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Alkoxymagnesium Halide Supports for Heterogeneous Ziegler–Natta Polymerization Catalysts

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Solid ClMg(OEt) (**1**) has been prepared and characterized for the first time as a pure, spectroscopically homogeneous material. The novel material, Cl_3Mg_2OEt (**2**), has also been prepared and characterized as a pure, spectroscopically homogeneous solid. These materials are made by stepwise alcoholysis and chlorination of butylethylmagnesium. CP/MAS ^{13}C NMR (cross-polarization/magic angle spinning carbon-13 nuclear magnetic resonance) spectra of **1** and **2** show well-defined ethyl group environments in each material: **1** (δ, ppm), 59.3 (OCH_2CH_3), 19.7 (OCH_2CH_3); **2**, (δ, ppm), 63.4 (OCH_2CH_3), 19.1 ppm (OCH_2CH_3). X-ray powder diffraction pattern measurements show that **1** (d_{max} = 9.30 Å) and **2** (d_{max} = 9.93 Å) are different from each other from $MgCl_2$ (d_{max} = 8.26 Å) and $Mg(OEt)_2$ (d_{max} = 9.82 Å). These compounds are high surface area, microporous materials (**1**, 233 m^2/g by BET (Brunauer–Emmett–Teller adsorption isotherm) and pore volume 0.33 cm^3/g at P/P_0 = 0.98; **2**, 299 m^2/g by BET and pore volume 0.42 cm^3/g at P/P_0 = 0.98). After reaction with $TiCl_4$ and activation with $Al(i\text{-}Bu)_3$, these materials are active Ziegler–Natta polymerization catalysts (30 psig H_2, 100 psig total C_2H_4 pressure, 85 °C: **1** yields 30.4 kg of PE/(g of Ti h) (kg of polyethylene/(g of titanium hour)), M_w = 144 000, M_n = 9020; **2** yields 56.9 kg of PE/(g of Ti h), M_w = 110 000, M_n = 13 800).

Introduction

Solid materials composed of chlorine, magnesium and alkoxide (e.g. ClMgOEt) are being employed with increasing frequency as precursors for, or components in, Ziegler-Natta catalysts.[1–4] Most often, these materials are converted to high surface area magnesium chloride and, sometimes in the same step, impregnated with titanium salts. The resulting catalysts show high activities for α-olefin polymerization, and can be made stereospecific for propylene polymerizations.

Most of the work on alkoxymagnesium halides is built upon the suggestions of Turova and Turevskaya,[5] who made a systematic study of alkoxymagnesium halides. Work in this area since then has simply refined the basic approaches they outlined: Combinations or reactions involving one or more of magnesium metal, halogens, hydrogen halides, metal halides, alcohols, magnesium alkoxides, and magnesium halides (e.g. eqs 1 and 2);[3] or reactions of Grignard reagents with oxygen, or oxygen containing organics

$$Mg(OR)_2 + (1/n)ZX_n \rightarrow 1/n\,(RO)_nZ + ROMgX \quad (1)$$

$$ZX_n = \text{e.g. } MgX_2, SiX_4, TiX_4, HX, \text{etc.}$$

$$X = \text{halogen}$$

$(MgOR)_2$ either preformed or made in situ
from, e.g., Mg + excess xs ROH

$$MgX_2 + 2ROH + Mg \rightarrow H_2 + 2ROMgX \quad (2)$$

$$RMgX + (1/n)Z(OR)_n \rightarrow ROMgX + (1/n)R_nZ \quad (3)$$

$$Z(OR)_n = \text{e.g. } HOR, C(OR)_4, Si(OR)_4, Ti(OR)_4, \text{etc.}$$

RMgX either preformed or made in situ
from, e.g., Mg + RX

$$RMgX + Z(C{=}O)Z' \rightarrow RZZ'COMgX \quad (4)$$

$$Z(C{=}O)Z' = \text{e.g. aldehydes, ketones, esters, etc.}$$

$$RMgX + {}^1/_2O_2 \rightarrow ROMgX \quad (5)$$

other oxygen donors, besides molecular
oxygen, could be used

(e.g. eqs 3–5).[4] Relatively little work, outside of Ziegler–Natta applications, on alkoxymagnesium halides has been done.[6]

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Table I. Summary of Reaction Conditions

	alcoholysis step			halogenation step					
run	mol of BEM[a]	mol of EtOH	reflux duration, h	g of C_7H_{16}	mol of $SiCl_4$	heating duration, h	washes,[b] mL	yield, g	yield,[c] %
A	0.28	0.16	2	120	0.22	17	4 × 150	24.8	79.1
B	0.29	0.18	2	127	0.23	12	5 × 200	25.3	80.1
C	0.27[d]	0.17	2		0.22	16	4 × 300	21.5	70.3
D	0.38	0.27	2	192	0.27	12	3 × 250		
E	0.30	0.23	3	200	0.22	18	3 × 200	24.4	76.4
F	0.39	0.31	1.5	160	0.48	18	4 × 200	34.2	73.3
G	0.30	0.31	2	198	0.15	2	2 × 300	26.4	81.2
H	0.31[d]	0.35	3		0.15	14	3 × 150	32.1	84.2
I	0.25	0.29	3	149	0.13	15	3 × 200		
J	0.38	0.50	2	132	0.19	16	2 × 300	39.3	82.0
K	0.21	0.28	2.5	241	0.10	2			

[a] Butylethylmagnesium. [b] Washes used heptane or hexane. [c] Based on recovery of magnesium, using magnesium analyses reported in Table II. [d] 10.5% BEM in heptane, no further heptane added.

None of this previous work has treated the problem of preparing solid alkoxymagnesium halides in terms of solid state chemistry. While solids with a composition such as $Cl_{1.0}Mg_{1.0}(OEt)_{1.0}$ have been prepared, the chemical uniformity of such samples has not been demonstrated spectroscopically. In the majority of cases, solid compounds are never isolated or characterized before subsequent reactions are conducted. In other cases, the alkoxymagnesium halide is present in solutions, where it may be coordinated, or subject to equilibria analogous to the Schlenk equilibrium for Grignard reagents. In fact, in those cases where solids are isolated and characterized with techniques that would differentiate between mixtures and substantially pure, uniform substances, mixtures are found. These mixtures only had average compositions that approached $Cl_{1.0}Mg_{1.0}(OEt)_{1.0}$.[2b,3f]

In our laboratories, we have made a systematic study of alkoxymagnesium halide supported Ziegler–Natta catalysts. The first step in this study was preparation of well-defined, homogenous alkoxymagnesium halide starting materials. Ethoxymagnesium chloride is a simple and representative alkoxymagnesium halide and was chosen as the initial synthetic target.

The synthetic strategy to prepare ClMgOEt as a solid with uniform composition and purity needed to have several characteristics. So that contamination by binary compounds did not occur, this strategy had to insure that $Mg(OEt)_2$ or $MgCl_2$ were never formed. It was also necessary for the product to be deposited from a homogenous reaction mixture so that the solid composition did not change as the reaction proceeded. We chose selective alcoholysis of dialkylmagnesium compounds in hydrocarbons to form soluble alkylmagnesium alkoxides, followed by selective chlorination with $SiCl_4$, as the synthetic strategy.

$$\text{BuMgEt} + \text{EtOH} \rightarrow \text{RMgOEt} + \text{RH} \qquad (6)$$

$$\text{R} = \text{ethyl and/or butyl}$$

$$\text{RMgOEt} + \text{SiCl}_4 \rightarrow \text{ClMgOEt} + \text{RSiCl}_3 \qquad (7)$$

This strategy meets the above requirements, and has several other advantages. Reaction between butylethylmagnesium (BEM) and ethanol would be rapid and quantitative, allowing precise control of the alkoxymagnesium alkyl stoichiometry. Because alkylmagnesium alkoxides are known not to undergo Schlenk type equilibria[7] and are soluble in hydrocarbons, the alkylmagnesium alkoxide would be a well-defined, stable, homogeneous solute in hydrocarbons. $Mg(OEt)_2$ would not be present. There would be a sufficient difference in reactivity between alkyl and alkoxy group to allow a selective reaction with halogenating agents such as $SiCl_4$. As alkyl groups were halogenated, the insoluble ClMgOEt product would deposit, leaving the reaction mixture more dilute, but otherwise unchanged in composition.

This strategy was successful, given sufficient care in choosing reaction conditions and stoichiometry. We report here the preparation and characterization of homogenous, well-defined solid ClMgOEt and Cl_3Mg_2OEt; materials with high surface areas and clean, characteristic, CP/MAS NMR spectra, which can be converted to active Ziegler–Natta catalysts.

Experimental Section

General Methods. All manipulations were carried out using standard air-free methodology in a nitrogen-filled Vacuum Atmospheres Model HE-43-2 Dri-Lab, on a Schlenk Line, or in Schlenk type apparatus interfaced to a high vacuum line ($<10^{-5}$ Torr). Unless otherwise noted, all solvents and reagents were thoroughly dried and deaerated by conventional techniques,[8] and all reagents were obtained from commercial suppliers. If necessary, reagents and solvents were purified by conventional techniques. Butylethylmagnesium (BEM) was obtained from Akzo Chemicals Inc. as a 20.2 wt % solution in heptane and contained less than 0.5% aluminum compounds as stabilizers/viscosity modifiers. Carbon and hydrogen combustion analyses, and Si analyses, were performed by Galbraith Laboratories. Magnesium,[9] chlorine[10] and titanium[11] determinations were carried out in house, using wet chemical methods. SEM analyses were performed on an Amray 1830T instrument, using a lanthanum hexaboride source and an accelerating voltage of 20 kV. All samples were coated with approximately 150 Å of gold prior to examination.

Surface area analyses were carried out on a Micromeritics 2400 ASAP instrument. Samples were degassed at ambient temperature until outgassing was no longer observed (typically, overnight). A 55 point BJH adsorption/desorption isotherm was collected and plotted. Four to five points in the partial pressure region 0.05–0.20 were used for BET surface area calculations.[12]

Solid-state ^{13}C NMR spectra were recorded on a Bruker MSL-200 spectrometer operating at the ^{13}C resonance frequency of 50.3 MHz. A Doty broadband high speed magic angle spinning probe was used for all experiments. Transients were accumulated using both single pulse and cross polarization magic angle spinning techniques. All NMR experiments employed a proton decoupling field of sufficient magnitude to ensure full decoupling over the entire spectral width. ^{13}C spectra were externally referenced to the methyl signal in hexamethylbenzene.

General Method for Preparation of Ethoxymagnesium Chlorides. Specific amounts and other conditions can be found in Table I. Specific results are summarized in Tables II and III. A 1 L three-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet/outlet port, was charged with butylethylmagnesium in heptane solution and enough additional heptane to bring the butylethylmagnesium

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Table II. Summary of Product Properties[a]

run	ROH:Mg[b]	SiCl$_4$:Mg[c]	anal., wt % C	H	Cl	Mg	Si	[OEt],[d] mmol/g	Cl:Mg[e]	[OEt]:Mg[f]	BET, m^2/g	pores, cm^3/g	wt % C$_7$H$_{16}$	sum,[g] %
A	0.59	0.79			48.3	22.1		5.30	1.50	0.58	288	0.41		
B	0.60	0.80	14.88	3.40	49.1	22.5	0.20	5.12	1.50	0.55	299	0.42		98.3
C	0.61	0.81			46.0	21.7		5.15	1.45	0.58	313	0.36		
D	0.71	0.73	17.93	3.89	45.9	23.0	0.51	5.45	1.37	0.58	271	0.41	1.7	100.0
E	0.74	0.69	16.85	3.64	47.1	23.2		5.65	1.39	0.59	277	0.37	1.4	99.8
F	0.81	1.12			41.1	20.2		6.22	1.39	0.75	208	0.26		
G	1.03	0.50	22.75	5.05	36.8	22.2	0.14	7.93	1.14	0.87	90	0.08	0.2	99.6
H	1.12	0.50			30.6	19.7		8.59	1.06	1.06	63	0.17		
I	1.16	0.52	23.41	5.06	33.4	21.6	0.68	9.21	1.06	1.04	6.1			98.0
J	1.31	0.49	24.35	5.20	31.9	22.4		9.44	0.98	1.02	223	0.33	1.1	98.9
K	1.30	0.49	25.56	5.45	30.4	20.7	0.14	9.80	1.01	1.15[h]	205	0.42		97.9

[a] Analytical precision has not been determined statistically. Estimated precision is as follows: C, ±0.02 wt %; H, ±0.03 wt %; Si, ±0.03 wt %; Cl, ±0.1 wt %; Mg, ±0.1 wt %; [OEt], ±0.15 mmol/g; BET surface area, ±10% above 10 m^2/g, ±20% below 10 10 m^2/g; pore volumes, ±10%. [b] Mole ratio of ethanol to BEM in the alcoholysis step. [c] Mole ratio of SiCl$_4$, used for halogenation, to initial BEM charge. [d] Measured as total base in an acid–base titration after hydrolysis. [e] Mole ratio of chlorine to magnesium in the product. [f] Mole ratio of total base to magnesium in the product. [g] Analytical closure: sum of C, H, Cl, Mg, Si, and the amount of O required by the [OEt] analyses. [h] This material was not washed and was known to contain residual M–R groups, which would contribute to excess base content.

Table III. CP/MAS ^{13}C NMR Results

run	Cl$_1$Mg$_1$(OEt)$_1$ δ(CH$_2$), ppm	Cl$_1$Mg$_1$(OEt)$_1$ δ(CH$_3$), ppm	Cl$_3$Mg$_2$(OEt)$_1$ δ(CH$_2$), ppm	Cl$_3$Mg$_2$(OEt)$_1$ δ(CH$_3$), ppm
A			63.5	19.4
B			63.4	19.1
C			63.3	19.2
D			63.0	18.9
E	59.1	[18.9][a]	63.2	18.9
F	59.6	20.0	63.3	[20.0]
G	59.3	19.9	63.2	[19.9]
H	59.4	19.9	63.8	[19.9]
I	59.3	19.9	63.0	[19.9]
J	59.3	19.7		
K	59.3	19.9		

[a] When a peak is believed to be masked by a stronger signal, the chemical shift of the stronger signal is shown in brackets.

concentration down to about 10 wt %. This solution was then stirred and heated to 50–60 °C, and a calculated amount of absolute ethanol (dried over activated 4A sieves) added slowly, causing the temperature to rise to 60 °C. This temperature was maintained throughout the ethanol addition. External heat was then applied to reflux the solvent. After refluxing, a homogenous alkylmagnesium alkoxide solution was obtained.

The reaction solution was then cooled to –15 °C and stirred. Silicon tetrachloride was added all at once, and no immediate exotherm or reaction was observed. The solution temperature was increased by 1 °C/min to about 60 °C, where precipitation was observed to begin, and held there. Finally, the reaction mixture was cooled, solids allowed to settle, and the supernate decanted. The solids were washed with fresh solvent, collected by filtration or decantation and vacuum dried at ca. 50–100 mTorr.

X-ray diffraction analyses were conducted with representative samples of these materials. In general, these powders diffracted weakly, giving poor signal to noise ratios. However, the characterization was sufficient to determine that novel materials were present in samples containing predominantly ClMgOEt (run H) and Cl$_3$Mg$_2$OEt (run D). In run H the major reflections were at d = 9.30 and 4.17 Å, and the lowest angle reflection was at d = 9.30 Å. In run D the major reflections were at d = 4.17 and 8.66 Å, and the lowest reflection was at d = 9.93 Å.

General Method for Preparation of Catalysts. Specific amounts and other conditions can be found in Table IV. Specific results are summarized in Table V. A 500 mL three-neck round bottom catalyst flask equipped with bottom frit, mechanical stirrer, thermometer, and gas inlet was charged with solid support material. The catalyst flask and solids were cooled to + 5 °C, and titanium tetrachloride (neat, 10 mL/g of support) and n-heptane (10 mL/g of support) were slowly added to the flask. The temperature of the mixture was slowly increased with stirring to the desired temperature (Table IV), and held for 6 h. At this point stirring was stopped, and the supernate was removed, while hot, through the bottom frit. The solids were allowed to cool to room temperature.

At room temperature, fresh titanium tetrachloride (10 mL/g of support) was added to•the solids. The mixture was heated with stirring to the desired temperature (Table IV) and held there for 2 h. The supernate was again removed by hot filtration and the solids washed with hot n-heptane several times. The solids were dried in vacuo at 50–100 mTorr and room temperature.

Ethylene Polymerizations. Polymerization tests were conducted in a 1 L stainless steel autoclave. Catalysts were activated with Al(i-Bu)$_3$ at an Al:Ti ratio of 50:1. The activated catalysts, hexane solvent, 30 psig H, and finally ethylene to 100 psig were charged to the reactor at 80 °C. As polymerization proceeded, the temperature was controlled at 85 °C and ethylene was supplied on demand. The autoclave was equipped with a three-bladed propeller type impeller, and was stirred at ca. 1200 rpm. Results are summarized in Table VI.

Results and Discussion

The synthetic strategy of eqs 6 and 7 was applied as shown in eq 8. The ratio of ethanol to magnesium (x) is the most important factor in this reaction, and it directly controls the stoichiometry of the product. The chlorine to magnesium ratio (z) found in the insoluble reaction products from eq 8 is plotted against x in Figure 1. Because a few of the ethoxide groups, in addition to all of the alkyl groups, react with the SiCl$_4$, z is generally somewhat more than 2 – x. Figure 1 illustrates the approximately linear relationship between final composition and reaction stoichiometry. The line shown in Figure 1 is a least squares line that was constrained to pass through z = 2.0 when x = 0, since under those conditions one must obtain MgCl$_2$. If the reaction of SiCl$_4$ with RMgOEt only resulted in replacement of the R group with Cl, this line would have a slope of –1. In fact, it has a slope of –0.81, which indicates that, on average, 19% of the MgOEt groups are consumed, in addition to all of the MgR groups, in the RMgOEt intermediate.

$$\mathrm{BuMgEt} + x\mathrm{EtOH} \rightarrow \mathrm{R}_{2-x}\mathrm{Mg(OEt)}_x + x\mathrm{RH}$$

$$\mathrm{R} = \text{ethyl and/or butyl}$$

$$0 < x < 2 \qquad (8)$$

$$\mathrm{R}_{2-x}\mathrm{Mg(OEt)}_x + y\mathrm{SiCl}_4 \rightarrow \mathrm{Cl}_z\mathrm{MgOEt}_{2-z} + y\mathrm{R}_{(2-x)/y}\mathrm{SiCl}_{4-z/y}(\mathrm{OEt})_{(x+z-2)/y}$$

$$2 - x < z < 2$$

Although the overall product composition varies smoothly with changes in the reaction stoichiometry, the other properties vary less simply. The most important feature of the products isolated in these reactions is that the change in bulk composition shown in Figure 1 is due to the presence of systematically varying amounts of two ethoxymagnesium chloride materials with different compositions. Figure 2 shows that the change in average composition occurs as the ratio of two spectroscopically distinct

Table IV. Catalyst Preparation Conditions

	first titanation step						second titanation step					
	support											
catalyst run	run	amt, g	mL of $TiCl_4$	mL of C_7H_{16}	*T*, °C	*t*, h	mL of $TiCl_4$	*T*, °C	*t*, h	washes, mL	isolated yield, g	method
1	J	10.9	100	100	80	6	100	80	2	5 × 75	11.6	mild
2	H	5.9	60		110	5	60	110	2	3 × 75	6.7	vigorous
3	D	7.7	70	70	80	6	70	80	2	5 × 150	7.5	mild
4	C	4.6	45		110	6	45	110	2	5 × 50	4.1	vigorous
5	F	4.0	40	40	80	6	40	80	2	4 × 150	4.0	mild
6	F	4.2	42		110	6	42	110	2	5 × 50	4.6	vigorous

Table V. Catalyst Analyses[a]

		anal., wt %					
catalyst run	support run	Ti	Mg	median PS, μ	BET, m^2/g	pores, cm^3/g	% Mg recovery
1	J	8.93	14.3	5.3	486	0.34	68
2	H	8.31					
3	D	2.47	20.0	35.9	303	0.38	85
4	C	2.47	22.0	9.6			
5	F	4.13		6.8	331	0.31	
6	F	3.56		7.5	401	0.37	

[a] Analytical precision has not been determined statistically. Estimated precision is as follows: Mg, ±0.1 wt %; Ti, ±0.03 wt %; BET surface area, ±10%; pore volumes, ±10%.

Table VI. Ethylene Polymerizations Results

support run	catalyst run (type)	yield, kg of PE/ (g of Ti h atm)	M_w	M_w/M_n
J	1 (mild)	3.9	144 000	16.0
H	2 (vigorous)	7.3	145 000	13.0
D	3 (mild)	7.3	110 000	8.0
C	4 (vigorous)	14.0	73 800	8.4
F	5 (mild)	12.1	138 000	14.5
F	6 (vigorous)	18.2	114 000	12.3

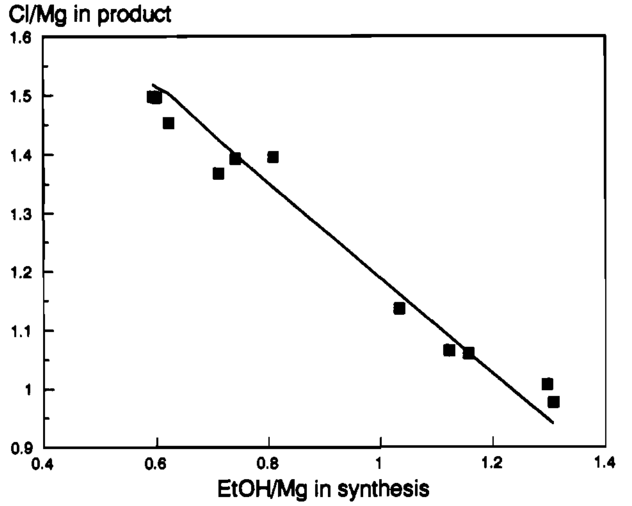

Figure 1. Composition of the product from eq 8, expressed as the atomic ratio of Cl to Mg (*z* in eq 8), shown as a function of the amount of ethanol used (*x* from eq 8).

product components varies. At conditions where $x = 1.31$, and $y = 0.49$ (run J), a spectroscopically pure product with the composition $Cl_{0.98}Mg_{1.00}(OEt)_{1.02}$ is obtained. This product is formulated as stoichiometric ClMgOEt (**1**). The CP/MAS NMR spectrum of **1** is presented in Figure 2-1: the signal at δ 59.3 ppm is assigned to the methylene carbon, and the signal at δ 19.7 is assigned to the methyl carbon of the ethoxy group. As *x* is reduced, and the chlorine to magnesium ratio in the product increases, a new signal for the methylene carbon of a magnesium bound ethoxy group appears at about δ 63.4 ppm. As *x* decreases from 1.3 to 0.6, the signal at δ 63.4 ppm increases in strength, the signal at δ 59.3 ppm decreases, and the methyl carbon signal shifts from ca. δ 20.0 ppm to ca. δ 19.0 ppm (Figure 2-1–5). Only when $x = 0.60$ and $y = 0.80$ (run B) is another material which is not an obvious mixture of ethoxide containing species, obtained (Figure 2-6, spurious peaks in the approximate range of δ 14–32 ppm are from solvent, see below). This product has the composition $Cl_{1.50}Mg_{1.00}(OEt)_{0.55}$ and consequently is formulated as Cl_3Mg_2OEt (**2**). Phenomenologically, it appears that in this compound every other ethoxide has been replaced with Cl.

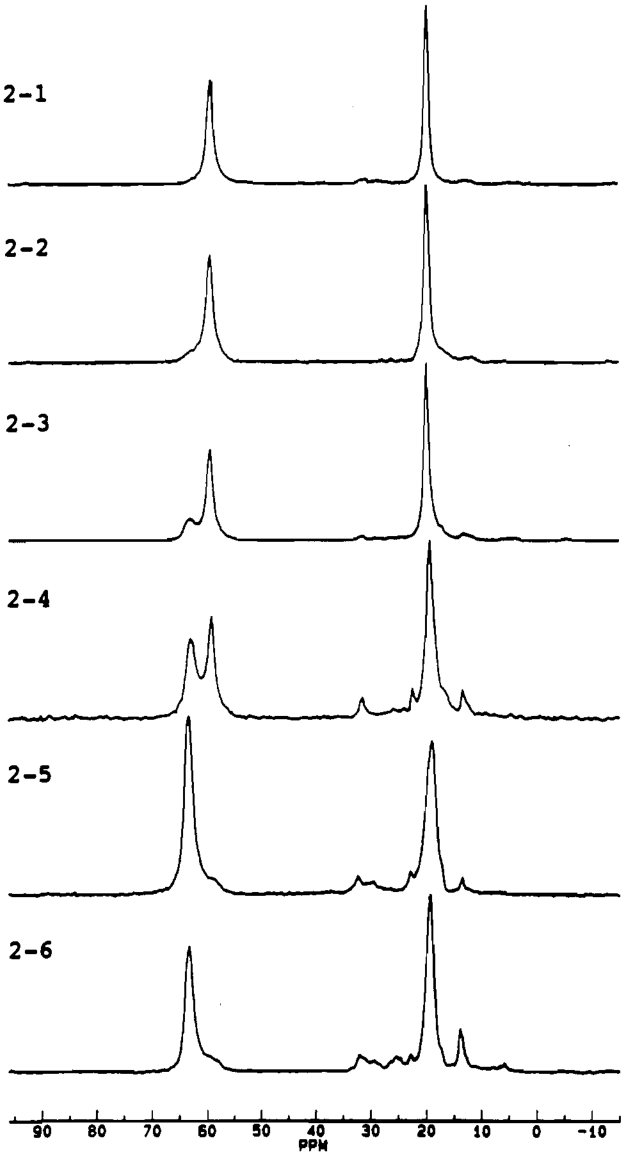

Figure 2. Changes in the composition of the product from eq 8 as observed by CP/MAS ^{13}C NMR. Spectrum 2-1 is that of pure 1 (run J in Table II). Spectrum 2-2 is the product from run I, spectrum 2-3 is from run G, spectrum 2-4 is from run F, and spectrum 2-5 is from run E. Spectrum 2-6 is that of pure 2 (run B in Table II).

Several other features of Figure 2 and Table II require clarification. One feature is that in run F (Figure 2-4), the ratio of Cl to Mg is measured as 1.39, indicating a product mixture containing more **2** than **1**. However, the peak from **1** (at δ 59.3 ppm) is more intense than the peak from **2** (at δ 63.4 ppm). There

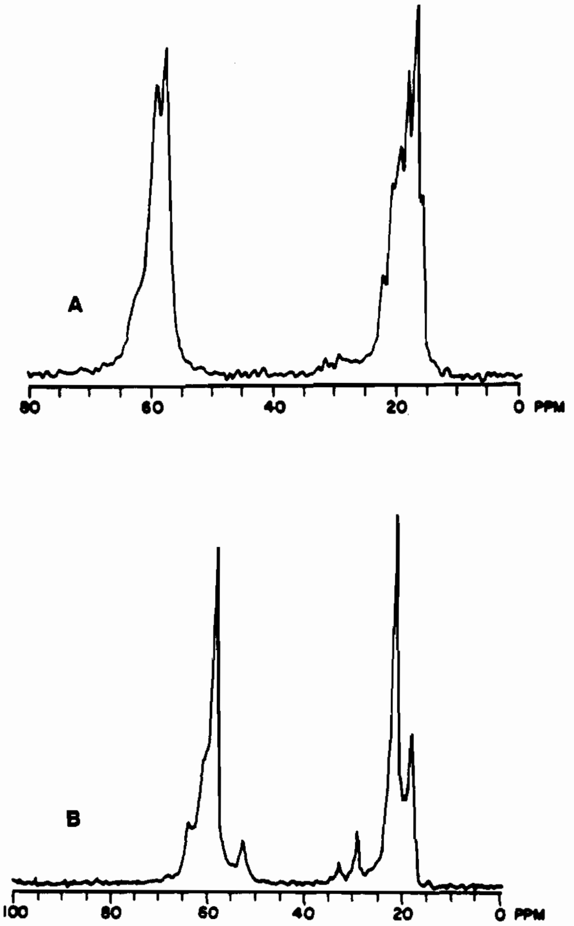

Figure 3. CP/MAS ^{13}C NMR spectra previously reported[3b] for materials with the composition $Cl_1Mg_1(OEt)_1$. Spectrum a is the product from the reaction of magnesium metal with butyl chloride in heptane, followed by addition of ethanol. Spectrum b is the product from the reaction of magnesium metal with ethanol, followed by treatment with HCl. The prominent peaks in spectrum b are probably due to $Mg(OEt)_2$.

are several possible explanations for this behavior. ^{13}C CP/MAS NMR is not a quantitative technique so peak areas and intensities may no reflect composition, although groups in similar environments do tend to give similar intensities. Additionally, **1** contains more ethoxide per gram than **2**, so it would take about twice as much **2** as **1** to obtain the same signal in a quantitative experiment. Finally, the peak from **2**, while less intense, is somewhat broader that the signal from **1**, so relative areas may not track peak heights.

Another noticeable feature of Figure 2 is that signals due to residual heptane or hexane are always more prominent in samples containing **2**. Samples containing **2** typically showed a significant level of hysteresis in the BET isothermal adsorption/desorption curves. This behavior is characteristic of materials with "ink-bottle" shaped pores, where there is restricted egress (i.e. through a narrow opening) from the pores. In **2**, this break usually occurred at a pressure corresponding to desorption of nitrogen from pores of about 40 Å diameter. The larger heptane signals observed for **2** may be due to heptane retained in these restricted egress pores.

Figure 2 should also be compared to previously published spectra for ClMgOEt. Examples of ^{13}C CP/MAS NMR spectra of materials described as ClMgOEt are shown in Figure 3. Figure 2 contains spectra of either two well defined components, or simple mixtures thereof. The spectrum of Figure 3a shows at least two methylene signals, and up to six methyl signals, indicating as many as six compounds could be present. The spectrum of Figure 3b is dominated by single methylene and methyl signals. These are at δ 58.6 and 22.2 ppm (36.4 ppm difference), and can probably by assigned to $Mg(OEt)_2$. In our spectrometer, a sample of $Mg(OEt)_2$ obtained from Aldrich had CP/MAS ^{13}C NMR signals at δ 58.1 and 21.7 ppm (36.4 ppm difference).

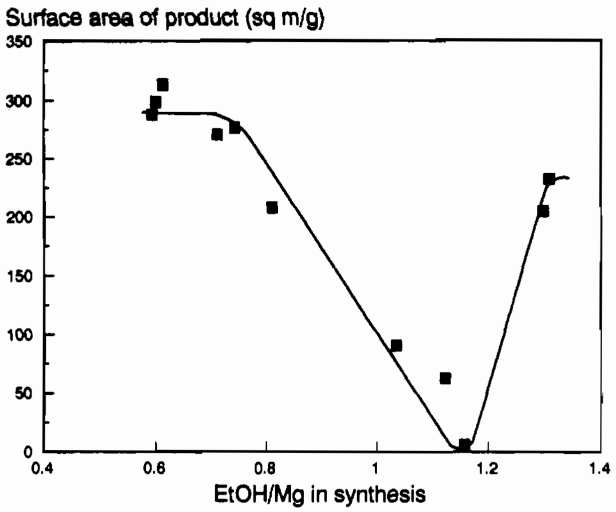

Figure 4. Surface area of the product from eq 8 as a function of the amount of ethanol used (x from eq 8).

As x is varied, other properties besides gross composition and CP/MAS ^{13}C NMR spectral characteristics vary. Figure 4 shows the dependence of BET surface area upon reaction stoichiometry. Unlike the dependence of composition on reaction stoichiometry, which varied monotonically, a more complex behavior is seen here. At the conditions which give **1** (spectroscopically pure ClMgOEt, run J), a relatively high surface area and pore volume material is produced (223 m^2/g, 0.33 cc/g). At $x = 1.16$ and $y = 0.52$ (run I), where a material with nearly the same composition as **1** ($Cl_{1.06}Mg_{1.00}(OEt)_{1.04}$, **3**) and of similar spectroscopic purity (Figure 2-2) is obtained, the surface area is dramatically lower (6.1 m^2/g, trivial pore volume). The proximate cause of this is revealed by SEM examination of the products from runs K and I (Figure 5). The morphologies are completely different: run I (**3**, Figure 5b) produced smooth massive particles with dimensions near 5 μm, while run K (**1**, Figure 5a) produced a more continuous solid, but with a much finer structure. This change in structure is not sufficient to cause the change in surface area, since a surface area of 200 m^2/g implies roughness on the 10–100 Å scale, but it does suggest that there are significant differences in the way these two materials are formed. The structural and surface area differences are probably consequences of the same process.

As x is reduced further, and the amount of **2** present in the samples increases, the surface area also increases. This increase is well correlated with the Cl:Mg ratio in the product and the changes in the ^{13}C CP/MAS NMR (Compare Figures 1, 2, and 4). As the fraction of **2** present in the sample increases, the surface area of the sample increases. The surface area of **2** is typically about 300 m^2/g with a pore volume of about 0.42 cm^3/g (e.g. Run B). It should also be noted that **2**, unlike **1**, shows hysteresis in the BET isothermal adsorption/desorption curve, with nitrogen desorbing at $P/P_0 \approx 0.5$. This behavior could be indicative of pores with restricted access (i.e. ink-bottle shapes).[12]

As was alluded to above, the alkoxymagnesium chlorides reported here show three distinct morphologies, corresponding to the three distinct combinations of surface area and composition. The high surface area form of ClMgOEt (**1**) has an extremely fine structure, with sub-micron sized primary particles that are fused together into an extended random structure (Figure 5a). The low surface area form of ClMgOEt (**3**) has a completely different morphology. SEM examination (Figure 5b) shows it to be composed of smooth solid particles with primary dimensions from 1 to 20 or more microns. The high surface area Cl_3Mg_2OEt product (**2**) is almost a hybrid of the first two morphologies. It

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(12) Lowell, S.; Shields, J. E. *Powder Surface Area and Porosity*; Chapman and Hall: New York, 1987.

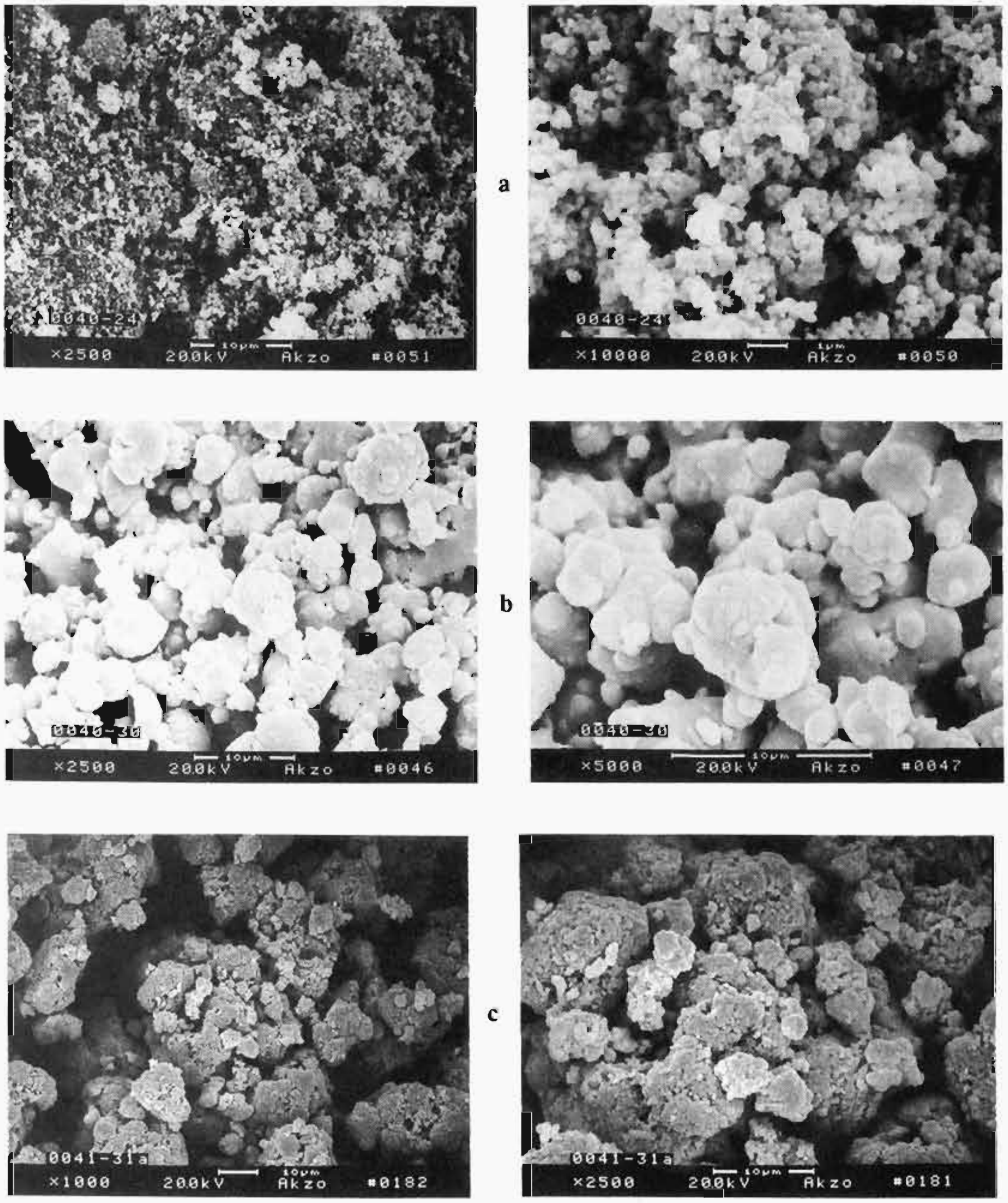

Figure 5. SEM photos of high surface area $Cl_{1.0}Mg_{1.0}(OEt)_{1.0}$ (**1**, photo a), low surface area $Cl_{1.0}Mg_{1.0}(OEt)_{1.0}$ (**3**, photo b), and $Cl_{1.5}Mg_{1.0}(OEt)_{0.5}$ (**2**, photo c).

shows primary dimensions on the order of a micron or less, in the form of surface roughness on relatively large particles, with sizes from 10 to 100 µm (Figure 5c).

Tables IV–VI summarize some preliminary work with these materials in ethylene polymerization. Catalyst runs 1 and 2 show typical results when **1** is treated with $TiCl_4$. Fairly high incorporation of titanium is observed, and good activities in ethylene polymerization are found. The polyethylene produced has a broad molecular weight distribution.[13] In catalyst runs 3 and 4, the titanium incorporation is much lower, indicating that **2** is less reactive toward $TiCl_4$, than **1**. However, the activity is significantly higher here, and the polymer product shows a more narrow molecular weight distribution. This provides evidence that the nature of the support precursor influences catalyst performance. The best activity results (runs 5 and 6) when mixtures of **1** and **3** are titanated. Using a mixture of supports appears to give a catalyst that has the activity of **2** and the molecular weight distribution of **1**. Note also, that the surface area of catalysts made from **2** is about the same as **2** itself. In other cases, where the catalyst is made from **1** or from mixtures of **1** and **3**, higher surface areas result.

Conclusions

This work demonstrates that, given appropriate synthetic strategy and analytical tools, a systematic solid-state chemistry emerges for alkoxymagnesium halides. At least 2 well defined compositions of ethoxymagnesium chloride exist, with distinctive spectroscopic and physical properties. In the case of $Cl_1Mg_1(OEt)_1$ it can be demonstrated that the physical form of the material is highly dependent on synthetic reaction conditions. These novel alkoxymagnesium halides can be converted with the usual techniques to active olefin polymerization catalysts.

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[13] Sufficient H_2 was present so that ≤25 mol % was consumed during polymerization.