

The Effect of Metal Promoters in an Mo-Supported HZSM-5 Catalyst for Microwave-Assisted Methane Dehydroaromatization to Aromatics

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Introduction

Microwave (MW)-assisted methane dehydroaromatization (MDHA) using an Mo-supported HZSM-5 catalyst (Mo/HZ5) can convert methane into value-added aromatic products in modular microwave reactor systems, enabling producers to generate revenue from an otherwise wasted resource. Modifying the local environments of active Mo species with metal promoters potentially regulates the reaction/deactivation pathways and improves the heating properties of the Mo/HZ5 under microwaves. Herein, metal promoters (M), including monovalent K⁺ and bivalent Co²⁺ and Ni²⁺, were incorporated to form M-Mo/HZ5 and their MDHA performance was investigated.

Catalyst Synthesis Mo 1st < Mo 2nd

M 1st-Mo/HZ5: K⁺, Co²⁺, or Ni²⁺ were first introduced to HZ5 via incipient wetness incorporation (IWI), followed by calcination at 550 °C in air. Mo was subsequently incorporated using similar IWI and calcination procedures.

M 2nd-Mo/HZ5: The order of adding promoters and Mo on HZ5 was reversed.



MDHA Testing

MDHA testing: 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 CH₄/H₂ (10:90) at 700 °C. MW-assisted MDHA was carried out at 700 °C in 450 sccm of CH₄/N₂ (70/30) for 60 min (WHSV = 6,000 mL g⁻¹ h⁻¹).

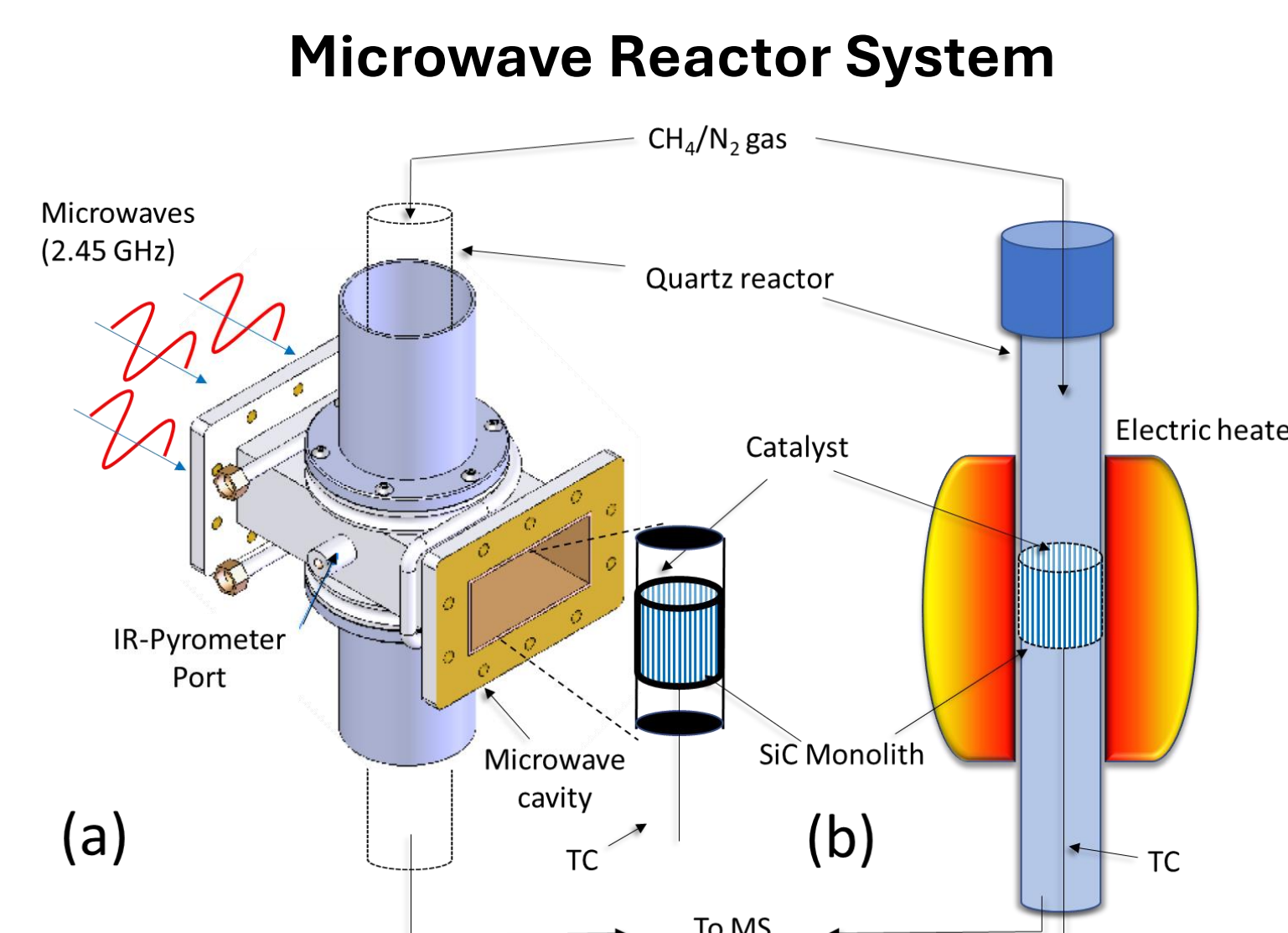
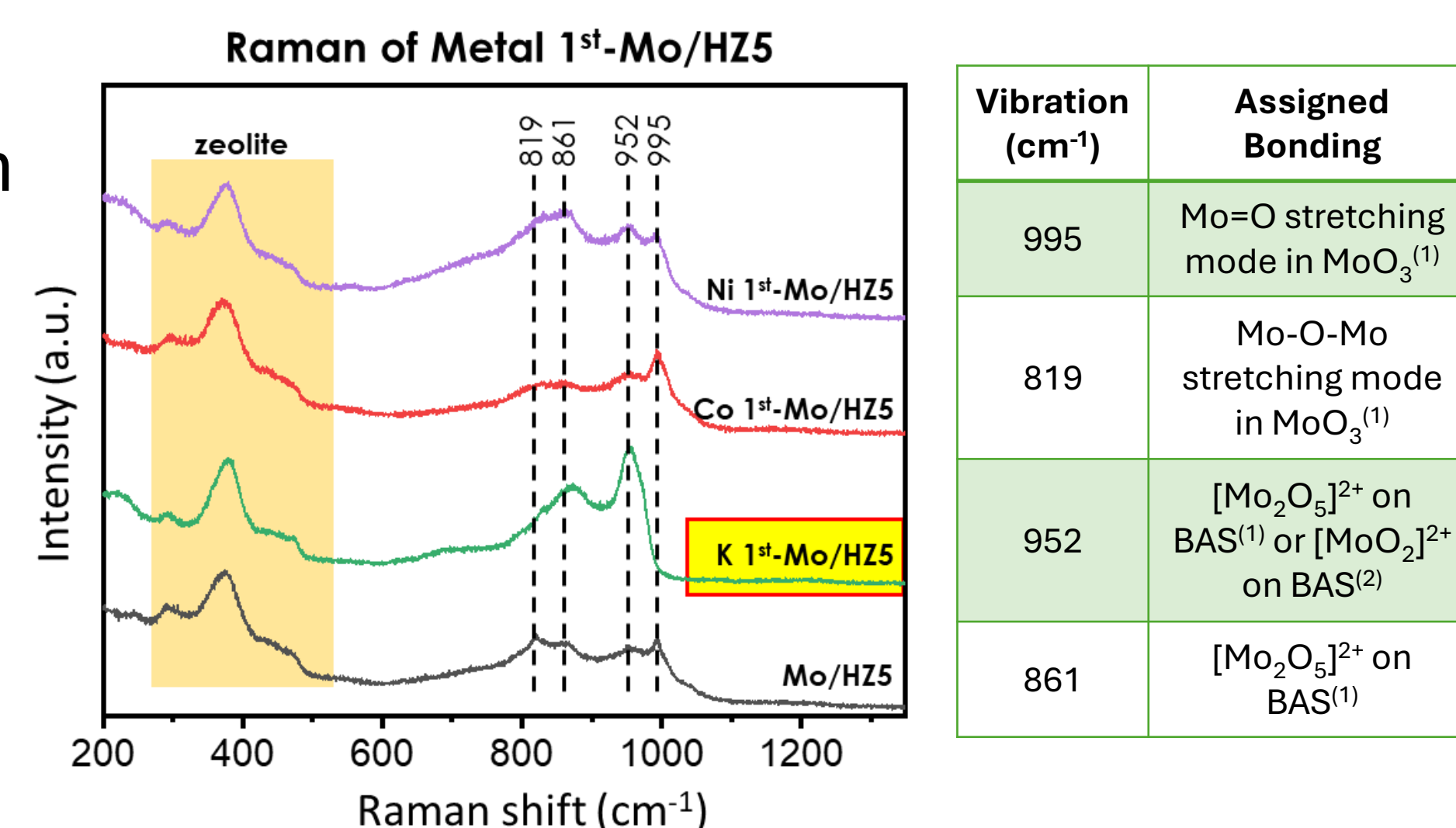
Changes in Mo Types and Dispersion

Raman:

- There were no changes in vibration of Mo species upon adding metal promoters: no direct interaction.
- K⁺ enriched the BAS-anchored Mo species (monomeric or dimeric), leading to improved Mo dispersion.

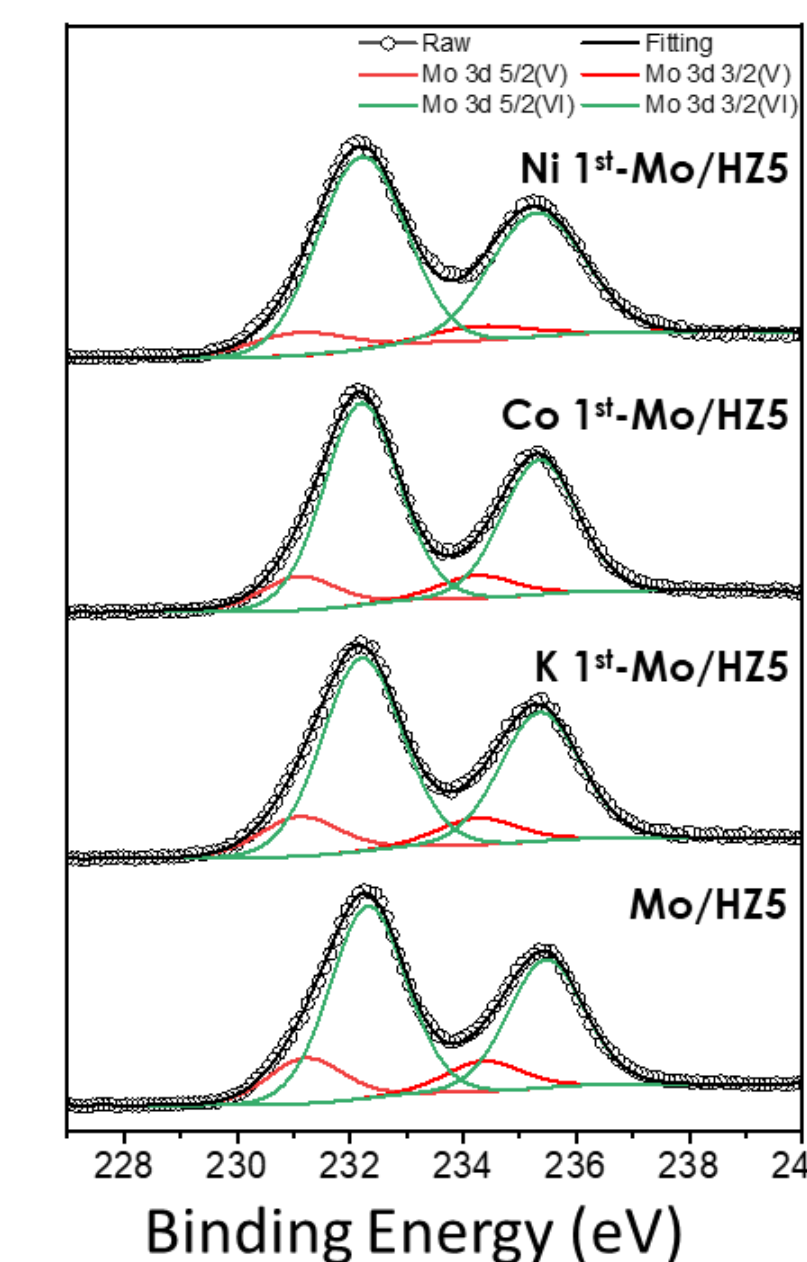
XPS:

- Insignificant shift in binding energy upon adding metal promoters indicates no direct interaction, which is consistent with Raman.



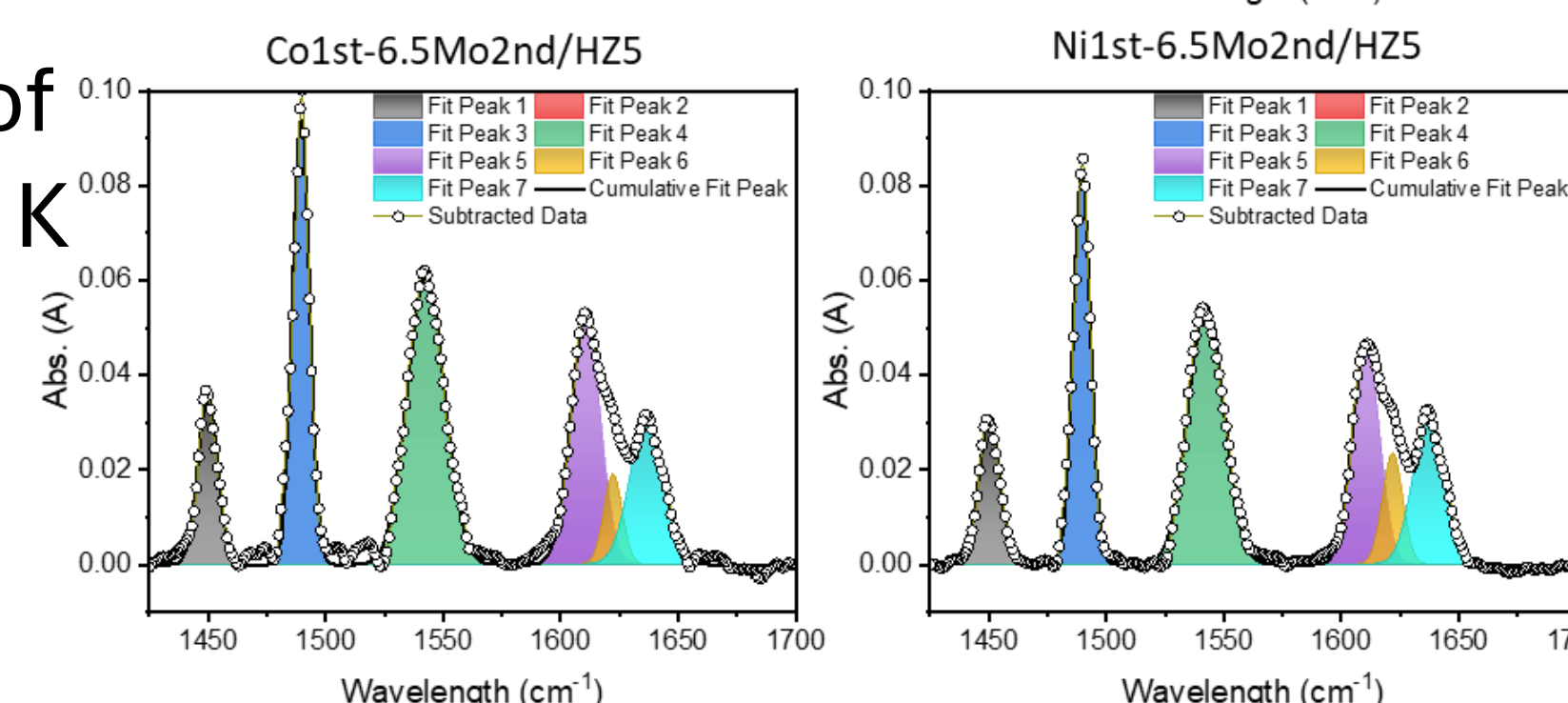
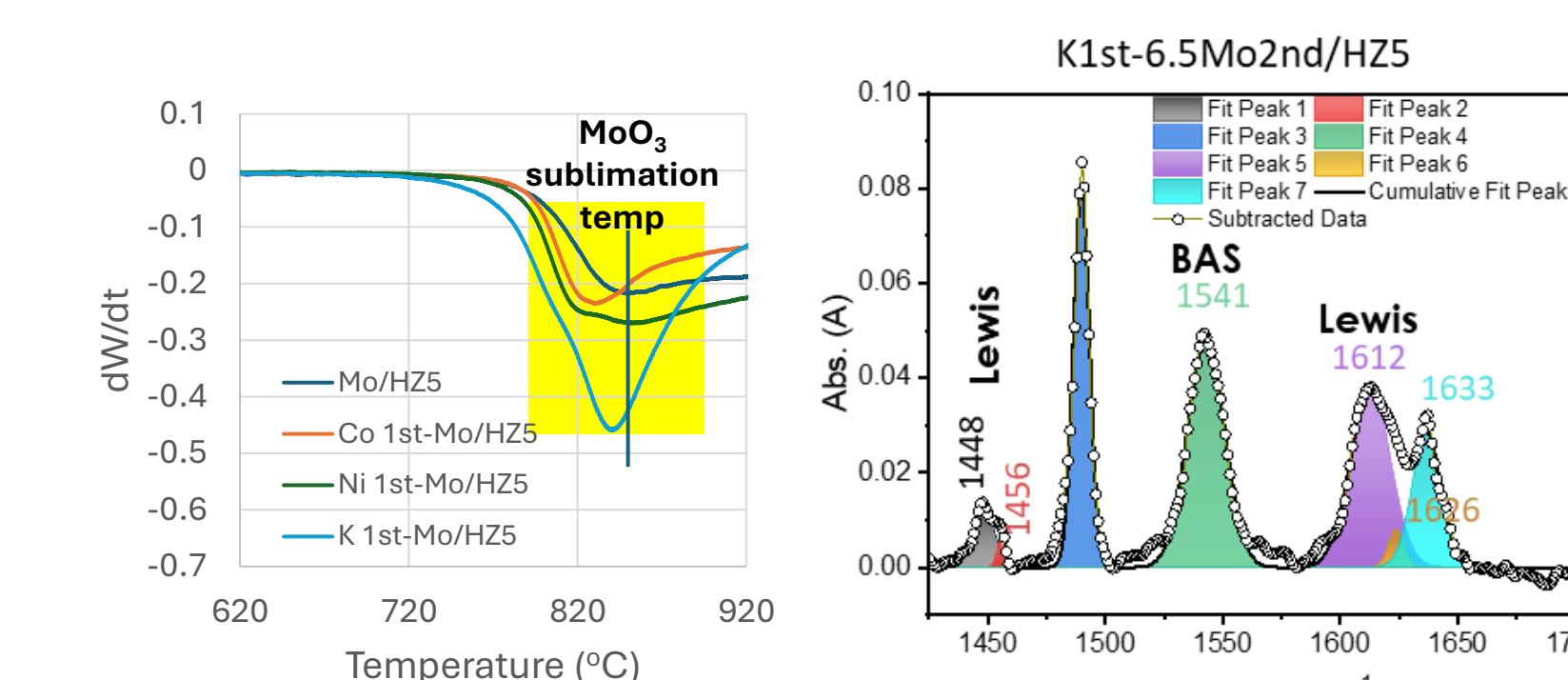
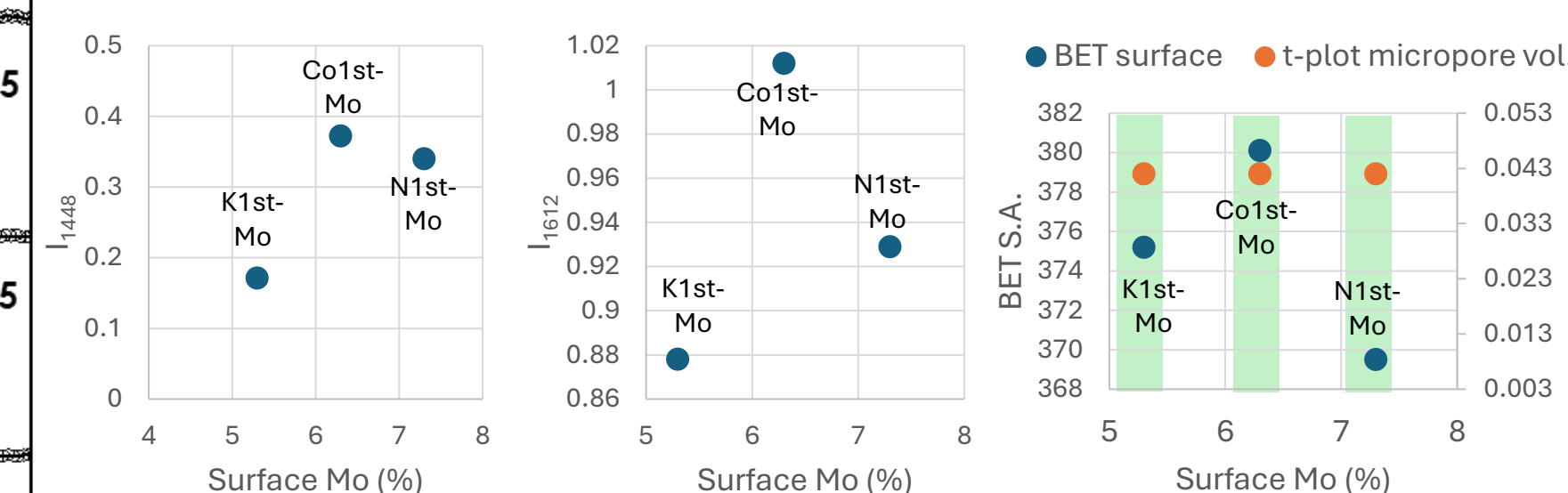
XPS, BET, pyridine-FTIR:

- K and Co reduced Mo surface content from 6.5% to 5.3 and 6.3%, respectively: more Mo anchored on BAS inside the pores.
- Addition of Ni had the opposite effect which enriched surface Mo (7.3%).
- Surface area decreased upon adding metal promoters: Mo/HZ5 > Co > K > Ni.
- Lewis and BAS in K-promoted were much lower than those of Co and Ni: more BAS-anchored Mo for K-promoted.
- TGA showed that sublimation temperature of metal promoted is lower than Mo/HZ5, with K showing the most intensified sublimation, likely due to more BAS-anchored Mo that forms aluminum molybdate at high temperatures.³

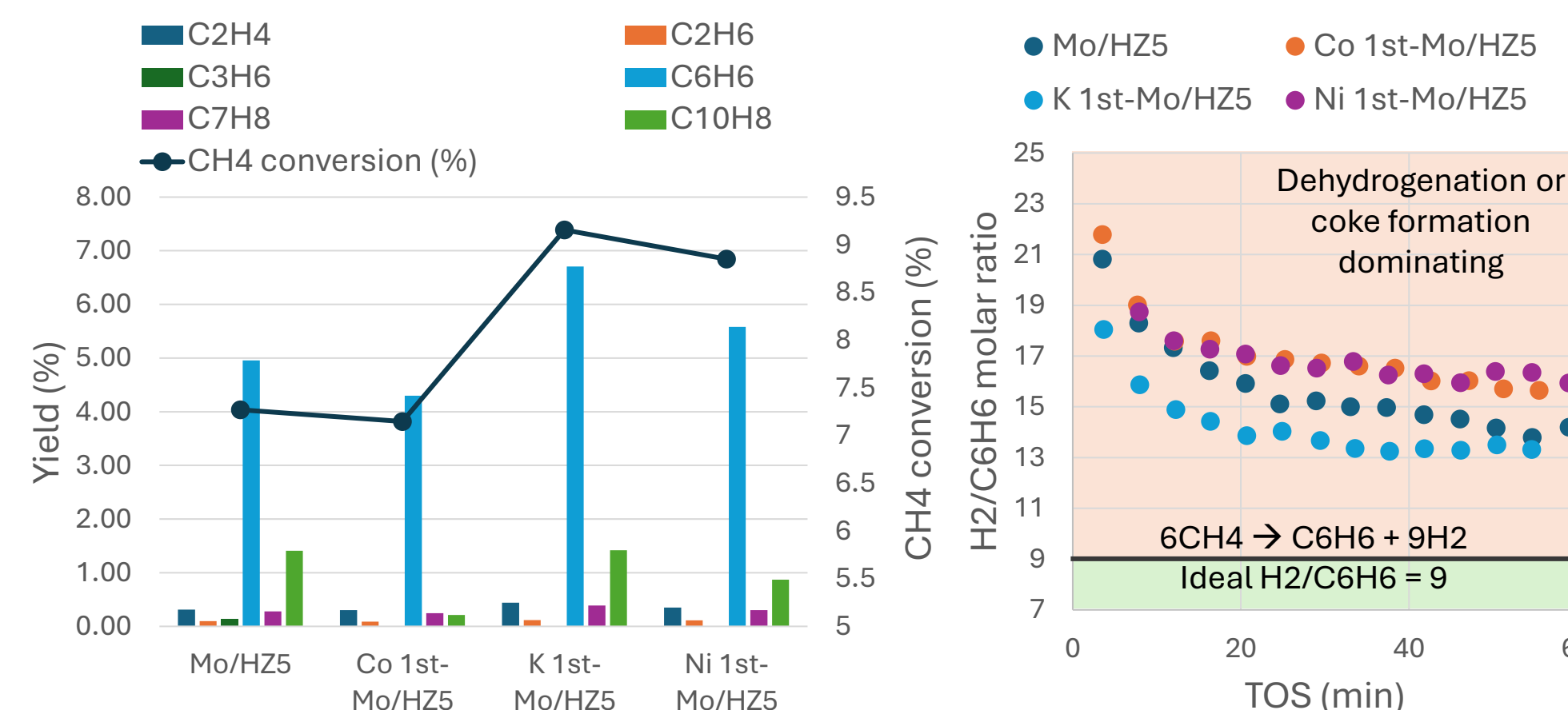


Summary of Material Characterizations (XPS, BET, and pyridine-FTIR)

Samples	Mo (%)	Mo/Al	Al/Si	Mo/M	S.A.	Pore	I ₁₄₅₀	I ₁₆₂₀
Mo/HZ5	6.5	3.6	0.10	n.a.				
Co 1st-Mo/HZ5	6.3	3.3	0.12	31.5	380.1	0.042	0.372	1.012
K 1st-Mo/HZ5	5.3	3.1	0.11	10.6	375.2	0.042	0.171	0.878
Ni 1st-Mo/HZ5	7.3	3.8	0.12	24.3	369.5	0.042	0.340	0.929



Microwave-Assisted MDHA Performance



- K led to higher CH₄ conversion (9.2%) and aromatic yield (8.5%) than Mo/HZ5, due to a higher quantity of BAS-anchored Mo.
- K balanced the ratio of catalytic sites for dehydrogenation and ring formation which led to less coke and more aromatic products.

Conclusions

- The use of K as a promoter led to an increased quantity of BAS-anchored Mo species as indicated by Raman, XPS, FTIR, and TGA.
- K 1st-Mo/HZ5 led to 60% higher aromatic and less coke compared to Mo/HZ5.

- Gao J. et al. Science 348 (2015) 686.
- Julian I. et al. Catal. Sci. Technol. 9 (2019) 5927.
- Kosinov N. et al. J. Catal. 346 (2017) 125.

Disclaimer

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