The dark reaction of artificial photosynthesis:
Catalytic hydrogenation of CO$_2$

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Abstract:
This lecture presents the research progress made on CO$_2$ hydrogenation which could be considered as a dark reaction for artificial photosynthesis as long as the hydrogen is produced from solar energy. A thermal catalytic hydrogenation of CO$_2$ utilizing the hydrogen from photocatalysis essentially coincides with the photosynthesis where the photoreaction and dark reaction take place separately in order. A solid solution metal oxide catalyst ZnO-ZrO$_2$ [1] was found to be highly active and selective for CO$_2$ hydrogenation to methanol, and that the Zn site is more active for hydrogen activation and the Zr site is responsible for CO$_2$ adsorption and activation. A synergetic effect between the two sites makes the selectivity high (CH$_3$OH selectivity >90%) even at temperatures over 300 °C. Furthermore, we demonstrated that a tandem catalyst based on the ZnO-ZrO$_2$ catalyst combined with SAPO zeolite can selectively produce low olefins (C$_2^+$ - C$_4^+$ selectivity > 80%) [2]. It was revealed that a kinetic and thermodynamic coupling between the methanol synthesis and olefin formation greatly enhances the conversion and selectivity in low olefins production.

The hydrogen can be produced from water splitting by photocatalysis, photoelectrocatalysis and electrolysis with solar energy. The great challenge of solar energy conversion photocatalysis lies in its complicated processes including light absorption (harvesting), charge separation and transfer, and catalytic reactions [3]. In order to achieve high solar energy conversion efficiency, the photocatalytic system must harmonically guarantee high efficiencies of all these three processes instead of only one of them. Among the three aspects, the photogenerated charge separation could be regarded as a central issue of photocatalysis. A brief discussion focuses on the photogenerated charge separation driven by phase junction [4], cocatalysts [5, 6] and different facets [7-12].

Keywords: Photocatalysis, photoelectrocatalysis, water splitting, Hydrogen production, Carbon dioxide, hydrogenation, methanol synthesis, artificial photosynthesis, dark reaction, light reaction.

References