

Toward Single-Site, Immobilized Molecular Catalysts: Site-Isolated Ti Ethylene Polymerization Catalysts Supported on Porous Silica

Michael W. McKittrick and Christopher W. Jones*

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology,
311 Ferst Drive, Atlanta, Georgia 30332

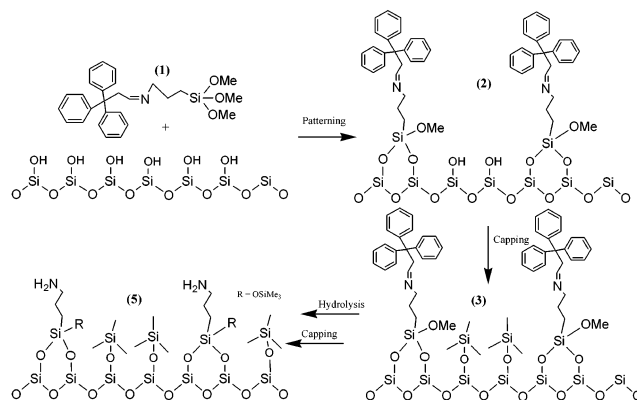
Received December 15, 2003; E-mail: cjones@chbe.gatech.edu

Soluble transition metal complexes are nearly ideal catalysts because of the versatile chemical properties that can be incorporated into them — the symmetry, sterics, and electronics of the active center can all be controlled using molecular design principles. However, industrial implementation of catalytic technologies often requires a solid catalyst. Thus, transition metal complex catalysts have been immobilized on solid supports for decades.¹ Usually, the performance of the supported catalysts is significantly inferior as compared to the homogeneous analogues. This is due to many factors, with a primary cause being the formation of multiple types of ill-defined metal species on the solid support. For example, single-site transition metal complexes such as Group 4 metallocenes and related complexes have been developed as revolutionary new olefin polymerization catalysts.² However, the preparation of well-defined (single-site) solid-supported polymerization catalysts has not progressed as rapidly.³ This is because synthetic protocols that lead to the creation of uniform, isolated organometallic catalysts on surfaces are not well-developed.⁴ Hence, a general methodology for immobilizing metal complex catalysts while maintaining single-site behavior would be a major advance. A potential technique is demonstrated here with Group 4 olefin polymerization catalysts.

To illustrate the pitfalls in catalyst design, consider literature reports of Ti and Zr constrained geometry-inspired catalysts (CGCs)⁵ covalently supported on oxides. Two different covalent immobilization strategies have been reported. In the first approach, a derivatized organometallic precatalyst is contacted with a support.⁶ This method routinely leads to multiple types of surface species due to solid–metal atom interactions. In the alternate approach, the complex is assembled stepwise on the solid.⁷ This also can result in multiple types of sites due to steric crowding on the support and the heterogeneous nature of the support surface. From these reports, it is clear that a method is needed to prepare catalysts with (i) isolated sites, (ii) uniform sites, and (iii) structures that are amenable to detailed characterization. To this end, here we report a new, general methodology that can be utilized to create site-isolated organometallic catalysts on a silica surface. A model silica support is functionalized using a molecular patterning technique to incorporate isolated aminopropyl groups on the surface.⁸ Primary amine groups can serve as versatile ligands or scaffolds for the assembly of well-defined, isolated complexes on the surface. This methodology is demonstrated here through the assembly of Ti CGCs⁵ on a porous silica surface. These new catalysts are up to 10 times more active than multisited catalysts that are prepared using traditional techniques, perhaps due to the isolated nature of the sites.

A patterning molecule has been designed and synthesized that allows for the effective spacing of aminosilane groups on a silica surface. The patterning molecule (1) is contacted with hexagonal mesoporous silica materials such as SBA-15 with an average pore diameter of ~50 Å. The large trityl groups on the patterning agent prevent incorporation of the silane on the surface at sites im-

Scheme 1



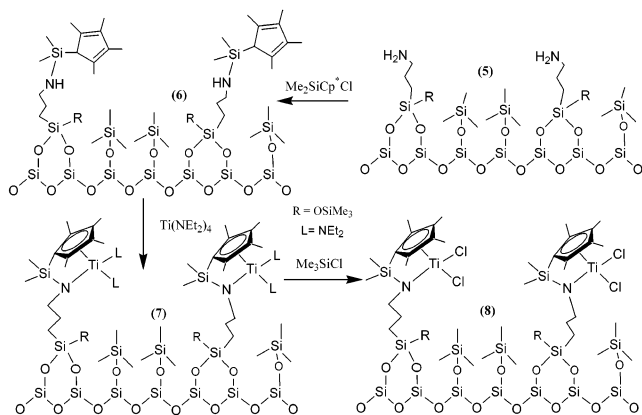
mediately adjacent to each other,⁸ as shown in Scheme 1. After this functionalization, any additional, unreacted silanols on the surface are covered via treatment with hexamethyldisilazane yielding material (3). The imine bond is then selectively hydrolyzed to remove the trityl groups from the functionalized surface, leaving aminopropyl species on material (4). A final capping step is used to cover any additional silanol groups that might be produced in the hydrolysis step, giving material (5). At every stage of the surface functionalization, the materials have been characterized by a battery of techniques including solid-state ²⁹Si and ¹³C NMR, nitrogen physisorption, and FT-Raman spectroscopy. Using these methods, the proposed structure of the solid at each stage of the synthesis has been verified to be as described in Scheme 1.⁸ Probe reaction studies of the amine-functionalized silica materials indicate that the amine groups on the surface of the patterned material behave chemically as if they are isolated and fully accessible.⁸

This silica material with isolated amine sites can be easily utilized as a scaffold for a variety of organometallic catalysts. For preparation of a CGC,⁵ treatment of functionalized silica with chlorodimethyl-(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl) silane yields a CGC precursor ligand on the surface, material (6).⁹ This species is then treated with tetrakis(diethylamino)titanium in toluene for 24 h under reflux to metalate the surface ligands. The resulting immobilized titanium species [material (7)] is then treated with 5 equiv of trimethylsilyl chloride to yield the more stable and easily characterizable titanium chloride complex [material (8)]. This synthetic protocol is shown in Scheme 2. Materials (6) and (8) were characterized by ¹³C CPMAS NMR to verify the structure of the surface species (Supporting Information). Elemental analyses yielded metal loadings with a Ti–N ratio of nearly 1, with literature methods resulting in substantially less Ti incorporation (~0.5 Ti/N) due to the presence of multiple types of surface ligands.⁷ This stoichiometric metalation is consistent with the preparation of well-defined surface species.

Table 1. Catalytic Polymerization with Silica-Supported CGC/BARF Catalysts^a

entry	catalyst	Ti loading (mmol/g of cat)	temp (°C)	polymerization time (min)	Al:Ti	alkyl aluminum	activity (kg of PE/mol of Ti·h)	T _m (°C)	M _w (polymer)	PDI
1	8 – patterned	0.38	25	10	400	TMA	28.7	134.1	660 000	3.1
2	8 – patterned	0.38	25	10	400	TIBA	24.8	133.8	1 000 000	1.9
3	9 – control	1.6 ^b	25	10	400	TIBA	19.8	132.8	470 000	2.8
4	10 – control	0.17	25	10	400	TMA	4.2	131.5	ND	ND
5	10 – control	0.17	25	10	400	TIBA	5.1	132.6	620 000	2.5
6	11 – control	0.53	25	10	400	TMA	2.7	133.5	500 000	broad
7	11 – control	0.53	25	10	400	TIBA	1.5	133.1	1 000 000	2

^a TMA = trimethylaluminum; TIBA = triisobutylaluminum. ^b Homogeneous catalyst.

Scheme 2

The immobilized Ti-CGC⁵ precatalyst derived from the patterned silica support (8) was evaluated in the catalytic polymerization of ethylene. In addition, three control catalysts were prepared for comparison. The first control was the homogeneous Ti-CGC precatalyst (9).⁶ A second control was prepared via addition of a preformed complex to silica as previously reported (10).⁶ Catalyst (11) was assembled using the same protocol as was used for the patterned catalyst (8), with the exception that the complexes were assembled on a densely functionalized aminosilica surface. The precatalysts were contacted with a toluene solution containing tris-(pentafluorophenyl)borane and an alkylaluminum (trimethylaluminum or triisobutylaluminum) as activator and were subsequently exposed to 60 psi of ethylene pressure at 25 °C. The produced polymers were analyzed by GPC and TGA-DSC. The catalytic results are described in Table 1.

The patterned precatalysts show significantly higher productivity than the control materials. Furthermore, the patterned catalyst exhibits increased activity even when compared to the homogeneous analogue (catalyst 9). There are several possible explanations for the observed improvement in performance as compared to solid catalysts made via traditional techniques. It is clear that the patterning process allows for more efficient assembly of surface species based on the essentially quantitative yield of each step of the synthesis, something that is unique as compared to previous reports.⁷ Furthermore, if the sites are more uniform and significantly more isolated than sites on densely functionalized materials (control 11), the patterned sites may be more accessible for activation by the borane/alkylaluminum cocatalysts and also could more easily incorporate monomer. In addition, the spectroscopic results and the quantitative assembly of the supported complex imply that it is less likely that there are non-CGC metal species on the patterned catalyst. Another potential advantage of the patterning protocol is

it may limit unwanted interactions of the complex with the oxide surface. Addition of a preformed complex to silica (control 10) likely results in the formation of multiple types of metal sites.⁶ The patterning protocol developed may prevent such surface–metal interactions (silanols are capped), allowing for a more well-defined, active material. Continuing work is focusing on a full molecular level characterization of the new supported species to fully elucidate the cause of the promising catalytic results.

In summary, a new, general patterning methodology that can be utilized to create organometallic catalysts on a silica surface that may be site-isolated is reported here. Ti-CGC-inspired sites are prepared on this support and are demonstrated to be more active than covalently tethered catalysts prepared via traditional techniques. The isolated aminosilica scaffold is a versatile support for metal complex immobilization and may allow for the preparation of a wide array of single-site immobilized organometallic catalysts.

Acknowledgment. C.W.J. thanks the NSF for support through the CAREER program (CTS-0133209). M.W.M. thanks the Molecular Design Institute (N00014-95-1-1116, Office of Naval Research) for partial support through a graduate fellowship. We thank the Coughlin group at UMass for GPC analysis.

Supporting Information Available: Synthetic protocols for Ti catalysts, polymerization procedures, and ¹³C NMR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA031725G