CHAPTER V

PROPYLENE POLYMERIZATION WITH SILICA-SUPPORTED ALUMINOXANES AS COACTIVATORS

5.1 Introduction

It is well known that support have very important impact on Ziegler-Natta catalyst for propylene polymerization. In the early stage, the favored method for increasing the activity was to support the active species on the surface of inorganic materials with chemical reactions. A reaction of $TiCl_4$ with the hydroxyl group on such a support as silica, alumina, or Mg(OH)Cl was regarded as a good tool. So far SiO_2 is known to be an ideal support for the preparation of industrial olefin catalytic polymerization [189] and now constitutes the best support for metallocenes and methylaluminoxane (MAO) because of its excellence features as high surface area and porosity, good mechanical properties, good morphology and thermostability and it is stable and inert under reaction and process conditions [190,191].

For Ziegler-Natta catalyst, various generations of electron donor (Lewis base) including monoester, diester, alkoxysilane, diether and succinates were sequentially successful developed. Each generation has constituted to higher productivity of the process and to significant improvement of the stereospecificity of the propylene polymerization [192]. However, highly active Ziegler-Natta catalyst is still the important issue for catalyst research. Modification of catalyst supports [193] and introduction of other components such as grignard reagent [194,195] have been applied to enhance polymerization activity. Recently, trimethylaluminium-free MAO together with a certain amount of an alkylaluminium showed a notable effect on activity improvement for propylene polymerization at high temperature [196,197]. In fact, MAO is a particularly prominent activator for metallocene catalyst system. The formation of active sites undergoes by alkylation of transition metal complexes subsequent to methyl anion abstraction to yield cationic transition metal species which is active for olefin polymerization [198,199]. Nevertheless, alkylaluminium cocatalyst serves as alkylating agent in a similar way as MAO, but greater capability.

Moreover, it further reduces Ti oxidation state to lower valence species and possibly form bimetallic complexes with Ti species [152,188].

In Chapter IV, it is clear that CaO, without any modification, have a pronounced effect on an increase of polymerization activity during *in situ* propylene polymerization. On the contrary, the preliminary study here, under the same polymerization conditions, showed that the small addition of SiO_2 caused a marked reduce in catalytic activity. This phenomena was in agreement with the catalyst deactivation by the deposition of microparticle SiO_2 on the outer surface of the catalyst as reported by García *et al.* [185].

Therefore, in this chapter the surface of amorphous SiO_2 was tentative to be modified with aluminoxane compounds in order to reduce hydrophobicity surrounding the bulk silica surface and act as a co-activator for polymerization. To serve this purpose, several immobilized SiO_2 with MAO, MMAO, dMMAO and unsupported dMMAO were prepared and used as co-activator in propylene polymerization using $TiCl_4/DEP/MgCl_2$ catalyst in combination with TEA as cocatalyst. The activation mechanism of the combination between aluminoxane compound and alkylaluminium component might differ from the conventional activation process and it perhaps generate new active species which give high activity and novel polymer properties. The influence of the supported aluminoxanes on the catalytic activity and polymer properties were further investigated and discussed.

5.2 Materials

The chemicals employed in a present chapter were chemical 1. The polymerizations of these series were all done under very similar conditions with varying types of silica-supported MAOs at fix $Al_{aluminoxanes}/Ti$ mole ratio = 13. Propylene polymerizations were tested over catalyst 1 with reactor 1. The immobilized supports were characterized in terms of SEM-EDX, BET and TGA analysis. The polymer analytics were done on ^{13}C NMR 1 and DSC measurement. Details on the experimental procedure and used equipment are described in Chapter III.

5.3 Results and discussion

5.3.1 Characterization of SiO_2-supported MAOs

Table 5.1 shows the $[Al]_{MAOs}$ contents by means of EDX measurement of different co-activators supported on SiO_2. The treated SiO_2 particles were not coated and microtomed prior to the analysis, thus only concentrations on the external surface were observed. The $[Al]_{MAOs}$ quantities of various immobilized aluminoxane compounds on the SiO_2 surface increased in the following order: $MAO/SiO_2 < MMAO/SiO_2 < dMMAO/SiO_2$. These behaviors could reflect the distinction in their adsorption ability between the aluminoxane compounds and the surface of silica particles. Due to the fact that surface hydroxyl group of SiO_2 has high reactivity towards exchange reaction, it can result in high capability to be tailored by interaction with the external agents. In this regard, it is possible for the aluminoxane compounds to be able to bind on the SiO_2 surface via the hydroxyl groups [200].

Table 5.1 Characterization of different aluminoxanes supported on SiO_2

Modified-SiO_2	%Al[a]	BET (m^2/g)	Pore size (nm)	Pore volume (ml/g)	Number of Al ($atoms/nm^2$)[b]
SiO_2	-[c]	305	20.0	1.53	-[c]
MAO/SiO_2	7.3	299	12.8	0.95	5.4
$MMAO/SiO_2$	8.7	243	15.0	0.91	7.9
$dMMAO/SiO_2$	10.2	301	8.0	0.60	7.5
dMMAO	20.13	-[c]	-[c]	-[c]	-[c]

[a] Determined by EDX analysis.
[b] Calculated by Al contents and specific surface area of final support.
[c] Not determined.

As also shown in Table 5.1, the individual SiO_2 had the largest specific surface area, whereas heterogenization caused an influence on decreasing of specific surface area accompanied by lowering the average pore diameter and consequently the total pore volume. The pore size distribution curve indicated that the modified-SiO_2 still had only one kind of pore with narrower their size distribution (see Figure 5.1). In fact, surface area has a pronounced influence on the determination of dispersion states of the supported aluminoxane. The calculation of the supported Al amounts on the silica surface (Al atoms/nm^2) indicated the highly dispersed aluminoxane species on the support ranging from 5 to 8 atoms of Al/nm^2. To confirm the homogeneous dispersion for all aluminoxane compounds employed, the typical EDX mapping images were applied with each modified SiO_2 and shown in Figure 5.2. It was obviously seen that aluminoxanes were well distributed throughout the external surface of the particles in all samples. However, SEM micrographs demonstrated that the impregnation of dMMAO brought about an altering in the SiO_2 morphology and surface characteristics. These results were in agreement with the remarkable decrease of pore size diameter and its distribution of dMMAO/SiO_2 as seen in Tables 5.1 and Figure 5.1.

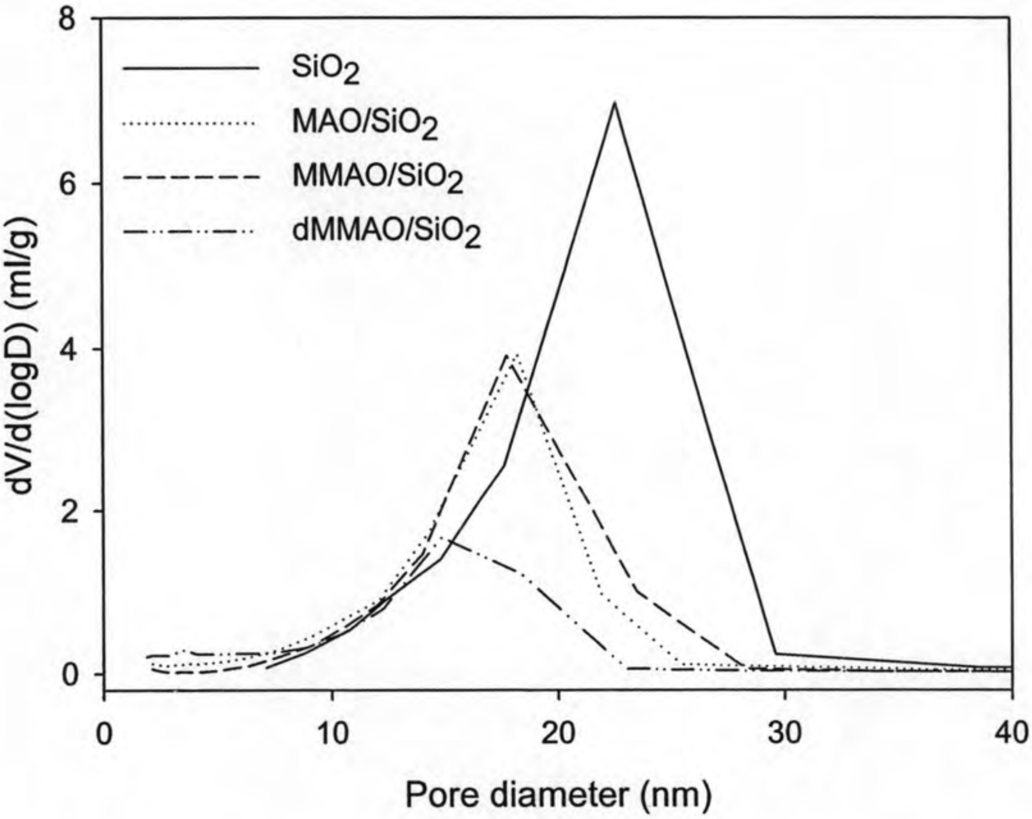

Figure 5.1 Pore size distribution of different SiO_2-supported aluminoxanes.

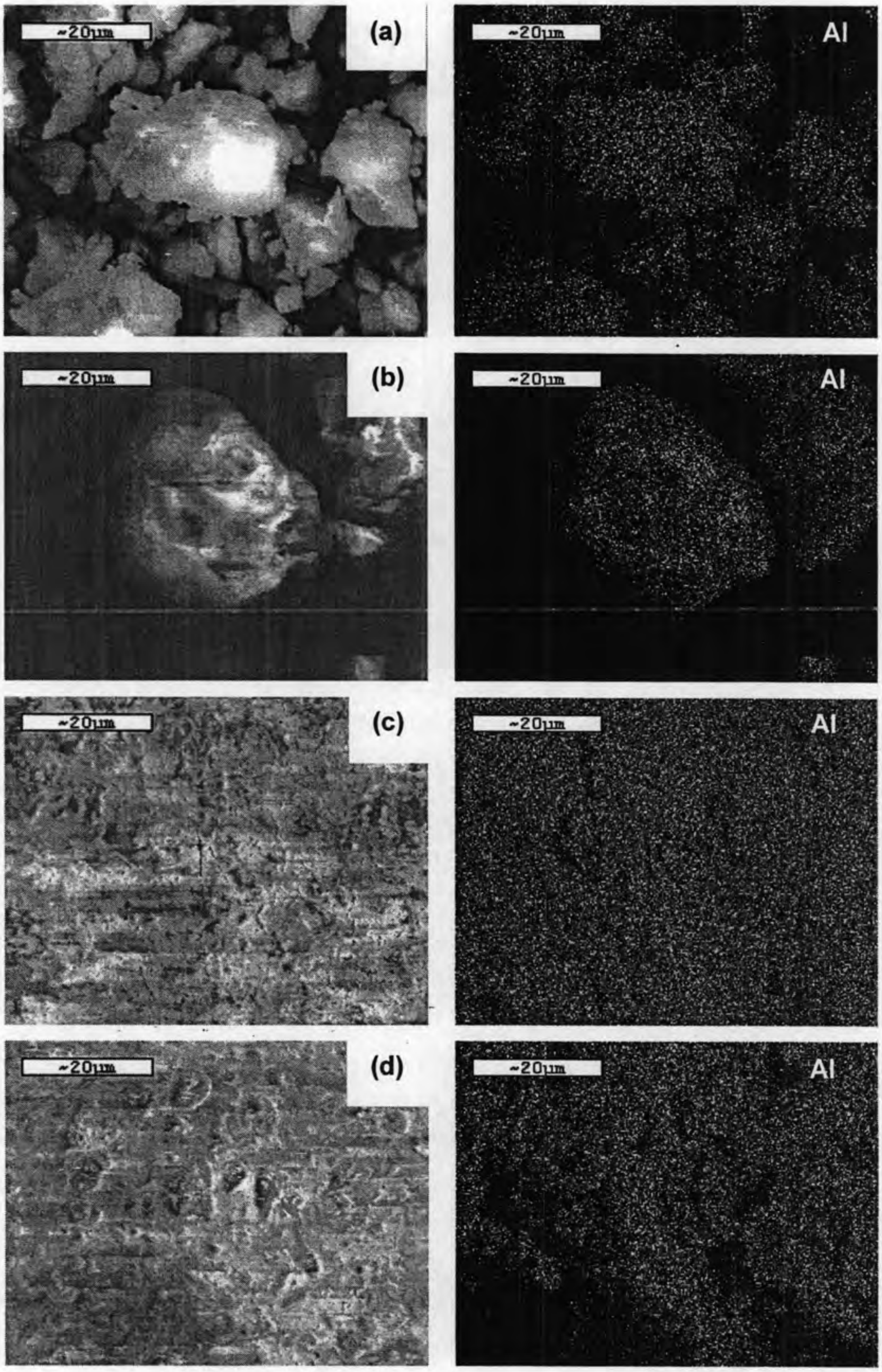

Figure 5.2 SEM micrograph and EDX mapping for Al distributions of various supported aluminoxanes; (a) MAO/SiO_2, (b) MMAO/SiO_2, (c) dMMAO/SiO_2, (d) dMMAO.

One of crucial factors for the heterogeneity of immobilized SiO_2 is the degree of interaction between supported aluminoxane and silica surface. Severn *et al.* [201] have reported that these two compounds were possibly linked to each other via the $O_{support}$–$Al_{cocatalyst}$ bonding. We also have investigated the correlation between these interactions and the catalytic activity towards ethylene/α-olefin copolymerization using metallocene catalyst [202,203]. In this study, TGA analysis was performed to identify the degree of interactions by monitoring the weight loss and removal temperature. For MAO/SiO_2, $MMAO/SiO_2$ and $dMMAO/SiO_2$, it is apparent from Figure 3 that all three aluminoxanes-SiO_2 sample showed essentially the same TGA behavior with a single removal temperature of aluminoxane compounds from the support at around 277°C. In comparison, dMMAO with a similar TGA profile presented a larger weight loss at 360°C. The typical weight loss for all cases, measured at the end of thermal treatment at 800°C, were in the order of dMMAO (39.8%) > $dMMAO/SiO_2$ (19.2%) > MAO/SiO_2 (18.6%) > $MMAO/SiO_2$ (16.9%). The influences of the degree of interaction strength on the polymerization behavior are discussed further.

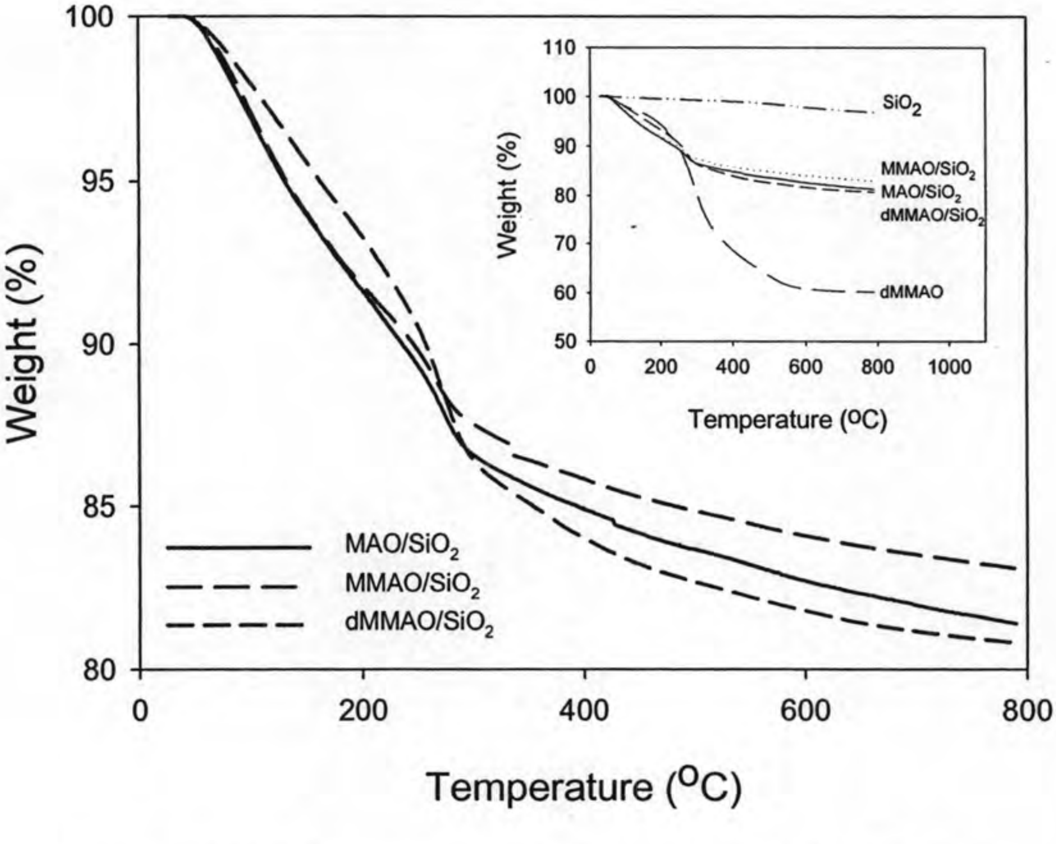

Figure 5.3 TGA thermogrammes of several SiO_2-supported aluminoxanes.

5.3.2 Effects on Catalytic Activity

A detailed study has also been extended for the evaluation of different supported aluminoxane effects on the catalytic activities and polymer properties towards $MgCl_2/DEP/TiCl_4$–TEA catalytic system. Propylene polymerizations were carried out with minimal amount addition of different aluminoxane compounds supported on SiO_2 as a third component. For a comparative study, the polymerization with and without the presence of calcined SiO_2 was tested and denoted as SiO_2 and SiO_2-free, respectively.

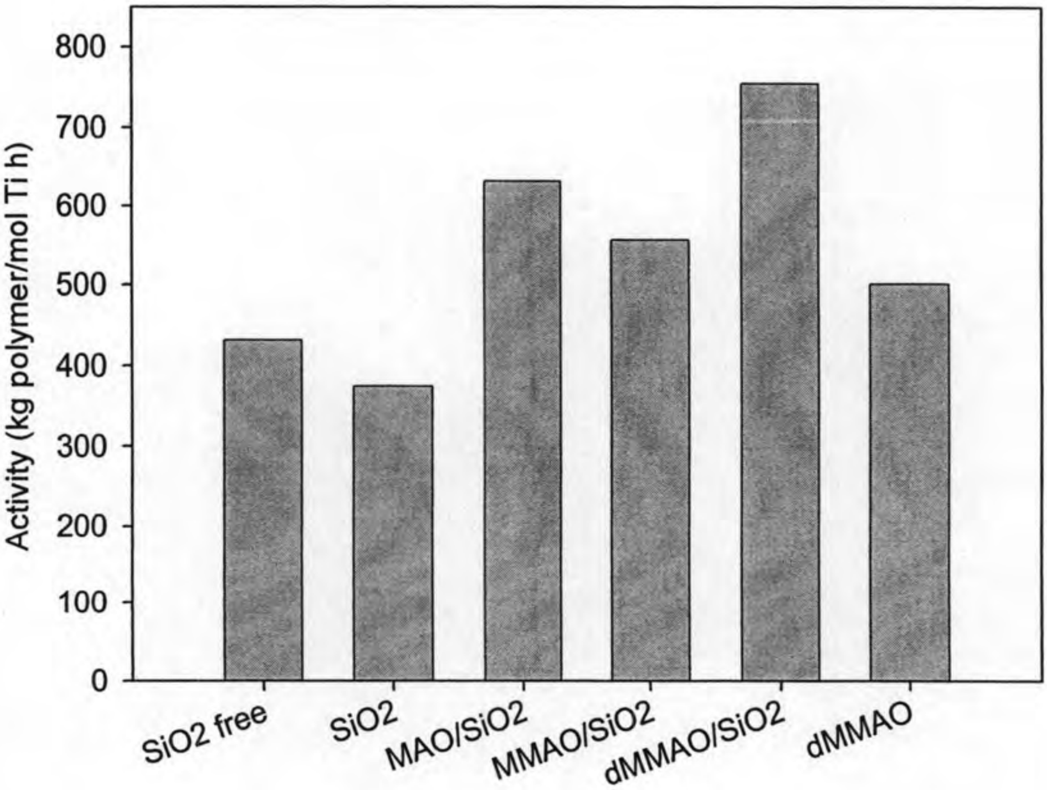

Figure 5.4 Catalytic activity in propylene polymerization; catalyst: 10 mg, cocatalyst: TEA, Al_{TEA}/Ti (mol/mol) = 167, $Al_{aluminoxanes}/Ti$ (mol/mol) = 13, solvent: *n*-hexane (30 ml), *P*: 60 psi, *T*: 60°C, *t*: 30 min.

Figure 5.4 presents the polymerization activities, which were clearly dependent upon the types of supported aluminoxanes. They decreased as the following order: $dMMAO/SiO_2$ > MAO/SiO_2 > $MMAO/SiO_2$ > SiO_2-free > SiO_2. It was demonstrated that the unmodified SiO_2 caused a decrease in the catalytic activity, whereas the other three types of SiO_2-supported aluminoxanes gave rise to the enhancement of productivity. Based on García *et al.* [185] experiment, the modified microsized-silica with a silane coupling agent was applied in order to prevent catalyst deactivation. However, the activity profile obviously showed fast decay indicating the presence of catalyst destruction. We also have reported in the previous chapter that the addition of metal oxide to some extent level during the *in situ* propylene polymerization yielded a polypropylene with lower activity comparing to the reference polymerization. This was attributed to the fact that active sites were sensitive to the hydroxyl species, which can remove chlorine atoms from the coordination sphere of titanium species. Therefore, hydroxyl moieties remained on the silica surface was more likely to play an important role for the catalyst deactivation.

The observed activity revealed interestingly that the dMMAO/SiO_2 rendered the highest polymerization activity, whereas the unsupported dMMAO possessed the lowest catalytic activity. This phenomenon was probably due to the supporting effect, which can influence the reactivity of dMMAO towards titanium active species or TEA cocatalyst. Moreover, the supported aluminoxane appeared to be promising to promote the polymerization activity rather than the use of the sole unsupported aluminoxane. In general, it is accepted that during the activation process the alkyl aluminum co-catalysts, i.e. trimethylaluminum (TMA), triethylaluminum (TEA) and triisobutylaluminum (TIBA), are the key components for the alkylation and reduction of Ti species to form catalytic active centers. Their reducing ability is closely related to the Lewis acidity nature and bulkiness structure. That is to say, higher Lewis acidic property with less steric hindrance provided higher reducing ability as listed in the order of TMA > TEA > TIBA. For the supported series, it should be noted that MAO containing free TMA, whereas the MMAO having either free TMA or TIBA, which possibly took part in the activation of active sites to some extent level. However, here, the large amount of TEA was consumed as a cocatalyst, thus we believed that the major influences of the additional aluminoxane compounds came from the nature and structure of the aluminoxanes themselves. From this point of view, the higher activity of dMMAO comparing to MMAO could be attributed to higher actual amount of alkylaluminum-free MMAO present on the silica supported. Moreover, MAO was more active than MMAO as a cocatalyst. It was, however, still unclear that how it could activate active species for propylene polymerization. Zhong *et al.* [196]

reported that alkylaluminum-free MAO was not active for propylene polymerization at high temperature, but a combination of that with small amount of various alkyaluminums increased catalytic activity due to the formation of separated ion pairs formation of active species. Nath *et al.* [204] stated that in $CoCl_2$ catalyst system, TMA was indispensable for alkylation of $CoCl_2$, and then MAO abstracted the methyl anion from the alkylated cobalt compound to generate the cationic cobalt species, which was perhaps the active species. In this sense, further investigations of the polymerization behavior in the absence of TEA were carried out at the same aluminoxanes/Ti molar ratio = 13 (MAO/SiO_2, MMAO/SiO_2, dMMAO/SiO_2, dMMAO). It was found that no polymerization occurred in the use of only aluminoxane compounds. This would confirm the idea mentioned above that the aluminoxane compounds could not act as a polymerization activator, but only a combination with alkylaluminum that efficiently activated propylene polymerization.

Besides, it was interesting that the order of activating power of the supported aluminoxane had a reverse correlation with its degree of interaction as the stronger interaction gave lower polymerization activity (see Figures 5.3 and 5.4). It was feasible that strong interaction decreased its reactivity towards Ti species in the course of activation process resulting in a relative decrease of catalyst activity for polymerization. However, the features of the actual activation mechanism are still not clear since the third co-activator component makes the catalytic system more complicated. In fact, the solid-solid interaction between the supported catalyst and silica-supported MAOs was considered to be hardly existed. The solid additive probably affects the active species though the modification of TEA in some way. Thus the steric effect of the bulky structure for the aluminoxane compound or its reducing ability could be of great important factor that controls the activation behavior.

5.3.3 Effects on polymer properties

Table 5.2 showed properties of polymer obtained with various co-activators. Polymer crystallinities (X_c) slightly increased with the addition of silica-supported MAOs whereas the *mmmm* pentad and melting temperature (T_m) were almost constant. Particularly, the literatures had reported that the incorporation of an inorganic particle could improve the degree of polymer crystallinity since the filler component can act as nucleating agents [205]. This could be realized that the supported aluminoxanes possibly took part in the active site formation and still contained in the resulting polymer as they increased the polymer crystallinity from 24.7% up to 28%. In general, the most important factor affecting activity promotion comes from an increase in active site concentration [C*] or propagation rate constant (k_p). In addition, a number of relevant contributions have reported that k_p of isospecific sites is much more higher than k_p of aspecific sites [113,206]. And even different trialkylaluminums were employed for the activation process of ZN catalyst, the identical active species formation, which possessed a comparable k_p value with varying in active site concentrations still took place [121]. On the basis of this consideration, the appearance of constant values of the *mmmm* pentad suggested that the addition of SiO_2-supported MAOs gave no evidence for the altering of k_p as well. Both the aluminoxane compound and triethylaluminum cocatalyst presumably generate the same active species in the course of activation process, resulting in the production of polymer without any change in their microstructure and thermal properties. Thus, the important activity enhancement was likely due to the increase in the number of active centers.

Table 5.2 Polymer characterization with different SiO_2-supported MAOs

Supported-SiO_2	*mmmm*[a]	T_m (°C)[b]	X_c[b]
SiO_2 free	77	159.5	24.7
SiO_2	78	160.9	28.0
MAO/SiO_2	76	160.9	30.3
MMAO/SiO_2	77	160.3	28.5
dMMAO/SiO_2	78	160.9	29.9
dMMAO	75	159.7	27.5

[a] Obtained by ^{13}C NMR.
[b] Measured by DSC.

5.4 Summary

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 supports showed decrease in specific surface area along with 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 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 changes in k_p.