Topics in Catalysis Vol. 34, Nos. 1–4, May 2005 (© 2005)
DOI: 10.1007/s11244-005-3790-8

Design of silica-tethered metal complexes for polymerization catalysis[†]

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Metal complex catalysts that are covalently tethered to oxide supports have been utilized for many years as hybrid molecular/heterogeneous catalysts. In this work, recent results from our laboratory in the area of silica-tethered metal complex polymerization catalysts are reviewed. The critical parameters for catalyst design when catalyst recovery and recycle are important are discussed in the context of silica-immobilized CuBr complexes for atom transfer radical polymerization (ATRP) as well as silica-tethered Zn-β-diiminate (BDI) complexes for lactide or epoxide/CO_2 polymerization. Additionally, a new strategy for the preparation of site-isolated metal complex catalysts on a silica surface is illustrated through the design of tethered constrained geometry catalysts (CGCs) for ethylene polymerization. The novel synthetic protocol is demonstrated to result in catalysts that appear to be more well-defined and that have improved catalytic properties. Major challenges and future directions in the field of oxide-tethered metal complex catalysis are discussed.

KEY WORDS: catalyst immobilization; tethered catalyst; ATRP; leaching.

1. Introduction

Homogeneous, molecular catalysts and heterogeneous, material catalysts are both widely utilized for lab scale chemistry. However, in large scale commercial operations, heterogeneous catalysts are more frequently used due to the ease of separating the solid catalysts from fluid media. Indeed, whereas the strengths of most solid, heterogeneous catalysts are low cost and ease of catalyst and product recovery, the strengths of homogeneous catalysts are their inherently higher catalytic selectivities. Ideally, a catalyst that combines the recoverability/recyclability of heterogeneous systems with the selectivity of homogeneous catalysts is desired. For this reason, molecular catalysts have been immobilized on solid supports for many years [1]. In this work, we will briefly review recent developments from our laboratory in the use of immobilized metal complex catalysts on oxide supports for liquid phase polymerization reactions.

There are many synthetic techniques that have been utilized to immobilize molecular organometallic catalysts on oxide supports (Figure 1) [2]. One of the oldest and simplest approaches is to ion-exchange a cationic metal complex [3] onto an anionic solid support, such as an aluminosilicate [4]. While this approach can work quite well, it is limited to use in non-polar media that will not disrupt the ionic interaction between the support and the complex. Another approach is to functionalize the support with an additional phase, for example a grafted fluorous phase [5] or an adsorbed aqueous phase [6]. The metal complex catalyst can then be dissolved/adsorbed in this phase and applied in catalytic reactions in a non-soluble phase (e.g., supported aqueous phase catalysis in non–polar organic solvents). Like the first case, this methodology will only work with a limited range of solvents. An approach that is applicable to essentially all types of liquid media is catalyst immobilization *via* ship-in-the-bottle synthesis [7,8]. In this case, a catalyst is assembled within the micropores of a solid, typically zeolitic support. If the size of the complex is larger than the size of the pore opening, it will be effectively immobilized and can be used as a recyclable catalyst. However, the restricted size of the pores thrusts a limitation on this type of catalyst – they are only useful for substrate and product molecules that are relatively small in size, as they must diffuse into and out of the small pores of the solid.

The approach that is, in principle, most widely applicable is ligand tethering. In this methodology, the organic ligand of the metal complex is covalently anchored onto the solid oxide. For cases where this ligand does not dissociate in the catalytic cycle, these catalysts can be used as recyclable systems in nearly any solvent. The key drawback to this methodology, however, is that the preparation of catalysts of this type can be quite complex [2].

In this work, we review recent developments in ligand-tethered metal complex polymerization catalysis from our laboratory and speculate about future directions for the field.

2. Recovery and reuse of tethered homogeneous polymerization catalysts

As noted above, metal complex catalysts have been immobilized on supports for many years in an effort to aid catalyst recovery. In nearly all cases, the catalytic reactions of interest are common transformations involving small molecules such as hydrogenations, hydroformylations, etc. In these cases, the steps in the catalytic cycle are the same as in heterogeneous catalysis

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[†] Invited paper for a special issue on "The Interface between Heterogeneous and Homogeneous Catalysis" in Topics in Catalysis

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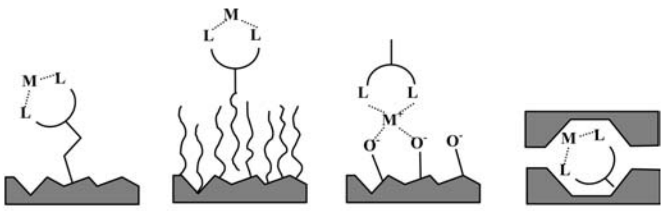


Immobilization Method	covalent ligand binding	physisorption	ion pair	encapsulation
Applicability	broad	restricted	restricted	restricted
Drawbacks	preparation	competition with solvents	competition with polar or ionic substrates	substrate size, diffusion

Figure 1. Summary of common methodologies for metal complex immobilization, adapted from reference [2].

with simpler, more traditional catalysts such as supported metals. For example, in the traditional picture of small molecule conversion over a solid catalyst, the reactant first diffuses into the catalyst pore system, binds to the active site, reacts, and the product desorbs from the surface and diffuses out of the pore system. An analogous image can be envisaged for a tethered molecular catalyst, with a reactant diffusing into the catalyst pore system, binding to the metal complex and entering the catalytic cycle. The product is then expelled from the complex and diffuses out of the pore system.

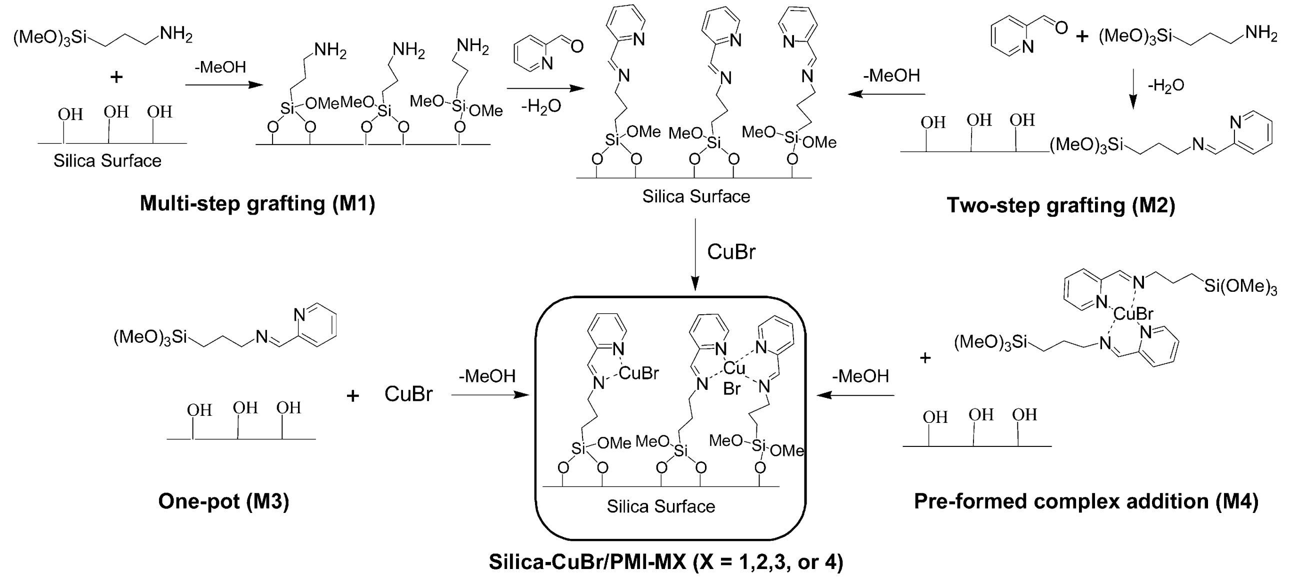
For polymerization reactions where catalyst recovery is desired, this picture becomes more complicated. When the product of the reaction is a polymer, the product may not diffuse out of the pore system. As high molecular weight polymer is formed, the pores become filled and this slows subsequent monomer additions. This can have a significant impact on the course of the polymerization, affecting the structure of the polymer produced, the reaction kinetics, and the ultimate recyclability of the catalyst.

2.1. *Silica-tethered CuBr complexes in atom-transfer radical polymerization (ATRP)*

In most commercial polymerization reactions (i.e. olefin polymerization with Zigler Natta catalysts or supported metallocenes), the catalyst is designed for a single use [9,10]. However, in other cases, the ability to recover and reuse the catalyst would be critical for economic or environmental reasons. One of the most exciting recent developments in radical polymerization is the advent of atom transfer radical polymerization by Wang and Matyjaszewski [11] and Kato et al. [12]. This technology allows for living/controlled radical polymerizations to be carried out where the polymer structure can be exquisitely fine-tuned – the molecular weight, and polydispersity can be easily controlled and novel polymer architectures can be prepared [13]. A key drawback to this technology, however, is the large amount of metal salts that are used to control the polymerization that must be separated from the product polymer. This is a case where catalyst immobilization on a solid support could have a major impact, potentially allowing for facile separation of the catalyst from the polymer. Furthermore, because in ATRP relatively low molecular weight polymer is usually produced and the polymerization is carried out under conditions where the polymer is soluble, the ability to recover and reuse the catalyst without clogging the pores appears possible.

There are two primary methods by which oxide-tethered metal complex catalysts have been prepared, (i) pre-formed complex addition and (ii) step-wise synthesis of the complex on the support. We hypothesized that method (i) would lead to a catalyst with more well-defined surface species and therefore better catalytic properties for ATRP. Subsequently, we investigated the role of complex synthesis and support properties (pore size, structure) on the ATRP of methyl methacrylate [14,15].

An immobilizable pyridylmethanimine (PMI) CuBr complex was designed and tethered to several solid supports as described in Scheme 1. The synthetic protocols included three multi-step grafting protocols of decreasing complexity (3 steps – Method 1; 2 Steps – Method 2; One Pot metallation and grafting – Method 3), and a preformed complex addition method (Method 4). Each method was applied to three different support materials, hexagonally-ordered mesoporous silicas (SBA-15) with a 48 Å and 100 Å average pore diameter, and Cab-O-Sil EH5 fumed, nonporous silica. The spectroscopic results and elemental analyses of the catalysts are consistent with each material having a similar primary surface species (CuBr-PMI complexes) and hence one might assume that all the catalysts based on a given support would behave the same. This was not observed to be the case, perhaps due to the different distribution of species on the surface. Whereas, the



Scheme 1. Preparation of tethered CuBr/PMI ATRP catalysts.

catalysts made by Methods 2–4 can likely have only complete PMI ligands, CuBr, and CuBr-(PMI)$_{N=1or2}$ complexes, materials made *via* Method 1 can have free amine sites and free pyridylaldehyde groups as well. Indeed, using Method 1, only 92% of the surface amines react with pyridylaldehyde groups by TGA [14], assuming all the aldehyde added reacts with amine groups. On the SBA-15 supports, the final organic ligand loading was found to be relatively independent of the synthetic method used [14]. In contrast, on the nonporous Cab-O-Sil support, the simplest approaches, Methods 3 and 4 gave the largest ligand loading. In all cases, nearly quantitative metallation was achieved, assuming that two ligands were bound to each CuBr molecule [14].

Despite the potentially similar primary surface species, for a given support, different synthetic methods yielded catalysts with different properties. In general, catalysts prepared *via* Methods 3 and 4, the simplest methods, behaved the best, giving polymers with narrower PDIs and controlled molecular weights [15][1]. Of the three supports used, poor control was generally observed over the narrow pore SBA-15, moderate control was achieved on the 100 Å pore SBA-15 samples made via Method 3 and 4, and good control was achieved on Cab-O-Sil EH5 supports for all synthetic methods used (Table 1). All catalysts allowed for the recovery of the vast majority of the copper used (usually greater than 99%), but in every case, at least some leaching was observed. The large pore and non-porous catalysts could be effectively recovered and reused in several cycles [15].

Based on the results of this study, the most promising synthetic strategy, Method 4, was explored further with a different ATRP ligand, a bipyridine that was modified for tethering to oxide supports (Scheme 2) [16]. Because of the improved polymerization performance with non-porous and large-pore supports in the PMI case, the ligand was studied over an additional large pore support, controlled pore glass (CPG), which has interconnected 240 Å pores. This support differs from SBA-15 in that the pores are larger and interconnected, whereas in the hexagonal mesoporous support the pores are effectively isolated (small micropores connect the pores, but on the scale of the polymer chains produced, these pores are likely not relevant). As noted in Table 2, it was determined that the polymerization was controlled best by sites on nonporous and interconnected large pore supports, with narrow PDIs and controlled molecular weights [16]. Like the PMI system, a small amount of leaching was observed in nearly all cases and the catalysts were recoverable and recyclable [16].

These studies brought to light several important points: (1) in some cases, ligand-tethered metal complex polymerization catalysts can be recovered and reused; (2) good polymerization control and effective recycling is aided by use of a nonporous support or a support with large, interconnected pores; (3) the simpler, preformed complex addition approach yielded the best catalysts; and (4) catalysts that *appear* to have a similar primary surface structure based on spectroscopy and elemental analysis can behave very differently in catalytic reactions. In reference to point 4, we hypothesize that the materials do not in fact have the same types of surface species present. Instead it is expected that the spectroscopic methods used simply were not capable of identifying the subtle differences in the structure of the

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[1] Note that in ATRP, poor transport in solid catalysts manifests itself as poor control over the polymerization rather than as reduced reaction rates as is typically seen in small molecule reactions.

Table 1
Polymerization of MMA with CuBr/PMI immobilized on silica[1]

Entry	Catalysts	Time (hrs)	% Conv	$M_{n,\ Th}$	$M_{n,\ Exp}$	PDI	R_{Cu}[2] (ppm)
1	CuBr/PPMI	12	73	7300	7800	1.13	—
2	SBA(50)-CuBr/PMI-M1	24	82	8200	15,400	1.97	42
3	SBA(50)-CuBr/PMI-M2	24	70	7000	13,600	1.96	47
4	SBA(50)-CuBr/PMI-M3	24	67	6700	8700	1.58	10
5	SBA(50)-CuBr/PMI-M4	24	82	8200	10,300	2.27	34
6	SBA(100)-CuBr/PMI-M1	7	64	6400	11,000	2.05	169
7	SBA(100)-CuBr/PMI-M2	7	83	8300	13,900	1.90	80
8	SBA(100)-CuBr/PMI-M3	7	84	8400	14,200	1.52	191
9	SBA(100)-CuBr/PMI-M4	7	78	7800	12,100	1.60	10
10	Cab-O-Sil-CuBr/PMI-M1	7	83	8300	11,200	1.46	186
11	Cab-O-Sil-CuBr/PMI-M2	6	85	8500	12,200	1.64	317
12	Cab-O-Sil-CuBr/PMI-M3	8	81	8100	13,600	1.66	23
13	Cab-O-Sil-CuBr/PMI-M4	8	80	8000	12,500	1.57	56

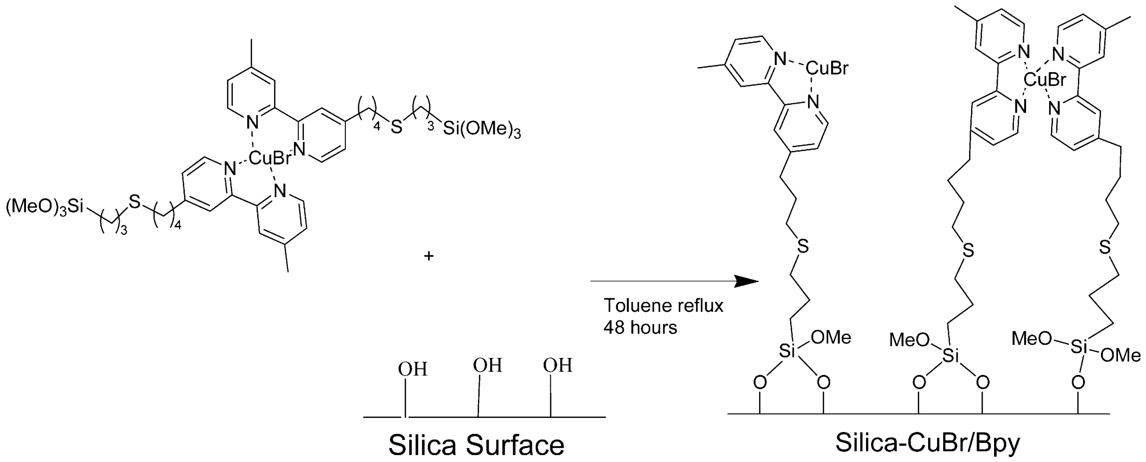
Polymerization conditions: [MMA]/[Cu]/[BPN] = 100/1/1 in 25% by v/v MMA in toluene at 90 °C.
[1]Adapted from [15].
[2]Residual copper content determined by elemental analyses (detection limit was 10 ppm).

metal complexes that were formed on the surface. This issue will be discussed further below.

2.2. Silica-tethered Zn-β-diiminate (BDI) complexes as recycleable? green catalysts for biodegradable polymer production

The work described above, as well as the work of others [17–21], indicated that recoverable, recyclable silica-tethered catalysts for radical polymerizations could be developed. In this case, the growing polymer chain is never bonded to the metal center, making catalyst recovery at the end of the polymerization as simple as filtering off the solid catalyst from the reaction media. A significantly greater challenge would be recovery and recycle of a coordination-insertion catalyst, where the polymer grows off the metal atom. To this end, we explored the literature for a potentially recyclable coordination-insertion polymerization catalyst. Systems for lactone and lactide polymerization based on bi and tridentate amine ligands coordinated to metal alkoxy species were identified as promising candidates [22–24], as the polymerizations are often quenched via addition of alcohol and alkoxy species are good initiating groups. Furthermore, if a recoverable and recyclable lactide polymerization catalyst were introduced, it would allow for the ultimate "green" polymerization system: a monomer derived from renewable resources, a recoverable and recyclable catalyst with no metal waste, and a biodegradable polymer product.

Coates' Zn-BDI complex [22] was identified as a good candidate for immobilization and synthetic strategies for the production of ligand-tethered complexes were developed (Scheme 3) [25]. Three synthetic strategies were used, including a preformed complex addition method (Method A), a two step grafting protocol (Method B) and a stepwise grafting method (Method C).



Scheme 2. Preparation of tethered CuBr/Bpy ATRP catalysts.

In the copolymerization of carbon dioxide and cyclohexeneoxide to produce poly(cyclohexene carbonate), all catalysts effectively produced copolymer with varying amounts of homopolymer as a side product

Table 2
Polymerizations of MMA with CuBr/Bpy immobilized on silica[1]

Entry	Catalyst	Time (hrs)	% Conv	$M_{n,\ Th}$	$M_{n,\ Exp}$	PDI	R_{Cu}[2] (ppm)
1	CuBr/dMBpy	10	74	7400	8600	1.22	6840
2	SBA15(50)-CuBr/SdMBpy	24	44	4400	11,600	4.74	< 10
3	SBA15(100)-CuBr/SdMBpy	24	77	7700	10,600	2.11	< 10
4	CPG(240)-CuBr/SdMBpy	24	72	7200	8400	1.35	< 10
5	Cab-O-Sil-CuBr/SdMBpy	17	78	7800	13,000	1.29	< 10
6	CuBr/dMBpy	16	79	23700	24,900	1.30	1324
7	SBA15(100)-CuBr/SdMBpy	24	79	23800	31,200	1.81	48
8	CPG(240)-CuBr/SdMBpy	24	70	21000	25,700	1.38	168
9	Cab-O-Sil-CuBr/SdMBpy	24	76	22800	27,700	1.52	< 10

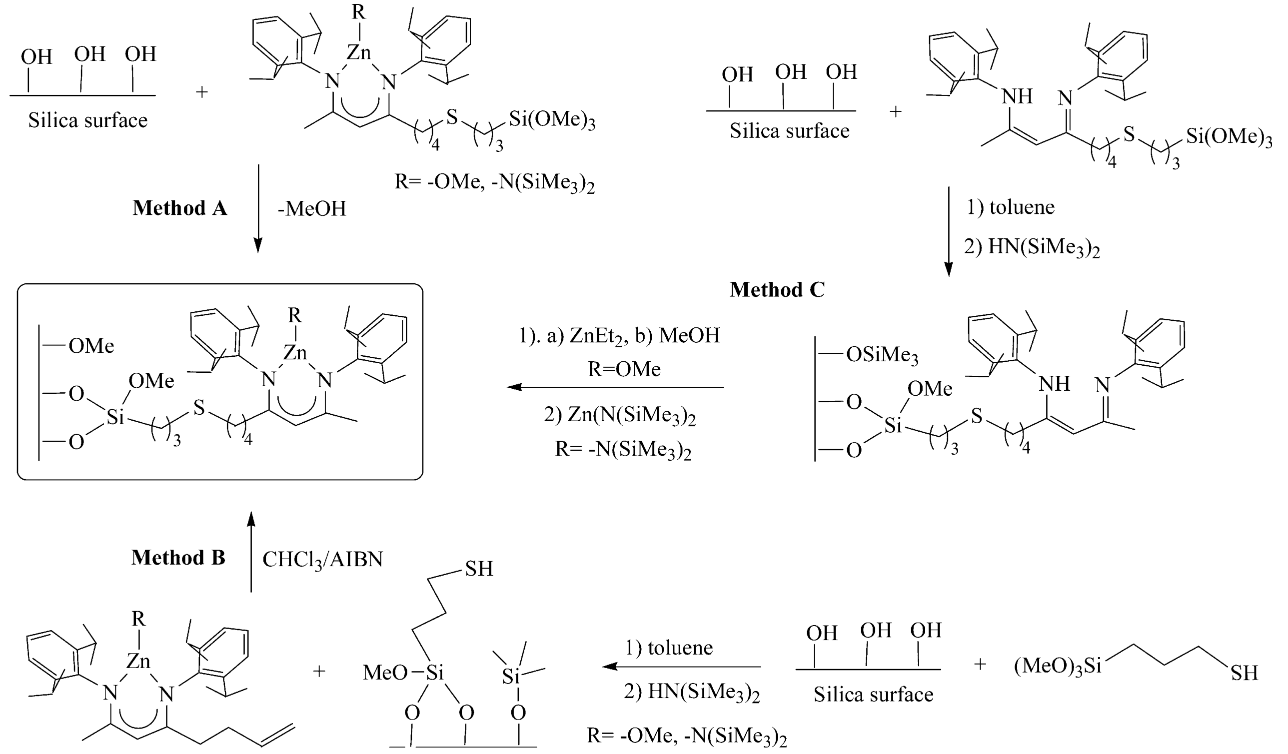
Polymerization conditions: [MMA]/[Cu]/[BPN] = X/1/1 in Y% by v/v MMA in toluene at 90 °C. For entries 1–5, $X = 100$, $Y = 25$; entries 6–9, $X = 300$, $Y = 50$.

[1] Adapted from [16].

[2] Residual copper content determined by elemental analyses (detection limit was 10 ppm).

(polycyclohexene ether). The fraction of polycarbonate produced decreased in the order Method A (65–78%) > Method B (69–43%) > Method C (33–41%), over SBA-15 and CPG supports [25]. As in the ATRP case discussed above, the results indicate that preformed complex addition resulted in the best catalyst. It is noteworthy that the homogeneous catalysts gave much higher yields of polycarbonate (91–98%) [25], implying that some change in the active site structure may have occurred during immobilization. Indeed, it is hypothesized that upon immobilization, some sites are formed that are specific for polyether formation. However, conclusive evidence for this has not yet been obtained. In addition, it was shown that over the course of the reaction, the polycarbonate content decreases with time, which is partly due to transport limitations that prevent carbon dioxide from effectively entering the pore system after the pores fill with polymer [25].

It is noteworthy that the pre-formed complex addition method worked only with mesoporous supports such as SBA-15 and CPG. However, when this method was applied to Cab-O-Sil EH5 supports, significant complex decomposition was observed [25]. This was hypothesized to result from interactions between the zinc center and accessible silanols on the concave Cab-O-Sil silica surface. This is in sharp contrast to the



Scheme 3. Preparation of tethered Zn-BDI catalysts.

CuBr/Bpy and CuBr/PMI cases, where the best catalysts were prepared on Cab-O-Sil supports. This illustrates how no single simple immobilization strategy works for all systems. In the case where the metal center is sensitive to mildly acidic silanols and these silanols are accessible, significant metal-surface reactions can occur yielding undesired sites.

The Zn-BDI catalysts prepared via Method A and B were also used in the polymerization of lactide [26]. In the copolymerization case above, the catalysts readily made polymer with a relatively narrow polydispersity. For lactide polymerization, it was found that the residual silanol groups on the silica surface were detrimental to the molecular weight. The silanols acted as chain transfer agents giving low molecular weight polymer, as verified by capping reactions (silanol removal resulted in higher molecular weights) [26]. By supporting the Zn-BDI complex on the external surface of surfactant-filled, nonporous SBA-15 and thereby removing it from the pore system where there is a large local concentration of silanols, polymer with a relatively high molecular weight was produced (1285 for immobilization in the mesopores; 12,460 when immobilized on the outer surface) [26].

After lactide polymerization, the catalyst could be recovered by filtration/centrifugation if the reaction was not quenched with alcohol, although it still contained polymer (as measured by TGA). This polymer in the pores precluded effective recycling of the catalyst and no subsequent turnovers of the catalyst were detected. If the reaction was quenched with methanol as is usually done in the homogeneous systems, it was found that the solid could be recovered effectively but that a substantial portion of zinc leached off the solid. Apparently, under the conditions used, the methanol leads to significant complex decomposition during quenching. Thus, in our preliminary studies, the solid catalyst was recoverable, but not recyclable.

The Zn-BDI studies reinforce some of the findings from the ATRP case, while differing in some ways as well. As in the CuBr/Bpy and CuBr/PMI systems, preformed complex addition gave the best-behaved catalysts. However, this observation has to be modified with the caveat that they have the best catalytic properties in cases where interactions with surface silanols are either not significant (CuBr cases) or where the thermodynamically downhill reactions are not possible due to steric constraints (Zn-BDI on mesoporous supports). In both systems it was observed that pore constraints can affect the polymerization, as CPG was a more effective support than SBA-15 in each case. The pore constraints manifested themselves in the form of a selectivity change in both systems. Poorer control over the radical polymerizations was observed over SBA-15 supports, leading to broader PDIs and higher molecular weights. In the Zn-BDI system, lower copolymer content was observed when SBA-15 supports were used, partly resulting from restricted access to carbon dioxide in the pore system as the reaction progressed.

3. A patterned aminosilica scaffold for isolated, well-defined metal complex catalysts

The zinc and copper systems described above illustrate that effective polymerization catalysts can be prepared via ligand tethering to oxide supports. However, it is clear that a molecular-level understanding of the immobilized catalysts is not in hand. The nature of the surface species on the molecular level is unknown and it is highly probable that the surface-tethered complexes have a distribution of structures. In some cases, such as with the CuBr/Bpy system for ATRP of methyl methacrylate, the presence of multiple types of species does not seem to be detrimental, as the polymer produced is very similar to that produced with a pure, homogeneous complex. However, more often, a distribution of types of sites can lead to sites with different structures that behave differently in the presence of monomer, potentially producing different types of products.

The molecular level speciation of the metal complexes in the systems described above is lacking due to the difficulty in characterizing multi-sited solids. Spectroscopy routinely gives you insight into the average surface species but rarely gives definitive information when a large number of types of sites are present. Thus, if a true molecular level understanding of these ligand-tethered systems is to be developed, a methodology for the preparation of truly single-site immobilized complexes must be elaborated. To this end, we have developed a new synthetic protocol to give a well-defined, potentially single-site scaffold for the immobilization of metal complex catalysts.

The Zn-BDI system described above illustrates a key difficulty in immobilizing many metal complexes that contain oxophilic metal atoms – the reactivity of residual silanols on the surface. Blocking all the surface silanols is one possible option, although this would decrease the available surface area for complex immobilization *via* the methoxysilane moiety (which react with both siloxane bridges and silanols [27,28]). One other option is to remove most of the silanols *via* calcination at high temperature. Unfortunately, both of these methods can lead to lower surface loadings, making characterization of immobilized surface species more difficult. For this reason, we developed a multistep grafting technique that was designed to: (i) give a versatile scaffold group, a single type of primary amine site; (ii) prevent amine-silanol and metal-silanol interactions, and (iii) isolate the surface groups a specific minimum distance from each other [29].

A molecular patterning process (Scheme 4) was used to functionalize a mesoporous SBA-15 silica material with primary aminopropyl groups on the surface [29]. Due to the nature of the synthesis, the deprotected amine groups should be free of surface silanol interactions, readily accessible and uniformly reactive. Although it has not been explicitly proven that the amines are free of silanol interactions, stoichiometric probe reactions lead to quantitative conversion of the amines. This is unusual and is not observed in materials prepared by traditional grafting processes [30–32].

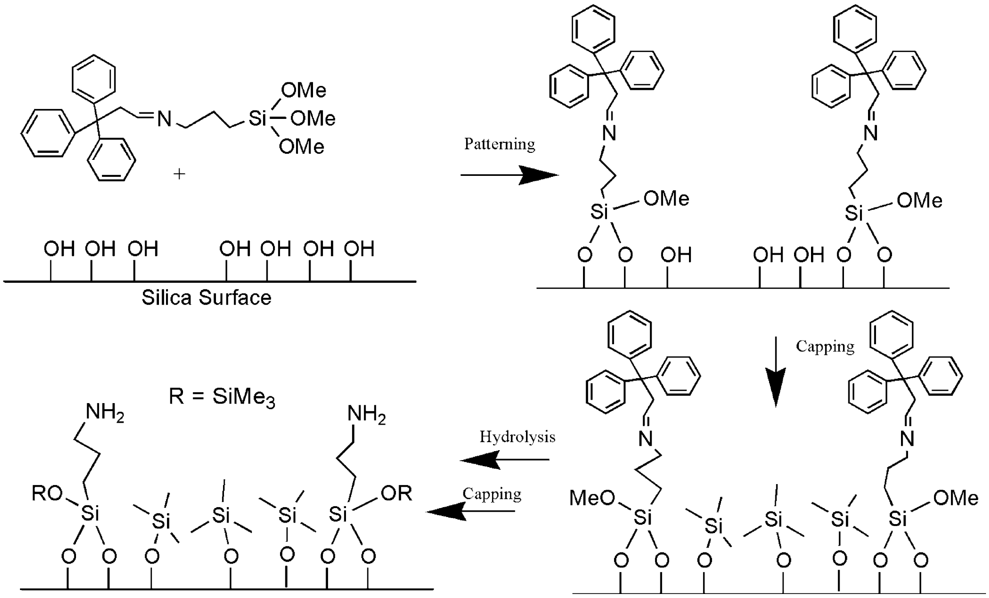
The resulting "patterned aminosilica" scaffold may be an ideal support for the immobilization of a wide array of well-defined metal complex catalysts. To evaluate the materials as a metal complex support, Ti [33,34] and Zr [35] constrained geometry complexes (CGCs) were immobilized at the amine sites. These complexes were chosen as model systems for several reasons. First, immobilized Group IV transition metal complexes have been widely applied as single-use, heterogeneous polymerization catalysts commercially [10]. Additionally, these early transition metal complexes are extremely oxophilic and are therefore difficult to prepare in single-site form on silica, thus presenting a significant synthetic challenge. For example, the preformed complex addition approach that resulted in the best catalysts in the cases described above has been shown to result in multi-sited, ill-defined catalysts in the Ti CGC case [36]. This is due to the fact that the CGC contains a very sterically open active center, making it among the most difficult Group IV complexes to support without having serious metal-support interactions. For this and other reasons, Dow has commercialized [37] this polymerization catalyst in an unsupported form, which is quite rare for single site polymerization catalysts.

Utilizing the patterned aminosilica as a scaffold, we successfully immobilized Ti [33,34] and Zr [35] CGC-inspired catalysts (Scheme 5) that behaved substantially better than ligand-tethered catalysts made via traditional techniques (Table 3). Methylalumoxane was found to cause substantial complex leaching, whereas the use of alkylaluminum/borane cocatalyst systems led to no observed loss of transition metal. Thus, the use of this cocatalyst system gives an immobilized polymerization system that may be amenable to the development of true structure/property relationships.

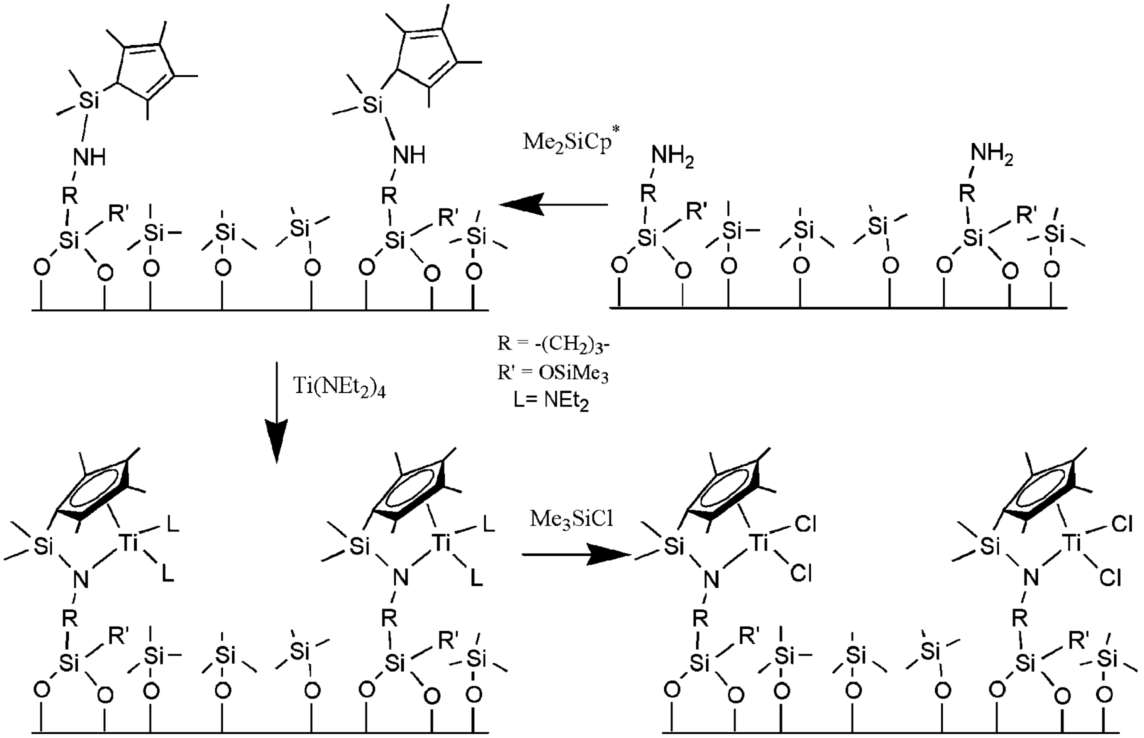
To develop such relationships, detailed knowledge about the structure of the immobilized sites must be obtained. Although the Ti CGC-inspired sites that were prepared on the patterned aminosilica scaffold may be substantially more uniform than on catalysts prepared in traditional ways (based on grafting stoichiometry, spectroscopy, etc.) conclusive proof of a single type of titanium site could not be obtained [34]. Work continues towards this goal, with a focus on the use of spectroscopic methods such X-ray Absorption Spectroscopy (XAS) that directly probe the titanium metal center.

4. Long term challenges for oxide-tethered metal complex catalyst design

Ideally, an immobilization method should result in a catalytic site that is identical to the homogeneous system. In practice, this is almost never the case, as the complex inevitably interacts with support in a non-scripted manner. In some cases, this results in immobilized catalysts that are more selective than their homogeneous analogues [38,39] and in other cases it leads to catalysts that are inferior to their unsupported



Scheme 4. Molecular patterning protocol for creation of the aminosilica scaffold.



Scheme 5. Functionalization of the aminosilica scaffold with Ti-CGC sites.

Table 3
Polyethylene polymerization results for silica immobilized CGCs[*]

Entry	Catalyst	Ti loading[a] (mmol/g Cat)	Co-catalyst	Productivity[e] (kg PE/mol Ti-hr)
1	Patterned	0.38	MAO	19.7
2	Patterned	0.38	Borane[b]/TMA[c]	28.7
3	Patterned	0.38	Borane[b]/TIBA[d]	24.8
4	Homogeneous Analogue	2.83	MAO	11.4
5	Homogeneous Analogue	2.83	Borane[b]/TMA[c]	15.6
6	Homogeneous Analogue	2.83	Borane[b]/TIBA[d]	21.4
7	Self-Immobilized Complex[f]	0.17	MAO	26.5
8	Self-Immobilized Complex[f]	0.17	Borane[b]/TMA[c]	4.2
9	Self-Immobilized Complex[f]	0.17	Borane[b]/TIBA[d]	5.1
10	Alkyllithium Method[g]	0.65	MAO	4.2
11	Alkyllithium Method[g]	0.65	Borane[b]/TMA[c]	1.5
12	Alkyllithium Method[g]	0.65	Borane[b]/TIBA[d]	2.2
13	Densely Loaded[h]	0.53	MAO	5.9
14	Densely Loaded[h]	0.53	Borane[b]/TMA[c]	2.7
15	Densely Loaded[h]	0.53	Borane[b]/TIBA[d]	1.5
16	Densely Loaded[h]	0.38	MAO	5.4
17	Densely Loaded[h]	0.38	Borane[b]/TMA[c]	4.3
18	Densely Loaded[h]	0.38	Borane[b]/TIBA[d]	2.3

[*] Adapted from reference [34].

[a] Titanium loadings determined by elemental analysis.

[b] Borane = tris(pentafluorophenyl)borane.

[c] TMA = trimethylaluminum.

[d] TIBA = triisobutylaluminum.

[e] polymerization conditions: T = 25 °C; solvent: toulene; ethylene pressure: 60 psi; reaction time: 10 min.

[f] prepared via literature methods using a self-immobilizable CGC complex.

[g] prepared via literature methods using an alkyllithium to immobilized cyclopentadienyl functionality on aminosilica.

[h] prepared by same method as shown in Scheme 5, only a densely functionalized aminosilica was used as a starting scaffold.

counterparts [40,41]. Unfortunately, although well-behaved catalysts are known [38,42–44], no general immobilization methodology exists that is applicable for all (or even most) metal complexes. Furthermore, there are no long-term, systematic studies that have been undertaken that elaborate a general set of rules that will guide catalyst design. As noted above, it is exceedingly difficult to a priori predict how an immobilized catalyst will behave. Because in almost all cases the tethered catalyst behaves differently than the homogeneous ones, new structure/property relationships for the tethered catalysts must be developed; it is very uncommon for all structure/function relationships that exist for the soluble, homogeneous complex to be directly translated to the immobilized system.

The generation of structure/property relationships for immobilized molecular catalysts is hampered by the existence of multiple types of immobilized metal complexes on the surface. Whenever multiple types of sites are formed, generation of structure/function relationships is complicated by the difficulty in unambiguously characterizing the structure of the supported species. As spectroscopy routinely gives insight into the average or composite surface structure, understanding the structure of the surface complexes on multi-sited solids becomes a major challenge. Thus, *a major challenge in the design of oxide-tethered metal complex catalysts is the development of general methods for the preparation of isolated, single-site complexes on oxide surfaces that are fully characterizable*. Our work described above illustrates our initial efforts toward this goal.

In addition to the long term objective described above, there are several other major challenges that the research field still needs to address.

4.1. Understanding and controlling metal leaching

Perhaps the key issue that has prevented widespread implementation of immobilized metal complex catalysts commercially is their propensity to leach metal species [45]. In some cases the cause of leaching is clear, for example, phosphine dissociation is a necessary part of many catalytic cycles and hence complexes that are tethered via an immobilized monodentate phosphine will almost always leach [46]. However, in other cases, the causes of complex leaching are less clear and in some cases there is evidence that leaching occurs via rupture of the bonds between the silane tether and the oxide surface [34].

4.2. Coupling experimental catalyst design and characterization with quantum and molecular modeling

Generation of a complete understanding of porous oxide tethered metal complex catalysts will require the careful combination of experiment and modeling. Quantum calculations will aid in understanding changes in electronic structure of the metal complex that result from immobilization, while molecular models can aid in understanding the sterics and dynamics of the ligand tethered species within the catalyst pores. Indeed, initial promising studies along these lines have recently been reported [47].

4.3. Integrating tethered single-site metal complexes with imprinted cavities containing secondary organic groups

Great strides have been made in the development of artificial enzyme mimics via molecular imprinting [48]. Creation of well-defined, local cavities in oxide materials via a sol-gel imprinting process allows for the positioning of multiple active sites within a porous space of prescribed size [49]. Initial efforts at incorporating metal complexes in imprinted solids have also shown promise [50–55]. In the future, the possibility of combining tethered metal complexes in imprinted cavities with additional secondary organic groups will undoubtedly be explored as a further stride towards enzyme mimicking materials [56].

5. Conclusions

There are number of factors that affect that performance of silica-tethered metal complex catalysts for polymerization applications. In cases where catalyst recovery and recycle are important, the porosity of the support has a major influence on catalytic performance, with nonporous and large pore supports giving better catalytic results. The method of metal complex assembly was also shown to have a large influence on catalytic performance. For metal complexes that are not susceptible to reaction with the silanols on the support, it was demonstrated that immobilization of catalysts via preformed complex addition results in materials with the best catalytic behavior. In contrast, for metal complexes with a propensity to react with the silanols of the support (early transition metals complexes as well as complexes with protolytically labile groups), this approach is less useful as the detrimental interactions between the metal atoms and free surface silanols lead to unwanted reactions of the complex with the support. For these situations, a new synthetic strategy was introduced that leads to a well-defined aminosilica scaffold that is free of accessible surface silanols. This scaffold is useful for immobilization of a variety of metal complexes, but particularly those that are expected to react with surface silanols. In the case where Ti and Zr CGCs were immobilized on this scaffold, catalysts that had substantially improved activities were obtained. Future directions in this research area are expected to include mechanistic investigations of complex leaching, increased use of tethered metal complexes in molecularly imprinted, enzyme-mimicking catalysts, and the combined use of experimental studies with quantum and molecular modeling to generate an understanding of these systems on the molecular level.

Acknowledgements

CWJ acknowledges the Catalysis and Biocatalysis Program at NSF (CTS-0133209, CTS-0210460), the

Catalysis Science Initiative in Basic Energy Sciences at DOE (DE-FG02-03ER15459), and the Shell Oil Company Foundation for research support. MWM thanks the Georgia Tech Molecular Design Institute (N00014-95-1-1116, Office of Naval Research) for partial support through a graduate fellowship. JVN thanks the Georgia Tech NanoScience and Technology Initiative for partial support via a graduate fellowship.

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