SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL STABILITY OF $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$

Lauro Pavanello[1], Antonio Marigo[1], Silvano Bresadola[1*] and Giovanni Valle[2]

[1] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università, via Marzolo 1, I-35131 Padova (Italy) and Centro di Studio del C.N.R. sulla Stabilità e Reattività dei Composti di Coordinazione, Università di Padova, Italy

[2] Centro di Studio del C.N.R. sui Biopolimeri, Università di Padova, Italy

Abstract

The reaction of α-$MgCl_2$ with dimethylformamide affords the $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ adduct which was obtained as crystals suitable for X-ray analysis. M_r = 423.62, triclinic, space group $P\bar{1}$, with a = 8.171(2) Å, b = 8.946(2) Å, c = 8.170(2) Å, α = 91.7(2)°, β = 111.7(2)°, γ = 91.4(2)°, V = 554.2(8) Å^3, D_x = 1.27 g cm^{-3}, λ(Mo Kα) = 0.71069 Å, observed reflections 1407, R = 0.104, R_w = 0.094. Such adduct shows a polymeric structure formed through hydrogen bonds between the coordinated H_2O molecules and the chloride ions. Each magnesium atom appears to be octahedrally coordinated by four dimethylformamide molecules through the carbonyl oxygen atom and by two water molecules through the oxygen atom. The thermal stability of this adduct has been investigated by thermogravimetric analysis and the obtained TG curve shows that the thermal elimination of the coordinated molecules is the result of more than one step.

Introduction

The interaction between anhydrous α-$MgCl_2$ and electron-donor compounds is of current

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*To whom correspondence should be addressed

interest, especially in order to prepare activated δ-$MgCl_2$ useful as support for Ziegler-Natta type catalysts of the high yield α-olefin polymerization processes.

The treatment of α-$MgCl_2$ with Lewis bases yields well defined adducts. The successive thermal elimination of the coordinated bases carried out under controlled conditions produces a $MgCl_2$ form having a disordered structure, which appears to behave like a very active supporting material. The preparation of such $MgCl_2$ supports, especially by treatment of α-$MgCl_2$ with aromatic esters [1] or ethanol [2], is claimed in several patents. On considering that the performance of the supported Ziegler-Natta catalysts can be related to both structural and chemical features of the supporting materials we have investigated the role of the Lewis base used for the α-$MgCl_2$ activation. We have recently reported the synthesis and characterization of some $MgCl_2$-Lewis base adducts, such as $MgCl_2$-ethyl formate [3], $MgCl_2$-benzyl alcohol [4], $MgCl_2$-ethyl acetate [5], $MgCl_2$-ethyl alcohol [6], $MgCl_2$-formamide [7] $MgCl_2$-dimethylacetamide [8] together with a study of the thermal elimination of the coordinated base from these adducts [9]. We now report here the preparation and the single crystal structure determination of the $MgCl_2[HCON(CH_3)_2]_4(H_20)_2$ adduct, as well as the results of an investigation of the coordinated base elimination carried out by means of thermogravimetric measurements .

Materials and Methods

Reagent grade α-$MgCl_2$ (content of water *ca.* 0.4 % w/w) was supplied by Himont Italia S.p.A.; dimethylformamide (DMF), Aldrich A.C.S. reagent, was purified appropriately by standard method prior to use.

X-ray diffraction data on a single crystal were collected at room temperature using a Philips PW 1100 four circle automatic diffractometer with graphite-monochromated MoKα radiation (λ = 0.71069 Å), and a θ-2θ scan mode up to 2θ = 56°.

The powder X ray diffraction patterns were scanned in the transmission technique using a GD-2000 diffractometer (Ital Structures, Riva del Garda, Italy) operating in the Seemann-Bohlin geometry and equipped with a quartz-curved crystal monochromator of the Johansson type aligned on the primary beam. The Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å) was employed, and an instrumental 2θ step of 0.1° every 10 s was selected.

The thermogravimetric analysis was carried out with a Perkin-Elmer TGS-2 thermobalance and the TG data were collected and processed by a Perkin-Elmer 3700 Data Station, under a nitrogen flow of 60 ml min^{-1}, with a heating rate of 20 °C min^{-1} in the temperature range between 30 and 600 °C.

α-$MgCl_2$ and the obtained adduct were weighed and manipulated inside a recycle Braun MB-150 I/II dry box under strictly controlled inert atmosphere (oxygen = 1 ppm, water = 0.2 ppm).

Table 1 Crystal data and measuring conditions

Empirical formula	$C_{12}H_{32}N_4O_6Mg_1Cl_2$
Crystal system	Triclinic (monoclinic "C" was excluded)
Space group	P^{-},1
Z	1
Unit cell dimension	a = 8.171(2) Å; α = 91.7(2)°
(T=294 K)	b = 8.946(2) Å; β=111.7(2)°
	c = 8.170(2) Å; γ= 91.4(2)°
Volume	554.2(8) $Å^3$
μ	3.49 cm^{-1}
Formula Weight	423.62
Density (calc)	1.269 g/cm^3
Absorption Coefficient	3.15 cm^{-1}
F(000)	226
Diffractometer Used	Philips PW 1100
Radiation	MoKα (λ=0.71069 Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ Range; Scan Type	4.6° to 56.0°; θ-2θ
Standard reflections	2 measured every 200 reflections
Index Ranges	-10<h<10; -11<k<11; 0<l<10
Independent reflections	2692
Observed reflections	1407 [F≥ 3.0 σ(F)]
Number of refined parameters	179
Data to parameter ratio	7.9 :1

Results

Dimethylformamide (20 ml) was added drop by drop at 0 °C under a nitrogen atmosphere to α-$MgCl_2$ (1.2 g) contained in a 50 ml flask equipped with a reflux condenser. The

slurry so formed was heated to 60° C under stirring for 12 h. After cooling to room temperature the mixture was filtered under inert atmosphere and then in the course of three months thin strip-like crystals of $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ were formed.

Table 2. Fractional coordinates with equivalent isotropic thermal parameters $(Å^2)^{ab}$. U_{eq} is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U_{eq}
Mg	1.000000	0.000000	1.000000	0.0323(8)
Cl(1)	1.3974(2)	-0.1846(2)	0.7658(2)	0.0567(6)
O(3)W	1.2427(5)	0.0392(5)	0.9732(5)	0.046(1)
O(1)	0.9177(5)	-0.1019(4)	0.7575(5)	0.044(1)
N(1)	0.7584(6)	-0.1854(5)	0.4800(5)	0.043(2)
C(1)	0.7747(7)	-0.1244(6)	0.6346(7)	0.042(2)
C(2)	0.5853(9)	-0.217(1)	0.3410(9)	0.069(3)
C(3)	0.911(1)	-0.231(1)	0.443(1)	0.074(3)
O(2)	1.0898(5)	-0.2042(4)	1.1124(5)	0.044(1)
N(2)	1.2142(6)	-0.4272(5)	1.1174(7)	0.048(2)
C(4)	1.1583(6)	-0.2988(6)	1.0472(7)	0.041(2)
C(5)	1.204(1)	-0.4651(9)	1.284(1)	0.073(3)
C(6)	1.2836(9)	-0.5355(7)	1.027(1)	0.069(3)

[a] In this and following tables standard deviations in the least significant digit(s) are given in parentheses.

b The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(1/3)S_iS_jU_{ij}a_i^*a_j^*a_ia_j$.

The obtained crystals are less stable than those of the $MgCl_2$ adducts with formamide or dimethylacetamide isolated as described previously [7,8] and attempts to transfer them from the mother solution into a Lindemann quartz capillary filled with vaseline petrolatum failed. However, we have found that silicon oil is more suitable than the

vaseline petrolatum as protective medium in the case of this $MgCl_2$-DMF adduct. Therefore, a diffraction-quality crystal with dimension 0.4x0.4x0.4 mm was inserted directly into a quartz capillary previously filled with dry and oxygen free silicon oil. The crystal data and X-ray intensity measurements are summarized in Table 1.

The data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct method using SHELX86 [10] programs and refined by full-matrix least-squares procedure employing anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located from a different map and isotropically refined. The atomic scattering factors for Mg atom were taken from the International Tables for X-ray Crystallography [11], while the other factors together with all the computations were performed using the SHELX76 [12] program. The full-matrix least-squares refinement, based on F using weights $w=[\sigma^2(F_o)+gF_o^2]^{-1}$, where $g=4.64x10^{-4}$, gave final values R=0.104 and Rw=0.094, S= 0.605 for 179 variables and 1407 observed reflections having $F_o>7\sigma(F_o)$; $(\Delta/\sigma)_{max}=0.577$. The high values found of both R and 7σ may be due to the presence of the silicon oil used as stabilizating agent of the crystal and with the need to carry out the data collection with an adequate high speed owing the crystal instability. The final maximum residual electron density is $\Delta\rho=0.78$ $eÅ^{-3}$.

Discussion

Table 2 gives the fractional atomic coordinates with the equivalent isotropic thermal parameters. Selected bond distance, hydrogen-bonds geometry and selected bond angles are listed in Tables 3, 4 and 5, respectively. The crystal analysis of $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ shows an ionic structure in which the magnesium ion, that lies on a cristallographic centre of inversion, is octahedrally coordinated by four dimethylformamide moieties through the oxygen atoms of the carbonyl groups and by two water molecules, as shown in Fig. 1. Bond lengths and angles of this compound resemble those shown by the adducts $[MgCl_2(C_7H_7OH)_6]$ and $[MgCl_2(C_2H_5OH)_6]$ [4, 6]. In particular the average values of the Mg-O and O-C distances fall in the expected ranges. Furthermore, the crystallographic data (see Tables 5 and Figures 1 and 2) are in agreement with a structure in which hydrogen bonds between the chloride ions and the coordinated water molecules gives rise to a linear polymeric structure in the solid state.

Fig. 3. shows the thermogram recorded in the temperature range 30-600 °C. The overall weight loss below 340 °C is equal to 76 %, corresponding practically to the elimination of

all the six coordinated molecules from the $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ adduct (the theoretical value is 77.5 %). The elimination of the coordinated Lewis bases appears to be the result of three consecutive steps. This behaviour is due to both steric and electronic factors. The elimination of the donor molecules occurs at temperatures progressively higher as the elimination goes on. In fact, the decrease of the number of the coordinated donors increases the electrophilicity of the metal center and then also the activation energy of the elimination reaction increases [8]. At temperature around 400 °C it is observed evolution of HCl due to the reaction of $MgCl_2$ with residual coordinated water. Compared with the adducts with ethanol, ethyl acetate or benzoate [13] the $MgCl_2$ adduct with dimethylformamide appears more thermally stable. In fact, a thermal treatment at 220 °C and 10^{-2} mmHg for 160 h leaves a $MgCl_2$ residue containing again 0.74 % w/w of dimethylformamide.

Table 3. Selected bond distances (Å)

Mg-O(3)W	2.096(4)	Mg-O(1)	2.021(5)
Mg-O(2)	2.094(5)	O(1)-C(1)	1.235(6)
N(1)-C(1)	1.320(8)	N(1)-C(2)	1.464(8)
N(1)-C(3)	1.45(1)	O(2)-C(4)	1.237(8)
N(2)-C(4)	1.314(7)	N(2)-C(5)	1.45(1)
N(2)-C(6)	1.45(1)		

Table 4. Hydrogen-bonds geometry.

O(3)W-H(2)W (Å)	O(3) ··· Cl(1) (Å)	H(2)W(3)···Cl(1) (Å)	O(3)W-H(2)W(3)··· Cl(1) (degree)
0.883	3.160	2.742	110.39

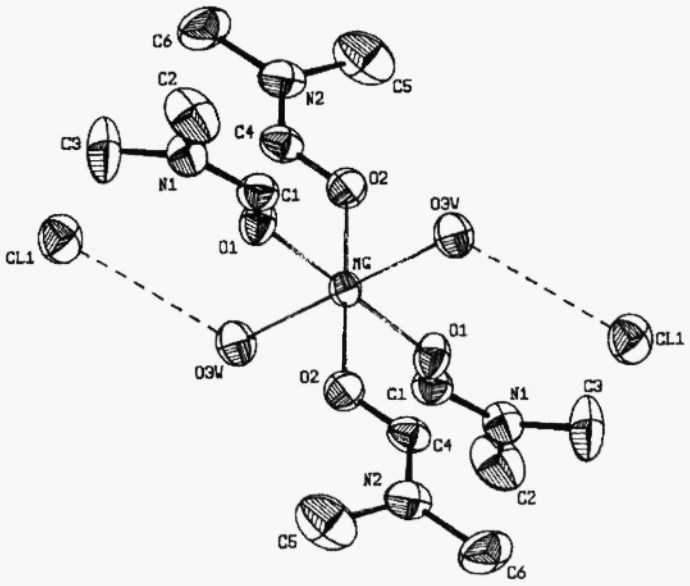

Figure 1. A perspective view showing the coordination around the magnesium atom and the hydrogen bonds between water molecules and chloride ions, with the atomic numbering scheme.

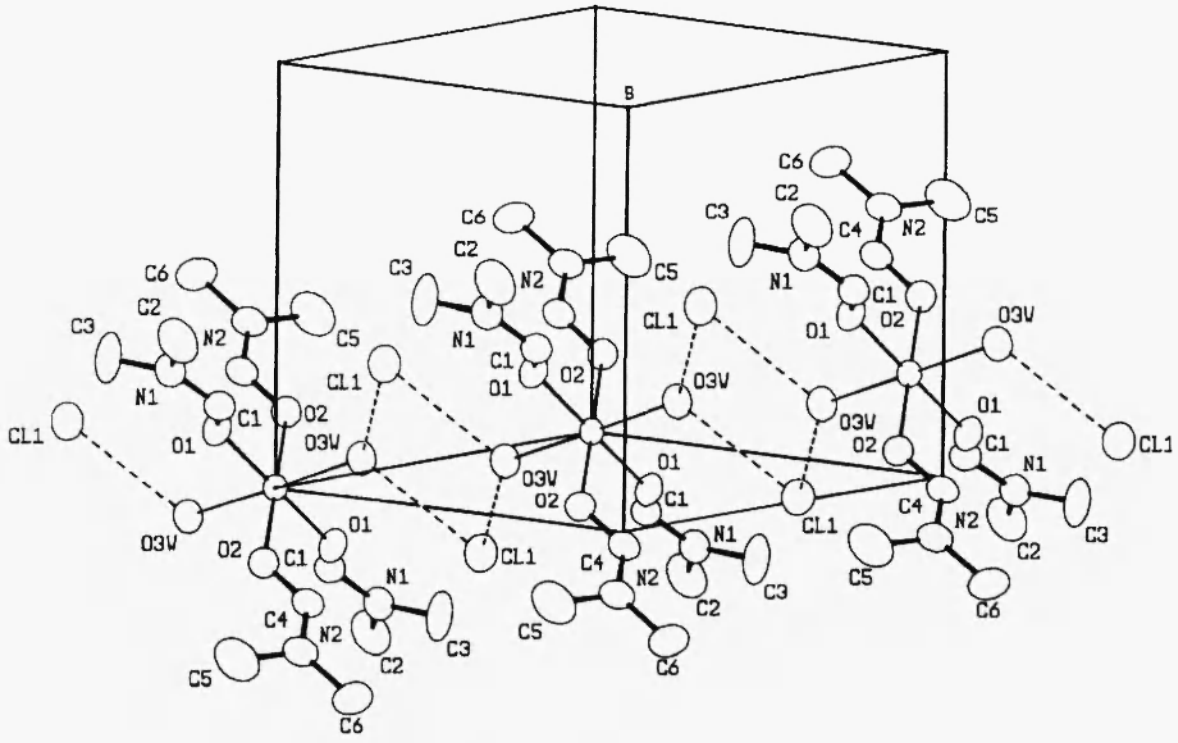

Figure 2. Unit cell projection

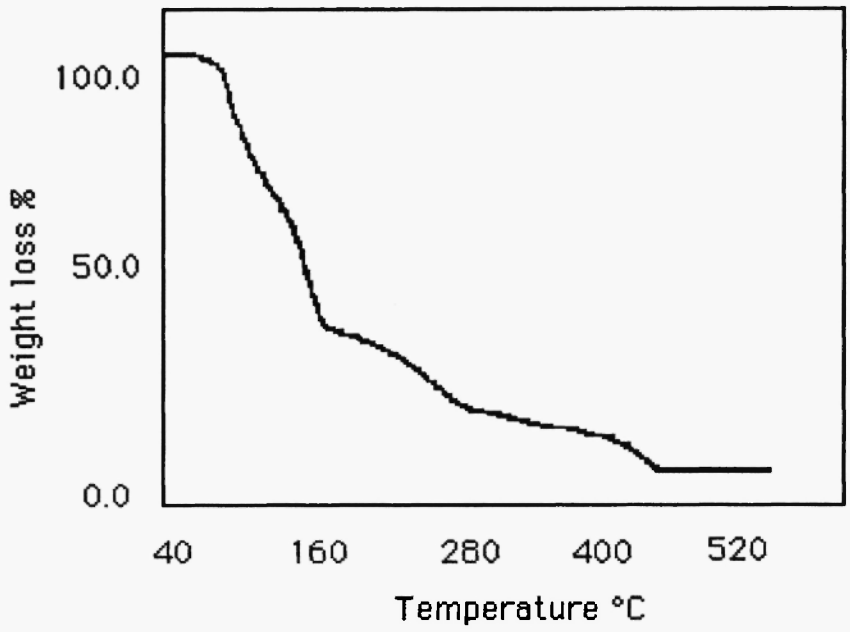

Figure 3. Thermogram of the elimination reaction from $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ (heating rate 20 °C min^{-1}).

Table 5. Selected bond angles (degree).

O(1)-Mg-O(2)	89.7(4)	O(3)W-MG-O(2)	89.2(5)
O(3)W-Mg-O(1)	86.7(4)	Mg-O(1)-C(1)	135.6(8)
C(2)-N(1)-C(3)	116.8(7)	C(1)-N(1)-C(3)	121.6(7)
C(1)-N(1)-C(2)	121.5(9)	O(1)-C(1)-N(1)	123(1)
Mg-O(2)-C(4)	124.2(5)	C(5)-N(2)-C(6)	118.6(8)
C(4)-N(2)-C(6)	120.6(7)	C(4)-N(2)-C(5)	120.8(9)
O(2)-C(4)-N(2)	124.3(7)		

Furthermore, as shown by the XRD analysis of this residue, it is not possible to obtain a fully disordered $MgCl_2$ species by treatment of $MgCl_2$ with dimethylformamide followed

by thermal elimination of the coordinated base. Figures 4a and 4b exhibit the XRD spectra of the $MgCl_2$ adduct and the product of the thermal decomposition, respectively. Figure 5 shows the XRD spectrum of α-$MgCl_2$. The XRD spectrum of the product formed by thermal decomposition of the adduct shows a large band that partially overlaps on the peaks

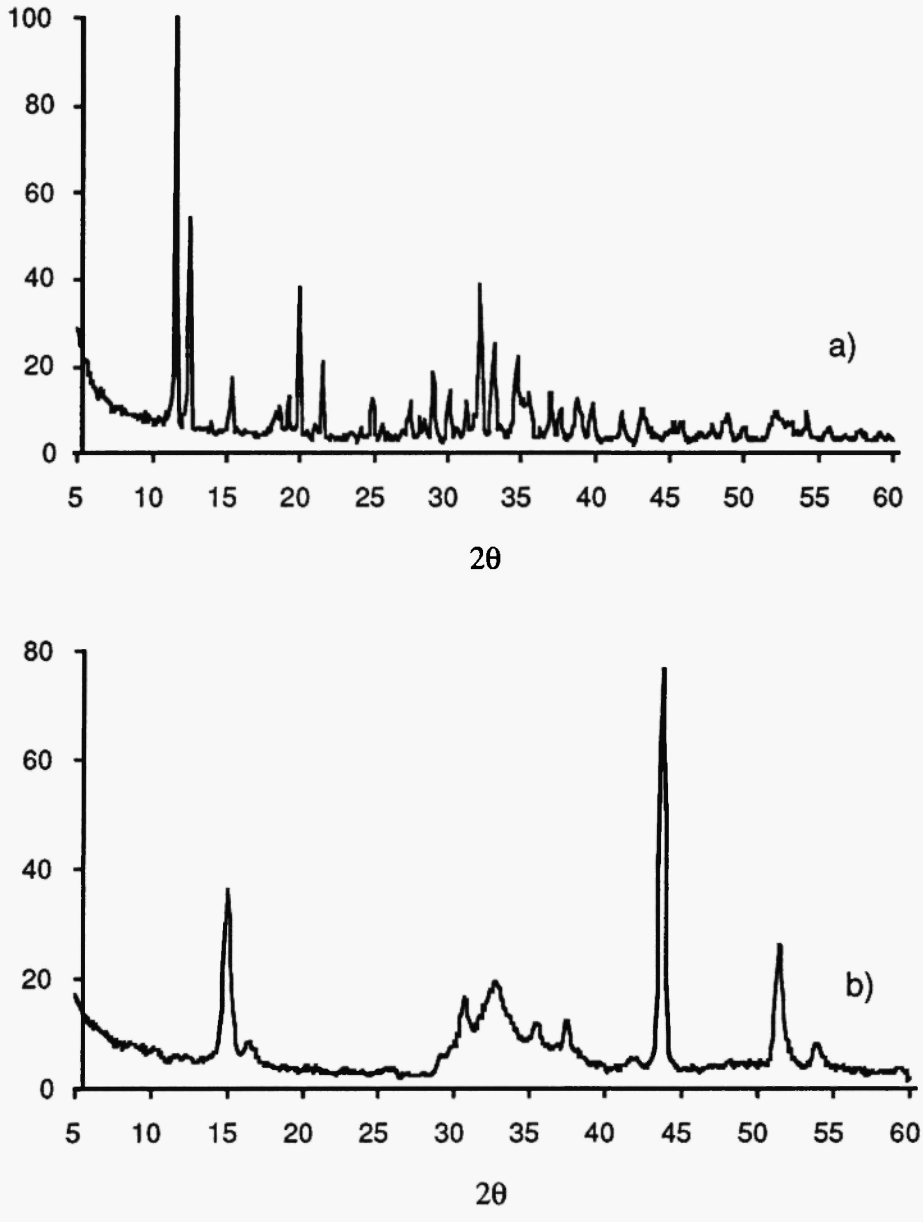

Fig. 4. Powder XRD patterns of: a) $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$; b) $MgCl_2[HCON(CH_3)_2]_4(H_2O)_2$ after thermal treatment at 220 °C under vacuum (10^{-2} mmHg) for 160 h (intensities in arbitrary unit).

centered at 2θ=31° and 2θ=36° which are characteristic of the α-$MgCl_2$ species. On the other hand, this XRD spectrum shows new peaks centered at 2θ=38° and 2θ=44° which are probably due to a discrete compound rather than to the disordered species. Finally, the observed peak at 2θ = 15° is currently

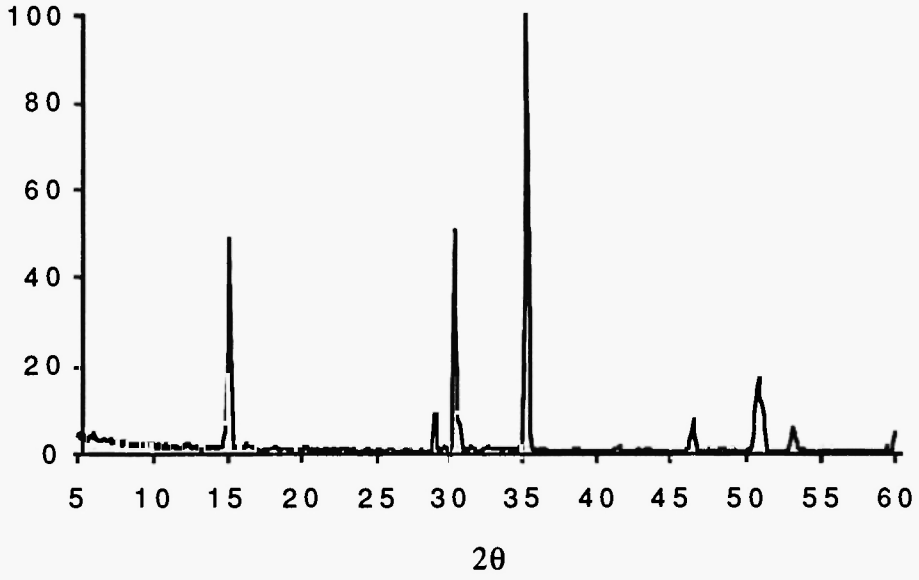

Fig. 5. Powder XRD patterns of α-$MgCl_2$.

associated with the stacking of the Cl-Mg-Cl layers along the c crystallographic direction of α-$MgCl_2$ [2]

Experiments are now in progress in order to evaluate the effectiveness of this material to act as catalyst support in the propene polymerization.

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