

Effect of ethylene monomer pressure on BCE Ziegler-Nata catalyst fragmentation in the early stage of polymerization

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Abstract

In order to investigate ethylene monomer pressure on fragmentation and in the morphology of the BCE Ziegler-Nata catalyst particles ($\text{TiCl}_4/\text{MgCl}_2$) in the early stages of polymerization reaction, polymerization was carried out at a 3.0 bar to 4.5 bar of the ethylene monomer pressure. Scanning electron microscope (SEM) has been used to investigate the effect of ethylene monomer pressure on morphology of the catalyst particles. SEM images show that with increasing pressure size of pores and cracks of the catalyst increases. Meanwhile activity of the catalyst was linearly increased from 16.0 to 18.6 ($\text{gPE} \cdot \text{mmolTi}^{-1} \cdot \text{h}^{-1}$) with increasing of the monomer pressure.

Keywords: Ziegler-Natta catalyst, ethylene polymerization, fragmentation, morphology, SEM

Introduction

Undoubtedly one of remarkable discoveries in the field of polyolefins was the discovery of the Ziegler-Nata catalyst [1]. In the catalytic polymerization of polyolefins, the final polymer morphology produced is under influence of the changes which may happen in the morphology of the catalyst and its fragmentation in the early stages of the polymerization [2]. The catalyst fragmentation requires a high porosity in the catalyst to lead the monomer into the catalyst particles and carry out the polymerization on the internal active sites. The hydraulic pressure of the polymer produced inside the catalytic pore causes the catalyst fragmentation [3, 4].

Experimental/Theoretical

Polymerization reaction of ethylene was carried out in a buchi metal reactor of 1 L in the presence of triethylaluminum (TEA) as a cocatalyst. In order to investigate the effect of pressure on BCE Ziegler-Natta catalyst ($\text{TiCl}_4/\text{MgCl}_2$) fragmentation, the polymerization reaction was carried out at to 3.0 bar to 4.5 bar of ethylene monomer pressures, 84

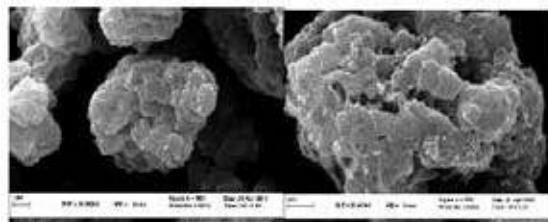


Fig. 1. The original SEM image of the catalyst.

°C, reaction time of 5 min and 25:1 M ratio of cocatalyst to catalyst. In all of the reactions, slurry polymerization was carried out in hexane. At the end of the polymerization catalyst particles was washed using hexane containing anhydrous THF (THF/Ti: 200/1 mole ratio) [5] and dried under vacuum.

Results and Discussion

SEM images of the original catalyst are shown in Fig. 1, with an average catalyst particle diameter of about 12.0 μm . In order to investigate the effect of ethylene pressure on morphology and the catalyst activity in the early stages of the polymerization, polymerisation was performed at different pressures of ethylene monomer. The results of the activity analysis indicate that by increasing of the pressure of ethylene monomer, activity of the catalyst was linearly increased (Fig. 2). SEM images show that with increasing

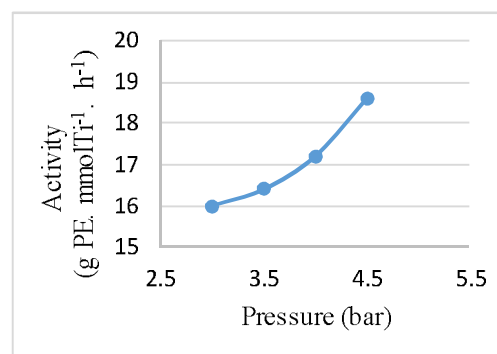


Fig. 2. Effect of monomer pressure on activity of the catalyst.

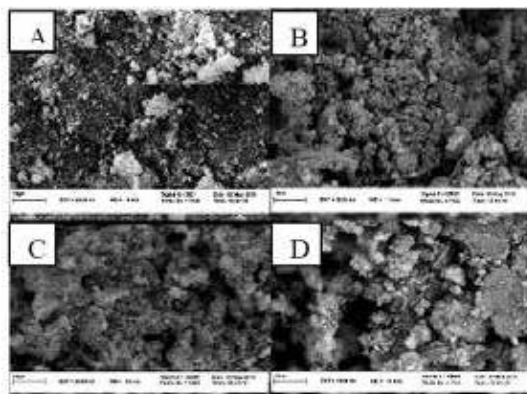


Fig. 3. SEM images of monomer pressure on the catalyst fragmentation: (A) 3.0 bar, (B) 3.5 bar, (C) 4.0 bar, and (D) 4.5 bar.

of the monomer pressure, size of the porosity and cracks in the catalyst was increased. The behavior could be due to the greater penetration of the monomer into the catalyst particle and the polymerization in the active sites, which produce higher hydrolytic pressure into the pores of the catalyst (Fig. 3).

Conclusion

The polymerization results was shown that with increasing pressure of the monomer, the catalyst activity was linearly increased. The SEM images was shown that the size of pore and catalyst cracks tends to increase with increasing of the monomer pressure too.

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