

## Design of New Multifunctional Materials for Heterogeneous Catalysis

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### Introduction

Organically functionalized mesoporous materials have recently shown importance in the area of heterogeneous catalysis. These materials exhibit desirable properties, such as ease of functionalization, high surface areas, high chemical stability, reusability, etc., that allow for significant improvements in the rates and selectivities achievable in certain chemical reactions. A large variety of materials have been synthesized bearing numerous different functionalities ranging from Lewis acids, Bronsted acids and bases, metal centers, as well as multiple types of sites on these surfaces.

Previous work has shown that the precise placement of adjacent sulfonic acid sites caused enhancements in reaction rate and selectivity towards Bisphenol A in the condensation reaction between phenol and acetone, presumably due to some form of cooperative, catalytic effect occurring between neighboring sulfonic acid sites [1]. The precise nature of this cooperativity, however, was not clear or understood mechanistically. Homogeneous control experiments provided insights into the factors affecting selectivity and rate in this reaction, and were used to guide the synthesis of bifunctional materials containing immobilized sulfonic acids with thiols. Dramatic improvements in catalytic activity were observed with these new materials thus validating the homogeneous findings and allowing for the preparation of heterogeneous catalysts that could outperform similar homogeneous reactions[2]. These findings also led to the development of materials bearing different combinations of immobilized functional groups that were capable of achieving cooperative, catalytic behavior not achievable in solution (ie, acids used in combination with bases)[3]. The potential to synthesize materials capable of carrying out chemical reactions with unprecedented selectivity and reactivity as well as new ways of thinking about using incompatible functionalities together are outlined herein.

### Materials and Methods

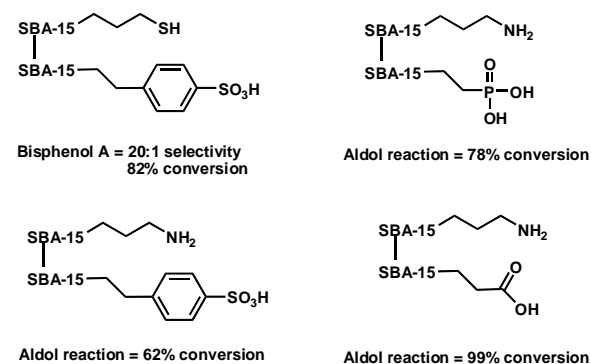
Organically functionalized mesoporous materials were synthesized using co-condensation methods under acidic conditions with P123 to afford SBA-15 type materials. Catalysts were characterized by solid state NMR, XRD, TGA, and N<sub>2</sub> adsorption. Catalysis experiments were run under inert atmosphere and were monitored by HPLC or NMR analysis with an internal standard.

### Results and Discussion

Homogeneous model systems indicated the possibility of unoxidized thiols remaining on the surface of the prepared materials bearing neighboring sulfonic acid sites. Guided by these findings, materials bearing combinations of thiol and sulfonic acid sites distributed throughout the SBA-15 material were synthesized and tested[2]. Upon immobilization of these two groups, dramatic improvements in reaction selectivity and rate were observed beyond the best case homogeneous reactions, and selectivities of nearly 20:1 were observed for bisphenol A with corresponding conversions of 82% (Figure 1). Through

simple immobilization of these functional groups, cooperative catalysis is observed due to their proximity on the surface.

**Figure 1.** Bifunctional SBA-15 materials synthesized containing thiol/acid groups and acid/base groups.



As an extension of this idea of immobilization of functional groups for cooperative catalysis, we have also synthesized materials bearing immobilized combinations of acid and base groups that are incompatible in solution[3]. These materials, despite bearing incompatible functional groups, are efficient catalysts of the aldol reaction between acetone and 4-nitrobenzaldehyde and unexpectedly exhibit a cooperative, catalytic effect compared to the individual functional groups. With these acid/base materials, carefully choosing the acid component with a pK<sub>a</sub> closest to that of the base component allows for a catalyst that provides nearly quantitative conversion to the aldol products. This presumably is reflective of the state of the equilibrium between free acid/free base and the neutralized ion pair resulting from neutralization, and a weaker acid component would result in less neutralization and hence more active free acid and free base sites.

### Significance

These results illustrate the significant improvements in reactivity achievable upon understanding reaction mechanism on a fundamental level and rationally designing materials based on the mechanism that contain immobilized combinations of reactive functional groups for cooperative catalysis. Through immobilization, unique reactivity between functional groups due to their placement on the surface in proximity to one another allows for significant improvements in reaction rates and selectivities.

### References

1. Dufaud, V.; Davis, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9403-9413.
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3. Zeidan, R.K.; Hwang, S.J.; Davis, M.E. *Angew. Chem. Int. Ed.* **2006**, 6332-6335.