Catalysis for upgrading C_1 feedstocks

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Abstract: Monofunctional catalytic strategies to activate apolar C-H bonds in CH_4 are limited by formidable kinetic bottlenecks and thermodynamic constraints. Our efforts in circumventing these challenges rely on polyfunctional strategies that selectively scavenge byproducts to overcome thermodynamic limitations in methane upgrading. We illustrate the efficacy of polyfunctional strategies for upgrading of C_1 sources with accelerated rates and increased desired selectivity based on the systematic assessment of mechanisms and site requirements involved in the non-oxidative conversion of methane.

Keywords: methane dehydroaromatization, hydrogen-selective adsorbent, continuous reaction-regeneration.

1. Introduction

Non-oxidative CH_4 reactions on Mo/ZSM-5 produce ethene, benzene, and naphthalene with high selectivity through bifunctional cascades. MoC_x species catalyze the primary reaction converting methane to ethene/ethane, zeolitic H^+ sites couple olefins for chain growth, and MoC_x species catalyze dehydrogenation of aliphatics to aromatics. Yields of ethylene, benzene, and naphthalene on Mo/H-ZSM-5, under typical CH_4 dehydroaromatization conditions, approach values prescribed by equilibrium ($6CH_4 \leftrightarrow C_6H_6 + 9H_2$; equilibrium conversion ~10% at 973 K). We discuss two distinct strategies to improve aromatics yield beyond equilibrium values in CH_4 dehydroaromatization: (i) co-processing low molecular weight oxygenates so that in effect CH_4 acts as a hydrogen carrier for deoxygenation reactions; and (ii) introducing an additional function that scavenges byproduct hydrogen thereby lifting thermodynamic constraints on attainable yields and increasing rates of products formation.

2. Experimental

Intimate mixtures of HZSM-5 (Si/Al = 11.7, CBV 2314) and MoO_3 powders (Sigma-Aldrich, 99.9%) were thermally treated in flowing air at 973K for 10 h to give Mo-oxo species within zeolite pores. After treatment, the molybdenum-to-aluminum ratio was determined to be 0.25 from elemental analysis. Chemical transient experiments show that 2.35±0.2 O/Mo are lost as CO, CO_2 and H_2O during initial CH_4 reactions with MoO_x precursors in a stoichiometric reaction that leads to MoC_x consistent with the putative formation of $(Mo_2O_5)^{2+}$ dimers upon treatment of MoO_3/H-ZSM-5 physical mixtures at 973 K in air. This synthetic protocol gives a Mo/H-ZSM-5 formulation with nearly identical steady-state benzene formation rates (2.5×10^{-4} mol (g-atom Mo)$^{-1}$ s^{-1}) as those reported previously for similarly prepared formulations [1].

3. Results and discussion

We report that co-processing oxygenates (HCOOH, CH_3COOH, CO_2) and CH_4 results in a two-zone, staged reactor configuration consisting of upstream oxygenate/CH_4 reforming and downstream CH_4 dehydroaromatization at 950K and atmospheric pressure. Forward rates of C_6H_6 synthesis are unaffected by the introduction of an oxygenate co-feed after rigorously accounting for the thermodynamic reversibility caused by the H_2 produced in oxygenate reforming reactions and the fraction of the bed unavailable for methane dehydroaromatization reactions ($6CH_4 \leftrightarrow C_6H_6 + 9H_2$). All effects of co-processing oxygenates with CH_4 on Mo/H-ZSM-5 formulations can therefore be kinetically described in terms of an approach to equilibrium for methane dehydroaromatization [2-4].

Benzene and naphthalene rates are enhanced while hydrogen synthesis rates are suppressed upon addition of Zr particles to Mo/H-ZSM-5 methane dehydroaromatization catalysts in interpellet mixtures (Figure 1 and Table 1). We attribute this enhancement to the formation of Zr-hydrides under reaction conditions, thereby lifting thermodynamic constraints for methane dehydrogenation. Subsequent thermal treatment of the polyfunctional catalyst results in desorption of hydrogen and in regeneration of the Zr-adsorbent. The transients in rates and selectivity noted for the Zr + Mo/H-ZSM-5 formulation simply represent spatial gradients in hydrogen concentration across the reactor length conferred by the gradual, stoichiometric reduction of the adsorbent to form a hydride.

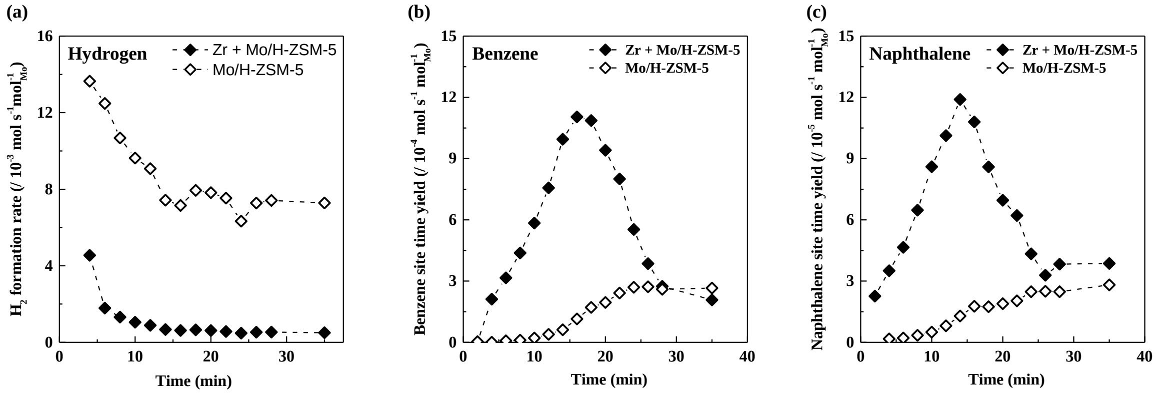

Figure 1. (a) Hydrogen, (b) Benzene, and (c) Naphthalene synthesis rates as a function of time-on-stream during reactions of CH_4/Ar (90%/balance; ~0.22 cm^3s^{-1}) mixtures at 950K, 0.4g Mo/H-ZSM-5 and 0.4g Mo/H-ZSM-5 + 2.4g Zr interpellet mixture, 1 atm.

Table 1. Product yield for Mo/H-ZSM-5 catalyst (0.4 g) and for a 6:1 weight ratio interpellet mixture of Zr (2.4 g) and Mo/H-ZSM-5 catalyst (0.4 g) at 950 K and 1 atm. CH_4/Ar = 90 vol %/balance, flow rate ~0.22 cm^3 s^{-1}.

Product yield at 35 min. on-stream ($mol_{Product}$ mol_{Mo}^{-1})	**Mo/H-ZSM-5 (0.4 g)**	**Mo/H-ZSM-5 (0.4g) + Zr (2.4g)**
C_2	0.145	0.096
Benzene	0.336	1.250
Naphthalene	0.038	0.139

4. Conclusions

Our results demonstrate (i) a critical limitation in attempting to couple deoxygenation and dehydrogenation chemistries on Mo/H-ZSM-5 formulations by co-processing oxygenates and CH_4 – the preferential selectivity to remove oxygen as CO instead of as H_2O – and (ii) the efficacy of polyfunctional formulations that comprise a hydrogen-selective adsorbent with the Mo/H-ZSM-5 methane dehydroaromatization catalyst in enhancing selectivity to desired aromatic products in non-oxidative methane conversion.

References

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