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AFM observation of silicon wafer supported Ziegler catalyst for olefine polymerization

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Introduction

Polyolefin, particularly polyethylene and polypropylene, are among the most widely used polymeric materials. One of the most important catalysts used industrially is Ziegler catalyst, by which various polyolefins such as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and isotactic polypropylene (*iso*-PP) have been commercially produced. At present it is for industrial propylene polymerization still the main catalyst to Ziegler catalyst.

Ziegler catalysts, composed of titanium chloride and alkyl aluminum, provided dramatic advances in process engineering in the polyolefin industry. However, the molecular-level scientific elucidation of structures and reaction mechanisms of the new system did not follow this technological progress. The barriers to development in the understanding of the Ziegler catalyst system were the complexity of the high-surface-area catalyst, the extreme sensitivity of the catalyst to oxygen and moisture and the lack of spectroscopic data detecting the active sites during polymerization.

Accordingly, many researchers have been reported aiming at the improvement in the activity and stereospicificity of polymerization since discovery. Consequently, improvement by the increase in the surface area of a carrier or a donor addition has been repeatedly reported. But this catalyst has not been fully understood concerning active sites and polymerization mechanism. Co-catalyst is indispensably required for activation of this catalyst. The state of active site changes with polymerization time. Two or more reactions are proceeding parallel reaction during polymerization. The composition of the catalyst is complicated for this catalyst system. The grain form of Ziegler catalyst is not uniform. Analysis of Ziegler Catalyst is difficult due to these factors.

Surface analyzing method is effective, for the catalytic reaction occurs on the catalyst surface.[1,2] Above all, direct observation of the catalyst is one of the most effective means. In this study, we use atomic force microscopy (AFM), which is a very useful tool for surface configuration analysis.[3] However a flat surface is required for AFM measurement. Therefore, we prepared a thin film model Ziegler catalyst. This approach has an advantage with a simple composition ingredient and simple preparation procedure with 100% of surface area exposed for observations. The silicon wafer used as a substrate is flat and smooth on an atomic level. The preparation of thin uniform films, which has mainly been investigated in relation to its industrial application as a method to deposit Ziegler catalyst on silicon wafer.[4] It is thought that acquisition of the direct knowledge about active species of silicon wafer-supported Ziegler catalyst can be performed.

Experiment Part

Materials

Material
Titanium tetrachloride (Wako Pure Chemical Industries, Ltd.)
Triethyl Aluminum (TEA) (Tosoh Fine Chem Co.)
Benzene (Wako Pure Chemical Industries, Ltd.)
Ethanol (Wako Pure Chemical Industries, Ltd.)
Pure air (Nippon Sanso Co.Ltd.)
Nitrogen (Uno Sanso Co.)
Propylene (TakaTiho Chem. Co.)
Silicon wafer (100) (Komatsu Silicon)

Catalyst preparation

Briefly, **silicon wafer washed with benzene and ethanol(6:4).** Si (100) silicon wafer was calcined at 750℃ for 6h to obtain an oxide layer for generation of a surface hydroxyl group. Then, the wafer was treated in boiling water for 1h to the surface hydroxyl group layer.

Deposited catalysts were prepared by $TiCl_4$ vapor deposition on silicon wafer. $TiCl_4$ depends on liquefaction nitrogen was purified by several freeze-thaw cycles to remove contamination. Vapor depositions of $TiCl_4$ were carried out at room temperature for 5 hours. After that the sample was vacuum pumping for 15 mins in order to remove an excessive $TiCl_4$.

Direct observation of surface by Atomic force microscopy (AFM)

In order to observe their change of the surface, AFM observation was carried out. AFM observation was performed under N_2 atmosphere. AFM observation in tapping mode was carried out with a scan rate of 1Hz .AFM observation was performed under nitrogen atmosphere.

Measurement of the binding energy by X-ray photoelectron spectroscopy (XPS)

In order to observe the change of the binding energy of titanium, XPS measurement was carried out. XPS measurement was performed with a measurement time of 2 h for each sample. Monochromic Al Ka radiation (1486.6eV) was used for the analysis.

Co-catalyst preparation and polymerization

Deposited co-catalysts were prepared by TEA vapor deposition on silicon wafer deposited with $TiCl_4$. Polymerization was carried out with propylene flowing at the same time on $TiCl_4$ film deposited TEA. The catalyst surface studied direct observation by AFM. In order to observe the morphology of the catalyst surface,.

Result and Discussion

By performing all the processes of preparation and observation of catalyst in nitrogen atmosphere, it can be expected that silicon wafer prepared catalyst isn’t deactivated by gases.

AFM measurement was performed in order to investigate the flat silicon wafer surface configuration. Fig.1,5 shows the AFM images of silicon wafer.

According to the AFM images and its profile, silicon wafer has less than 0.3nm roughness. The roughness is enough for AFM observation of possible difference between difficult compounds because the height of the $TiCl_4$ one molecule is about 0.35nm. Consequently, it was succeeded in preparation of silicon wafer on which AFM observation is possible.

Fig.1,5 shows the AFM image of silicon wafer. Fig.2,6 supported Ziegler catalyst after $TiCl_4$ vapor deposition, after TEA(Fig.3,7) vapor deposition, after propylene introduction(Fig.4,8) for 3h.According to the AFM image and its profile, about 2nm of height differences in surface roug hness was observed between $TiCl_4$ vapor deposition and TEA vapor deposition. Moreover, the roughness of the surface was about 25nm before polymerization. As for Fig.4,8, surface morphology was changed clearly after polymerization. It turns out that it generated from polymer was observed XPS analysis of the thin film after polymerization because Fig.9 shows the XPS measurement Si 2p and C 1 s peak before and after propylene ga s introduction. After propylene gas introduction, only the peak at which Si 2p belongs to SiO_2 was detected. It was speculated from the above reason that propylene polymerization occurred, and polymerization activity was confirmed using silicon wafer supported Ziegler catalyst.

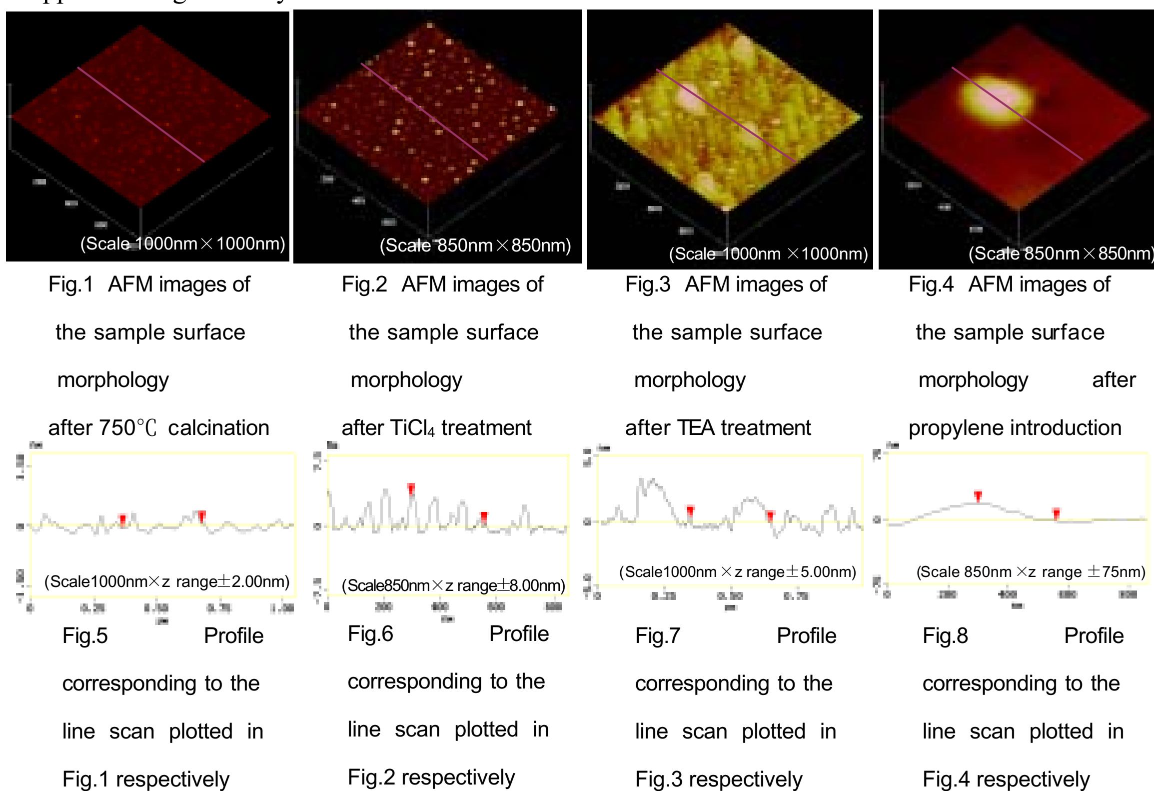

Fig.1 AFM images of the sample surface morphology after 750℃ calcination

Fig.2 AFM images of the sample surface morphology after $TiCl_4$ treatment

Fig.3 AFM images of the sample surface morphology after TEA treatment

Fig.4 AFM images of the sample surface morphology after propylene introduction

Fig.5 Profile corresponding to the line scan plotted in Fig.1 respectively

Fig.6 Profile corresponding to the line scan plotted in Fig.2 respectively

Fig.7 Profile corresponding to the line scan plotted in Fig.3 respectively

Fig.8 Profile corresponding to the line scan plotted in Fig.4 respectively

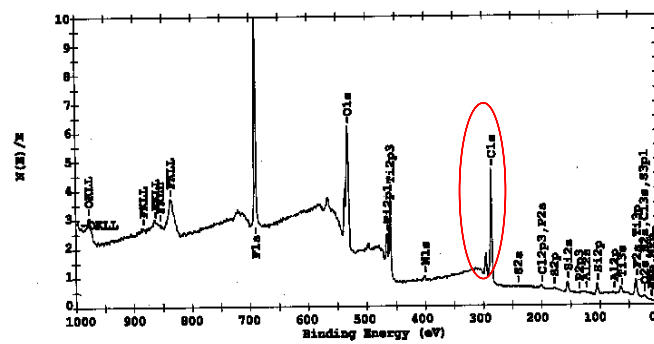

Fig.9 XPS spectra of propylene polymerization wafer

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