

CHAPTER I

INTRODUCTION

1.1. Introduction

Polyolefin industries began in the 1950s due to the discovery of $TiCl_3$ catalysts by Ziegler and Natta. However, catalyst activities and stereospecificities were very low. In 1968, $MgCl_2$ has been almost invariably used for all supported catalysts of practical interest, because it allows the catalysts the high activity and stereospecificity.

Supported catalysts enable the use of high activity polymerization system with negligible reactor fouling, and the same time producing polymer powders of good morphology and high bulk density. Catalyst preparation methodology is the great commercial interest, as it can influence catalyst activities and kinetics, catalyst morphologies and polymer properties. Choice of support, support treatment and use of electron donor and novel Ti species are important.

The most important factor is the morphology of the catalyst particles replicated from its support. The spherical of support is the key point of preparation. Several methods have been used to prepare the "active" $MgCl_2$ are as follows: [1]

- 1) Chlorinating an organomagnesium compound such as butyloctyl magnesium (BOMAG) or butylethyl magnesium (BEM), or Grignard agent and precipitating the formed $MgCl_2$ from a hydrocarbon solvent [2].

- 2) Dissolving or dispersing $MgCl_2$ into a hydrocarbon by using certain surfactants with partial polarity to form a solution, emulsion or suspension, then precipitating $MgCl_2$ to be solid particles [3-6].

- 3) Direct chlorination and titanation of coarse magnesium ethoxide ($Mg(OEt)_2$) to form both the support component and catalyst component *in-situ* at the same time [7,8].

4) Dissolving $\text{Mg}(\text{OEt})_2$ into a long chain alcohol like 2-ethyl hexanol, or ethanol under pressure of carbon dioxide. $\text{Mg}(\text{OEt})_2$ is converted to magnesium hydrocarbyl carbonate, followed by titanation with TiCl_4 [10].

The $\text{Mg}(\text{OEt})_2$ supported catalysts synthesized were used for olefin polymerization. In the preparations reported in the literature, the high hygroscopic nature of MgCl_2 caused a problem that its reaction with TiCl_4 needs to be done in the absence of alcohol. Further, problem concerning morphology control of polymer, for example, particle size and shape, particle size distribution and bulk density still exists. This is due to the rough shape and big particle size closely 700 micron of $\text{Mg}(\text{OEt})_2$. At the first time, mechanical wet-milling or jet-stream impact milling $\text{Mg}(\text{OEt})_2$ was applied to increase surface area. However, the particle size distribution of milled support is still broader and milling time is too long [9].

It has been reported that the magnesium precursor prepared by solution route showed good morphology of polymer compared with the solid route. For example, the use of butyloctyl magnesium (BOMAG) or butylethyl magnesium (BEM) is found to control morphologies of particles to spherical shape more easily than using $\text{Mg}(\text{OEt})_2$ or MgCl_2 .

Recently, it has been reported the morphology of starting magnesium ethoxide can be controlled by conversion to magnesium ethyl carbonate via the reaction of magnesium ethoxide with carbon dioxide [10]. However, several factors affecting the preparation have not been studied such as particle size of supported catalyst, type of chlorinating agent and reaction time of preparation etc. Therefore, in this work we are interested in the study of preparation of supported Ziegler-Natta catalyst via solution route with carbon dioxide in order to control the morphology of the supported catalyst and utilize the prepared catalyst for producing high density polyethylene.

1.2. Objectives

- 1). To synthesize supported Ziegler-Natta catalysts from magnesium ethyl carbonate and to control morphologies of *in-situ* formed magnesium chloride support.
- 2). To evaluate performances of the synthesized supported Ziegler-Natta catalysts in ethylene polymerization.

1.3. Scope of the research

- 1). Search the literature.
- 2). Prepare and characterize magnesium ethyl carbonate.
- 3). Prepare and characterize supported Ziegler-Natta catalysts.
- 4). Perform ethylene polymerization and characterize polyethylene powder.
- 5). Compare the properties of the polyethylene obtained from this work with those prepared from commercial catalyst.
- 6). Summarize the results and write thesis.