Analysis of heterogenized zirconocene catalysts using a micro-PIXE technique

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Et(Ind)$_2$ZrCl$_2$ and the MAO co-catalyst, which polymerize ethylene and propylene, were heterogenized on partially dehydroxylated Davison silica 955, following the method of equilibrium adsorption. The dispersion of these catalyst components on the silica support was investigated by measuring the spatial concentration profiles of Si, Al, and Zr using a micro-PIXE technique. These components were found to be uniformly distributed over the support irrespective of the variation in the heterogenization procedures and the experimental conditions used. The Si:Al ratios determined by the micro-PIXE technique were similar to those measured by the spectrophotometric method. However, the Al:Zr ratios measured by the former were somewhat lower than those determined by the latter. Micro-PIXE measurements confirmed the presence of several trace impurities such as K, Ca, Ti, Fe, Ni, Cu, and Zn which may potentially poison the resulting catalyst.

Introduction

Metallocene catalysts are becoming increasingly important for the polyolefins industry because they are much more active and versatile than the current Ziegler-Natta catalysts.[1] They control precisely the polyolefin resin microstructure. However, a cost- and energy-effective, metallocene-based commercial olefin polymerization process must use heterogenized catalysts to (1) overcome the problem of solvent devolatilization and (2) attain the desired particulate morphology for the resin. A solvent-free process favors the economics whereas the resin morphology dictates the packing density, particulate flow behavior, and processability.[2] Therefore, heterogenizing the metallocene catalyst precursors on a suitable support is highly important. However, heterogenization of the metallocene catalysts is more difficult than that of the Ziegler-Natta ones because of the bulkier metallocene precursors which hinder diffusive mass transfer process on the support. Activity and lifetime of a catalyst, and the resulting properties of the polymer can be affected by inhomogeneous distribution of the active metals on the support. Therefore, the knowledge of the degree of dispersion of the metallocene precursors on the support is important to evaluate the performance of these catalysts.

The present study investigates the elemental distribution profiles of a bridged zirconocene catalyst heterogenized on silica support, using the micro-PIXE technique.[3] Heterogenization of the zirconocene over the silica support was tried by several methods. In addition to the spatial elemental distribution profiles, concentration ratios of the major elements were also determined from the micro-PIXE data. These elemental ratios were compared to the corresponding bulk ratios obtained from spectrophotometric analysis.

Experimental

Catalyst materials

The catalyst precursor used was ethylene-bis(indenyl) zirconium dichloride [Et(Ind)$_2$ZrCl$_2$]. The zirconocene was selected because its performance in olefin polymerization is well-known.[1] The co-catalyst used was methyl alumoxane (MAO) (10% by wt. in toluene). The silica support was Davison 955 having a surface area of 300 m^2/g, average pore volume of 1.65 cm^3/g, and pore size of 220 Å.

Support dehydroxylation

The silica support was partially dehydroxylated in vacuum by heating at 548 K for 24 hours in a Büchi furnace, then cooled to room temperature and stored under argon. Partial dehydroxylation was considered because it has been reported to increase olefin polymerization activity.[4]

Catalyst heterogenization

The zirconocene catalysts prepared were heterogenized on the partially dehydroxylated silica following three different procedures, according to the principle of equilibrium adsorption:

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Procedure 1: Adsorb MAO, then add the metallocene.

Procedure 2: Adsorb metallocene, then treat the supported metallocene with MAO.

Procedure: Add MAO-pretreated metallocene to the support.

The equilibrium adsorption avoids undesirable side reactions causing precipitation of the catalyst precursors off the support.

In the first heterogenization method, the dehydroxylated silica was first slurried in toluene. Then MAO solution was added to this slurry and was stirred at 60 °C for 4 hours. The excess liquid was removed using a pipette. The solid part was then washed with toluene to obtain the MAO/silica precursor. $Et(Ind)_2ZrCl_2$ was dissolved in toluene at 60 °C and the solution was added to the MAO/silica precursor. The mixture was thoroughly stirred at 60 °C for 2 hours to promote the diffusive mass transport process, then at room temperature for 16 hours. The excess liquid was removed using a pipette and the solid part was washed three times with toluene. It was then dried under vacuum at 50 °C to a free-flowing powder and stored under argon.

In the second heterogenization method, the above procedure was repeated, reversing the order of addition of MAO and $Et(Ind)_2ZrCl_2$. However, the concentration gradient and the mixing condition with respect to the diffusing components were kept the same.

In the third method, $Et(Ind)_2ZrCl_2$ was first preactivated with MAO according to a molar concentration ratio of 1:23 to generate the zirconocenium cation before heterogenization. The rest of the heterogenization procedure essentially remained as above.

Spectrophotometric analysis

The bulk aluminum and silicon concentrations in the prepared catalysts were determined using sodium hydroxide fusion. The catalyst samples were first fused with sodium hydroxide, then diluted with deionized water. For the spectrophotometric determination of silicon, an aliquot of the above solution was treated with ammonium molybdate to form a molybdosilicic acid complex at a pH of 1.5. For the determination of aluminum, the solution was treated with pyrocatechol violet at a pH of 6.0. The zirconium content was determined by decomposing the loaded $Et(Ind)_2ZrCl_2$ with H_2SO_4 and oxidizing the resulting products with concentrated HNO_3. Arsenazo III was reacted with the above acidified products in the presence of 9M HCl. The details of the above analysis procedure are available elsewhere.[5]

Micro-PIXE measurements

The heterogenized $Et(Ind)_2ZrCl_2$ catalyst samples were first pressed into pellets. These pelletized samples were scanned using the micro-PIXE facility on the 3 MV Tandetron accelerator at the Center for Applied Physical Sciences of the Research Institute,[6] King Fahd University of Petroleum & Minerals, Dhahran.

Figure 1 shows a schematic of the micro-PIXE set up used. X-rays from the target, produced by the proton microbeam, were detected by the Si(Li) detector placed at an angle of 135° with respect to the incident beam direction. Signals from the detector were amplified, and processed by the CERN's VALET-Plus data acquisition and experiment control software[7] based on a VME computer interfaced through a PC. The data acquisition system produced simultaneously an X-ray energy spectrum and several two-dimensional elemental distribution maps from the scanned area on the target. The energy spectrum identified the elements present in the sample and the distribution maps showed the spatial concentration profiles of the elements.

In the present measurements, a pellet area of about 500 µm×500 µm, divided into 64×64 pixels, was scanned at a time using a 2.5 MeV proton microbeam of about 5 µm resolution. The resulting elemental distribution maps were analyzed and printed on a grey concentration scale using the Kmax software.[8] The elemental spectra were analyzed by the PIXE quantitative analysis software GUPIX[9] to obtain the relative elemental concentrations listed in Table 1.

Table 1. Comparison of the elemental atomic ratios of the heterogenized zirconocene catalyst precursors determined by spectrophotometric and micro-PIXE methods

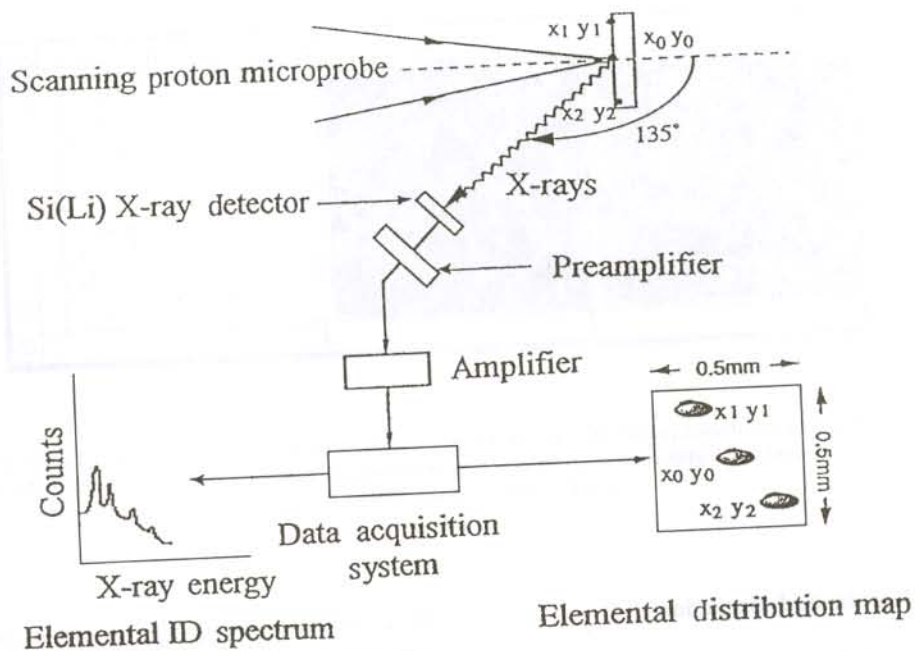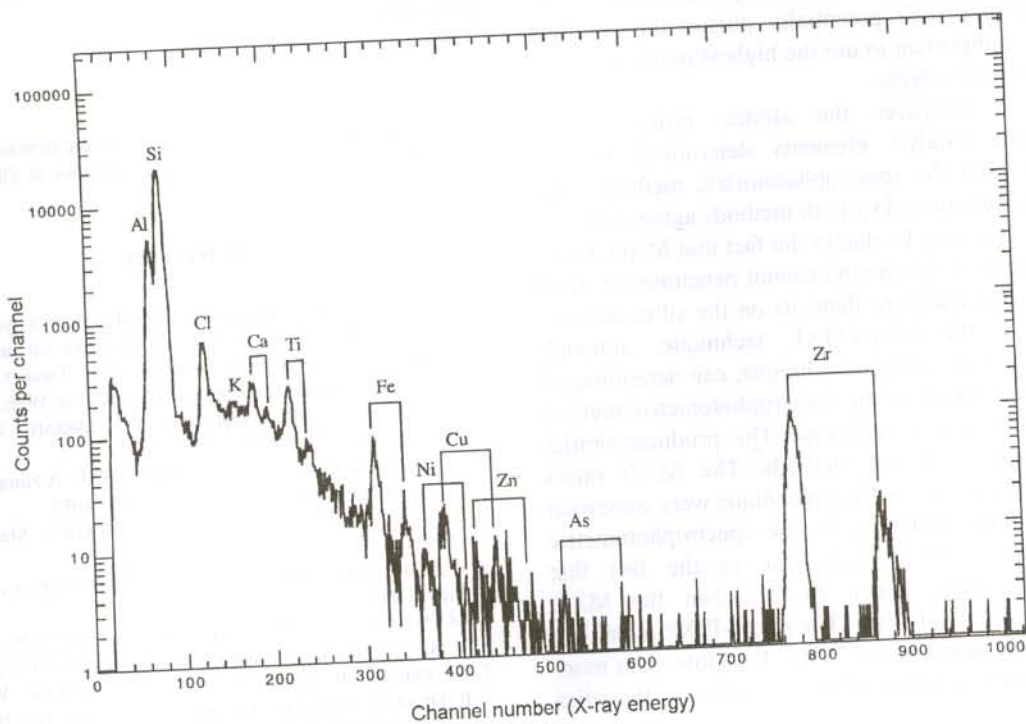| Sample No.	Heterogenization procedures	Elemental ratios (atomic)			
		Spectrophotometric		Micro-PIXE	
		Si:Al	Al:Zr	Si:Al	Al:Zr
1	Silica/MAO/Et(Ind)$_2$ZrCl$_2$	2.6±5%	94.0±5%	2.6±2.8%	71.9±5.2%
2	Silica/Et(Ind)$_2$ZrCl$_2$/MAO	2.6±5%	100.5±5%	2.6±2.7%	73.4±5.6%
3	Silica/MAO-Pretreated Et(Ind)$_2$ZrCl$_2$	2.7±5%	216.6±5%	2.7±2.5%	204.3±5.8%

Fig. 1. A schematic diagram of the micro-PIXE set up used

Fig. 2. A typical X-ray energy spectrum from a scanned area of about 500 μm×500 μm on the catalyst pellet of sample #1, showing the presence of several trace element impurities

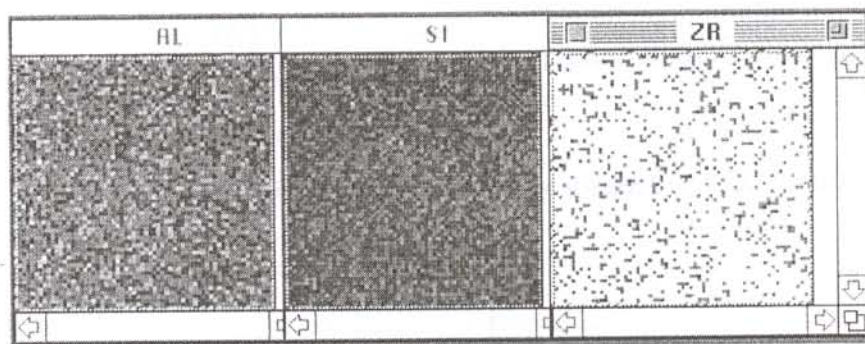*Fig. 3.* Spatial elemental distribution profiles from a scanned area of about 500 μm×500 μm on the catalyst pellet of sample #1. Darker shades indicate higher concentrations. The total raw gross counts in these maps are 36070±190 for Al, 159419±399 for Si and 792±28 for Zr

Results and discussion

A typical micro-PIXE energy spectrum from one of the samples is shown in Fig. 2. It indicates the presence of several trace element impurities such as K, Ca, Ti, Fe, Ni, Cu, and Zn. The source of these impurities was determined to be the starting catalyst materials. Since these impurities may potentially poison the resulting catalyst, it is important to use the highest purity materials to minimize their effects.

Table 1 compares the atomic ratios of the heterogenized catalyst elements determined by the micro-PIXE and the spectrophotometric methods. The Si : Al ratios determined by both methods agree well with each other. This may be due to the fact that MAO, being a bulky oligomeric compound cannot penetrate the small silica pores and therefore deposits on the silica surface. As a result, the micro-PIXE technique, although relatively a surface analysis technique, can determine all the available Al as does the spectrophotometric method which is a bulk analysis technique. This produces similar Si : Al ratios by both the methods. The Al : Zr ratios determined by the micro-PIXE technique were somewhat lower than those measured by the spectrophotometric method. This is most likely due to the fact that $Et(Ind)_2ZrCl_2$, being much smaller than the MAO penetrates the pores of silica. The micro-PIXE technique with its probing depth of 10–20 m^2, therefore, sees more Zr than Al which is deposited on the surface of the silica matrix.

The elemental distribution maps obtained showed that the dispersions of Al and Zr on the silica support were uniform for all the three types of samples prepared by different heterogenization methods. Figure 3 shows the distribution profiles of Al, Si and Zr for sample #1 as an example of such homogeneous dispersions. This important feature of a good catalyst as demonstrated for all the three samples studied indicate that the bulky MAO co-catalyst having a degree of oligomerization of 14 does not affect the heterogenization process, irrespective of the variations in the heterogenization procedures.

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