Influence of Mo- and Ga-Supported HZSM-5 Co-Catalyst Configuration in Microwave-Assisted Methane and Ethane Dehydroaromatization

Duy Hien Mai[1,2]; Swarom Kanitkar[1,2]; Evgeniy Myshakin[3,4]; Xinwei Bai[1,2]; Wissam Saidi[3]; Daniel J. Haynes[1]

[1]National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26505, USA; [2]NETL Support Contractor, 3610 Collins Ferry Road, Morgantown, WV 26505, USA; [3]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA; [4]NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

Introduction

Microwave (MW)-assisted dehydroaromatization (DHA) using an Mo-supported HZSM-5 catalyst (Mo/HZSM-5) enhances the value of natural gas resources by converting stranded or underutilized natural gas into value-added chemicals in modular microwave reactor systems. This approach offers the potential to generate economic value. However, natural gas mixtures often contain multiple components, including ethane (C_2H_6) and propane (C_3H_8), which complicate the reaction pathways. Ga-supported HZSM-5 (Ga/HZSM-5) catalysts are generally inactive toward CH_4 but exhibit higher activity toward C_2H_6 and C_3H_8. Therefore, investigating the combination of Mo/HZSM-5 and Ga/HZSM-5 in various catalyst bed configurations is essential. This study explores different co-catalyst bed configurations and CH_4/C_2H_6 feed compositions to determine the most effective way for enhanced natural gas conversion and benzene production.

Catalyst Synthesis

Ga/HZSM-5 and Mo/HZSM-5: 1 wt.% Ga/HZSM-5 and 4 wt.% Mo/HZSM-5 were prepared via incipient wetness incorporation (IWI). The powder was dried at 105 °C and calcined at 550 °C in air. Citric acid was used to assist the metal loading in IWI. HZSM-5 used in these studies has a silicon to alumina ratio (SAR) of 23.

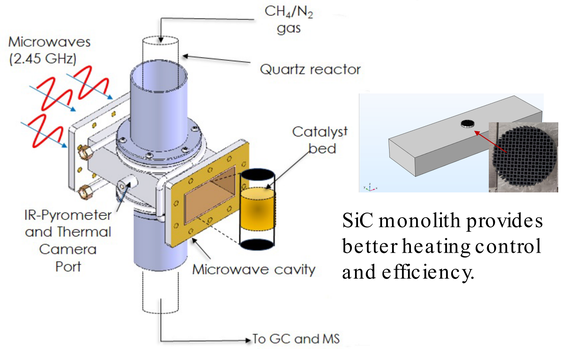
Ga 1st-Mo/HZ5: 1 wt.% of Ga was first introduced to HZSM-5 via IWI, followed by calcination at 550 °C in air. 4 wt.% of Mo was subsequently incorporated using similar IWI and calcination procedures.

CH_4 and C_2H_6 DHA Testing

Separate Ga/HZSM-5 and Mo/HZSM-5: MW tests were performed using a 1.2 kW, 2450 MHz fixed-bed microwave reactor system. Catalyst pellets (4.5 g) were filled in a silicon carbide (SiC) monolith and activated in-situ in CH_4/H_2 (10:90) at 700 °C. MW-assisted CH_4 and C_2H_6 DHA were carried out at 700 °C in 450 sccm of gas feeds, with various $CH_4/C_2H_6/N_2$: 70/0/30, 65/5/30, 60/10/30, 55/15/30, 50/20/30, and 0/20/80 for 60 min (WHSV = 6,000 mL g^{-1} h^{-1}).

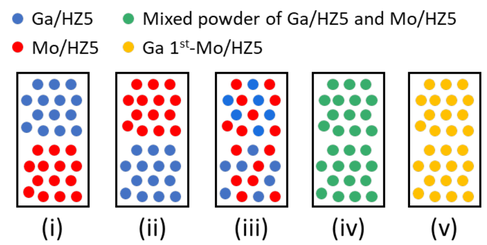
Combined catalyst bed: Five different catalyst bed configurations (4.5 g) were tested for MW-assisted CH_4/C_2H_6 DHA at 700 °C in 450 sccm of gas feed with $CH_4/C_2H_6/N_2$ of 50/20/30 for 60 min (WHSV = 6,000 mL g^{-1} h^{-1}).

Microwave Reactor System

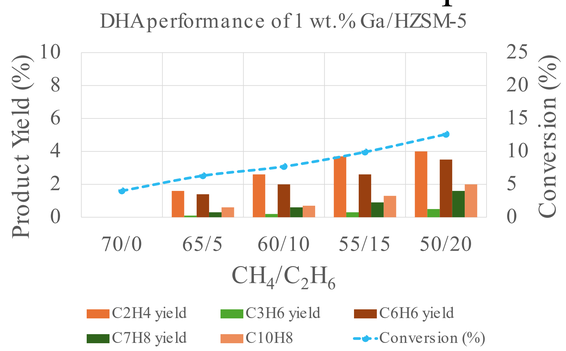


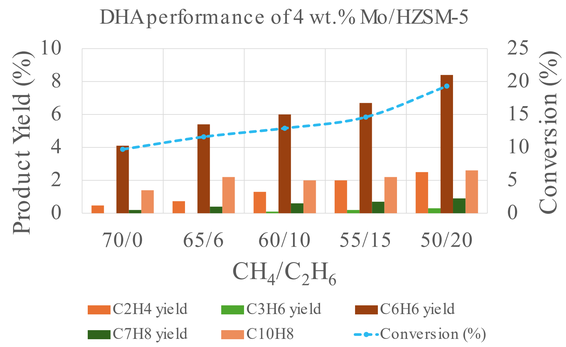
SiC monolith provides better heating control and efficiency.

Catalyst Bed Configuration



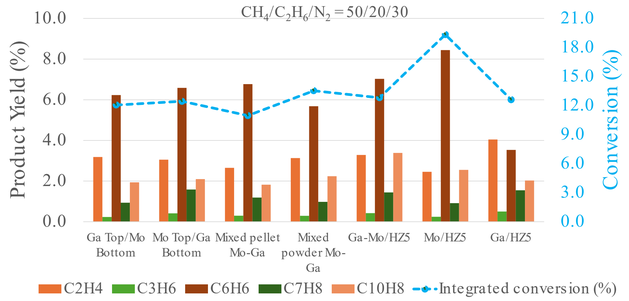
MW-Assisted DHA of Separate Ga/HZSM-5 and Mo/HZSM-5

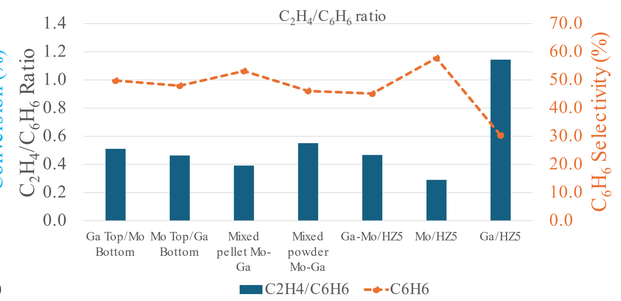




- Ga/HZSM-5 showed no activity with pure CH_4, producing no aromatics.
- With C_2H_6 addition, both C_2H_4 and aromatics increased.
- High C_2H_4/C_6H_6 ratio (>1) indicates Ga promotes C_2H_6 dehydrogenation.
- Mo/HZSM-5 exhibited enhanced conversion (up to 20%) with increasing C_2H_6 feed, reflecting the greater ease of C_2H_6 activation compared to CH_4.
- Aromatic yield (C_6H_6, C_7H_8, and $C_{10}H_8$) reached 11% at CH_4/C_2H_6=50/20, which doubled that obtained at 70/0.
- The low C_2H_4/C_6H_6 ratio (0.1–0.3) highlights preferential aromatization.

MW-Assisted DHA of Combined Catalysts





- Although the mixed pellets of Mo/HZSM-5 and Ga/HZSM-5 exhibited lower conversion (~13%) compared with Mo/HZSM-5 (20%), the C_6H_6 yield (7%) and selectivity (55%) remained comparable with Mo/HZSM-5.
- All combined catalyst configurations showed an elevated C_2H_4/C_6H_6 ratio, confirming that Ga species enhanced C_2H_6 dehydrogenation in the combined catalyst bed.

Conclusions

- Ga/HZSM-5 promoted C_2H_6 dehydrogenation (higher C_2H_4/C_6H_6).
- Mixed pellets Mo-Ga gave comparable C_6H_6 yield/selectivity to Mo/HZSM-5; further CH_4 and C_2H_6 conversion analysis is needed to clarify the role of Ga and Mo sites.

Disclaimer

This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

U.S. DEPARTMENT of ENERGY

Driving Innovation and Delivering Solutions