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Tuning the selectivity of methanol-to-hydrocarbons conversion on H-ZSM-5 by co-processing olefin or aromatic compounds

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ABSTRACT

The product selectivity of dimethyl ether (DME) conversion to hydrocarbons on H-ZSM-5 was systematically tuned by co-feeding small amounts of ^{13}C-propene and ^{13}C-toluene (4 kPa) with ^{12}C-DME (70 kPa) under isoconversion conditions (20.8–22.7 C%) at 548 K. The selectivity to ethene (14.5–18 C%) and aromatics (7.1–33.7 C%) increased while selectivity to C_4–C_7 aliphatics (42.8–16.9 C%) decreased with increasing amounts of toluene (0–4 kPa) in the co-feed. Similar trends were also observed at lower conversions (4.6–5.1 C%) at 548 K and at higher temperatures (623 K), showing that the olefin-to-aromatic ratio can be used as a parameter to propagate the olefin- and aromatic-based carbon pools to varying extents within the range of conditions studied in this work. The co-reaction of ^{13}C-propene with ^{12}C-DME showed that C_5–C_7 olefins are formed almost exclusively from methylation reactions while butenes are formed from both olefin cracking and methylation reactions. The high fraction of propene (55.1%) with at least one ^{12}C indicated that a large fraction of propene is a product of olefin cracking reactions. Under conditions in which the aromatic-based cycle is dominant (increasing amounts of toluene in the co-feed), both ethene and propene contained approximately 10% ^{13}C atoms, showing that when the olefin-based cycle is suppressed, these light olefins primarily originate from the aromatic-based cycle. The ^{13}C content of toluene in the effluent was unchanged compared to that in the ^{13}C-toluene feed, implying that toluene is not formed as a significant product. Additionally, at least 9.8% of *p*-xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene isotopomers were entirely ^{12}C-labeled, while less than 2% of toluene and *o*-xylene isotopomers were entirely ^{12}C-labeled, showing that under the conditions studied in this work, cyclization reactions occur predominantly for C_{8+} aliphatics to form *p*-xylene and larger aromatics. Because the olefin- and aromatic-based cycles are not isolated from one another, understanding communication between the two cycles is an important step in controlling selectivity of MTH on H-ZSM-5.

1. Introduction

Nontraditional carbon-based feedstocks will be critical in supplying the planet with fuel and chemicals in the future. The conversion of methanol to hydrocarbons (MTH) over an acidic zeolite catalyst has received considerable attention since its discovery by Mobil Research Laboratories in 1976 [1], both for its ability to grow carbon chains and because methanol can be produced from any gasifiable carbon-based feedstock, including natural gas [2], coal [3,4], and biomass [5,6]. Using either methanol or its dehydration product, dimethyl ether, as a feed, a wide variety of hydrocarbons can be formed, such as gasoline-range hydrocarbons (methanol to gasoline, MTG) [1,7–14], light olefins (methanol to olefins, MTO) [15–19], branched alkanes [20,21], and aromatics [22–24], though not typically with high selectivity to any particular class of hydrocarbons [10,25].

Although early mechanistic work in MTH focused on the formation of the first carbon–carbon bond [8,14], recent experimental [13,26] and theoretical [27–29] work has shown that direct methanol coupling does not occur, because of the requirement for unstable intermediates and high activation energy barriers. Experiments using fractionally distilled methanol demonstrated that the catalyst induction period for methanol to hydrocarbons on H-ZSM-5 and H-SAPO-34 is so sensitive to the impurity concentration in the methanol feed that if direct C_1 coupling does occur, it operates at a rate so low that it is irrelevant compared to the rate at which trace impurities initiate the reaction [13]. Methanol conversion over zeolite and zeotype catalysts instead proceeds through a "hydrocarbon pool" mechanism in which carbon–carbon bond formation occurs via an indirect route wherein organic co-catalysts entrained within the zeolite pore act as scaffolds for carbon–carbon bond formation [16–18]. These organic co-catalysts undergo successive methylation reactions to eventually eliminate light olefin products such as ethene and propene. The identity of the active hydrocarbon pool species is likely dependent on the zeolite or zeotype topology [30–34].

Extensive theoretical and experimental studies have focused on the role of aromatics, particularly polymethylbenzenes (polyMBs),

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as the active hydrocarbon pool species for light olefin formation. In two early studies, Mole et al. [35] noted a co-catalytic effect of toluene when co-fed with methanol over H-ZSM-5 and Langner [36] showed that the catalyst induction period decreased 18-fold when methanol was co-fed with cyclohexanol, indicating the importance of cyclic species for MTH. By reacting a series of two 20-μL pulses of methanol over H-SAPO-34, Haw and co-workers [37] showed that methylbenzenes (MBs) can act as organic co-catalysts for MTO, increasing methanol conversion from 14% to 100% between the first and second pulse. Mikkelsen et al. [24] observed the incorporation of ^{12}C atoms from benzene and toluene into ethene and propene when ^{12}C labeled aromatics were co-reacted with ^{13}C-methanol over H-ZSM-5, H-BEA, and H-MOR, providing further evidence that polymethylbenzenes are active hydrocarbon pool species for light olefin formation. Isotopic switching experiments coupled with HF dissolution of the spent catalyst have shown that on large-pore zeolites (H-BEA and H-SAPO-34), pentaMB, hexaMB, and ethene have similar ^{13}C content and, therefore, penta- and hexaMB are active for light olefin formation [32–34]. In contrast, on medium-pore zeolite, H-ZSM-5, the ^{13}C content of di-, tri-, and tetraMBs are similar to ethene, hence suggesting these MBs are active for olefin formation for this zeolite [30–32,34]. Experimental [7,11,37–42] and theoretical [9,23,43–48] work has postulated that light olefin formation occurs via either a paring mechanism or a side-chain mechanism. In the side-chain mechanism, gem-methylation of a MB species results in elimination of a methyl hydrogen, resulting in an exocyclic double bond, which can undergo side-chain methylation. Subsequently, the side chain can crack to form ethene or propene [35,46]. The paring mechanism is also initiated by gem-methylation of a MB, which in this mechanism results in ring contraction, generating an alkyl substituent. The alkyl substituent can then crack to form light olefins such as propene and isobutene [9,49].

In addition to aromatic hydrocarbon pool species, emerging research based on computational and experimental studies suggests that olefins also act as hydrocarbon pool co-catalysts, depending on the identity of the zeolite. Chen and Reagan [50] originally reported the autocatalytic effect of olefins for MTH and Langner [36] also noted that by co-feeding higher alcohols that readily dehydrate to linear olefins under reaction conditions, the kinetic induction period could be substantially reduced, indicating the important catalytic role of olefins in MTH. Dessau and LaPierre [51,52] proposed an olefin-based catalytic cycle for MTH in which propene is successively methylated to form higher olefin homologues, which can then crack to form lighter olefins such as propene and butene, or undergo hydrogen transfer steps to form aromatics and alkanes. ONIOM calculations over 46T zeolite clusters have shown that energy barriers for olefin methylation are of similar magnitude (60–80 kJ mol^{-1}) to those for lower methylbenzenes in H-ZSM-5, suggesting that the contribution of an olefin-based hydrocarbon pool is significant [48]. Recent work using isotopic switching experiments on the unidirectional 10-MR zeolite H-ZSM-22 has shown that aromatics are inactive on this zeolite, based on the low rate of ^{13}C incorporation into aromatics compared to olefins. Therefore, under space-limiting conditions in H-ZSM-22, MTH proceeds exclusively through an olefin-based hydrocarbon pool mechanism, resulting in a product mixture that is rich in branched alkenes [53,54]. Similar experiments have also shown the existence of an olefin-based carbon pool, as well as an aromatic-based carbon pool, on H-ZSM-5, leading to the formulation of a dual catalytic cycle for MTH on H-ZSM-5 (Scheme 1) [31].

Understanding the role these two different cycles play on H-ZSM-5 is key to understanding how selectivity for MTH can be controlled on this zeolite. In this work, we demonstrate that by co-processing small amounts of propene and toluene (total 4 kPa) with dimethyl ether (70 kPa) on H-ZSM-5 at 548 K, we can control the composition of the organic hydrocarbon pool and thus modulate the relative contributions of olefin and aromatic methylation cycles in MTH, resulting in systematic variation in the selectivity of ethene (14.5–18 C%), C_4–C_7 aliphatics (42.8–16.9 C%) and aromatics (xylenes, triMBs, and tetraMBs: 7.1–33.7 C%) at isoconversion (20.8–22.7 C%).

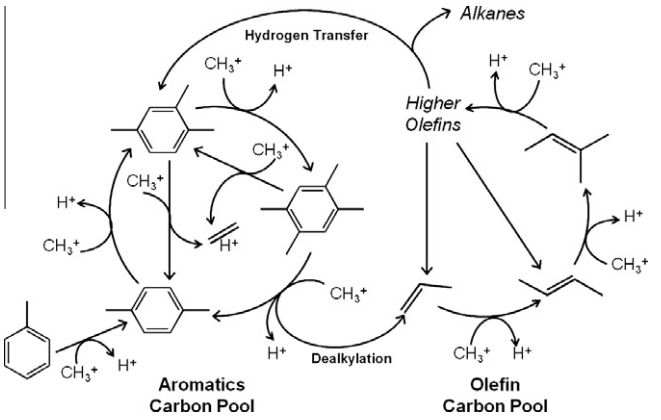
2. Materials and methods

2.1. Catalyst preparation

The catalyst H-ZSM-5, Si/Al = 42.6, was obtained in the ammonium form from Zeolyst International. Structural and chemical characterization of the H-ZSM-5 sample used in this study is reported in Section S.1 of the Supplemental Information. The silicon-to-aluminum ratio was determined by ICP–OES elemental analysis (performed by Galbraith Laboratories). The ammonium-form zeolite was sieved to obtain aggregate particle sizes between 180 and 425 μm (40–80 mesh) and treated in 1.67 $cm^3\ s^{-1}$ of dry air (20–21% O_2, <10 ppm H_2O, Minneapolis Oxygen), heated at a rate of 0.0167 K s^{-1} to 773 K, and held for 4 h to convert it to the proton-form zeolite. The catalyst was pretreated in situ in 1.67 $cm^3\ s^{-1}$ of helium flow (99.995% purity, Minneapolis Oxygen) at 773 K overnight at a heating rate of 0.0167 K s^{-1} prior to reaction.

2.2. Catalytic reactions of DME with and without co-feeds over H-ZSM-5

A stainless steel packed-bed reactor (0.25 in. o.d.; 0.215 in. i.d.) equipped with a concentric thermal well (0.0625 in. o.d.; 0.0485 in. i.d.) aligned along the tube center was used for the conversion of dimethyl ether (DME). The catalyst bed was supported between quartz wool plugs and operated under isothermal conditions using an ARI heating coil regulated by a Watlow Temperature Controller (96 Series). Reactions were run at 548 K using 50 mg of catalyst and at 623 K using 5 mg of catalyst. Under these conditions, a flow rate of 0.45 $cm^3\ s^{-1}$ DME (Matheson Tri-Gas, 99.5% purity) was used. Propene (50% propene, 50% argon, Praxair) and toluene (99.9% purity, Sigma–Aldrich) co-reactants were fed so that the total co-feed gas flow rate was 0.025 $cm^3\ s^{-1}$. Toluene was fed as a liquid using a Cole Parmer EW-74900–00 syringe pump. Methane (10% methane, 90% argon, Airgas), fed at 0.16 $cm^3\ s^{-1}$, was used as an internal standard. A balance of helium was used to achieve a total flow rate of 0.83 $cm^3\ s^{-1}$. The total pressure in the reactor was 130 kPa. The resulting partial pressure of DME was 70 kPa, and the total co-feed pressure was 4 kPa. All results shown are for data recorded at



Scheme 1. Dual olefin and aromatic methylation catalytic cycle for methanol to hydrocarbons on H-ZSM-5.