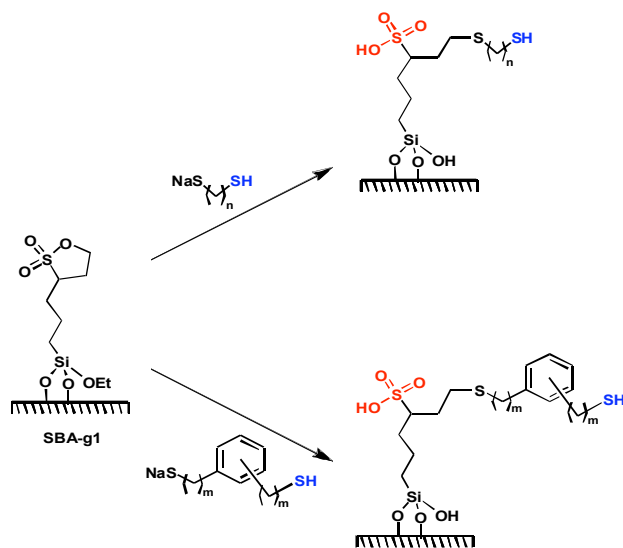


## **Final Report for DOE Grant DE-FG02-04ER15601**

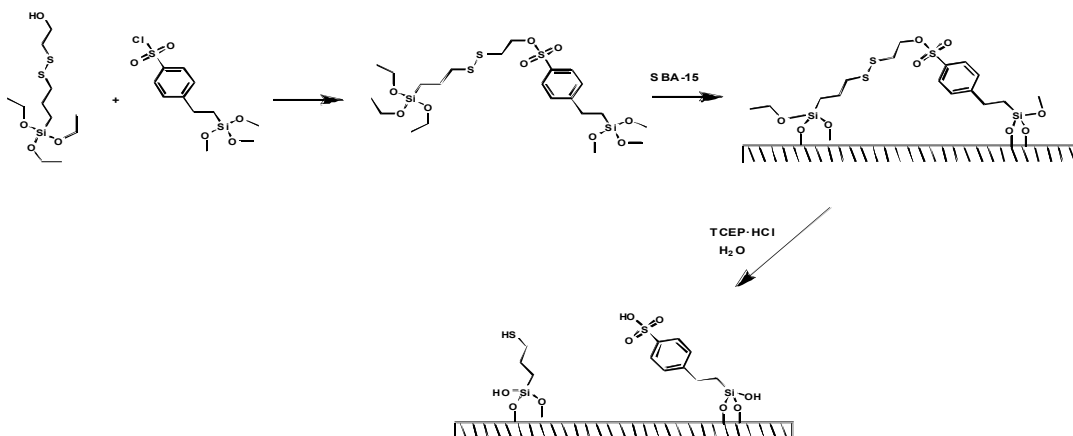
**Mark E. Davis, Chemical Engineering, California Institute of Technology, Pasadena, CA**

**Objectives:** The objectives of our work are: (i) to create solid catalysts with active sites that can function in a cooperative manner to enhance reactivity and selectivity, and (ii) to prepare solid catalysts that can perform multiple reactions in a network that in some cases would not be possible in solution due to the incompatibilities of the various catalytic entities (for example an acid and a base).

**Summary of Work:** We began this project with the observation that two sulfonic acids placed in close proximity of each other on a mesoporous solid (SBA-15) appeared to provide enhanced reactivity and selectivity over what was achievable with individual sulfonic acid sites on the solid or in solution for the condensation reaction of acetone and phenol to bisphenol A (Dufaud and Davis, J. Am. Chem. Soc. **2003**, *125*, 9403-9413). We carried out extensive homogeneous reactions using combinations of thiols and sulfonic acids to test the nature of the cooperative effect that was observed to investigate if the cooperativity was caused by sulfonic acid/sulfonic acid interactions or thiol/sulfonic acid interactions [1]. Next, we created a series of materials to test the effect of distance between the two functional groups. The methodology is illustrated below.

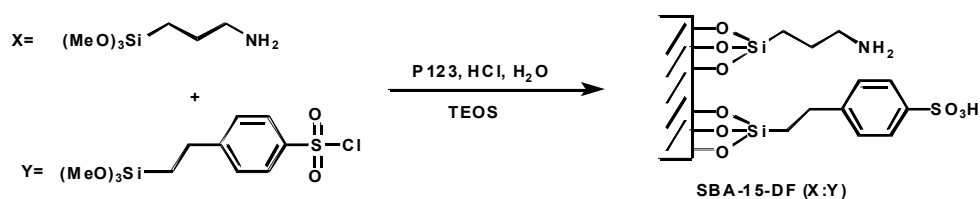


The catalytic data show that the further the thiol is placed from the acid, the slower the reaction kinetics [4]. Thus, the thiol should be as close to the acid center as possible. In order to create a strong acid/thiol combination, we developed a better synthetic strategy as illustrated below.

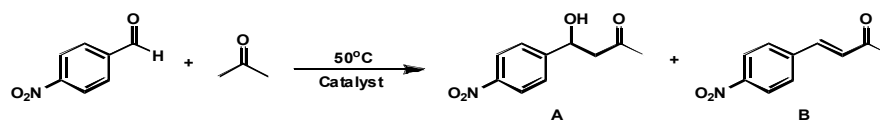


This catalyst gave the best overall performance [6]. The acid/thiol combination provided an example where the two organic groups should be positioned as close to one another as possible. We also studied a system where this is not possible (acid – base).

We investigated simultaneously incorporating acid and base groups into the same material. Looking to natural enzymes for inspiration, we began by investigating the possibility of incorporating acids and base, two mutually incompatible functional groups, into one material. Initial attempts were carried out using amines as the base and sulfonic acids as the acid under similar conditions as described above for the acid-thiol. When placing the acid and base next to one another in a methodology similar to that in [4], there was no reactivity, presumably due to the acid and base neutralizing each other. Therefore, we continued with synthetic methodology like that in [1] to give materials having primary amines and sulfonic acids (shown below) that can function in a cooperative manner [2].



Additionally, we prepared materials with different acid strengths and found that carboxylate groups performed the best in combination with primary amines as shown by the data below [3].



Entry	Catalyst (10 mol%)	%A	%B	Total Yield
1		45	17	62
2		62	16	78
3		75	24	99

Thus, for the case of acid and bases, there is an optimal separation distance (too close allows for neutralization while too far eliminates any cooperative behavior).

### **Publications:**

1. R. K. Zeidan, V. Dufaud and M. E. Davis, "Enhanced cooperative, catalytic behavior of organic functional groups by immobilization," *J. Catal.*, 239, 299 (2006).
2. R. K. Zeidan, S. J. Hwang and M. E. Davis, "Multifunctional Heterogeneous Catalysts: SBA-15 Containing Primary Amines and Sulfonic Acids," *Angew. Chemie Int. Ed.*, 45, 6332 (2006).
3. R. Zeidan and M. E. Davis, "The Effect of Acid-Base Pairing on Catalysis: An Efficient Acid-Base Functionalized Catalyst for the Aldol Condensation," *J. Catal.*, 247, 379 (2007).
4. E. L. Margelefsky, R. K. Zeidan, V. Dufaud and M. E. Davis, "Organized surface functional groups: Cooperative catalysis via thiol/sulfonic acid pairing," *J. Am. Chem. Soc.*, 129, 13691 (2007).
5. E. L. Margelefsky, R. K. Zeidan and M. E. Davis, "Cooperative catalysis by silica-supported organic functional groups," *Chem. Soc. Rev.*, 37, 1118 (2008).
6. E. L. Margelefsky, A. Bendjeriou, R. K. Zeidan, V. Dufaud and M. E. Davis, "Nanoscale Organization of Thiol and Arylsulfonic Acid on Silica Leads to a Highly Active and Selective Bifunctional, Heterogeneous Catalyst," *J. Am. Chem. Soc.*, 130, 13442 (2008).

**Presentations:**

“Design of Hybrid Organic-Inorganic Heterogeneous Catalysis for Bisphenol A Production,” EMRS Conference, Strasbourg, France (June 2005).

“Rationally Designed Hybrid Catalysts for Heterogeneous Catalysis,” ICCOSS Conference, UCLA, Los Angeles, CA (July 2005).

“Nanostructured Catalysts for Improving the Environment Impact of Chemical Synthesis,” PacifiChem Conference, Hawaii (December 2005).

“Design of Multifunctional Hybrid Inorganic-Organic Materials for Heterogeneous Catalysis,” Pacific Coast Catalysis Society, Pasadena, CA (Nov. 2007).

“Porous Organic-Inorganic Hybrid Materials,” AIChE Meeting, Salt Lake City, UT (Nov. 2007).

“Design of Multifunctional Hybrid Inorganic-Organic Materials for Heterogeneous Catalysis,” AIChE Meeting, Salt Lake City, UT (Nov. 2007).

“Mesoporous Silica Catalysts Containing Sulfonic Acid and Thiol Groups Organized on the Surface at Various Distances,” AIChE Meeting, Salt Lake City, UT (Nov. 2007).

“Design of Hybrid Inorganic-Organic Materials for Heterogeneous Catalysis,” Wilhelm Lecture, Princeton University, Princeton, NJ (Feb. 2008).

“Design of Hybrid Inorganic-Organic Materials for Heterogeneous Catalysts,” ACS Meeting, New Orleans, LA (Apr. 2008).