Preparation of Heterogeneous Constrained-Geometry Catalysts of Group 4 Transition Metals by Amine Elimination Reaction

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Three heterogeneous constrained-geometry catalysts $[(C_5H_4)SiMe_2(N(CH_2)_3SiMe_2{-}O{-})]M(NMe_2)_2$ (M = Hf (catalyst **1**), Zr (catalyst **2**), and Ti (catalyst **3**) were prepared by anchoring of metal amides ($M(NMe_2)_4$, M = Hf, Zr, or Ti) to a bifunctional ligand surface on SiO_2. Preparation of the bifunctional ligand on silica surface was carried out in two steps. First the silica surface was functionalized with aminopropyldimethylethoxysilane (APDMES) by using saturated gas−solid reactions. Second a reaction of the amino groups on the silica surface with *n*-BuLi was carried out, producing lithiated amido groups, which were allowed to react further with chlorides of (cyclopentadienyl)dimethylchlorosilane ($Me_2Si(C_5H_5)Cl$). Anchorage of the metal amides on the prepared surface was carried out by the amine elimination route. The heterogeneous catalysts were comprehensively characterized by ^1H, ^{13}C, and ^{29}Si solid state NMR and FTIR spectroscopy.

Introduction

Constrained-geometry catalysts have been the most recent discovery in the field of monocyclopentadienyl complexes. Soon after Bercaw and co-workers[1,2] had introduced the first constrained-geometry complexes of scandium for olefin polymerization catalysis, corresponding group 4 catalysts were also developed by Okuda,[3] Dow,[4] and Exxon.[5]

A convenient method to prepare constrained-geometry catalysts is the amine elimination route developed originally by Lappert[6] for metallocene compounds. This strategy has already been utilized for constrained-geometry catalysts by Carpenetti et al.,[7] Eisen et al.,[8] and Herrmann et al.[9]

Even though homogeneous polymerization catalysts are always thoroughly studied and well characterized, they are not suitable for industrial applications without modification. Heterogeneous catalysts are much more important from an industrial point of view, but they are rarely well defined because characterization of supported catalysts is difficult.[10]

Heterogenization of constrained-geometry catalysts has been studied but only to a small extent. Exxon[11] and Vega et al.[12] have reported heterogenization of the constrained-geometry catalysts in their patents and Eisen et al.[8] in their paper.

In our earlier studies[13,14] we have prepared immobilized constrained-geometry zirconium and hafnium catalysts with tetramethyl-substituted cyclopentadienyl groups. Despite our numerous attempts, we did not manage to prepare the corresponding titanium catalysts with the tetramethylcyclopentadienyl group, and therefore we decided to study bifunctional surfaces containing amine and nonsubstituted cyclopentadienyl groups for preparation of a heterogeneous constrained-geometry catalyst of titanium.

In this paper we report preparation and characterization of heterogeneous constrained-geometry titanium, zirconium, and hafnium catalysts that have been constructed in stepwise fashion. The first step, the modification of silica surface with aminopropyldimethylethoxysilane (APDMES), was introduced in our earlier paper.[15] In the second step (cyclopentadienyl)chlorodimethylsilane is immobilized on the APDMES-modified silica using liquid-phase reaction. In the final step three different metal amides [$M(NMe_2)_4$, M = Ti, Zr, Hf] are

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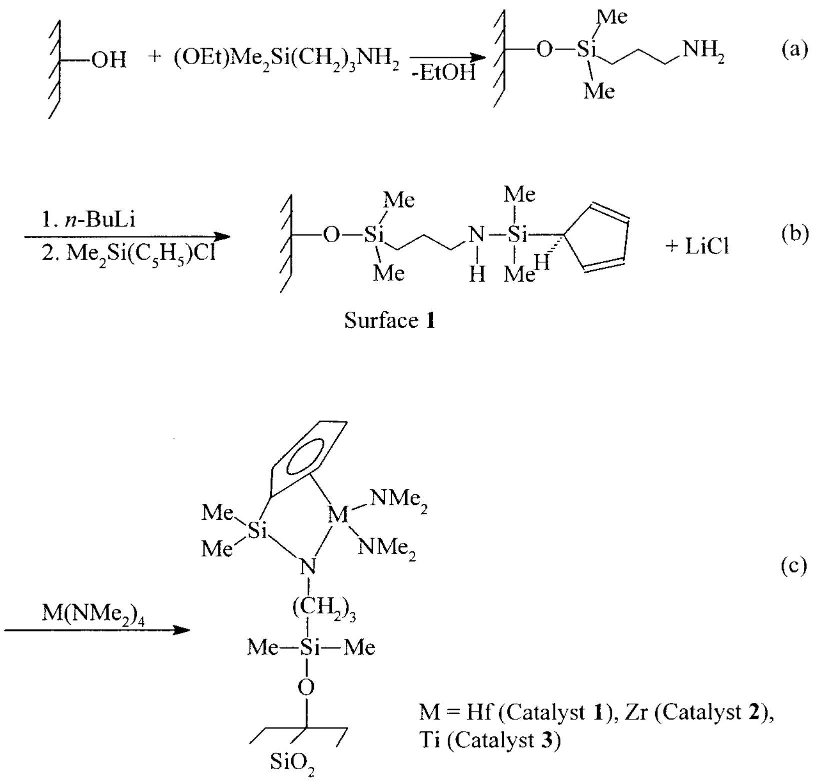
Scheme 1



Surface **1**

M = Hf (Catalyst **1**), Zr (Catalyst **2**), Ti (Catalyst **3**)

immobilized on this prepared surface by amine elimination reaction. The heterogeneous catalysts are characterized ^{1}H, ^{13}C, and ^{29}Si solid state NMR and FTIR spectroscopy.

Results and Discussion

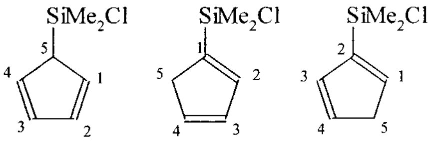
Preparation of Bifunctional Silica Surface. Silica surface (pretreated at 600 °C) was first functionalized with APDMES in an ALCVD (atomic layer chemical vapor deposition) reactor utilizing saturated gas−solid reactions (Scheme 1a). The nitrogen analysis after modification corresponds to 1.4 N atoms (or APDMES molecules)/nm^2 of SiO_2.

Second, (cyclopentadienyl)chlorodimethylsilane ($Me_2Si(C_5H_5)Cl$) was reacted with *n*-BuLi (*n*-butyllithium)-treated amino groups of APDMES-modified silica (Scheme 1b). The *n*-BuLi treatment produces not only lithiated amido groups but also directly silica surface bound butyl and lithium groups as a result of the siloxane bridges opening.

Already in early 1970s it was shown by NMR measurements[16,17] that the (cyclopentadienyl)silanes occur as three isomers resulting from intramolecular sigmatropic rearrangement of the hydrogen atom (Scheme 2). On the basis of ^{29}Si NMR the isomer distribution of $Me_2Si(C_5H_5)Cl$ corresponds to about 80% of allylic (5-isomer) and 20% of vinylic isomers (1- and 2-isomers).

The carbon analysis after immobilization of $Me_2Si(C_5H_5)Cl$ corresponds to about 13 C atoms/nm^2 of silica and nitrogen analysis 1.4 N atoms/nm^2 of silica; therefore the C/N ratio is 9.3. The expected C/N ratio for a complete reaction of amino groups was 12, and so there are still some unreacted amino groups left on the surface.

Scheme 2



5-isomer 1-isomer 2-isomer

The proof for successful immobilization of $Me_2Si(C_5H_5)Cl$ on the APDMES-modified surface (surface **1**) was obtained from FTIR and ^{13}C and ^{29}Si NMR. The IR spectrum of surface **1** shows weak bands between 3056 and 3095 cm^{-1}, which are characteristic of η^1-cyclopentadienyl groups (Figure 1a). A new band at 3413 cm^{-1} can be assigned to the N−H stretching band of the secondary amine group, indicating that a new bond has formed between nitrogen and silicon. Herrmann et al.[9] have observed the corresponding N−H stretching band for homogeneous constrained-geometry ligands at about 3385 cm^{-1}.

The ^{13}C NMR spectrum of surface **1** (Figure 2a) shows two new signals at 132 and 130 ppm that can be assigned to vinylic carbons of the cyclopentadienyl ring (5-isomer). Signals due to the 1- and 2-isomer cannot be exactly assigned because of their minor quantity, but between 135 and 150 ppm there are weak resonances that can be caused by these isomers. The signal at 53.8 can be assigned to the allylic carbon of the ring (5-isomer). Moreover the signal of the methyl groups bound to the silane (Si−Me) has slightly shifted from −2.9 to −1.5 ppm as a result of the presence of the methyl groups of the $Me_2Si(C_5H_5)$ moiety.

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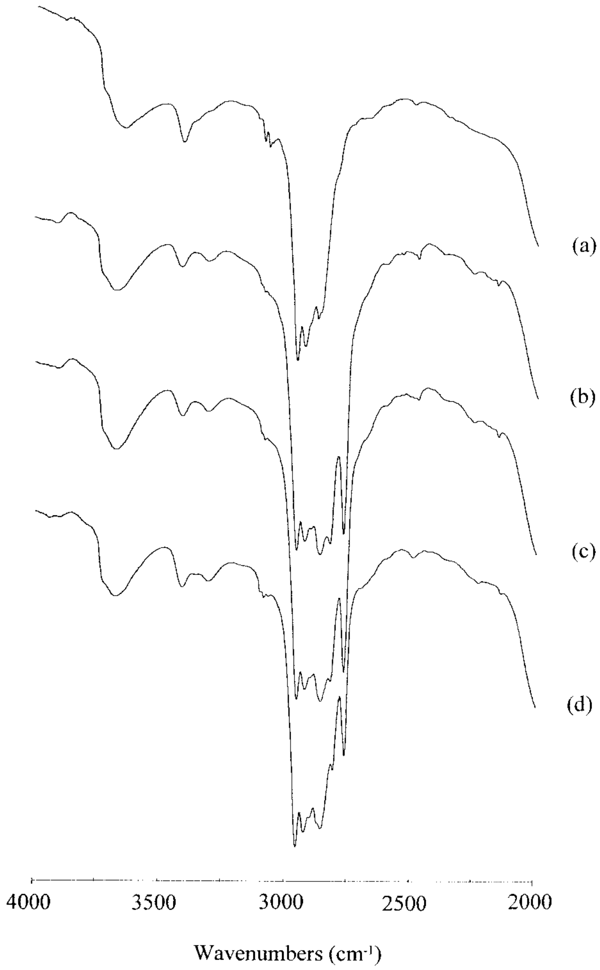

Figure 1. IR spectra of (a) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5H_5)Cl$, (b) catalyst **1**, surface **1** after anchorage of $Hf(NMe_2)_4$, (c) catalyst **2**, surface **1** after anchorage of $Zr(NMe_2)_4$, (d) catalyst **3**, surface **1** after anchorage of $Ti(NMe_2)_4$.

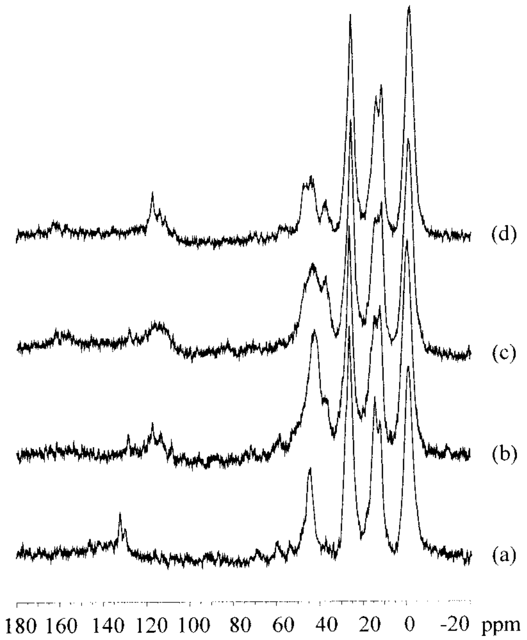

Figure 2. CP/MAS ^{13}C NMR spectra of (a) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5H_5)Cl$, (b) catalyst **1**, surface **1** after anchorage of $Hf(NMe_2)_4$, (c) catalyst **2**, surface **1** after anchorage of $Zr(NMe_2)_4$, (d) catalyst **3**, surface **1** after anchorage of $Ti(NMe_2)_4$.

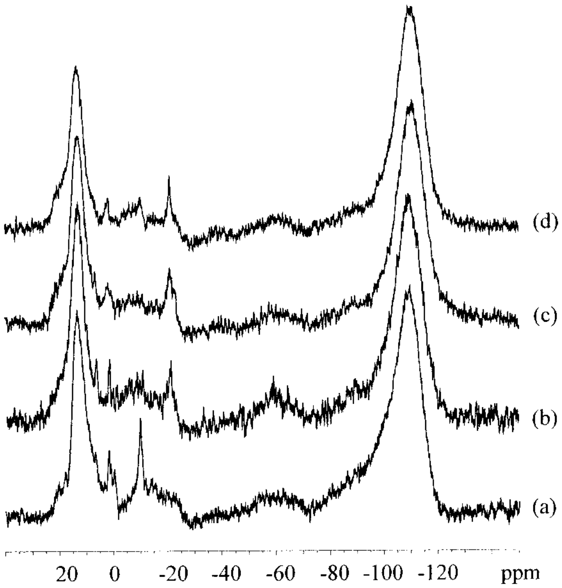

Figure 3. CP/MAS ^{29}Si NMR spectra of (a) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5H_5)Cl$, (b) catalyst **1**, surface **1** after anchorage of $Hf(NMe_2)_4$, (c) catalyst **2**, surface **1** after anchorage of $Zr(NMe_2)_4$, (d) catalyst **3**, surface **1** after anchorage of $Ti(NMe_2)_4$.

The ^{29}Si NMR spectrum of surface **1** (Figure 3a) shows two new signals, in addition to the signals of the silica (−110 ppm) and the silane of the APDMES (13.8 ppm). Both new signals at 2.1 and −9.7 ppm can be assigned to the amine-bound $Me_2Si(C_5H_5)$ groups. The two signals are due to isomerism of the Cp ring.

Preparation of Heterogeneous Constrained-Geometry Catalysts. Immobilization of metal amides ($M(NMe_2)_4$, M = Hf, Zr, Ti) onto the bifunctional surface **1** was carried out in a metal/ligand mole ratio of 1.5 by amine elimination reaction (Scheme 1c). Metal amides are expected to react with both the cyclopentadienyl ring and the amino group of surface **1** with the evolution of NMe_2H.

Reactions of the metal amides with the bifunctional surface were carried out in toluene with reflux. In the case of titanium amide it was noticed that extending of the reflux time did not enhance the titanium loading on the surface. In the cases of zirconium and hafnium longer reflux times not only increase the metal contents on the surfaces but also cause to some extent side reactions, and the surface structures were no longer the desired ones.

Reaction of $Hf(NMe_2)_4$ with surface **1** resulted in catalyst **1** containing 5.9 wt % of hafnium, which corresponds to a Hf loading of ca. 0.66 Hf/nm^2 of support (Table 1). Comparison of the Hf loading of catalyst **1** with nitrogen loading of surface **1** suggests that about 47% of the amino groups have reacted with $Hf(NMe_2)_4$. The corresponding reaction with zirconium amide, $Zr(NMe_2)_2$, produced catalyst **2** with 0.59 Zr atoms/nm^2 of support and with about 42% of the amino groups reacted. Reaction of $Ti(NMe_2)_4$ with surface **1** gave catalyst **3** with 0.5 Ti atoms/nm^2 of support and about 36% of amino groups reacted. According to these

Table 1. Elemental Analyses of Modified Surface and Catalysts

modified support	Anal. C (wt %)	Anal. N (wt %)	N/nm^2	Anal. M (wt %)	M/nm^2	N/M
surface **1**	7.7	1.0	1.4			
catalyst **1** (M = Hf)	7.77	1.50	2.15	5.9	0.66	3.3
catalyst **2** (M = Zr)	8.05	1.59	2.28	2.7	0.59	3.9
catalyst **3** (M = Ti)	7.96	1.58	2.26	1.2	0.50	4.5

analyses, the best metal loading was achieved with hafnium amide.

Spectroscopic Characterization of the Catalysts. Structural characterization of the catalysts was carried out with solid state ^{1}H, ^{13}C, and ^{29}Si NMR and IR measurements. IR spectra of the prepared catalysts **1**–**3** are very similar (Figure 1b–d), and by comparing them with the IR spectrum of surface **1**, the changes caused by metal anchorage can be clearly seen. The IR spectra of each catalyst show two new intense bands at 2771 and 2815 cm^{-1} that can be assigned to CH stretching of the NMe groups bound to the metal. The IR spectra of catalysts **1**–**3** also show that the intensity of the characteristic bands of the η^1-Cp groups of the modified silica at 3056–3095 cm^{-1} has decreased. This indicates that the electronic nature of the Cp rings has changed as a result of coordination of metal amides to the Cp ring.

The ^{13}C NMR spectra of each catalyst (Figure 2b–d) show the same changes when compared to the spectrum of ligand surface **1** (Figure 2a). The carbon signals of the Cp ring have shifted to around 118 and 114 ppm. The weak signal of the bridgehead carbon of the ring can be observed at about 108 ppm, more clearly in the case of hafnium than in the other two catalyst cases. The carbon signals of the Cp ring for corresponding homogeneous constrained-geometry catalysts have been observed at about 108, 115, and 118 ppm.[9]

The signal of the methyl groups of the metal amide at about 44 ppm is in the same area as the signal of the CH_2–N group. The intensity of this broad signal varies for the prepared catalysts. In the case of hafnium the 44 ppm signal is strongest and in the case of titanium, the weakest. The differences in intensities of the signals can be explained on the basis of the metal contents of the catalysts (metal loadings on the surface: 0.5 Ti atoms/nm^2, 0.59 Zr atoms/nm^2, and 0.66 Hf atoms/nm^2). In the ^{13}C NMR spectra of catalysts **1**–**3** an extra signal at about 37 ppm can be observed. This signal has been assigned in the literature[7,8] to a NMe_2H molecule coordinated to metal. In addition, in the IR spectra of catalysts **1**–**3** a new band at 3303 cm^{-1} probably due to the coordinated NMe_2H molecules is observed.

The ^{29}Si NMR spectra of catalysts **1**–**3** (Figure 3b–d) show the same silica and APDMES resonances at −110 and 12.8 ppm as in the earlier stage (surface **1**, Figure 3a), while the ^{29}Si signals of the $Me_2Si(C_5H_4)$ group have now shifted from 2.1 and −9.7 to −21 ppm due to the coordination of metal species. Herrmann et al.[9] has measured ^{29}Si NMR spectra of the constrained-geometry ligands before and after anchorage of metals. The shifts of the ^{29}Si resonances of the ligand are almost congruent with our results. For example in the case of $Me_2SiCp(N\text{-}t\text{-}Bu)$ and $Zr(NEt_2)_4$ shifts from −1.8, −3.33, and −4.19 to −23.26 were observed. There is only one new signal because of disappearance of isomerism after coordination of the metal to the Cp ring. The resonance shift indicates a significant enhancement in the shielding at silicon due to the coordination of metal amide to the Cp and NH functional groups of the ligand surface. However, the weak signals at 2.1 and −9.7 ppm can still be observed in every catalyst spectra, indicating that there are still unreacted $Me_2Si(C_5H_5)$ groups on the surface.

Both IR and NMR results support the conclusion that $M(NMe_2)_4$ has coordinated to both amino and Cp groups and produced heterogeneous constrained-geometry catalyst.

Polymerization of Ethylene. The activities of the three heterogeneous catalysts (catalysts **1**–**3**) were studied in the polymerization of ethylene in the presence of MAO cocatalyst. The polymerizations were performed under unoptimized reaction conditions by using toluene as a reaction medium. Polymerization temperature was 80 °C, and the other conditions varied slightly from one polymerization to another. A summary of the polymerization conditions and results is shown in Table 2. According to Jordan[18] and our own observations[13] a large excess of MAO is needed for methylation and activation of metal amide catalysts, and therefore an Al/M ratio of around 5000 was used in the polymerizations. The highest activity, obtained with zirconium catalyst (catalyst **2**), was about 700 kg of polyethylene/(mol of Zr·h). When the polymerization was done by using an ethylene overpressure of 2 bar, the activity of 378 kg of polyethylene/(mol of Zr·h) was obtained. This value is about 2 times higher than that obtained under the same polymerization conditions for analogous tetramethylcyclopentadienyl-functionalized zirconium catalyst (Table 2).[13] Polymerization with hafnium catalyst (catalyst **1**) resulted in activity of 220 kg of polyethylene/(mol of Hf·h) when ethylene overpressure of 2.5 bar was used.

The melting temperatures of polyethylenes made with catalysts **1** and **2** were between 137 and 138 °C, which are typical of linear high-density polyethylene. Also, the IR spectra of the polyethylenes made with catalysts **1** and **2** show no sign of the branching, which also supports the linear structure. The molecular weight distributions for polyethylenes obtained with catalysts **1** and **2** were relatively narrow (polydispersity index between 3 and 4).

The polymerizations with titanium catalyst (catalyst **3**) produced polyethylene with very low activities. Due to the high silica content in the polyethylene prepared by catalyst **3**, the molecular weights could not be determined. DSC gave for polyethylenes made with titanium catalyst two different melting temperatures (128 and 140 °C), which can be assigned to two polyethylene materials produced by two different catalytic sites. One possible explanation for multisite catalysis could be the leaching of the metal complex from the support during the polymerization.

Conclusion

We have prepared three heterogeneous constrained-geometry catalysts by attaching metal amides [$M(NMe_2)_4$, M = Hf, Zr, Ti] on the bifunctional silica surface with amine elimination reaction. The bifunctional ligand

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Table 2. Results of Ethylene Polymerizations[a] with the Heterogeneous Constrained-Geometry Catalysts as Well as Properties of the Polymers

catalyst ($A = SiO_2$/APDMES)	ethylene pressure (bar)	time (min)	n_M (μmol)	Al/M	yield (g)	A_m (kg/mol of M·h)	T_m (°C)	M_w (g/mol)	M_w/M_n
catalyst **1** (M = Hf)	2.0	30	15.5	5000	1.24	160	137.2	216 000	2.8
catalyst **1** (M = Hf)	2.5	30	7.27	5000	0.80	220	138.2	281 000	3.2
catalyst **2** (M = Zr)	2.0	30	6.66	5000	1.36	378	138.2	208 000	4.0
catalyst **2** (M = Zr)	2.5	30	5.80	5000	2.04	703	137.6	218 000	3.5
catalyst **3** (M = Ti)	2.0	20	12.3	5400	0.06	15	128.9, 133.9		-
catalyst **3** (M = Ti)	2.0	15	11.1	5400	0.05	18	128.3, 133.6		-
$A/Me_2(C_5Me_4H)Cl/Zr(NMe_2)_4$[11]	2.0	30	20.0	3400	1.80	180	139.7	204 000	2.1

[a] Polymerization temperature 80 °C.

surface, containing amino and cyclopentadienyl groups in the same coupling agent molecule, was prepared in two steps.

We observed in our polymerization studies that the activity was higher for catalysts containing a less sterically hindered unsubstituted Cp group in the constrained-geometry ligand than for catalysts with a tetramethyl-substituted Cp group. The polymerization results also showed that our immobilized constrained-geometry complexes, especially of zirconium and hafnium, act in the presence of MAO as single-site catalysts and produce linear polyethylene structure.

Experimental Section

General Considerations. All manipulations were performed under nitrogen using a vacuum line and Schlenk techniques. SiO_2 (EP 10, Crosfield Ltd.) was heat treated in air for 16 h at 600 °C. The pretreated silica was functionalized with APDMES in a commercial F-120 ALCVD reactor manufactured by Microchemistry Ltd., Finland, according to published procedures.[15] $Me_2Si(C_5H_5)Cl$ was prepared according to published procedures.[19] $Zr(NMe_2)_4$, $Ti(NMe_2)_4$, and $Hf(NMe_2)_4$ (Strem Chemicals) were used as received. The solvents used were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Methylaluminoxane (30%) was purchased from Witco GmbH. Ethylene was passed through a purification system containing molecular sieves and activated Cu just before feeding to the reactor.

Characterization of the Catalysts. IR spectra of the solid samples were recorded on a Nicolet Impact 400D FTIR spectrometer equipped with DRIFT (diffuse reflectance infrared-Fourier transform) and connected in an airtight manner to a glovebox. The solid state ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer equipped with a magic angle spinning probehead using the parameters described in ref 20. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with a Carlo Erba Instruments EA 1110 CHNS-O analyzer. Metal analyses were carried out with an inductively coupled plasma atomic emission spectrometer (ICP).

Polymer Analysis. The melting temperatures of the polyethylenes were measured with a Mettler Toledo Star DSC 821 system of powdered samples. The samples were heated first at a heating rate of 20 °C/min, cooled, and then heated again at a heating rate of 10 °C/min. The second heating curve was used for analysis. The molecular weights and molecular weight distributions were determined using a Waters 150-C ALC/GPC instrument equipped with Waters Styragel columns and RI detector. The solvent, 1,2,4-trichlorobenzene, was applied at a flow rate of 1.0 mL/min. The calibration of the columns was done with a universal method by using polystyrene standards with narrow molecular weight distribution.

Immobilization of (Cyclopentadienyl)dimethylchlorosilane ($Me_2Si(C_5H_5)Cl$) on APDMES-Modified Silica. Aminopropyl-functionalized silica (2 g) was degassed and purged with nitrogen. Pentane (20 mL) was added, with a double-ended needle, into the flask. Solution of *n*-BuLi (1.1 mL, 2.86 mmol of a 2.5 M solution in hexane) was syringed at room temperature into the stirred suspension of the aminopropyl-functionalized silica. The reaction mixture was stirred overnight. The solution was filtered off, and the resulting solid was washed two times with pentane. The reaction was continued directly by adding pentane (20 mL) into the flask containing the resulting solid. The solution of $Me_2Si(C_5H_5)Cl$ (0.31 g) in pentane (5 mL) was added into the stirred reaction mixture, and stirring was continued overnight. The solution was filtered off, and the resulting white solid was washed first twice with THF and then three times with pentane. Finally the solvent residues were evaporated under reduced pressure.

^1H NMR (400 MHz) δ: -0.1 ($Si-CH_3$), 0.6 (CH_2Si and CH_2), 2.6 (CH_2N), 3.5 (allyl CH), 6.2 (vinyl CH) ppm. ^{13}C NMR (100.6 MHz) δ: -1.5 ($Si-CH_3$), 14.2 (CH_2), 26.0 (CH_2), 44.1 (CH_2), 53.8 (allyl CH), 130.0 (vinyl CH), 132.1 (vinyl CH) ppm. ^{29}Si NMR (79.5 MHz) δ: 2.1 ($Si-CH_3$), -9.7 ($Si-CH_3$), 13.8 (silica-$Si-CH_3$), -110 (silica) ppm.

Reaction of $Hf(NMe_2)_4$ with Surface 1. Modified silica (surface **1**, 0.5 g) was packed into a flask in the glovebox, and toluene (15 mL) was added with a syringe. $Hf(NMe_2)_4$ (0.19 g, 0.54 mmol) was diluted with toluene (5 mL), and both mixtures were cooled to -60 °C. The solution of $Hf(NMe_2)_4$ in toluene was added to the flask dropwise, with a double-ended needle, while stirring. After the reaction mixture had warmed to room temperature, it was refluxed for half an hour. The solution was filtered off, and the resulting light yellow solid was washed three times with toluene and twice with pentane. Finally the solvent was evaporated under reduced pressure.

Catalyst **1**: ^1H NMR (400 MHz) δ: -0.2 ($Si-CH_3$), 0.6 (CH_2Si and CH_2), 2.6 (CH_2N, NCH_3), 6.0 (olefin CH) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ: -0.8 ($Si-CH_3$), 11−14.4 (CH_2), 26.2 (CH_2), 42.9 (NMe_2), 108 (olefin C), 112 (olefin CH), 117 (olefin CH) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ: 13.8 (silica-$Si-CH_3$), -20.8 ($Si-CH_3$), -110 (silica) ppm.

Reaction of $Zr(NMe_2)_4$ with Surface 1. The reaction was performed with the same procedure as in the previous case using 0.4 g of modified silica and 0.11 g (0.41 mmol) of $Zr(NMe_2)_4$. The product was light yellow.

Catalyst **2**: ^1H NMR (400 MHz) δ: -0.04 ($Si-CH_3$), 0.6 (CH_2Si and CH_2), 2.6 (CH_2N, NCH_3), 6.0 (olefin CH) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ: -0.6 ($Si-CH_3$), 11.8−15 (CH_2), 26.1 (CH_2), 37.3 (NMe_2), 43.5 (NMe_2), 110−120 (olefin CH) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ: 13.3 (silica-$Si-CH_3$), -20.9 ($Si-CH_3$), -110 (silica) ppm.

Reaction of $Ti(NMe_2)_4$ with Surface 1. Reaction was performed with the same procedure as in the previous case except that the reflux time was 6 h (0.5 g of modified silica and 0.12 g (0.54 mmol) of $Ti(NMe_2)_4$). The product was brown-yellow.

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Catalyst **3**: ^{1}H NMR (400 MHz) δ: −0.2 (Si−CH_3), 0.6 (CH_2-Si and CH_2), 2.6 (CH_2N, NCH_3), 5.8 (olefin CH) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ: −0.8 (Si−CH_3), 11.8−14.3 (CH_2), 26.0 (CH_2), 37.4 (NMe_2), 44.3 (NMe_2), 108 (olefin C), 114 (olefin CH), 117.5 (olefin CH) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ: 13.8 (silica-Si−CH_3), −20.8 (Si−CH_3), −110 (silica) ppm.

Ethylene Polymerization. Ethylene polymerization was carried out in toluene in a 0.5 dm^3 stainless steel autoclave. Toluene (250 mL) and the MAO (30%) used as cocatalyst were introduced into the evacuated and nitrogen-purged reactor under nitrogen flow. The heterogeneous catalyst was rinsed into the reactor with toluene under nitrogen flow. MAO and the catalyst were allowed to prereact for 15 min, while the temperature of the reactor was raised to the polymerization temperature (80 °C). The feeding of ethylene was begun, and the ethylene pressure was regulated to 2 or 2.5 bar. The consumption of ethylene was regulated with a mass flow controller. The polymerization time was 15−30 min. After polymerization, the reactor was allowed to cool to room temperature and then degassed. The polymerization product was stirred with a mixture of ethanol and concentrated hydrochloric acid (20−40 mL) and filtered. Finally the polymer was washed with ethanol and dried in an oven at 60 °C.

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