POLYMERIZATION OF ETHYLENE OVER PLANAR MODEL ZIEGLER-NATTA CATALYST: TESTING A HIGH PRESSURE REACTOR

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Polymers like polyethylene (high density polyethylene) and polypropylene are tough materials and therefore resistant to harsh conditions of the environment. The increased use of polymers relates to the economic reasons. They are lighter materials and they can be manufactured and processed with lower energy input than metals and glass. In the present work polymerization of ethylene (at low pressures) using a flat model system by deposition of $MgCl_2$ from ethanol solution, by means of spin coating, on silica wafers, followed by treatments of $TiCl_4$ and contact with the cocatalyst (AlR_3) has been initially tested using a Schlenk reactor. These systems are active for ethylene polymerization and offer highly favourable opportunities for surface characterization and imaging. Additionally, a new autoclave reactor is introduced and tested for ethylene polymerization utilizing a Ziegler-Natta catalytic system. The aim was to compare activities and morphologies of the polymer films obtained by these catalytic systems in both reactors bearing in mind that the autoclave reactor allows variation of both temperature and pressure in ethylene polymerization.

Keywords: Ziegler-Natta catalysts, high pressure reactor, catalytic activity

Introduction
Prevoius work on Ziegler-Natta catalysis demonstrated an approach to build a flat model system using deposition of $MgCl_2$ from ethanol solution, by means of spin coating, on silicon/silica wafers, followed by treatments to introduce $TiCl_4$ and before contact with the cocatalyst, Andoni (2009). These systems were active for ethylene polymerization and offered highly favorable opportunities for surface characterization and imaging. A similar approach incorporating donor molecules was shown to be successful with regard to the formation of polypropylene.

While this method led to the formation of nanoparticles/nanograins, controlled annealing of a spin-coated layer by Ostwald ripening proved to be a feasible method to prepare well-defined crystallites of the $MgCl_2$-support, Andoni et al (2007). This opened the possibility to study Ziegler-Natta catalysis on surfaces with different structures. This is a usual feature of surface science on extended single crystals, but is less obvious for magnesium chloride phases. Using such samples, the role of internal donors such as 9,9–bis(methoxymethyl)fluorene, diisobutyl phthalate and ethyl benzoate in the formation of magnesium chloride crystallites was demonstrated, along with implications for the location and nature of the catalytically active titanium chloride species.

In the present work we will introduce a new autoclave reactor which has been tested for ethylene polymerization utilizing a Ziegler-Natta catalytic system. The aim was to demonstrate that kinetic studies are possible, bearing in mind that the autoclave reactor allows variation of both temperature and pressure in ethylene polymerization.

Experimental/Materials/Catalyst/sample preparation and reactor for ethylene polymerization
Anhydrous magnesium chloride (beads, 99.9 %), absolute ethanol (99.9 %), titanium tetrachloride (99.9 %) and triethylaluminium (25 wt% in toluene) were purchased from Aldrich Chemicals and used as received. HPLC-grade toluene was taken from an argon-flushed column packed with alumina and stored over 4 Å molecular sieves. Ethylene was supplied by Praxair (3.5).

All manipulations of air- or water-sensitive compounds were carried out using standard glove box techniques. The $MgCl_2 \cdot n$EtOH support and SiO_2/Si(100) wafer used in this work for ethylene polymerization (autoclave reactor) were prepared as described in the preceding work, Andoni et al (2007). The wafers were treated with a 10 % v/v $TiCl_4$ solution in toluene at room temperature for 30 min. After washing with toluene to remove the physisorbed $TiCl_4$, the model catalyst was dried under nitrogen.

The reactor used for ethylene polymerization was a new autoclave reactor as displayed in Fig. 1 (left picture). This set up consists of two reactors, each of which is 100 mL in volume and equipped with a magnetic stirrer. In each reactor independently, the temperature can be set between room temperature and $150^{o}C$ and pressures up to 10 bar can be applied. A metal holder, shown in Fig. 1 (right picture), is made to hold wafer samples in the reactor. Five pieces of wafer of 2×2 cm^2 can be placed into the reactor at the same time by using this holder.

The set up allows us to compare catalysts under the same conditions. The right-hand reactor serves as a pre-mixing vessel, in which solvent and cocatalyst (e.g. $AlEt_3$) are pressurized with ethylene at a desired pressure and temperature. The left-hand reactor is the actual polymerization reactor, where the $SiO_2/Si(100)$ wafers with the immobilized catalysts are located. The reactors are connected by a pipe. After the solvent with cocatalyst is saturated with ethylene in the pre-mixing reactor, the transfer to the polymerization reactor through the pipe may occur and the polymerization can start instantly. This procedure yields a well-defined starting point of the polymerization. The ethylene pressure remains constant during the polymerization in the actual reactor. Release of the ethylene pressure and removal of the wafer samples out of the solution will stop the polymerization.
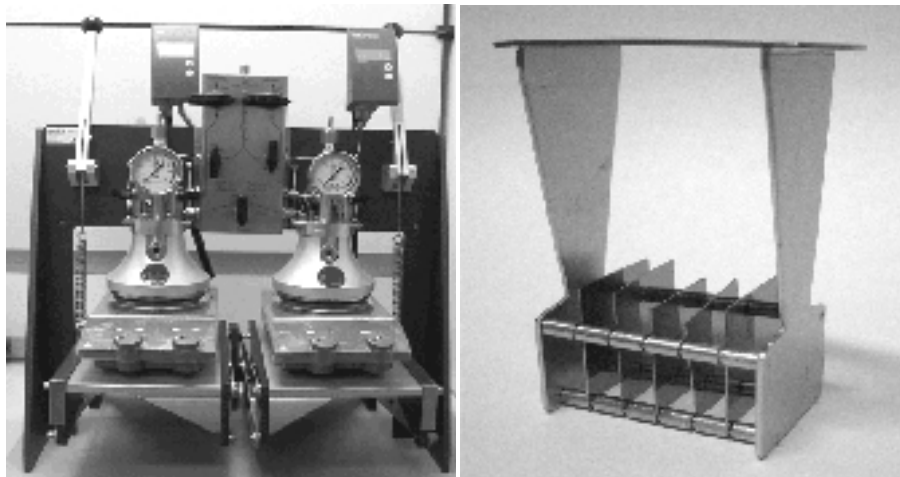

Fig. 1: Autoclave reactor setup for polymerizations and a sample holder with five pieces of $SiO_2/Si(100)$ wafer samples.

Results and dicussion

In the preceding work ethylene or propylene polymerizations were carried out in a Schlenk reactor, Andoni et al (2007, 2009). The polymer layer of polyethylene grown after 16 hours reached a thickness of ~ 100 µm. Furthermore, scanning electron microscopy of these films revealed pillary polymer growth, in the direction perpendicular to the flat support surface. In the present work, the spin coated support was treated with $TiCl_4$ and transferred in a sealed bottle to another glove box in which the autoclave reactor was located. The polymerization was run at room temperature and 2 bar ethylene pressure for 16 hours (note that concentration of the cocatalyst in toluene was 10 times the concentration used in the preceding work).

The polymer film produced with Ziegler-Natta catalyst was imaged by SEM. Fig. 2 displays lateral views of polyethylene grown on the Si wafer after 16 hours polymerization under very mild conditions, similar to the conditions of the former work. As can be observed from these images, the thickness of the polymer layer does not exceed more than ~ 30 µm, which may indicate some deactivation during the sample transfer. Water adsorbs on the edges and corners of $MgCl_2$, which is a very hygroscopic substance. Fig. 2d represents a SEM image of a $MgCl_2$ crystallite obtained after the spin coated layer was subjected to Ostwald ripening process and exposed to air very shortly before imaging. Water adsorption along the edges of the crystallite is indicated by the arrows.
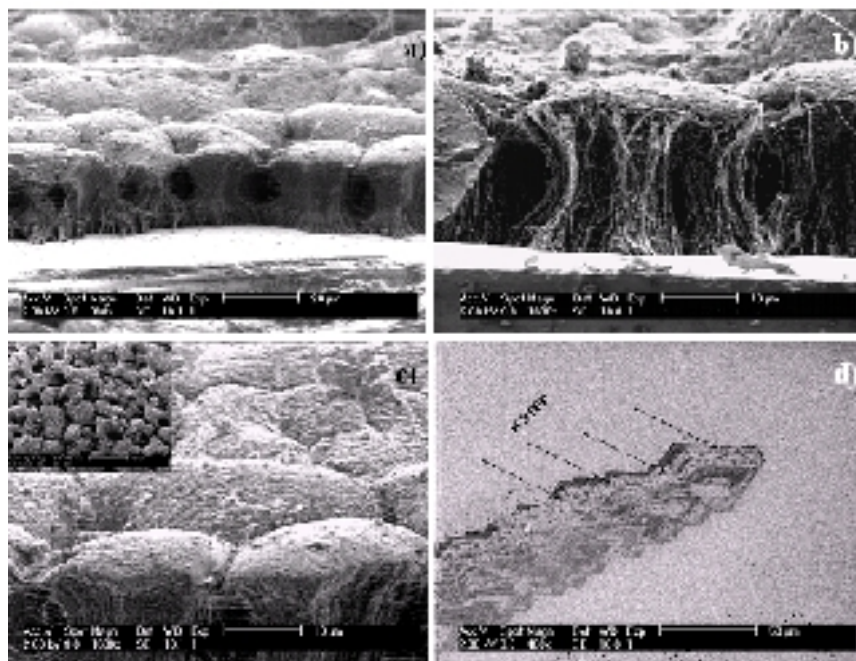
Fig. 2: a), b) and c) SEM (side view) images of polyethylene grown on a Si wafer-immobilized MgCl$_2$/EtOH/TiCl$_4$ catalyst after 16 hours polymerization at 2 bar monomer pressure and room temperature. The inserted SEM image represents the top view of the polyethylene. d) MgCl$_2$/ethanol deposited on Si wafer via spin coating and subjected to Oswald ripening process and exposure to air.

However, the most important observation from the above images (lateral views) is the pillary structure also noticed in the polyethylene films produced with the Schlenk reactor. These pillars appear to be separated from each other. In the SEM images of former work, Andoni (2009) the lateral views indicated formation of densely packed pillary structure for polyethylene, which is not the case in the images in Fig. 2a, b and c. Again, this may be due deactivation of the MgCl$_2$/TiCl$_4$ catalytic system by water, giving rise not only to a decrease in the thickness of the polymer layer (i.e. yield) but also causing shrinkage of the polymer film. The latter can be also observed from the inserted top-view SEM image in Fig. 2c. Placement of the spin coating device in same glove box where the autoclave reactor is located should prevent water contamination during transfer and provide realistic activities.

Conclusion

In the current study we described briefly that a new autoclave reactor can be applied to Ziegler-Natta catalysts aiming to obtain kinetic information for this system. SEM images indicated yet again formation of the pillary structures for the polyethylene films. This morphology was comparable with the one obtained with the former method (polymerization in Schlenk reactor). The decrease in the activity of the catalyst when comparing both systems was attributed to water contamination during sample/catalyst transfer.

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