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Role of Electron Donor in Polymer Catalyst Synthesis: An XPS Study

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Abstract X-ray photoelectron spectroscopy (XPS) has been applied to the study pertaining to preparation and characterization of catalysts used in propylene polymerization. The analysis has indicated support/donor interaction in active support (adduct) and active support/$TiCl_4$ interaction during catalyst preparation process. A systematic study has been made to identify suitable adduct from a set of three adducts for catalyst synthesis. Precise binding energy of Titanium species on catalyst surface has been measured and its dispersion on support has been evaluated to correlate catalyst performance with the surface spectroscopic parameters.

Keywords XPS · Polypropylene · Catalyst · Dispersion · Electronic interaction · Electron donor · Titanium · Catalyst performance

1 Introduction

Recent advances in the technology of $MgCl_2$ supported catalysts, and the development of bulk and gas phase process has led to production of a large range of propylene polymers. These polymers are suitable for an unlimited number of applications since they can now be tailored for one determined specification. In spite of the significant technical challenge in the development of the products and processes of polymerization, the catalyst is always the key factor, and the industrial success of a polymerization process depends greatly on the development of a proper catalyst system [1, 2].

It is well known that $MgCl_2$ supported $TiCl_4$ catalyst in combination with an electron donor such as ethyl benzoate exhibit a high activity and a high stereospecificity [3, 4]. The use of phthalate and alkoxy silane compounds as an internal and external donor further enhances the activity and stereospecificity of the catalyst [5, 6]. In fact, these donors are most important key factors in determining the performance of the catalyst in stereospecific polymerization.

X-ray photoelectron spectra (XPS) is useful for benchmarking and characterization studies of catalyst surface [7, 8]. The present investigation deals with systematic study on supported catalysts from their preparation stage to the production of polypropylene. XPS has also been used in understanding various possible electronic interactions, identifying active Titanium species, dispersion of these species on the support and also in correlating performance of the catalyst with these parameters [9].

Understanding the role of donor in catalyst synthesis will be very useful in development of desired catalysts.

2 Experimental

2.1 Preparation of $MgCl_2$–MEG Adduct (Adduct A)

About 51.5 mmol of anhydrous $MgCl_2$ was added in 100 ml chlorobenzene taken in round-bottomed flask connected with overhead stirrer. The round-bottomed flask was heated by oil bath. About 241.2 mmol of mono ethylene glycol (MEG) was added very slowly for 10 min and reaction was carried out for one hour at 110 °C.

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Chlorobenzene was decanted after cooling of reaction mixture. Again 100 ml chlorobenzene was added, stirred and decanted. Two hexane washes were given and decanted after settling. Solid after reaction was dried by nitrogen till weight of solid become constant to ensure complete drying. Magnesium content of solid was determined by ethylene diamine tetra acetic acid (EDTA) titration.

2.2 Preparation of $MgCl_2$–DEG Adduct (Adduct B)

About 50.5 mmol of anhydrous $MgCl_2$ was added in 75 ml dichloromethane (DCM) taken in round-bottomed flask connected with overhead stirrer. Round bottom flask was heated by oil bath. About 58.0 mmol of di-ethylene glycol (DEG) and 25 ml of DCM was taken in addition funnel and added very slowly for 15–20 min to round–bottom flask. Reaction was done at room temperature with proper stirring for 15 min. DCM was decanted after solid settling.

Two DCM wash were given to solid and dried in nitrogen till constant weight of solid was achieved. Magnesium content of solid was determined by EDTA analysis.

2.3 Preparation of MgCl2–TEG Adduct (Adduct C)

About 52.6 mmol of anhydrous $MgCl_2$ was added in 100 ml Dichloromethane (DCM) taken in round-bottomed flask connected with overhead stirrer. The round-bottomed flask was heated by oil bath. About 56.2 mmol of tri-ethylene glycol (TEG) was added very slowly to round-bottomed flask. Reaction was done at room temperature with proper stirring for one hour. DCM was decanted after solid settling.

Two DCM wash were given to solid and dried in nitrogen till constant weight of solid was achieved. Magnesium content of solid was determined by EDTA analysis.

2.4 Catalyst Synthesis Using $MgCl_2$–MEG Adduct

About 14.6 mmol of $MgCl_2$–MEG adduct (Adduct A) was taken into three neck jacketed catalyst reactor. About 410 mmol of $TiCl_4$ and 441 mmol of chlorobenzene (112.6) were added at room temperature. Reaction mixture was stirred at 110 °C and reaction was carried out for 1 h. Mixture of TiCl4 and chlorobenzene was decanted very cautiously after solid settling for 15 min.

About 684 mmol of $TiCl_4$ and 733 mmol chlorobenzene were added into solid (remained after decantation), stirred continuously and heated to 110 °C for 1 h. Mixture of $TiCl_4$ and chlorobenzene was decanted after solid settling. Again, 684 mmol of $TiCl_4$ and 733 mmol chlorobenzene was added into solid (remained after decantation) and same procedure was repeated. Washing of reaction solid was done by 100 ml of *n*-hexane with proper stirring and hexane was decanted after solid settling for 5 min. Solids were dried in nitrogen till constant weight achieved.

2.5 XPS Experiments

XPS measurements were carried out using VG Scientific ESCALAB MK II spectrometer fitted with Al Kα and Mg Kα twin anode X-ray source. Sample preparation for XPS measurements were performed under inert (argon) atmosphere through fast entry lock attached to the preparation chamber. Samples were dusted on double side adhesive tape placed on sample holder and transferred to Analysis Chamber of the spectrometer for XPS measurements. X-ray source was operated at 100 W power (10 kV × 10 mA). Quantitative data for each element were collected using 50 eV pass energy and high resolution data for binding energy measurements were collected using 20 eV pass energy of analyzer. Acquisition time for each measurement was $\sim$10 min. Spectrometer was calibrated using Ag(3d5/2) photoelectron line at 368.3 eV [10] and base vacuum in analysis chamber was maintained better than 10^{-8} mbar during spectra acquisition. Spectra shown in Fig. 1–Fig. 5 have been recorded using Mg Kα source.

These spectra were recorded using DELL computer interfacing the spectrometer. Each measurement was carried out at least three times and reported binding energies (BE) are average of these three values with uncertainty of ± 0.2 eV. C(1 s) photoelectron line from aliphatic carbon at 284.8 eV was used as internal reference in binding energy measurements. All experiments were performed under identical conditions.

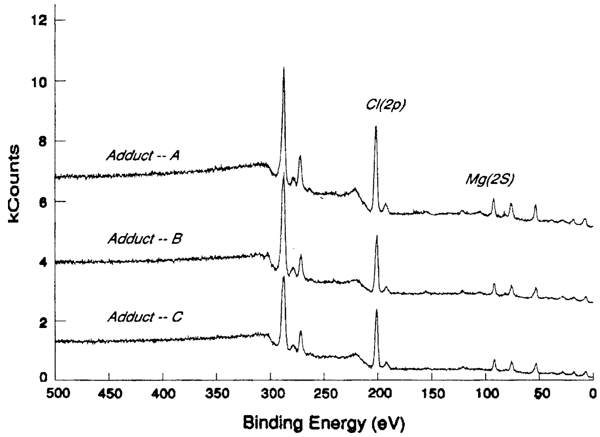

Fig. 1 Scans of Adducts A, B and C recorded in 0–500 eV range

2.6 High Pressure Slurry Polymerization of Catalyst

Dry *n*-hexane was taken in preheated moisture free SS jacketed reactor fitted with magnetic stirrer. $MgCl_2$ supported catalyst, Cocatalyst (triethylaluminium), in cocatalyst/catalyst ratio of 200:250 & external donor (paraethoxy ethylbenozate) in cocataylst/donor molar ratio of 3:5 was taken in decane. Hexane was saturated with propylene. Mixture of catalyst/cocatalyst and donor was added in reactor and hydrogen was added as chain transfer agent as per requirement of melt flow index. Reactor temperature was maintained at 70 °C by heating/cooling system. Simultaneously propylene pressure was maintained to 5.0 kg/cm^2. Polymerization reaction was carried out for 1 h. After 1 h of reaction, hexane was removed and polymer was collected/dried. Productivity of catalyst was calculated based on polymer yield and catalyst amount.

The catalyst productivity was found in the range of 2.9 ± 0.5 kg PP/g_{Cat}.

3 XPS Study

XPS studies have been made on Ziegler–Natta catalysts by Somorjai group [11–13], Terano group [14, 15] and recently by Andoni et al. [16].

This study involve following four steps of experiments and analysis

(a) *XPS of Catalyst Support*

XPS have been recorded for $MgCl_2$ support and precise binding energies of Mg(2p) and Cl(2p) photoelectron lines have been measured using C(1s) photoelectron line from hydrocarbon contamination at 284.8 eV as internal reference. Binding energies of Magnesium and chlorine photoelectron lines are given in Table 1.

(b) *XPS of Adducts*

XPS survey scans of three different adducts i.e., $MgCl_2$ with internal donors (ID) have been recorded to see the changes in support spectrum on take up of these donors.

Figure 1 shows spectra of these three adducts A, B and C. From the comparison of line intensities of Mg and Cl photoelectron lines, it is clear that Mg and Cl atoms of support are better dispersed on the surface of Adduct A (compositional data reported in Table 1 also support this statement). Such adduct is more suitable for catalyst synthesis as it will take up more $TiCl_4$ and hence more titanium species for polymerization reaction.

The high-resolution C(1s) photoelectron spectra showing resolved functionalities C–OH [17] of electron donor and relative ratios of and C–OH and C–C + C–H functional groups are shown in Fig. 2. OH^- group being an electron donor group will interact strongly with $TiCl_4$ and

Table 1 Binding energies of magnesium and chlorine photoelectron lines

Sample	XPS results[a]				Additional experimental data
$MgCl_2$	Mg(2p) = 51.6 ± 0.2 eV				
Support	Mg(2s) = 90.6 ± 0.2 eV				
	Cl(2p) = 199.6 ± 0.2 eV				
$MgCl_2$+electron donor	Mg(2p) = 51.1 ± 0.2 eV				
Adduct A	Mg(2s) = 90.0 ± 0.2 eV				
	Cl(2p) = 199.1 ± 0.2 eV				
	C–OH = 286.5 ± 0.2 eV				
	C–Adduct = 289.1± 0.2 eV (?)				
Atomic composition		Mg Atoms	Cl atoms	Mg:Cl	
Adducts	Adduct A	179	257	41.0:59.0	
	Adduct B	90	127	41.5:58.5	
	Adduct C	74	110	40.2:59.8	
Adduct A+$TiCl_4$	Ti(2p3/2) = 459.3 ± 0.2 eV				
Catalyst	Mg(2s) = 90.3 ± 0.2 eV				
	Mg(2p) = 51.4 ± 0.2 eV				
	Cl(2p) = 199.4 ± 0.2 eV				
	[Ti/Mg] Atomic ratio = 0.054				Surface area = 245 m^2/g
	Titanium index = 13.2				
	Estimated productivity				Productivity in Slurry phase polymerization = 2.9 ± 0.5 kg/g_{Cat}
	= 3.46 log (titanium index)				
	= 3.8 kg/g_{Cat}.				

[a] Binding energy measurements were made using C(1s) photoelectron line from aliphatic carbon at 284.8 eV as internal reference

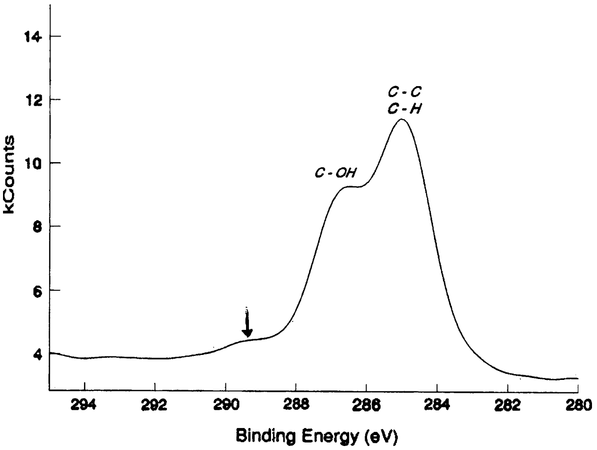

Fig. 2 High resolution C(1s) photoelectron spectrum of Adduct A

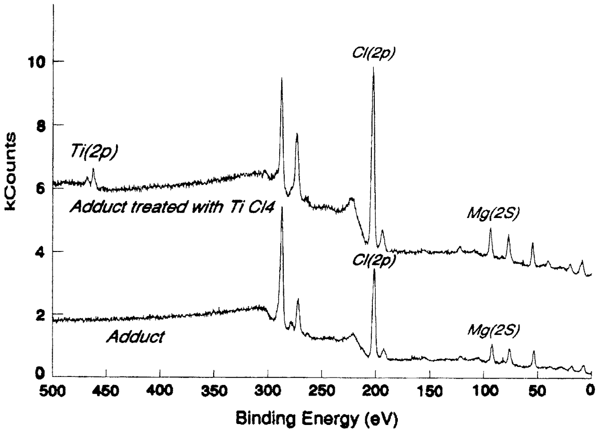

Fig. 3 Scans of Adduct A and Adduct A treated with $TiCl_4$ in 0–500 eV range

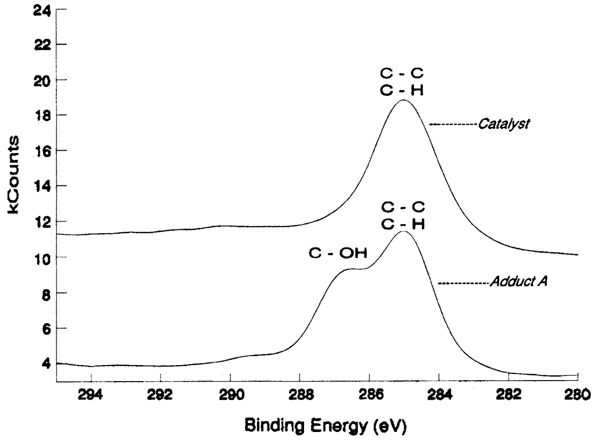

Fig. 4 High resolution C(1s) spectra of catalyst and adduct

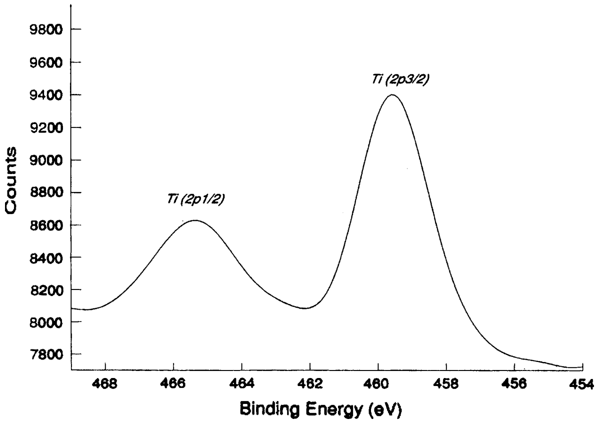

Fig. 5 High resolution Ti(2p3/2; 2p1/2) photoelectron lines of catalyst

hence a balance in number of electron donor groups on the surface is very critical in $TiCl_4$ treatment of adduct for catalyst preparation. The C(1s) photoelectron spectrum of adduct also indicate presence of third carbon functionality ~289.1 eV which although not assigned but is indicative of $MgCl_2$/electron donor interaction. This is strongest in the case of Adduct A may be indicative of higher activity of this support/electron donor combination on addition of $TiCl_4$.

Table 1 shows change in the binding energy of support Mg(2S) and Mg(2p) photoelectron lines on take up of electron donor for Adduct A. This shift in the binding energy indicates transfer of electronic charge between donor and $MgCl_2$ support. In fact, negative shift in binding energy data indicate that the internal donor (ID) interacts with the support to form $MgCl_2 \cdot ID$ complex in which electronic charge is transferred from internal donor to the $MgCl_2$ support to form adduct.

(c) *XPS of Catalyst*

On take up of $TiCl_4$, adduct surface interacts with$TiCl_4$ resulting into formation of active Titanium species dispersed on the support.

Figure 3 shows XPS scans of Adduct A and of catalyst after take up of Ti Cl_4 on this adduct surface. Besides dispersion of titanium on catalyst surface, electron acceptor (Ti^{4+}) interacts with the electron donor (OH^-) and lowers the binding energy (electronic state) of titanium species on the catalyst surface. This interaction is also reflected in high-resolution C(1s) photoelectron spectra of catalyst and adduct shown in Fig. 4 where C–OH functional group of Adduct A has disappeared on take up of $TiCl_4$.

(d) *XPS Measurements*

A multiscan high resolution spectrum of Ti(2p3/2; 2p1/2) photoelectron line is shown in Fig. 5 and precise binding energy value of Ti(2p3/2) photoelectron line using this spectrum is given in Table 1. Comparison of this value with the reported value [18] for $TiCl_4$ [Ti(2p3/2) = 459.8 eV; Cl(2p) = 199.2 eV] indicate transfer of electronic charge from adduct to Titanium on take up of $TiCl_4$.

Once the electronic state of active titanium species has been established [9], Ti/Mg atomic ratio indicates dispersion of these active species on Magnesium based support. Evaluated Ti/Mg ratio with other parameters given in Table 1 has been used to estimate productivity of the catalyst [9]. Evaluated Ti/Mg ratio was 0.054, a value typical for Ziegler–Natta catalyst used for propylene polymerization [19].

4 Discussions

The present investigation is a step in understanding the role of internal donor in Polypropylene catalyst that has prime importance for consideration in the mechanism of catalyst improvement.

Our XPS investigations reveal that "Internal donor interacts with the support by which the amount and the situation of $TiCl_4$ on $MgCl_2$ are regulated to improve catalyst performance".

Such direct information on the role of internal donor in catalyst is not possible because of the following uncertain reasons (a) Majority of the experimental information available in the literature comes from the detailed structural analysis of the polymer product. (b) Some kind of internal donors, such as ethyl benzoate (EB) are eluted from $MgCl_2$ supported catalysts [1, 20] under the general polymerization condition.

5 Conclusions

Based on the present study. It can be concluded that (a) the nature of the active species on the $MgCl_2$ supported Ziegler–Natta catalysts are affected by the change in the electronic environment around the titanium species through the interaction of internal donor with $MgCl_2$ support. (b) titanium electronic state, its dispersion on support and surface area of catalysts are indicative of catalyst's productivity performance.

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