CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

7.1.1 Incorporation of CaO during *in situ* polymerization of propylene employing the Ziegler-Natta catalyst showed activity enhancement during the initial stage of polymerization through the reduction of Ti^{4+} to Ti^{3+} which was verified by ESR results. The effect was maximum at Ca/Ti mole ratio = 6. The results also suggested that the presence of inorganic filler even in smaller amounts could improve catalyst against deactivation. However, while the overall catalytic activity increased the stereo selectivity apparently decreased. The properties of the resulting polymer such as T_m, X_c and morphology did not change with varying the mole fractions of Ca/Ti.

7.1.2 The effects of aluminoxane compounds were studied in propylene polymerization with Ziegler-Natta catalyst. TEA was used as activator while MAO/SiO_2, MMAO/SiO_2, dMMAO/SiO_2 and dMMAO were employed as co-activator. The impregnated support showed high surface area and high Al dispersion, but less pore size and pore size distribution. All aluminoxane compounds were active in the polymerization. Catalyst activity was improved in the order of dMMAO/SiO_2 > MAO/SiO_2 > MMAO/SiO_2 > SiO_2-free > SiO_2, which was in a reverse trend according to the degree of interaction. In other words, the strong interaction caused a decrease in catalytic activity. Moreover, polymer crystallinity slightly increased, whereas no significant change in the melting temperature was observed. The constant of *mmmm* pentad suggested that an increase in the number of active centers plays an important role in activity enhancement rather than the improved k_p.

7.1.3 Poisoning materials showed a remarkably effect on the lowering of catalytic activity without improving in catalyst stereospecificity. Methanol exhibited the strongest deactivation power comparing to acetone and ethyl acetate due to its high reactivity to form titanium chloride alkoxide which was inactive in polymerization. In alcohol series, 1-butanol clearly provided stronger poison ability as

a consequence of the higher dissolve capability to the catalyst support and high steric complex formation presented beside the active site. The interaction of acetone and ethyl acetate might obstruct or impose some restrictions on the Ti coordination leading to active site destruction. A precise kinetic study with the stopped-flow method for the effect of the methanol pretreatment revealed that the deactivation was completed due to the decrease of the number of the active centers by methanol, and quite insensitive to the types of the active sites, keeping the k_p value as well as the stereoregularity of the obtained polymers at constant in the presence and absence of methanol pretreatment.

7.2 Recommendations

7.2.1 In the preliminary study on the effects of metal oxide, we have attempted on testing several families of such compounds. The results showed interestingly for the case of ZnO which have a similar influence on the polymerization performances as well as CaO. Further investigation of the controlled amount of hydroxyl group on the CaO or ZnO appears to be an interesting issue since there were no surface modification in this study and these hydroxyl moieties are more likely to suppress the active site formation or even alter the cocatalyst chemistry. Regarding to the observation, the clarification of the incorporated metal oxide during active site formation is still far from clear. In the sense that metal oxide have some interaction with the catalytic site, it should distribute throughout the polymer even small amount were used. Therefore, the use of X-ray photoelectron spectroscopy (XPS) would be a powerful tool to detect the presence of metal oxide atom on the surface of polymer.

7.2.2 Although the supporting effects of dMMAO on amorphous silica as co-activator were found to polymerize propylene with higher activity, more detailed studies on the aluminoxane compounds, i.e. MAO, MMAO, without any immobilization could present benefits on obtaining a better understanding of their roles in the course of polymerization. They could moreover take part in the chain transfer process. Therefore, GPC analysis on the molecular weight of resulting polymer should be further investigated.

7.2.3 For the case of poisoning effect elucidation, more detailed study on the polymer properties including the distribution state of polypropylene crystallinities which reflect the distribution state of isospecific sites should be further investigated in terms of temperature rising elution fractionation analysis (TREF). This is considered to answer the question what and how active sites have been altered by the poisoning materials, and it is supposed to confirm whether such reagents could kill the active site selectively. Furthermore, it would be beneficial to perform more detailed kinetic studies in the presence of ethanol, 1-butanol or even more bulky structure alcohol such as 2-ethyl-1-hexanol to investigate not only the destruction impact but also the steric effect on the catalyst nature.