

Role of Amine Structure and Site Isolation on the Performance of Aminosilica-Immobilized Zirconium CGC-Inspired Ethylene Polymerization Catalysts

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Received April 2, 2004

The homogeneous zirconium complex (CpSiMe₂Cl)ZrCl₃ is immobilized onto three different aminosilica supports, resulting in supported constrained-geometry-inspired zirconium complexes that, when combined with methylalumoxane (MAO), are active for the homopolymerization of ethylene to produce linear polyethylenes. The structure of the immobilized metal species is shown to depend on both the nature of the amine groups on the surface (primary vs secondary) and the amine surface density (densely loaded vs site-isolated). Diffuse-reflectance ultraviolet–visible (UV–vis) spectra of the metallated solids indicates that a true, immobilized constrained-geometry catalyst (CGC) is likely only produced on the silica that contains isolated primary amine sites. The polymerization data support the hypothesis that a traditional constrained-geometry Zr catalyst exhibits higher catalytic activity compared to a more open metal center that is likely the primary species produced on a densely loaded aminosilica surface. MAO causes significant leaching of the immobilized catalysts, possibly due to the cleavage of the Si–O–Si surface linkage.

Introduction

Constrained-geometry catalysts (CGCs) containing a cyclopentadienyl ring and an amido ligand, linked together with a dimethylsilyl unit, are currently under intensive study and development as a new generation of highly active catalysts for olefin polymerization.^{1–10} Soon after Bercaw and co-workers¹¹ introduced the first constrained-geometry scandium complexes for olefin polymerization, corresponding group 4 CGCs were also

developed by Okuda,² Dow,¹² and Exxon.¹³ There are several strategies by which the group 4 constrained-geometry complexes have been synthesized. One route is to synthesize [C₅R₄HSiMe₂NHR] (R = CH₃, H), followed by a metathetical reaction of its dilithium salt with MCl₄ (M = Ti, Zr).^{14,15} As an alternative, titanium and zirconium CGCs can be prepared through an amine elimination reaction.^{16–20} A third method, developed by Royo et al., involves the initial formation of the (C₅H₄-SiMe₂Cl)MCl₃ (M = Ti, Zr, R = H, Me) complexes, which upon subsequent reaction with *tert*-butylamine afford the corresponding constrained-geometry complexes.^{1, 21}

To date, almost all the *ansa*-monocyclopentadienyl-amido catalysts that have been introduced have been homogeneous. However, for the purpose of commercial

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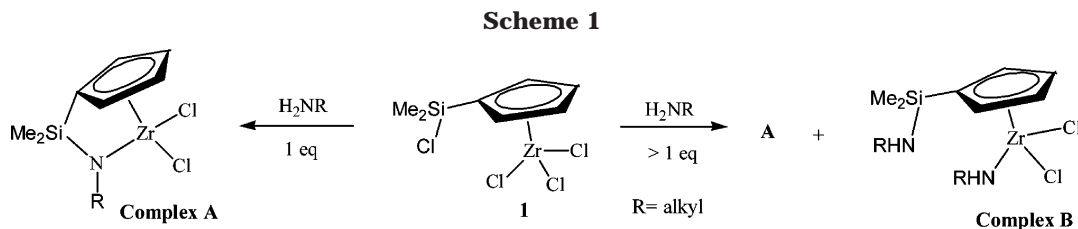
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application, heterogenization of the homogeneous catalysts on solid supports is practical and sometimes preferred. Both Exxon¹³ and Vega et al.²² have heterogenized these constrained-geometry catalysts in their patents, although Dow has commercialized this technology in solution under the INSITE name.^{12b} In an alternate immobilization approach, Pakkanen et al.²³ have reported the preparation of heterogeneous zirconium CGCs through a stepwise approach by building the ligand and metal complex on the support surface. In comparison to their homogeneous analogues, supported catalysts usually become less reactive and selective. This is due to many factors, with a primary cause potentially being the formation of multiple types of ill-defined metal species on the surface. Hence, it is clear that if a molecular level understanding of supported CGCs is to be developed, a method is needed to prepare well-defined catalysts with (i) isolated sites, (ii) uniform sites, and (iii) structures that are amenable to detailed characterization.

The most widely applied method to immobilize homogeneous olefin polymerization catalysts consists of anchoring metallocene/single-site catalysts onto silicas that are pretreated with methylalumoxane (MAO).^{24,25} While this method is often preferred for commercial application, the large excess of the ill-defined MAO that is used (~100–1000 Al:M) makes characterization of the supported transition-metal complexes difficult. To make immobilized complexes that are amenable to detailed characterization leading to an understanding of the molecular structure of the metal species, metal complexes can be tethered to the support surface via a covalent ligand–surface linkage, as Pakkanen²³ and others^{19,26} have reported for CGC-type complexes. However, the multistep approach involving several synthetic steps on the solid support²³ and the addition of a preformed CGC complex to a silanol-containing support¹⁹ likely lead to multisited solids. An alternate, elegantly simple approach has been recently introduced by Coughlin using Royo's metalation strategy to assemble Ti–CGCs on an amine-substituted polymer in one step.²⁶

Despite all the previous work on covalently tethered CGCs,^{19,22–23,26,27a} the exact speciation of the Ti or Zr atoms on the surface has not been elucidated. This is

due to the difficulty in characterizing the bonding of the metal center when it is present in low concentrations on a support. In fact, no definitive proof has been presented which illustrates that true CGC complexes have been produced on the surface.^{23,26,27a} Indeed, one could achieve many different types of transition-metal complexes depending on the surface amine type, site density, and reactivity.

Recently, we have illustrated that Ti complexes with substantially improved productivity in ethylene polymerizations can be prepared using a novel aminosilica support material,^{27b} with relatively isolated primary amines on the surface (relative to catalysts prepared on a densely loaded aminosilica surface).^{27a} It has been hypothesized that this observation could be attributable to increased accessibility of the complexes on the silica surface and/or to production of a different type of surface metal complex when isolated amines are used. To further probe these issues, here we report the preparation of Zr CGC-inspired complexes on three different types of amine-functionalized silica supports utilizing the Royo/Coughlin metalation strategy. The nature of the surface species and polymerization activities are found to be strongly dependent on the structure of the aminosilica support.

Results and Discussion

Catalyst Preparation. There are two general routes that have been applied to prepare ligand-tethered CGC-inspired catalyst systems onto silica: (i) stepwise building of the ligand and metal complex at the surface^{23,27a} and (ii) immobilizing a presynthesized catalyst precursor containing an anchorable functionality.^{19,26} Often, the second route is preferred, as it can result in a more well-defined system that requires characterization of only one solid material, whereas the first route requires the characterization of the solid after each step and sometimes such detailed characterization is simply not practical. Royo and co-workers²¹ have demonstrated that contacting complex **1** with a primary amine or LiNHR results in the formation of a constrained-geometry zirconium complex in solution (Scheme 1, species A). Coughlin²⁶ recently utilized this approach to assemble a Ti CGC on a cross-linked (aminomethyl)-polystyrene. Here three different amine-functionalized SBA-15 silicas have been prepared and complex **1** is subsequently immobilized on these supports. The resulting silica-supported Zr complexes are up to 50 times more reactive than their Ti analogues under similar reaction conditions.²⁸

SBA-15²⁹ is a well-defined, hexagonal mesoporous silica material with straight mesopores that are con-

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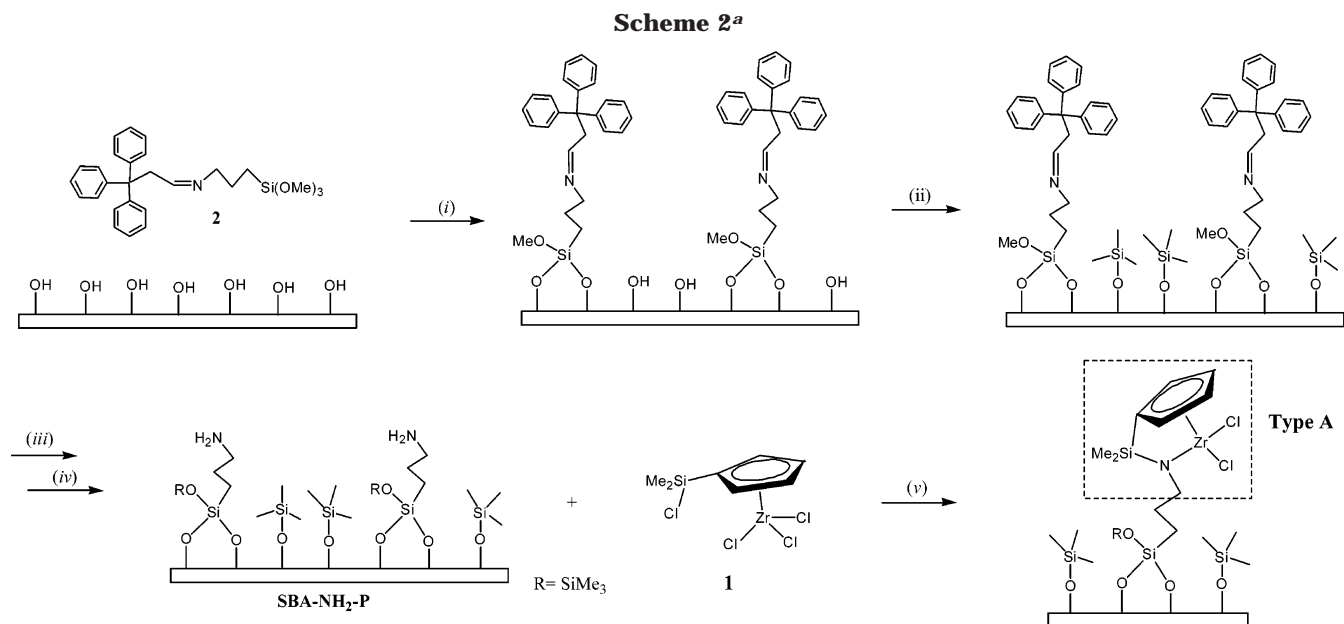
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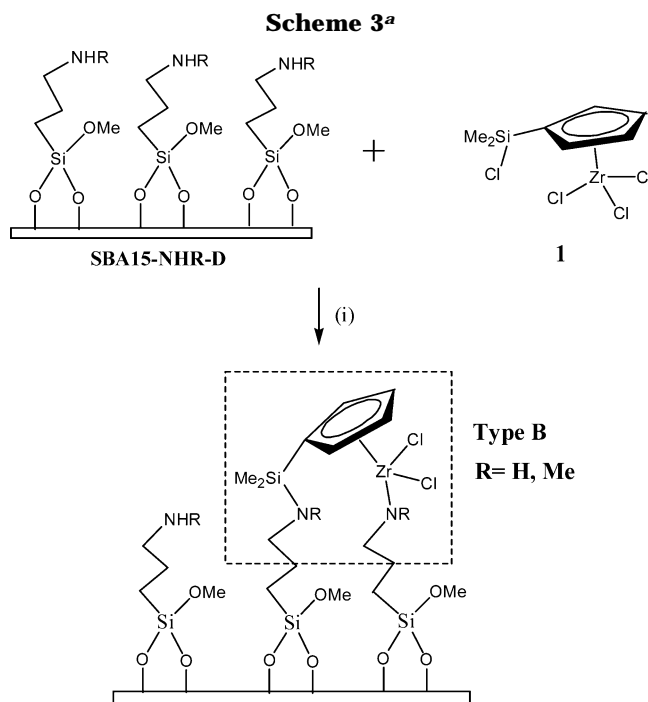
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^a Conditions: (i) toluene, room temperature, 24 h; (ii) HN(SiMe₃)₂, toluene, room temperature, 24 h; (iii) H₂O/MeOH/HCl (2:2:1, v:v:v); (iv) HN(SiMe₃)₂, toluene, room temperature, 24 h; (v) toluene, 2,6-di-*tert*-butylpyridine, 24 h, room temperature.

nected through small, random micropores. Hexagonal mesoporous silicas of this type are useful model supports, because they have well-defined, tailorable mesopore systems with low polydispersity. Primary amine and secondary amine functionalized SBA-15 were prepared by reacting SBA-15 with (3-aminopropyl)trimethoxysilane (APTS) and ((methylamino)propyl)trimethoxysilane (MAPTS), respectively, in a toluene suspension at room temperature. Any remaining accessible surface silanol (Si–OH) groups in the as-prepared aminosilica materials were capped by further reaction with excess HN(SiMe₃)₂. The resulting densely functionalized aminosilica materials (SBA-NH₂-D and SBA-NHMe-D) have a typical amine loading around 0.8–1.0 mmol of amine site per gram of support. The fact that amine sites on these two solids are not isolated from each other may allow for the creation of catalytic centers with multiple types of sites during the immobilization of complex **1**. In an effort to create an environment that will allow for the synthesis of a single type of site, a material with more isolated amines has been developed as a support scaffold.^{27,30} A patterning molecule has been designed and synthesized that allows for the effective spacing of primary amino groups on a silica surface, with an average spacing between neighboring amine groups to be ~8 Å or more (SBA-NH₂-P; Scheme 2, steps i–iv).^{27b}

The homogeneous zirconium complex **1** was treated with the amine-functionalized silica supports SBA-NH₂-D, SBA-NHMe-D, and SBA-NH₂-P in the presence of excess 2,6-di-*tert*-butylpyridine to scavenge the 2 equiv of HCl generated. The reaction was carried out in a toluene suspension at room temperature for 24 h, followed by filtration in a drybox with extensive washing



^a Conditions: (i) toluene, 2,6-di-*tert*-butylpyridine, 24 h at room temperature.

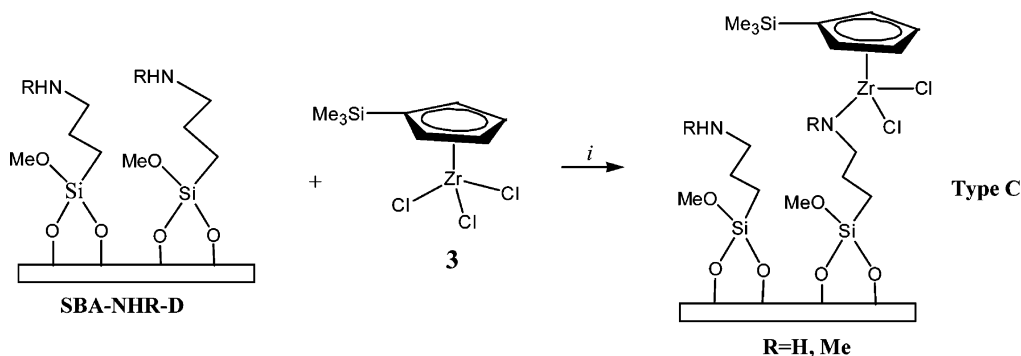
with toluene, dichloromethane, and hexane. The resulting light-colored solid materials were dried under high vacuum to afford the catalysts SBA-NH₂-P-1 (Scheme 2) and SBA-NHR-D-1 (R = H, Me; Scheme 3). The catalyst SBA-NHR-D-3 was also prepared in a similar manner by reacting complex **3** with SBA-NHR-D (R = H, Me; Scheme 4).

Catalyst Characterization. Both the Zr–Cl and Si–Cl bonds in complex **1** can react with primary amine groups. In the presence of the proton scavenger, contacting **1** with 1 equiv of primary amine results in the formation of a traditional constrained-geometry zirconium complex (complex **A**; Scheme 1). However, in the presence of more than 1 equiv of primary amine, a

(28) We also immobilized (CpSiMe₂Cl)TiCl₃ on SBA-NH₂-P and SBA-NH₂-D, and under identical ethylene polymerization conditions used here, the supported Ti catalysts only showed a productivity of ~60 kg of PE/(mol of Ti) h.

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Scheme 4^a

^a Conditions: (i) toluene, 2,6-di-*tert*-butylpyridine, 24 h at room temperature.

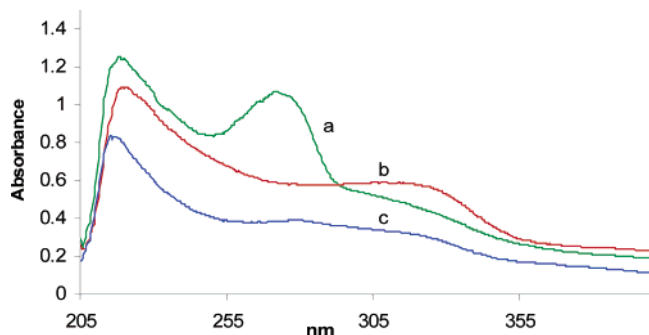


Figure 1. UV-vis spectra (vs PTFE) of **1** immobilized on (a) SBA-NH₂-P, (b) SBA-NH₂-D, and (c) SBA-NHMe-D.

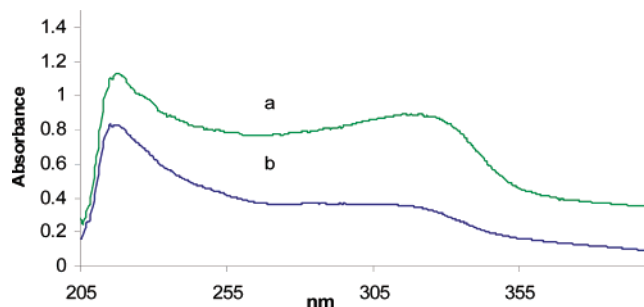
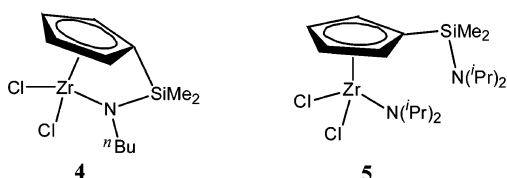


Figure 2. UV-vis spectra (vs PTFE) of **3** immobilized on (a) SBA-NHMe-D and (b) SBA-NH₂-D.

Scheme 5



mixture of **A** and **B** is expected (Scheme 1) if both Zr-Cl and Si-Cl bonds react with separate amine groups. Analogously, reaction between complex **1** and primary amine groups with site-isolated amine silica, SBA-NH₂-P, is expected to form only a type A metal center, a true supported CGC (Scheme 2). Immobilizing **1** on a secondary amine functionalized silica support (SBA-NHMe-D) should result in a type B active site (Scheme 3), the heterogeneous analogue to homogeneous complex **B** (Scheme 1).

The metalated solids were characterized by TGA/DSC, FT-Raman spectroscopy, diffuse-reflectance UV-vis spectroscopy, and, in some cases, elemental analysis. FT-Raman spectra of the metalated materials showed two bands around 2963 and 2905 cm⁻¹, which can be assigned to the CH stretching of the alkyl linkage (spectra not shown). However, due to sample fluorescence, we were not able to obtain additional information relating to the chemical bonding around the bridging Si or Zr atoms. The solid-state UV-vis spectrum (Figure 1a) of the material made by contacting SBA-NH₂-P with complex **1** (SBA-NH₂-P-1 in Scheme 2) showed an absorbance band at 275 nm, which is assigned as a ligand-metal charge transfer (LMCT),³¹ a charge transfer from the Cp ring to the Zr metal center. This is consistent with a solution UV-vis absorbance of the homogeneous Zr CGC complex **4** (Scheme 5), which

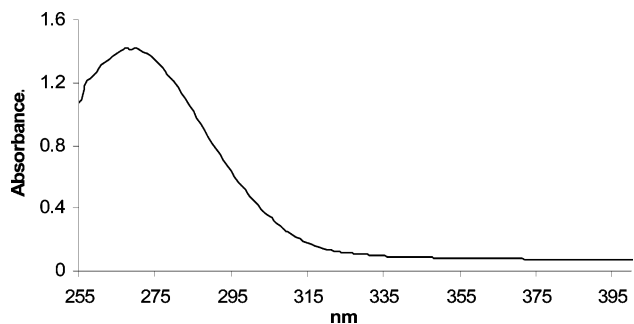


Figure 3. Solution UV-vis spectrum of complex **4** (λ_{max} 272 nm, toluene as solvent).

showed an absorbance band at 272 nm (Figure 3). In contrast, in the UV-vis spectrum of the material made by contacting SBA-NHMe-D with complex **1** (SBA-NHMe-D-1 in Scheme 3), the absorbance band at 275 nm is notably absent, while a broad new band is present at 326 nm (Figure 1c). As the reaction of SBA-NHMe-D with complex **1** is not expected to produce a CGC site due to the nature of the amine used (secondary amine instead of primary amine), this observation was not surprising. Instead, this material is expected to have a surface structure akin to that of the homogeneous complex **5** (Scheme 5), with the Zr and Si atoms interacting with different amines to produce type B sites as shown in Scheme 3. Hence, the absorbance at 326 nm is assigned to this new species. This represents a red shift of the LMCT absorbance from a material with

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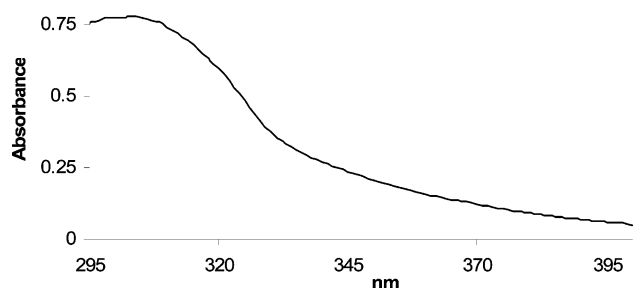


Figure 4. Solution UV-vis spectrum of complex **5** (λ_{max} 306 nm, toluene as solvent).

Table 1. Elemental Composition of the Supported Catalysts

| supported catalyst | anal. (wt %) | | | | anal. (found) Zr:Cl:N |
|--------------------------|--------------|------|------|------|--------------------------|
| | C | N | Cl | Zr | |
| SBA-NH ₂ -D-1 | 12.14 | 1.41 | 2.75 | 3.25 | 1:2.18:2.83 |
| SBA-NHMe-D-1 | 12.35 | 1.69 | 2.52 | 3.10 | 1:2.09:3.55 |
| SBA-NH ₂ -P-1 | 11.53 | 0.75 | 2.14 | 2.87 | 1:1.91:1.70 |

type A sites compared to type B sites. A similar red shift in the absorbance band was also observed in moving from homogeneous complex **4** to complex **5**, which has a band at 306 nm (Figure 4). Interestingly, contacting **1** with SBA-NH₂-D could result in a material that contains a mixture of type A and type B metal centers, yet this is not what is observed on the basis of UV-vis data. The UV-vis spectrum for this material looks essentially identical with the material SBA-NHMe-D-1 (Figure 1), leading to the conclusion that immobilizing **1** on densely loaded primary aminosilica supports predominantly results in type B metal centers. Hence, when a dense loading of amines is present, true CGC sites may not be produced.

Reacting complex **3** with amine-functionalized silica supports SBA-NHR-D (R = H, Me) forms the materials SBA-NHMe-D-3 and SBA-NH₂-D-3, in which the zirconium complex is postulated to be chemically tethered onto the amine support through a single Zr-N bond, forming a type C metal center (Scheme 4). UV-vis spectra of these materials showed a similar absorbance band around 326 nm (Figure 2), which is almost identical with that of the materials SBA-NHMe-D-1 and SBA-NH₂-D-1. This provides evidence that supports the structures postulated in Schemes 3 and 4 and indicates that the materials SBA-NHMe-D-1, SBA-NH₂-D-1, SBA-NHMe-D-3, and SBA-NH₂-D-3 all have similar metal coordination. Finally, it is noteworthy that all the aminosilica-supported materials with type A, B, or C sites showed an absorbance band around 220 nm, characteristic of tetrahedrally coordinated Zr(IV) and the silica support.^{30,31}

Elemental analyses of the type A and type B materials are summarized in Table 1. All the Cl to Zr ratios of these materials are very close to a theoretical value of 2, suggesting that both the Zr-Cl and Si-Cl bonds of complex **1** have been reacted with the amine silica surface. The N to Zr ratio of 1.70 in type A materials indicates that not all the amine sites in the patterned amine silica, SBA-NH₂-P, are incorporated with a zirconium CGC, with up to 40% of the amine sites left unreacted. Similarly, about 30% and 45% of the amine sites in the materials SBA-NHMe-D-1 and SBA-NH₂-

D-1 are left unreacted based on elemental analysis. This could be due to steric constraints on the surface.

Polymerization Results. The supported catalysts were evaluated in the catalytic polymerization of ethylene. The cocatalyst used in these polymerization studies was MAO (10 wt % in toluene from Aldrich). An excess of cocatalyst was used (~1000 equiv) to activate the supported catalysts. Ethylene polymerizations were conducted by charging a mixture of ~10 mL of dry toluene and ~1000 equiv of MAO along with ~10 mg of the supported catalyst in a thick-walled tubular glass pressure vessel. The resulting slurry was premixed for about 20 min before it was pressurized with 60 psi of ethylene for 5–10 min with constant stirring at 25 °C in a water bath. The reaction slurry became very viscous as time progressed, and at the end of the polymerization, the ethylene supply was stopped and the reactor was vented. The addition of acidic methanol resulted in the precipitation of the polymer, which was collected through filtration and dried at 70 °C overnight. The yield of the polymer, polymerization activity, molecular weights, and melting points of the PEs are summarized in Table 2.

The material SBA-NH₂-P-1, which contained type A sites (true CGC sites), exhibited high activity for the polymerization of ethylene (Table 2, entry 3). Pakkanen prepared a material described as a Zr CGC by immobilizing Zr(NMe₂)₄ on a heterogenized (tetramethylcyclopentadienyl)amino ligand, and the resulting material had an activity of only 60 kg of PE/(mol of Zr) h (Al:Zr = 1400, reaction temperature 80 °C, 2 bar of ethylene pressure for 30 min)^{23a,32} compared to an activity of 3086 kg of PE/(mol of Zr) h observed here. Although the polymerization conditions used here are different from those of Pakkanen, the observed activity of the material with type A sites is still unusually high, especially considering the mild conditions used here. GPC analysis of the resulting PE yields an M_w value of 130 000 and a PDI value of 2.3. High-temperature ¹³C NMR showed a single peak at 30.1 ppm, indicating that the PE obtained is very linear. Surprisingly, the material SBA-NH₂-P-1 with type A sites is twice as active as the homogeneous CGC **4** under the conditions used here, although this observation must be tempered by the knowledge that the detailed kinetics of the polymerization as well as the catalyst deactivation profile have not been enumerated. Furthermore, the amount of MAO used can strongly impact homogeneous CGC activity, with homogeneous CGC requiring substantially more MAO to reach maximum activities.³³

The materials SBA-NH₂-D-1 and SBA-NHMe-D-1, which are postulated to have similar surface structures (type B sites) based on UV-vis spectra, are observed to have similar ethylene polymerization activities (Table 2, entries 1 and 2). This is further evidence for a common type of active center in these materials. GPC analysis indicated that the resulting PEs from those two catalysts have almost identical M_w values with an M_w

(32) The stepwise approach used in preparing the supported Zr catalyst described previously²³ could result in immobilized CGC species as well as metal complexes with other, unintended structures. Indeed, there is no direct evidence reported in previous studies that conclusively demonstrates formation of a true CGC site.^{23,26,27a}

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Table 2. Ethylene Polymerization Using Silica-Supported Zr–CGCs and Homogeneous Zirconium Complexes^a

| entry | catalyst | Zr loading ^b (mmol/g of cat) | polymer yield (g) | time (min) | MAO/Zr | productivity (kg of PE/(mol of Zr) h) | <i>T</i> _m | 10 ³ <i>M</i> _n | PDI |
|-------|--------------------------|--|----------------------|---------------|--------|--|-----------------------|---------------------------------------|-------|
| 1 | SBA-NH ₂ -D-1 | 0.35 | 0.561 | 5 | 1000 | 1891 | 138.8 | 63 | 2.1 |
| 2 | SBA-NHMe-D-1 | 0.34 | 0.432 | 5 | 1000 | 1920 | 134.6 | 60 | broad |
| 3 | SBA-NH ₂ -P-1 | 0.31 | 0.676 | 5 | 1000 | 3086 | 132.1 | 130 | 2.3 |
| 4 | SBA-NH ₂ -D-3 | 0.35 | 0.137 | 5 | 1000 | 548 | 139.2 | 450 | broad |
| 5 | SBA-NHMe-D-3 | 0.37 | 0.147 | 5 | 1000 | 588 | 140.0 | 530 | 1.98 |
| 6 | 1 | n.a. | 0.192 | 10 | 300 | 82 | 134.0 | n.d. | n.d. |
| 7 | 4 | n.a. | 1.48 | 5 | 400 | 1460 | 131.5 | n.d. | n.d. |
| 8 | 5 | n.a. | 1.32 | 5 | 360 | 1286 | 129.7 | n.d. | n.d. |

^a About 9–15 mg of catalyst (entries 1–5) was mixed with 1000 equiv of MAO in ~10 mL of dry toluene in a thick-walled tubular glass vessel; about 5 mg of **1**, **4**, and **5** were used in each test. ^b Zr loadings of entries 1–3 were determined by elemental analysis, while Zr loadings of entries 4 and 5 were estimated by TGA/DSC analysis.

value of 63 000 for SBA-NH₂-D-1 and 60 000 for SBA-NHMe-D-1, respectively. A homogeneous analogue, complex **5**, was also prepared (Scheme 5), in which the Si–N and Zr–N bonds closely mimic those of the postulated structure of the supported catalysts SBA-NH₂-D-1 and SBA-NHMe-D-1 (type B sites). The catalytic activity from **5** is lower than that from the supported materials, which is similar to the trend seen in the materials that have a true CGC structure (complex **4** and SBA-NH₂-P-1). The catalysts SBA-NH₂-D-3 and SBA-NHMe-D-3 also should share a common structure (type C sites), and indeed, their polymerization activities and the *M*_w values of the resulting PEs are very similar as well, with activities of 548 and 588 kg of PE/(mol of Zr) h and *M*_w values of 450 000 and 530 000 for SBA-NH₂-D-3 and SBA-NHMe-D-3, respectively.

Catalyst Leaching. To determine if the immobilized catalysts are covalently bonded to the amine silica supports, leaching tests were undertaken. Initially, it is clear that the complexes are fixed strongly to the supports. The materials SBA-NH₂-P-1 and SBA-NHR-D-1 (R = H, Me) were washed with hot toluene, filtered, and then dried, and the catalytic activities of the recovered solids showed no significant change. Furthermore, when the filtrate was mixed with a large excess of MAO (1000 equiv), no ethylene polymerization activity was observed. In addition, trialkylaluminums were found to induce no leached metal species that are active for ethylene polymerization. For example, the catalyst SBA-NH₂-P-1 was stirred with an excess (500 equiv) of AlMe₃ or Al(*i*Pr)₃ in toluene for 10 min and the slurry was then filtered inside a drybox. Excess MAO (1000 equiv) was added into the filtrate, and the mixture was subjected to standard ethylene polymerization conditions. No polyethylene was formed from this reaction mixture, indicating that contact with trialkylaluminums alone does not induce any leaching of active species. In contrast, MAO is found to induce some leaching of active metal species from the solids. Precontacting the supported catalysts with MAO (1000 equiv) in toluene for 20 min, followed by filtration in a drybox and evaluation of the filtrate for ethylene polymerization reactivity, revealed that the filtrate had substantial catalytic activity. For example, with the catalyst SBA-NH₂-P-1 and 1000 equiv of MAO, the filtrate had a catalytic activity of 1646 kg of PE/(mol of Zr) h, corresponding to ~50% of the activity from a regular polymerization run. Additionally, it was observed that the catalytic activity of the filtrate is dependent on the amount of

MAO used. When SBA-NH₂-P-1 was allowed to precontact with 300 equiv of MAO for 20 min followed by filtration, the filtrate yielded a catalytic activity of only 480 kg of PE/(mol of Zr) h, about 15% of that for a regular test.

It is important to note that it is very difficult to accurately determine the amount of *active* zirconium species leached from the solid. Thus, the leaching activity mentioned above was calculated on the basis of the total amount of zirconium in the solid. It is noteworthy that the activity of the homogeneous catalyst **4** (1460 kg of PE/(mol of Zr) h) is of the same order as the leached species from the patterned material (1646 kg of PE/(mol of Zr) h). This might lead one to assume that the additional activity observed with SBA-NH₂-P-1 is due to immobilized sites. However, this is not a safe assumption. As the leached species could be more active than the supported ones (although homogeneous complexes are found to be less active here; vide supra), a minor fraction of Zr may be removed from the solid, yet these species may provide almost all of the activity observed using the solid catalyst. Furthermore, the MAO-activated species are extremely sensitive, and although all manipulations are performed in a drybox, it is possible there is still some deactivation through handling. Thus, the results of these leaching experiments should be viewed as only a lower bound on the activity of the leached species. Hence, in the case of SBA-NH₂-P-1, for example, the activity due to leached species could range from ~53 to 100% of the total activity.

Similar leaching results were also obtained with the catalysts SBA-NH₂-D-1 and SBA-NHR-D-1. MAO has been shown to cause leaching in other solid-supported systems as well.^{34,35} However, the nature of the leached active species is still unknown. Two potential sites are likely to be susceptible to cleavage by MAO: one is the Si–O–Si linkage to the silica backbone, and the other is the Zr–N and/or Si–N linkages. The fact that homogeneous complex **1** has such low catalytic activity (82 kg of PE/(mol of Zr) h, Table 2, entry 6) suggests that the leached species likely has retained the CGC

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structure, suggesting the possibility that MAO leaches the CGC by cleaving the Si–O–Si linkage.

Conclusions

In summary, we have successfully prepared immobilized zirconium complexes on three different types of amine silica supports. The nature of the immobilized metal species is shown to depend on both the nature of the amine groups on the surface (primary vs secondary) and the amine surface density. The supported Zr catalysts exhibit good activity for ethylene homopolymerization, resulting in linear PEs with high melting points. It was demonstrated that MAO causes significant leaching of the immobilized catalysts, possibly due to the cleavage of the Si–O–Si linkage. The data support the hypothesis that a traditional constrained-geometry Zr catalyst (type A site) exhibits higher catalytic activity compared to a more open metal center (type B site) that is the primary species produced on a densely loaded aminosilica surface.

Experimental Section

(A) Materials and Instrumentation. All reactions were carried out under a dry nitrogen/argon atmosphere in an MBraun UniLab 2000 drybox and/or using standard Schlenk line techniques. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Mercury VX instrument. Nitrogen physicochemical measurements were conducted on a Micromeritics ASAP 2010 system. Samples were pretreated by heating under vacuum at 150 °C for 8 h. Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 409 PC Luxx simultaneous thermal analyzer (TGA/differential scanning calorimetry) with heating to 1000 °C at 20 K/min in air. FT-Raman spectra were obtained on a Bruker FRA-106 instrument. At least 128 scans were collected for each spectrum, with a resolution of 2–4 cm^{-1} . Diffuse-reflectance ultraviolet–visible (UV–vis) spectroscopy was performed on solid materials in a drybox with an Ocean Optics USB2000 fiber optic spectrometer using a PTFE diffuse reflectance standard. Solution UV–vis spectroscopy was performed using a Hewlett-Packard Model 8453 spectrometer with toluene as a solvent. Gel permeation chromatography (GPC) was performed at the University of Massachusetts, Amherst with Polymer Laboratories PL-220 high-temperature GPC equipped with a Wyatt MiniDawn (620 nm diode laser) high-temperature light-scattering detector and refractive index detector at 135 °C using 1,2,4-trichlorobenzene as solvent and calibrated using polystyrene standards. Polyethylene was extracted from silica at 130 °C using TCB as the solvent prior to the GPC analysis.

Toluene was distilled over Na/benzophenone, and all other solvents used were obtained from a solvent purification system.³⁶ $\text{C}_5\text{H}_4(\text{SiMe}_2\text{Cl})(\text{SiMe}_3)$ and complex **1** were prepared according to literature procedures.³⁷ All other reagents were obtained from commercial sources and generally used without further purification. The silica support, SBA-15, was synthesized using literature methods.²⁹ The calcined material has an average pore diameter about 105 Å and a surface area of 830 m^2/g .

(B) Synthesis of Amine-Functionalized SBA-15. SBA-NH₂-D. Densely functionalized aminosilica SBA-15 was synthesized by stirring a toluene (40 mL) suspension of SBA-15 (1 g) and 3-aminopropyltrimethoxysilane (1 g) at room temperature for 24 h. The solid was filtered and washed with

anhydrous toluene and then dried under vacuum. Capping of the remaining surface silanols was achieved by stirring the as-synthesized materials with an excess of hexamethyldisilazane (1.0 g) in toluene (30 mL) at room temperature overnight. The solid was then filtered and washed with toluene in a drybox and dried under vacuum at room temperature overnight. TGA showed that ~1.0 mmol/g of SiO_2 of the amine was immobilized on the SBA-15.

SBA-NHMe-D. SBA-15 densely functionalized with secondary amine groups was prepared in a manner identical with that described above, except (3-(methylamino)propyl)trimethoxysilane was used in place of (aminopropyl)trimethoxysilane. TGA showed that ~0.80 mmol/g of the amine was immobilized on the SBA-15 surface.

SBA-NH₂-P. The site-isolated patterned amine silica was synthesized according to our previously reported procedure.²⁷ TGA showed ~0.4 mmol/g of the amine was immobilized on the SBA-15.

(C) Synthesis of Homogeneous Zirconium Complexes 3–5. Complex **3** was synthesized in a manner analogous to that for complex **1**.³⁷ $(\text{C}_5\text{H}_4)(\text{SiMe}_3)_2$ (670 mg, 3.19 mmol) was added to a dry toluene (15 mL) suspension of ZrCl_4 (750 mg, 322 mmol). The reaction mixture was slowly warmed to 100 °C with vigorous stirring. As the temperature was raised, the formation of a brown solution was observed. The solution was filtered in a drybox and cooled to –30 °C to give the crude complex **3** as a white solid, which was collected through filtration and then washed with cold hexane. Recrystallization from toluene/hexane afforded pure **3** as an off-white powder. Yield: 897 mg, 84%. ^1H NMR (CDCl_3): δ 6.98 (m, 2H, C_5H_4), 6.94 (m, 2H, C_5H_4), 0.35 (s, 9H, SiMe_3) ppm. Anal. Calcd for $\text{C}_8\text{H}_{13}\text{Cl}_3\text{SiZr}$: C, 28.70; H, 3.91; Found: C, 28.92; H, 3.82.

Complex **4** was synthesized on the basis of a modified literature procedure.¹ A solution of *n*-BuNH₂ (100 mg, 1.37 mmol) and NEt_3 (277 mg, 2.74 mmol) in 15 mL of toluene was slowly added to a toluene solution (20 mL) of complex **1** (487 mg, 1.37 mmol) at –78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for 12 h, resulting in a pale yellow solution. Subsequent filtration in a drybox and solvent removal under vacuum afforded a sticky solid. Recrystallization from toluene at –30 °C gave **4** as a white crystalline solid. Yield: 35% (170 mg). ^1H NMR (C_6D_6): δ 7.07 (m, 2H, C_5H_4), 6.98 (m, 2H, C_5H_4), 2.24 (t, $J = 7.2$, 2H), 1.32 (m, 2H), 1.20 (m, 2H), 0.85 (m, 3H), 0.58 (s, SiMe_2) ppm. Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{Cl}_2\text{NSiZr}$: C, 37.17; H, 5.39; N, 3.94. Found: C, 37.43; H, 5.52; N, 4.05.

Complex **5** was synthesized in a manner analogous to that for **4** by using **1** (250 mg, 0.70 mmol) and $\text{NH}(\text{Pr})_2$ (284 mg, 2.82 mmol). Yield: 248 mg (73%). ^1H NMR (CDCl_3): δ 6.91 (m, 2H, C_5H_4), 6.63 (m, 2H, C_5H_4), 3.45 (m, 4H, $J = 6.6$, CHMe_2), 1.42 (d, 24H, $J = 6.6$, CHMe_2), 0.37 (s, 6H, SiMe_3) ppm. Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{N}_2\text{Cl}_2\text{SiZr}$: C, 47.08; H, 7.90; N, 5.78. Found: C, 47.25; H, 8.02; N, 5.91.

(D) Synthesis of Immobilized Catalysts. SBA-NH₂-D-1. Complex **1** (60 mg, 0.169 mmol) and the proton scavenger 2,6-di-*tert*-butylpyridine (200 mg, 1.05 mmol) were added to a 40 mL toluene suspension of SBA-NH₂-D (300 mg). The reaction mixture was stirred at room temperature for 24 h, at which point it was filtered in a drybox and washed extensively with dichloromethane, hexane, and toluene. The resulting silica-supported catalyst SBA-NH₂-D-1 was dried under high vacuum for several hours.

SBA-NHMe-D-1 and SBA-NH₂-P-1. These catalysts were prepared in a manner analogous to that for SBA-NH₂-D-1, except SBA-NHMe-D (350 mg) and SBA-NH₂-P (500 mg) were used during the synthesis, respectively.

SBA-NH₂-D-3. Complex **3** (60 mg, 0.179 mmol) and the proton scavenger 2,6-di-*tert*-butylpyridine (200 mg, 1.05 mmol) were added into a 40 mL toluene suspension of SBA-NH₂-D (300 mg). The reaction mixture was stirred at room temperature for 24 h, at which point it was filtered in a drybox and

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washed extensively with dichloromethane, hexane, and toluene. The resulting silica supported catalyst SBA-NH₂-D-3 was dried under high vacuum for several hours.

SBA-NHMe-D-3. This catalyst was prepared in a manner analogous to that for SBA-NH₂-D-3, except SBA-NHMe-D (300 mg) was used during the synthesis.

(E) General Ethylene Polymerization Procedures. In a typical polymerization, the immobilized precatalyst (~10 mg), toluene (~10 mL), and MAO (10% toluene solution) were added to the polymerization reactor along with a stirbar in a drybox. The mixture was stirred for about 20 min for sufficient activation of the precatalyst. The reactor was then placed in a 25 °C water bath and pressurized with 60 psi of ethylene. The polymerization was allowed to continue for a prescribed amount of time (5–10 min) with constant stirring. The ethylene supply was stopped, and the reaction was then terminated by venting off the ethylene followed by the addition of acidic methanol. The precipitated polymers were collected

through filtration, washed with ethanol, and dried in an oven at 70 °C. PE was then weighed to give the polymer yield. The catalytic productivity of each catalyst was estimated by dividing the weight of the dry polymer by the reaction time (in hours) and the molar amount of Zr catalyst.

Acknowledgment. The National Science Foundation is gratefully acknowledged for support of this work through the CAREER program (Grant No. CTS-0133209). M.W.M. thanks the GT Molecular Design Institute (under the prime contract N00014-95-1-1116 from the Office of Naval Research) for partial support through a graduate fellowship. We thank the Coughlin group at the University of Massachusetts, Amherst, for high-temperature GPC analysis.

OM049765W