CHAPTER IV

CALCIUM OXIDE INFLUENCE ON POLYMERIZATIONS AND POLYMER CHARACTERISTICS

4.1 Introduction

The titanium-based Ziegler-Natta catalytic system is extensively used in an industry for polyethylene and polypropylene production. Over the years, the catalyst has evolved from simple $TiCl_3$ crystals into the nowadays used high-surface-area industrial catalyst consists of $TiCl_4$ supported on activated $MgCl_2$ particles [107]. The preparation of highly active $MgCl_2$ was first announced by ball milling of anhydrous $MgCl_2$ and $TiCl_4$ together [18]. This led to the breaking of the $MgCl_2$ layered structure and the reduction of its crystallite size. The consequence is that the specific surface area of the catalyst and its activity increase significantly, however, the morphology of the catalyst cannot be controlled [44]. On the other hand, the reaction of $MgCl_2$ with a Lewis base, typically an alcohol, treated with an excess of $TiCl_4$ can produce super active catalyst with morphology improvement [34]. The use of these spherical $MgCl_2$ adducts as the catalyst support gives rise to the increased activity and also controls polymer morphology via a replica phenomenon [174,175].

$MgCl_2$ is considered an efficient dispersant of active titanium, and its electronic interaction with the active titanium species is believed to enhance polymerization activity [176,177]. Some literatures have reported the modification of $TiCl_4/MgCl_2$ based catalysts by doping inorganic compounds in the support, such as $ZnCl_2$ [43], $MnCl_2$ [178], $AlCl_3$ [179] and NaCl [180]. The modified support appeared to change the crystal structure of $MgCl_2$ leading to the variation in potential active site. Therefore, doping the catalyst support becomes an effective way of regulating active site distribution through an increased catalyst heterogeneity that produces polymer mixtures with widely varying molecular weights and microstructures.

The other example of incorporated inorganic particles is *in situ* polymerization. In contrast to the doping support, the direct addition of inorganic material during polymerization is conducted to produce polymer composite instead of using conventional extrusion [181] or injection molding [182]. The former appears to be superior to the latter in several ways including high particle distribution and improved mechanical properties with low filler-particle concentration. However, some drawbacks have been faced. The chemical incompatibility of nonpolar propylene around hydrophilic inorganic metal such as surface silanol functionalities of metal oxide [183] and the catalyst sensitivity toward these oxophilic species [184] cause the process not facile. Moreover, microsized filler particles can cause masking or pore blockage thereby obscuring the active sites in the course of polymerization resulted in lowering of activity [185].

In our previous study, Suwaree [186] have demonstrated the effects of Fe_2O_3 on the catalytic activity improvement over the classical unsupported ZN catalyst. The result showed the enhancement of initial polymerization rate with the addition of Fe_2O_3 at a Fe/Ti mole ratio of 0.02. It might be speculated that the Fe_2O_3 have a capability to oxidize the lower Ti valence state to higher value through the exchanged oxidation-reduction process between Fe ions and Ti species resulting in an increase of active site concentration. However, color of the obtained polymer turned out to be changed from the white product to the red one which was not commercially desirable. In this sense, for the next stage it may be useful to look more closely at the interesting feature of the metal oxide that could improve catalyst performance along with to obtain a better understanding of the metal oxide influences.

The study presented here was intended primarily to perform *in situ* polymerization synthesis of PP/CaO composites using $TiCl_4$/DEP/$MgCl_2$ catalyst in combination with TEA as a cocatalyst which has not been reported before. The influence of the Ca/Ti mole ratio on the catalytic activity and kinetics of propylene polymerization, as well as the properties and morphology of the polymer obtained, were investigated and discussed further.

4.2 Materials

The experimental details of these polymerization series are described in Chapter III. All chemicals used were chemical 1. Catalyst 1 was prepared and employed to polymerize propylene and ethylene by using reactor 1 under the same polymerization condition. CaO, with the mole ratio of Ca/Ti between 3 and 28, were added into the reactor before starting the polymerization. ESR was used to determine Ti^{3+} of a mixture of employed catalyst and TEA cocatalyst at room temperature under argon atmosphere. Polymer characteristics were analyzed by means of Soxhlet extraction, DSC, GPC 1 and SEM.

4.3 Results and Discussion

4.3.1 Titanium Oxidation States

It is well known that three various titanium valences; Ti^{4+}, Ti^{3+} and Ti^{2+} are formed by reacting $TiCl_4$ with an alkylaluminium such as AlR_3 (R = alkyl group). Ti^{3+} species is considerably active for the polymerization of both ethylene and propylene while over-reduction of Ti^{3+} to Ti^{2+} leads to ethylene polymerization only [76,86]. These transition metal oxidation states have been widely investigated through electron spin resonance (ESR) spectroscopy which is useful in detecting free radicals from paramagnetic solid materials. The ESR spectra of the catalyst solution with different addition of CaO are shown in Figure 4.1. It was noted that the amount of Ti^{3+} species could be obtained from relative intensity of a signal with a g-factor of 1.970 which was presented in all cases [71]. Increasing the Ca/Ti mole ratio was found to result in a gradual increase in the Ti^{3+} species, reaching a maximum value at the mole ratio of 6, and then the content of Ti^{3+} started to decrease. Although it is generally believed that the organoaluminium co-catalyst plays an important role in active site formation by alkylation and reduction of the titanium species, the results obviously demonstrated that small amounts of CaO addition could have some effect on the induction of Ti^{3+} species as well.

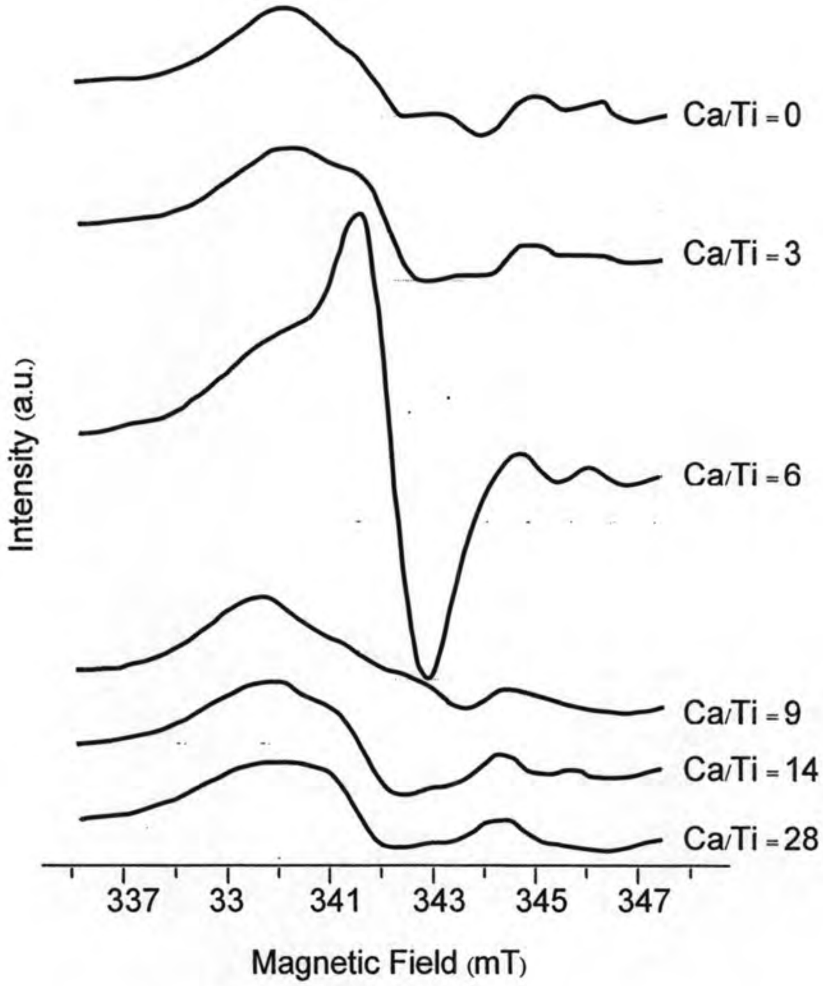

Figure 4.1 ESR spectra of the catalyst $TiCl_4/DEP/MgCl_2$–TEA treated with various Ca/Ti mole ratios.

4.3.2 Activity

In order to develop a better understanding of the effect of CaO addition, the polymerization of propylene was carried out in the semi-batch type autoclave reactor under different reaction conditions of Ca/Ti mole ratio varying from 3 to 28. The propylene consumption was measured by a mass flow meter in order to obtain the activity profiles as shown in Figure 4.2. The activity of all these catalysts exhibited a decay profile. Interestingly, without CaO addition the polymerization proceeded at low reaction rate while the incorporation of which could activate most of the active center in a first few minutes and then followed a fast decay but in higher level. To provide explanations for the aforementioned results, the catalyst activities during the ethylene polymerization were additionally determined and compared with those obtained from the propylene polymerization as shown in Figure 4.3. Only a slight increase in the value of polymerization activity of ethylene was observed while that of propylene was enhanced to attain a maximum value (the precise activity values were reported in Tables 4.1 and 4.2), in which the highest intensity of Ti^{3+} was detected, and then decreased. It was apparent that the addition of a small amount of CaO had an influence on both ethylene and propylene polymerization by increasing the values of active centers leading to monomer insertion acceleration. However, in excess amount CaO can induce over-reduction of titanium to its lower oxidation states, i.e. Ti^{3+} to Ti^{2+}, resulting in poisoning of the catalytic sites for propylene polymerization without a decrease in ethylene polymerization. It should be noted that as reported by Kashiwa *et al.* [76], the presence of Ti^{2+} was more preferred for polymerization of ethylene. The other reason to explain this behavior can be attributed to the influence of microparticle size of fillers used on catalyst deactivation.

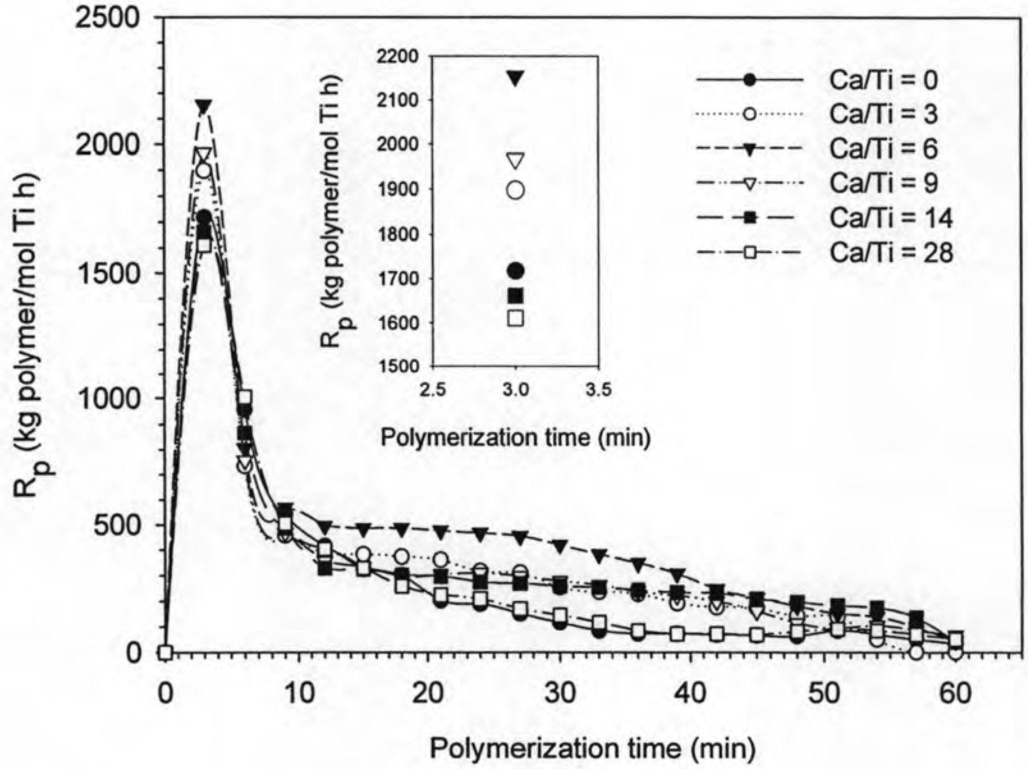

Figure 4.2 The influence of Ca/Ti mole ratio on *in situ* propylene polymerization kinetics.

Table 4.1 Catalytic activity of polypropylene at different CaO addition[a]

Ca/Ti mole ratio	Yield (g)	Activity (kg polymer/mol Ti h)
0	2.2390	355
3	2.4810	394
6	2.8406	451
9	2.3310	370
14	2.1087	335
28	1.7833	283

[a]Polymerization conditions: catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 167, solvent: *n*-hexane (30 ml), *P*: 60 psi, *T*: 60°C, *t*: 60 min.

Table 4.2 Catalytic activity of polyethylene at different CaO addition[a]

Ca/Ti mole ratio	Yield (g)	Activity (kg polymer/mol Ti h)
0	2.6905	427
6	2.7985	444
14	2.9008	460
28	2.9600	470

[a]Polymerization conditions: catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 167, solvent: *n*-hexane (30 ml), *P*: 60 psi, *T*: 60°C, *t*: 60 min.

As seen from Figure 4.4, the particle size of CaO determined by the laser light scattering analysis exhibited a very broad uni-modal particle size distribution ranging from 0.3 μm to 60 μm with an average particle size of 3 μm. García *et al.* [185] studied the *in situ* polymerization of propylene incorporation with silica employing the forth generation Ziegler-Natta catalyst and observed that SiO_2 had some implications on the catalyst deactivation by its physical deposition on the outer surface of the catalyst.

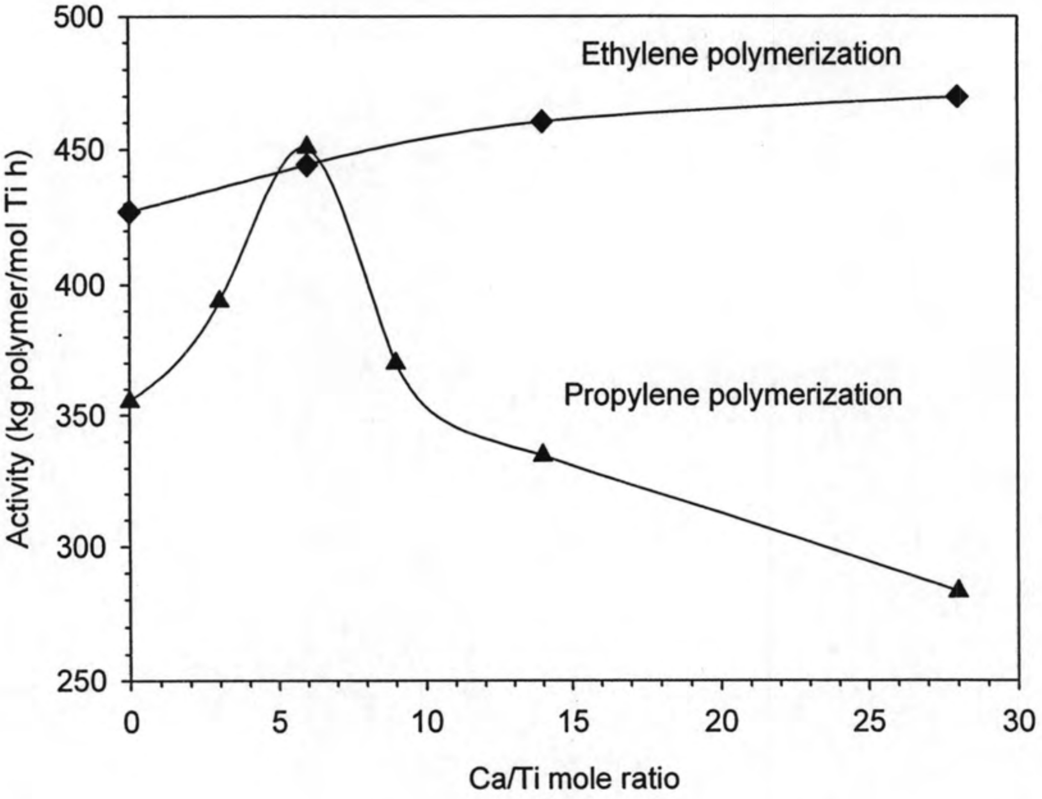

Figure 4.3 Activity comparison between propylene and ethylene polymerization.

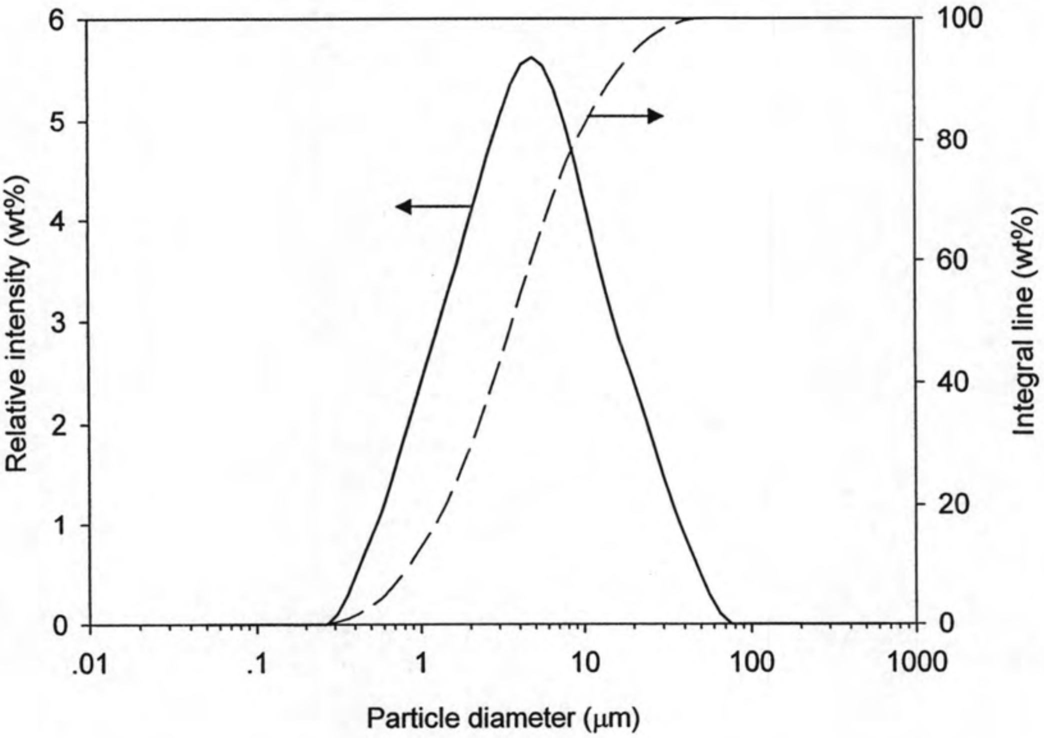

Figure 4.4 Particle size distribution for microsized calcium oxide.

4.3.3 Isotacticity

The polymers obtained were characterized and the results are illustrated in Table 4.3, consisting of yield, isotacticity index (I.I.), isotactic weight and atactic weight. It was evident that the optimum Ca/Ti mole ratio was reached at 6 in which the highest yield was obtained. In contrast, the isotacticity of polypropylene decreased with an increase in CaO content (see Figure 4.5). Although a number of active sites including aspecific sites and isospecific sites were enhanced, it was obvious that CaO had more significant effect on increasing of the atactic part while high concentrations of the doping treatment led to poisoning the isotactic sites more than the atactic sites as clearly shown in Figure 4.6.

It is generally accepted that in the presence of internal donor as a Lewis base, it competes with the $TiCl_4$ to coordinate with the vacant coordination sites especially on (110) faces of $MgCl_2$ which in turn higher acidic properties and non-stereospecific active centers. Consequently, Ti species can adsorb on the $MgCl_2$ (100) face instead to form stereospecific sites [57,187]. However, it is important to note in this work that the DEP coordinates much more weakly with the catalyst surface, so it can be easily extracted by TEA from catalyst surface during polymerization resulting in poor stereo selectivity of polymer received.

Table 4.3 Isotacticity of polypropylene obtained

Ca/Ti mole ratio	Yield (g)	I.I.[a]	isotactic PP (g)	atactic PP (g)	*mmmm*[b]
0	2.2390	87.3	1.9536	0.2854	75
3	2.4810	78.6	1.9500	0.5310	76
6	2.8406	76.1	2.1629	0.6777	74
9	2.3310	73.6	1.7165	0.6145	74
14	2.1087	71.7	1.5118	0.5969	75
28	1.7833	71.1	1.2686	0.5147	75

[a] I.I. of the insoluble boiling heptane polymer fraction.
[b] Determined by ^{13}C NMR analysis.

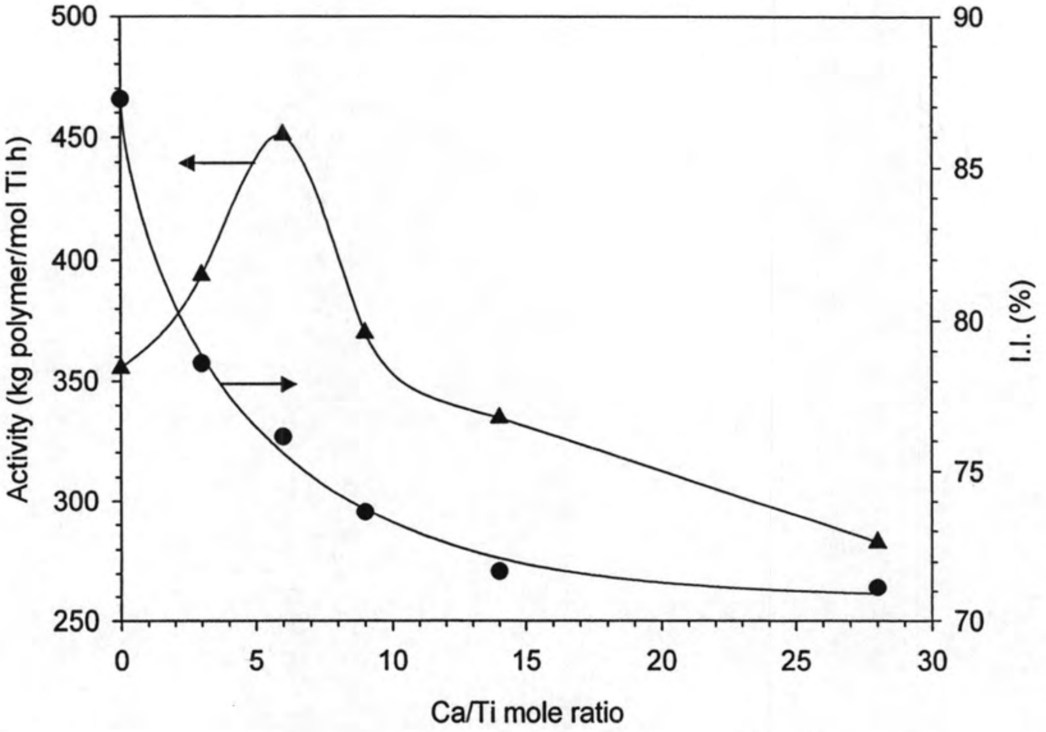

Figure 4.5 Effects of Ca/Ti mole ratio on catalyst performances.

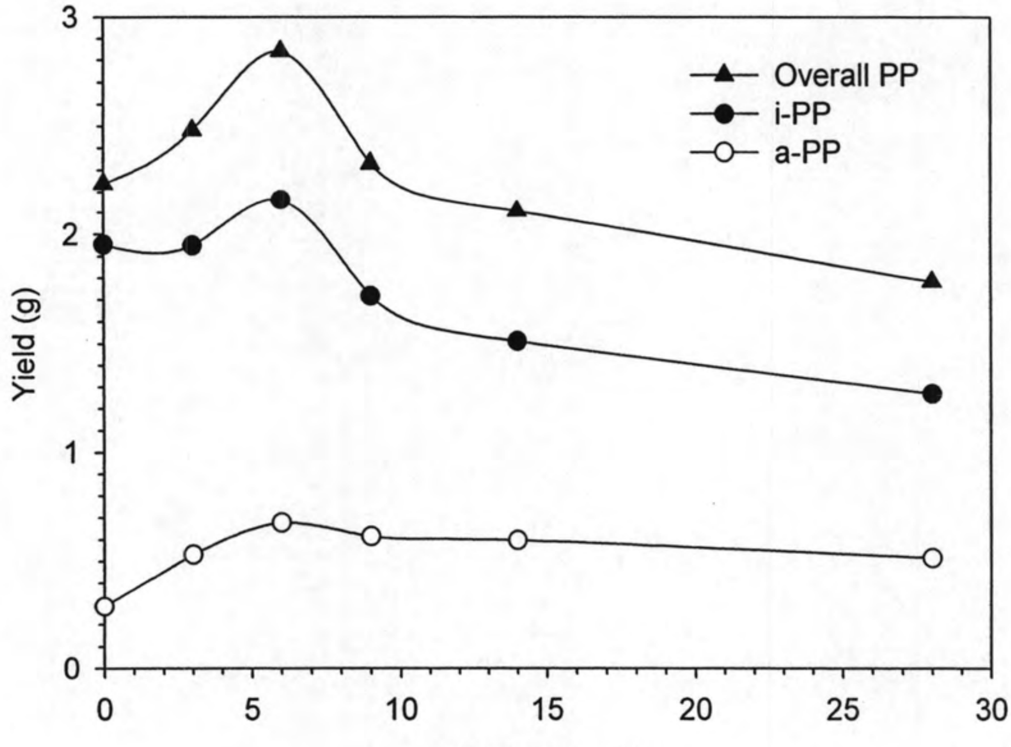

Figure 4.6 Influence of Ca/Ti mole ratio on the yields of overall PP, i-PP and a-PP.

4.3.4 Thermal Properties and Molecular Weight

However, it is unclear that how CaO can have a strong decrease in the tacticity of the polymer. By considering the M_w, X_c and T_m of the product (Tables 4.4 and 4.5), its crystallinity and melting point remained high while the M_w slightly decreased. One possible explanation is that in the presence of CaO the low molecular weight isotactic polypropylene was produced and could be dissolved in boiling *n*-heptane during Soxhlet extraction resulted in low I.I. detected. It can, moreover, be noted that the addition of small amount of fillers did not affect the melting behavior and crystallinity of the resulting polymer. This was confirmed by the constant of mmmm as measured by ^{13}C NMR (Table 4.3).

Table 4.4 Thermal properties of polypropylene obtained

Ca/Ti mole ratio	T_m (^{o}C)[a]	ΔH_m (j/g)[a]	X_c
0	155.3	52.7	25.2
3	156.9	55.9	26.8
6	153.3	57.1	27.3
9	153.4	60.6	29.0
14	158.0	58.3	27.9
28	157.8	56.8	27.2

[a] Determined by DSC.

Table 4.5 Molecular weight of polypropylene obtained

Ca/Ti mole ratio	M_w[a]	M_n[a]	M_w/M_n
0	309,387	19,765	15.7
3	–[b]	–[b]	–[b]
6	291,819	18,321	15.9
9	–[b]	–[b]	–[b]
14	–[b]	–[b]	–[b]
28	281,688	17,256	16.3

[a] Determined by GPC.
[b] Not determined.

4.3.5 Morphology

SEM micrographs (see Figure 4.7) demonstrated that the morphology of all polymers produced with different Ca/Ti addition were virtually similar and showed globule like structure.

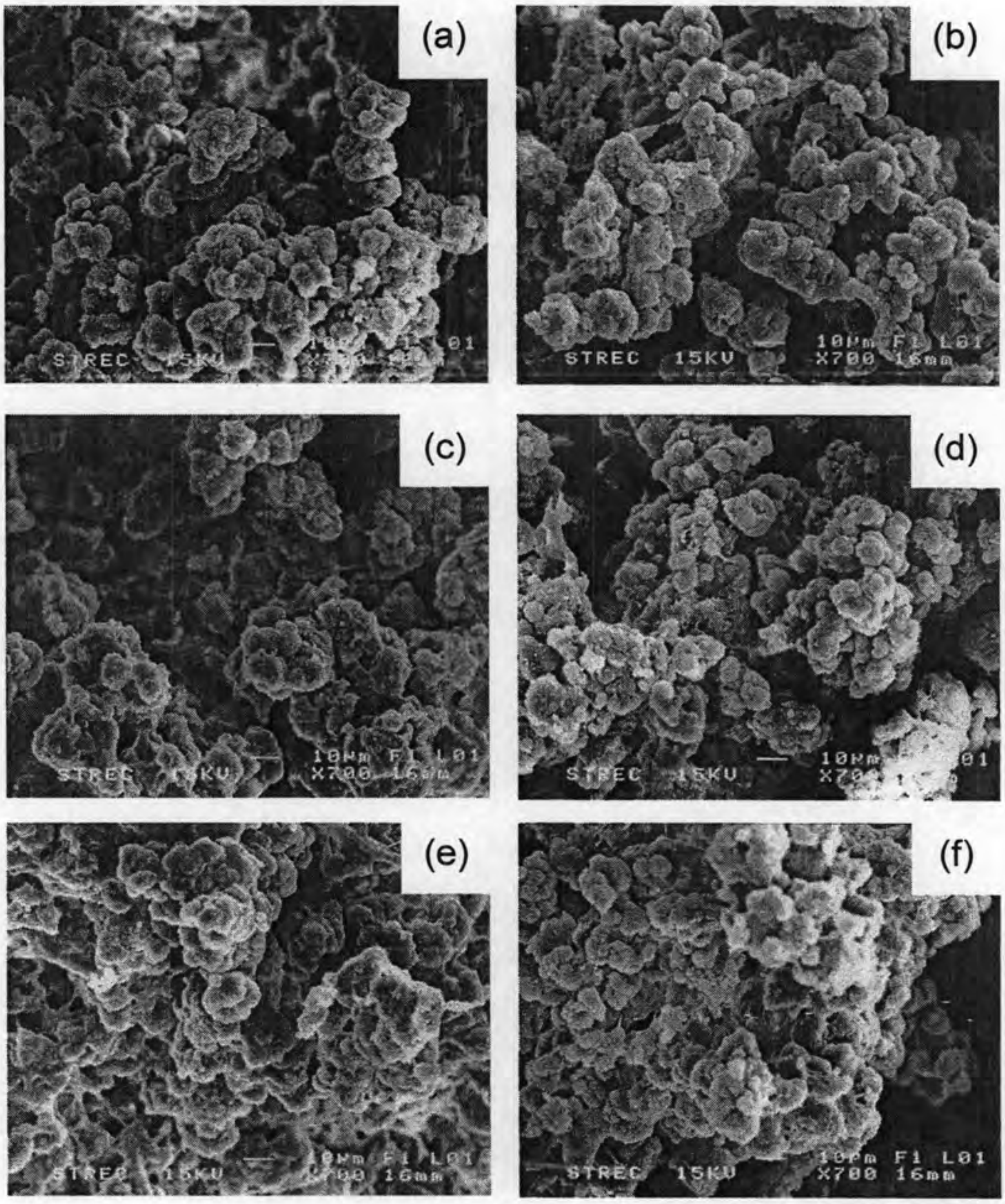

Figure 4.7 SEM micrographs of polypropylene particles obtained with catalyst prepared with Ca/Ti mole ratios = 0 (a), 3 (b), 6 (c), 9 (d), 14 (e) and 28 (f).

4.3.6 Activation Mechanism

Nitta *et al.* [188] and Liu *et al.* [152] reported that even in the existence of internal electron donor, the alkyl aluminium can transform the monometallic active sites (aspecific or less isospecific) into bimetallic active sites (highly isospecific) by coordinating with the catalyst. Taking this phenomenon into account, the effect of CaO on the active site formation may be attributed to the vacancy occupation by the O^{2-} anions from CaO on the titanium species after its alkylation by cocatalyst as shown in Figure 4.7. These O^{2-} provide an increase in the electron density of cationic metal center to form active polymerization site and may stabilize the interaction between this metal and coordinated olefin which could be the main reason for improving resistance of the catalyst to deactivation. It is interesting that the addition of CaO may convert nonstereospecific site to isospecific one by occupying vacancies with O^{2-} anions. On the contrary, this interaction could block the bimetallic active site formation which gives highly isospecific polypropylene. However, it may be expected that excess amount of O^{2-} may convert the active center to an inactive one by occupying all vacancies on active species.

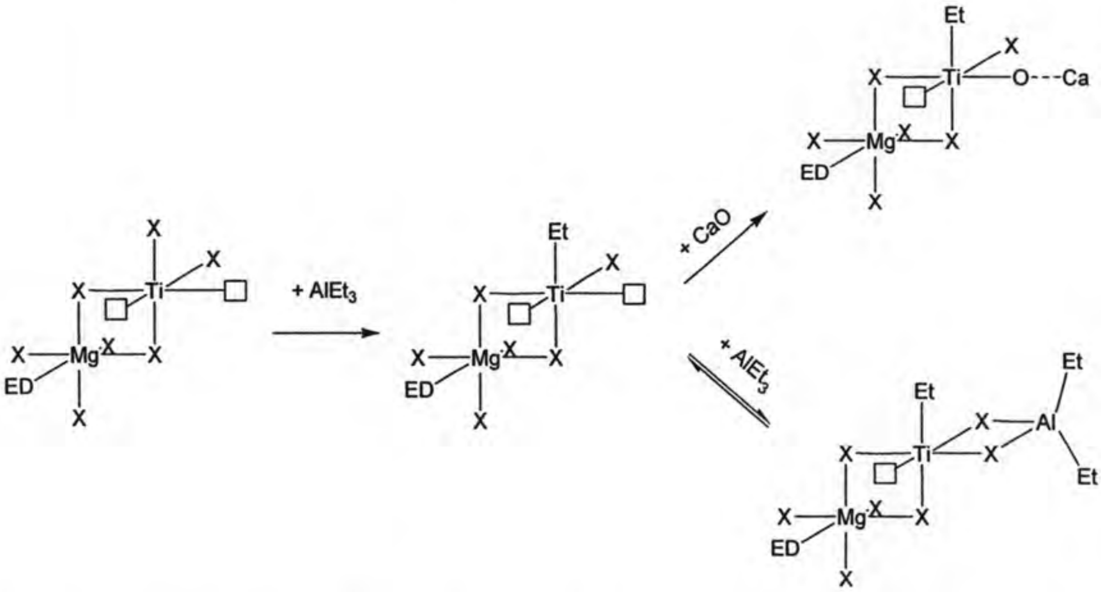

Figure 4.8 Suggested mechanism of active site formation catalyzed by CaO in the presence of internal electron donor (ED) (X: -Cl or –Et; □: coordination vacancy).

4.4 Summary

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.