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Hot Carrier-Driven Photocatalysis for the Partial Oxidation of Methane

(Thesis Outline)

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Chapter 1. Introduction

In facing a soaring demand for energy, natural gas, of which methane is the major constituent, has been considered as the most essential fossil fuel in this century. Partial oxidation of methane (POM) into syngas ($CO+H_2$) with O_2 is a significant reaction which is conducive to the effective utilization of the abundant methane resources. However, high reaction temperatures are required in conventional thermocatalytic systems. Photocatalysis is an alternative approach, by which the transformation of photon energy to chemical energy is expected to reduce the reaction temperature. The photocatalytic properties of metallic nanostructures are prospective for POM owing to the function of photogenerated hot carriers derived from the interband electron transition in metals. The Auger relaxation of hot carriers results in photothermal conversion. The direct interaction between hot carriers and surface-adsorbed molecular is possible to induce photochemical reactions. A number of previous studies have reported the use of hot carriers to enhance the activity for methane reforming and other heterogeneous catalytic reactions. However, their photocatalytic mechanisms were ambiguous or controversial, and the photocatalytic POM under mild temperatures has not been accomplished. Therefore, this thesis dedicates to construct hot carrier-driven photocatalytic system for POM using supported metallic catalysts and metal-semiconductor composites. The objectives of this thesis are to realize the photocatalytic POM at a mild temperature of 423 K with high activity, identify the functional mechanisms of hot carriers in POM, and finally justify the hot carrier concept with solid evidence.

Chapter 2. Photocatalytic Partial Oxidation of Methane over Noble Metals Incorporated in Mesoporous Silica

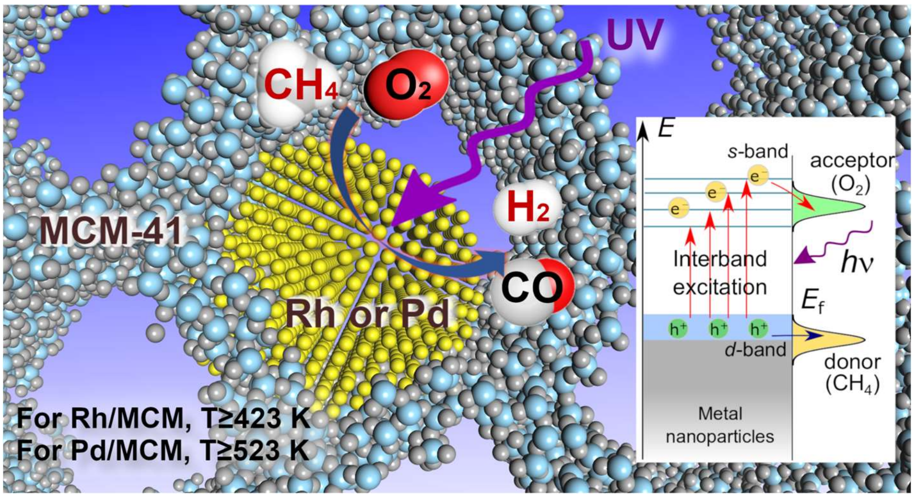

Figure 1. Schematic diagram of the photocatalytic POM over Ru/MCM and Pd/MCM.

The supported metallic photocatalysts, noble metals (Rh, Pd, Ru, and Pt) incorporated in mesoporous silica (MCM-41) were prepared via a one-pot process. TEM observations confirmed that Rh and Pd nanoparticles with sizes of 3.5 and 3.8 nm, respectively, were successfully embedded in the mesoporous channels. Under UV irradiation, Rh/MCM exhibited superior photocatalytic performance at operating temperatures as low as 423 K with a stable output of syngas and CO selectivity of about 50%. Pd/MCM can also initiate POM under illumination, but a higher temperature of 523 K is required. Action spectra and surface temperature measurement demonstrated that the high activity under UV irradiation is attributed to the synergistic photothermal and nonthermal effects of hot carriers.

The catalyst surface temperature was elevated due to the relaxation of hot carriers, but not high enough to induce the thermocatalytic POM individually. The nonthermal effect, which can be ascribed to the direct activation of O_2 and CH_4 adsorbed state by hot electrons and holes is considered as a critical reason for the high activity.

Chapter 3. Photocatalytic Partial Oxidation of Methane over Palladium-Loaded Strontium Tantalate

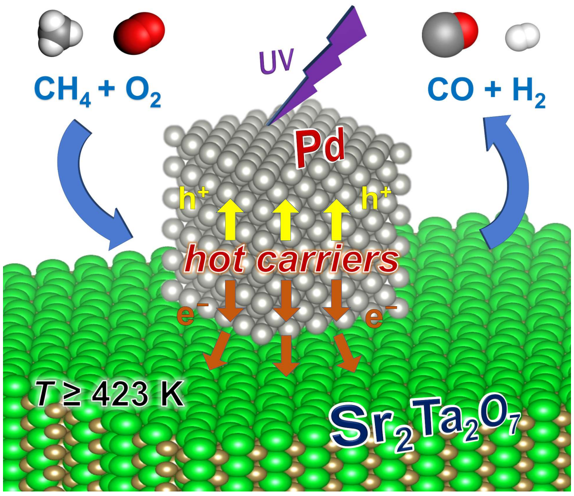

Figure 2. Schematic diagram of the photocatalytic POM over $Pd/Sr_2Ta_2O_7$.

To further improve the activity and reduce the operating temperature of Pd-based catalyst. Metal-semiconductor composite photocatalysts were prepared by loading Pd on the surface of ultra-wide bandgap (UWBG) $Sr_2Ta_2O_7$. The influence of Pd loading amount and loading method was investigated. The catalyst prepared by photodeposition method with 1 wt% Pt amount was the optimized sample, which successfully induced POM at 423 K with CO selectivity of 43%, under UV irradiation, exhibiting better performance than Pd/MCM developed in Chapter 2. Comparative studies were carried out using other semiconductors with relatively narrow bandgap such as ZnO and TiO_2 to replace $Sr_2Ta_2O_7$. These conventional semiconductors showed much lower activity than $Sr_2Ta_2O_7$. The *in situ* EPR analysis demonstrated that the enhanced photocatalytic activity was owing to the hot electron injection from Pd to the CB of $Sr_2Ta_2O_7$ which realized the charge separation. The injected electrons in the CB of $Sr_2Ta_2O_7$ with high energy can promote the reduction and activation of O_2. On the other hand, the polarized $Pd^{\delta+}$ hot holes are high reactive centers for CH_4 cracking, which operate by extracting the CH_4 σ electrons. By contrast, the low activity of those such as Pd/ZnO is ascribed to the competition between bandgap excitation and hot carrier generation.

Chapter 4. Perspectives

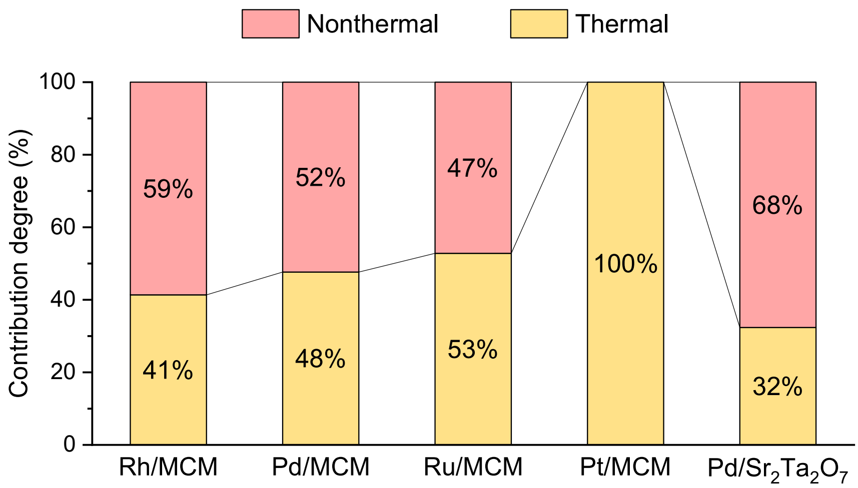

Figure 3. Contribution degrees of the thermal effect (including external heating and photothermal effect) and the nonthermal effect of hot carriers in the photocatalytic POM using M/MCMs (M = Rh, Pd, Ru, and Pt) and Pd/$Sr_2Ta_2O_7$ catalysts.

Quantitative estimation of thermal and nonthermal contributions in the hot carrier-driven POM was carried out using the temperature and activity data in Chapter 2 and 3, based on the Arrhenius equation. The result gave solid evidence that, in most cases, hot carriers' nonthermal effect is the dominant factor to drive the photocatalytic POM. This study helped address the debate involving the reasonability of nonthermal hot carrier effect, and exhibited significant contribution to the field of photocatalysis and plasmonic physics and chemistry. Besides, the hot carriers' nonthermal effect in Pd/$Sr_2Ta_2O_7$ was more evident than that in Pd/MCM, suggesting that the use of a UWBG semiconductor as the catalyst support is a critical and an effective path to establishing a high-efficient hot carrier-driven photocatalytic system. The contribution of this thesis to the field of engineering was demonstrated by comparing the photocatalysts with a conventional thermocatalyst, Ni/Al_2O_3. Both the turnover numbers (TONs) and stability of the photocatalysts developed in this thesis were superior to those of the conventional thermocatalyst, exhibiting the practical prospects of the concept of hot carrier-driven photocatalysis. Finally, the contributions of this thesis to the society and industry were clarified.

Chapter 5: Summary

This chapter summarized this thesis and concluded the key factors in the design of a hot carrier driven photocatalytic system.