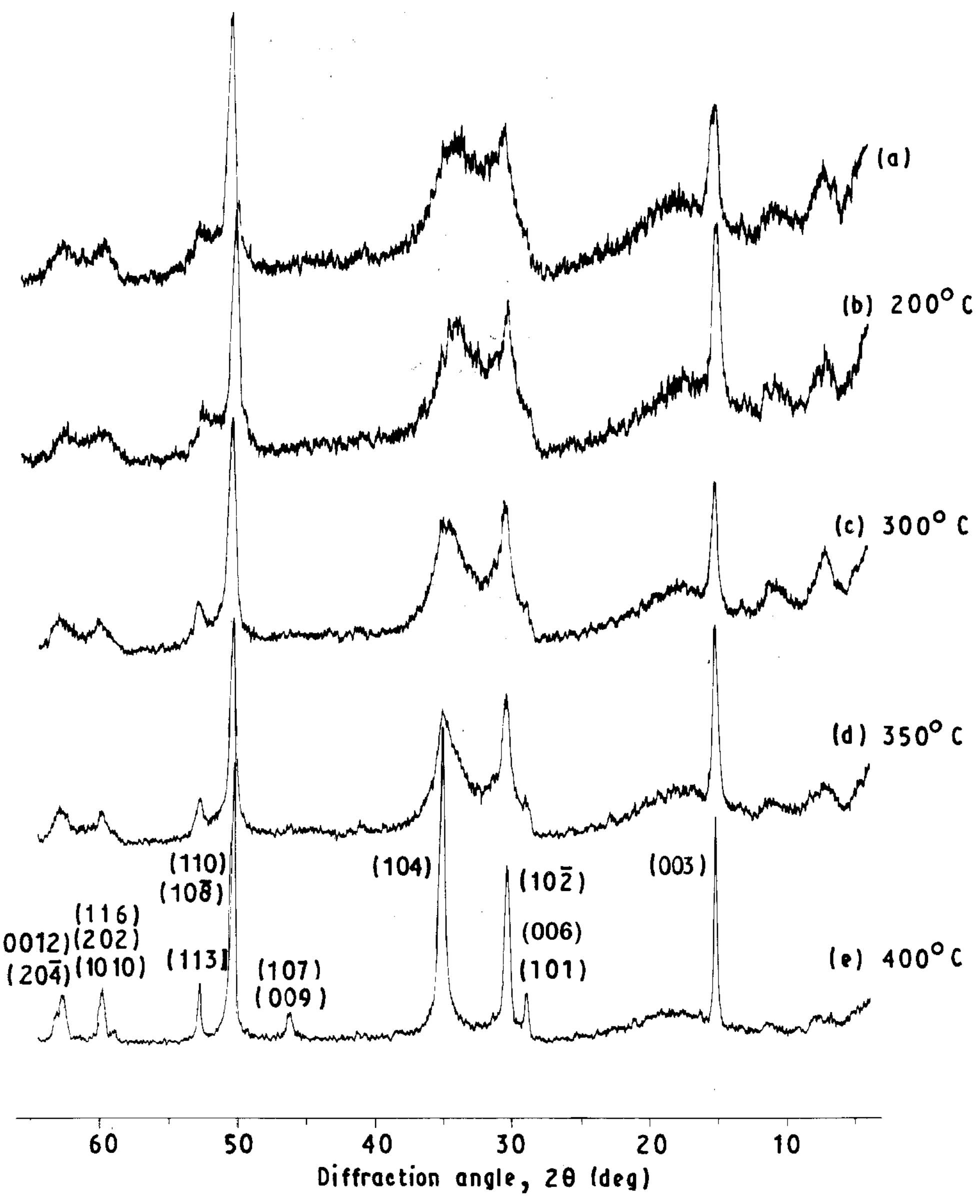

Figure 4 X-ray powder diffraction patterns (CuK_α radiation) of disordered $MgCl_2$ (200 h in vibratory mill) after various post-treatments: (a) 3 h ultrasonic agitation; (b–e) annealing at 200–400 °C for 8 h.

ing of the chlorine atom planes along the c-axis, which is of the cubic close packing (. .ABCABC. .) type in α-$MgCl_2$ as opposed to hexagonal close packing (. .ABAB. .) in β-$MgCl_2$. Under the influence of milling, the strong shear forces easily overcome the weak van der Waals forces between the Cl–Mg–Cl double layers and sliding of the layers of chlorine atoms leads to disorder in the stacking which becomes essentially random after prolonged intense grinding.

The stacking faults affect the diffraction peaks to various extents. The observed intensities of the reflections with $h - k \neq 3n$ of both α- and β-$MgCl_2$ are especially greatly influenced by the disorder in the succession of chlorine atom planes in the c-axis direction. Typically, under mild milling conditions, the strong (1 0 4) reflection is still present though with a line profile asymmetrically enlarged towards low 2θ angles and a half-peak width being larger than that of unmilled $MgCl_2$. The intensities of $h - k = 3n$ reflections are modified to a lesser extent. The relative sharpness of these reflections is due to the conservation of the close-packed structure in the milling process. Amongst the $h - k = 3n$ reflections, (1 1 0) broadens more slowly than (0 0 3). This is understood if we consider that cleavage of the $MgCl_2$ crystallites along the double layers (shear planes) accounts for the broadening of the (0 0 3) peak, whereas the strong bonding within the $MgCl_2$ layers is most difficult to break and explains the slow broadening of the (1 1 0) reflection. In this context it is also to be noticed that due to the close packing of the anions in the hexagonal and cubic arrangements, the lattice spacings of the reflections are very similar [3].

Particularly significant is the formation of broad haloes in the diffraction pattern of extensively milled $MgCl_2$, in correspondence to the disappearance of the reflections with $h - k \neq 3n$. The disorder of the layer stacking is interpreted by a statistical distribution in the sequence of structural layers with cubic or hexagonal packing mode, originating by gliding between the chlorine and magnesium planes. In the angular region of the X-ray spectrum of $MgCl_2$ which we have considered, a statistical model of stacking corresponding to complete translational disorder of the layers (equal probabilities for cubic and hexagonal sequences) gives rise to two broad haloes centred at

$2\theta = 31.3°$ and $33.6°$, in fairly good agreement with the positions of the two gaussians, calculated for the extensively milled samples of $MgCl_2$.

The change in the crystal structure of the aggregates from the α- or β-modifications to the less ordered δ-form is accompanied by crystallite size reduction. As may be seen by the results reported in Table I, the surface area of the material is a crude measure of the intensity of milling. However, it is equally noticed that is is possible to induce various degrees of stacking (dis)order for equal values of the surface area by applying various treatments. The effectiveness of crystallite size reduction by extensive ball milling of $MgCl_2$, far beyond what would normally be expected from a grinding treatment, stands in direct relation to the particular lattice structure which allows layer sliding under the action of sufficiently intense shear. With the slide distance at the interface of two double Cl–Mg–Cl layers being only a small fraction of the layer size, the resulting thin protruding sections of the worked crystal may easily be broken off. Formation of "activated" $MgCl_2$ by low-temperature chemical synthesis routes probably takes advantage of non-equilibrium conditions leading to disordered structures with small crystallite size, as opposed to well-crystallized ordered (α-$MgCl_2$) material with low surface area resulting from high-temperature synthesis. Hence, so-called "activated" $MgCl_2$ invariably exhibits the X-ray diffraction pattern of the δ-form.

Distortion of $MgCl_2$ can be relieved by annealing. This process is rapid at 350 and 400 °C (Fig. 4). In isothermal conditions the practical limit below which the relieving process takes place at a very slow rate is probably about 250 °C. It is then not surprising that α- rather than δ-$MgCl_2$ is obtained by high temperature ($T > 400$ °C) decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ with HCl [4]. The fact that disorder in $MgCl_2$ can be removed by annealing lends further support to the idea that the observed properties are due to shear in the layer structure of $MgCl_2$. The crystallite-size data and trend in the I(disorder)/I(total) ratio indicate that although the degree of crystallinity of untreated $MgCl_2$ powder is initially higher than that of the milled ones, annealing out of crystal defects at high temperatures transforms the previously milled powder into a more perfect (highly crystalline, non-oriented) material than the original one. A similar fact has been noticed by grinding of nickel powder [11].

The few experiments performed on β-$MgCl_2$ show that grinding leads to disorder similar to that induced in α-$MgCl_2$. As annealing leads to an almost complete conversion to α-$MgCl_2$, this form is thermodynamically more stable than the β-form.

Other lattice-type structures (e.g. graphite) exhibit similar effects as observed in the case of $MgCl_2$. Apart from the stable hexagonal graphite modification ($D^4_{6h} - C\,6/m\,m\,c$) a second form exists with a rhombohedral structure ($D^5_{3d} - R\,\bar{3}m$) [12]. In this case the hexagonal form may be transformed into the rhombohedral one by mild mechanical treatment involving shear (grinding) [13, 14]. Also the change in phase relation between zinc blende and würtzite caused by preliminary grinding has been reported [15].

Appendix

For the sample of the shortly milled α-$MgCl_2$ (2 min in vibratory mill) we have performed an X-ray diffraction spectrum (CuK_α radiation) at high angular resolution

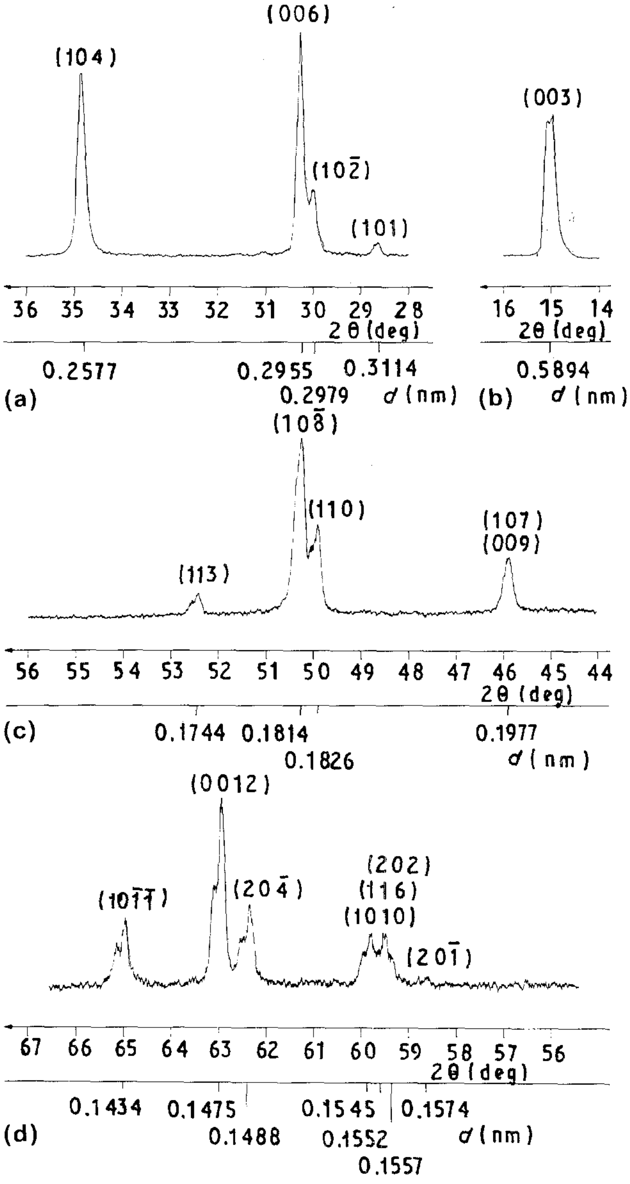

Figure 5 X-ray diffraction spectrum of a 2 min milled $MgCl_2$ sample. (a) × 1, (b) × 4, (c) × 10, (d) × 20.

TABLE III

$h\,k\,l$	d_{obs} (nm)	d_{calc} (nm)	$I\,(h\,k\,l)$
0 0 3	0.5894	0.5904	> 100
1 0 1	0.3114	0.3113	7
1 0 $\bar{2}$	0.2979	0.2978	31
0 0 6	0.2955	0.2952	100
1 0 4	0.2577	0.2574	91
1 0 7 0 0 9	0.1977	0.1976 0.1968	13
1 1 0	0.1826	0.1825	19
1 0 $\bar{8}$	0.1814	0.1814	49
1 1 3	0.1744	0.1744	4
2 0 $\bar{1}$	0.1574	0.1575	3
2 0 2	0.1557	0.1557	1
1 1 6	0.1552	0.1553	7
1 0 10	0.1545	0.1546	7
2 0 $\bar{4}$	0.1488	0.1489	9
0 0 12	0.1475	0.1476	21
1 0 $\bar{1}\bar{1}$	0.1434	0.1435	8

(Fig. 5). From this (oriented) spectrum we have obtained the following refined values of the unit-cell parameters of α-$MgCl_2$: $a = b = 0.3653(1)$ nm, $c = 1.771(1)$ nm, which differ significantly from previously determined values [2, 16]. A comparison between the calculated and observed values of the interplanar spacings are reported in Table III; for the evaluation of $I\ (h\,k\,l)$ it should be considered that the sample was oriented in spite of the application of a rotating sample holder.

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