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Modulating the Reactivity of an Organometallic Catalyst via Immobilization on a Spatially Patterned Silica Surface

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Molecular catalysts such as organometallics and coordination compounds have been immobilized on inorganic solids for many years.[1] Most often, the goal of such studies is to produce a solid catalyst with molecular reactivity characteristics and catalyst recoverability. However, frequently, immobilization leads to creation of a distribution of surface species that can lead to reduced catalytic selectivities. Nonetheless, in rare cases, immobilization actually improves the catalytic performance. For example, Raja, Thomas, and co-workers have reported that the tethering of asymmetric organometallic catalysts on a mesoporous silica support increases the enantioselectivity of the catalysts as compared to the analogous homogeneous complex.[2] It has also been recently shown that tailoring the silica support structure in supported constrained geometry complex-inspired (CGC) catalysts can affect the catalyst activity and the resulting polymer properties.[3]

Recently, we introduced a simple molecular patterning process by which we prepared silica materials derivatized with isolated aminopropyl groups. The amine sites react with probe molecules in a consistent way due to their relative spatial isolation (Figure 1).[4] From this designed silica surface, we subsequently showed that CGC-type sites could be prepared and that the immobilized sites were 10× more active than when the same synthesis procedure was applied to a traditionally functionalized aminopropyl silica.[5] In this work, we show that immobilization of organometallic complexes on the spatially patterned silica support can give not only improved reactivity in a known reaction (10× increase in ethylene polymerization activity[5a]) but also novel reactivity in reactions that the homogeneous complex does not effectively promote. Ti CGC-inspired sites supported on patterned silica allow for both the homopolymerization of the bulky monomer (norbornene) and the copolymerization of bulky functional norbornenes and ethylene. As noted below, there are two key attributes to the catalyst design that are hypothesized to facilitate this catalytic behavior: the accessibility of the metal center (from above the surface and laterally) due to the spatial distribution of the amine sites on the surface (laterally) and the steric constraints that are imposed by the silica surface (from below the complex).

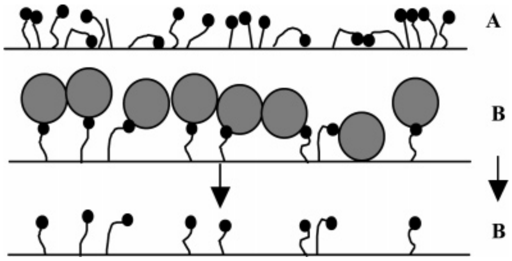

Figure 1. Traditional aminosilicamaterial with a random amine distribution (A) and spatially patterned aminosilica material prepared using bulky spacer molecules (B).

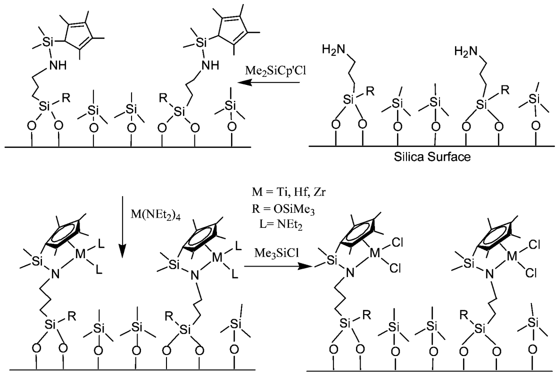

Figure 2. Methodology for immobilization of CGC-inspired complexes.

Mesoporous silica SBA-15 with roughly 50 Å diameter pores was prepared via literature procedures.[6] This silica material was then functionalized with aminopropyl groups using two different routes: a traditional grafting process that produces a distribution of types of amine sites (i.e., clustered, silanol complexed, and isolated amine sites) and a molecular patterning process that yields spatially patterned sites that behave as if they are isolated on the surface.[4] From these two amine scaffolds, Ti, Zr, and Hf CGC-inspired sites are assembled via a methodology previously reported (Figure 2).[5a,7] Whereas complexes assembled on the traditionally functionalized aminosilica result in substantially less than quantitative yields in every step, assembly of the complexes on the patterned support gives near quantitative conversions in every step (Table 1), regardless of the metal used (Ti, Zr, Hf) as evidenced by the Ti/N ratio of ∼1. This provides

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Table 1. Material Characterization for Synthesis of CGC−Inspired Complexes

	titanium		zirconium		hafnium	
material	patt. silica	rand. silica	patt. silica	rand. silica	patt. silica	rand. silica
amine loading (mmol/g)	0.36[a,b]	1.35[a]	0.36[a,b]	1.35[a]	0.36[a,b]	1.35[a]
Cp′ loading (mmol/g)	0.37[b]	0.82[b]	0.37[b]	0.82[b]	0.37[b]	0.82[b]
metal loading (mmol/g)	0.39[b]	0.52[b]	0.37[b]	0.41[b]	0.40[b]	0.37[b]

[a] Loading determined by TGA. [b] Loading determined by elemental analysis.

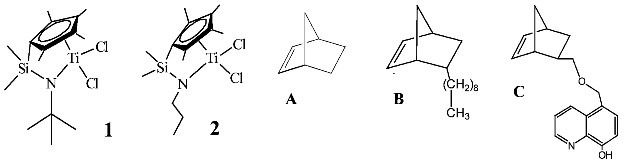

Figure 3. Homogeneous constrained geometry catalysts (**1**, **2**) and norbornene monomers (A−C) utilized in this study.

indirect evidence of the greater uniformity and lateral spatial accessibility of the amine sites on the patterned surface, in accord with previous probe reaction studies.[4]

Ethylene−norbornene copolymers have properties, such as high glass transition temperatures, high thermal stability, and high clarity, that make them viable for applications in microelectronics, pharmaceutical packaging, and optical media.[8] Homogeneous CGCs of the structure **1** shown in Figure 3 are known to promote the catalytic polymerization of bulky monomers, such as norbornene, as well as the copolymerization of ethylene and norbornene.[8] CGC **1** has been reported as having an ethylene−norbornene copolymerization productivity in excess of 500 kg of copolymer/mol of M•h, with a norbornene incorporation of 10−40% (depending on reaction conditions).[8] However, CGCs such as **2** (Figure 3) do not effectively promote the reaction (vide infra). Indeed, it has been shown before that subtle changes in the sterics and electronics of CGCs strongly affect catalytic performance. For example, Stevens reported changing the *tert*-butylamido group (seen in **1**) to phenylamido or phenylphosphido groups led to lower productivity in the polymerization reactions.[9] Interestingly, here we show that complexes that are inactive under homogeneous conditions, such as **2**, can be made active in immobilized form by using the molecular patterning protocol to disperse the catalytic sites on the silica surface.[10]

The polymerization data in Table 2 clearly show that the homogeneous catalyst **2** has very little activity when exposed to toluene solutions of norbornene and ethylene. In contrast, when the complex is assembled on a patterned aminosilica support, the immobilized species effectively polymerize ethylene and norbornene with good activities that are similar to those observed in ethylene homopolymerizations.[7] However, when the same synthetic procedure is applied to a traditionally functionalized aminosilica solid, the resulting sites are inactive for the polymerization. Thus, it appears that the spatial patterning of the surface directly influences the catalytic properties, perhaps allowing for the necessary space around the metal centers for bulky monomers such as norbornene to be effectively incorporated.

Analysis of the polymers produced by the homogeneous catalyst and the spatially patterned silica-supported catalyst indicates that different types of polymers are produced in each case (Supporting Information). Polymers produced by the homogeneous catalyst **2** had melting points and ^{13}C NMR spectra that were consistent with formation of ethylene homopolymers, even when the polymerization was done in the presence of norbornene. In contrast, corresponding data for the polymers prepared by the patterned catalyst (with borane/triisobutylaluminum as a co-catalyst) indicate that a true ethylene−norbornene polymer was prepared, with approximately 20% norbornene incorporation as estimated by ^{13}C NMR. Thus, the patterned catalyst behaves more like the homogeneous catalyst **1**, which is reported to be active in the copolymerization,[8] than catalyst **2**, which we show here to be virtually inactive. One may infer from these data that the silica surface below the amine group ligated to the metal center could provide the steric constraints below the complex necessary to have a good catalyst, as the *tert*-butyl group does in the homogeneous catalyst **2**.

In addition to allowing for the copolymerization of ethylene and norbornene, the spatially patterned catalyst allows for several other polymerizations to proceed that do not effectively occur with the homogeneous catalyst **2** or the catalyst immobilized on the traditionally prepared aminosilica surface. Table 3 shows data gathered during the homopolymerization of norbornene and the copolymerization of bulkier, functionalized norbornenes with ethylene. The norbornene homopolymerization results further suggest the patterned catalyst has a more accessible active site than the densely functionalized catalyst. As norbornene (Figure 3A) has a substantially greater size than ethylene, a more isolated catalytic site should be more capable of polymerizing the monomer. The homogeneous CGC shows a lower activity than the patterned catalyst as well, which is similar to results previously seen in ethylene polymerizations.[5a,7]

The addition of bulky polar or nonpolar functional groups to the monomer can drastically change the reactivity of the monomers. To this end, the copolymerization of ethylene with functionalized norbornenes was investigated. The first monomer tested had a long alkyl chain attached to the norbornene ring, 5-nonyl-bicyclo[2.2.1]hept-2-ene (Figure 3B). Again the densely loaded catalyst showed very little activity in this polymerization, not unexpected due to its lack of activity in the copolymerization of norbornene and ethylene. The homogeneous catalyst **2** also showed only slight activity. The patterned catalyst again showed the highest productivity in the polymerization.

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Table 2. Ethylene−Norbornene Copolymerization Results

catalyst	Ti loading[a] (mmol/gcat)	co-catalyst	ethylene productivity (kg of PE/mol of Ti·h)[e]	copolymer productivity (kg of polymer/mol of Ti·h)[f]
patterned	0.38	borane[b]/TMA[c]	28.7	27.9
patterned	0.38	borane[b]/TIBA[d]	24.8	25.2
2	2.83	borane[b]/TMA[c]	15.6	3.6
2	2.83	borane[b]/TIBA[d]	21.4	3.4
traditional	0.53	borane[b]/TMA[c]	2.7	no activity
traditional	0.53	borane[b]/TIBA[d]	1.5	no activity

[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: toluene; ethylene pressure: 60 psi; reaction time: 10 min. [f] Same conditions as footnote *e* with norbornene added to reactor prior to ethylene exposure.

Table 3. Polymerization Results with Norbornene and Functionalized Norbornene−Ethylene Copolymerizations

				comonomer	
catalyst	Ti loading[a] (mmol/g of catalyst)	co-catalyst	norbornene productivity (kg of PNB/mol of Ti·h)[d]	nonyl−norbornene (N) copolymer productivity (kg of polymer/mol of Ti·h)[e]	quinoline−norbornene (Q) copolymer productivity (kg of polymer/mol of Ti·h)[e]
patterned	0.38	borane[b]/TIBA[c]	23.4	16.6	8.5
2	2.83	borane[b]/TIBA[c]	2.4	1.5	no activity
traditional	0.53	borane[b]/TIBA[c]	trace	0.9	no activity

[a] Titanium loadings determined by elemental analysis. [b] Borane = tris(pentafluorophenyl)borane. [c] TIBA = triisobutylaluminum. [d] Polymerization conditions: $T = 50$ °C; solvent: toluene; pressure tube reactor; reaction time: 10 min. [e] Polymerization conditions: $T = 25$ °C; solvent: toluene; ethylene pressure: 60 psi; reaction time: 10 min; addition of norbornene to reactor prior to ethylene exposure.

The second functionalized monomer, 5-[(6-bicyclo[2.2.1]-hept-5-en-2-yl-hexylamino)methyl]-quinolin-8-ol, is illustrated schematically in Figure 3C. This is a heteroatom-functionalized monomer containing a strongly metal-coordinating group that has been polymerized via ROMP to synthesize polymeric electron transport layers in light-emitting diodes.[11] The control materials are again nearly inactive in the copolymerization. However, the patterned catalyst maintains some polymerization activity in this system. This is unique from two perspectives. First, this norbornene monomer contains a quinoline moiety that could easily coordinate with the Ti metal center. However, it is known that this ligand coordinates to Al species as well. Thus, interactions with the co-catalyst, which is present in large excess, may decrease the likelihood that the quinoline group coordinates with the Ti center.[11] The second unique aspect is that this is a rare example of an immobilized Group 4 polymerization catalyst that is active in the polymerization of a polar group functionalized monomer.[12] The lack of activity by the control catalysts and the depressed rate of the patterned catalyst as compared to other polymerizations could be a consequence of several factors. First, the bicyclic rings on the monomer create a large steric profile, thus having isolated catalytic sites may allow for better incorporation compared to catalysts prepared on traditionally functionalized silica. The depressed activity compared to the other copolymerizations could be the result of quinoline−catalyst interactions. It is possible the titanium metal center interacts with the quinoline functionality, creating titanium sites that are unavailable for polymerization. This may account for the lack of activity of the homogeneous CGC **2** in this copolymerization. Evidence for the importance of aluminum−quinoline interactions is provided by the observation that the order of addition of the reagents directly affects the catalytic performance of the catalysts. In experiments where the catalyst (supported or homogeneous) is not contacted with the trialkylaluminum co-catalyst before exposure to the quinoline functionalized monomer, no polymerization activity is observed. This observation is consistent with previous work on related systems, where it has been shown that protecting a heteroatom functionalized monomer with a trialkylaluminum can allow for polymerization with otherwise sensitive Group 4 systems.[12f,13]

The spatial patterning of the surface imparted by the protocol developed has been shown to improve the catalytic properties of an organometallic catalyst. The reactivity characteristics of this system are hypothesized to result from two key attributes of the system. First, the spatial distribution of the sites on the surface creates a more accessible metal center than traditionally immobilized sites. This allows for the necessary space around the metal centers for bulky monomers such as norbornene to be effectively incorporated. Second, the steric constraints below the complex imparted by the use of the silica surface have a similar effect to an increase in ligand steric bulk in a homogeneous catalyst structure, for example, moving from **2** to **1**. These aspects

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of the catalyst may be what allow for improved reactivity in ethylene polymerization[5a] as well as the ability to perform novel norbornene–ethylene copolymerizations via a silica-tethered complex. It is anticipated that the patterned aminosilica material may be a useful support for many other immobilized molecular catalysts.

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Supporting Information Available: Synthetic procedures for Ti catalysts, polymerization procedures, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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