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A Nanostructured, Scandium-Containing Polymer for Heterogeneous Lewis Acid Catalysis in Water

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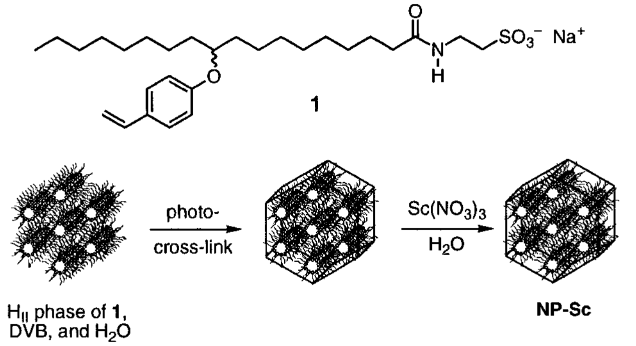
Scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$) is a versatile Lewis acid catalyst that can accelerate a variety of organic reactions using water as an environmentally benign solvent or cosolvent.[1] For example, $Sc(OTf)_3$ can catalyze aldol, Mannich, Michael addition, tin-mediated allylation, and Diels−Alder reactions in water at ambient temperature. Recently, there has been interest in heterogeneous Sc(III)-based catalysis in water, with the goal of modifying catalyst behavior and facilitating catalyst recovery. For example, Lewis acid catalysis in micelles using Sc(III)-exchanged surfactants has been investigated.[2] More importantly, several groups have developed solid-state, polymer-supported Sc(III) catalysts that can be recycled via simple filtration. Polymer-supported Sc(III) catalysts have been produced by binding $Sc(OTf)_3$ to Nafion,[3] derivatized polyacrylonitrile,[3] polystyrene microcapsules,[3] sulfonated polystyrene resin,[4] and dendrimers.[5] While these initial polymer-supported scandium catalysts exhibit good reactivity and recyclability, they are inherently amorphous in nature.

In heterogeneous catalysis, nanometer-scale architecture is often synonymous with high reactivity and selectivity. For example, zeolites are believed to facilitate reactions with high selectivity by localizing reactants in their ordered micropores and providing a high local concentration of active sites.[6] Layered ionic clays[7] and MCM-41 mesoporous sieves[8] also serve as excellent heterogeneous catalysts because of their ordered microstructures. On the other hand, organic polymers offer better chemical tunability and mechanical properties as well as more facile processing. It would obviously be advantageous if these features could be combined with the reactivity and selectivity afforded by a nanostructured scaffold. A nanostructured polymer support for Sc(III) may yield different reactivities and selectivities compared to amorphous Sc(III) catalysts due to a anisotropic, confined catalyst environment. Recent studies of Lewis acid catalysis with Sc(III) in calix[6]arene cavities[9] and La(III) inside an anthracenebisresorscinol coordination network[10] lend support to this idea. Unfortunately, there are very few examples of nanostructured polymers available for heterogeneous catalysis.[11]

Scheme 1



We present here the first example of a nanostructured, polymer-supported Sc(III) catalyst (**NP−Sc**). This catalyst utilizes a cross-linked inverted hexagonal (H_{II}) lyotropic liquid-crystal (LLC) phase as the polymer support.[11] The resulting material, **NP−Sc**, possesses regular channel structures similar to those of MCM-41 mesoporous sieves, and it is within these nanochannels that the reactive Sc(III) centers are localized. **NP−Sc** not only functions in water at ambient temperature and can be efficiently recycled, but it also affords different product stereoselectivities in Mukaiyama aldol and Mannich test reactions compared to existing isotropic solution and solid-state scandium catalysts.

NP−Sc was prepared by initially making a cross-linked H_{II} phase of a new LLC monomer containing a sodium sulfonate headgroup (**1**), and then quantitatively exchanging Sc(III) for Na^+ in the polymer using aqueous $Sc(NO_3)_3$ (Scheme 1). (Several transition-metal salts of monomers structurally similar to **1** have been found to form the H_{II} phase;[12] however, attempts to prepare the Sc(III) salt of **1** directly for subsequent polymerization were unsuccessful. Spontaneous polymerization occurred during ion exchange.[13]) Monomer **1** was prepared by reacting racemic 10-(4-vinylphenoxy)octadecanoic acid[14] with *N*-hydroxysuccinimide to form the corresponding ester, followed by reaction with 1.5 equiv of

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[1] For a recent review of $Sc(OTf)_3$-catalyzed reactions, see: Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15−27.

[2] (a) Manabe, K.; Mori, Y.; Wakabayashi, T.; Nagayama, S.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 7202−7207. (b) Kobayashi, S.; Wakabayashi, T. *Tetrahedron Lett.* **1998**, *39*, 5389−5392.

[3] For a recent review of polymer-supported Lewis acid catalysts based on rare earth metals, see: Kobayashi, S. *Top. Organomet. Chem.* **1999**, *2*, 285−305.

[4] Nagayama, S.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 567−569.

[5] Reetz, M. T.; Giebel, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2498−2501.

[6] For reviews of the catalytic applications of zeolites, see: (a) Corma, A. *Chem. Rev.* **1997**, *97*, 2373−2419. (b) Chen, N. Y. In *Catalysis*; Ward, J. W., Ed.; Elsevier Science: Amsterdam, 1987; pp 153−163.

[7] For a review of clays in catalysis, see: Vaccari, A. *Catal. Today* **1998**, *41*, 53−71.

[8] For recent reviews on mesoporous sieves and their applications, see: (a) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 56−77. (b) Sayari, A. *Chem. Mater.* **1996**, *8*, 1840−1852.

[9] Tian, H.-Y.; Chen, Y.-J.; Wang, D.; Zeng, C.-C.; Li, C.-J. *Tetrahedron Lett.* **2000**, *41*, 2529−2532.

[10] Dewa, T.; Saiki, T.; Aoyama, Y. *J. Am. Chem. Soc.* **2001**, *123*, 502−503.

[11] Miller, S. A.; Kim, E.; Gray, D. H.; Gin, D. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3021−3026.

[12] Gray, D. H.; Gin, D. L. *Chem. Mater.* **1998**, *10*, 1827−1832.

[13] Upon mixing $Sc(NO_3)_3$ with **1** in water, a sparingly soluble precipitate formed. Subsequent NMR analysis of the soluble fraction of the precipitate revealed the absence of olefin groups, consistent with polymerization of the stryene ether moieties. It was just reported that lanthanide triflates are capable of cationic polymerization of *p*-alkoxystyrenes in water. See: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660−4666.

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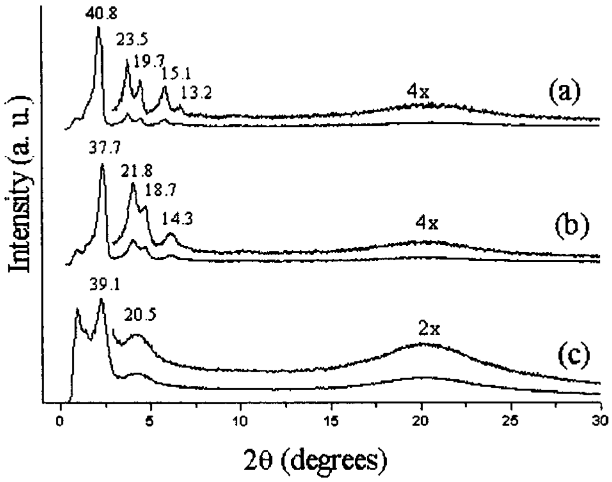
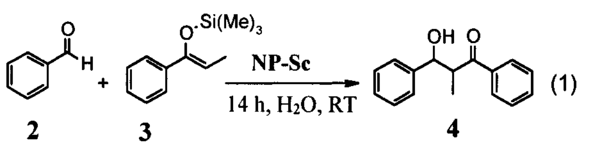


Figure 1. XRD profiles of (a) H_{II} phase formed by monomer **1**/water/DVB/photoinitiator (82/6/10.2/1.8 w/w/w/w) prior to photopolymerization; (b) the same H_{II} phase after photopolymerization; and (c) the cross-linked H_{II} phase after quantitative Sc(III) exchange. The values shown above the diffraction peaks are the *d* spacings in Å.

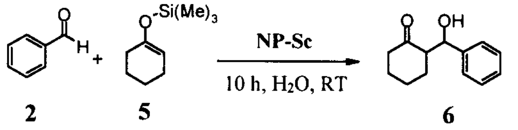
2-aminoethanesulfonic acid in the presence of 1.5 equiv of Na_2CO_3 (90% yield). The H_{II} phase of **1** was prepared by mixing 82/6/10.2/1.8 (w/w/w/w) **1**/water/divinylbenzene(DVB)/2-hydroxy-2-methylpropiophenone and then cross-linked by irradiating the sample with 365-nm light overnight at ambient temperature. The X-ray diffraction (XRD) profiles of the material before and after photopolymerization (Figure 1a,b) were consistent with a H_{II} phase (*d* spacings: 1, $1/\sqrt{3}$, 1/2, $1/\sqrt{7}$,...).[12,14] After cross-linked **1** was refluxed in aqueous $Sc(NO_3)_3$ overnight, the resulting material was found to contain 2.72% Sc and <0.12% residual Na by elemental analysis, indicating that Sc(III) exchange was nearly quantitative. The Sc(III)-exchanged polymer **NP−Sc** shows a slightly larger primary XRD peak and broad and coalesced secondary and tertiary peaks compared to cross-linked **1** (see Figure 1c). However, the optical textures of thin films of cross-linked **1** under crossed polarizers before and after Sc(III) exchange were similar. Thus, it can be inferred that the material did not change phase (e.g., to a lamellar phase) upon ion exchange but rather underwent a slight distortion of the original H_{II} structure.

To test the reactivity and selectivity of **NP−Sc**, variations of the Mukaiyama aldol in water at ambient temperature (21 °C) were used as test platforms (eqs 1 and 2). In particular, the Mukaiyama reaction between **2** and **3** (eq 1) has been employed as a model reaction



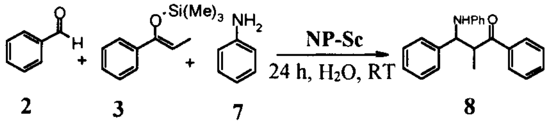
(1)

in evaluating the performance of several Sc(III) catalyst systems.[1−3,5,9] The loading of **NP−Sc** in our test reactions was 1.5 mol % Sc with respect to benzaldehyde, the limiting reagent in the reaction. Under these conditions, benzaldehyde (**2**) reacted with (Z)-1-phenyl-1-trimethylsiloxypropene (**3**) to give 88% yield of product **4** as a mixture of four stereoisomers with a syn/anti ratio of 64/36, as determined by ^1H NMR analysis.[15] In contrast, aldol reactions of **2** and **3** catalyzed by $Sc(OTf)_3$,[1] Sc(III)-exchanged surfactants,[2] and amorphous polymer-supported Sc(III) catalysts[3−5] afford similar product yields but essentially no diastereoselectivity (syn/anti = ca. 50/50), while calix[6]arene-supported Sc(III) catalysts exhibit diastereoselectivities favoring the anti isomers (syn/anti = 31/69 to 40/60).[9] Similarly, **2** and 1-trimethylsiloxycyclohexene (**5**) in the presence of **NP−Sc** catalyst gave 78% of product **6** with a syn/anti ratio of 76/24 (eq 2). These results show that the



(2)

diastereoselectivity afforded by this catalyst is very consistent within this reaction manifold. Also, Mannich reaction of **2**, **3**, and aniline (**7**) (eq 3)[5] in the presence



(3)

of **NP−Sc** gave 72% yield of product **8** with a syn/anti ratio was 62/38 (no **4** was detected). The recycled **NP−Sc** catalyst gave comparable product yields and diastereoselectivities in both the aldol and Mannich reactions. In addition, the isolated supernatant from these heterogeneous reactions exhibited only background reactivity with fresh reagents; thus, Sc(III) is apparently not leached from the solid material.[16]

Although selectivity ratios of ≥10/1 are generally desired for stereoselective reactions, our initial results suggest that the use of a nanostructured polymer support is a promising first step for achieving such selectivities with a heterogeneous catalyst. It should also be noted that Diels−Alder test reactions between 3-acryloyl-1,3-oxazolidin-2-one (or naphthaquinone) and cyclopentadiene in water at room temperature were also performed. However, we were not able to definitively separate the rate enhancement afforded by the nanostructured Sc(III) catalyst from that promoted by water alone.[17] The observed endo/exo selectivity ratio (>95/5)

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(14) Reppy, M. A.; Gray, D. H.; Pindzola, B. A.; Smithers, J. L.; Gin, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 363−371.

(15) (a) Denmark, S., E.; Wong, K.-T.; Stavenger, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 2333−2334. (b) Kobayashi, S.; Nagayama, S.; Busujima, T. *Tetrahedron* **1999**, *55*, 8739−8746.

(16) Control experiments: The Mukaiyama aldol reaction between **2** and **3** was performed in the absence of **NP−Sc** to determine background reactivity in water. After 21 h at room temperature, the reaction gave less than 6% yield of the product with a syn/anti ratio of ca. 50/50. This observed background reactivity for **2** and **3** in pure water is comparable to that in the literature. See: Kobayashi, S.; Wakabayashi, T.; Nagayama, S.; Oyamada, H. *Tetrahedron Lett.* **1997**, *38*, 4559−4562. In a separate experiment, the supernatant from a reaction with **NP−Sc** was extracted with ethyl acetate to remove organic products. It was then evaporated to dryness, and an exact amount of water was added to the flask, together with **2** and **3**. The reaction afforded similar results as in pure water described above (background reactivity), indicating that Sc(III) ions were not leached into the water layer during the initial reaction.

(17) For a recent review on the role of water in Diels−Alder reactions, see: Kumar, A. *Chem. Rev.* **2001**, *101*, 1−19.

obtained with **NP−Sc** was similar to that observed with isotropic Sc(III) catalysts in the literature.[1,3,4]

In summary, we have developed a nanostructured, polymer-supported Sc(III) catalyst (**NP−Sc**) based on a cross-linked LLC assembly that is capable of heterogeneous Lewis acid catalysis in water. Our initial studies using **NP−Sc** to catalyze the Mukaiyama aldol and Mannich reactions in water indicate that it affords condensation products with consistent syn/anti diastereoselectivity ratios of ca. 2/1. In contrast, isotropic Sc(III) catalysts in solution and on amorphous solid supports used in previous studies do not show any significant syn/anti diastereoselectivity under similar conditions. Although our use of cross-linked LLC assemblies as nanostructured supports for Lewis acid catalysis was initially demonstrated using Sc(III) and the H_{II} phase, we believe that this concept can be applied to other metals and LLC phases to afford heterogeneous catalysts with different properties and small-scale architectures. We are currently working on making Sc(III) salts of LLC monomers that are not susceptible to Lewis acid-catalyzed cationic polymerization to obtain better control over catalyst structure. We are also applying these concepts to other polymerizable LLC phases to investigate the effect of different nanostructures on catalyst performance.

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Supporting Information Available: Experimental procedures for the synthesis and polymerization of **1** in the H_{II} phase; Sc(III) exchange of cross-linked **1** to afford **NP−Sc**; and the aldol and Mannich test reactions with **NP−Sc** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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