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Heterogeneous Constrained-Geometry Zirconium Catalysts

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Heterogeneous constrained-geometry catalysts were prepared by immobilizing $Zr(NMe_2)_4$ on a heterogenized *ansa*-cyclopentadienylamino ligand of type $(RN)R'R''Si(C_5R'''_4)$: surface **1**, $R = -O\text{-}Me_2Si(CH_2)_3$; $R', R'', R''' = Me$; surface **2**, $R = -O\text{-}Me_2Si(CH_2)_3$; $R', R''' = Me$, $R'' = H$. The preparation of the constrained-geometry catalyst ligand on a silica surface has been carried out in two steps: first, functionalizing the silica surface with aminopropyldimethylethoxysilane (APDMES) by using saturated gas−solid reactions, and then immobilizing two different (tetramethylcyclopentadienyl)chlorosilanes, $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$, on the APDMES-functionalized silica by utilizing *n*-BuLi (*n*-butyllithium). $Zr(NMe_2)_4$ was immobilized on the heterogeneous surfaces using the amine elimination reaction. The two heterogeneous monocyclopentadienylamido zirconium catalysts were characterized with ^1H, ^{13}C, and ^{29}Si solid-state NMR and FTIR spectroscopy and tested for ethylene polymerization.

Introduction

Constrained-geometry catalysts having the formula $(\eta^5\text{-}C_5R_4)SiR'_2(\eta^1\text{-}NR'')MX_2$ ($M = Ti, Zr, Hf$; $X = Cl, Me, NR_2$; $R, R', R'' =$ alkyl or aryl) are currently under intensive study and development[1−27] as a new generation of highly active and selective Ziegler−Natta-type catalysts[28−32] for the copolymerization of ethylene and α-olefins. The initial designs of *ansa*-monocyclopentadienylamido catalysts were introduced by Bercaw and co-workers, who developed scandium complexes for olefin polymerization catalysts.[33,34] Later Okuda[3] reported the synthesis of analogous titanium complexes, and soon afterward Dow and Exxon[35,36] detailed the synthesis and catalytic activities of group 4 constrained-geometry complexes in the patent literature.

The method initially used for preparation of these complexes involves the metathetical reaction of the dilithio salt of $[(C_5R_4)L(NR')]^{2-}$ with an appropriate metal halide. Alternatively a more efficient method is the amine elimination reaction developed originally by Lappert for metallocene compounds.[37] This reaction

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strategy was subsequently utilized by Teuben,[38,39] Herrmann,[20,40−42] and Gauthier[43] for *ansa*-cyclopentadienyl or indenyl complexes, and recently by Jordan[44−48] for stereoselective syntheses of chiral *ansa*-metallocenes. Carpenetti and co-workers[18] have prepared *ansa*-monocyclopentadienylamido group 4 complexes using a neat amine elimination reaction.

To date almost all the *ansa*-monocyclopentadienylamido catalysts that have been introduced have been homogeneous. Only Exxon[49] and Vega et al.[50] have tested heterogenization of these constrained-geometry catalysts in their patents.

In this paper we introduce novel heterogeneous *ansa*-monocyclopentadienylamido catalysts which have well-defined active sites. The catalysts have been prepared in three stages. In the first stage the silica surface was modified with aminopropyldimethylethoxysilane (APDMES) utilizing saturated gas−solid reactions. In the next step different (tetramethylcyclopentadienyl)chlorosilanes ($Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$) were immobilized on the surface using liquid-phase reactions. These two stages have been described previously.[51] In our present paper we describe immobilization of a zirconium complex ($Zr(NMe_2)_4$) onto these previously prepared bifunctional surfaces using the amine elimination reaction. The final heterogeneous catalysts were characterized with solid-state ^1H, ^{13}C, and ^{29}Si NMR and FTIR spectroscopy and have been tested in ethylene polymerization.

Results and Discussion

Preparation of Bifunctional Silica Carriers. The pretreated silica surface (calcinated at 600 °C) was modified first 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 1.2−1.5 N atoms (or APDMES molecules)/nm² of SiO_2 (see Table 1).

In the next step, two different (tetramethylcyclopentadienyl)methylchlorosilanes, $Me_2Si(C_5Me_4H)Cl$ (surface **1**) and $MeHSi(C_5Me_4H)Cl$ (surface **2**), were immobilized on the APDMES-functionalized silica by utilizing *n*-BuLi (Scheme 1b,c). The reaction of the amino group of the modified silica surface with *n*-BuLi in pentane produces a lithiated amido group, which reacts further with the chloride of the silane, and a chemical bond between nitrogen and silicon of the silane, as well as lithium chloride (LiCl) as a byproduct, is formed. Detailed modification and analyses of the catalyst carriers were described in our earlier report,[51] and the elemental analysis results are given in Table 1.

Scheme 1

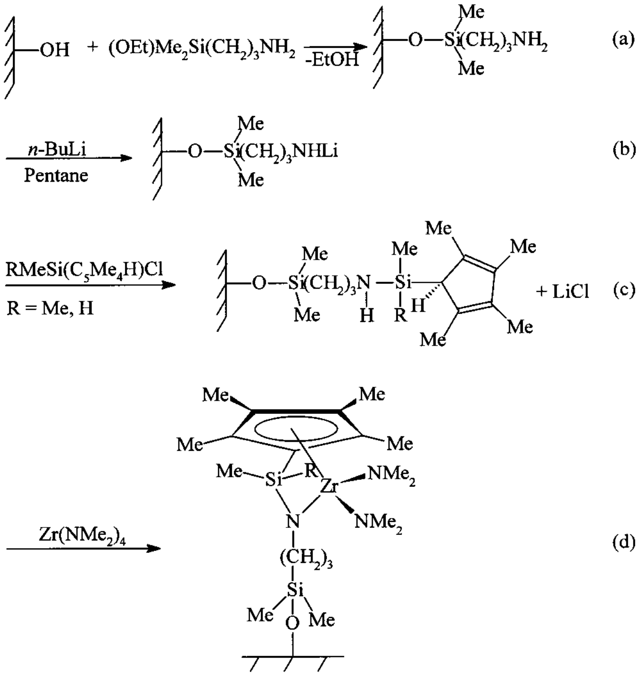

Table 1. Elemental Analyses of the Modified Surfaces and Catalysts

modified support	anal. C (wt %)	anal. N (wt %)	N/nm²	anal. Zr (wt %)	Zr/nm²	N/Zr
SiO_2 + APDMES	4.7	1.1	1.5			
surface **1**	8.38	0.80	1.1			
catalyst **1**	9.49	1.98	2.7	4.38	0.9	3.0
SiO_2 + APDMES	4.1	0.9	1.2			
surface **2**	8.86	0.74	1.0			
catalyst **2**	8.92	1.67	2.2	2.38	0.5	4.4

Preparation of Heterogeneous Catalysts. The synthetic route chosen for the attachment of tetrakis(dimethylamido)zirconium, $Zr(NMe_2)_4$, to the above prepared bifunctional supports is presented in Scheme 1d. $Zr(NMe_2)_4$ is expected to react with both the cyclopentadienyl ring and the amino group of the surfaces **1** and **2** with the evolution of NMe_2H. This amine elimination reaction does not require the use of an organolithium reagent, and therefore one step in the synthetic route is eliminated.

Immobilization of $Zr(NMe_2)_4$ on Surface 1. The $Zr(NMe_2)_4$-treated surface **1** (catalyst **1**) contains 4.38 wt % of zirconium, corresponding to a Zr loading of ca. 0.9 Zr atoms/nm² of support (Table 1). The nitrogen content of the catalyst was 1.98 wt %, corresponding to ca. 2.7 N atoms/nm² of support, which refers to a N/Zr ratio of 3.0. This ratio indicates that two NMe_2H molecules have been eliminated from the immobilized $Zr(NMe)_4$, and we could assume that zirconium has

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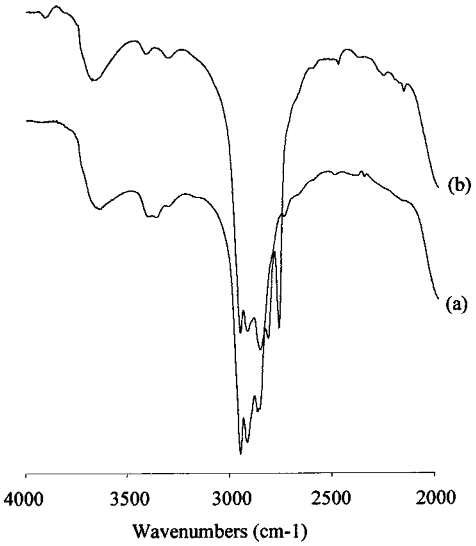


Figure 1. IR spectra of (a) surface **1,** APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$, and (b) catalyst **1**, surface **1** after anchorage of $Zr(NMe_2)_4$.

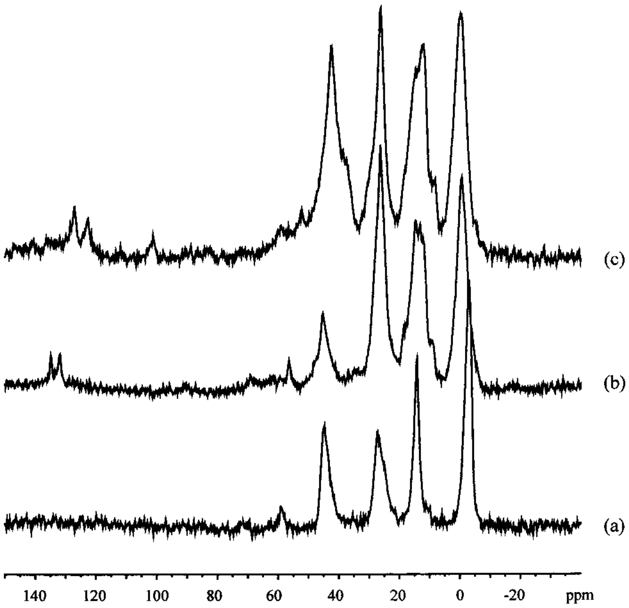


Figure 2. CP/MAS ^{13}C NMR spectra of (a) APDMES-modified silica, (b) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$, and (c) catalyst **1**, surface **1** after anchorage of $Zr(NMe_2)_4$.

reacted with both the Cp ring and the amino group of the surface. However, the elemental analyses give a too ideal view of the situation. On the basis of elemental analyses, surface **1** was not totally saturated with the $Me_2Si(C_5Me_4H)Cl$ molecules before immobilization of $Zr(NMe_2)_4$, and therefore these are also free $-NH_2$ sites on the silica.

In the IR spectrum of catalyst **1** (Figure 1b) a weak band, which is typical for a η^5-Cp group, is observed at 3907 cm^{-1}. This band is clear evidence of the coordination of Zr to the Cp ring. Two other new bands in the IR spectrum at 2859 and 2765 cm^{-1} can be assigned to the CH stretching of the CH_3N group bonded to zirconium.

The ^{13}C NMR spectrum of catalyst **1** (Figure 2c), when compared to that of the surface **1** (Figure 2b), shows some new features in the area of 130 ppm, where the carbons of the Cp ring are observed. The resonances due to the four cyclopentadienyl *C*Me carbons at 132 and 135 ppm have shifted to 123 and 127 ppm due to their coordination to zirconium. Also, the signal of the fifth carbon of the Cp ring has shifted from 56 to 101 ppm due to the elimination of hydrogen.[10,18] An intense signal of the methyl groups of the zirconium amide at 42 ppm overlaps the signal of the CH_2-N group at 45 ppm.

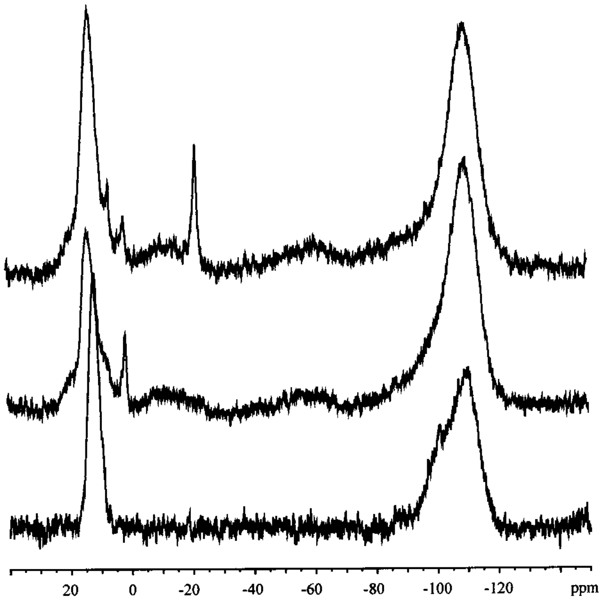


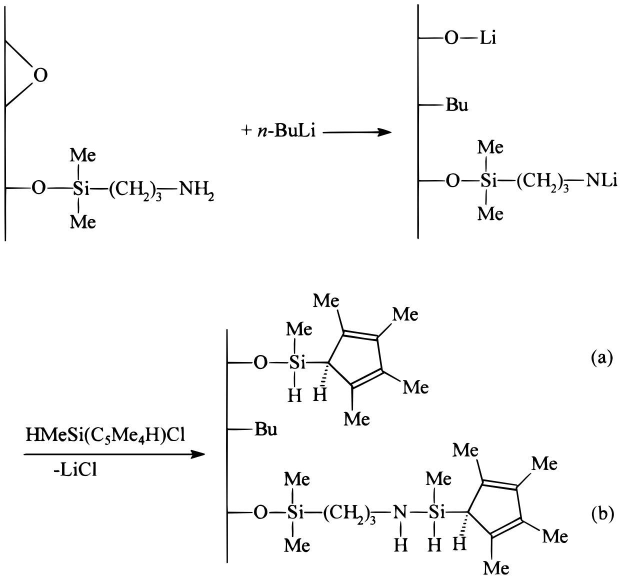
Figure 3. CP/MAS ^{29}Si NMR spectra of (a) APDMES-modified silica, (b) surface **1**, APDMES-modified silica after immobilization of $Me_2Si(C_5Me_4H)Cl$, and (c) catalyst **1**, surface **1** after anchorage of $Zr(NMe_2)_4$.

The ^{29}Si NMR spectrum of catalyst **1** (Figure 3c) shows the same silica and APDMES resonances as in the earlier stage (surface **1**, Figure 3b), but the ^{29}Si signal of the $Me_2Si(C_5Me_4)$ group has shifted from 1.6 to −21.8 ppm due to coordination of the zirconium.

Immobilization of $Zr(NMe_2)_4$ on Surface 2. In our earlier study[51] we found that *n*-BuLi treatment of the APDMES-modified silica produced not only lithiated amido groups but also cleavage of the siloxane bridges of the silica when the butyl and lithium groups reacted directly with the silica surface (Scheme 2). Because $MeHSi(C_5Me_4H)Cl$ can react with the lithium sites of both of these groups, there are actually two differently bonded $MeHSi(C_5Me_4H)$ groups on the surface **2**: one that is bonded to the amino groups (Scheme 2b), and the other that is bonded directly to the surface (Scheme 2a).

Before immobilizing the $Zr(NMe_2)_4$, the nitrogen content of surface **2** was 0.74 wt %, corresponding to ca. 1 N atoms/nm^2 of support (Table 1). The immobilization of $Zr(NMe_2)_4$ on surface **2** (catalyst **2**) increased the nitrogen content to 1.67 wt %, corresponding to 2.2 N atoms/nm^2 of support. The zirconium content for catalyst **2** was 2.39 wt %, corresponding to 0.49 Zr atoms/nm^2 of support. These chemical analysis results indicate that $Zr(NMe_2)_4$ has reacted with only about half of the amino groups when the zirconium content of catalyst **2** is compared to the nitrogen content of surface **2**. We deduced that due to steric reasons, $Zr(NMe_2)_4$ reacts preferably with $MeHSi(C_5Me_4H)$ groups that are bonded to the amino groups (Scheme 2a). This claim is sup-

Scheme 2



ported by the IR results. In the spectrum of surface **2** the Si−H band at about 2100 cm^{-1} is quite broad, and actually there are two bands: the band at 2113 cm^{-1} is specified as $MeHSi(C_5Me_4H)$ groups bonded to the amino groups, and the band at 2159 cm^{-1} is assigned to $MeHSi(C_5Me_4H)$ groups bonded directly on the surface. In the spectrum of catalyst **2**, the band at 2113 cm^{-1} has disappeared, and there is a new band at 2081 cm^{-1}. We can assume that the 2113 cm^{-1} band has shifted because zirconium amide has coordinated to the adjacent atoms of the SiMeH group. The band at 2159 cm^{-1} is still at the same wavenumber, but the intensity of the band is smaller when compared to the band at 2081 cm^{-1}. There is also a weak band at 3907 cm^{-1} in the spectrum of catalyst **2**, which is typical for a η^5-Cp group. Two other new bands at 2860 and 2765 cm^{-1} can be assigned as CH stretching of the CH_3N group bonded to zirconium.

The ^{13}C NMR of catalyst **2** cannot be as easily interpreted as that of catalyst **1**. The most intensive signals in the area around 130 ppm are at 123 and 128 ppm, which can be assigned to four cyclopentadienyl *C*Me carbons. However, there is a broad resonance at about 135 ppm, which is probably due to unreacted Cp groups. The signal of the fifth cyclopentadienyl ring carbon of the ring at about 100 ppm is not resolved. The methyl groups of the zirconium amide give two signals at 37 and 42 ppm. We assume that there are two signals because $Zr(NMe_2)_4$ has coordinated to both of two different surface sites (a and b) in Scheme 2. The ^{29}Si NMR spectrum of catalyst **2** shows the same silica and APDMES resonances as in the earlier stage (surface **2**), but the signal of the immobilized $MeHSi(C_5Me_4)$ group has shifted from −9 to −38 ppm due to coordination of the zirconium.

Polymerization of Ethylene. The activities of catalysts **1** and **2** were studied in the polymerization of ethylene in the presence of cocatalyst MAO. $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ was tested as a reference catalyst by using the same reactor and the same unoptimized polymerization conditions (ethylene pressure 2 bar, temperature 80 °C, reaction time 30 min, and toluene as a reaction medium) as in the case of catalysts **1** and **2**. A reaction temperature of 40 °C was also tested for catalyst **1**, but because it resulted in a very low activity (10 kg of PE/(mol of Zr·h)), the temperature was raised to 80 °C. The polymerization results and polymerization conditions are summarized in Table 2. The only variable factor in the polymerizations with catalysts **1** and **2** was the Al/Zr ratio. The polymerization results for catalyst **1** with different Al/Zr ratios indicate that a large amount of MAO is needed for methylation and activation of catalysts **1** and **2**. Kim and Jordan[52] have reported that zirconium amido complexes cannot be efficiently alkylated with MAO. The highest activities for the heterogeneous catalysts under these reaction conditions were around 200 kg of polyethylene/(mol of Zr·h). Our heterogeneous zirconium catalysts were almost 20 times less active than the homogeneous constrained-geometry reference catalyst $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$, which showed under the same polymerization conditions an activity of 3550 kg of polyethylene/(mol of Ti·h) when the Al/Ti ratio of 5000 was used. The molecular weight distributions of the polyethylenes were narrow (about 2), which is typical for polymers prepared with single-site metallocene catalysts. The melting temperatures of the polyethylenes prepared with heterogeneous catalysts **1** and **2** were between 140 and 141 °C, values typical for linear HD polyethylene. Also, the IR spectra of the polyethylenes made with heterogeneous catalysts **1** and **2** show no sign of the branching in the polyethylenes supporting the linear structure.

Conclusion

Heterogeneous constrained-geometry catalysts for ethylene polymerization were prepared by anchoring tetrakis(dimethylamido)zirconium ($Zr(NMe_2)_4$) on the bifunctional silica surfaces. The bifunctional carrier, containing amino and tetramethylcyclopentadienyl groups in the same coupling agent molecule, was prepared in two stages. The reaction of the zirconium compound with tetramethylcyclopentadienyl and amino groups proceeds via elimination of amine, yielding the constrained-geometry structure based on IR and ^{13}C and ^{29}Si CP/MAS NMR results.

Both heterogeneous catalysts were shown to be active in the polymerization of ethylene in the presence of a cocatalyst, MAO. Linear high-density polyethylene with narrow molecular weight distribution was obtained, indicating that our heterogeneous constrained-geometry catalysts function as single-site catalysts.

To improve the activity of the present catalysts, a comprehensive study on activation of heterogeneous constrained-geometry zirconium catalysts is in process. In addition we are currently preparing corresponding titanium and hafnium catalysts.

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 (aminopropyldimethylethoxysilane) in a commercial F-120 ALCVD (atomic layer chemical vapor deposition) reactor manufactured by Microchemistry Ltd., Finland, ac-

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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	*n* of Zr (mol)	Al/Zr	yield (g)	A_m (kg/mol of Zr·h)	T_m (°C)	M_w (g/mol)	M_w/M_n
catalyst **1**	2.2×10^{-5}	1400	0.7	60	141.3	231 000	2.2
catalyst **1**	2.0×10^{-5}	3400	1.8	180	139.7	204 000	2.1
catalyst **2**	1.1×10^{-5}	5000	1.0	180	139.8	214 000	2.2
catalyst **2**	9.5×10^{-6}	6000	1.0	210	140.0	226 000	2.3

[a] Polymerization conditions: temperature, 80 °C; ethylene pressure, 2 bar; time, 30 min.

cording to published procedures.[51] $Me_2Si(C_5Me_4H)Cl$ and $MeHSi(C_5Me_4H)Cl$ were prepared and immobilized on the APDMES-functionalized silica according to published procedures.[51] The solvents used were distilled from sodium benzophenone ketyl under nitrogen atmosphere. $Zr(NMe_2)_4$ (Strem Chemicals) and $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ (Boulder Scientific Co.) were used as received. Methylaluminoxane (10% and 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 using a Nicolet Impact 400D FTIR spectrometer equipped with DRIFT (diffuse reflectance infrared-Fourier transform), and the connection to a glovebox was airtight. 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 53. Elemental analyses for carbon, hydrogen, and nitrogen were determined with a Carlo Erba Instruments EA 1110 CHNS-O analyzer. Zirconium 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 cm^3/min. The calibration of the columns was done with a universal method by using polystyrene standards with narrow molecular weight distribution.

Anchoring of Tetrakis(dimethylamido)zirconium ($Zr(NMe_2)_4$) on the $Me_2Si(C_5Me_4H)Cl$-Modified Surface (Surface 1). Modified silica (surface **1**) was packed into the flask in the glovebox, after which toluene (15 mL) was added with a syringe. $Zr(NMe_2)_4$ was diluted in toluene (5 mL), and both mixtures were cooled to −60 °C. The solution of $Zr(NMe_2)_4$ in toluene was added dropwise with a double-ended needle into the flask while stirring. The reaction mixture was allowed to warm to room temperature. The mixture was refluxed for an hour, producing a light yellow solid. The solution was filtered off, and the resulting solid was washed once with toluene and three times with pentane. Finally the solvent was evaporated under reduced pressure.

Catalyst **1**: ^1H NMR (400 MHz) δ: −0.01 ($Si-CH_3$), 0.6 (CH_2-Si and CH_2), 2.2 (ring CH_3), 2.6 (CH_2N, NCH_3) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ: −0.2 ($Si-CH_3$), 12 (ring CH_3), 26.2 (CH_2), 42.4 (NMe_2), 101.3 (ring C), 122.7 (ring C), 127.1 (ring C) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ: 13.5 (silica-Si−CH_3), −21.8 ($Si-CH_3$), −110 (silica) ppm.

Anchoring of Tetrakis(dimethylamido)zirconium ($Zr(NMe_2)_4$) on the $MeHSi(C_5Me_4H)Cl$-Modified Surface (Surface 2). Anchorage was done using the same procedure as in the previous case with the exception that the reflux time was half an hour. The product was light yellow.

Catalyst **2**: ^1H NMR (400 MHz) δ: −0.05 ($Si-CH_3$), 0.7 (CH_2-Si and CH_2), 2.2 (ring CH_3), 2.6 (CH_2N, NCH_3) ppm. ^{13}C CP/MAS NMR (100.6 MHz) δ: −0.3 ($Si-CH_3$), 9.0 (ring CH_3), 11.6 (ring CH_3), 26.1 (CH_2), 36.9 (NMe_2), 42.1 (NMe_2), 123.3 (ring C), 128.5 (ring C) ppm. ^{29}Si CP/MAS NMR (79.5 MHz) δ: 13.8 (silica-Si−CH_3), −38.8 ($Si-CH_3$), −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 MAO (10% for $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]TiCl_2$ and 30% for catalysts **1** and **2**), used as a cocatalyst, were introduced into the evacuated and nitrogen-purged reactor under a nitrogen flow. The heterogeneous catalyst was rinsed into the reactor with toluene under a 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. The feeding of ethylene was begun, and the ethylene pressure was regulated to 2 bar. The consumption of ethylene was regulated with a mass flow controller. The polymerization time was 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 a small amount of concentrated hydrochloric acid and filtered. Finally the polymer was washed with ethanol and dried in an oven at 60 °C.

Supporting Information Available: CP/MAS ^{13}C and ^{29}Si NMR and IR spectra of surface **2** and catalyst **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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