

TESTING IN-SITU COORDINATION OF AN INTERNAL DONOR TO SUPPORTED ZIEGLER-NATTA CATALYST: AN ATR-IR STUDY

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Combinations of transition metal salts and aluminum alkyls (Ziegler-Natta catalysts) are able to polymerize ethylene at low temperature and pressures, giving HDPE (high density polyethylene) and polypropylene (PP) in the presence of an electron donor. HDPE and PP weigh less and are usually more corrosion resistant as opposed to metals. Similar to metals they are blended to improve their properties. Commodity polymers are characterized by low cost. In this work, a sensitive method is introduced for investigation of the planar Ziegler-Natta model catalysts by attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR). A solution of $MgCl_2$ in ethanol, containing an internal donor (diisobutyl phthalate), is spin coated directly onto a planar ZnSe ATR crystal. The internal donor is an essential element in supported Ziegler-Natta catalysts for propylene polymerization, because it determines the stereospecificity of the catalyst. Internal donors are known to bind strongly to the $MgCl_2$ support. Infrared spectroscopy is a useful research tool for the study of surface species in solid catalysts. It probes the state of carbonyl groups in ester internal donors, as the $C=O$ absorption band is very sensitive upon coordination to the $MgCl_2$ support. In the present work the in-situ coordination of diisobutyl phthalate ester onto $MgCl_2$ support is studied by attenuated total reflectance infrared spectroscopy (ATR-IR) and is compared with ex-situ coordination.

Keywords: Ziegler-Natta catalysts, internal donor, ATR-IR infrared spectroscopy

Introduction

The internal donor is an important component in supported Ziegler-Natta catalysts for propylene polymerization, as it is a major factor determining the stereospecificity of the catalyst, Andoni (2009). Internal donors strongly bind to the $MgCl_2$ support as it blocks particular sites on the $MgCl_2$ surface which otherwise, upon coordination with $TiCl_4$, would generate precursors of non-stereospecific active sites Andoni et al. (2009). Infrared (IR) spectroscopy is one of the most useful research tools for the study of surface species in solid catalysts. It can be applied to probe the state of carbonyl groups in ester internal donors, since the $C=O$ absorption band is very sensitive to coordination with a Lewis acid. IR spectroscopy has been extensively applied to Ziegler-Natta catalysts, Andoni (2009). With regard to propylene polymerization catalysts, most of the work has focused on the spectral changes in the $C=O$ of the internal aromatic ester in various stages of catalyst preparation. Analogous to this spin coating onto the planar carrier (wafer), Andoni et al. (2007) we are now using a ZnSe crystal to deposit the $MgCl_2$ (with donor) from ethanol solution via spin coating, aiming to investigate the Ziegler-Natta catalysts by means of a new technique (for us): attenuated total reflectance (ATR) infrared spectroscopy. To this end, the wafer has now been replaced by an internal reflection element such as ZnSe, which allows application of ATR-FTIR spectroscopy. The purpose of the present work is to explore the feasibility of applying ATR-FTIR to monitor in-situ coordination of an electron donor and, most importantly, to investigate the interactions of an internal donor such as a diester with the $MgCl_2$ support.

Experimental/Materials/Analytical technique

Experiments were carried out by flowing solutions of diisobutyl phthalate in ethanol or toluene onto a ZnSe or Si crystal contained in a closed cell within the ATR-FTIR set up. The spectra were measured in transmittance mode using ZnSe with ethanol or toluene as background, masking in this manner ethanol or toluene and allowing the visibility of only monoester signals. In this way ethanol or toluene is masked and the characteristic bands of the esters can become evidently visible in the spectra. The data points of the collected spectra were the average of 4 scans at a spectral resolution of 4 cm^{-1} . Diisobutyl phthalate (DIBP) (99 %) was provided by Aldrich and used as received. Absolute ethanol (99.9%) was purchased from Aldrich Chemicals and used as received. HPLC-grade toluene was taken from an argon-flushed column packed with aluminum oxide and stored over 4 \AA molecular sieves. A schematic representation of the ATR-IR flow cell set up for in-situ experiments is shown in Fig. 1.

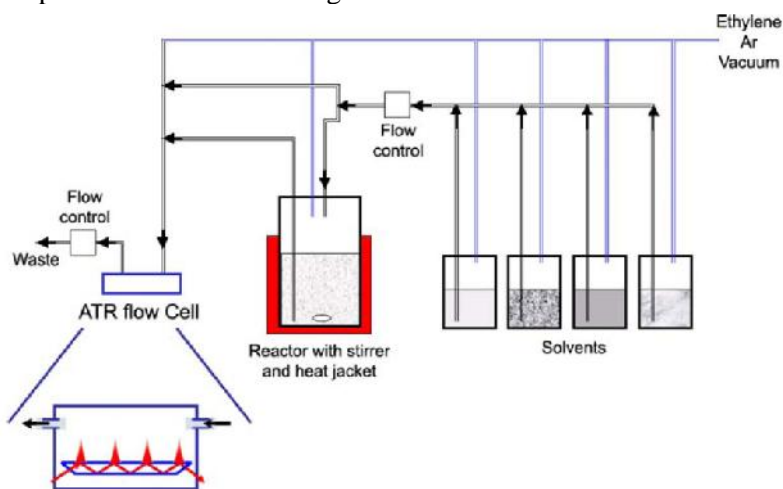


Fig. 1: Schematic representation of the ATR-IR flow cell set up for in-situ experiments.

Results and discussion

In this section we have attempted to prove that investigation of in-situ coordination of the donors is achievable. In other words, instead of dissolving the donor in the solution of MgCl_2 in ethanol followed by spin coating and subsequently measurement with ATR-FTIR, the spin coated layer of $\text{MgCl}_2/\text{EtOH}$ is brought in contact with a solution of donor in toluene. The deposition of MgCl_2 onto a Si crystal (cut-off 1500 cm^{-1}) was carried out via spin coating. Meanwhile a solution of DIBP donor in toluene was prepared ($20\text{ }\mu\text{L}$ DIBP/mL toluene) under glove box conditions, poured into a bottle, sealed and transferred to the new modified ATR-FTIR set up as shown in Fig. 2 (bottom panel). Initially a transmittance ATR-FTIR spectrum of the background was measured (Si crystal located in cell was filled with toluene and measured afterwards). The in-situ measurement was carried out in a timeframe of 20 min. As the DIBP in toluene flows into the cell, a band at ca. 1728 cm^{-1} appears in the ATR-FTIR spectrum. This band corresponds to the C=O stretching frequency of uncoordinated DIBP.

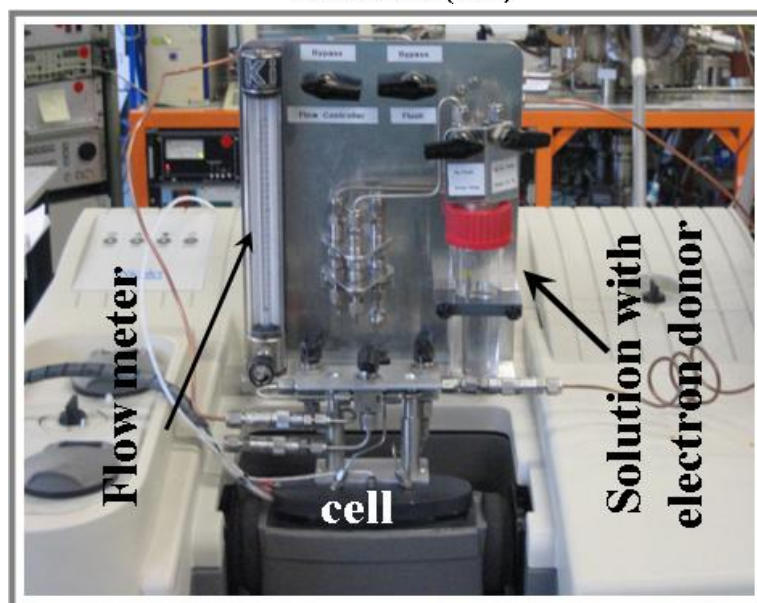
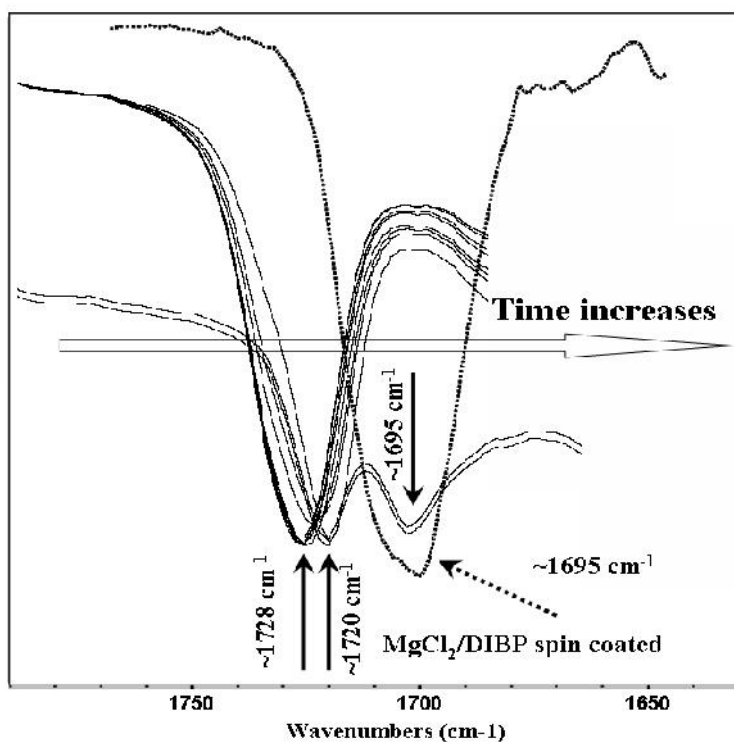


Fig. 2: Top panel represents spectra (solid lines) of the in-situ coordination of DIBP (from toluene solution) on to $\text{MgCl}_2/\text{EtOH}$ film in the C=O region. The measurements were carried out using ZnSe with toluene as a background. The dashed line spectrum represents coordination of DIBP onto $\text{MgCl}_2/\text{ethanol}$ ex-situ (spin coating of a solution which contains MgCl_2 and DIBP in ethanol). The bottom panel represents a picture of the set up enabling in-situ coordination of the donor onto $\text{MgCl}_2/\text{ethanol}$ film. The solution of the donor in toluene (or other solvents) flows from the bottle into the cell with a definite speed which is controlled via the flow meter as indicated in the picture. In this particular experiment the flow speed was maintained at 0.5 ml donor solution/min. In a meantime, a new band becomes visible at ca.

1720 cm^{-1} . The band at 1720 cm^{-1} is close to the carbonyl stretching vibrations in neat ester and can be attributed to carbonyl groups in loosely coordinated DIBP. The striking observation in the ATR-FTIR spectra of Fig. 2 is that with time (while the solution of the donor flows in the cell) the band at ca. 1720 cm^{-1} appears as a twin peak with stretching frequencies at about 1720 cm^{-1} and 1695 cm^{-1} . This value corresponds to the C=O band of the coordinated donor. The position of the peak/component at 1695 cm^{-1} completely overlies the position of the C=O band originated from the spin coated DIBP/MgCl₂ layer (ex situ coordination) indicated by a dashed line spectrum in Fig. 2. The splitting of the C=O band into two peaks suggests/implies the co-existence of loosely coordinated (1720 cm^{-1}) and coordinated (1695 cm^{-1}) species of DIBP on the surface of the MgCl₂ support. Therefore with time, as the solution of the donor slowly flows in the cell, one would expect disappearance of the twin peak and appearance of a single peak at ca. 1695 cm^{-1} . Unfortunately, contamination of water in the system/set up hampered the complete coordination of DIBP onto the MgCl₂ support. Nonetheless the present experiment shows the possibility to investigate in-situ coordination of electron donors onto the surface of the MgCl₂ support (provided that the system is water-free).

Conclusion

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) can be applied to the detection of carbonyl group of electron donors in their free states and upon complexation with a MgCl₂ support for Ziegler-Natta catalysts. ATR-FTIR offers in this manner the application of a new method for in situ/ex situ experiments. It is established that coordination of a diester donor on MgCl₂ occurs via the functional group C=O (ester).

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