The chemical potential stored in the earth’s methane reserves is either untapped or wasted because we lack an economically viable process for converting the gas to a liquid from that can safely be transported for use remote from the source. We are therefore seeking a low-temperature catalytic cycle, using $O_2$ as the terminal oxidant, to functionalize methane with the selectivity typical of non-radical, organometallic reactions.

Stable catalysts which have shown the fastest turnover for the selective formation of methanol or intermediate products such as methyl bisulfate or methyl chloride have used electrophilic metals: Pt, Au, Hg, and Pd. These metals react preferentially with the electron-rich C-H bond of methane over the C-H bonds of oxidized products. Also, C-O bond formation by $S_n2$ attack on M-CH$_3$ intermediates is facile since these metals in high oxidation states are good leaving groups. However, this reactivity has not been commercialized because the electrophilic metals require strong or exotic oxidants or are poisoned by small concentrations of water or methanol in an otherwise pure sulfuric acid medium.

While we have not abandoned the electrophilic metal paradigm, our recent progress has supported the viability of the opposite approach: electron-rich metals which are not poisoned by basic solvents. Methane activation processes in this regime feature a transfer of charge from the metal to the C-H antibonding orbital. Challenges include maintaining the reduced state of the metal catalyst in the presence of the required oxygen atom donor, and identifying C-O bond forming mechanisms to replace the reductive reactions of the late transition metals. We have found that metal carbon bonds which are polarized $M^\delta^+\cdot CH_3^\delta^-$ are susceptible to a number of electrophilic functionalization routes.