Effect of metallation protocol on the preparation and performance of silica-immobilized Ti CGC-inspired ethylene polymerization catalysts

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Abstract

Titanium constrained-geometry-inspired complexes (CGCs) are assembled on aminosilica surfaces using two metallation protocols, a single-step method using a piano-stool complex, and a multi-step surface grafting approach that uses amine elimination from a $M(N(Et_2))_4$ precursor. Two scaffolds are used in the study, one that has spatially patterned amines on the silica surface and another that has a distribution of different amine species prepared by a traditional amine-grafting approach. The materials are characterized by thermogravimetric analysis, elemental analysis, diffuse reflectance UV–vis spectroscopy, and subsequently, are evaluated in the polymerization of ethylene. Using both metallation protocols, the catalysts prepared on the patterned aminosilica are more productive than the materials prepared using traditional supports. The materials made via the single-step metallation method are more productive in the polymerization of ethylene per mole of metal atoms than the materials made using the amine elimination approach. However, on all supports, the single-step method results in significantly lower metallation efficiency than the amine elimination route, which allowed nearly quantitative surface functionalization. As a result, the materials made via amine elimination have a substantially higher metal loading that gives a higher catalytic productivity per gram of catalyst. It is also shown that the catalysts made via the amine elimination method are less susceptible to complex leaching caused by the co-catalyst methylalumoxane than the materials made via the single-step approach. Furthermore, when alkylaluminum/borane co-catalysts are used, leaching of active metal species from the support is not detected.
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1. Introduction

In recent years, constrained-geometry catalysts (CGCs) have emerged as an important class of organometallic complexes [1]. Used mainly as olefin polymerization catalysts, these homogeneous species offer unique advantages due to the ligand environment around the metal center. The open nature of the reactive center allows for the production of very high molecular weight polymers, as well as long-chain and short-chain branched polymers and co-polymers.

A common synthetic route for the preparation of homogeneous metallocenes or CGCs utilizes an alkyllithium reagent to deprotonate the cyclopentadienyl (Cp) ring. This is followed by metallation with the metal tetrachloride salt. However, with silica-supported systems, this methodology can result in side reactions with the surface. For example, metal chlorides can react directly with the surface silanols instead of the Cp ring, leading to the formation of multiple types of sites [2]. The alkyllithium reagent can also react with the silica surface by opening siloxane bridges, again resulting in the possible formation of a multi-sited material [2]. Therefore, alkyllithium reagents must be avoided when a single type of site is desired.

In the synthesis of homogeneous CGCs, there are two additional major methods of metallation, which have been shown to be more amenable for surface immobilization protocols. The amine elimination route was developed by

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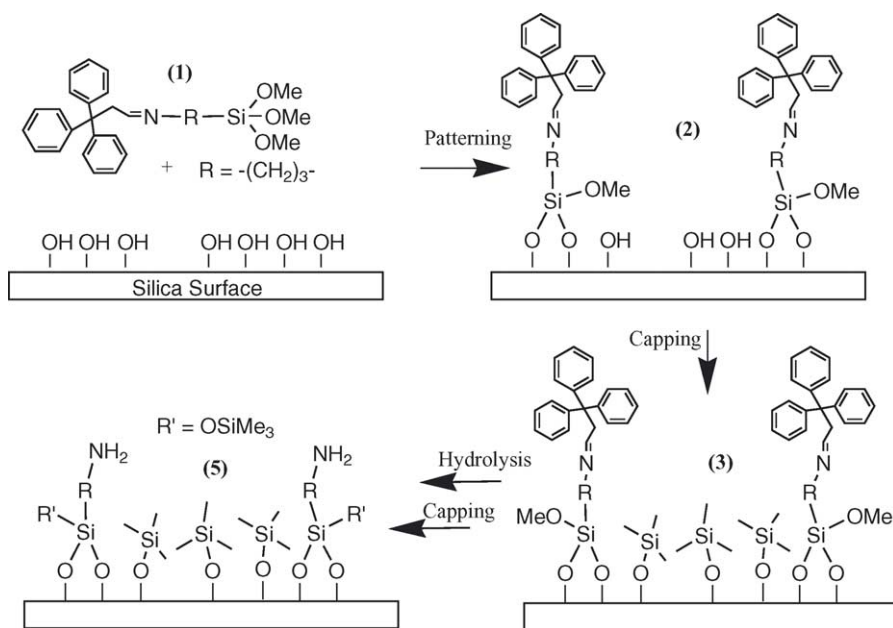
Scheme 1.

Peterson and Jordan for making Group IV metallocenes, then applied to the synthesis of CGCs [3,4]. In this case, for CGCs, tetrakis(diethylamino)titanium is reacted with a cyclopentadienyl functionalized amine. Two of the amine ligands are replaced in the titanium coordination environment, being substituted for ligation to the cyclopentadienyl ligand and the tethered amine. Another major method was developed by Royo et al. [5]. This method entails the reaction

of a piano-stool type complex with an amine to form the CGC. This metallation scheme requires both the metal atom and silyl chloride to react with a single amine.

Both the amine elimination and the Royo method have been used in the synthesis of supported catalysts where the CGC structure was targeted. For example, Pakkanen and co-workers reacted a cyclopentadienyl ligand on an amine-functionalized silica surface and then metallated the sur-
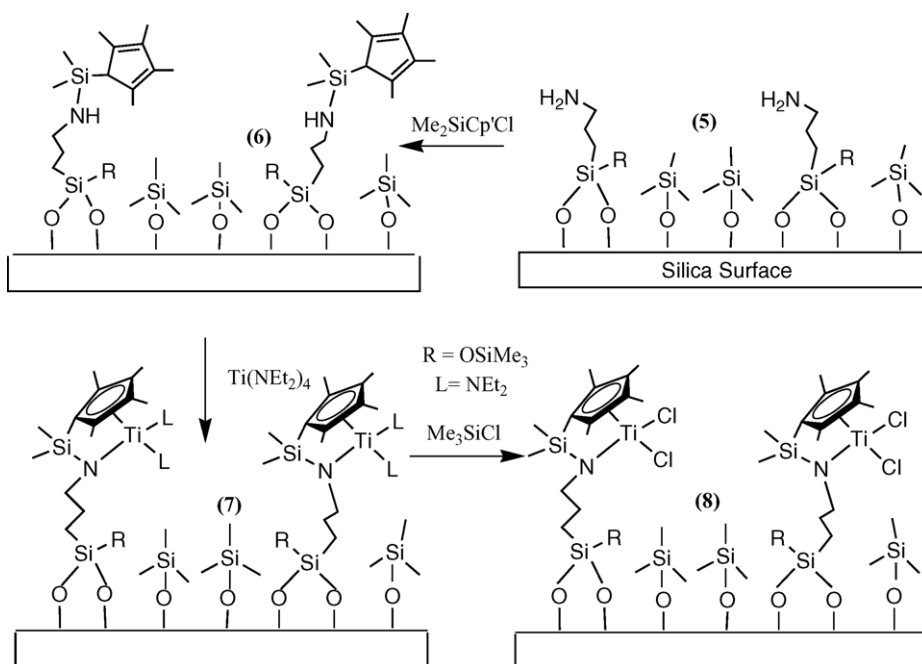
Scheme 2.
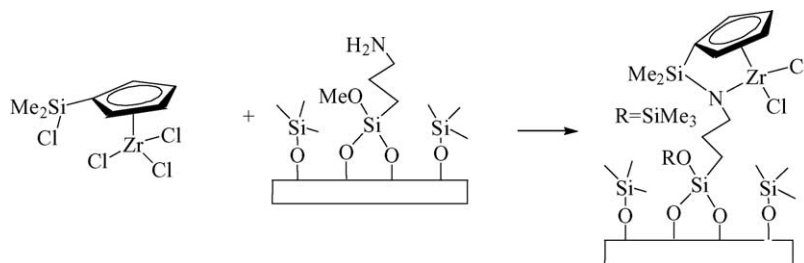
Scheme 3.

face with a variety of Group IV tetrakis(dialkylamino) complexes [6–13]. Kasi and Coughlin have synthesized supported CGC-type complexes using the Royo method on amine-functionalized polystyrene [14].

We have recently reported a patterning protocol that allows for the preparation of a well-defined amine-functionalized silica (Scheme 1)[1], with amine sites that behave as if they are isolated and uniform [16]. Using this patterned aminosilica as a scaffold, protocols to synthesize supported constrained-geometry-inspired catalysts on the surface were subsequently developed. We previously reported the synthesis of a supported titanium CGC-inspired complex made via an amine elimination route, as illustrated in Scheme 2 [17,18]. Additionally, the synthesis of silica-supported zirconium CGC-inspired complexes via the Royo method, as shown in Scheme 3, was also reported [19].

As shown in the literature, both the amine elimination and Royo methods have been used to synthesize supported CGC type complexes that are active for the polymerization of ethylene as well as the co-polymerization of ethylene and other olefins [6–14,17–19]. However, it is of interest to determine the impact of the metallation method on the catalyst performance and the resulting polymer properties, as there are no reports that directly compare catalysts with similar *intended* structures prepared by both the Peterson/Jordan and Royo methods. To this end, the role of the metallation method and the type of amine scaffold (isolated versus dense) used in the construction of CGC-inspired catalysts are evaluated in the polymerization of ethylene.

2. Experimental

2.1. General considerations

The following chemicals were commercially available and used as received: 3,3,3-triphenylpropionic acid (Acros), 1.0 M LiAlH$_4$ in tetrahydrofuran (THF) (Aldrich), pyridinium dichromate (Acros), 2,6 di-*tert*-butylpyridine (Acros), dichlorodimethylsilane (Acros), TEOS (Aldrich), 3-aminopropyltrimethoxysilane (Aldrich), hexamethyldisilazane (Aldrich), tetrakis(diethylamino)titanium (Aldrich),

trimethyl silyl chloride (Aldrich), trimethylaluminum (Aldrich), triisobutylaluminum (Aldrich), methylaluminoxane (MAO: Aldrich, 10 wt% in toluene), and *n*-butyllithium in hexanes (Aldrich). Tetramethyl-cyclopentadiene (Aldrich) was distilled prior to use. Anhydrous toluene (Acros) was distilled over sodium metal prior to use. Tris(pentafluorophenyl)borane (Aldrich) was purified via sublimation. Anhydrous methanol (Acros) was further dried over 4-Å molecular sieves prior to use. Anhydrous ether, anhydrous THF, anhydrous dichloromethane, and anhydrous hexanes were obtained from a packed bed solvent purification system utilizing columns of copper oxide catalyst, and alumina (ether, hexanes) or dual alumina columns (tetrahydrofuran, dichloromethane) [20]. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques under dry, deoxygenated argon or in a drybox under a deoxygenated nitrogen atmosphere. Ethylene was passed over a metallic catalyst (Matheson 641-01 cartridge) to remove oxygen and water, before being fed to the reactor.

2.2. Synthesis of SBA-15

Mesoporous silica SBA-15 with approximately 100 Å diameter pores was synthesized via literature methods [21,22]. Calcination of the material was done in air using the following temperature program: (1) increasing the temperature (1.2 °C/min) to 200 °C, (2) heating at 200 °C for 1 h, (3) increasing at 1.2 °C/min to 550 °C, and (4) holding at 550 °C for 6 h. Prior to use, the SBA-15 was dried under vacuum at 200 °C for 3 h and stored in a drybox.

2.3. Aminosilica scaffold synthesis

Densely loaded and patterned aminosilica materials were prepared using an SBA-15 host as described previously [16].

2.4. Immobilization via multi-step grafting (amine elimination method)

From these aminosilica scaffolds, Ti-CGC inspired complexes were prepared using the methodology previously reported [17]. Complex **9**, (1-(chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium trichloride, was synthesized via a literature procedure [14].

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[1] After independently developing this methodology, it was discovered that a similar approach had been used previously [15].

2.5. Immobilization via a piano-stool complex (Royo method)

The immobilization protocol was adapted from a literature procedure [19]. Complex **9** (50 mg, 0.14 mmol), and the proton scavenger, 2,6-di-*tert*-butyl-pyridine (200 mg, 1.05 mmol) were added into a toluene (40 ml) suspension of patterned amine-functionalized SBA-15 (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 was dried under high vacuum for several hours. A similar procedure was used for immobilizing the complex on densely functionalized aminosilica.

2.6. Materials characterization

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. Thermogravimetic analysis (TGA) and differential scanning calorimetry was performed on a Netzsch STA409. TGA samples were heated under air from 30 to 1000 °C at a rate of 5 °C/min. The organic loading was measured by determining the weight loss from 200 to 650 °C. DSC samples to determine polymer melting points were heated under nitrogen with a heating cycle from 30 to 160 °C at 2°/min, cooling to 100 °C at 2°/min, and then repeating the cycle. The melting point was taken from the second heating cycle. Elemental analysis was performed by Desert Analytics. Gel permeation chromatography (GPC) was performed at the Dow Chemical Company, at 160 °C using 1,2,4-trichlorobenzene as solvent. Polyethylene was extracted from silica at 160 °C using TCB as the solvent prior to the GPC analysis.

3. Ethylene polymerizations

3.1. MAO co-catalyst

The immobilized pre-catalyst was added to a pressure glass reactor with toluene and methylalumoxane (800 Al:1 Ti) in a drybox. The solution was stirred for 20 min to allow for sufficient activation of the catalyst. The reactor was then sealed and removed from the glovebox, placed in a 25 °C waterbath, and subsequently, connected to an ethylene source at 60 psi. The ethylene was delivered for a prescribed amount of time and the polymerization was terminated by releasing the ethylene pressure and adding acidic ethanol. The precipitated polymers were washed with ethanol, and then dried at 70 °C.

3.2. Borane co-catalyst

In a typical polymerization, the immobilized pre-catalyst was added to the pressure glass reactor with toluene,

tris(pentafluorophenyl) borane (1.5 B:1 Ti), and either trimethyl aluminum or triisobutyl aluminum (400:1 Al:Ti ratio) in a drybox. The mixture was allowed to stir for 30 min to allow for sufficient activation of the catalyst. The reactor was then sealed and removed from the glovebox, placed in a 25 °C waterbath, and ethylene at 60 psi was introduced as described above. The polymerization was allowed to continue for a prescribed amount of time, and then terminated as noted above. The precipitated polymers were washed with ethanol, and then dried at 70 °C.

3.3. Leaching experiments

The immobilized pre-catalyst, toluene, and methylalumoxane (800:1 Al:Ti) or alkylaluminum (400:1 Al:Ti) were added to a flask in a drybox. The mixture was allowed to stir for 20 min. The mixture was then filtered in the drybox, the filtrate was added to the pressure glass reactor with toluene and an additional portion of MAO (200:1 Al:Ti). The reactor was then removed from the glovebox, placed in a 25 °C waterbath, and contacted ethylene at 60 psi as described above. The polymerization was allowed to continue for a prescribed amount of time, and then terminated by adding acidic ethanol. The precipitated polymers were washed with ethanol, and then dried at 70 °C.

4. Results and discussion

4.1. Catalyst synthesis and characterization

Two aminosilica scaffolds were used in this work. Patterned aminosilica was synthesized via the protocol shown in Scheme 1. Traditionally grafted, densely functionalized aminosilica was made via literature methods [16]. The patterning protocol afforded 0.57 mmols NH_2/g SiO_2. Note that this loading is higher than previously reported [16] because a more open, large pore SBA-15 material was used here. Grafting 3-aminopropyltrimethoxysilane onto the silica surface gave a densely loaded material with a loading of 1.35 mmol NH_2/g SiO_2.

For metallation using the amine-elimination route, as shown in Scheme 2, the aminosilica was functionalized first with chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (Cp′Si). On the patterned amine, this reaction was nearly quantitative, as seen previously [16]. Next, Cp′Si was reacted with the surface bound amines yielding 0.54 mmol of Cp′/g of SiO_2, corresponding to ~95% functionalization of the patterned amines. Metallation via an amine elimination route with tetrakis(diethylamino)titanium resulted in 0.56 mmols Ti/g of silica, a nearly quantitative metallation of the Cp′ (perhaps within experimental error). A final ligand exchange, accomplished by reacting the metallated solid with trimethylsilylchloride, afforded 1.05 mmol Cl/g SiO_2. This suggests that nearly all of the immobilized Ti species retain their exchangeable

Table 1
Characterization of functionalized silica materials

Material description	Amine elimination		Royo method	
	Patterned silica	Densely functionalized	Patterned silica	Densely functionalized
Amine loading (mmol/g)	0.57[a,b]	1.35[a,b]	0.57[a,b]	1.35[a,b]
Cyclopentadienyl loading (mmol/g)	0.54[a,b]	0.84[a,b]	NA[c]	NA[c]
Reaction yield[d] (%)	94.7	62.2	–	–
Ti loading (mmol/g)	0.56[b]	0.68[b]	0.12[b]	0.34[b]
Reaction yield[d] (%)	98.2	50.4	21.1	25.2

[a] Loading determined by TGA.
[b] Loading determined by elemental analysis.
[c] Not applicable, in this method amine is not functionalized directly with a cyclopentadienyl moiety.
[d] Reaction yield based on functionalization of immobilized amines.

ligands (∼94%). Elemental analysis results are tabulated in Table 1.

The densely functionalized aminosilica was used in the same synthetic protocol (Scheme 2). This material had a loading of 1.35 mmols amine/g SiO_2. Upon reaction with multiple aliquots of Cp′Si, 62% of the amines were found to react, giving a loading of 0.84 mmols Cp′Si/g of SiO_2. This proportion of amine-functionalization is similar to previous results [16]. Metallation via amine elimination yielded 0.68 mmol Ti/g SiO_2, which corresponds to ∼75% metallation of immobilized Cp′Si and ∼50% metallation of immobilized amine sites. After exchanging the diethylamino ligands with chlorides, elemental analysis showed 1.22 mmol Cl/g SiO_2. Thus, 89% of the titanium sites have retained their exchangeable ligands in the immobilization process. These results are consistent with our previous studies, where the surface reactions on the traditional aminosilica supports are substantially less than quantitative and those on the patterned silica gave quantitative or nearly quantitative yields [18].

Using the same aminosilica supports, the Royo method for synthesizing supported CGC-type complexes was used. From the patterned silica, the supporting protocol shown in Scheme 4 afforded 0.12 mmol Ti and 0.34 mmol Cl/g SiO_2. With densely functionalized silica, 0.34 mmols Ti were immobilized and 0.82 mmols Cl/g SiO_2 were retained on the complex. Complete elemental analyses of these materials are also shown in Table 1.

The amine elimination route provided nearly quantitative metallation of the patterned amine, evidenced by the ∼1:1 N:Ti ratio. When applied to the densely functional-

ized aminosilica, the method resulted in an amine–titanium ratio of 2:1. This ratio is similar to previous results [18]. In contrast, using the Royo method with a patterned aminosilica support, metallation with 9 gave a N:Ti ratio of roughly 5:1. Metallation of densely functionalized materials provided similar results.

It appears that the amine elimination route provides a more efficient means of metallation when compared to Royo method. There are several possible reasons why the metallation via the Royo method is not as efficient on the silica surface. On the SBA-15 support, the majority of the amine sites will be located within the mesopores, with a smaller number located on the external surface. As the piano-stool complex has more steric bulk than the individual reactants in the amine elimination metallation, it may block access to some amines in the pore structure. Additionally, the formation of bridged complexes (Scheme 5) would result in a larger amine–titanium ratio as well. This will be discussed further below.

Characterization of supported complexes is difficult due to the fact that traditional spectroscopic techniques, such as NMR, FT-IR, and FT-Raman, rarely give useful information concerning the bonding of many transition metal centers when the metal species are present at such low concentrations. As previously shown, characterization by UV–vis spectroscopy can be used to partially elucidate the speciation of the metal center [18,19]. The comparison of the UV–vis spectra of the materials in this work is shown in Fig. 1.

In the patterned materials made via amine elimination, there is a broad signal with a maximum intensity at 250 nm.
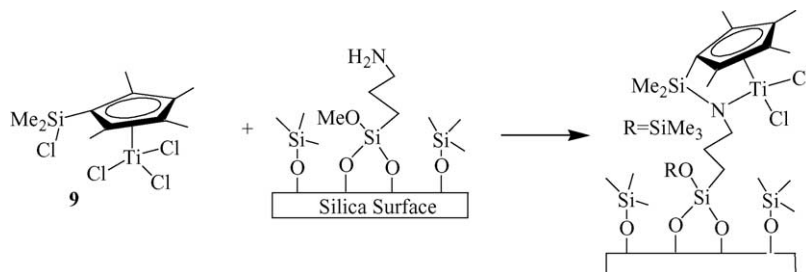
Scheme 4.
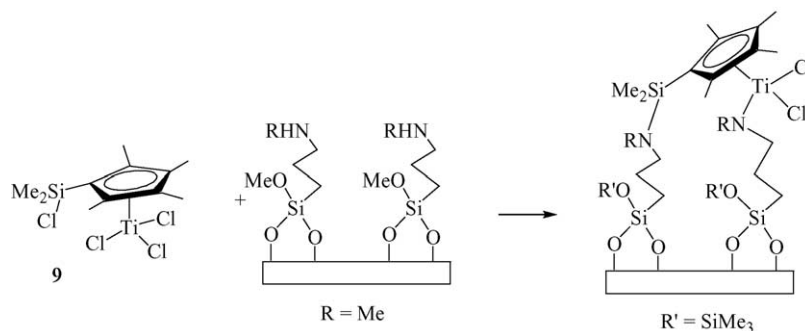
Scheme 5.

In our previous work, this transition could not be correlated to an exact structure, however it was suggested the peak could be a combination of the 220 nm signal from the SBA-15 scaffold and the transition from titanium (expected to appear around 260 nm) [18]. The shoulder centered around 330 nm is attributed to the ligand to metal charge transfer (LMCT) from the cyclopentadienyl ring to the Ti [23]. The densely loaded amine elimination material showed a broad signal with a maximum intensity at 240 nm and the LMCT expected around 350 nm was not as prominent as in the patterned material. As noted earlier [18], the UV–vis spectra for materials made via amine elimination look similar on both densely functionalized and patterned silica. Thus, this technique does not provide any evidence for formation of different types of Ti species on the two supports, although the possibility cannot be ruled out.

In the patterned material prepared from the piano-stool complex, there is a signal at 220 nm, likely from the silica scaffold. The transition at 260 nm can be attributed to the immobilized titanium complex. A second weaker peak assigned to the LMCT starts at approximately 325 nm. In the densely functionalized Royo material, there is a broad transition centered around 225 nm, again assigned to a combination of the silica transition and a titanium transition. The LMCT is much more pronounced than in the other materials, while also beginning at a lower wavelength (280 nm). This large LMCT shoulder is likely the result of incomplete complex formation or formation of the bridging species [19], similar to those shown in Scheme 5. To test this hypothesis, a densely functionalized secondary aminosilica was used as a scaffold for complex immobilization (shown in Scheme 5 with R = CH$_3$). With this secondary amine-functionalized silica, it is not possible to form a CGC and there is a high probability of incomplete complex formation or bridged titanium species [19]. As seen in Fig. 2, the UV–vis spectrum of this material is nearly identical to that of the densely functionalized Royo material. This suggests the high density of the amine sites on traditionally grafted materials creates a different primary titanium species on the surface.

Characterization via UV–vis spectroscopy failed to provide conclusive evidence of the formation of different sites from the different metallation methods (with the exception of the densely loaded Royo material). While, the UV–vis spectra of the materials made via amine elimination show some variations from the Royo materials, the basic transitions expected in an immobilized CGC are present in both materials,
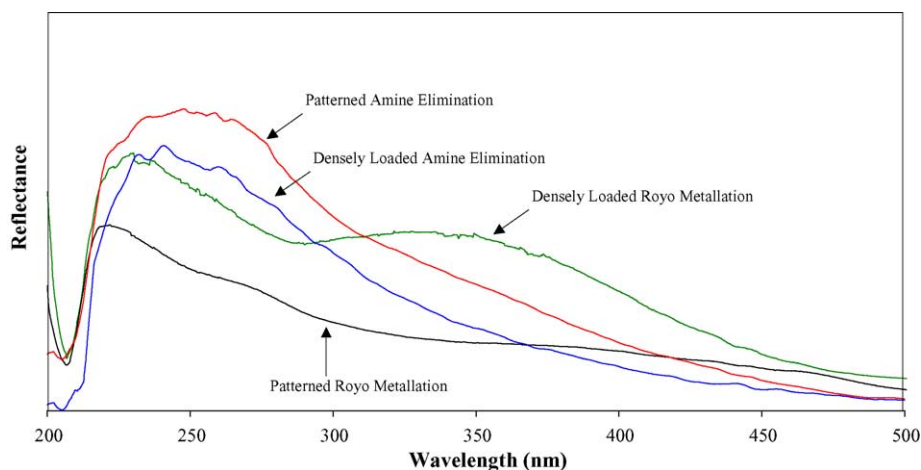

Fig. 1. Diffuse-reflectance UV–vis spectra of patterned amine elimination material, densely loaded amine elimination material, patterned Royo material, and densely loaded amine elimination material.
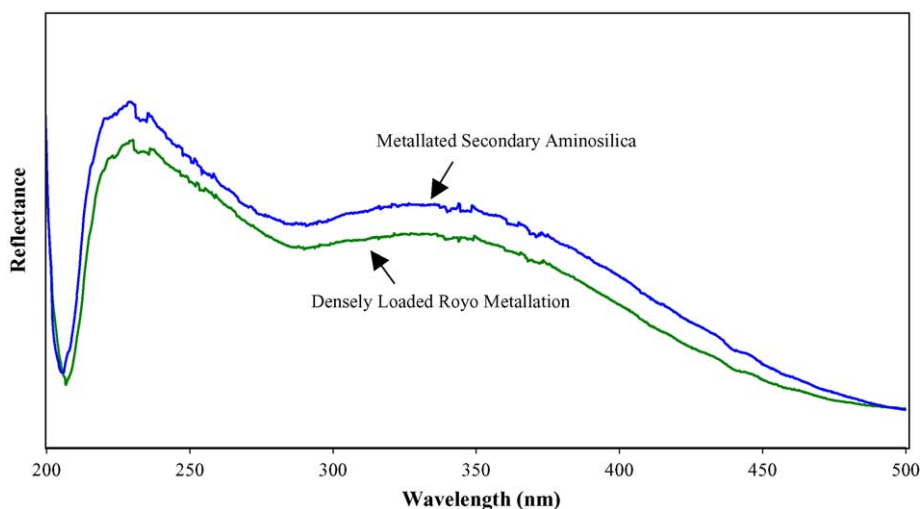
Fig. 2. Diffuse-reflectance UV–vis spectra of densely loaded Royo materials using primary and secondary aminosilica scaffolds.

albeit with differing intensities which may result from the different titanium loadings on the respective samples. The major structural variation seen via this technique is the large LMCT in the densely loaded Royo materials, attributed to the bridging complexes.

5. Polymerization results

The ethylene polymerization behavior of the patterned and densely functionalized catalysts made via the two metallation routes was studied. The polymerizations were performed with methylaluminoxane (MAO) and borane/alkylaluminum co-catalysts. The results of the polymerizations using MAO are shown in Table 2. The data indicate that the patterned catalysts made via the Royo method are significantly more active per gram of titanium than those made via the amine elimination method. This result is also seen in comparing the densely functionalized materials. While the data suggest that the Royo method makes more productive catalyst, there are subtleties in the data.

As seen previously in work with these supported CGC-type complexes, the MAO co-catalyst can leach metal complex from the support [18,19]. This makes it more

difficult to determine the active species, whether it is the leached species, immobilized species, or some combination of the two. To attempt to quantify this leaching phenomenon, the supported pre-catalyst and MAO co-catalyst were stirred in the drybox with toluene. After a prescribed period of time, the mixture was filtered and the filtrate was collected. The filtrate was added to the reactor along with additional co-catalyst and exposed to ethylene as described previously. The polymerization results using the leached, soluble species are shown in Fig. 3. The filtrate from the patterned catalyst made via the Royo method showed an activity of 38.9 kg polymer/mol Ti-h, nearly 70% of the activity of the supported catalysts. The catalysts made via amine elimination also show significant leaching, with over 50% of the activity due to leached metal complex.[2] It is important to note that the leached activities determined are a lower bound for the fraction of activity that may be due to leached species. This is because there is the possibility for deactivation of catalytic species during sample manipulation steps such as filtrations in the drybox. Thus, with MAO as co-catalyst, it is possible that all activity is derived from leached species. Indeed, the melting points of polymers made using filtrate from the leaching experiments are similar to those using the solid catalysts.

To probe the activity of the actual immobilized species, it has been shown that a borane/alkylaluminum co-catalyst does not leach metal complex from the surface [18]. The leaching tests described above for MAO were repeated using alkylaluminums (either trimethylaluminum or triisobutylaluminum) as co-catalysts. The filtrate collected showed no polymerization activity upon exposure to ethylene, even in the presence of additional MAO. This suggests the activity seen in studies performed with borane systems will provide the productivity of an immobilized species.

Table 2
Catalytic productivity in ethylene polymerization using MAO as co-catalyst

Metallation method	Support	Productivity (kg PE/mol Ti-h)	T_m (°C)
Amine elimination	Patterned	22.1	138
Amine elimination	Patterned	19.0	134
Amine elimination	Densely loaded	8.0	131
Amine elimination	Densely loaded	8.6	135
Royo	Patterned	58.1	133
Royo	Patterned	61.2	138
Royo	Densely loaded	15.5	142
Royo	Densely loaded	14.3	140

[2] This complex may be free in solution or it may re-adsorb onto the silica support under reaction conditions.
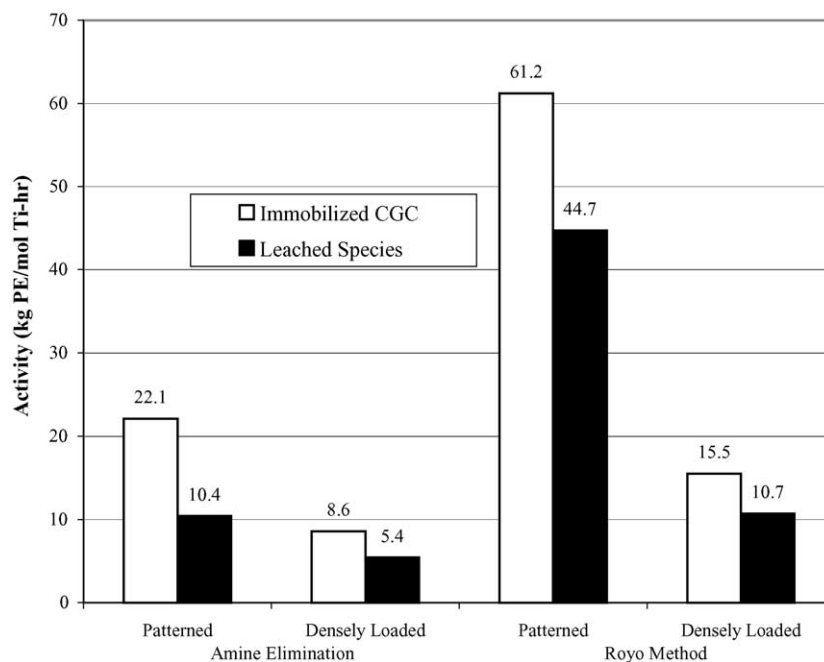
Fig. 3. Comparison of the polyethylene productivity of the supported catalysts with the leached filtrate using methalumoxane as a co-catalyst.

The results of the ethylene polymerization with the supported pre-catalysts and a borane/alkylaluminum co-catalyst are given in Table 3. Again the patterned catalysts made via the Royo method were shown to be significantly more active than those made via the amine elimination route. However, the magnitude of all the productivities decreased compared to the MAO results. Nonetheless, the patterned Royo material is still 1.5–2 times more active than the patterned amine elimination material. Only limited molecular weight data was gathered, although it is clear that high molecular weight polymer is produced by the patterned catalyst, as was observed in previous studies [17, 18].

The productivity results presented thus far in this work were based on yield of polymer per mole of immobilized titanium. However, the efficient functionalization that occurred during the amine elimination protocol yielded materials that had a much greater loading of titanium. Thus, it is also useful to look at the catalytic productivities measured per gram of catalyst. When this is done, it is clear that the additional loading afforded by the amine elimination route gives a more productive system overall (Table 4).

These results suggest that the methodology of the Royo metallation may allow for the synthesis of fewer, yet more accessible sites on the aminosilica scaffold, compared to the amine elimination method. The SBA-15 material used for a support in this work had a pore diameter of approximately 100 Å. In the amine-elimination method, the aminosilica is first functionalized with a cyclopentadienyl moiety and then metallated, with all the steps involving relatively small components. With a porous silica support, a number of these metal sites will be immobilized on the interior of the pore wall. When ethylene is added, polymerization at sites near the pore entrance can lead to pore blockage, preventing monomer from reaching other sites within the pore system. This would yield a lower catalytic productivity per site than a case where most of the sites are near pore mouths or are on the external surface of the solid.

In comparison, the Royo method uses a single-step immobilization protocol. Despite using identical aminosilica

Table 3
Catalytic productivity in ethylene polymerization using alkylaluminum/borane co-catalysts

Metallation method	Support	Alkyl aluminum	Productivity (kg PE/mol Ti-h)	M_w ($\times 10^3$)	T_m (°C)
Amine elimination	Patterned	TMA	12.1	–	135
Amine elimination	Patterned	TIBA	10.4	1300	133
Amine elimination	Densely loaded	TMA	1.4	–	135
Amine elimination	Densely loaded	TIBA	1.3	15	136
Royo	Patterned	TMA	20.1	–	133
Royo	Patterned	TIBA	15.3	42	134
Royo	Densely loaded	TMA	Trace	–	–
Royo	Densely loaded	TIBA	2.8	21	144

Table 4
Catalytic productivity per gram of catalyst

Metallation method	Support	Co-catalyst	Productivity (g PE/g cat-h)
Amine elimination	Patterned	Borane/TMA	6.8
Amine elimination	Patterned	Borane/TIBA	5.8
Amine elimination	Densely loaded	Borane/TMA	1.0
Amine elimination	Densely loaded	Borane/TIBA	0.9
Royo	Patterned	Borane/TMA	2.4
Royo	Patterned	Borane/TIBA	1.8
Royo	Densely loaded	Borane/TMA	Trace
Royo	Densely loaded	Borane/TIBA	1.0

scaffolds, the materials made via the Royo method have significantly lower titanium loadings than the materials made via amine elimination. If a piano-stool complex molecule reacts with an immobilized amine site near the entrance of a pore, it may be difficult for additional piano-stool complexes to pass by to react with amines further down the pore. This effect should be exacerbated in the Royo method compared to the amine elimination route, where individual, relatively small components are added stepwise to the surface. Thus, it is hypothesized that the formation of a CGC type site at the pore mouth using the Royo method decreases the effective pore diameter, preventing a large number of amines in the mesopores from reacting. As such, there are fewer immobilized CGCs within the pore which will potentially be blocked once polymerization begins, and catalytic productivity per mole of metal will be high. This hypothesis is also consistent with the observed higher reactivity of leached catalyst on materials made via the Royo method, as the propensity to leach complexes would be expected to be higher on the external surface and at the pore mouth than from within the mesopores.

In our previous work using the Royo method for immobilization of CGC-inspired complexes, a zirconium piano-stool complex was used [19]. The activities of the Ti-Royo materials reported here are 25–50 times lower than the Zr-Royo materials reported previously. However, it is difficult to directly compare the two studies due to the use of different aminosilica scaffold materials, polymerization vessels, and polymerization conditions. In particular, when studying the Zr-Royo materials, only MAO was used as a co-catalyst and this lead to significant complex leaching in all cases. Nonetheless, in comparing data in both cases with MAO as the co-catalyst, it appears that the leached sites from the Zr-Royo materials are significantly more active than those from the Ti-Royo materials. This observation is consistent with previous work using immobilized CGC-type catalysts prepared using MAO as co-catalyst [2]. In that case, the Zr complexes were 25–50 times more active than the analogous titanium species.

Finally, it is noteworthy that the Zr-Royo catalysts previously reported had metal loadings nearly three-fold greater than the titanium materials. This suggests that the Royo metallation efficiency is more dependent on the metal used than when using the amine elimination method, where metallation efficiencies are similar.

6. Summary

The results presented here provide evidence that using a Royo metallation scheme to synthesize an immobilized CGC-type may lead to a more active catalyst than those prepared by an amine elimination route. Characterization of the immobilized complexes indicate that CGC-type complexes may be prepared in all cases except when the Royo metallation method was used on a densely loaded support, in which case a more open, bridged complex was likely formed. The catalysts synthesized by the Royo method were more productive per mole of supported titanium. However, the Royo method had significantly lower metallation efficiency than the amine elimination route, which showed nearly quantitative functionalization. This was hypothesized to stem from limited metallation of sites within the mesopores of the support. As a result of the nearly quantitative functionalization, the amine elimination materials had a much greater loading of titanium, which allows them to produce more polyethylene per gram of supported catalyst than the Royo materials.

Acknowledgements

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