

Mechanistic Understanding of Microwave-Assisted Thermal Catalysis in Upgrading Shale Gas

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Highlights

- Propane dehydrogenation under microwaves shows performance advantages over conventional methods.
- Insights into molecular-level mechanisms for the microwave-assisted dry reforming of methane.

1. Introduction

The transformation of shale gas into chemicals, such as through nonoxidative propane dehydrogenation (PDH) and dry reforming of methane (DRM), presents significant challenges, including equilibrium-limited reactions, high operational temperatures, catalyst sintering, and coking. Microwave (MW)-assisted heterogeneous catalysis has recently emerged as a viable alternative, offering increased energy efficiency and improved catalytic performance, including higher activity, selectivity, and enhanced resistance to deactivation compared to conventional heating (CH) processes [1]. The unique ability of MWs to achieve selective and volumetric heating [2] leads to unique temperature profiles that benefit catalyst activity and durability, primarily by suppressing gas-phase chemistry. Nonetheless, the precise mechanisms underlying these improvements are subject to ongoing discussion, partly due to the difficulties in measuring temperatures accurately under MW irradiation [3]. To tackle these challenges, we utilized fiber Bragg grating (FBG) sensors, ensuring temperature measurements comparable to those in conventional heating systems. This approach facilitated a comprehensive investigation into the mechanisms driving MW-assisted reactions. We performed reactivity tests, extensive characterization, and post-mortem analyses to elucidate the impact of MWs on catalytic performance.

2. Methods

The PDH and DRM reactions were carried out using a single-mode cylindrical MW resonator, operating in the TE₁₁₁ mode at a consistent 2.45 GHz [4, 5]. This setup generated a homogeneous electromagnetic field around the catalyst. The catalysts were sieved to 60-100 mesh and fixed in the electromagnetic field using a quartz tube with a quartz frit. Surface and core temperatures in the reactor were measured using a pyrometer, infrared (IR) thermal camera, and high-temperature FBG sensors. CH reactions were similarly set up in an electric furnace with a thermocouple in the catalyst bed to monitor temperature. We used PtSn/SiO₂ catalysts for PDH ($C_3H_8 \rightarrow C_3H_6 + H_2$) and zirconia-doped ceria catalysts (CZO, Ce_xZr_y) for DRM ($CO_2 + CH_4 \rightarrow CO + 2H_2$).

3. Results and discussion

Our MW configuration allows for an equitable comparison with CH (**Fig. 1A**). To ensure a uniform temperature distribution, we utilize both digital and IR imaging techniques. Within the SiC monolith and bed of quartz beads, temperature measurements at the center (obtained via FBG) and at the wall (captured by IR camera) showed a discrepancy of around 6%. The temperature profile under MWs exhibited minor radial variations, with the edges being slightly cooler. Propylene selectivity is higher under MW heating than CH at 700 °C (**Fig. 1B**). With CH, gas-phase reactions dominate at high temperatures. In contrast, MWs enhance propylene selectivity by reducing gas-phase reactions. Under CH conditions, coking and agglomeration adversely affect the active sites. Alternatively, MWs keep PtSn nanoparticles stable, although occasional premature carbon formation on SiO₂ is observed through TEM analysis. Temperature programmed oxidation (TPO) studies with O₂ show that carbon deposits from CH are oxidized at lower temperatures, indicating proximity to active metal sites. Conversely, under MW conditions, carbon is eliminated at higher temperatures, suggesting coke is deposited further

from the active metal sites and thereby reducing its effect on PDH. Our detailed post-mortem analyses, including Raman spectroscopy, microscopy, and thermogravimetric studies, demonstrate that MWs offer superior PDH performance over CH by minimizing deactivation caused by gas-phase reactions at elevated temperatures.

The interaction between the electromagnetic field and the cerium-zirconium oxide catalyst in DRM operates differently. CO₂ is dissociatively adsorbed at active sites made available by reactive lattice oxygens (O_L) and vacancies (V_O) on ceria surfaces. The presence of a dense population of oxygen vacancies in reduced ceria-based catalysts significantly boosts their electrical conductivity and dielectric loss, rendering them highly effective for MWs. This synergy was investigated in DRM experiments conducted at 800 °C using cerium-zirconium (Ce_xZr_y) catalysts under CH and MWs (**Fig. 1C**). Altering the zirconium content resulted in a marked change in the methane consumption rate. Under MWs, the Ce₁Zr₁ catalyst showed significant improvements in both reaction rate and hydrogen selectivity. Such enhancements are ascribed to the relationship between the DRM rate and the concentration of Ce³⁺-V_O pairs, with the effects of MWs becoming more pronounced at elevated Ce³⁺-V_O pair densities. Reactant step-jump experiments further corroborated the proposed mechanism, indicating that catalyst reduction improves dielectric MW coupling. This enhancement leads to a rise in V_O density via a positive feedback mechanism, thereby hastening the reaction process. This discussion highlights the complex relationship between catalyst composition, MWs, and DRM efficiency.

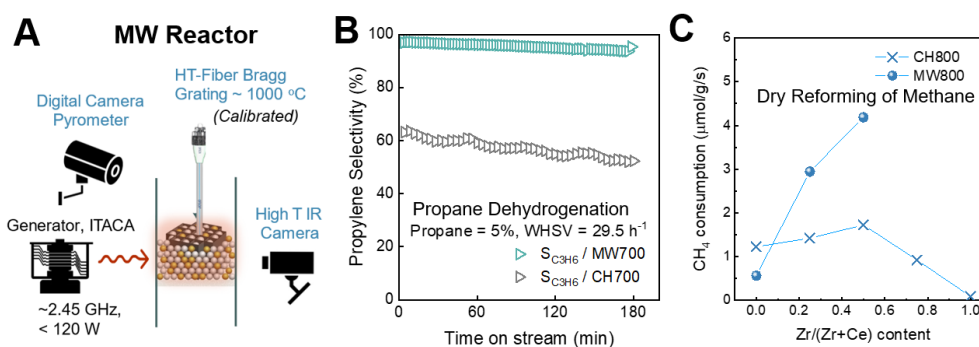


Figure 1. (A) MW reactor schematic. (B) C₃H₆ selectivity under MWs and CH for PDH. Reaction conditions: 700 °C, 60 cc/min of 5% propane in He. (C) Effect of Zr content on the CH₄ consumption rate of DRM over Ce_xZr_y catalysts under MWs and CH. Reaction conditions: 800 °C, 100 cc/min of 5% CH₄ and 10% CO₂ in N₂.

4. Conclusions

This study demonstrates the advantages of MW-assisted thermal catalysis in upgrading shale gas and offers critical insights into its mechanistic foundations. The observed benefits of MW electrification for chemical processes emphasize its potential role in facilitating a zero-carbon transition, especially as renewable electricity sources become more accessible.

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Keywords

Microwaves; Shale gas conversion; Propane dehydrogenation; Dry reforming of methane