

Title: Stereoselective heterogeneous catalytic cyclopropanation of structurally diverse alkenes in aqueous medium

Cyclopropanation is a significant chemical process in modern chemistry. Metal porphyrins play a crucial role as active centers in most biological catalysts (enzymes), demonstrating high catalytic efficiency, regioselectivity, and stereoselectivity in suitable environments. However, enzyme-based catalysts have drawbacks including lengthy synthesis time, low stability, recyclability, and yield. Furthermore, enzyme systems are homogeneous in nature. To address these limitations, we aim to develop a heterogeneous catalyst for cyclopropanation in an aqueous medium by employing metal-porphyrins within confined spaces, such as micelles inside silica core-shell structures and metal-organic frameworks (MOFs), to achieve high regioselectivity and stereoselectivity.

In our research, we specifically investigated micelles such as CTAB, as well as MOFs like ZIF-8, which are highly water-stable and capable of creating an asymmetric environment around the porphyrins.

We have chosen as alkene styrene and utilize the readily available metal-porphyrin, Hemin. After observing that encapsulating hemin within CTAB did not significantly alter selectivity, we modified hemin to hydrophobic hemin by amidation. As micelles are dynamic structures and homogeneous in nature, we encapsulated CTAB micelles containing hemin n-octylamide with a mesoporous SiO₂ core-shell structure (Hemin amide_CTAB@SiO₂) to enhance selectivity, regioselectivity, and yield. We have observed significant increment of product formation in Hemin_amide_CTAB@SiO₂ but no change in selectivity.

In other studies, we encapsulated hemin within ZIF-8 (Hemin@ZIF-8) in an aqueous medium at room temperature. We observed a significant shift in selectivity, where the cyclopropanation reaction of styrene with EDA predominantly yielded the cis-cyclopropanation product. Therefore, the encapsulation of hemin within ZIF-8 resulted in a reversal of selectivity compared to the free hemin system, but it has the limitation of side reactions due to stability issue.