

Improving Methanol-to-olefins Turnover Capacity of CHA Materials by Controlling Methanol Transfer Dehydrogenation Rates

Praveen Bollini,^{1*} Aditya Bhan²

¹ Assistant Professor, Department of Chemical & Biomolecular Engineering, University of Houston, 4722 Calhoun Drive, Houston, TX 77004

² Associate Professor, Department of Chemical Engineering & Materials Science, University of Minnesota

*Corresponding author: ppbollin@central.uh.edu

Highlights

- Two strategies for improving methanol-to-olefins catalyst lifetime were developed based on a mechanistic understanding of the deactivation chemistry
- 4X reduction in carbon loss at low turnover numbers was achieved by seeding the hydrocarbon pool before exposure to methanol
- 2.5X enhancement in catalyst lifetime was achieved by cofeeding water
- Transient kinetic data was interpreted to establish a mechanistic basis for observed improvements in catalyst lifetime

1. Introduction

Methanol-to-olefins (MTO) conversion – the final processing step in converting gasifiable carbon-based feedstocks to light-olefins (ethene and propene)- is an unsteady state fluidized bed process in which catalyst lifetime is a key metric for economical process operation. Recent work¹⁻³ 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. In this study, we present two examples (seeding and water cofeeds) in which we exploit this mechanistic understanding of chemistries mediating deactivation to develop strategies for improving catalyst lifetime in methanol-to-olefins conversion. Firstly, we reasoned that introducing active hydrocarbon chain carriers into an otherwise empty pore *before* the first turnover i.e. seeding should mitigate formaldehyde formation at low turnover numbers/early times-on-stream. Significant increases in light-olefin yields (upto 2X) and reduction in carbon loss (4X) at low turnover numbers were achieved using acetaldehyde as a seed source. In the second example, we hypothesized that cofed water should react with electrophilic hydroxymethyl intermediates to form methanediol. We demonstrate that cofeeding water under MTO conditions increases formaldehyde conversion to methanediol, thereby increasing HSSZ-13 turnover capacity by a factor of 2.5. 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.

2. Methods

A 5 weight% acetaldehyde (Acros Organics, 99.5%) in deionized water solution was used in seeding experiments. Seed loadings and H/C ratios were measured by treating the catalyst bed under a flow of 1%O₂ in He. 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. Water was cofed by mixing appropriate amounts of deionized water and methanol and loading into the syringe pump before being delivered to the reactor.

3. Results and discussion

The effect of seeding was studied at three different seed loadings: $0.02\text{C}/\text{H}^+$, $0.1\text{C}/\text{H}^+$, and $0.5\text{C}/\text{H}^+$. Light olefin yields (ethane and propene) were found to increase monotonically with seed loading, consistent with the co-catalytic nature of MTO chemistry in which methylbenzene molecules act as scaffolds for light-olefin formation. Cumulative carbon loss decreased monotonically with seed loading (Figure 1, left), consistent with the hypothesis that incorporation of the seed leads to the introduction of chain propagation steps that compete with methanol transfer dehydrogenation reactions. Seeding was also found to be more effective at conditions having higher methanol pressures as a consequence of the greater relative preponderance of methanol transfer dehydrogenation at higher methanol pressures.

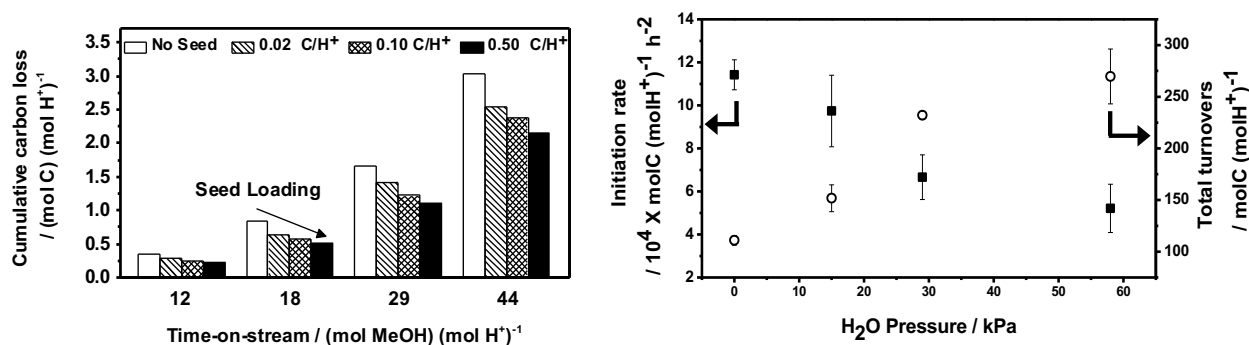


Figure 1. Effect of seeding on cumulative carbon loss as a function of time-on-stream (left), and effect of inlet water partial pressure on initiation rates and HSSZ-13 methanol-to-olefins turnover capacity (right)

Both initiation and termination rates decreased monotonically with increasing water pressure, resulting in a 2.5X enhancement in HSSZ-13 turnover capacity (Figure 1, right). Scavenging of hydroxymethyl intermediates at MTO-relevant temperatures was verified by desorbing persistent chloromethyl intermediates with water to form formaldehyde and HCl. Enhancement in turnover capacity at a certain temperature was found to correlate with the fraction of formaldehyde formed present as methanediol, suggesting that the scavenging of formaldehyde as methanediol has a major impact on catalyst lifetime.

4. Conclusions

Two strategies for improving methanol-to-olefins turnover capacity were developed by inhibiting and scavenging formaldehyde formed in methanol transfer dehydrogenation events. These results reinforce the importance of developing a detailed mechanistic understanding of chemistries mediating deactivation in hydrocarbon conversion processes.

References

- [1] Hwang, A.; Kumar, M.; Rimer, J. D.; Bhan, A. J. *Catal.* 346 (2017) 154–160.
- [2] Hwang, A.; Bhan, A. *ACS Catal.* 7 (2017) 4417–4422.
- [3] Müller, S.; Liu, Y.; Kirchberger, F. M.; Tonigold, M.; Sanchez-Sanchez, M.; Lercher, J. A. J. *Am. Chem. Soc.* 138(49) (2016) 15994–16003.

Keywords

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