CHAPTER I

INTRODUCTION

The discovery of metallocene catalysts along with a methylaluminoxane (MAO) cocatalyst was revealed to be highly active for homogeneous polymerization of α-olefins [1,2], aroused an economic interest, as it became clear that this could compete with the conventional Ziegler-Natta catalysts. These new generation catalysts are capable of producing a variety of polyethylene copolymers, all with different chain compositions and architecture. However, they are more active than Ziegler-Natta catalysts only as homogeneous metallocene systems. In order to apply metallocene catalysts in modern gas-phase and slurry olefin polymerization processes, they need to be heterogenized on a support.

Homogeneous metallocene catalysts have two major disadvantages : the lack of morphology control and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks. Many inorganic supports such as SiO_2, Al_2O_3 and $MgCl_2$ have been investigated [3-9]. It was reported that silica is perhaps the most attractive support so far. However, the properties of silica itself may not be completely satisfied for all purposes based on the polymers produced. Thus, the modification of silica properties is necessary in order that it can be used efficiently. It has been reported that a new immobilization method of introducing a spacer group between the support and metallocene resulted in higher catalytic activity [10,11].

The use of silane-modified silica-supported methylaluminoxane (MAO) with $Et[Ind]_2ZrCl_2$ catalyst for ethylene/α-olefin copolymerization was studied by Jongsomjit *et al.* [12]. The copolymerization of ethylene/α-olefin via mixed Ti/Si supported MAO with zirconocene catalyst was also investigated in our Laboratory [13,14]. It was found that mixed Ti/Si supported resulted in an increase in the activity of ethylene/α-olefin copolymerization. It was reported that zirconia can be used as a modifier for supports such as silica [15] and alumina [16]. It revealed that catalytic properties increased with the zirconia modification as well. Therefore, it would be

interest to investigated how the zirconia modification can do in the supported metallocene catalytic system.

This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literatures dealing with metallocene catalysis for olefin polymerization were presented. The literature review was accentuated metallocene catalyst system used for copolymerization of ethylene with α-olefins. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers were also described in Chapter III.

In Chapter IV, the results on ethylene and α-olefins copolymerization were presented. The impact of zirconia modification on silica-supported metallocene catalyst via ethylene/1-olefins copolymerization including develop a better understanding on how zirconia modification changed the nature of silica-supported metallocene catalyst in terms of activities and stereospecificity were investigated. The characteristics of the modified supports and catalyst precursors using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetic analysis (TGA) and N_2 physisorption. The obtained copolymers were characterized using SEM, differential scanning calorimetry (DSC) and ^{13}C-nuclear magnetic resonance (^{13}C NMR).

Finally, conclusions of this work and some recommendations for future research work were provided in Chapter V.

1.1 Objectives of the thesis

1.1.1 To investigate the impact of zirconia modification on supported metallocene catalyst via ethylene/1-olefin copolymerization.

1.1.2 To develop a better understanding on how the zirconia modification changes the nature of supported metallocene catalyst in terms of activities and properties.

1.2 Scope of the thesis

In this thesis, impact of zirconia modification on the silica-supported metallocene catalyst was investigated. Experimentally, the zirconia-modified silica was prepared by impregnation of a zirconium (IV) n-propoxide solution onto the silica subsequently, reacted with MAO. Then, to use the modified support as the supported metallocene catalyst to perform copolymerization of ethylene/1-olefin. The characteristics of the modified support and catalyst precursors were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX), thermogravimetic analysis (TGA) and N_2 physisorption. The obtained copolymer using SEM, differential scanning calorimetry (DSC) and ^{13}C nuclear magnetic resonance (^{13}C NMR).