

Titanium distribution on the surface of Ziegler–Natta catalysts observed by scanning Auger electron microscopy

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Abstract

Scanning Auger electron microscopy (SAM) with a field emission electron gun was used to analyze the surface of two different types of Ziegler–Natta catalysts. The SAM revealed the chemical composition, morphology, and distribution of the specific elements on the surface of the catalysts. The analysis also showed the difference between the surface distribution of titanium on MgCl₂-supported catalyst and that on TiCl₃. The results obtained in this study demonstrate that the SAM has great potential as an effective tool for the characterization of Ziegler–Natta catalyst.

Keywords: Ziegler–Natta catalyst; Titanium; Surface distribution; Scanning Auger electron microscopy

1. Introduction

Ziegler–Natta catalyst has been 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 paid on the improvement of the catalyst performance, such as activity and stereospecificity. Nevertheless, the catalyst nature, which means the state and structure of the active sites on the catalyst, has not been sufficiently understood yet. High-performance surface analytical methods have progressed greatly just recent year, which can be applied for the detailed characteri-

zation of the active sites on the catalyst. Therefore, only a few researchers performed the study of the surface characterization of the Ziegler–Natta catalysts by using X-ray photoelectron spectroscopy [1] and X-ray absorption spectroscopy [2,3]. They, however, gave the limited information about the surface composition and the environment of titanium, respectively.

Scanning Auger electron microscopy (SAM) is one of the useful surface analytical techniques and has been used for the characterization of various inorganic materials [4–10]. It can be operated as Auger electron spectroscopy (AES) and scanning electron spectroscopy (SEM) at the same time. AES analysis provides the surface chemical composition for a few nm in depth, while SEM observation gives the surface morphological information. Furthermore, two-

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dimensional maps of specific elements can be obtained by the combination of the two techniques, which gives the information concerning the distribution of specific element on the surface of the sample. SAM has a high lateral resolution of 20 nm under the optimum condition with a field emission electron gun, which are enough to analyze the specific element on the outermost surface of the catalyst. Thus, the technique can be recognized to be suitable for the investigation of the Ziegler–Natta catalysts.

In this study, as a part of our programs for the investigation of active sites on the Ziegler–Natta catalyst, the SAM is applied to the two different types of the catalysts, that is T-type TiCl_3 and MgCl_2 -supported catalyst. The purpose of this research is to observe the surface distribution of titanium on the catalysts and demonstrate the usefulness of SAM analysis for the basic study of the Ziegler–Natta catalyst.

2. Experimental part

2.1. Materials

A gallium plate (Nilaco, 99.9999%) was used after washing with acetone as a substrate to fix the catalyst for the SAM analysis. Nitrogen of 99.99% purity (Uno Sanso) and other chemicals were used without further purification.

2.2. Catalyst preparation

T-type TiCl_3 supplied from Toho Titanium was used after removing the large particles. Titanium content in the TiCl_3 obtained by a titration method was 6.5 mmol Ti/g cat. MgCl_2 -supported catalyst was prepared as follows. MgCl_2 (30 g; 11 m^2/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. Titanium content in the catalyst obtained by the titration method was 0.40 mmol Ti/g cat.

2.3. SAM measurement

The SAM analysis was carried out on a PHI670 Auger Nanoprobe (Φ Physical Electronic) with a field emission gun in an ultra-high vacuum of about 10^{-10} Torr at room temperature. In the SAM instrument, an Auger electron detector located at the position above the sample. The system is called ‘Cylindrical Mirror Analyzer’ by which the influence of sample geometry can be minimized. While a secondary electron detector for SEM observation located at the left-hand side of the sample. The catalyst was embedded on the gallium plate (13 mm \times 13 mm) to be fixed on the sample holder. The sample introduction chamber of the SAM was covered by a polyethene glove bag filled with dry nitrogen. The sample was always treated under nitrogen in the bag to prevent the sample from moisture and oxygen in atmosphere. The peaks obtained by AES were assigned according to the previously reported data [11]. SEM images and two-dimensional titanium maps were obtained for each catalyst particle. In the two-dimensional analyses, background corrections were made by a three-point acquisition because small titanium Auger signal rode on a sloping positive background. A low-energy (10 keV) of electron beam at current of 10 nA with a large beam diameter (0.1 μm) was used to minimize sample damage and charging on the nonconducting catalysts. The size of pixels in the map was adjusted to 0.3 μm in order to reduce the measurement time. The acquisition time of a catalyst was about 2 h. Under the condition, SEM image, AES signal, and two-dimensional map were obtained clearly at all samples without time-dependent change.

3. Results and discussion

The SAM was used to characterize the surface of the two typical types of the Ziegler–Natta catalysts. In generally, Ziegler–Natta catalyst is

sensitive to moisture and oxygen in the atmosphere. The unfavorable reactions of the catalyst with them proceed spontaneously to lose the activity for olefin polymerization. The states and structure of active sites on the catalyst seem to be change quickly by the reaction. In this study, the two types of the catalysts were always deal under dry nitrogen to prevent the catalysts from the reaction with moisture and oxygen.

The particle forms of the TiCl_3 and the MgCl_2 -supported catalyst were observed by SEM measurement. The various forms of the catalyst particles were visualized on the gallium plate, such as aggregate forms and isolated particles. The surface compositions of the typical isolated particles with about $10 \mu\text{m}$ diameter were analyzed using AES mode in SAM. By the AES measurement, the elements existing on the outermost surface of the catalyst could be detected with a sensitivity of several percent. The investigation involved a series of point analysis (3–6 different points per each particle). Fig. 1 shows the AES signal $N(E)$, the back scattered electron number with the kinetic energy E , of the typical particles of the catalysts. The peaks at about 195, 260, 397, 530, and 1190 eV are attributed to Cl, C, Ti, O, and Mg, respectively. Cl and Ti were observed on the TiCl_3 surface (Fig. 1(a)), while Mg, Cl, and Ti were found on the surface of the MgCl_2 -supported catalyst (Fig. 1(b)). These results indicate that the constituent atoms of the catalyst exist on the outermost surface with a depth of a few nm. C and O

found in both samples could be attributed to contaminants on preparing SAM samples, which was the same as reported by Furuta using X-ray photoelectron spectroscopy [1]. It was difficult to evaluate the absolute values of a specific peak accurately, but not so hard to compare the relative values in the AES spectrum. Thus, the intensities of Cl and Ti peak were compared relatively in each spectrum. Though the peak of Cl was larger than that of Ti in the spectrum of the MgCl_2 -supported catalyst, they were almost equal in the case of TiCl_3 . It was reflected the composition of the catalysts obtained by titration method, that is, the molar ratio of Ti to Cl was about 0.3 for the TiCl_3 and about 0.02 for the MgCl_2 -supported catalyst.

The SAM analysis was also applied for the determination of the two-dimensional distribution of the specific element over the surface using a mapping procedure. In the Ziegler–Natta catalyst, it is very important to know the distribution of titanium compounds on the catalyst surface, because it is directly related to the catalyst performance. Thus, mapping of titanium on each catalyst surface was performed with SAM. Figs. 2 and 3 show the Auger maps of titanium (b) together with the corresponding SEM image (a) for a typical particle with about $10 \mu\text{m}$ diameter of each catalyst. In both the SEM images, the dark area in the right-hand side of a particle is a shadow, which is formed by the position of a secondary electron detector located at the left-hand side of the sample. Fig. 2(b) and Fig. 3(b) show the maps of the AES intensity at the titanium peak subtracting the baseline from AES spectra at each analytical point, in which the contrast corresponded to the amount of the element existing. Accordingly, the bright part indicated the presence of titanium, whereas the dark part reflected the absence of the element. As shown in Fig. 2(b), titanium existed evenly on the surface of the TiCl_3 , although some area presenting less titanium was found on the catalyst, where carbon was detected more than other area. The Auger electrons emitted from titanium was probably

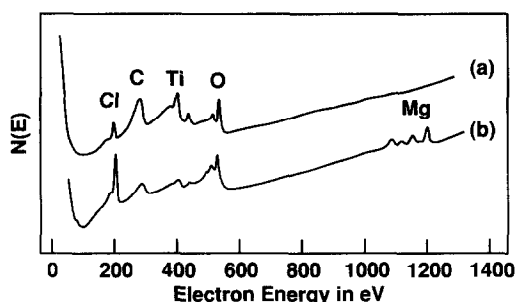
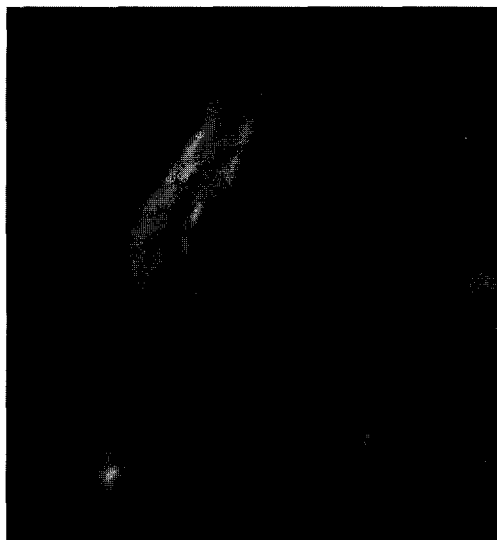
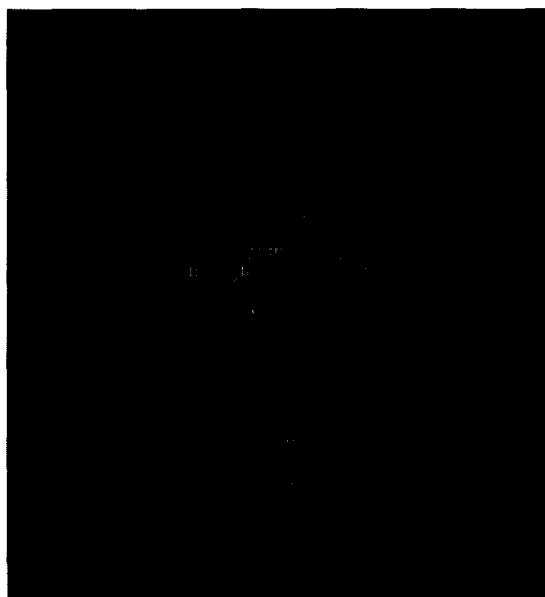


Fig. 1. Auger electron spectroscopy signals of two types of Ziegler–Natta catalysts: (a) T-type TiCl_3 ; (b) MgCl_2 -supported.



(a) $10\ \mu\text{m}$

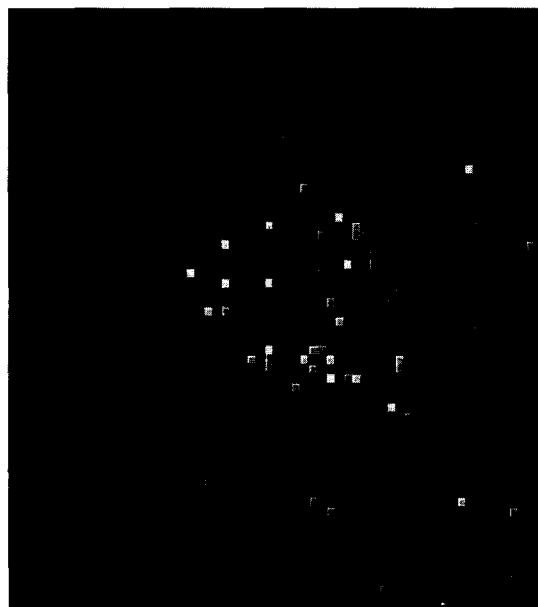


(b) $10\ \mu\text{m}$

Fig. 2. Auger map of a T-type TiCl₃ particle: (a) SEM image; (b) titanium map.



(a) $5\ \mu\text{m}$



(b) $5\ \mu\text{m}$

Fig. 3. Auger map of a MgCl₂-supported catalyst particle: (a) SEM image; (b) titanium map.

concealed by the carbon crust covering the catalyst partially. All particles of the TiCl_3 showed the similar tendency, suggesting that the catalyst had the homogeneous surface composition. These results seemed to be plausible from the structure of the TiCl_3 crystal. In the case of the MgCl_2 -supported catalyst, the signal to noise ratio is not so good (Fig. 3(b)) because the titanium content of the catalyst is very small. In the figure, titanium was observed as white patches on the surface. These were several types of the patches having different contrast, suggesting that the various states of titanium clusters existed. In some particles no titanium was found on the surface. They suggest that TiCl_4 can not be supported evenly on all over the surface of the MgCl_2 by the preparation method employed in this study. As described above, the difference of the distribution states of the titanium on the surfaces of both catalysts were distinctly observed by using SAM.

In this study, SAM was successfully applied for the observation of the titanium distribution on the surface of Ziegler–Natta catalysts. In particular, it is demonstrated that the titanium exists unevenly on the surface of the MgCl_2 -supported Ziegler catalyst used in this study. It is generally accepted that the structure and performance of MgCl_2 -supported Ziegler catalyst are strongly dependent on the preparation method of the catalyst. From this point of view, it is inferred that the catalyst prepared by the different method shows the different distribution state of the titanium on the catalyst. More de-

tailed studies using several kinds of MgCl_2 -supported Ziegler catalysts are now on progress using this technique, the results of which will be reported in our forthcoming paper.

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References

- [1] M. Furuta, *J. Polym. Sci. Polym. Phys. Ed.* 19 (1981) 135.
- [2] P.J.V. Jones and R.J. Oldman, in: *Transition Metals and Organometallics as catalysts for Olefin Polymerization*, W. Kaminsky and H. Sinn (Eds.) (Springer-Verlag, Berlin, Heidelberg, 1988) p. 223.
- [3] L. Aleandri, V. Fraaije and G. Fink, *Macromol. Rapid Commun.* 15 (1993) 453.
- [4] T. Bertrams, F. Winkelmann, T. Uttich, H.J. Freund and H. Neddermeyer, *Surf. Sci.* 333 (1995) B 1515.
- [5] M.A. Baker and P. Tsakiroopoulos, *Surf. Interface Anal.* 20 (1993) 589.
- [6] J.M. Cowley and J. Liu, *Surf. Sci.* 298 (1993) 456.
- [7] I. Olefjord and A. Nylund, *Surf. Interface Anal.* 21 (1994) 290.
- [8] S.D. Bohmig, B.M. Reichl, M.M. Eisl and H. Stori, *Surf. Interface Anal.* 22 (1994) 304.
- [9] N.C. Alstrup, N. Langvad and I. Chorkendorff, *Surf. Interface Anal.* 22 (1994) 441.
- [10] Y. Huang and J.M. Cowley, *Surf. Sci.* 328 (1995) 277.
- [11] L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach and R.E. Weber, in: *Hand Book of Auger Electron Spectroscopy* 2nd Ed. (Physical Electronics Industries, Inc., Eden Prairie, MN, 1976).