

# DRIFT study of internal donors in supported Ziegler–Natta catalysts

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## Abstract

The state of internal donor (ID) in the supported titanium–magnesium ( $\text{TiCl}_4/\text{ID}/\text{MgCl}_2$ ) catalysts for stereospecific propylene polymerization has been studied by diffuse reflectance infrared spectroscopy (DRIFT). The samples were prepared via interaction of highly dispersed  $\text{MgCl}_2$  with different IDs (ethyl benzoate, EB; di-*n*-butyl phthalate, DBP) and  $\text{TiCl}_4$ . It was found that the DRIFT spectra of carbonyl groups of IDs adsorbed on  $\text{MgCl}_2$  could be best described as a superposition of several overlapping vibration bands from a variety of surface complexes. Within this model the content of individual EB and DBP complexes on the  $\text{MgCl}_2$  surface was calculated. In the case of EB, three main complexes were found on the  $\text{MgCl}_2$  support in about equal proportions. In the case of DBP, only one of three complexes was preferentially formed. The surface content of both EB and DBP was found to decrease in presence of  $\text{TiCl}_4$ . At the same time  $\text{TiCl}_4$  had influenced the distribution pattern of EB but not DBP complexes. The most likely scenario of competitive adsorption of  $\text{TiCl}_4$  and IDs on the  $\text{MgCl}_2$  support is discussed. A model describing surface distribution of  $\text{TiCl}_4$  on  $\text{MgCl}_2$  is proposed for  $\text{TiCl}_4/\text{EB}/\text{MgCl}_2$  and  $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$  catalysts.

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## 1. Introduction

The internal donor (ID) is an important component in supported Ziegler–Natta catalysts for propylene polymerization responsible for stereospecificity of these catalysts [1–3]. It was demonstrated that the internal donor was strongly bound to the  $\text{MgCl}_2$  support and did not interact with adsorbed  $\text{TiCl}_4$  [4–7]. It is believed that the internal donor blocks particular sites on the  $\text{MgCl}_2$  surface, which otherwise upon coordination with  $\text{TiCl}_4$  would produce precursors of non-stereospecific active sites [4,8,9]. It was also suggested, that when adsorbed on the catalyst's surface the internal donor could convert aspecific active sites into specific ones [2,10–16]. Several theoretical studies have been performed to address the possible role of internal donors in Ziegler–Natta catalysts [17–19]. At the same time only limited experimental data on the distribution of the internal donor on the  $\text{MgCl}_2$  support has been reported so far. One  $^{13}\text{C}$  CP-MAS NMR study had found two esters (EB, ethyl benzoate and DIBP, di-*iso*-butyl phthalate) coordinated by non-equivalent surface sites on the  $\text{MgCl}_2$  surface, with diester demonstrating somewhat different behaviour than monoester [6].

DRIFT spectroscopy is one of the most useful research tools in studying variety of surface species in solid catalysts. It can also be applied to probe the state of carbonyl groups in the molecules of internal donors, since the  $\nu(\text{C}=\text{O})$  adsorption band is very sensitive to coordination. Typical spectra of carbonyl groups of internal donors would have asymmetric shapes due to many different complexes co-existing on the surface [5,20–22]. In this work we have analyzed the  $\nu(\text{C}=\text{O})$  regions in the DRIFT spectra of samples prepared via interaction of highly dispersed  $\text{MgCl}_2$  with EB (ethyl benzoate), DBP (di-*n*-butyl phthalate) and  $\text{TiCl}_4$ . Broad and asymmetric  $\nu(\text{C}=\text{O})$  bands were deconvoluted into several components from individual surface complexes involving internal donors. Using this approach it was possible to obtain quantitative information on the content of different complexes of EB and DBP. The likely mechanism of competitive adsorption of internal donors and  $\text{TiCl}_4$  is discussed.

## 2. Experimental

### 2.1. Materials

Heptane, butylchloride, chlorobenzene (PhCl), EB and DBP were used after dehydration over molecular sieves. All the preparation and manipulation with samples were performed under

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argon atmosphere. Argon gas was additionally dried with molecular sieves and using a Drierite gas drying unit with anhydrous calcium sulfate.

## 2.2. Support

The highly dispersed  $\text{MgCl}_2$  support was prepared via interaction of magnesium metal powder with  $\text{C}_4\text{H}_9\text{Cl}$  (molar ratio  $\text{C}_4\text{H}_9\text{Cl}/\text{Mg} = 3$ ) in heptane at  $98^\circ\text{C}$  with subsequent washing with heptane [23]. The resulting  $\text{MgCl}_2$  support contained ca. 10 wt.% of organic residue and had a surface area of ca.  $90\text{ m}^2/\text{g}$ .

## 2.3. ID/ $\text{MgCl}_2$ samples

The  $\text{MgCl}_2\cdot 0.35\text{EB}$ ,  $\text{MgCl}_2\cdot 0.1\text{EB}$ ,  $\text{MgCl}_2\cdot 0.35\text{DBP}$  and  $\text{MgCl}_2\cdot 0.1\text{DBP}$  samples were prepared by interaction of a suspension of  $\text{MgCl}_2$  in heptane (2.5 ml/g of  $\text{MgCl}_2$ ) with corresponding ester (loading ester/ $\text{MgCl}_2$  molar ratio of 0.35:1 for the  $\text{MgCl}_2\cdot 0.35\text{ID}$  samples and 0.1:1 for the  $\text{MgCl}_2\cdot 0.1\text{ID}$  samples) at  $103^\circ\text{C}$  for 5 h. The samples were washed twice with heptane.

The  $\text{EB}/\text{MgCl}_2$  ( $-50^\circ\text{C}$ ) and  $\text{DBP}/\text{MgCl}_2$  ( $-50^\circ\text{C}$ ) samples were prepared by dosing ester ( $\text{EB}/\text{Mg}$  ratio of 0.0057 and  $\text{DBP}/\text{Mg}$  ratio of 0.00085 and 0.0017) to a suspension of  $\text{MgCl}_2$  in heptane (25 ml/g of  $\text{MgCl}_2$ ) at  $-50^\circ\text{C}$  for 0.5 h. After dosing, the temperature was increased to  $20^\circ\text{C}$  and the reaction mixture was kept at this temperature for 1 h.

The  $\text{EB}/\text{MgCl}_2$  ( $20^\circ\text{C}$ ) and  $\text{DBP}/\text{MgCl}_2$  ( $20^\circ\text{C}$ ) samples were prepared by dosing ester ( $\text{EB}/\text{Mg}$  ratio of 0.014 and 0.028 and  $\text{DBP}/\text{Mg}$  ratio of 0.014) to a suspension of  $\text{MgCl}_2$  in heptane (25 ml/g of  $\text{MgCl}_2$ ) at  $20^\circ\text{C}$  for 0.5 h and kept at this temperature for 1 h. The samples were washed once with heptane.

The  $\text{EB}/\text{MgCl}_2$  ( $105^\circ\text{C}$ ) sample was prepared by adding EB to a suspension of  $\text{MgCl}_2$  ( $\text{EB}/\text{MgCl}_2 = 0.1$ ) in  $\text{PhCl}$  (25 ml/g of  $\text{MgCl}_2$ ) at  $105^\circ\text{C}$  and keeping the reaction mixture at this temperature for 1 h. The resulted sample was washed once with  $\text{PhCl}$  at  $105^\circ\text{C}$  and twice with heptane.

The  $\text{DBP}/\text{MgCl}_2$  ( $115^\circ\text{C}$ ) sample was prepared by adding DBP to a suspension of  $\text{MgCl}_2$  ( $\text{DBP}/\text{MgCl}_2 = 0.07$ ) in  $\text{PhCl}$  (25 ml/g of  $\text{MgCl}_2$ ) at  $115^\circ\text{C}$  and keeping the reaction mixture at this temperature for 1 h. The resulted sample was washed once with  $\text{PhCl}$  at  $115^\circ\text{C}$  and twice with heptane.

## 2.4. Catalysts

Titanium–magnesium catalyst (**I**) with a composition of  $\text{TiCl}_4/\text{EB}/\text{MgCl}_2$  (0.77 wt.% of Ti, 1.5 wt.% of EB) was prepared via treatment of  $\text{MgCl}_2$  with a mixture of  $\text{TiCl}_4/\text{PhCl}$  (1:1 vol.,  $\text{Ti}/\text{Mg} = 10$ ) in presence of EB ( $\text{EB}/\text{MgCl}_2 = 0.1$ ) at  $105^\circ\text{C}$  for 1 h and followed by two treatments with the same  $\text{TiCl}_4/\text{PhCl}$  mixture at  $105^\circ\text{C}$  for 0.5 h. The catalyst was washed once with  $\text{PhCl}$  and three times with heptane.

Titanium–magnesium catalyst (**II**) with a composition of  $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$  (0.82 wt.% of Ti, 2.8 wt.% of DBP) was prepared via treatment of  $\text{MgCl}_2$  with a mixture of  $\text{TiCl}_4/\text{PhCl}$  (1:1 vol.,  $\text{Ti}/\text{Mg} = 10$ ) in presence of DBP ( $\text{DBP}/\text{MgCl}_2 = 0.07$ ) at  $115^\circ\text{C}$  for 1 h and followed by two treatments with the same  $\text{TiCl}_4/\text{PhCl}$  mixture at  $115^\circ\text{C}$  for 1 and 0.5 h. The

catalyst was washed once with  $\text{PhCl}$  and three times with heptane.

## 2.5. Chemical analysis

Titanium content in the samples was determined with inductively coupled plasma-atomic emission spectrometry (ICP-AES). To determine DBP content the samples were suspended in heptane and decomposed by 10%  $\text{H}_2\text{SO}_4$ . The organic phase was separated, washed twice with distilled water, dried and weighted. The EB content was determined by GC analysis of the organic phase after hydrolysis of the samples in heptane with 10%  $\text{H}_2\text{SO}_4$ .

## 2.6. DRIFT measurements

Prior to DRIFT measurements all samples were dried in vacuum at room temperature. The DRIFT spectra were recorded on a Bruker Vector 22 FT-IR spectrometer equipped with a dry nitrogen chamber and sealed cells with  $\text{CaF}_2$  windows. All spectra were recorded with a nominal resolution of  $4\text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Interaction of EB with $\text{MgCl}_2$

On the surface of highly dispersed polycrystalline  $\text{MgCl}_2$  there are three types of low-coordinated Mg ions, i.e.  $\text{Q}^5$  sites, five-coordinated Mg ions at the (100) face;  $\text{Q}^4$ , four-coordinated Mg ions at the (110) face, and  $\text{Q}^3$ , three-coordinated Mg ions at the edges and corners of  $\text{MgCl}_2$  crystals [8,10]. These low-coordinated Mg ions demonstrate pronounced Lewis acidic properties and are capable of strong coordination of ester molecules, including EB and DBP internal donors studied in this work. Since there are several different Mg sites on the  $\text{MgCl}_2$  surface, it is typical to observe several types of carbonyl groups in the corresponding IR spectra of adsorbed IDs [24]. The individual  $\nu(\text{C})$  absorption bands would often overlap and produce a broad asymmetric feature covering the whole range of vibrations of carbonyl groups. As an example, the DRIFT spectra of the  $\text{MgCl}_2\cdot 0.35\text{EB}$  and  $\text{MgCl}_2\cdot 0.1\text{EB}$  samples (see Section 2) are shown in Fig. 1. In this spectrum the absorption bands of carbonyl groups  $\nu(\text{C})$  can be seen in the range of  $1600\text{--}1750\text{ cm}^{-1}$  with at least four distinct maxima at ca. 1649, 1675, 1697 and  $1724\text{ cm}^{-1}$ . The band at  $1724\text{ cm}^{-1}$  is close to the  $\nu(\text{C})$  carbonyl stretching vibrations in neat EB ester (ca.  $1720\text{ cm}^{-1}$ ) and can be attributed to carbonyl groups in loosely coordinated EB or EB in  $\text{MgCl}_2\cdot 1\text{EB}$  and  $\text{MgCl}_2\cdot 2\text{EB}$  complexes [22]. On the other hand it is known, that upon coordination of ester molecules to metal ions via carbonyl oxygen, the corresponding  $\nu(\text{C})$  frequencies would decrease relative to free ester [5]. Thus, we suggest that three remaining  $\nu(\text{C})$  bands in the DRIFT spectrum of this sample are most likely from three distinct types of EB species bound strongly to  $\text{Q}^3\text{--Q}^5$  Mg ions of  $\text{MgCl}_2$ . The ratio between individual complexes can be determined via computer-assisted deconvolution of the DRIFT spectra into separate bands. In this work such deconvolution

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