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On Route to the Chiral Imprinting of Bulk Silica

Santiago Ini, Jessica L. Defreese, Nicholas Parra-Vasquez and Alexander Katz
Department of Chemical Engineering, University of California at Berkeley
Berkeley, CA 94720-1462, U.S.A.

ABSTRACT

Shape-selective pores have been synthesized in bulk silica via imprinting. The synthetic approach relies on a sol-gel process to immobilize the imprint within a hybrid organic/inorganic material. Cleavage of the carbamate linkage from this material generates a primary amine within a microporous binding site. Characterization studies, including potentiometric titration and solid-state nuclear magnetic resonance spectroscopy, indicate that most imprinted amine sites are accessible during binding with small molecule probes. However, larger probes are unable to adsorb to the same material, indicating significant shape-selectivity in binding. Additionally, an investigation of framework pore size effects in a catalytic system shows that shape-selectivity can be solely a result of the imprinted active site and not the framework structure.

INTRODUCTION

Shape-selective catalysis originating from specific imprinted pockets has been observed in a variety of imprinted systems [1]. Previous studies of silica imprinting have largely focused on surface imprinting, utilizing both covalent [2,3] and non-covalent [4,5] strategies to prepare selective sites for adsorption and catalysis by functional group organization. Covalent imprinting in silica has recently been extended to three dimensions, and the control of local functional group density was demonstrated by organizing up to three primary amines within a microporous cavity [6]. Importantly, the porosity generated during the imprinting process was quantified with argon physisorption. The material demonstrated shape-selective catalysis in the Knoevenagel condensation of isophthalaldehyde and malononitrile, by inhibiting a second addition of malononitrile to the aldehyde, whereas an amorphous aminopropyl-functionalized silica gel catalyzed both additions [6]. The present study investigates the role of imprinted as well as framework porosity in achieving shape-selectivity in this catalytic system. Shape-selective binding in a silica synthesized from an asymmetric imprint is also described.

EXPERIMENTAL DETAILS

Imprint molecules were prepared by the reaction of a parent alcohol with 3-aminopropyltriethoxysilane and 1,1'-carbonyldiimidazole in the presence of a catalytic amount of sodium ethoxide. A chiral imprint was synthesized from (*R*)-(+)-*sec*-phenethyl alcohol (Figure 1), and a non-chiral imprint was synthesized from benzyl alcohol.

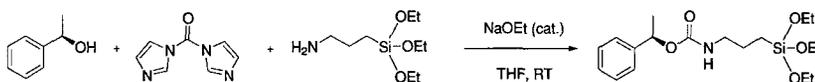


Figure 1. Synthesis of the chiral imprint molecule.

Microporous bulk silicas were prepared by co-condensing the appropriate imprint with 50 equivalents of tetraethylorthosilicate (TEOS) in an acid-catalyzed sol-gel process (Figure 2). The resulting optically clear glasses were Soxhlet extracted with acetonitrile over calcium hydride, and the internal silanols were capped with an equimolar mixture of hexamethyldisilazane and trimethylsilylchloride. The imprints were removed by reaction with trimethylsilyliodide in acetonitrile for 24 hours at 40 °C, followed by treatment with triethylamine in methanol for 24 hours at room temperature. The final materials were Soxhlet extracted with benzene over *p*-toluenesulfonic acid to remove the remaining triethylamine. The mesoporous imprinted silica was synthesized from TEOS and the benzyl carbamate imprint via a base-catalyzed condensation route. The remaining processing steps were carried out as with the microporous materials.

The presence of amine sites in each of the materials was quantified by a non-aqueous titration with perchloric acid in glacial acetic acid. Condensations of aldehydes with the imprinted amines were performed in toluene with continuous water removal and 1,3,5-trimethoxybenzene as an internal standard. Reactions of carboxylic acids with the imprinted amines were performed in chloroform also using 1,3,5-trimethoxybenzene as an internal standard. Gas chromatography (GC) was performed on an Agilent 6890 equipped with a Cyclosil-B column for aldehyde analysis and an Innowax column for analysis of acids. The

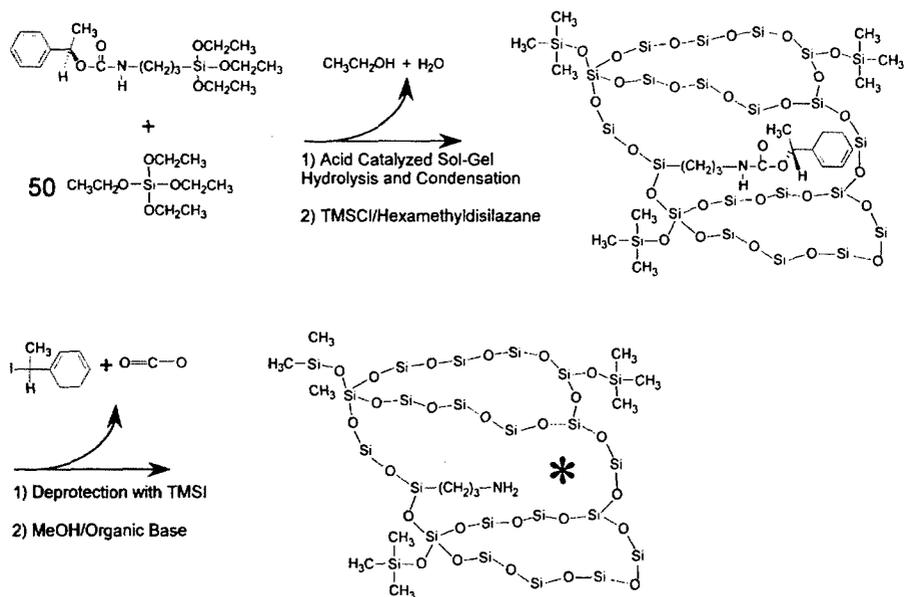


Figure 2. Schematic illustration of microporous bulk silica imprinting synthesis.

catalytic Knoevenagel reactions were performed at 60 °C and 80 °C with 0.75 mmol of isophthalaldehyde, 0.75 mmol of hexamethylbenzene (internal standard), 1.5 mmol of malononitrile, and 0.22 mol% of catalyst in 50 mL of acetonitrile. Solid-state NMR spectroscopy was performed on Bruker AM-300 spectrometer equipped with solids accessories. Nitrogen physisorptions were carried out on a Quantachrome Autosorb 1. Solid-state UV-Vis spectra were obtained on a Cary 400 Bio equipped with solids accessories.

DISCUSSION

Material Characterization

Solid-state NMR spectroscopy was performed to investigate the state of the imprint during material synthesis. As seen from the ^{13}C CP/MAS spectra in Figure 3a, the protected material shows high-field signals from the carbamate functionality. After deprotection (Figure 3b), the high-field signals are eliminated while the propyl tether signals remain. This result indicates near quantitative removal of the imprint. Variable contact time experiments were consistent with a lack of rotation about carbons labeled 4 and 5 in the protected material. The result for a typical potentiometric titration of the material is presented in Figure 4 and shows the presence of approximately 0.17 mmol primary amine sites per gram of silica.

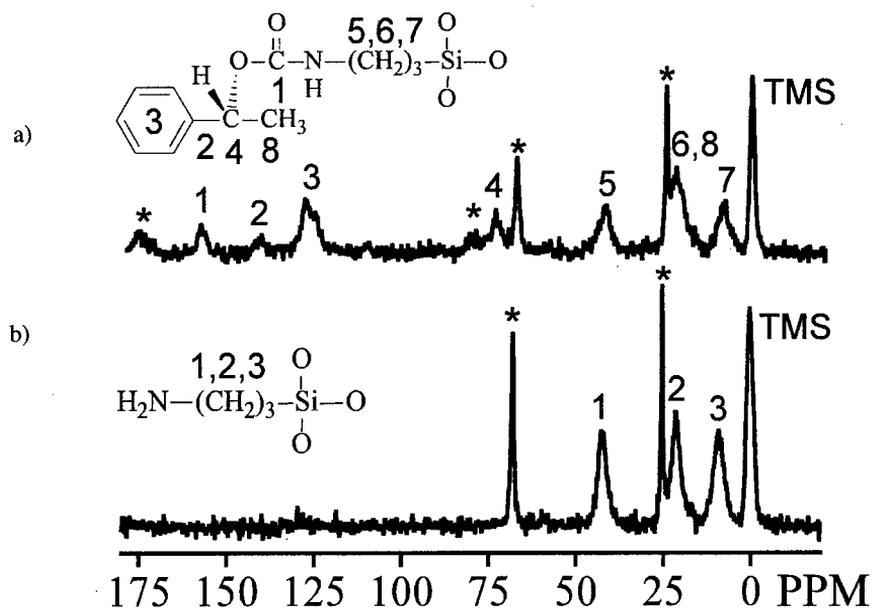


Figure 3. ^{13}C CP/MAS solid-state NMR spectra of a protected (a) and deprotected (b) bulk imprinted silicate. Asterisk (*) denotes either a spinning sideband or solvent (THF) resonance.

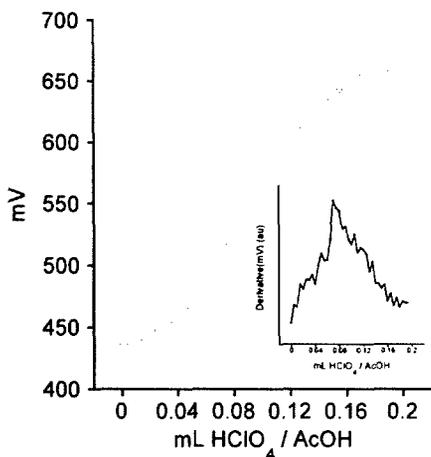


Figure 4. Potentiometric titration of imprinted amine sites in deprotected material.

Probe Molecule Binding

The shape-selectivity of the chiral imprinted system was investigated via covalent and non-covalent probe molecule binding. Salicylaldehyde was bound into the imprinted material by stirring with two equivalents of the aldehyde in refluxing toluene for 5 days. As assessed by GC, almost all (95%) of the imprinted sites were accessed via formation of the hydrogen bond-stabilized imine. A solid-state diffuse reflectance UV-Vis spectrum of the material before and after salicylaldehyde treatment (Figure 5) shows a strong band at 390 nm associated with the Schiff base.

Non-covalent binding into the material was explored via carboxylic acids. Benzoic acid bound to 51% of the imprinted sites at room temperature and 42% at 50 °C, while the larger acids 3-phenylbutyric acid and α -methylhydrocinnamic acid bound to less than 5% of the sites under the same conditions. This shape-selectivity in acid binding was especially significant considering the accessibility of almost all sites to salicylaldehyde. As an additional control experiment, the isostructural aldehyde 3-phenylbutyraldehyde of 3-phenylbutyric acid was successfully bound, as evidenced by solid-state NMR and GC. In summary, imprinted sites in microporous silica were accessible to salicylaldehyde, benzoic acid, and 3-phenylbutyraldehyde; however, the larger probes comprising 3-phenylbutyric acid and α -methylhydrocinnamic acid were unable to bind under identical conditions.

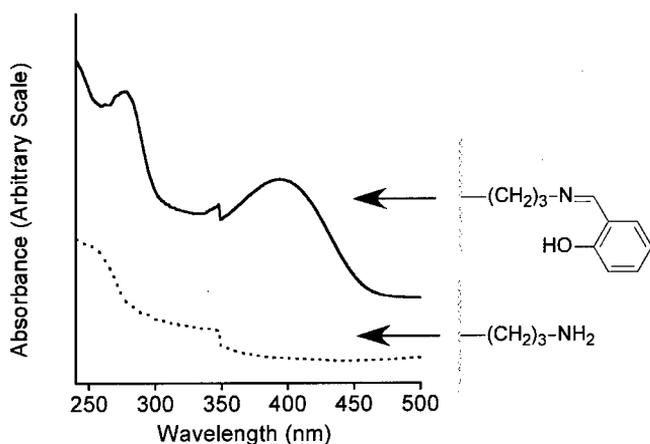


Figure 5. Diffuse reflectance UV spectra of salicylaldehyde-bound material (top) and control material (bottom).

Knoevenagel Catalysis

A mesoporous imprinted silica was synthesized to separate the role of the imprinted pore from the framework porosity in performing shape-selective molecular recognition. The nitrogen physisorption isotherm of this material exhibited the presence of microporosity from the imprinted sites and mesoporosity from the framework (Figure 6). Possible effects of the framework pore size were studied by running a catalytic Knoevenagel condensation of isophthalaldehyde with malononitrile in the presence of both microporous and mesoporous imprinted silicas, as well as a post-synthetically functionalized amorphous control silica (aminopropyl-functionalized mesoporous silica). Figure 7 shows the product distribution for each of these materials. Both imprinted systems suppressed the formation of the double-addition product C, suggesting shape-selectivity arising from the imprinted sites. In other words, the imprinted systems were able to selectively catalyze the synthesis of the mono-addition product B from isophthalaldehyde A, whereas the surface-functionalized material non-selectively catalyzed the synthesis of A to the double-addition product C. Given the stark contrast in framework pore sizes between the microporous and mesoporous imprinted materials, the catalytic selectivity must be due to the imprinted active site characteristics rather than an effect of the bulk framework porosity.

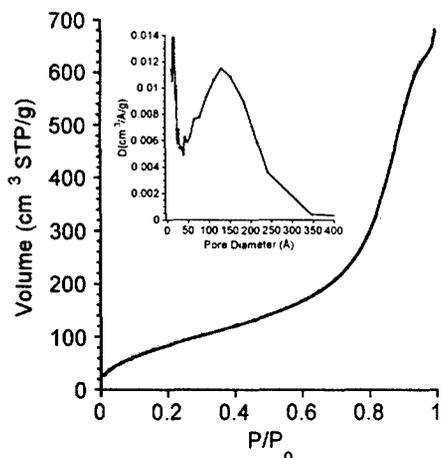


Figure 6. Nitrogen physisorption isotherm of imprinted mesoporous silica. Inset: Barrett-Joyner-Halenda (BJH) size distribution [7] showing bimodal microporosity (imprinted) and mesoporosity (framework).

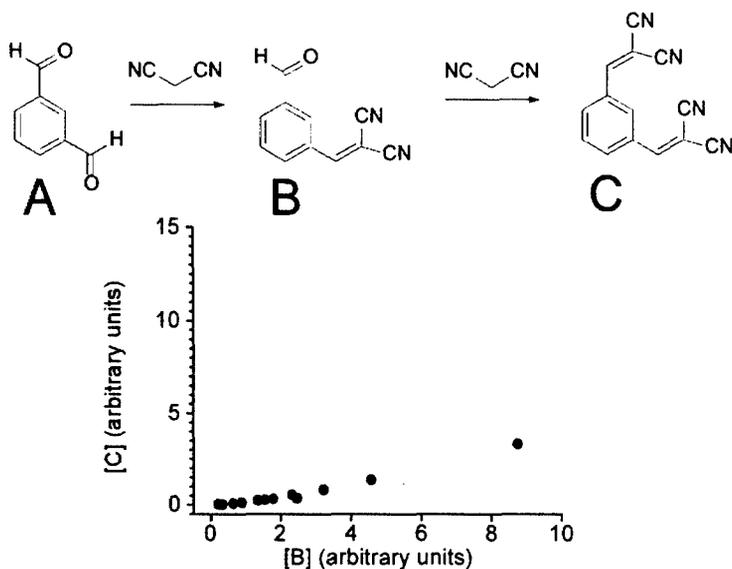


Figure 7. Relative concentration of di-addition product, C, versus mono-addition product, B, for surface-functionalized (hollow circles), mesoporous imprinted (solid circles) and microporous imprinted (crosses) silicates.

CONCLUSIONS

Shape-selectivity in bulk imprinted silica was studied using probe molecule adsorption experiments and Knoevenagel catalysis. Results indicate that imprinted silica can perform shape-selective molecular recognition in binding carboxylic acids. Comparison of shape-selective catalysis observed in a microporous versus mesoporous bulk imprinted silica suggests that shape-selectivity arises due to the effect of the active site rather than the bulk framework structure. These results point to the promise of an imprinting-based approach in bulk silicates for selective catalysis and adsorption, including enantioselective recognition.

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