# 学 位 論 文 内 容 の 要 旨

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## 学 位 論 文 題 名

Solar Energy-Driven Photothermal Catalytic $CO_2$ Hydrogenation over Nanometals/Oxides Catalysts

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Solar energy-driven photothermal catalytic $CO_2$ hydrogenation to valuable fuels and chemicals is a promising technology to alleviate the gradually deteriorating environment and energy problems simultaneously. Nanometals/oxides catalysts, featuring good catalytic activity for $CO_2$ activation and conversion, are considered as promising candidates for photothermal catalytic $CO_2$ hydrogenation. With the plausible design of the nanostructures, nanometal-based catalysts, such as Cu- and Ru-based composites, can exhibit a remarkable performance via the synergetic effects of light-to-heat conversion and photo-induced hot charge-carrier-mediated activation of the reactants. However, although many efforts have been taken to investigate photothermal catalysis over the past few years, it still remains challenging to develop catalysts with high efficiency, good stability and desired product selectivity for photothermal $CO_2$ hydrogenation, and also to clarify the mechanism of photo-driven $CO_2$ conversion and illustrate the influence of metal-support interaction on the process. Thus, this thesis focuses on the rational design of nanometals (Cu, Ru)/oxides catalysts for efficient and stable photothermal catalytic $CO_2$ hydrogenation at mild conditions by coupling solar heating effect and photo-induced activation of the reactants via hot carriers, as well as selectively generating highly valuable solar methanol under ambient pressure.

In chapter 1, a general background about photothermal $CO_2$ hydrogenation reaction and the fundamentals of photothermal processes is introduced. Then, the recent development of $CO_2$ conversion reaction driven or promoted by solar energy is summarized.

In chapter 2, a Ga-Cu/$CeO_2$ catalyst was synthesized by direct pyrolysis of the Ga and Cu-containing Ce-metal-organic frameworks for efficient photothermal catalytic $CO_2$ hydrogenation to CO via RWGS reaction. Due to the highly dispersed Ga and Cu species in $CeO_2$, the optimized catalyst 10Cu5Ga/$CeO_2$ (10 wt% Cu and 5 wt% Ga) achieved a CO production rate of 111.2 $mmol \cdot g^{-1} \cdot h^{-1}$ with nearly 100% selectivity under full solar spectrum irradiation, which was superior to most reported Cu and other earth-abundant metals-based photothermal catalysts. Mechanism studies demonstrated that the synergy of photothermal heating and light-promotion contributed to the substantially increased CO production. In situ DRIFTS results revealed that the introduction of Ga enhanced the formation of formate species, the key intermediates in $CO_2$ hydrogenation, and light-induced hot carriers facilitated

the decomposition of formate species to carbonyl, thus enhancing CO production.

In chapter 3, to enhance the long-term stability of catalysts in photothermal catalysis, which is an important factor for further application, a joint strategy was utilized to fabricate an efficient and stable metal-oxide ($ZrO_2$) modified Cu/MgO-$Al_2O_3$ photothermal catalyst via the pyrolysis of LDH precursors followed by the loading of $ZrO_2$. Due to the highly dispersed Cu and the stabilization by the addition of metal oxide ($ZrO_2$), the modified catalysts exhibited not only efficient activity of CO production but also remarkably improved long-term stability. After 12 h reaction process, the CO yield was still remaining 93% as that on fresh catalyst. Detailed study suggested that the addition of metal oxide stabilized the architecture of Cu nanoparticles and prevented the aggregation of active Cu, thus preserving the active sites of catalysts during the reaction process.

In chapter 4, in order to achieve efficient solar methanol ($CH_3OH$) production, a much more valuable product than CO, a Ru/$In_2O_3$ catalyst was synthesized by a facile method for effective photothermal methanol production from $CO_2$ hydrogenation under atmospheric pressure. With the light irradiation, the Ru/$In_2O_3$ catalyst exhibited a remarkable solar methanol production of 280.4 $\mu$ mol $g^{-1}$ $h^{-1}$, which was 50 times higher than that of pure $In_2O_3$ under the same conditions and surpassed previously reported $In_2O_3$-based photothermal catalysts. Detailed characterizations demonstrated that the synergy of photothermal heating effect and hot-carriers-induced activation of reactants on Ru together with the interaction between Ru and $In_2O_3$ enhanced the activation of $CO_2$ and $H_2$ to generate the key intermediate *CO. Moreover, Ru modulated the electronic structure of $In_2O_3$ and promoted the formation of oxygen vacancies, which was favorable for the hydrogenation process of *CO to form methanol, thereby contributing to the efficient solar methanol production.

In chapter 5, an overall summary of this dissertation was presented. This thesis carried out a systematic study on photothermal catalytic $CO_2$ hydrogenation over nanometals/oxides catalysts, including photothermal RWGS reaction and solar methanol production under atmospheric pressure. Highly efficient $CO_2$ conversion to CO and lower apparent activation energy were achieved in photothermal catalysis over Cu-based catalysts with the coupling of solar heating and light-induced hot carrier-mediated activation of reactants, and the modulation of catalysts succeeded in excellent stability. At atmospheric pressure, solar methanol was considerably generated with the assistance of solar heating and hot carriers on Ru as well as the interaction between Ru and $In_2O_3$. The findings in this study strengthened the understanding of the interaction between light-induced hot carriers and surface reactants, and provided a potential strategy for realizing efficient and stable $CO_2$ hydrogenation with desired product selectivity for future application through the rational design of nanometals/oxides catalysts.