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Improving HSAPO-34 methanol-to-olefins turnover capacity by seeding the hydrocarbon pool

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Abstract

Seeding the hydrocarbon pool before exposure to methanol ensures the presence of active olefinic and aromatic chain carriers in the HSAPO-34 cavity before the first methanol-to-olefins turnover. The primordial hydrocarbon pool enables the introduction, at low turnover numbers, of chain propagation steps that compete with methanol transfer dehydrogenation mediated chain termination steps, thereby increasing the fraction of converted methanol used for productive turnovers during methanol-to-olefins catalysis over HSAPO-34. Seeding the hydrocarbon pool results, concurrently, in higher light olefin yields and lower rates of carbon loss. The increasing relative preponderance of methanol transfer dehydrogenation steps with increasing methanol pressure renders seeding more effective at higher methanol pressures. Under the conditions used in this study, seeding appears to accelerate the buildup of the hydrocarbon pool without significantly altering its composition. The results reported here outline a strategy for mitigating the deleterious effects of methanol transfer dehydrogenation reactions while reemphasizing their primacy in effecting catalyst deactivation during methanol-to-olefins conversion.

1 Introduction

Methanol-to-olefins (MTO) conversion – the final processing step in converting gasifiable carbon-based feedstocks to light-olefins (ethene and propene)^[1] – is an autocatalytic process,^[2,3] the propagation steps of which can be compendiously described using a dual-cycle hydrocarbon pool schematic comprised of olefinic and aromatic methylation cycles.^[4–10] Olefins undergo successive methylation reactions as part of the olefin methylation cycle to from higher olefins, which can crack to form lighter olefins like ethene, propene, and butenes, or undergo hydrogen transfer and cyclization reactions to form aromatics, that can then participate in the aromatic cycle. Methylbenzene molecules constituting the aromatic cycle act as co-catalytic scaffolds, undergoing dealkylation reactions to form ethene and propene.

The dual-cycle schematic, used widely in the mechanistic interpretation of MTO data, describes the interconversion between hydrocarbon chain carriers and their role in ethene and propene formation, but does not address the transformation of active chain carriers to inactive ones. Recent work^[11–18] has helped elucidate the role of formaldehyde, formed by the transfer dehydrogenation of methanol, as an accelerant for catalyst deactivation mediated by the transformation of monocyclic to polycyclic aromatic hydrocarbons. Rates of chain termination relative to propagation necessarily increase with methanol pressure, and hence, decreasing local methanol pressures by lowering inlet methanol pressures,^[11] operating in a continuous stirred tank configuration (CSTR) instead of a plug flow reactor configuration (PFR),^[15] or using dimethyl ether as feed instead of methanol^[17,19] have all been shown to increase catalyst lifetime. These effects of local methanol pressure, in addition to the deleterious effects on catalyst lifetime observed on co-feeding formaldehyde with methanol over HSSZ-13^[11] and HZSM-5^[17] implicate formaldehyde, formed in methanol transfer dehydrogenation events, as crucial for catalyst deactivation in methanol-to-hydrocarbons conversion. Additionally, significantly higher hydrogen transfer product yields (5x greater) for methanol-containing feeds compared to pure olefin feeds, and the greater sensitivity of hydrogen

transfer product yields to contact time below 100% methanol conversion than above emphasize the relevance of methanol as a hydride donor during methanol-to-hydrocarbons conversion.^[13,14] The hydride abstractor in methanol transfer dehydrogenation steps can either be a surface methoxide or C_2^+ alkoxides (Scheme 1), with methoxides being the predominant hydride abstractors at low turnover numbers, as evinced by high initial methane selectivities on HSSZ-13 at 623K and 6.1-23kPa methanol,^[11] and the much higher contents of CH₄, CH₃D, CD₃H, and CD₄ (93%) compared to CH₂D₂ detected when CD₃ covered HSAPO-34 is pulsed with CH₃OH at 673K.^[20]



Scheme 1. Formaldehdye formation via bimolecular methanol transfer dehydrogenation involving either a methoxide (methanol disproportionation) or a C_2^+ alkoxide

Strategies proposed so far for mitigating formaldehyde-induced catalyst deactivation include suppressing methanol transfer dehydrogenation to formaldehdye by lowering local methanol pressures (vide supra), and scavenging formaldehyde, once formed, using rare-earth metal oxide domains proximal to Brønsted acid sites.^[12]. In this study, we use a hydrocarbon seed comprised of active chain carriers to lower the rate of methanol disproportionation. When starting from an empty HSAPO-34 cavity, a surface methoxide can undergo one of two reactions at low turnover numbers: abstract hydrogen from methanol or undergo nucleophilic attack via the oxygen atom to form dimethylether. By incorporating hydrocarbon chain carriers into the cavity before the first methanol-to-olefins turnover (Scheme 2), seeding should, at low turnover numbers, introduce reaction pathways for consumption of the methoxide that can compete with the deleterious methanol disproportionation reaction, thereby reducing the fraction of unproductive turnovers leading to formaldehyde formation. Xu and coworkers^[21,22] have demonstrated that pretreating HSAPO-34 with oxygenates before exposure to methanol leads to higher cumulative ethylene and propylene yields and a longer catalyst lifetime, as measured by the time required for complete catalyst deactivation. They do not, however, propose a mechanistic basis for either of these effects. Based on the observation that methanol disproportionation predominates until the hydrocarbon pool matures to an extent where propagation reaction sequences compete with methanol disproportionation and methanol dehydration to DME, we reasoned that introducing active hydrocarbon chain carriers into an otherwise empty pore *before* the first turnover should mitigate formaldehyde formation at low turnover numbers/early times-on-stream. We demonstrate, using acetaldehyde (0.02-0.5 C/H⁺) and DME (2-4.5 C/H⁺) as seed sources, that seeding the

CH₃CHO C,H,, CH₂OH **CH**₄ CH₃OH CH₃OH **CH**₄ **CH**₄ C.H.CH. Seeding HOH₂ CH₃ HOH CH₃+ CH₃ CH₃+ C+H2OH

hydrocarbon pool by pretreating the catalyst can increase light-olefin yields while simultaneously mitigating carbon loss during methanol-to-olefins catalysis over HSAPO-34.



2 Experimental

2.1 Catalyst synthesis and characterization

The synthesis procedure and material characterization for the HSAPO-34 sample used in this study have been reported elsewhere.^[12]

2.2 Acetaldehyde seeding

25.3 mg of templated HSAPO-34 (40-80 mesh) and 330 mg quartz sand (40-80 mesh, treated in 2M HNO₃, washed in deionized water, and treated under flowing dry air at 1273K for 12h) were loaded into a quartz reactor having an inner diameter of 4mm. The quartz tube was placed in a custom-built single-zone copper furnace, the temperature of which was controlled using two 250W Omega Engineering cartridge heaters (CSH-202250). The temperature was measured using a K-type thermocouple inserted axially and penetrating the top of the catalyst bed. The sample was treated in a 1%O₂/ He mixture (0.42 cm³ s⁻¹; Minneapolis Oxygen custom gas mixture UN1956) by ramping to 823K at 0.018 K s⁻¹ to remove the organic template used in zeolite synthesis. The temperature of the catalyst bed was increased to 673K under the same O₂-He atmosphere by ramping at 0.042 K s⁻¹, after which it was exposed to a flow of 0.83 cm³ s⁻¹ He (Minneapolis Oxygen, 99.997%) for 3.6ks. A 5 weight% acetaldehyde (Acros Organics, 99.5%) in deionized water solution was prepared and delivered using a syringe pump at a rate of 2.1 mol CH₃CHO $(molH^+)^{-1}$ h⁻¹ into a gas line heated to 383K. Helium was used as a diluent in the seeding experiments. Seed loadings were measured by treating the catalyst bed under a flow of $1\%O_2$ in He. After exposure to acetaldehyde for the desired amount of time (0-16h), the catalyst bed was ramped up to 823K at 0.17 K s⁻¹ under a 0.83 cm³ s⁻¹ helium flow, followed by exposure to 0.42 cm³ s⁻¹ 1%O₂ in He and 0.17 cm³ s⁻¹ Ar. The seed loading was calculated based on the amount of CO₂ evolved during this step, which was quantified using the m/z=44 peak on a Cirrus 2 quadrupole mass spectrometer system with argon as the internal standard. The H/C ratios were calculated from the ratio of H_2O and CO_2 evolved during burnoff.

2.3 Methanol-to-olefins catalysis

Aldrich CHROMASOLV HPLC grade (>99.9% purity) methanol was used in the MTO runs. The reactor setup described above with a copper furnace and internal thermocouple was used for these studies. After seeding, the catalyst was brought to reaction temperature (623K) at 0.028 K s⁻¹, kept under a 0.84 cm³ s⁻¹ flow of helium for 0.9ks, then exposed to a gas stream containing methanol, helium, and argon (internal standard for GC quantification). Reaction products were quantified using an Agilent 7890A GC system with a HP-PLOT Q column connected to a thermal conductivity detector (He as reference gas) and an HP-

1 column connected to a flame ionization detector. The argon peak on the TCD was used as the internal standard for quantification. The rate of carbon loss was calculated by subtracting the molar flow rate of carbon exiting the bed from that entering the bed. Integration of the rate of carbon loss thus obtained (molC/molH⁺/s) with respect to time then yielded the cumulative carbon loss (molC/molH⁺) at a specific time-on-stream. The conversion in all cases was significantly less than 100%; specifically, the highest conversion attained in the experiments reported in this study was 47.2%.

3 Results

3.1 Seed loading

Seed loadings increase monotonically with time of exposure to acetaldehyde before leveling off at higher values, suggesting that partial deactivation of Brønsted acid sites may occur during the seeding process. H/C atomic ratios are independent of time of exposure (Figure 1), and are equal, within error, to that of acetaldehyde (H/C atomic ratio = 2). The H/C atomic ratio suggests that the presence of aromatics in the seed (H/C<2), if any, is accompanied by the presence of hydrogen rich molecules like paraffins (H/C>2). Stoichiometric constraints necessitate that the formation of aromatics be accompanied by the concomitant formation of hydrogen-rich paraffins. The H/C ratios reported in Figure 1 suggest that not only the hydrocarbons formed during the seeding step but also the hydrocarbons *retained* within the HSAPO-34 cavity, i.e. the seed, conform to this stoichiometry, implying that active chain carriers occluded within these cavities are not hydrogen deficient relative to the methanol feed they are exposed to (CH₃OH = CH₂ + H₂O; H/C atomic ratio = 2).



Figure 1. Seed loading (left) and H/C atomic ratio (right) in acetaldehyde seeding experiments over HSAPO-34; seeding conditions: 673K, 0.1 kPa CH₃CHO, 2.1 (mol CH₃CHO) (molH⁺)⁻¹ h⁻¹

3.2 Effect of seeding on product yields and carbon loss

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Three different seed loadings (0.02, 0.1, and 0.5 C/H⁺) were used to study the effect of seeding on MTO catalysis by choosing exposure times corresponding to the three target seed loadings (Figure 1). Consistent with the dual-cycle mechanism, early times-on-stream in MTO catalysis are characterized by induction periods during which accumulation of olefinic and aromatic chain carriers occurs.^[23–25] Seeding with acetaldehyde introduces chain carriers into the SAPO-34 cavity before the first turnover and their concentration increases with increasing seed loading. Cumulative ethene and propene yields – the total moles of ethene and propene formed in an MTO run up to a certain time-on-stream – increase monotonically with seed loading (Figure 2), consistent with increasing chain carrier concentration with seed loading. The abscissae in Figure 2 represent the time-on-stream multiplied by methanol molar space velocity, which equates to the cumulative moles of methanol fed to the reactor per mole Brønsted acid sites. Methane can be formed either via methanol reacting with a surface methoxide forming methane and an adsorbed hydroxymethyl species or via hydrocarbon chain carriers reacting with a surface methoxide forming methane and a C₂⁺ alkoxide. Rates of carbon loss indicate that seeding inhibits the former reaction (*vide infra*), suggesting that increasing methane yields with seed loading (Figure 2) are caused by increasing rates of hydrogen transfer from hydrocarbon chain carriers to surface methoxides.





Seeding conditions: 673K, 0.1 kPa CH₃CHO, 2.1 (mol CH₃CHO) (molH⁺)⁻¹ h⁻¹ Reaction conditions: 623K, 6.1 kPa MeOH, 923 (mol MeOH) (molH⁺)⁻¹ h⁻¹

Seeding should, as a consequence of the predominance of methanol disproportionation at low turnover numbers, mitigate carbon loss by introducing competing reaction pathways for the consumption of the

surface methoxide (*vide supra*). Cumulative carbon losses calculated from a carbon balance (carbon flow rate in – carbon flow rate out) decrease monotonically with seed loading (Figure 3), validating the mechanistic hypothesis predicating this study. Additionally, the increasing relative preponderance of methanol disproportionation with methanol pressure dictates that the same seed loading should be more effective at mitigating carbon loss at higher methanol pressures relative to lower methanol pressures. Although this effect of methanol pressure is not clearly discernible at the lowest seed loading used in our study (0.02 C/H^+ ; Figure 4), clear trends appear in the case of higher seed loadings ($0.1 \text{ and } 0.5 \text{ C/H}^+$; Figure 4), with carbon loss decreasing monotonically with methanol pressure. Additionally, this concept is not limited to acetaldehyde as the seed source. Monotonically increasing trends in light-olefin yields and monotonically decreasing trends in carbon loss with seed loading were achieved using DME as a seed source instead of acetaldehyde (Supplementary Information).



Figure 3. Effect of seeding on cumulative carbon loss as a function of time-on-stream Seeding conditions: 673K, 0.1 kPa CH₃CHO, 2.1 (mol CH₃CHO) (molH⁺)⁻¹ h⁻¹ Reaction conditions: 623K, 6.1 kPa MeOH, 923 (mol MeOH) (molH⁺)⁻¹ h⁻¹



Figure 4. Effect of seeding on cumulative carbon loss as a function of turnover number at various methanol pressures (6.1-30 kPa); 0.02 C/H⁺ (left), 0.1 C/H⁺ (middle), and 0.5 C/H⁺ (right)

Seeding conditions: 673K, 0.1 kPa CH₃CHO, 2.1 (mol CH₃CHO) (mol H⁺)⁻¹ h⁻¹

Reaction conditions: 623K, 6.1-30 kPa MeOH, 923 (mol MeOH) (mol H⁺)⁻¹ h⁻¹

3.3 Effect of seeding on the evolution of the hydrocarbon pool

Turnover number – the cumulative moles of product carbon formed per mole Brønsted acid sites – is a more rigorous descriptor of reaction progress compared to the more commonly used time-on-stream.^[11,23] When plotted against turnover number as a descriptor of reaction progress, ethene and propene yields do not vary with seed loading (Figure 5). Cumulative product yields as a function of turnover number that are invariant with seed loading suggest that seeding does not necessarily alter the *speciation* of active chain carriers constituting the hydrocarbon pool; instead, it merely serves to *accelerate* the evolution of the hydrocarbon pool, as reflected in the greater number of turnovers it effectuates over a given length of time-on-stream. Seeding the hydrocarbon pool under the conditions used in this study has a twofold effect on HSAPO-34 MTO performance at low turnover numbers/early times-on-stream: a reduction in the fraction of methanol lost as (inactive) polycyclic aromatic hydrocarbons by inhibiting methanol transfer dehydrogenation chemistry, and an acceleration of the buildup of the hydrocarbon pool without significantly altering the constitution of active chain carriers. Yield of C₂-C₄ paraffins, necessitated by stoichiometric constraints, also tracks with turnover number, and is invariant with seed loading (Figure 5), consistent with a seed H/C atomic ratio of 2 (Figure 1) identical to that of the methanol feed (CH₂ + H₂O).



Figure 5. Cumulative ethene, propene, and C₂-C₄ paraffin yield as a function of turnover number for acetaldehyde seeding experiments

Seeding conditions: 673K, 0.1 kPa CH₃CHO, 2.1 (mol CH₃CHO) (mol H⁺)⁻¹ h⁻¹

Reaction conditions: 623K, 6.1-30 kPa MeOH, 923 (mol MeOH) (mol H^+)⁻¹ h⁻¹

4 Conclusions

Introduction of active chain carriers into the HSAPO-34 cavity by seeding the hydrocarbon pool results in a reduction in the length of the induction period, leading to cumulative ethene and propene yields that increase monotonically with seed loading. By introducing, at low turnover numbers, reaction pathways that compete with methanol disproportionation and transfer dehydrogenation, seeding enables a reduction in carbon loss at equivalent times-on-stream. The higher the methanol pressure, the greater the extent of carbon loss mitigation, consistent with the greater relative preponderance of methanol disproportionation and transfer dehydrogenation and reaction conditions used in this study, seeding accelerates the buildup of chain carriers constituting the hydrocarbon pool without significantly altering their identity. Favorable effects of seeding on HSAPO-34 MTO performance have been demonstrated using both acetaldehyde and DME as carbon sources for seeding, and point to the general efficacy of this strategy in mitigating deleterious effects of methanol transfer dehydrogenation on methanol-to-olefins catalysis.

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Supporting Information

Results of the DME seeding experiments are reported as supplementary figures, and are available free of charge via the internet.

Keywords

Methanol-to-hydrocarbons, zeolites, deactivation

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Controlled introduction of methanol-to-olefins conversion chain carriers into the HSAPO-34 cavity before the first turnover is shown to simultaneously accelerate the buildup of the hydrocarbon pool and inhibit methanol transfer dehydrogenation events responsible for catalyst deactivation without altering the speciation of active chain carriers constituting the hydrocarbon pool.

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