Studies on highly active coordination catalysts for polymerization of α-olefins: 2. Thermal investigations of the support system anhydrous magnesium chloride–ethyl benzoate

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The interaction between anhydrous $MgCl_2$ and ethyl benzoate (EB) involves a two-step exothermic process. The thermal effect indicates a rapid first stage attributed to the adsorption of EB on the surface of $MgCl_2$ followed by a considerably slower second stage of the complex formation. The amount of EB bonded in the complex increases with increase in the molar ratio of EB to $MgCl_2$, temperature, and reaction time. During the thermal decomposition of this system, up to its boiling point unreacted or adsorbed EB escapes, then decomposition of the complex takes place resulting in evaporation of the bonded EB. The reaction between EB and $MgCl_2$ is accompanied by a dilation.

INTRODUCTION

Electron donor compounds such as esters, amines, ethers etc. used for the conventional coordination catalysts also have considerable importance in regulation of the stereospecificity of supported Ziegler–Natta catalysts[1–4]. They are supposed to exert their influence by adsorption on the more accessible non-stereospecific active sites of the catalyst, blocking them with respect to the polymerization[5,6]. This effect is important in the formation of active sites but it may be altered by the interaction between the electron donor compound and the catalyst support.

The present work aimed to study the interaction between anhydrous magnesium chloride ($MgCl_2$) and ethyl benzoate (EB) as one of the frequent support–electron donor systems in the coordination polymerization of olefins.

In a previous paper[7], formation of a new crystalline phase was detected by X-ray diffractometry in the reaction product of these components. Thermal effects of the EB–$MgCl_2$ reaction and thermal stability of its products are discussed in the present paper.

EXPERIMENTAL

Preparation and grinding of EB/$MgCl_2$ samples at different molar ratios were described previously[7].

Calorimetric measurements

These were carried out by a Setaram–Calvet isothermal differential microcalorimeter in a glass cell divided into two chambers by a glass membrane. The reaction was started by breaking the membrane allowing the components to get into contact with each other.

Thermoanalytical and thermogravimetric

Curves were simultaneously recorded by a Derivatograph/System Paulik–Paulik–Erdey, Hungarian Optical Works, Budapest/ at a heating rate of 4.5 K min^{-1} up to 1273K. Introduction of samples was preceded by purging the sample chamber with argon for 16 h. The argon stream was continued during the measurements.

Densities

Measured in a pycnometer with n-octane medium at 298K.

RESULTS AND DISCUSSION

Dependence of enthalpy of the EB–$MgCl_2$ interaction on the temperature and the molar ratio of the components

$MgCl_2$ was reacted with EB at a molar ratio of 1:1 at 323K. Heat flux was recorded as a function of time and two exothermic peaks were obtained (Figure 1).

At higher temperatures, the second maximum occurred in less time resulting in overlapping with the first maximum. Overall enthalpies and reaction times at different temperatures are presented in Table 1. It can be seen that the overall enthalpy decreases only slightly while the process is getting much more rapid with increasing temperature. The magnitude of enthalpy suggests a formation of secondary bonds rather than a real chemical reaction.

The binodal course of the thermal effect leads to the conclusion that two successive processes take place. The first process might be an adsorption of EB on the surface of $MgCl_2$ indicated by the facts that its rate is relatively high and the size of its thermal peak decreases markedly with increasing temperature (curves at 323 and 353K in Figure 1).
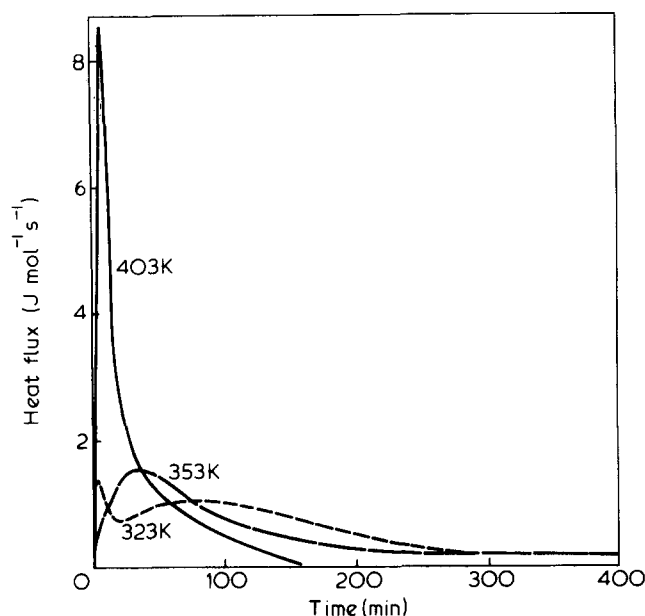
Figure 1 Heat flux of the reaction between EB and MgCl₂ plotted against time at different temperatures

Table 1 Temperature dependence of the interaction between EB and $MgCl_2$ at molar ratio of 1

Temperature K	Overall enthalpy J mol^{-1}	Reaction time min
323	226	580
353	213	540
403	201	160

The second, slower process is presumably the result of the endothermic destruction of the $MgCl_2$ crystal lattice and the exothermic complex formation between EB and $MgCl_2$. Its rate increases with the increase in temperature.

The overall enthalpy and the course of the thermal effect are shown at different molar ratios of EB to $MgCl_2$ in *Table 2* and *Figure 2*, respectively.

Binodality of the enthalpy curve is enhanced by increasing molar ratio (*Figure 2*). Though the overall enthalpy involves the complex formation as well as the adsorption and the destruction of the original $MgCl_2$ crystals, its value in terms of either $MgCl_2$ or EB suggest an equilibrium process. Its rate and extent depends on the initial molar ratio of the components and on the temperature.

Thermal decomposition of the EB/MgCl₂ system

Thermogravimetric (t.g.) and differential thermo-analytical (d.t.a) measurements were made for unground $EB/MgCl_2$ systems at molar ratios of 0, 0.10, 0.17, 0.50, 1.0, and 2.0 and for that at molar ratio of 0.17 ground for 100 or 120 h.

Pure $MgCl_2$ showed a mass loss of ~2.6% in the temperature range of 483 to 553K, possibly, due to releasing some bonded water. The following results were corrected for this value.

Thermal decomposition of $EB/MgCl_2$ systems proceeds in two steps (*Figure 3*). Mass losses are accompanied by endothermic d.t.a. peaks (*Figure 4*). The first endothermic effect at 373K preceding the mass losses may be attributed

to the desorption of adsorbed or physically bonded EB from the surface of $MgCl_2$.

The first decomposition step starts above 373K and comes to an end in the 458–483K range dependeng on the initial EB content but, in any case, below the boiling point of EB (485.6K). In this step, the desorbed excessive EB is escaping.

Table 2 Overall enthalpies of the interaction between EB and $MgCl_2$ at different molar ratios at 323K

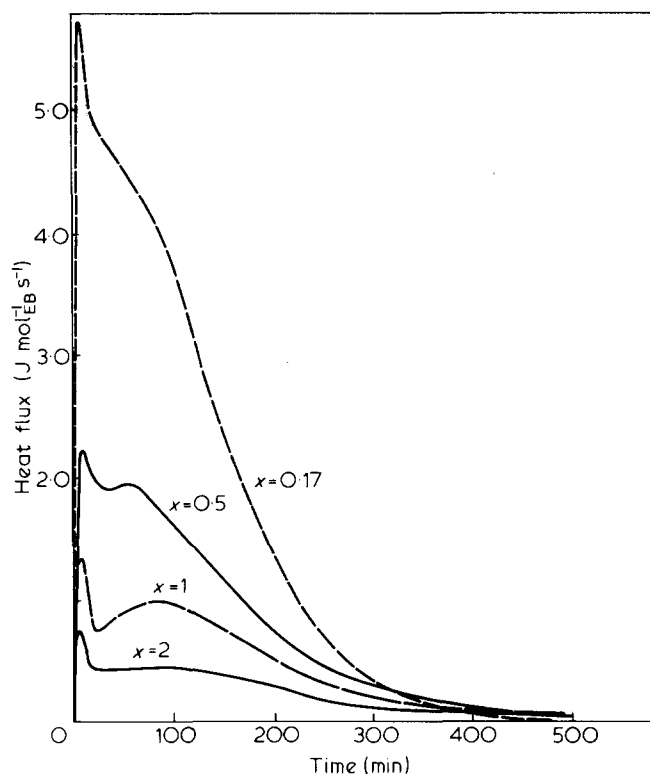| Molar ratio EB to $MgCl_2$	Overall enthalpy	
	J mol^{-1} of $MgCl_2$	J mol^{-1} of EB
0.17	130	779
0.25	173	695
0.50	180	160
1.00	226	226
2.00	360	180

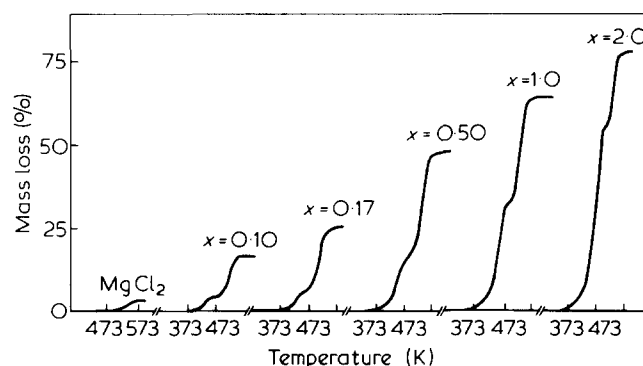Figure 2 Heat flux of the reaction between EB and MgCl₂ plotted against time at different molar ratios

Figure 3 Thermogravimetric t.g. curves of MgCl₂ and EB/MgCl₂ systems at different molar ratios (x = molar ratio of EB to MgCl₂)
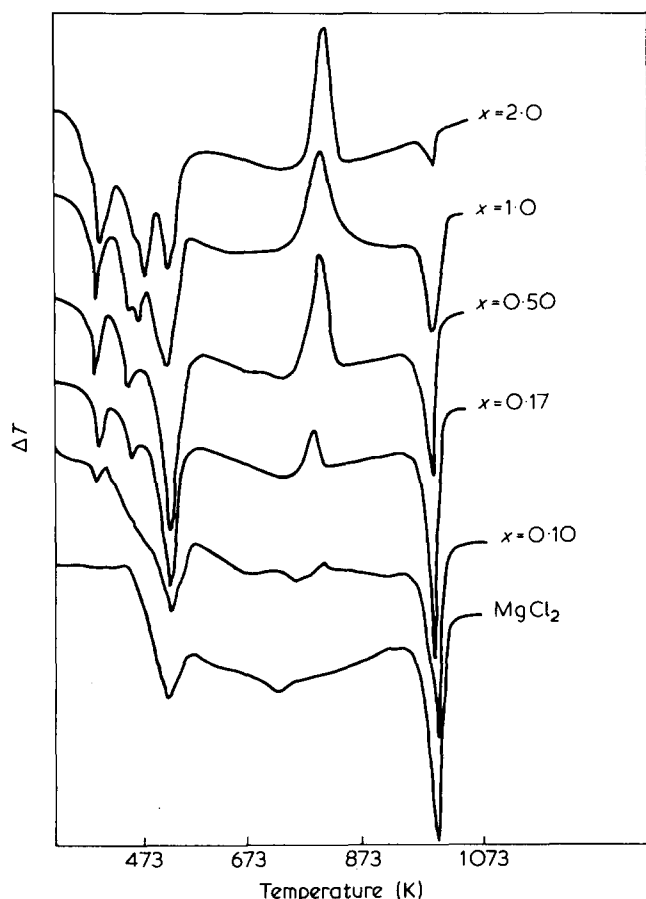
Figure 4 D.t.a. curves of MgCl₂ and EB/MgCl₂ systems of different molar ratios (x = molar ratio of EB to MgCl₂)

Table 3 Thermal decomposition of EB/MgCl₂ systems of different compositions

Molar ratio EB to MgCl₂	Mass loss in terms of EB content (%)	
	Step 1	Step 2
0.10	31.1	86.9
0.17	29.2	82.7
0.50	33.2	65.7
1.0	53.6	46.2
2.0	71.9	28.9

Above the boiling point of EB, the complexed ester is released up to about 550K. At molar ratios of 0.5, 1.0, and 2.0, the total mass loss in the two steps corresponds to the initial EB content (Table 3). At low molar ratios, the surplus could be attributed to some decomposition products from the relatively high amount of MgCl₂.

These decomposition steps are followed by an exothermic effect at 813K (*Figure 4*) due presumably to the decomposition of the charred residue of EB. The last endothermic effect at about 981K refers to the melting of MgCl₂.

Decomposition behaviour of ground samples (for 100 or 120 h) is markedly different from that of the unground system at the molar ratio of 0.17 (*Figure 5*). Grinding reduced the proportion of EB volatilizing in the first step to 24.0 and 10.3%, respectively while the second step was enhanced correspondingly, suggesting that a higher proportion of EB was complexed with MgCl₂ in the ground

samples. This proposal is supported by the observation that the first and second endothermic d.t.a. peaks, referring to the desorption and the first volatilization step of EB, respectively, are markedly reduced after 100 h grinding and disappear completely for samples ground for 120 h (*Figure 6*).

It can be established that a longer reaction period together with the formation of new surfaces promotes the complex formation so that 120 h grinding at a molar ratio of 0.17 results in complexing of about 90% of EB.

Changes in the density of EB/MgCl₂ systems with the molar ratio of the components

Densities of MgCl₂ reacted with EB were measured picnometrically. It was revealed that measured values were lower than those calculated from the densities of the components by using the additivity rule (*Table 4*). It should be noted that measured densities involve a systematic error since n-octane medium dissolves ethyl benzoate (it can be detected by gas chromatography) which may shift the equilibrium of the EB/MgCl₂ complex. Although the correct densities of the initial systems are not measured, results are reproducible and convincing since the differences are much higher than the possible error.
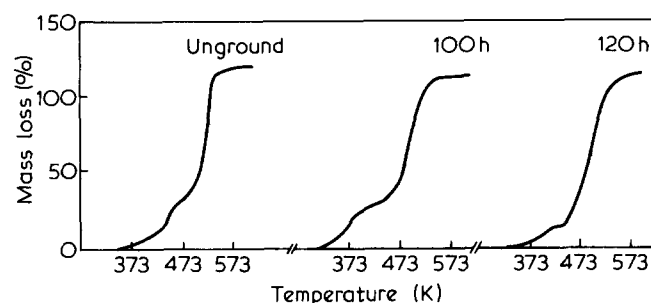
It can therefore be concluded that the reaction between

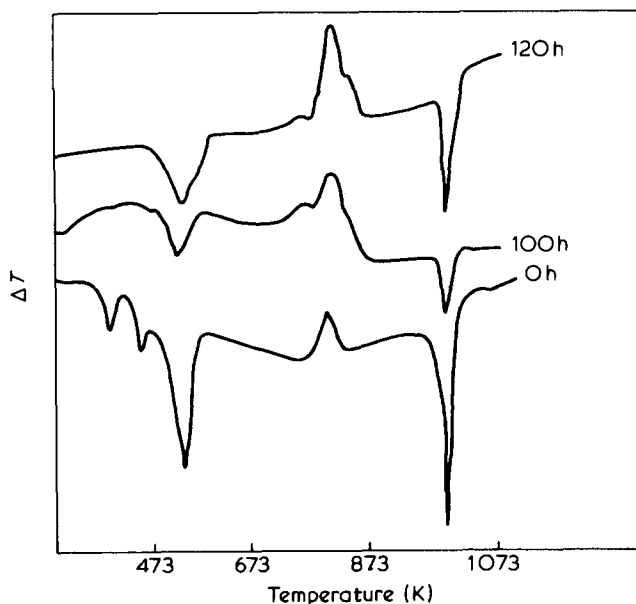*Figure 5* T.g. curves of EB/MgCl₂ systems at molar ratio of 0.17 after different grinding periods

Figure 6 D.t.a. curves of EB/MgCl₂ systems at molar ratio of 0.17 after different grinding periods

Table 4 Comparison of densities measured picnometrically and calculated by the additivity rule as a function of the composition of EB/MgCl$_2$ systems

Molar ratio EB to MgCl$_2$	Density		Deviation in density g cm^{-3}
	measured g cm^{-3}	calculated g cm^{-3}	
MgCl$_2$	2.3018	2.3018	–
0.05	1.81	2.2097	0.40
0.10	1.78	2.1301	0.35
0.17	1.74	2.0396	0.30
0.50	1.54	1.7460	0.20
1.00	1.45	1.5302	0.08
2.00	1.30	1.3496	0.05
EB	1.0412	1.0412	–

EB and MgCl$_2$ involves dilation supporting the previous suggestions that their interaction results in a new phase which appears as new reflections in the wide-angle X-ray diffractograms of EB/MgCl$_2$ systems[7].

Crystal hydration of MgCl$_2$ is also accompanied by dilation (the density of MgCl$_2$.6H$_2$O is 1.56 g cm^{-3} in contrast to the calculated value of 1.62 g cm^{-3}). Hence, it may be suggested that the nature of the interaction between MgCl$_2$ and EB is possibly similar to the crystal hydration.

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