CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

From the present work, it can be concluded that:

1. The in situ activated zirconocene system by supported borane co-catalyst improved the catalytic performance for ethylene polymerization over the pre-activated zirconocene system.
2. The in situ activated metallocene system showed better catalytic performance than the pre-activated metallocene system in time scales up to 60 min.
3. For in situ activated Cp_2ZrCl_2/TIBA system, the activity was independent of time while the pre-activated Cp_2ZrCl_2/TIBA system showed faster deactivation after their initial period.
4. MW and MWD of both pre-activated and in situ activated metallocene systems were not significantly different, but the bulk density was a factor of 3 and higher than the homogeneous system.
5. Both of the pre-activated and the in situ activated metallocene systems could reduce the fouling and produced good morphology polymer products with high density.
6. Stabilizing supported borane using carbenium and anilinium salts could reduce the extraction of borane from the surface of silica support.
7. The contribution of carbenium borate supported co-catalyst gave higher productivity for ethylene polymerization than that of anilinium borate supported co-catalyst.
8. Polyethylene produced from carbenium borate supported co-catalyst had higher MW and bulk density of polyethylene than that from anilinium borate supported co-catalyst.
9. Polyethylene particle produced from both carbenium and anilinium borate supported co-catalyst systems had good morphology and replicated the original shape of silica support.

10. The pretreatment of silica support with alkylaluminum improved the co-catalytic performance of carbenium borate supported co-catalyst.

11. Carbenium borate supported co-catalyst pretreated with TEA gave a higher productivity than that pretreated with TIBA.

12. The pretreatments with alkylaluminum did not affect the supporting borane over surface of the silica support.

13. The produced polyethylene was obtained spherical particle replicated from the original shape of silica support.

7.2 Recommendation for Future Work

7.2.1 Effect of Alkylating Agent on In-situ Metallocene by Supported Borate Co-catalysts

In "MAO-free" ethylene polymerization, a high productivity can be obtained by using organoborane compound as effective co-catalyst for metallocene instead of MAO, as well as using supported borane version. For the present work, TIBA has dual function of scavenging the impurities as well as being the alkylating agent for Cp_2ZrCl_2 to create dibutyl zirconocene (Cp_2ZrBu_2). In borane co-catalyst system, Cp_2ZrBu_2 was required for reacting with borane co-catalyst systems to create zirconocenium ion (Cp_2ZrBu^+). For borate co-catalyst system, Cp_2ZrBu^+ was generated over borate-silica bound surface and effective species for ethylene polymerization.

Since other available alkylaluminums, such as trimethylealuminum (TMA), triethylaluminum (TEA), trioctylaluminum (TOA), they could also be used as alkylating agents for metallocene dichloride. Due to different alkyl group of these alkylaluminum, it can directly influence the rates of alkylation and polymerization. For smaller alkyl group, it can provide higher speed rate of polymerization than the larger one, but compensate to increase deactivation rate of the catalyst. However, a high reaction rate can essentially improve productivity of the polymerization. Moreover alkyl-lithium compounds are alternative alkylating agents for the same purpose. Therefore, it is a good opportunity to employ these chemicals to improve and maintain stability of the active metallocenium species.

7.2.2 To Prepare a Supported Borate on Polymer Supports

Olefin polymerization based heterogeneous metallocene provides many advantages such as fouling-free reactor, high bulk density of polymer product, producing polymer with good morphology. Generally the active metallocene were supported on the surface of inorganic solids. From the present work, it was found that the chemical pretreatment of the support was of considerable importance to obtain high active supported co-catalyst. The desire to rationally modify the chemical and structural properties of the supporting material had recently led to investigations of organic supports for olefin polymerization. However, there was no general method currently available for the binding of these catalysts to a support that would allow the direct and rapid comparison of a wide variety of different catalysts under commercially relevant conditions.

Polymer supports such as crosslinked polystyrene beads or Merrified resin, posses several of the attributes of an idea catalyst support. They are unreactive to the metallocene cation, commercially available in different sizes and crosslinking densities, and amenable to numerous functionalization procedures utilizing both nucleophilies and eletrophiles. A particularly important property of lightly crosslinked beads is their ability to swell in organic solvents. Therefore, it is possible to functionalize the interior volume of the bead so that the catalytic species reside within a mobile, essentially isotropic, hydrocarbon-rich matrix. Such a microenvironment clearly bears closer resemblance to the organic solution in which metallocene catalyzed polymerization is typically studied than a traditional catalyst support in which the active species is localized at the interface between a rigid inorganic surface and the solution. Furthermore, the potential to vary the amount of crosslinker and the swelling behavior and flexibility of the support provides an opportunity to investigate directly the influence of the mechanical properties of the support on the progress of the polymerization.