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Absorptive hydrogen scavenging for enhanced aromatics yield during non-oxidative methane dehydroaromatization on Mo/H-ZSM-5 catalysts

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Abstract

The addition of Zr metal particles to MoC_x/ZSM-5 in interpellet mixtures (2:1 weight ratio) resulted in maximum single-pass methane conversion of ~27% for dehydroaromatization at 973 K – in significant excess of the equilibrium prescribed ~10% conversion at these conditions – and a concurrent 1.4 – 5.6 fold increase in aromatic product yields due to circumvention of thermodynamic equilibrium limitations by absorptive hydrogen removal by Zr while retaining the cumulative aromatic product selectivity. The absorptive function of the polyfunctional catalyst formulation can be regenerated by thermal treatment in helium flow at 973 K yielding above equilibrium methane conversion in successive regeneration cycles. Hydrogen uptake experiments demonstrate formation of bulk ZrH_{1.75} on hydrogen absorption by zirconium at 973 K. Cooperation between absorption and catalytic centers distinct in location and function enables circumvention of persistent thermodynamic challenges in non-oxidative methane dehydrogenation.

Dehydroaromatization (DHA) provides an attractive thermochemical route for CH₄ valorization in reference to indirect and oxidative routes that bring forth significant kinetic challenges in conferring high selectivity.^[1,2] Non-oxidative conversion of CH₄ by pyrolysis reactions to produce aromatics (benzene; at ~70% carbon selectivity) occurs with near equilibrium yield ($6\text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$; ~10% single pass conversion) on carbidic forms of Mo encapsulated in zeolites at temperatures ~950 K.^[3–5] Oxidic precursors of Mo deposited in H-ZSM-5 zeolitic channels via vapor phase solid state ion exchange result in formulations that catalyze CH₄ DHA at 950 K– 973 K.^[6] Formation of MoC_x clusters of 0.6 – 1.5 nm size after carburization of Mo-oxidic precursors in Mo/H-ZSM-5 catalyst and their involvement in catalytic C-H bond activation during CH₄ DHA reactions has been evidenced using spectroscopic studies.^[3–9] Although the stoichiometry and coordination of MoC_x clusters is still a topic of debate, the proficiency and reduced nature of active Mo-centers is no longer debated in literature.^[8,10–14] Four noteworthy publications in recent literature examine evolution and speciation of MoC_x species in CH₄ DHA^[10,12,15,16], however, we make no effort to probe identity of MoC_x species in this study and instead report in-situ absorptive-hydrogen removal as a strategy to overcome thermodynamic limitations that limit single pass conversion in CH₄ DHA to ~10%. A recent report proposes that addition of Zr metal as a hydrogen absorber to MoO_x/H-ZSM-5 formulations leads to increased CH₄ conversion and aromatic yields.^[17] These reports, however, do not arbitrate the effect of hydrogen acceptor function precisely as hydrogen/oxygen removal during the carburization transient of MoO_x conversion to MoC_x was not accounted for.

Here, we report that addition of Zr to pre-carburized Mo/H-ZSM-5 formulations (denoted as MoC_x/H-ZSM-5 in this work) in an interpellet mixture (2:1 weight ratio) leads to formation of ZrH_x species during CH₄ DHA at 973 K resulting in ~27% maximum single-pass CH₄ conversion

and enhanced yield of CH₄-derived hydrocarbon products at equivalent time-on-stream (TOS) because equilibrium limitations are transiently circumvented by the hydrogen-absorptive Zr function while the aromatic product selectivity is unperturbed. Thermal treatment of the Zr and MoC_x/H-ZSM-5 interpellet mixture in helium flow results in regeneration of the Zr absorbent leading to above-equilibrium CH₄ conversions in successive reaction-regeneration cycles.

X-ray absorption spectroscopy and computational chemistry studies have been reported to evidence formation of (Mo₂O₅)²⁺ dimers occupying two proximate Al sites on air treatment of MoO₃ and H-ZSM-5 physical mixtures at 973 K.^[4,5] Mo loadings ~ 5 wt% for H-ZSM-5 with Si:Al ~13 have been shown to cause irreversible damage to the zeolite framework leading to aluminum molybdate formation (inactive for CH₄ DHA).^[8] Consequently, we use Mo:Al_f ~0.25 (~3 wt% Mo loading) for H-ZSM-5 catalyst with Si:Al ~11.5 to ensure the required number of Al atom pairs are available for (Mo₂O₅)²⁺ dimer formation and stabilization within zeolite channels.^[18,19] Raman spectroscopy, HAADF-STEM, and chemical transients (Fig. 1 (a) – (c)) reported here exhibit evolution of catalyst structure during CH₄ DHA. Mo/H-ZSM-5 (Fig. 1(a)(ii)) showed a new band at 970 cm⁻¹ as compared to MoO₃ and H-ZSM-5 physical mixture (Fig. 1(a)(i)) and 973 K air-treated H-ZSM-5 (Fig. 1(a)(iii)). This band corresponds to a stretching mode characteristic of Mo=O bonds^[9] suggesting formation of (Mo₂O₅)²⁺ dimers within zeolite channels after MoO_x thermal exchange at 973 K. HAADF-STEM of Mo/H-ZSM-5 (Fig. 1(b)(ii)) demonstrated that crystallinity of the zeolite framework was preserved and Mo species dispersed atomically (weak white contrast clusters (<1.5 nm) marked by black arrows) during thermal treatment. Initial carburization of Mo/H-ZSM-5 on CH₄ exposure at 973 K resulted in transient evolution of CO, CO₂, and H₂ as dominant products (Fig. 1(c)), before evolution of any hydrocarbon products, yielding $\sim 2.44 \pm 0.1$ O:Mo during ~15.5 ks elucidating the stoichiometric reaction of (Mo₂O₅)²⁺

dimers with CH₄ to form MoC_x clusters. Carburization transients of ~15.5 ks resulted in deposition of $\sim 8.5 \pm 1.0$ C:Mo in line with ~10 C:Mo deposition reported previously for CH₄ DHA on Mo/H-ZSM-5 at ~973 K.^[3,12,20,21]

The induction (carburization) period and initial increase and subsequent reduction in aromatic formation rates with TOS (Fig. 1(e)) is suggestive of a bifunctional catalytic mechanism wherein C-H bonds in CH₄ are activated on MoC_x clusters formed during carburization to form C₂H_x species which subsequently undergo oligomerization/hydrogen transfer on residual Brønsted acid sites within zeolite channels to form aromatics. Previous reports showed that unsupported molybdenum carbide catalyzed CH₄ and ethane conversion to C₂ products and ethylene respectively but did not yield aromatics whereas MoC_x/H-ZSM-5 catalyzed ethane conversion to benzene suggesting that both carbidic MoC_x sites and residual Brønsted acid sites are involved in CH₄ DHA.^[22,23] Mo-based species are necessary to initiate CH₄ DHA reactions on Mo/H-ZSM-5 catalysts^[22,23], therefore, we normalized product rates by total number of Mo atoms to account for all available Mo atoms resulting in the lowest possible rate. We also enumerated the concentration of free Brønsted acid sites in H-ZSM-5 (Si/Al = 11.5) via NH₃ uptake as $1.21 \times 10^{-3} \text{ mol g}_{\text{cat}}^{-1}$ which is similar to concentration of Al in the zeolite based on Si:Al ratio ($1.33 \times 10^{-3} \text{ mol g}_{\text{cat}}^{-1}$).

C₂H_x (ethane and ethylene) products were formed immediately on exposure of Mo/H-ZSM-5 to CH₄ at 973 K whereas benzene evolution was observed only after an induction period of ~0.6 ks and reached a maxima at ~15.5 ks after complete carburization of (Mo₂O₅)²⁺ dimers to MoC_x (Fig. 1(c) and (d)) (C:Mo $\sim 8.5 \pm 1.0$ deposited after ~15.5 ks). C₂H_x rate monotonically increased to a steady value of $\sim 6 \times 10^{-5} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ whereas benzene, toluene, and naphthalene net formation rates achieved maxima of $2.70 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$, $1.21 \times 10^{-5} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$, and

$5.67 \times 10^{-5} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ respectively before monotonically decreasing at longer TOS (Fig. 1(d) and (e)). Forward rate of C_6H_6 formation (R_{for}) was calculated for the stoichiometric reaction of CH_4 to H_2 and C_6H_6 (equation 1) on Mo/H-ZSM-5 at 973 K using net rate of benzene formation (R_{net}) and effluent hydrogen, benzene, and CH_4 pressures in the regime (12 – 22 ks TOS) in which R_{net} was invariant. Using $R_{\text{net}} \sim 2.7 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ and $\eta \sim 0.5$ from equations 2 and 3 with $K_{\text{eq}} = 0.0302$ [4], we obtained $R_{\text{for}} \sim (5.05 \pm 0.09) \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$. The net and forward rates of benzene formation are similar to that previously reported for CH_4 DHA on Mo/H-ZSM-5 at 950 K– 973 K. [5,25,26] Mo/H-ZSM-5 showed near equilibrium conversion ($\sim 10\%$) at 973 K after carburization was complete at ~ 15.5 ks and monotonically decreased at long TOS (exceeding ~ 26 ks) (Fig. 1(e)).

$$\eta = \frac{p_{\text{C}_6\text{H}_6}^6 p_{\text{H}_2}^3}{p_{\text{CH}_4} K_{\text{eq}}} \quad (2)$$

$$R_{\text{for}} = \frac{R_{\text{net}}}{(1-\eta)} \quad (3)$$

Catalyst deactivation with TOS can be attributed to continuous buildup of carbonaceous deposits within zeolite channels which leads to reduction in Brønsted acid sites, thus inhibiting formation of aromatics, as evidenced via chemical titration with dimethyl ether, XPS, ion-scattering spectroscopy, and FT-IR measurements. [3,4,21,22] We observed benzene and naphthalene selectivity to be $\sim 67\%$ and $\sim 21\%$ respectively at ~ 15 ks TOS, typical for CH_4 DHA reactions on Mo/H-ZSM-5. [6,27] Aromatic selectivity decreased at longer TOS with a concurrent increase in C_2H_x selectivity, consistent with deactivation of oligomerization acidic sites in zeolites by coke deposition. [5,21]

Hydrogen co-feed studies at different catalyst loadings (0.1 – 1.0 g Mo/H-ZSM-5) and H₂:CH₄ co-feeds (0.03 – 0.11 molar ratio) at 950 K by Bedard et al.^[4] demonstrated that hydrogen does not (i) cause any irreversible structural or chemical modification to MoC_x moieties present in the catalyst and (ii) have any kinetic effect on the rate-limiting step of CH₄ DHA. Net benzene formation rates were lower in presence of hydrogen but R_{for} (equation 1) was invariant demonstrating that the abundant H₂ formed in catalyst bed limited aromatics production by enhancing the approach to equilibrium. This implies that single pass CH₄ conversion for CH₄ DHA can be enhanced by removal of hydrogen.

We performed CH₄ DHA on pre-carburized MoC_x/H-ZSM-5 formulations at 973 K as shown in Fig. 1(f). Initially, Mo/H-ZSM-5 exhibited a transient profile for ~15.5 ks where (Mo₂O₅)²⁺ dimers were carburized to MoC_x species with O_{removed}:Mo ~ 2.44 ± 0.1 (Table S1 and Fig. 1(f) catalyst labeled as Mo/H-ZSM-5). Subsequently, CH₄ DHA on the carburized sample (Fig. 1(f) labeled as MoC_x/H-ZSM-5) showed no induction period in aromatics formation because of the presence of catalytically active MoC_x moieties from pre-carburization. MoC_x/H-ZSM-5 formulation showed characteristics of Mo/H-ZSM-5 for CH₄ DHA after complete carburization of Mo-oxo species including (i) <10% CH₄ conversion (equilibrium conversion for 6CH₄ ↔ C₆H₆ + 9H₂ at 973 K) that decreased with TOS, (ii) benzene, toluene, and naphthalene as major products with C₂H_x formed at < 3% carbon selectivity, (iii) steady benzene formation rate for ~6 ks that subsequently declined with TOS, and (iv) a shift in product selectivity towards C₂H_x at longer TOS (Fig. 1(f)). The R_{for} was ~ (4.92 ± 0.06) × 10⁻⁴ mol s⁻¹mol_{Mo}⁻¹. HAADF-STEM of Mo/H-ZSM-5 after ~15.5 ks CH₄ reaction (Fig. 1(b)(iii)) showed Mo containing particles with sizes >2 nm (grey arrows) and Mo containing clusters <1.5 nm where concentration of particles (likely on external zeolite surface) and clusters increases after ~150 ks CH₄ reaction (Fig. 1(b)(iv)), suggesting the

change in morphology of some Mo species from atomically dispersed to agglomerates of MoC_x on CH₄ exposure at 973 K.^[28] Induction periods corresponding to carburization dynamics are avoided when initiating CH₄ DHA with pre-carburized catalyst formulations and allows for assessment of effects of a hydrogen-absorbent function on mitigating thermodynamic equilibrium limitations in CH₄ DHA.

Physical mixtures of Zr metal and MoC_x/ZSM-5 were constituted in an inert environment to avoid oxidation of MoC_x species due to their oxophilic nature.^[4,11] CH₄ flow over Zr particles at ~973 K did not yield any products (Fig. S4). Interpellet mixtures (2:1 weight ratio) of Zr metal and MoC_x/H-ZSM-5 CH₄ DHA catalyst showed maximum single-pass CH₄ conversion ~27% due to alleviation of thermodynamic equilibrium constraints (~10% equilibrium conversion) (Fig. 2(a)). Benzene, toluene, and naphthalene were major aromatic products observed (> 92% carbon selectivity) with xylenes, C₁₀⁺, and C₂H_x (ethane and ethylene) as minor products with < 6% carbon selectivity. CH₄ conversion, benzene, toluene, and naphthalene formation rates increased monotonically to ~27% at ~1.2 ks, $\sim 5.21 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ at ~1.2 ks, $\sim 2.84 \times 10^{-5} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ at ~1.8 ks, and $\sim 1.27 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ at ~0.5 ks, respectively, before decreasing with TOS accompanied by a concomitant increase in C₂H_x formation rate to $\sim 1.09 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{Mo}}^{-1}$ at ~9 ks (Fig. S1(a)). After an initial increase for ~0.27 ks in effluent H₂ flow rate, there was a monotonic decrease in H₂ eluted for ~5.1 ks (Fig. S1(b)) despite high CH₄ conversion and aromatics formation presumably due to in-situ absorptive H₂ removal by Zr particles resulting in hydride formation. A subsequent increase in instantaneous H₂ effluent rate after ~5.1 ks despite a continuing decrease in CH₄ conversion and aromatics formation can be attributed to saturation of Zr particles with hydrogen leading to reduction in hydrogen-removal sites in catalyst bed.

Benzene, naphthalene, toluene, and C_2H_x instantaneous selectivity calculated on a carbon basis were ~60%, ~30%, ~3%, and ~2%, respectively, at ~27% CH_4 conversion at ~0.3 ks TOS. The identity and sequence of appearance of products remained unchanged for $MoC_x/H-ZSM-5$ and $Zr + MoC_x/H-ZSM-5$ suggesting that bifunctional pathways effecting CH_4 DHA were unperturbed upon Zr addition. The observed enhancement in CH_4 conversion and aromatic product rates (Fig. S2) can be explained as a consequence of in-situ H_2 removal resulting in accelerated CH_4 conversion to aromatics.

Cumulative aromatic product selectivity (defined as ratio of aromatic product formed, in moles carbon, to total products observed, in moles carbon) of CH_4 DHA is retained on Zr addition leading to enhancement of aromatic yields (benzene, naphthalene, toluene, xylenes, C_{10}^+ , C_2H_x) and CH_4 turnovers (Fig. 3 and S3 and Table S1) where cumulative product yield at TOS, t , is defined as total number of moles of product formed per Mo at the end of time, t . A 2.1-fold increase in CH_4 converted with a concurrent 1.4, 1.6, 2.1, 2.1, and 5.4-fold increase in C_2H_x , benzene, naphthalene, toluene, and C_{10}^+ yields respectively (after 8.7 ks TOS, Table S1) were achieved via Zr and $MoC_x/ZSM-5$ interpellet mixtures as compared to $MoC_x/ZSM-5$. Concurrently, a 0.84x decrease in H_2 yield in reactor effluent was observed for $Zr + MoC_x/ZSM-5$ evidencing that Zr absorbs hydrogen (as discussed below) formed during CH_4 DHA. Catalyst deactivation evident from decreasing CH_4 conversion and product rates with TOS for $Zr + MoC_x/H-ZSM-5$ was faster as compared to $MoC_x/H-ZSM-5$ (Fig. 2 and S2) which can be a consequence of two factors: (i) gradual saturation of hydrogen-absorbing sites due to stoichiometric reduction of absorbent Zr to form a hydride and/or (ii) an increase in rate of deposition of unsaturated carbonaceous species owing to hydrogen removal leading to a reduction in available Brønsted acid sites for chain growth reactions. Our results to-date do not allow us to distinguish between these two scenarios. We

calculate ~3.46 C per Mo is deposited from a total of ~35.85 mol_{CH₄} mol_{Mo}⁻¹ CH₄ converted (after 8.7 ks TOS) with Zr addition (equation 4) while ~1.74 C per Mo is deposited from ~35.39 mol_{CH₄} mol_{Mo}⁻¹ converted (after 14.7 ks TOS) by a MoC_x/H-ZSM-5 formulation evincing the high efficiency of this polyfunctional catalyst formulation to convert CH₄ to aromatic products.

$$C_{\text{product}} = (2 \times C_2H_x + 6 \times C_6H_6 + 7 \times C_7H_8 + 8 \times C_8H_{10} + 10 \times C_{10}H_8 + 11 \times C_{10}^+) \quad (4)$$

The hydrogen absorption capacity of Zr metal at 973 K was determined by H₂ uptake experiments (Fig. 4 and S5 and Table S2) at different H₂ uptake pressures (3.28 – 95.13 kPa). Proportional decrease in breakthrough time and heavyside functions for uptake curves demonstrate that rate of H₂ uptake on Zr metal is not kinetically relevant and transport of H₂ from MoC_x moieties in zeolite to Zr limits bulk H₂ absorption by Zr during CH₄ DHA at 973 K. Temperature-programmed-desorption (TPD) at ~1193 K in helium flow following H₂ uptake (Fig. 4(b) and (d)) resulted in stoichiometric removal of absorbed H₂ demonstrating regeneration of Zr after H₂ absorption. These results demonstrate that (i) Zr metal absorbs H₂ at ~973 K consistently across a large H₂ pressure range (3.28 – 95.13 kPa) to form ZrH_{1.75}, and (ii) all absorbed hydrogen can be removed by helium TPD at ~1193 K to regenerate Zr metal. Bulk crystalline characteristics of metallic Zr and stoichiometry of Zr hydride post-hydrogen uptake were confirmed by X-ray diffraction (Fig. 4(e)).

The hydrogen-absorption function of polyfunctional Zr + MoC_x/H-ZSM-5 catalyst formulation was regenerated by treating the catalyst in helium flow at ~973 K after performing CH₄ DHA for ~3.6 ks resulting in above-equilibrium CH₄ conversions (equilibrium conversion ~10%) during each reaction-regeneration cycle (~ 22 – 15 % maximum conversion) (Fig. 2(a)). The Zr + MoC_x/H-ZSM-5 catalyst formulation consistently converted higher amounts of CH₄ (~ 10.73 –

19.8 mol mol_{Mo}⁻¹) compared to MoC_x/H-ZSM-5 (~ 8.34 mol mol_{Mo}⁻¹) at the end of each reaction cycle (Fig. 2(b) and Table S3). This regeneration protocol does not regenerate the Brønsted acid sites lost due to formation of unsaturated carbonaceous species in zeolite channels which would account for lack of complete regeneration post helium flush. Hydrogen stoichiometrically absorbed by Zr during CH₄ reaction desorbed during helium treatment at 973 K (Fig. S6).

Thermal treatment in helium flow (~0.83 cm³ s⁻¹) at ~1193 K of Zr + MoC_x/H-ZSM-5 following CH₄ DHA reaction at 973 K for ~9 ks (Fig. S1) resulted in H₂ and CH₄ elution from the reactor (Fig. 2(c)) presumably due to hydrogen desorption from Zr hydride and hydrogen-assisted hydrogenolysis of carbonaceous species. Removal of carbon deposits from Mo/H-ZSM-5 DHA catalysts by treatment in H₂ flow post-reaction at 973 K has been previously reported.^[22] The amount of hydrogen absorbed/accumulated during each CH₄ reaction on Zr + MoC_x/H-ZSM-5 (Tables S1 and S2) was calculated using equation 5. This calculation resulted in H_{missing}:Zr ~1.48 (Table S1) while quantification of desorbed hydrogen during post-reaction TPD resulted in H:Zr ~1.60, suggesting that all H₂ absorbed by Zr during CH₄ DHA was removed by desorption at ~1193 K. C:Mo ~ 1.69 was removed as CH₄ during TPD which was less than C:Mo ~ 3.46 deposited during reaction presumably due to the inability of hydrogen to hydrogenolyze all carbonaceous deposits.

$$H_{\text{missing}} = (2 \times H_2 + 4 \times C_2H_x + 6 \times C_6H_6 + 8 \times C_7H_8 + 10 \times C_8H_{10} + 8 \times C_{10}H_8 + 10 \times C_{10}^+) - (4 \times CH_4 \text{ reacted}) \quad (5)$$

In summary, a polyfunctional formulation comprising of MoC_x/H-ZSM-5 and Zr metal enhanced maximum CH₄ conversion (~27%), synthesis rates of aromatics, and benzene, naphthalene, toluene, xylene, and C₁₀⁺ product yields (1.4 – 5.4 times) as compared to MoC_x/H-

ZSM-5 due to hydrogen absorption by Zr without any deleterious effect on C₂-C₁₀ product selectivity. The absorptive-hydrogen removal function could be regenerated by thermal treatment in helium at 973 K resulting in above equilibrium CH₄ conversions (~ 22 – 15%) in successive reaction-regeneration cycles. We envision that a mathematical formulation of appropriate time and length scales for kinetic, diffusive, and convective phenomena in this polyfunctional catalytic system would reveal avenues for its further improvement.

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References

- [1] J. H. Lunsford, *Catal. Today* **2000**, 63, 165–174.
- [2] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, 417, 507–514.
- [3] D. Wang, J. H. Lunsford, M. P. Rosynek, *J. Catal.* **1997**, 169, 347–358.
- [4] J. Bedard, D. Y. Hong, A. Bhan, *J. Catal.* **2013**, 306, 58–67.
- [5] H. S. Lacheen, E. Iglesia, *J. Catal.* **2005**, 230, 173–185.
- [6] H. S. Lacheen, E. Iglesia, *Phys. Chem. Chem. Phys.* **2005**, 7, 538–547.
- [7] B. M. Weckhuysen, D. Wang, M. P. Rosynek, J. H. Lunsford, *J. Catal.* **1998**, 175, 347–351.

- [8] N. Kosinov, F. J. A. G. Coumans, G. Li, E. Uslamin, B. Mezari, A. S. G. Wijkema, E. A. Pidko, E. J. M. Hensen, *J. Catal.* **2017**, *346*, 125–133.
- [9] W. Li, G. D. Meitzner, R. W. Borry III, E. Iglesia, *J. Catal.* **2000**, *191*, 373–383.
- [10] I. Vollmer, B. Van Der Linden, S. Ould-Chikh, A. Aguilar-Tapia, I. Yarulina, E. Abou-Hamad, Y. G. Sneider, A. I. O. Suarez, J.-L. Hazemann, F. Kapteijn, et al., *Chem. Sci.* **2018**, *9*, 4801–4807.
- [11] N. Kosinov, F. J. A. G. Coumans, E. Uslamin, F. Kapteijn, E. J. M. Hensen, *Angew. Chemie Int. Ed.* **2016**, *55*, 15086–15090.
- [12] N. Kosinov, A. S. G. Wijkema, E. Uslamin, R. Rohling, F. J. A. G. Coumans, B. Mezari, A. Parastayev, A. S. Poryvaev, M. V. Fedin, E. A. Pidko, et al., *Angew. Chemie Int. Ed.* **2018**, *57*, 1016–1020.
- [13] B. Li, S. Li, N. Li, H. Chen, W. Zhang, X. Bao, B. Lin, *Microporous Mesoporous Mater.* **2006**, *88*, 244–253.
- [14] I. Vollmer, G. Li, I. Yarulina, N. Kosinov, E. J. Hensen, K. Houben, D. Mance, M. Baldus, J. Gascon, F. Kapteijn, *Catal. Sci. Technol.* **2018**, *8*, 916–922.
- [15] J. Gao, Y. Zheng, J.-M. Jehng, Y. Tang, I. E. Wachs, S. G. Podkolzin, *Science (80-.)*. **2015**, *348*, 686–690.
- [16] I. Lezcano-Gonzalez, R. Oord, M. Rovezzi, P. Glatzel, S. W. Botchway, B. M. Weckhuysen, A. M. Beale, *Angew. Chemie - Int. Ed.* **2016**, *55*, 5215–5219.
- [17] P. T. Tanev, D. E. Gerwien, S. Miao, A. T. Simpson, E. C. Howland, S. S. Lim, **2016**, U.S. Patent 0368836 A1.

- [18] A. I. Olivos Suarez, Á. Szécsényi, E. J. M. Hensen, J. Ruiz-Martínez, E. A. Pidko, J. Gascon, A. I. Olivos-Suarez, À. Szécsényi, E. J. M. Hensen, J. Ruiz-Martinez, et al., *ACS Catal.* **2016**, 6, 2965–2981.
- [19] B. R. Goodman, K. C. Hass, W. F. Schneider, J. B. Adams, *Catal. Letters* **2000**, 68, 85–93.
- [20] Y.-H. Kim, R. W. Borry, E. Iglesia, *Microporous Mesoporous Mater.* **2000**, 35–36, 495–509.
- [21] B. M. Weckhuysen, M. P. Rosynek, J. H. Lunsford, *Catal. Letters* **1998**, 52, 31–36.
- [22] D. Wang, J. H. Lunsford, M. P. Rosynek, *Top. Catal.* **1996**, 3, 289–297.
- [23] F. Solymosi, A. Szöke, *Appl. Catal. A Gen.* **1998**, 166, 225–235.
- [24] G. Wang, C. Gao, X. Zhu, Y. Sun, C. Li, H. Shan, *ChemCatChem* **2014**, 6, 2305–2314.
- [25] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági, A. Oszkó, *J. Catal.* **1997**, 165, 150–161.
- [26] S. Liu, L. Wang, R. Ohnishi, M. Ichikawa, *J. Catal.* **1999**, 181, 175–188.
- [27] Z. Liu, M. A. Nutt, E. Iglesia, *Catal. Letters* **2002**, 81, 271–279.
- [28] C. H. L. Tempelman, X. Zhu, E. J. M. Hensen, *Chinese J. Catal.* **2015**, 36, 829–837.

Figures and Tables

Figure 1. (a) Raman spectra of (i) MoO₃/H-ZSM-5 physical mixture, (ii) Mo/H-ZSM-5, and (iii) H-ZSM-5 air-treated at 973 K for 5 h. Lines shown as guide to eye for 376 cm⁻¹, 820 cm⁻¹, and 970 cm⁻¹ bands. (b) HAADF-STEM images of (i) H-ZSM-5 along [010], (ii) Mo/H-ZSM-5 along [010], (iii) MoC_x/H-ZSM-5 along [100], and (iv) Mo/H-ZSM-5 post CH₄ reaction for ~150 ks along [100]. TOS data for (c), (d), and (e) Mo/H-ZSM-5 and (f) Mo/H-ZSM-5 and MoC_x/H-ZSM-5. (c) Symbols and lines are GC and MS data respectively. ~0.21 cm³ s⁻¹ (90 vol% CH₄), Mo/H-ZSM-5 ~1.2 g, 973 K.

Figure 2. (a) CH₄ conversion vs TOS for MoC_x/H-ZSM-5 and Zr + MoC_x/H-ZSM-5 before (fresh) and after regeneration in He flow. Regenerations 1, 2, and 3 of Zr + MoC_x/H-ZSM-5 by flushing in He flow (~0.83 cm³ s⁻¹) at 973 K for 61.2 ks, 84.6 ks, and 34.2 ks respectively. MoC_x/H-ZSM-5 ~1.2 g, Zr ~2.4 g, ~0.21 cm³ s⁻¹ (90 vol% CH₄), ~973 K. Dashed black line indicates ~10% equilibrium conversion for 6CH₄ ↔ C₆H₆ + 9H₂ at 973 K. (b) Cumulative CH₄ converted from data shown in (a). (c) Effluent flow rates during He TPD post-CH₄ reaction on Zr + MoC_x/H-ZSM-5 for ~9 ks (Fig. S1).

Figure 3. Cumulative (a) CH₄ converted, (b) benzene, (c) naphthalene, (d) toluene, (e) xylenes, (f) C₁₀⁺, and (g) C₂H_x yield as a function of TOS for MoC_x/H-ZSM-5 and Zr + MoC_x/H-ZSM-5. MoC_x/H-ZSM-5 ~1.2 g, Zr ~2.4 g, ~0.21 cm³ s⁻¹ (90 vol% CH₄), reaction at ~973 K.

Figure 4. Normalized effluent flow rates during (a) H₂ uptake experiments for Zr and (b) helium TPD following H₂ uptake. (c) H:Zr molar ratio from H₂ uptake (H_{absorbed} : Zr) and helium TPD (H_{desorbed} : Zr). (d) XRD patterns of (i) Zr metal and (ii) Zr hydride formed by H₂ uptake of Zr. Zr ~2.4 g, Zr particle diameter ~ 3 × 10⁻⁴ m, feed ~1.7 cm³ s⁻¹, H₂/Ar ~ (3.28 – 95.13) kPa/balance, ~973 K. Zr metal (JCPDS PDF # 03-065-3366), ZrH_{1.66} (JCPDS PDF # 00-034-0649), and ZrH (JCPDS PDF # 00-034-0690).

Keywords: Heterogeneous catalysis, Carbides, Methane dehydroaromatization, Polyfunctional catalysis, Metal additive

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