

IMPROVING METHANOL-TO-OLEFINS TURNOVER CAPACITY OF CHA MATERIALS BY CONTROLLING METHANOL TRANSFER DEHYDROGENATION RATES

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Abstract

Recent work 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 over zeolite/zeotype materials. Two strategies for improving methanol-to-olefins turnover capacity on CHA materials (seeding and water cofeeds) 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 zeolite-catalyzed hydrocarbon conversion processes.

Keywords

Methanol-to-hydrocarbons; zeolites; deactivation; catalysis

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 work²⁻⁴ 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.

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Experimental

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. Transient experiments were performed by feeding dichloromethane and argon over HSSZ-13 at 673K while monitoring the reactor effluent using a mass spectrometer. In a second step, chloromethyl intermediates were then desorbed by exposing the catalyst material to a feed of water in helium (12kPa) while monitoring the reactor effluent for formaldehyde, hydrochloric acid, and water.

Results and Discussion

The effect of seeding was studied at three different seed loadings: 0.02, 0.1, and 0.5 C/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), 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 higher methanol pressures as a consequence of the greater relative preponderance of methanol transfer dehydrogenation at higher methanol pressures.

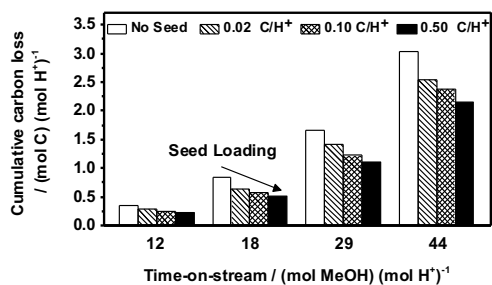


Figure 1. Effect of seeding on cumulative carbon loss as a function of time-on-stream

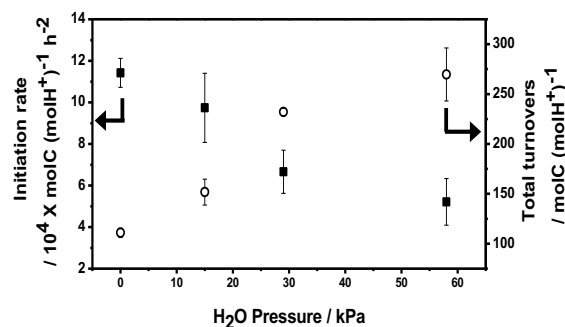


Figure 2. Effect of inlet water partial pressure on initiation rates and HSSZ-13 methanol-to-olefins turnover capacity

Both initiation and termination rates decreased monotonically with increasing water pressure, resulting in a 2.5X enhancement in HSSZ-13 turnover capacity (Figure 2). 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.

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 zeolite-catalyzed hydrocarbon conversion processes.¹

References

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