

PRF#: 58373-ND5

Project Title: Discovery of New Heterogeneous Catalysts for C-H Activation

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The primary goal of this project is to identify new heterogeneous catalysts for C-H activation. Our approach involves synthesizing and screening a library of solid-state materials as candidate catalysts. We focus on crystalline inorganic solids that require high-temperature solid-state reactions to form, because such materials are not typically within the scope of catalysts that are studied for such reactions. Just prior to receiving funding for this project, we found that bulk iron pyrite, FeS₂, catalyzes the selective hydrogenation of nitroarenes to their corresponding aniline derivatives (*Chem. Commun.* **2017**, 53, 4807). This result validated our hypothesis that bulk-scale crystalline inorganic solids could function as catalysts for such reactions, and therefore were appropriate for screening purposes.

We began this project by synthesizing a diverse range of solid-state materials so that we could screen them to identify new systems capable of catalyzing C-H activation and subsequent functionalization reactions. Since we were synthesizing bulk quantities of a diverse library of solid-state compounds, we decided to also screen them for other catalytic reactions that involved the selective functionalization of various classes of molecules. To synthesize the library of candidate catalyst materials, we used several types of solid-state reactions, including flux growth, arc melting, direct combination of constituent elements at high temperatures, and low-temperature topochemical manipulation of framework structures. The types of solid-state materials we synthesized as candidate catalysts included various transition metal oxides, borides, phosphides, and chalcogenides, with an emphasis on compounds that contained transition metals known to be active centers in related homogeneous catalyst systems.

We first screened catalysts for the C-H arylation of heteroarenes. We found that bulk Pd (our control), as well as a few Pd-based compounds, catalyzed C-H arylation. However, the new Pd-based compounds did not perform any differently than the Pd control, which itself performed analogous to previously reported Pd-based catalysts. We are currently exploring several other non-Pd systems, including mixed-metal compounds and alloys that are anticipated to function cooperatively to achieve selectivity for the C-H arylation of benzothiophene. We are also moving on to other reactions, including C-H thiolation, selenation, and phosphorylation, as well as selective hydrogenation.

During the course of our studies, we also screened a library of nanostructured materials that also are not mainstream catalysts for the reactions described above, thereby complementing and expanding on the scope of systems available through our solid-state catalyst library. We found that nanostructured colloidal WS₂, a well-known hydrogenation catalyst, catalyzes the selective hydrogenation of nitroarenes to their corresponding aniline derivatives in the presence of other reducible functional groups (*Chem. Sci.* **2019**, Advance Article). Following this discovery, our studies focused on understanding how this model two-dimensional (2-D) material achieves selectivity during catalytic hydrogenation using molecular hydrogen. In-depth electron microscopy experiments revealed that the nanostructured WS₂ colloids have abundant tungsten-terminated edge sites and a high density of sulfur vacancies on the basal planes. Computational studies revealed that functional group selectivity during hydrogenation is due to geometric effects, i.e. vertical adsorption of the nitroarene on the 2-D nanosheet surface and on regions of the basal planes having high concentrations of sulfur vacancies, as well as at the tungsten-terminated edges. In contrast, parallel adsorption of the nitroarene was favored on basal plane regions having low sulfur vacancy concentrations, and in this case, selectivity during hydrogenation was attributed to a lower kinetic barrier. The mechanism by which functional group selectivity was achieved on the 2-D nanosheet surfaces therefore depended on the adsorption geometry of the nitroarene, which itself depended on the types and densities of defects and adsorption locations. These insights will be useful in identifying other candidate catalysts for selective hydrogenation reactions.

This project has so far succeeded in seeding a new direction in my laboratory, focusing on screening diverse solid-state materials as selective catalysts for organic reactions where multiple functional groups are present. It has also provided the impetus for my group to learn how to synthesize a wide range of bulk-scale inorganic solids, as both powders and single crystals, using high-temperature solid-state reactions. While I have experience with this (from my graduate and postdoctoral work >16 years ago), it was new to my group, and this project has motivated us to learn how to synthesize several classes of materials that we will study more in the future. This project has also allowed the students it supports to gain expertise and knowledge that is outside of my group's typical infrastructure, including new-to-us aspects of catalysis, organic synthesis, and chemical analysis of molecular systems.