

Chapter 6

SUMMARY

My work has demonstrated several new ways of functionalizing mesoporous silica with discrete pairs of disparate organic functional groups. In Chapter 2, the ring-opening of surface-bound sultones was used to generate alkylsulfonic acid/thiol pairs attached to a single carbon tether. In Chapter 3, arylsulfonic acid/thiol pairs were generated using a two-point imprinting approach. In Chapter 4, the sultone approach was again used to create single-site pairs of alkylsulfonic acid and amines. And in Chapter 5, amino acid sites were pre-formed in an organosilane precursor and then grafted onto the silica surface.

The acid/thiol catalysts were shown to be very effective catalysts for the synthesis of bisphenols. Both the alkyl- and arylsulfonic acid catalysts exhibited high regioselectivity to the desired *p,p'* isomer of bisphenols A and Z, with isomer ratios of 14–19. It was shown that the promoting effect of thiols and the sensitivity to acid/thiol distance are both inversely related to the reactivity of the ketone. With trifluoroacetone, the effect of thiols is minimal. With acetone, acid/thiol pairing is important for catalysts with weaker acid sites (the two sites should be as close together as possible), but irrelevant when stronger acid sites are present. And finally, in the case of cyclohexanone, the least-reactive ketone studied, acid/thiol pairing leads to improved catalytic properties with both weaker and stronger acid sites.

With the acid/base catalysts discussed in Chapter 4, a different effect of pairing on aldol catalytic activity was demonstrated. When strong sulfonic acid sites coexist with weak base sites, pairing is not desirable, as the acid and base sites neutralize one another. When the two sites are randomly distributed on a catalyst surface, any observed acid/base cooperativity must be due to spatially isolated sites too far apart to neutralize.

With weaker acids, such as carboxylic acids, this isolation is unnecessary, which allows for homogeneous catalysts such as amino acids to remain active in solution. In Chapter 5, carboxylic acid and primary amine were used to catalyze the aldol reaction in solution, and the two groups exhibit cooperative catalysis, which is improved when the two groups are attached to each other with a short tether. When the acid and amine groups are untethered, binary diffusional limitations reduce the catalytic activity.

Heterogeneous silica catalysts functionalized with primary amine groups also exhibit cooperative catalysis in the aldol reaction. Amines and surface silanols are both necessary for good catalytic activity. Silanols activate reacting groups through hydrogen bonding interactions, so reaction solvents that have hydrogen-bonding ability (*e.g.*, alcohols) must be avoided.

In general, I have shown that the local arrangement of functional groups on the surface of a bifunctional heterogeneous catalyst plays a role in the catalytic activity of the material. The degree to which the catalytic activity depends on the group-to-group distance depends on the type of functional groups and the reaction being catalyzed.