Photocatalytic C—H functionalization of methane at ambient temperature by cerium photocatalyst

With the support by the National Natural Science Foundation of China, the research group directed by Prof. Zuo ZhiWei (左智伟) at ShanghaiTech University has recently developed a novel, photocatalytic methodology enabling the selective functionalization of methane, ethane and other gaseous alkanes to form valuable liquid products at ambient temperature. This intriguing result was published in *Science* (10.1126/science.aat9750).

Natural gas is typically viewed as a clean energy fuel and economical chemical feedstock by the chemical community. With dwindling oil supplies and the growing importance of reducing the worldwide dependence of petroleum-based chemical products, the recent discovery of huge volumes of unconventional reservoirs has made it an economically attractive raw material. Methane is the main chemical component of natural gas, hence the direct transformation of methane into high value liquid commodity chemicals has attracted enormous research attention across the scientific community over the last few decades. Recently, tremendous progress has been made in C—H functionalizations of methane utilizing transition metal catalyst such as Pt, Pd and Ir etc.; however, the development of efficient and sustainable catalytic systems under ambient conditions utilizing inexpensive catalysts still remains challenging.

Inspired by the recent advancement of photoredox catalysis, the young research team has developed an affordable and sustainable catalytic platform using light energy and economical catalyst for this process. High catalytic efficiency and selectivity were achieved using inexpensive cerium salts as photocatalysts. A ligand-to-metal charge transfer (LMCT) excitation process was employed to generate alkoxy radicals from simple alcohols, which in turn act as effective hydrogen atom transfer catalysts for methane activation. In this homogeneous catalytic system, challenging transformations of methane, including catalytic C—H amination, alkylation and arylation were realized under room temperature. Moreover, they successfully applied the mixed phase gas/liquid reaction in continuous-flow for the scalable conversion of these gaseous feedstocks, enabling a very perspective industry use of this new technique.

This work has provided a green, sustainable and mild catalytic platform for selective methane functionalizations, and will inspire more applications in natural gas upgrading chemistry.

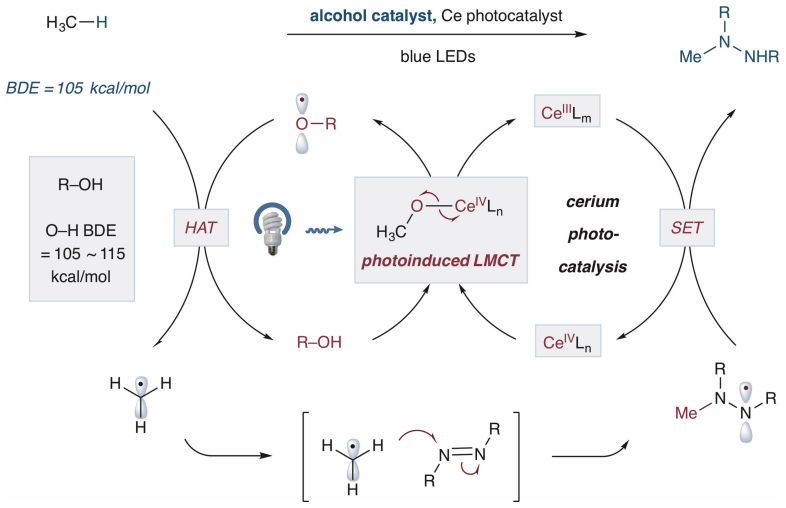

Figure The mechanism for the photocatalytic C—H functionalization of methane via the synergistic utilization of cerium photocatalyst and alcohol catalyst.