

Letter

X-ray photoelectron spectroscopy analysis for oxidation states of titanium chloride on the surface of Ziegler–Natta catalysts

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Received 29 November 1996; accepted 3 April 1997

Abstract

X-ray photoelectron spectroscopy was applied for Ziegler–Natta catalysts and the oxidation state of titanium chloride was studied from the analysis of the Ti 2p_{3/2} peak. It was observed that the state of titanium chloride on the catalysts was changed by the reaction with the co-catalyst. © 1997 Elsevier Science B.V.

Keywords: Ziegler–Natta catalyst; Titanium chloride; Oxidation state; X-ray photoelectron spectroscopy; Surface analysis

1. Introduction

More than forty years have passed since the Ziegler–Natta catalyst systems were discovered. It is widely used for the industrial production of high-density and linear-low-density polyethenes as well as isotactic polypropene. A great deal of effort has been made on the improvement of the catalyst performance, such as activity and stereospecificity. The active sites are considered to be titanium species formed by the reduction reaction of titanium chloride with a co-catalyst and the oxidation state of the active sites may exert a significant influence on the catalyst performance. However, the oxidation state of the active sites formed by the reaction with a co-catalyst has not been elucidated yet.

X-ray photoelectron spectroscopy (XPS) is used to analyze the elemental composition of materials and chemical bonding as well as the oxidation state of various atoms. Many titanium compounds have been analyzed by XPS and the binding energies of the Ti 2p peaks were reported [1–3]. For Ziegler–Natta catalyst systems, XPS was applied to homogeneous titanocene compounds to characterize a reactive catalytic intermediate by the chemical shift values of Ti 2p_{3/2} peak [4]. In the case of the heterogeneous systems, XPS was used to measure the area ratio of the Ti 2p_{3/2} peak to the Cl 2p peak on the TiCl₃ surface [5] and to define the effect of support on the electron density of titanium chloride in a supported Ziegler catalyst [6]. This study, however, gave limited information on titanium chloride before the activation by co-catalyst.

In this study, XPS is used to analyze the oxidation states of titanium chloride on the sur-

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¹ Delegated from Asahi Chemical Industry Co., Ltd.

face of two types of heterogeneous Ziegler–Natta catalysts by the chemical shift value and full width at half maximum intensity (FWHM) of the Ti $2p_{3/2}$ peak. To estimate the oxidation state of the catalytic species produced by the activation reaction with co-catalyst, the catalysts are also analyzed after the activation reaction and the oxidation states of the titanium compounds before and after the activation are compared.

2. Experimental

The $MgCl_2$ -supported catalyst in this study was prepared as follows. $MgCl_2$ (30 g; $11 \text{ m}^2/\text{g}$) and $TiCl_4$ (1.4 ml) were placed in a 1 l stainless steel vibration mill pot with 50 balls (25 mm diameter) and ground for 30 h at room temperature followed by washing with heptane. The titanium content in the catalyst was 0.40 mmol Ti/g cat. $TiCl_3$ donated from Toho Titanium was used as a reference for a typical non-supported catalyst. Each catalyst was embedded on the conductive tape made from copper and fixed on the sample holder in a grove bag filled with nitrogen gas. The sample holder was put into the vacuum transfer vessel (PHI Model 04-110, Perkin-Elmer) by which the sample could be introduced into the sample introducing chamber without atmospheric exposure. The XPS measurements of all catalysts were carried out on a PHI5600 ESCA system (Φ Physical Electronic) at room temperature. The acquisition times of the XPS analysis were 1 and 5 h for $TiCl_3$ and the supported catalyst, respectively.

The base pressure in the XPS chamber was typically about 5×10^{-9} Torr. Monochromic Al $K\alpha$ radiation having 14.0 keV and 350 W was used. In this study, the binding energy and the FWHM of Ti $2p_{3/2}$ peak were used for the analysis of titanium chloride on the catalyst surface. The binding energy of Ti $2p_{3/2}$ peak was estimated, which indicated the oxidation state of the titanium chloride. FWHM was measured to appraise the distribution of the oxida-

tion states of titanium chloride. The accurate binding energy of Ti $2p_{3/2}$ peak was determined by referencing with the Au $4f_{7/2}$ peak at 84.0 eV. During the preparation of the analytical samples, Au powder was added to all catalysts as an internal standard substance. The reaction of the supported catalyst with triethylaluminum (TEA) used as a standard co-catalyst for olefin polymerization was performed in heptane at room temperature. The concentration of TEA was 150 mmol/l and the molar ratio of TEA to titanium in the supported catalyst was 20. After the reaction, the catalyst was washed with heptane and dried in vacuo. The obtained catalyst powder was analyzed with XPS.

3. Results and discussion

A XPS survey scan was performed on the supported catalyst and $TiCl_3$ for the purpose of elemental analysis. Cl and Ti were observed on the $TiCl_3$ surface. Mg, Cl and Ti were found on the surface of the supported catalyst. The constituent atoms of the catalysts were shown to exist on the surface of the supported catalyst. To investigate the states of the titanium chloride in detail, a XPS narrow scan was performed for both catalysts. The spectra obtained by the analysis are shown in Fig. 1. The chemical shift and FWHM of a peak in a XPS spectrum indicate the electron density of the atom which corre-

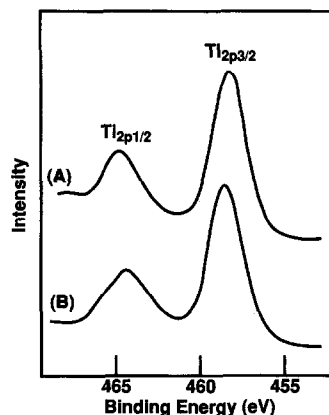


Fig. 1. XPS spectra of Ti 2p levels in Ziegler–Natta catalysts. (A) $TiCl_3$; (B) the supported catalyst.

Table 1
XPS data of the Ti 2p_{3/2} level in TiCl₃ and the supported catalyst reacted with triethylaluminium^a

Run No.	Catalyst	Reaction time (min)	Binding energy (eV)	FWHM ^c (eV)
1	TiCl ₃	0	457.8	2.1
2	the supported catalyst	0	458.8	2.7
3	the supported catalyst	5	458.5	3.1
4	the supported catalyst	10	458.2	3.2

^a The reaction was carried out under the following conditions: reaction temp. = r.t., [Al] = 150 mmol/l, Al/Ti molar ratio = 20.

^b Reference: Au 4f_{7/2} (84.0 eV).

^c Full width at half maximum intensity.

spond to the oxidation state and its distribution. The values of the binding energy and the FWHM of the peak in two types of Ziegler–Natta catalysts before activation were shown in Table 1 (run 1 and 2). From the comparison between the supported catalyst and TiCl₃, the binding energy of the peak was found to be higher for the supported catalyst (458.8 eV) than that for TiCl₃ (457.8 eV). The difference of the binding energy depended on the oxidation state of titanium in both samples, that is Ti⁴⁺ for the supported catalyst and Ti³⁺ for TiCl₃, respectively. The supported catalyst had a lower binding energy of the peak than TiO₂ [3] (459.2 eV) which is a typical Ti⁴⁺ compound. The reason is that the electron donation from the magnesium atom in MgCl₂ to the titanium atom through the chlorine bridge in the supported catalyst. This consideration was derived from the fact of the improvement of the activity for ethene polymerization with the increase of the electron density of titanium chloride by supporting [6]. For the FWHM, the value of the supported catalyst was larger than that of TiCl₃. The evaluation of the broadening behavior arising from supporting was performed by comparing with the FWHM of Mg 2p peak on original MgCl₂ and the supported catalyst. A sharp peak was observed in both cases and the values of the FWHM were almost the same (ca. 2.0 eV). It is suggested that the distribution of titanium chloride on the supported catalyst is broad because

of the different supporting state on MgCl₂. On the other hand, the distribution was relatively sharp for TiCl₃, indicating the more uniform existing state of Ti³⁺ in TiCl₃.

Table 1 also shows the states of titanium compounds produced by the activation reaction of the catalysts with TEA (run 3 and 4). It became clear from the comparison between before and after the reaction that the binding energy of the Ti 2p_{3/2} peak shifted to the lower binding energy side and the FWHM increased after the reaction. The binding energy decreased with the reaction time, indicating the proceeding of the reduction of titanium chloride. However, the value of the supported catalyst after the reaction was larger than that of TiCl₃. A part of titanium chloride on the supported catalyst was reduced by the reaction with TEA to have the activity for olefin polymerization.

In this study, the oxidation state of titanium compounds produced by the activation reaction of the supported catalyst with TEA was successfully analyzed by using XPS. The precise study on the reaction will be reported in a forthcoming paper.

Acknowledgements

The authors are grateful to Toho Titanium Co. Ltd. for their support and donation to our laboratory. The authors also thank Associate Professor Nobuhiko Yui for his valuable advice on this work.

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