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Borate and MAO Free Activating Supports for Metallocene Complexes

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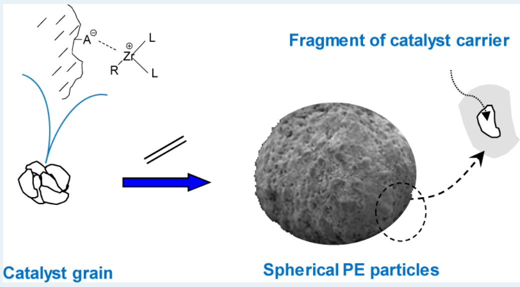
Supporting Information

ABSTRACT: Fluorinated activating supports (AS) for metallocene complexes were prepared via treatment of silica with $AlEt_3$ or $AlEt_2F$ followed by pyrolysis and combustion steps, and a subsequent fluorination step when $AlEt_3$ was used. This new family of activators appears to be universal for metallocene complexes leading to catalysts displaying high activities in ethylene polymerization without the addition of MAO. A productivity of 3200 g g_{AS}^{-1} was obtained in 1 h with the catalyst *rac*-$Et(Ind)_2ZrCl_2/AS_8/Al(iBu)_3$ at 80 °C under 10 bar of ethylene. An isotactic polypropylene with a melting transition at 145 °C was prepared using *rac*-$Me_2Si(2\text{-}Me\text{-}benz(e)Ind)_2ZrCl_2$ activated by AS9 and $Al(iBu)_3$. The spherical particle morphology of polyolefins was particularly adapted to slurry processes employed in industry.



KEYWORDS: *polyolefins, metallocene, supported catalysts, silica, polymerization process*

INTRODUCTION

Olefin polymerization catalysis started at the beginning of the 1950s with the discovery of Phillips (Cr) and Ziegler−Natta (Ti) catalysts.[1−3] These catalysts are heterogeneous because they are supported on a carrier (silica, $MgCl_2$) and thus insoluble in the polymerization medium. As they contain multiple families of active sites, they produce polymers with broad molar mass distributions and heterogeneous comonomer incorporation.

The field of polyolefins witnessed historical change with the discovery, in the 1970s, of the capability of group 4 metallocenes to be activated by methylaluminoxane.[4] This discovery attracted chemists working in the field of coordination chemistry to polyolefin synthesis and led to spectacular progress both in the development of group 4 metallocene catalysts, including stereospecific polymerizations of propylene in the 1980s,[5−8] and to the discovery of new families of catalysts covering a great range of transition metals.[9−12] These catalysts based on molecular precursors are called "single-site" catalysts.

The development of single-site catalysts has allowed the preparation of commodity polyolefins with homogeneous chemical composition distribution displaying improved properties. In spite of considerable research and developments on single-site technology, the commercialization of these catalysts has been slower than expected. Nevertheless, they are commercially important, and the metallocene-based LLDPE represents around 25% of the global LLDPE market.[13] One of the main impediments to the fast development of single site technology is the need to adapt metallocenes for "drop-in" use in commercial production facilities. The vast majority of commodity polyolefins processes are designed to accept heterogeneous catalysts (originally chromium and Ziegler−Natta catalysts), which means that it is also necessary to support the new metallocenes.

The preparation of supported single-site catalysts is indeed a big challenge since the polymer morphology must be controlled and the characteristics of molecular catalysts retained. Most olefin polymerization catalysts are formed by the combination of a precatalyst (transition metal complex) with an activator leading to a cationic active species. Different methods have been used to obtain solid catalysts by grafting either the precatalyst or the cocatalyst on a support.[14,15] The first method where the coordination complex is grafted on the support via the metal or a ligand (for instance a cyclopentadienyl ligand in the case of metallocenes) has encountered scarce success. The second method which is based on the preparation of supported activators has been developed on the industrial scale. Industrial supported activators are obtained by grafting homogeneous activators such as methylaluminoxane (MAO) or pentafluorophenylborate salts. However, both compounds have significant drawbacks. For instance, MAO is a poorly defined species

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(mixture of oligomers $(AlO(Me))_n$ evolving with time). In addition, both activators increase considerably the catalyst costs.

In the current paper, we will report our investigations on the synthesis of activating supports that can be used to overcome the difficulties associated with the use of compounds like MAO. This concept of activating supports uses the characteristics of the solid surface to permit isolation of highly reactive species. Thus, acid surfaces can be created and used as unique activators for molecular complexes without the need for grafting complex molecules onto a support. First insights on the use of acidic surface as activators have been reported by Soga and Kaminaka, who activated zirconocene complexes using various carriers such as Al_2O_3, $MgCl_2$, MgF_2, CaF_2, or AlF_3 in the presence of common alkylaluminiums.[16] Interestingly, the groups of Marks and Basset studied the adsorption of organometallic complexes, in particular metallocene type compounds, on inorganic oxide supports and discussed the formation of active species via abstraction of an alkyl group.[17,18] $MgCl_2$ based systems and particularly supports composed of $MgCl_2/AlR_n(OR')_{3-n}$ (R = Et, *i*Bu ; R′ = Et, 2-ethylhexanol) for activation of metallocenes and postmetallocene complexes have been intensively studied.[19−23] It was shown that the presence of Lewis acidic centers on $MgCl_2$ enables catalyst activation without the use of MAO. In addition, researchers at Chevron-Phillips developed solid acid activators for metallocenes on various inorganic supports.[24]

In the present study, we report the preparation of fluorinated aluminum-based activating supports and their use as activators for a range of metallocene complexes. This technology was originally patented by our group.[25,26]

■ MATERIALS AND METHODS

All manipulations were performed under pure and dry argon, using standard Schlenk techniques and a glovebox. 1-Hexene was distilled over CaH_2 prior to use. Toluene and *n*-heptane were dried on 3 Å molecular sieves. Methyl-aluminoxane (MAO), 10 wt % in toluene (Aldrich); methyl-aluminoxane, 30 wt % in toluene (Albemarle); diethylaluminium fluoride (Crompton); and triisobutylaluminium (Albemarle) were purchased from commercial suppliers.

Silica Grace Davison 332 (specific surface area = 300 $m^2\ g^{-1}$, mean particle size = 70 μm; porous volume = 1.65 mL g^{-1}; apparent density = 0.35 g cm^{-3}) and Crossfield ES70X (specific surface area = 276 $m^2\ g^{-1}$, mean particle size = 53 μm; porous volume = 1.54 mL g^{-1}; apparent density = 0.224 g cm^{-3}) were used as supports for the catalysts.

Polymerization Tests. Ethylene polymerizations were performed in a 500 mL glass reactor equipped with a stainless steel blade stirrer and an external water jacket for temperature control. $Al(i\text{-}Bu)_3$ (1 M solution in heptane), the activating support, the metallocene precatalyst (1 mM solution in toluene), and hexene were introduced successively in a flask containing 300 mL of heptane. The mixture was then immediately transferred in the reactor under a stream of argon. The argon was then pumped out before introducing the ethylene. Temperature and pressure were then progressively increased up to 80 °C and 4 bar. The pressure was kept constant during the polymerization. After 1 h of reaction, the polymerization was stopped. The resulting mixture was poured in 400 mL of methanol. The polymer was collected by filtration, washed with methanol, and dried under a vacuum.

Propylene polymerizations were performed in a 3.5 L Büchi type reactor. Inside a glovebox, in a 5 mL syringe, $Al(iBu)_3$ and dimethylsilyl-bis(2-methyl-4,5-benzoindenyl) zirconium dichloride ((*rac*-$Me_2Si(2\text{-}Me\text{-}benz(e)Ind)_2ZrCl_2$)) in 4 mL of heptane were contacted. This solution was then deposited onto 360 mg of the activating support. After a period of time of 5 min, the suspension was injected into the reactor containing liquid propylene (2 L) at a temperature of 70 °C. The polymerization was carried out for 1 h.

■ RESULTS AND DISCUSSION

Soga and Kaminaka reported the use of some metal fluorides (AlF_3, MgF_2, CaF_2) as carriers for metallocene catalysts in propylene polymerization.[16] However, the mechanism of activation is not clear, and the carriers are not really adapted for olefin polymerization processes which require a support with high surface area and are able to fragment.

In the present work, we assess the capability of aluminum fluoride grafted onto silica supports to activate metallocene precursors. Two routes for obtaining aluminum fluoride were investigated: (i) reacting silica with an aluminum fluoride compound or (ii) fluorinating aluminum derivatives grafted onto silica. This fluorination was based on the reaction of HF, which was released at a high temperature (typically 450 °C) from decomposition of the $(NH_4)_2SiF_6$ ammonium salt (Scheme 1), with the support.

Scheme 1. Decomposition of $(NH_4)_2SiF_6$ under Thermal Treatment

$$[NH_4]_2SiF_6 \longrightarrow 2\ NH_3 + SiF_4 + 2\ HF$$

Prior to any functionalization, the silica was subjected to a thermal treatment under a dynamic vacuum in order to dry the silica and to control the concentration of silanol groups. The reaction of the silica with $AlEt_3$ followed by a fluorination step provides a support with nearly no capability to activate a metallocene precursor in the presence of $Al(iBu)_3$. A thermolysis under argon and a combustion step were then introduced before fluorination in order to form some aluminum oxide species at the silica surface. A unique solid activator was formed when the fluorination step was performed right after the combustion (vide infra). Note that all the polymerization tests using the resulting activating supports were performed in the absence of MAO using common trialkylaluminium compounds as alkylating agents and scavengers. Alternatively, activating supports were also obtained by the reaction of $AlEt_2F$ with silica followed by pyrolysis and combustion steps. Scheme 2 summarizes the preparation of activating supports.

Two silicas, Grace 332 and ES 70, were used as carriers, and the wt % of NH_4SiF_6 was varied from 5 to 20% for each. The characteristics of the activating supports are summarized in Table 1.

Scheme 2. Preparation of Activating Supports

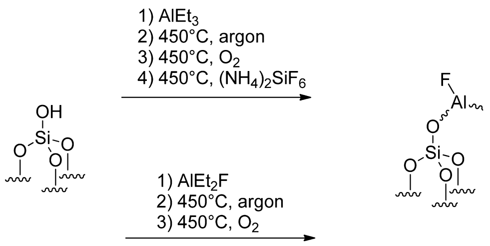

Table 1. Preparation and Elemental Analysis of Activating Supports

support	silica	Al complex	NH_4SiF_6 wt %	Al wt %	F wt %
AS1	Grace 332	$AlEt_3$	5	3.72	1.18
AS2	Grace 332	$AlEt_3$	5	4.75	1.74
AS3	Grace 332	$AlEt_3$	10	3.67	3.31
AS4	Grace 332	$AlEt_3$	20	3.81	5.30
AS5	Grace 332	$AlEt_2F$		4.56	2.21
AS6	Grace 332	$AlEt_3$	10	4.98	3.60
AS7	ES 70X	$AlEt_3$	10	3.01	3.98
AS8[a]	ES 70X	$AlEt_3$	10	3.2	2.2
AS9[b]	ES 70X	$AlEt_3$	5	3.26	2.34

[a] Step A: 200 °C. [b] Step A: 300 °C.

The spatial repartition of aluminum and fluorine was investigated on the particle surface and cross-section by EDX. The study aims at verifying that the different compounds were uniformly anchored in the particle, in order to ensure a uniform distribution of the active sites. It can be seen from Figure 1 that the spatial distribution of aluminum and fluorine for the support AS1 appears homogeneous.

The efficiency of the support AS1 for the activation of the complex *rac*-Et(Ind)$_2$ZrCl$_2$ was investigated (Table 2). Polymerizations were performed in heptane at 80 °C using Al(*i*Bu)$_3$ as an additional cocatalyst and scavenger. High activities in ethylene polymerization were obtained with these new activating supports, and a remarkable hexene activation effect was also observed. A maximum productivity of 900 g g_{AS1}^{-1} (in 1 h) was obtained under only 4 bar of ethylene. A decrease of the melting temperature was observed by increasing the hexene content in the feed, which is typical for metallocene catalysts.[27] Spherical polyethylene particles were obtained except for runs 5 and 6 due to the lower crystallinity of these polymers.

The impact of the fluoride content of the activating support on the catalysts' efficiency was investigated by increasing the amount of NH_4SiF_6 used for fluorination from 5 wt % to 20 wt % with respect to the support (AS2–AS4). Polymerization tests performed using this series of activating supports showed a high increase in activity as the wt % of F is increased on the carrier (Table 3). Note that the treatment of silica with a higher amount of fluorinating agent resulted in a degradation of the silica grain. At this point, the formation of Al–F compounds on a silica surface can be assumed. To further evaluate this assumption, silanol groups from silica were reacted with $AlFEt_2$ in order to localize the fluoride atom on aluminum. The resulting carrier showed little activator character without any thermal treatment. Again, a combustion step was necessary to get an efficient activator (run 10, Table 3). The activating

Table 2. Ethylene Polymerization with *rac*-EtInd$_2$ZrCl$_2$/AS1/Al(*i*Bu)$_3$[a]

run	hexene mol %	activity g mol_{Zr}^{-1} h^{-1}	prod.[b] g g_{AS1}^{-1}	M_w kg mol^{-1}	Đ	T_m °C
1	0	3.4×10^6	39	130	3.8	133
2	9	4.3×10^6	86	109	3.8	125
3	11	8.7×10^6	136	103	3.4	120
4	20	1.7×10^7	276	99	3.3	115
5	38	1.1×10^8	900	64	2.7	109
6	56	5.8×10^7	456	53	2.4	104

[a] 300 mL heptane, 19–23 mg of AS1, [*rac*-EtInd$_2$ZrCl$_2$] = 0.5 μM, [Al(*i*Bu)$_3$] = 1 mM, 4 bar, 80 °C, 60 min. Đ: dispersity. [b] Productivity in gram of isolated polymer per gram of catalyst (including the silica support).

Table 3. Influence of F Content of Activating Supports on Polymerization Activity[a]

run	AS mg	F wt %	activity g mol_{Zr}^{-1} h^{-1}	prod. g g_{AS}^{-1}	M_w kg mol^{-1}	Đ	T_m °C
7	AS2 (22)	1.74	2.1×10^7	155	123	4.1	111
8	AS3 (22)	3.31	6.9×10^7	504	105	3.8	111
9	AS4 (22)	5.30	1.0×10^8	750	99	3.8	114
10	AS5 (26)	2.21	1.9×10^7	110	119	3.9	110
11	AS6 (23)	3.6	7.5×10^7	550	97	3.7	111
12	AS7 (21)	3.98	9.1×10^7	725	125	3.6	112

[a] 300 mL heptane, [*rac*-EtInd$_2$ZrCl$_2$] = 0.5 μM, [Al(*i*Bu)$_3$] = 1 mM, 4 bar, 80°C, 60 min, 20 mol % of hexene.

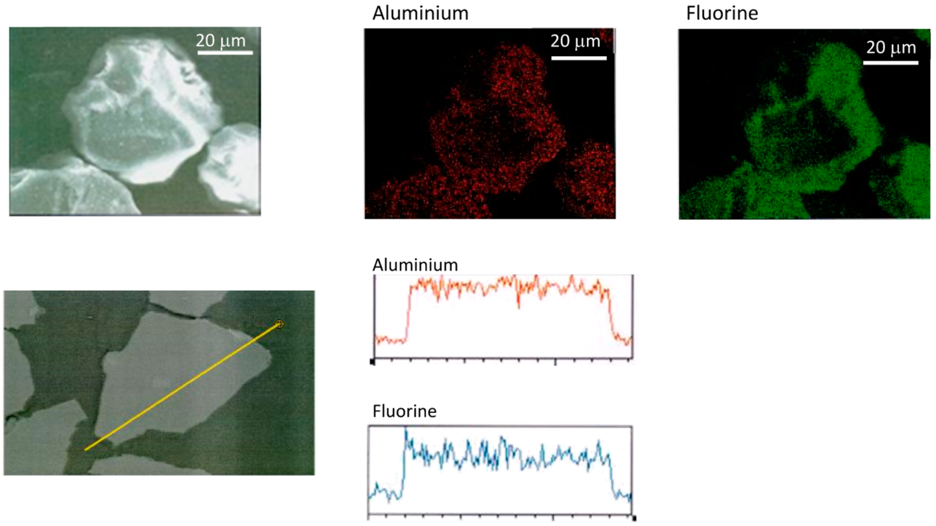

Figure 1. EDX analysis of the support AS1.

support AS5 showed comparable properties to support AS2 made using 5 wt % of NH_4SiF_6 having a similar content of F. Again the F wt % on the support seems to be correlated with the activity in ethylene polymerization. The activating supports AS2, AS3, and AS4 with increasing F content were analyzed by ^{27}Al solid-state NMR spectroscopy (Figure S1). $AlF_3{\cdot}3H_2O$, which was used as a reference, showed a signal at −15 ppm. Broad resonances were observed at 50, 32, and 3.5 ppm at a low F content (AS2). At a higher F content, a resonance at −15 ppm appears that can be assigned to $AlF_3{\cdot}3H_2O$. We assume that the hydration of AlF_3 formed during the fluorination step took place due to atmospheric moisture. For AS4, only $AlF_3{\cdot}3H_2O$ was detected on the NMR spectrum. However, the ^{19}F NMR spectrum of AS7 (Figure S2) showed a resonance corresponding to $AlF_3{\cdot}3H_2O$ (−8 ppm from C_6F_6) and one intense signal at 12 ppm. This last resonance is closed to the signal assigned to $^{VI}Al(O_5F)$ (9 ppm) and $^{VI}Al(O_4F_2)$ (20 ppm) by Fischer et al.[28] In conclusion, it appears that several acid species are present at the surface of the activating support. Further analyses are in progress to better understand the nature of the active sites.

A polymerization test was performed at 10 bar using AS8 (500 mL of heptane, [*rac*-$EtInd_2ZrCl_2$] = 1 μM, [Al(iBu)$_3$] = 2 mM, 73 mg of AS8, 10 bar, 80 °C, 6 mL of hexene). Under these conditions, a productivity of 3200 g g_{AS}^{-1} was obtained in 1 h. Particles of polyethylene were obtained without showing a presence of fines. The investigation of the particle morphology with SEM (Figure 2) showed the formation of spherical particles which replicate the catalyst grain.

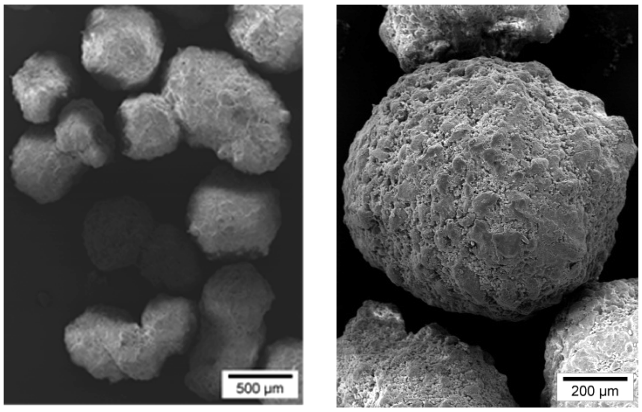

Figure 2. Polyethylene particles obtained using the catalyst *rac*-$EtInd_2ZrCl_2$/AS8/Al(iBu)$_3$ (heptane, 10 bar, 6 mL of hexene, 80 °C).

Table 4. Comparative Study of Copolymers Obtained Using *rac*-$EtInd_2ZrCl_2$ when Activated with MAO and an Activating Support[a]

run	activator	hex. in feed mol %	hex. in polymer mol %[d]	T_m °C	M_w kg mol^{-1}	Đ
13	MAO[b]	9	0.6	130	103	3.0
14	AS[c]	9	1.0	128	135	4.1
15	MAO[b]	11	0.7	127	113	3.1
16	AS[c]	11	1.1	127	134	4.7
17	MAO[b]	20	1.2	120	69	2.3
18	AS[c]	20	2.2	114	156	4.4
19	MAO[b]	38	2.5	115	57	2.0
20	AS[c]	38	3.5	111	58	2.6

[a] 300 mL heptane, 4 bar, 80 °C, 30 min. [b] Zr = 0.5 μM, [Al] = 3 mM (MAO 30%). [c] 20−25 mg of activating support, [Zr] = 2 μM, [Al(iBu)$_3$] = 3 mM. [d] Determined by ^{13}C NMR[33]

In the case of cationic active species, it has been shown that the counteranion must be included to model the chain growth reaction.[29,30] Interestingly, Sita et al. have reported that the dissociation of the ion pair can highly influence the reactivity ratios for ethylene/α-olefin copolymerization.[31] It was then expected that the ion pair formed by impregnation of a metallocene complex on an activating support was different than that obtained with MAO. The influence of the activating support on the properties of the copolymers was assessed. A series of polymers were produced using *rac*-$EtInd_2ZrCl_2$ activated with MAO or an activating support (Table 4). A better incorporation of hexene was observed with the activating support for all the runs. In order to verify that the difference of reactivity was not due to diffusional issues, polymerization were performed in slurry using a silica impregnated with MAO (SMAO) as described in the literature.[32] The analyses of the copolymers showed exactly the same composition as that obtained in solution using MAO.

The present results shed light on the unique behavior of activating supports. DSC and TREF analyses are in agreement with a higher incorporation of hexene when activation was performed using the activating support, which leads to a decrease of the crystallinity of the LLDPE. Figure 3 shows the TREF analyses of ethylene/hexene copolymers. As expected, the elution temperature decreased as the incorporation of 1-hexene rose. However, the chemical composition distribution of polymers was broader than that obtained with copolymers prepared using *rac*-$EtInd_2ZrCl_2$/MAO (run 17 in Figure 3). In the same vein, broader molecular weight distributions were obtained with the supported metallocene catalyst (Figure 4). Indeed, a high molar mass shoulder was observed on the SEC chromatogram. This might indicate the presence of multiple active sites for the ternary catalyst system *rac*-$EtInd_2ZrCl_2$/AS/Al(iBu)$_3$. We assume that the heterogeneity of the acid surface of the support leads to different ion pairs. The multisite nature of the supported catalyst based on the use of the single metallocene complex might be considered as an advantage since a molecular weight distribution higher than 2 is required for improved processability. This is generally obtained by the use of a mixture of metallocene precursors.

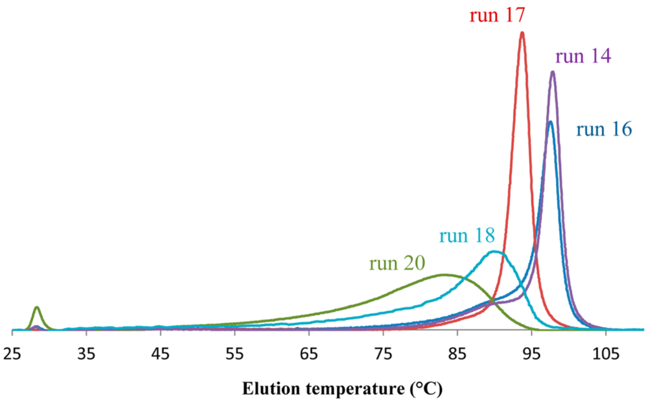

Figure 3. TREF analyses of copolymers obtained using the activating support (runs 14, 16, 18, 20: 1.0% to 3.5% of hexene) and MAO (run 17: 1.2% of hexene).

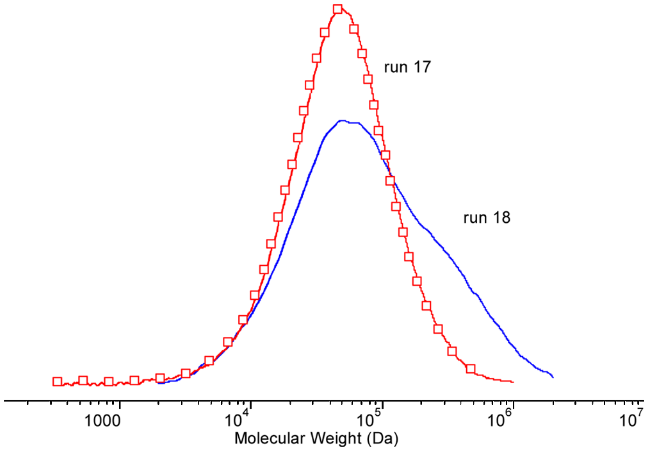

Figure 4. SEC analyses of copolymers obtained using the activating support (run 18) and MAO (run 17).

In order to assess the universality of a fluorinated activating support, a range of metallocene complexes were investigated ($(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$ (**2**), *rac*-$\mathrm{Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2}$ (**3**), $\mathrm{Me_2C(Cp)(9\text{-}Flu)ZrCl_2}$ (**4**), and $(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NtBu})\text{-}\mathrm{TiCl_2}$ (**5**)) using AS 6 and 7, which were prepared with the same protocol and were based on Grace 332 and ES70X silica, respectively (Table 5). Reference tests were also performed using MAO as an activator. All the complexes were activated using the activating supports. In addition, the activity measured compared well with that obtained when metallocene complexes were activated with MAO in solution. As already discussed in the case of *rac*-$\mathrm{EtInd_2ZrCl_2/AS/Al}(i\mathrm{Bu})_3$, a better response to hexene was obtained for all zirconocene supported catalysts. Interestingly, the metallocene complex $(n\mathrm{BuCp})_2\mathrm{ZrCl}_2$ showed a poor ability to insert hexene in solution, but its behavior is highly improved when using the activating support (runs 22, 23, and 25).

Polymerization of propylene was also performed using dimethylsilyl-bis(2-methyl-4,5-benzoindenyl) zirconium dichloride (*rac*-$\mathrm{Me_2Si(2\text{-}Me\text{-}benz(e)Ind)_2ZrCl_2}$) activated by AS9 in combination with $\mathrm{Al}(i\mathrm{Bu})_3$. The polymerization was performed in 2 L of liquid propylene at 70 °C (pressure 30 bar) for 60 min (360 mg of support, 6 μmol of Zr, Al/Zr = 225). An isotactic polypropylene (i-PP) of high molar mass was obtained (T_m = 145 °C, % mmmm = 95.9%, M_w = 296 000 g mol^{-1}, M_w/M_n = 2.9) with a productivity of 687 g g_{AS}^{-1}. Interestingly, the characteristics of *i*-PP are similar to those obtained using (*rac*-$\mathrm{Me_2Si(2\text{-}Me\text{-}benz(e)Ind)_2ZrCl_2}$/MAO (70 °C, liquid propylene, T_m = 146 °C).[34,35]

CONCLUSION

Activating supports based on fluorinated aluminum grafted onto silica appear as universal activators of metallocene compounds for ethylene and stereospecific polymerization of propylene. This new class of activators is obtained using readily available reactants and can compete with MAO. High productivities were obtained in slurry processes together with a good control of the particle morphology of the polymers.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation of activating supports and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

Table 5. Activation of a Range of Metallocene Complexes Using the Activating Supports AS6 and AS7[a]

run	complex	activator	hexene mol %	activity g $\mathrm{mol_{Met}^{-1}\ h^{-1}}$	activity g $\mathrm{g_{AS}^{-1}\ h^{-1}}$	M_w kg mol^{-1}	Đ	T_m
21	2	MAO (2000 equiv)	0	1.5×10^8		206	2.9	134
22	2	MAO (2000 equiv)	20	7.6×10^7		160	3.0	134
23	2	AS6 (21 mg)	20	9.1×10^6	71	102	3.0	124
24	2	AS7 (23 mg)	0	2.8×10^7	142	146	2.3	131
25	2	AS7 (21 mg)	20	2.2×10^7	162	94	3.1	119
26[b]	3	MAO (2000 equiv)	0	1.4×10^8		704	5.1	140
27[b]	3	MAO (2000 equiv)	20	2.7×10^7		154	2.1	90
28[b]	3	AS6 (20 mg)	20	2.4×10^7	196	346	5.2	81
29[c]	3	AS7 (43 mg)	0	4.2×10^6	29	557	3.6	131
30[b]	3	AS7 (26 mg)	20	3.0×10^7	189	193	3.3	84
31	4	MAO (2000 equiv)	0	2.6×10^6		161	3.7	131
32[b]	4	MAO (2000 equiv)	20	9.5×10^6		51	2.0	121
33[b]	4	AS6 (48 mg)	20	3.3×10^7	224	144	4.0	116
34	4	AS7 (41 mg)	0	2.9×10^6	23	342	4.1	135
35[b]	4	AS7 (42 mg)	20	4.3×10^7	338	122	3.5	111
36	5	MAO (2000 equiv)	0	1.1×10^6		173	3.3	138
37[b]	5	MAO (2000 equiv)	20	3.9×10^6		15	1.9	100
38[b]	5	AS6 (108 mg)	20	3.8×10^7	287	186	3.3	103
39	5	AS7 (112 mg)	0	3.3×10^6	24	1 022	5.7	133
40[b]	5	AS7 (112 mg)	20	1.2×10^7	95	356	5.5	101

[a] 300 mL heptane, 4 bar, 80 °C, 60 min, MAO 10 wt %. For **2** and **3**, [Zr] = 0.5 μM, [Al] = 1 mM; **4** [Zr] = 2 μM, [Al] = 4 mM; and for **5** [Ti] = 2.5 μM, [Al] = 5 mM. [b] 15 min. [c] [Zr] = 1 μM. $(^n\mathrm{BuCp})_2\mathrm{ZrCl}_2$ (**2**); *rac*-$\mathrm{Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2}$ (**3**); $\mathrm{Me_2C(Cp)(9\text{-}Flu)ZrCl_2}$ (**4**); $(\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2N^tBu})\mathrm{TiCl_2}$ (**5**).

■ ACKNOWLEDGMENTS

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