Direct photocatalytic CH_4 oxidation to oxygenates with O_2 at room temperature in water

With the support of the National Natural Science Foundation of China，the research work collaboratively conducted by Prof. Meng XianGuang（孟宪光）at the North China University of Science and Technology and Prof. Ye JinHua at the National Institute for Materials Science，reported direct and selective oxidation of CH_4 to oxygenates with O_2 at room temperature in water in the photocatalytic system，which was published in *Journal of the American Chemical Society*（2019，141：20507—15）.

Methane is an abundant and promising feedstock for the synthesis of various commodity chemicals，especially after the recent discovery of large reserves of shale gas and methane hydrate. Industrial approaches for transforming methane into liquid chemicals are performed indirectly through the production of syngas（a mixture of carbon monoxide and hydrogen）by strongly endothermic steam reforming，followed by further conversion of the syngas to liquid hydrocarbons through Fischer-Tropsch synthesis or methanol（CH_3OH）synthesis. The direct oxidation of methane into value-added oxygenates such as methanol and formaldehyde（HCHO），which could potentially avoid the energy-intensive reforming process，is still impeded by the sluggish C—H bond activation kinetics of methane at low temperature.

The photocatalytic reaction system developed by the joint research team enables direct oxidation of methane to methanol and formaldehyde using only molecular oxygen as the oxidant at room temperature. Just in water，oxide semiconductors such as ZnO and TiO_2 loaded with nanometal cocatalysts（Pt，Pd，Au，or Ag）could effectively catalyze the direct CH_4 oxidation reaction under mild light irradiation. Liquid oxygenates with ～95％ selectivity could be achieved over the Au/ZnO photocatalyst. Experiments with isotopically labeled oxygen and water reveal that molecular O_2，rather than water，is the source of oxygen for direct CH_4 oxidation. The high reaction rate of direct CH_4 oxidation benefits from the synergistic activation effect of the oxide photocatalyst and nanometal cocatalyst. They can respectively activate CH_4 and O_2 into methyl radical and mildly oxidative intermediate（hydroperoxyl radical）in water，which are two key precursor intermediates for generating oxygenated liquid products in direct CH_4 oxidation. Therefore，the photooxidation of CH_4 to liquid oxygenates is contributed by the two equally significant aspects，i. e.，efficient C—H bond activation of CH_4 and controllable activation of O_2. The aqueous reaction medium used in this study is much more advantageous than the previous gas phase reaction system in the suppression of CH_4 overoxidation. Moreover，hydroxyl radicals derived from photooxidation of H_2O will lead to the overoxidation of CH_4 into CO_2. Thus，compared with TiO_2，the ZnO with less hydroxyl radical generation obtains higher oxygenated product selectivity. This work offers valuable guidance for the direct catalytic oxidation of methane to high value-added liquid oxygenates with molecular oxygen at room temperature and highlights the opportunities in employing photocatalysis technology to drive methane conversion.

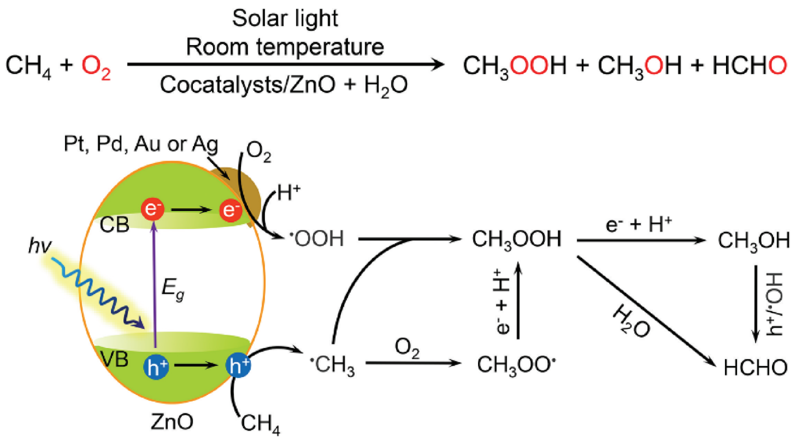

Figure The proposed reaction mechanism for photocatalytic CH4 oxidation to oxygenates.