

CHAPTER VI

IMPROVING THE PERFORMANCE OF HETEROGENEOUS BORANE CO-CATALYSTS BY PRETREATMENT OF THE SILICA SUPPORT WITH ALKYLALUMINUM COMPOUNDS

6.1 Summary

The treatment of silica with alkylaluminum compounds, tri-isobutylaluminum (TIBA) and tri-ethylaluminum (TEA), dramatically enhanced the co-catalytic performances of the $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$. We measured the productivity and ethylene consumption profiles for $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$ co-catalysts and $\text{Cp}_2\text{ZrCl}_2/\text{TIBA}$. Both of the treated co-catalyst systems improved the average molecular weight of the product over the untreated co-catalyst system. TIBA-treated co-catalyst provided a narrow molecular weight distribution while TEA-treated co-catalyst system gave a broad distribution.

6.2 Introduction

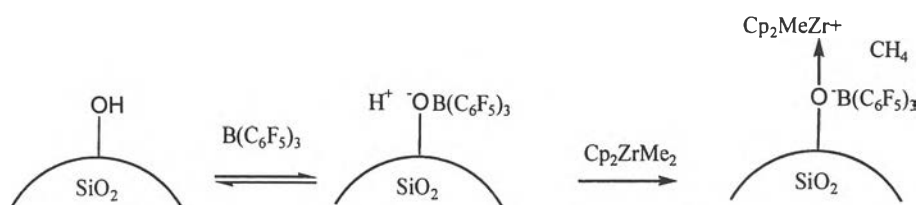
Single-site metallocene catalysts have been of intense interest in the last few decades in order to develop and improve their catalytic efficiency for olefin polymerization.^[1] These catalysts have many advantages for olefin polymerization such as narrow molecular weight distribution, low residual metal content and capability to control stereoregularity. Generally, a large excess of methylaluminoxane is used as a co-catalyst to increase the performance of metallocene catalysts.^[2]

If the role of the co-catalyst is to promote the formation of unsaturated “cation like” active centers. It might then be possible to devise other potent “Lewis acids” which are as effective as MAO but which can form isolable and characterizable catalysts with group IV metallocenes.^[3] Organoboranes such as tris(perfluorophenyl) borane ($\text{B}(\text{C}_6\text{F}_5)_3$) or “organoborates” such as tetrakis(perfluorophenyl) borate (e.g. $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$) when combined with dialkyl-metallocene produce highly active catalysts for olefin

polymerization. The character of the anion activator, which is the conjugate base of the Lewis acid activator, is also thought to be crucial to catalytic activity leading to highly active cationic catalysts.^[4]

In heterogeneous metallocene systems, oxide supports (e.g. SiO₂, Al₂O₃) modified with an alkyl aluminum reagent were treated with a solution of a metallocene catalyst and followed by adding an organoborane compound.^[5] The resulting catalyst system provided a low activity heterogeneous ion pair catalyst system.

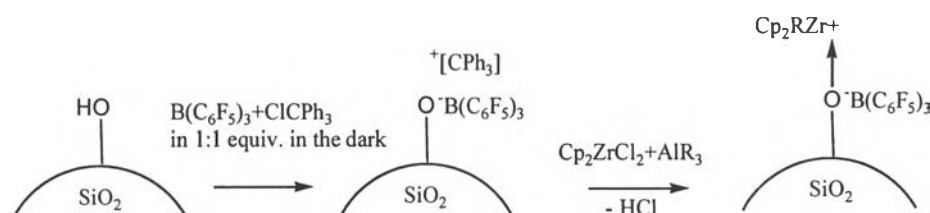
Recently, Tian et al. studied the functionalization of B(C₆F₅)₃ on partially hydroxylated silica and fully hydroxylated alumina.^[6] The reaction mechanism of borane functionalized or supported zirconocene on silica is proposed to be:



The use of heterogenized borane over polymer supports (e.g. Polystyrene, Merrifield resin) have also been reported by Roscoe et al.^[7] These findings have triggered the search for a new generation of “aluminum-free” supported catalysts. These supported catalysts work very well in ethylene and propylene polymerization with a low loading of alkylaluminums.^[6,7] Hlatky and Ward made heterogeneous organoboranes by providing a catalyst activator chemically bound directly to the support. This catalyst system reduced reactor fouling and increased the bulk density of the polymer product.^[8,9] Chein and coworkers reported an alternative route based on dichlorometallocene / [CPh₃]⁺[B(C₆F₅)₄]⁻/TEA, which avoids the synthesis of the dimethyl derivative. Because of the unstable form of dimethyl metallocenes, dichloride metallocenes reacted with alkylaluminum compounds have more potential to stay as living active centers for olefin polymerization.^[10]

In general the catalysis using metallocenes and organoboranes for olefin polymerization requires very pure solvent and reactor systems. The use of support materials with their high surface areas and porous structure is a source of impurities

which reduce catalytic activity. Therefore alkylaluminum compounds, which are scavengers for impurities, were used to modify the supports before preparing the supported co-catalyst system.^[11] In order to improve the catalytic performance. The present work reports the preparation of supported borane co-catalyst systems by treating the silica support with the alkylaluminums TIBA, TEA and TMA before functionalizing the silica support with $B(C_6F_5)_3$ and then stabilizing the resulting complex with CPh_3Cl as shown below. Because the amounts of borane co-catalyst used are comparable or equal to the amount of metallocene, preservation of activity is even more important than those cases where an excess of MAO is used:



Ethylene polymerization was carried out by using dichlorozirconocene/TIBA and the modified $[CPh_3]^+[B(C_6F_5)_3-SiO_2]^-$ co-catalysts. Our system is different than that of Tian et al [6] in that we used zirconocene dichloride (instead of di-methyl zirconocene) and our co catalyst is stabilized on the support by the carbenium ion.

6.3 Experimental Part

6.3.1 Chemicals

Polymerization grade ethylene and *UHP* grade nitrogen (Cryogenic, Michigan) were dried by passing through a column of oxygen-moisture trap (MATHESON). Tris(perfluorophenyl)borane ($B(C_6F_5)_3$) solution (11%wt in toluene) was purchased from Albemarle. Silica gel Sylapol 948, with a surface area of 309 m^2/g , and pore volume 1.62 cc/g , was bought from W.R. Grace Company, Maryland. Bis(cyclopentadiene)zirconiumdichloride (Cp_2ZrCl_2), triisobutylaluminum (TIBA, solution 1.0M in toluene), triethylaluminum (TEA, 25% in toluene), and trimethylaluminum (TMA, 2M in toluene) were obtained from Aldrich. Toluene

(Aldrich, anhydrous grade, $\text{H}_2\text{O} < 0.001\%$) was refluxed with sodium for 48 h, then degassed by distillation under N_2 with CaH_2 reflux. Hexane (Aldrich, anhydrous grade, $\text{H}_2\text{O} < 0.001\%$) was purged by bubbling N_2 . All solvents were stored over molecular sieves before use.

6.3.2 General

All of the catalyst preparation steps were carried out under anhydrous and anaerobic conditions in a glove box (O_2 and $\text{H}_2\text{O} < 1$ ppm).

To prepare the partially hydroxylated silica, silica gel support was washed repeatedly with DI-water and dried at 50°C under vacuum. The dried support was packed into a horizontal quartz tube and dried further at 500°C under oxygen flow for 6 h, and then cooled down with nitrogen flow to room temperature and stored under vacuum until use. The hydroxyl group content was approximately 1.42 OH mmol/g silica, determined by titration with trimethylaluminum.^[12]

Preparation of $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$ (co-catalyst #1)

The partially hydroxylated silica gel (~ 2 g) and toluene (14 ml) were slurried in a volumetric flask (100 ml) equipped with a magnetic stirrer bar and then $\text{B}(\text{C}_6\text{F}_5)_3$ (1.26 mmol in 6 ml of toluene) was added dropwise. After stirring for 3 h, ClCPh_3 (1.26 mmol or 0.351 g) in toluene (4 ml) was added dropwise to the mixture in the dark. The mixture was stirred for 12 h at room temperature. Finally, the solids in the mixture were settled overnight. The solid part was collected with a medium fritted-funnel. The final filtrate was washed with toluene (4x10 ml) and hexane (4x10 ml) and then dried in vacuum for 4 h.

Preparation alkyl aluminum treated silicas (2,3) and co-catalyst $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$ with alkyl aluminum treated silicas (4,5,6).

The partially hydroxylated silica gel (2 g) was slurried in 20 ml of toluene. 1 mmol of alkylaluminum (TEA or TIBA) in toluene was added to the mixture. After stirring the slurry for 30 min, the solid part was decanted and filtered in a medium fritted flask. The solid was washed with toluene (4x5 ml) and dried

under vacuum for 4 h. The product was alkyl aluminum treated support (TEA-treated-silica (2), and TIBA-treated-silica (3)). 14 ml of toluene slurry containing the treated-silica was mixed with 6 ml of $B(C_6F_5)_3$ in toluene solution. The mixture was stirred for 3 h. $ClCPh_3$ (1.26 mmol or 0.351 g) in toluene (4 ml) was added dropwise to the mixture in the dark. After stirring the mixture for 10 h at room temperature, the slurry was left to settle overnight. The solid part was collected with a medium fritted flask. The filtrate was washed with toluene (4x10 ml) and hexane (4x10 ml) and then dried in vacuum for 4 h. The product was $[CPh_3]^+[B(C_6F_5)_3-SiO_2]^-$ supported co-catalyst (TEA-treated (4), TIBA-treated (5)) and TMA treated (6)).

6.3.3 Ethylene polymerization

Ethylene polymerization was carried out in a 500 ml stainless steel reactor (Pressure Products) equipped with a magnetic stirrer and Teflon liner. The polymerization temperature was controlled using a PID temperature controller (OMEGA, CN-8502) with a heating jacket and a cooling U-coil (water as coolant) inside the reactor. The temperature was measured using a thermocouple (OMEGA, K-type) immersed in a thermowell, connected to the temperature controller. During the reaction the temperature was controlled within ± 1 °C of the set point. The rate of ethylene consumption was monitored by using a mass-flow-meter.

Prior to each run, the reactor was dried at 150 °C under vacuum for one hour. After drying, the reactor was cooled down while flushing with pure nitrogen several times and ethylene for the last cycle. The stirring speed was constant at 1000 rpm. All chemicals made as solutions in toluene were packed into a cylindrical bomb under an inert atmosphere to transfer into the reactor by N_2 overpressure. First, 200 ml of toluene was introduced into the reactor. The temperature was set to 40 °C and 0.5 ml of TIBA solution (1 M in toluene) was added. After 5 min, a weighed amount of the co-catalyst, suspended in 10 ml of toluene, was loaded into the reactor. To start the reaction prescribed amounts of Cp_2ZrCl_2 (2 μ mole) and TIBA (0.5 ml) were loaded into the reactor. Ethylene was supplied at 20 psig. After 30 min, the reactor was cooled to room temperature and depressurized. 10 ml of acidic-methanol was

injected into the reactor to quench the system. The final product was repeatedly washed with an excess of methanol, filtered, and left in the hood for 4 days.

6.3.4 Catalyst characterization

The changes brought about by pretreatment with alkylaluminums on the silica surface were investigated by diffuse reflectance FTIR. The measurements were carried out under a nitrogen atmosphere over the range of 4000-1500 cm^{-1} . The samples were mixed with dry-KBr and placed in the sample holder-cup. The bulk concentrations of boron (in $\text{B}(\text{C}_6\text{F}_5)_3$) and aluminum (in TEA and TIBA) absorbed onto the silica support were determined by using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES Leeman Labs Plasma-Spec ICP Model 2.5). Samples for testing were prepared by digesting the catalyst powder in 4 N aqueous solution of HNO_3 .

6.3.5 Polymer characterization

The average molecular weights (Mw) and molecular weight distributions (MWD) or polydispersity index (PDI) of the polyethylene products were determined by high-temperature gel permeation chromatography (GPC) using three Waters Ultrastyrigel columns in series at 150 °C with o-dichlorobezene as solvent. The columns were calibrated with narrow molecular weight distribution polystyrene samples. The morphology of the products was investigated using a scanning electron microscope (SEM, Philips XL30 SEM).

6.4 Results and Discussion

Figure 6.1 shows the IR spectra of dehydroxylated SiO_2 , (3), (1) and (5). Silica surface contains, isolated single hydroxyls, hydrogen bonded hydroxyls, paired hydroxyls, and adsorbed water. After heating silica support at 500 °C under oxygen flow, the adsorbed water and most of the peaks due to hydrogen bonded hydroxyls disappeared. However the single hydroxyl group (Si-OH) peak remained strong at

3658 cm^{-1} as seen in Figure 6.1a. Figure 6.1b shows that upon treating the silica support with the desired amount of TIBA the single hydroxyl peak intensity is reduced dramatically and the presence of surface bound TIBA is clearly seen by the presence of the CH stretch bands between 2850 and 2950 cm^{-1} . Alkylaluminum is known to react with accessible OH groups of silica at room temperature to form surface Si-O-AlR₂ groups and evolve alkane, RH [11,12]. Figure 6.1c is the spectrum of untreated co-catalyst $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$ (**1**). The reduced intensity of 3658 cm^{-1} single hydroxyl peak shows that $\text{B}(\text{C}_6\text{F}_5)_3$ is also interacting with the single hydroxyl groups of silica. Not all of the single hydroxyls have reacted and the incorporation of $\text{B}(\text{C}_6\text{F}_5)_3$ is clearly visible by the presence of 1645 and 1517 cm^{-1} bands [13]. Figure 6.1d shows the spectrum of $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-SiO}_2]^-$ with the TIBA pretreated silica (**5**). Comparing 6.1d to 6.1c, we see that the pretreated catalyst has fewer single hydroxyls and the 1517 cm^{-1} peak is also of much lower strength. Comparing with 6.1b we see that the CH₂ bands due to TIBA have almost disappeared.

Table 6.1 shows the measurements of adsorbed concentrations of B (boron) and Al (aluminum) on the silica support by ICP-AES. As we see, the amount of adsorbed Al of (**4**) is higher than (**5**). It is possible that TEA and TIBA react with the siloxane bonds to form surface Si-O-AlR₂ and Si-H groups and to evolve ethylene or isobutene. Increased aluminum incorporation with TEA is due to the higher reactivity of TEA and its smaller size. However, the pretreatment did not have an appreciable effect on the amount of adsorbed $\text{B}(\text{C}_6\text{F}_5)_3$ as demonstrated by the almost equal adsorbed boron amounts this is most likely due to the bulk of $\text{B}(\text{C}_6\text{F}_5)_3$ which will prevent it from reacting with isolated hydroxyls in small pores. Figure 6.2 shows the possible structure of functionalized borane on silica support. From the combined results of FTIR and ICP-AES, it can be seen that within error the alkyl aluminum pretreatment did not change the total amount of $\text{B}(\text{C}_6\text{F}_5)_3\text{-CPh}_3^+$ grafted to the surface. However, not all of the alkyl aluminums bonded to the surface are replaced by $\text{B}(\text{C}_6\text{F}_5)_3\text{-CPh}_3^+$. TIBA still occupies ~15-20% of the total surface hydroxyl sites and TEA occupies ~33%. This is consistent with the smaller size of TEA and the total number of hydroxyl groups determined by TMA titration. However, it is not possible to determine what other active surface sites are neutralized/blocked by the

alkyl aluminum treatment. Since the alkyl group of TEA is less bulky than the alkyl group of TIBA, it has more potential to scavenge impurities in porous silica, as well as to react with the siloxane bonds. Therefore, TEA treated co-catalyst (4) may have more available active $B(C_6F_5)_3^-CPh_3^+$ than TIBA treated co-catalyst (5), even though the adsorbed borane amounts of (4) and (5) are nearly equal.

The results of the ethylene polymerization are summarized in Table 6.2. The results show that the productivity is higher for the treated systems, almost double for (5) and almost four times for (4). TEA and TIBA by themselves were not active without the presence of borane and the stabilizing carbenium ion. The carbenium salt was used to reduce the extraction of borane from the silica surface, similar to the anilinium salt (NMe₂Ph) [13]. The kinetics of ethylene consumption during the polymerization, for (4) and (5), are shown in Figure 6.3. For (5) the profile of ethylene consumption is identical to (1) which showed a very slowly decaying activity curve for the 30 minutes of observation time. However, the activity with co-catalyst (5) is higher by almost a factor of two and also shows a very slow (or possibly constant) activity decay. The rate of ethylene consumption for TEA treated co-catalyst system (4) initially increases rapidly reaching 90-ml of ethylene/minute. This high activity plateau lasts only ten minutes after which a constant activity of ~60ml/min is observed. The initial rise in activity is similar to those seen with homogenous systems [14] and may be due to extraction of some of the catalyst into the solvent but we had no way of verifying this speculation.

The average molecular weight (Mw) of polyethylene produced from both (4) and (5) is higher than the polyethylene produced by (1). Moreover the molecular weight distribution (MWD) of the product was narrow for (1) and (5), corresponding to the single-site character of cationic metallocene. The distribution is significantly broader for (4), most likely due to leaching of the support surface giving rise to a mixture of homogenous and heterogeneous polymerization sites.

We also tested the overall activity with co-catalyst (6), made with TMA treated silica. However we were not successful in controlling the reactor temperature during the polymerization runs. The polyethylene produced had poor morphology and fouled the reactor. The product appeared to be segregated small polyethylene particles produced from leached active borane species and metallocene in toluene.

Reducing the concentration of TMA to 0.1 mmol for the pretreatment reduced the fouling effect but the temperature of the reactor still could not be controlled. Because TMA is smaller and more reactive, it probably reacts with all of the available surface hydroxyl groups of the support to form Si-OAlMe₂ and CH₄ [12]. The small addition of TMA was purposed only to kill impurities and occupy some Si-OH groups. Figure 6.4 shows the SEM micrographs of polyethylene particles produced by (1), (4), and (5). The polyethylene particles have the same general shape of the original support particles. The surfaces of the polyethylene particles from (4) and (5) appear to be marginally rougher than (1) particles. However the products of all three supported co-catalyst systems are free flowing.

6.5 Conclusion

Passivated silica support obtained by pre-treating with alkylaluminum compounds such TIBA and TEA enhances the catalytic performance of [CPh₃]⁺[B(C₆F₅)₃-SiO₂]⁻ co-catalyst, over untreated [CPh₃]⁺[B(C₆F₅)₃]⁻ SiO₂. The results show that the final productivity is in the order TMA>TEA>TIBA of treatment under the same preparation procedures and polymerization conditions. The average molecular weight of polyethylene produced by using co-catalysts with TEA and TIBA pretreated silica was higher than that produced by using a co-catalyst prepared with untreated silica. The final polyethylene grains are free-flowing, reduce fouling effect in the slurry phase polymerization, and yield high bulk density product.

6.6 References

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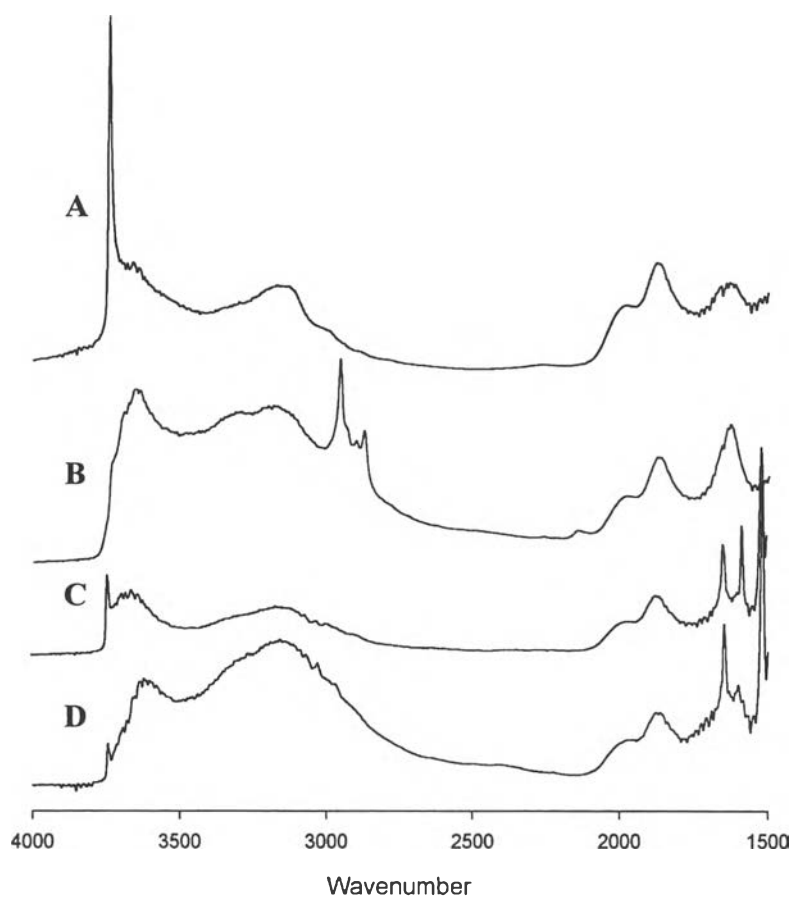


Figure 6.1 FTIR spectra measurements: **A.** Dehydroxylated silica support, **B.** TIBA-treated-silica (3), **C.** Co-catalyst #1 , **D.** Co-catalyst #5

Table 6.1 The components of the supported co-catalysts

Co-catalysts	Al ^{a)} (mmol/g)	B ^{b)} (mmol/g)	B:OH ^{c)}
(1)	-	1.15	0.81
(5)	0.25	1.05	0.74
(4)	0.56	1.12	0.79
B(C ₆ F ₅) ₃ (standard) ^{d)}	0.001 ^{e)}	3.64 ^{e)}	-

From ICP-AES measurement:

^{a)} Unit is mmol, compared to the original loaded amount of 1 mmol/g support

^{b)} Unit is mmol, compared to the original loaded amount of 1.26 mmol/g support

^{c)} Calculated from OH content of calcined silica (OH ~ 1.42 mmol/g)

^{d)} Standard solution of B(C₆F₅)₃ ~ 3.614 mmol

^{e)} Unit is mmol

^{e)} Unit is mmol

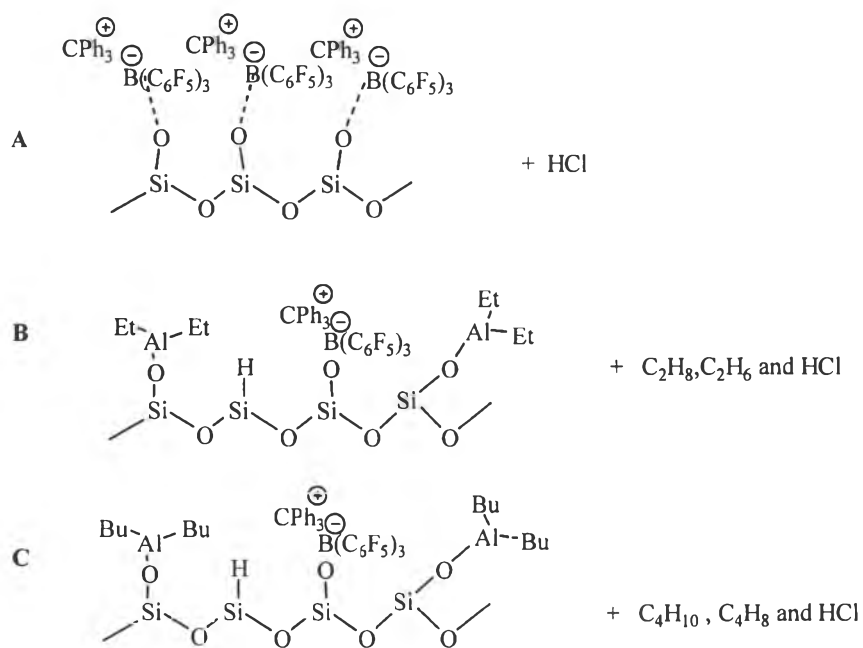


Figure 6.2 The functionalized surface of silica support; **A.** for (1), **B.** for (4), **C.** for (5).

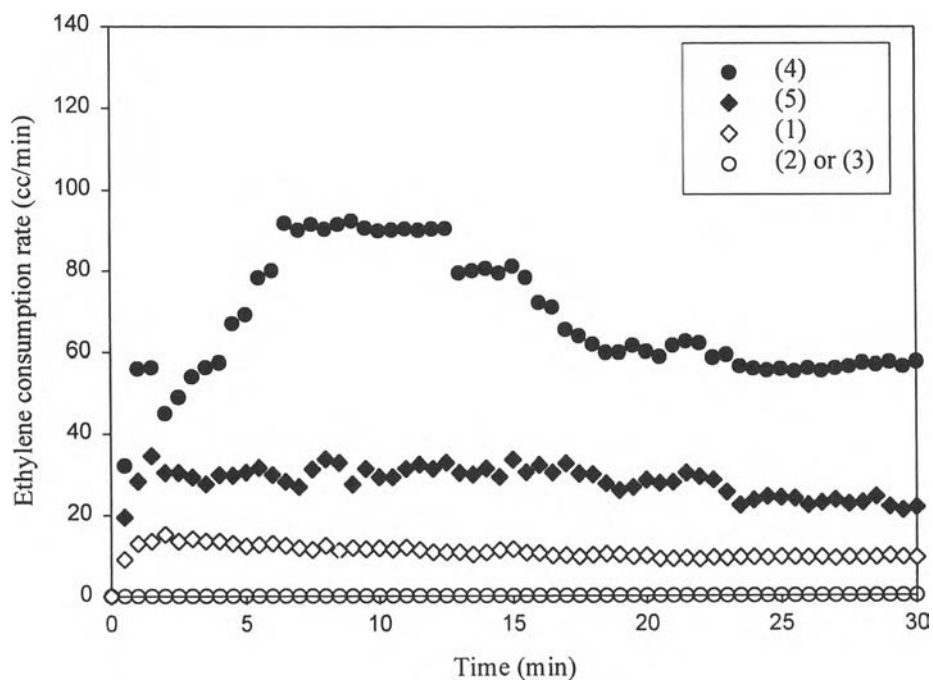


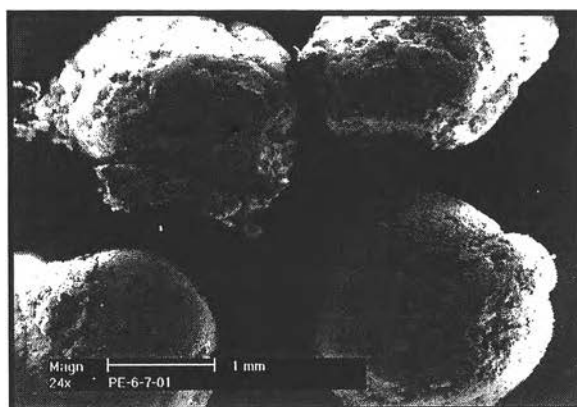
Figure 6.3 Effect of TIBA and TEA treatment of the silica used in preparing the co-catalysts on the ethylene consumption profiles during polymerization.

Table 6.2 The results of ethylene polymerization

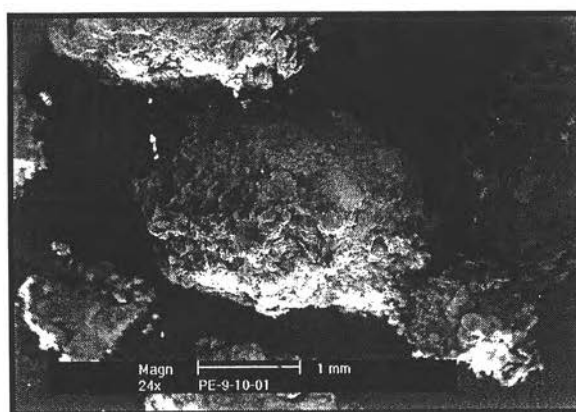
Co-catalysts Types	Productivity ¹	Mw	Mw/Mn	Bulk density (g/mL)
(1)	1.23	74000	3.01	0.35
(5)	2.01	108320	2.58	0.30
(4)	4.23	122237	10.12	0.24
(2)	0	-	-	-
(3)	trace	-	-	-

Polymerization conditions: Cp_2ZrCl_2 (2 μmol), TIBA (1 mmol), $T_p = 40\text{ }^\circ\text{C}$, ethylene = 20 psig, time = 30 min, supported co-catalyst = 0.15 g

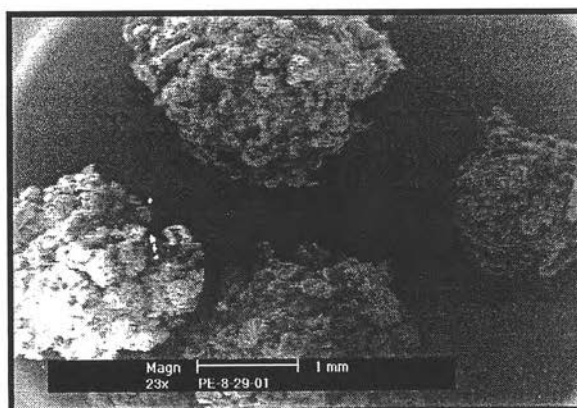
¹ kgPE/mmolZr x atm x hr



(A)



(B)



(C)

Figure 6.4 SEM micrographs of polyethylene grains from: A (1), B (5), C (4).