

## Heterogeneous Catalysis Using a Nanostructured Solid Acid Resin Based on Lyotropic Liquid Crystals

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Sulfonic acid-based solid acid resins such as Nafion and Amberlyst are used as heterogeneous catalysts in a large number of industrial<sup>1</sup> and laboratory<sup>2</sup> processes. One of the goals in acid resin research is control over fine pore size, structure, and chemical environment,<sup>1b</sup> with the ultimate goal of a catalyst with the versatility of a polymer and the selectivity of a nanostructured zeolite.<sup>3,4</sup> Organic acid moieties have been grafted onto inorganic mesoporous sieves;<sup>5</sup> however, these hybrid materials lack the processability of polymers. Phase-separated block copolymer assemblies containing acid groups have also been reported,<sup>6</sup> but catalysis with these systems has not yet been demonstrated. Our group recently developed a method for generating catalytic nanostructured polymer networks for enhanced base<sup>7</sup> and Lewis acid<sup>8</sup> catalysis using functionalized lyotropic liquid crystals (LLCs) as building blocks. However, a strong Brønsted acid analogue has remained elusive due to difficulties in designing strongly acidic amphiphiles with LLC properties. This problem was recently overcome via the use of LLC structure-directing agents to assist in the assembly of acidic amphiphiles.<sup>9</sup> Herein, we report the catalytic properties of the first example of a nanostructured strong acid resin (**1**), which was made using this approach. In esterification test reactions, resin **1** exhibits slightly lower overall reactivity but more than an order of magnitude higher product selectivity than amorphous Amberlyst-15 and Nafion NR50 resins. Experiments indicate that the regular nanostructure of **1** is responsible for a large part of its selectivity.

Resin **1** is made by the radical photo-cross-linking of a 5:1 mol/mol mixture of two acidic LLC monomers **2** and **3** that form the inverted hexagonal (H<sub>II</sub>) mesophase (Figure 1).<sup>9</sup> Monomer **2** carries the strong acid properties, whereas weak acid **3** directs the LLC assembly of **2** via amide H-bonding.<sup>9</sup> The heavily cross-linked networks (>90% acrylate conversion) exhibit X-ray diffraction (XRD) peaks at 41.2, 24.1, 15.6, and 13.8 Å, which is consistent with the 1:1√3:1√7:1√9 *d* spacing ratio of an H<sub>II</sub> phase with the 1/√4 peak systematically absent.<sup>9</sup> Titration studies showed that **1** contains 0.77 mequiv/g of accessible H<sup>+</sup> sites (i.e., 77% of the theoretical acid sites by mass). In contrast, Amberlyst-15 and Nafion NR50 have 4.5 and 0.85 mequiv/g of accessible H<sup>+</sup> sites, respectively, as determined by titration.<sup>1b</sup>

The esterification of benzyl alcohol with 1-hexanoic acid in dry toluene at 75 °C was used as a test platform to compare the catalytic performance of nanostructured resin **1** against that of amorphous Amberlyst-15 and Nafion NR50. This particular reaction was chosen because solid acid-catalyzed esterifications are important in industry and academia,<sup>1b,2</sup> and the participants are easily separated by gas chromatography. Acid-catalyzed esterifications can also produce ethers as a byproduct due to dehydrative coupling of two alcohols. Thus, this reaction was also a convenient platform for comparing

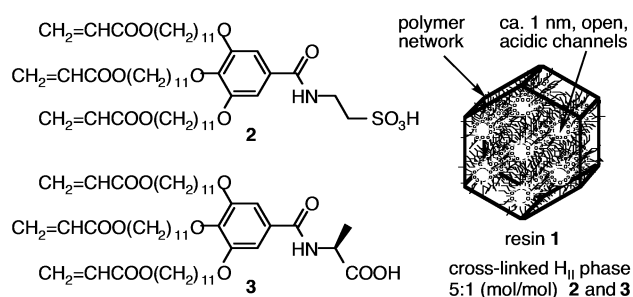


Figure 1. Nanostructured solid acid resin **1** and LLC monomers **2** and **3**.

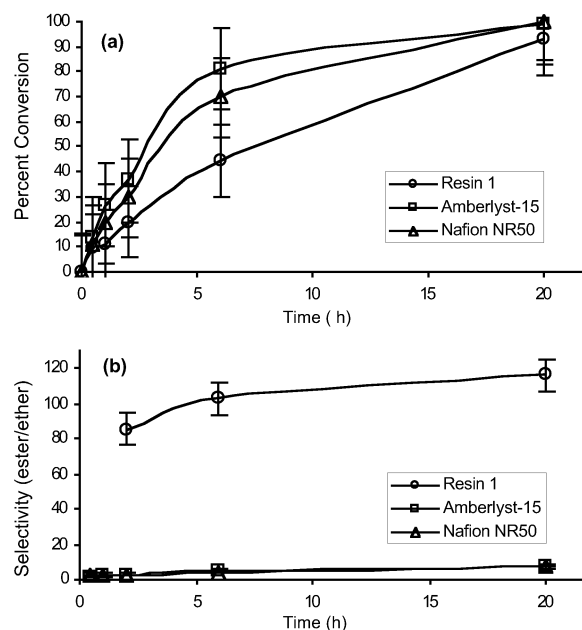


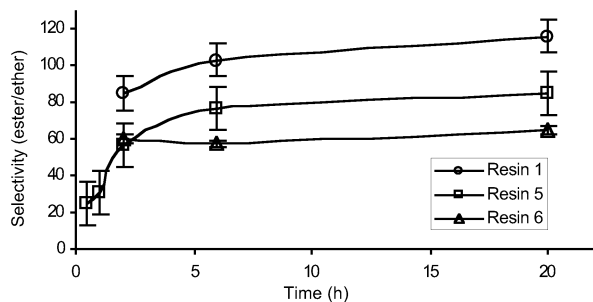
Figure 2. (a) Benzyl alcohol conversion versus time plots<sup>10</sup> and (b) ester/ether selectivity versus time plots for the three solid acid resin catalysts. Control experiments with different particle sizes and stirring rates were performed to ensure that the reactions were not limited by mass transfer.

catalyst selectivity. All test reactions were performed with a catalyst loading level of 5 mol % accessible H<sup>+</sup> sites relative to the reagents, with the catalysts in powdered form (270–400 mesh, 38–53 μm particles).

Initial studies showed that resin **1** has a slightly lower overall activity as compared to that of Amberlyst-15 and Nafion NR50. Figure 2a shows benzyl alcohol conversion versus time plots for the three solid acid catalysts<sup>10</sup> with the standard error over three independent runs superimposed on the data points. Resin **1** has a lower initial rate than the two amorphous resins; however, near-quantitative conversion is achieved after 20 h in all three cases.<sup>11</sup> In the absence of acid catalyst, no esterification takes place within 20 h under the aforementioned reaction conditions.

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**Figure 3.** Ester/ether selectivity versus time plots for resin **1** ( $H_{II}$  phase), resin **5** (mixture of LLC phases), and resin **6** (isotropic version of **1**).

When the reaction products were examined as a function of time, very different results were observed for the three solid catalysts. Amberlyst-15 and Nafion NR50 form significant amounts of dibenzyl ether in addition to the ester product (as confirmed by GC-MS), whereas resin **1** forms very little ether byproduct. As can be seen in Figure 2b, resin **1** exhibits an ester/ether selectivity of approximately 105:1 (mol/mol).<sup>11</sup> In contrast, the ester/ether selectivities of Amberlyst-15 and Nafion NR50 are both ca. 6:1,<sup>11</sup> even though perfluorinated sulfonic acid resins (i.e., Nafion) are much more acidic than polystyrene-sulfonic acid-based resins (i.e., Amberlyst).<sup>2</sup> This result suggests that the difference in selectivity between **1** and the two commercial resins is not due to acidity differences but rather due to the nanostructure present in **1**. We rationalized that part of the enhanced selectivity must be due to resin **1** having a regular nanostructure that offers a much more uniform local solid acid microenvironment for reaction, thereby favoring formation of one product.<sup>4b</sup> In contrast, amorphous acid resins have nonuniform morphologies and a distribution of micropore sizes that can lead to large variations in local acidity and subsequently multiple reaction pathways and products. It has been acknowledged that chemical and spatial uniformity of reactive sites in heterogeneous catalysts is very important for high selectivity and reactivity.<sup>4b</sup>

Several control experiments were performed to test this hypothesis. First, the relative acidities of the three resins were estimated by temperature-programmed desorption (TPD) studies<sup>12</sup> using aniline as a weak base. In TPD studies, a volatile base is absorbed onto the solid acid, and the temperature at which the base is thermally desorbed is a measure of the material's acidity.<sup>12</sup> The onsets of aniline desorption for **1** and Amberlyst-15 were found to be 475 and 485 K, respectively, indicating that the two nonfluorinated resins have similar acidities, as expected. For Nafion NR50, the onset of aniline desorption occurred at ~650 K (above the onset of decomposition of the resin), indicating that the fluorinated resin is much more acidic. Thus, the higher selectivity of **1** cannot be attributed to acidity differences. To confirm the effect of nanostructure on selectivity, reactions were run with a series of control resins: resin **4** formed by cross-linking pure weak acid **3**; resin **5** formed by cross-linking pure  $SO_3H$  monomer **2**; and resin **6** formed by cross-linking a 5:1 mol/mol mixture of **2** and **3** in the isotropic state. Resin **4** exists as a well-defined  $H_{II}$  assembly but is weakly acidic;<sup>9</sup> resin **5** is strongly acidic but exists as a mixture of LLC phases;<sup>9</sup> and resin **6** is an isotropic analogue of resin **1**. Resin **4** showed no catalytic activity due to its weak acidity. Resins **5** and **6** exhibited essentially the same reactivity as **1**; however, **5** showed ca. 25% lower selectivity, and amorphous **6** showed only about one-half the selectivity of nanostructured **1** (Figure 3). Collectively,

these studies indicate that differences in chemical composition between **1** and the commercial acid resins account for some of the selectivity differences, but clearly the presence of a more uniform solid catalyst nanostructure in **1** plays a major role in generating its much higher observed selectivity.

Recycling experiments with resin **1** showed that the recovered solid had nearly the same reactivity and selectivity as that of the initial catalyst and that the  $H_{II}$  XRD structure remained intact. The isolated supernatant only showed a very small activity that was always much lower than that of the original and recycled solids.

In summary, we have demonstrated a novel class of nanostructured, polymeric strong acid catalyst. This catalyst exhibits slightly lower reactivity but more than an order of magnitude higher selectivity than do amorphous solid acid resins. Studies indicate that the regular nanoporous structure present in this material is responsible for a large component of its higher reaction selectivity. Investigations to determine the applicability of these novel acid catalysts to more relevant reactions are currently underway. Future work includes studying the effect of different nanopore sizes and different sulfonic acid-to-amino acid monomer ratios on resin reactivity and selectivity. We are also in the process of designing LLC monomers for a new generation of acid resins with improved acidity and hydrolytic stability.

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**Supporting Information Available:** Full experimental details and characterization data for resin **1** and the control resins. Selectivity and reactivity plots for the recycling and other control experiments. XRD profiles of **1** before and after reaction (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Some benzyl alcohol is absorbed by Amberlyst-15 and not reacted, so the overall reaction rate for Amberlyst-15 is slightly overestimated in Figure 2a. Its reactivity is more accurately represented by the total yield of (ester + ether) as a function of time. See the Supporting Information.
- (11) It should be noted that all of the solid acid resins tested showed much lower reactivity and selectivity than a sulfonic acid (*p*-toluenesulfonic acid) in solution under the same reaction conditions. This can be attributed to the better transport and mixing inherent in a homogeneous reaction, as well as a more uniform reactive site environment for a catalyst in solution. See the Supporting Information.
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