Graphical Abstract

Isotopic tracer studies of methanol-to-olefins conversion over HSAPO-34: The role of the olefins-based catalytic cycle

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Abstract

The concurrent propagation of the aromatics-based and olefins-based catalytic cycles at early stages of the methanol-to-olefins reaction over HSAPO-34 and the resulting consequences on light olefins selectivities are demonstrated with $^{13}\text{C}_3$ -propylene/ $^{12}\text{C}_2$ -dimethyl ether isotopic tracing studies at 623 K and sub-complete dimethyl ether conversions. Transients in effluent product selectivities were rationalized by the maturation of the entrained hydrocarbon pool where catalyst turnover number is introduced as a compendious descriptor of reaction progress. The distinct ^{13}C -content of ethylene from other effluent products and its agreement with the ^{13}C -contents of entrained polymethylbenzenes indicate that ethylene is a product of aromatics-based dealkylation events while the match between methylation-predicted and experimentally observed ^{13}C -contents for C_{5+} olefins establishes that they are products of olefins-based methylation events. Methanol-to-olefins conversion proceeds through a dual cycle mechanism proposed earlier for methanol conversion over other solid acid catalysts where the topology of HSAPO-34 specifically engenders the prevalence of the aromatics-based cycle at $>\sim 200 \text{ mol}_\text{C} \text{ mol}_\text{H}^{-1}$ catalyst turnovers.

Keywords: methanol-to-olefins, HSAPO-34, hydrocarbon pool, dual cycle

1. Introduction

The methanol-to-olefins (MTO) process utilizes HSAPO-34, a silicoaluminophosphate zeotype acid catalyst, to selectively convert methanol to ethylene and propylene—high-value petrochemical building blocks for plastics and synthetics production [1]. MTO conversion occurs through an indirect [2–4], autocatalytic [5, 6] scheme called the ‘hydrocarbon pool’ mechanism [7–9] characterized by the hybrid organic-inorganic nature of the active center where unsaturated carbonaceous species localized in the catalyst pores, the hydrocarbon pool, act as scaffolds for carbon-carbon bond formation [10, 11]. The complex network

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of reactions for methanol conversion over acidic zeotype catalysts is summarized by dual catalytic cycles where the olefins-based chemistries of methylation and β -scission are coupled with the aromatics-based chemistries of methylation and dealkylation through hydrogen transfer and cyclization events [12–15]. The relative propagation of the two cycles ultimately regulates the product distribution [15–20] and is largely influenced by catalyst topology [21]. The 3.8 Å [22] chabazite-cage windows of HSAPO-34 restrict the effusion of large branched aliphatic and aromatic hydrocarbons rendering dominant the aromatics-based cycle which begets higher ethylene and propylene selectivities [23, 24] ($\sim 80\%$ carbon basis [25]) compared to methanol conversion with HZSM-5 ($\sim 40\%$ carbon basis [26]) where the ~ 5.5 Å [22] MFI-channel dimensions accommodate the egress of both olefins-based and aromatics-based cycle intermediates and thus propagation of both catalytic cycles [13].

Dahl and Kolboe, in their seminal work proposing and validating the operation of a yet vague “pool-type” mechanism for methanol conversion over HSAPO-34, characterized ethylene as a terminal product due to the tendency for $^{12}\text{C}_2$ -ethylene to emerge unreacted when co-fed (introduced into the reactor as $^{12}\text{C}_2$ -ethanol) with ^{13}C -methanol [8] and demonstrated the enhanced reactivity of co-fed propylene (introduced as $^{12}\text{C}_3$ -isopropanol) compared to ethylene noting the pronounced increase in the incorporation of labeled carbon atoms from the olefin co-feed into the effluent products [9]. Further studies into the hydrocarbon pool mechanism for MTO conversion over HSAPO-34 identified aromatics-based species as hydrocarbon pool intermediates for light olefins formation: the positive correlation between trends in effluent light olefins yields and entrained polymethylbenzenes concentrations, qualitatively evaluated via ^{13}C MAS NMR spectroscopy of quenched catalysts [23] or gas-chromatography/mass-spectrometry of extracted organics from acid-dissolved spent catalysts [27], and the incorporation of isotopic labels by polymethylbenzenes during $^{12}\text{CH}_3\text{OH}/^{13}\text{CH}_3\text{OH}$ switching experiments [24] provided evidence that polymethylbenzenes are the active participants comprising an aromatics-based hydrocarbon pool. Hereijgers et al. [28] performed additional isotopic switching experiments at either complete methanol conversion or during catalyst deactivation, i.e. for mature hydrocarbon pools, and concluded that ethylene, propylene, and butenes are predominantly formed from polymethylbenzene intermediates because of their matching isotopic compositions. At sub-complete methanol conversions and before catalyst deactivation, Dai et al. [29] observed di- and trimethylcyclopropane and dienes occluded in the cages of HSAPO-34 via UV/Vis and ^1H and ^{13}C MAS NMR spectroscopy and proposed these olefins-like species as precursors to the familiar aromatics-based intermediates for light olefins formation; these authors, however, did not suggest or provide evidence demonstrating these olefinic species as active hydrocarbon pool participants for light olefins formation. Wang et al. [30, 31] demonstrated the feasibility of olefins-based routes for ethylene and propylene formation during methanol conversion over HSAPO-34 by comparing computed overall reaction barriers for aromatics-based side-chain dealkylation and olefins-based β -scission events (~ 10 kJ mol $^{-1}$ difference) via dispersion-corrected density functional theory treatments.

Here, we present data from isotopic tracer studies to evaluate the mechanistic provenance of light olefins and the role of olefin methylation and β -scission reactions in constituting effluent product selectivities as a function of reaction progress during methanol conversion

over HSAPO-34. We introduce catalyst turnover number as a rigorous and comprehensive measure of reaction progress, demonstrate the operation of the olefins-based cycle at early turnover numbers, and show that ethylene is a product unique to the aromatics-based cycle. These data provide rationalization for observed transients in product selectivities, e.g. increase in ethylene-to-propylene selectivities, as consequences of the increased relative propagation of the aromatics-based cycle as compelled by the catalyst topology. These results support the hypothesis that methanol conversion over all zeotype acid catalysts comprises the same fundamental olefins- and aromatics-based chemistries where the topology of HSAPO-34 specifically regulates the hydrocarbon pool composition monotonically towards aromatics-based species with catalyst turnover.

2. Experimental methods

2.1. Catalyst characterization

SAPO-34 was obtained in its templated form from The Dow Chemical Company. The chabazite structure of the SAPO-34 sample was confirmed by powder X-ray diffraction patterns obtained on a Siemens D-500 diffractometer (see Figure S1 in Supporting Information). The Al, P, and Si contents, $(\text{Al}+\text{P})/\text{Si} = 12$, were measured by inductively coupled plasma optical emission spectroscopy (Analytical Geochemistry Lab, University of Minnesota). The micropore volume, $0.20 \text{ cm}^3 \text{ g}^{-1}$, and BET surface area, $470 \text{ cm}^2 \text{ g}^{-1}$, were measured via N_2 physisorption at 77 K—with prior degassing to $<6 \mu\text{m Hg}$, heating to 673 K at 0.167 K s^{-1} , and holding for 4 h—using a Micromeritics ASAP 2020 analyzer. The SAPO-34 crystals were determined as cubic in morphology and $\sim 1 \mu\text{m}$ in size from micrographs taken via scanning electron microscopy (JEOL JSM-6700F; see Figure S2 in Supporting Information). The elemental analyses [32–36], textural properties [35–37], and crystallite morphology [36, 37] are all consistent with previously reported characterization results of other SAPO-34 samples. The Brønsted acid site density was determined using NH_3 as a chemical titrant during temperature programmed desorption experiments following procedures analogous to those detailed by Bates et al. for isostructural aluminosilicate chabazite samples [38].

2.2. Catalytic reactions and isotopic tracer studies of dimethyl ether over HSAPO-34

Catalytic reactions of dimethyl ether with and without isotopic co-feeds were performed in a packed-bed stainless steel reactor (6.4 mm o.d., 5.5 mm i.d.) described accurately by plug-flow hydrodynamics. This reactor was held in a resistively heated furnace (National Element Furnace FA120 type) regulated by a Watlow Temperature Controller (96 Series); the bed temperature was monitored using a K-type thermocouple threaded through a concentric, co-axial stainless steel sheath (1.6 mm o.d., 1.2 mm i.d.) penetrating the catalyst bed. Templated SAPO-34 samples (crushed, pelletized, and sieved to 180–400 μm particle size) were mixed with quartz sand (triple-washed in aqueous HNO_3 and treated in flowing dry air at 873 K for 12 h), to avoid radial and axial thermal gradients, and supported between two quartz wool plugs. The structural template was removed by *in situ* oxidation treatment in flowing dry air ($1.67 \text{ cm}^3 \text{ s}^{-1}$; $<10 \text{ ppm H}_2\text{O}$, Matheson Tri-Gas): heated from ambient temperature to 823 K at 0.0167 K s^{-1} and held at 823 K for 6 h. The catalyst bed was

purged in flowing Helium ($1.67 \text{ cm}^3 \text{ s}^{-1}$; 99.999%, Matheson Tri-Gas) for 2 h at reaction temperature, 623 K, prior to catalytic reaction measurements.

Dimethyl ether (99.5%, Matheson Tri-Gas), helium (99.999%, Matheson Tri-Gas), methane (internal standard; 10% methane, 90% argon; Matheson Tri-Gas), and $^{13}\text{C}_3$ -propene (99% atom purity, Sigma-Aldrich) were metered using mass flow controllers (Brooks Instruments, 5850 series). All transfer lines were maintained at $>393 \text{ K}$ to prevent condensation of reactor influent and effluent mixtures. All reactor effluent compositions and mass fragmentation patterns were obtained via gas chromatography equipped with a methylsiloxane capillary column (HP-1, $50 \text{ m} \times 320 \mu\text{m} \times 0.52 \mu\text{m}$) connected to a flame ionization detector and an identical column connected to a mass spectrometer, respectively. Isotopomer distributions were quantified from mass fragmentation patterns using matrix methods that rigorously account for natural abundance [39]. The occluded species in the catalyst pores were analyzed following techniques introduced by Arstad and Kolboe [27] and Magnoux et al. [40]: rapidly quench the catalyst bed in an ambient temperature water bath (623 K to 300 K at $\sim (-20 \text{ K s}^{-1})$), dissolve the spent catalyst in hydrochloric acid (37 wt% HCl in water, Sigma-Aldrich), extract the organics into dichloromethane (99.5%, Sigma-Aldrich), and quantify using the aforementioned chromatographic techniques.

3. Results and discussion

3.1. Transient evolution of effluent product and retained hydrocarbons selectivities

Figure 1 shows the effluent product selectivity and retained hydrocarbon selectivity versus time-on-stream during the reaction of 18 kPa dimethyl ether at 623 K and a weight hourly space velocity (WHSV) of $210 \text{ g}_{\text{MeOH equiv}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ over HSAPO-34 where the Brønsted acid site density of the catalyst is $0.66 \text{ mmol}_{\text{H}^+} \text{ g}_{\text{cat}}^{-1}$ as determined by *ex situ* NH_3 titration (see Figure S3 in Supporting Information).

We introduce catalyst *turnover number* (TON), the cumulative moles of carbon in the effluent hydrocarbon products normalized by the number of Brønsted acid sites in the catalyst bed

$$\text{TON}(t) = \frac{1}{[\text{H}^+]_0} \sum_k \int_0^t d\tau k F_k(\tau)$$

where F_k is the effluent molar flow rate of hydrocarbon product with k carbon atoms (excluding methanol) and t is time-on-stream, as a more precise and complete measure of reaction progress than time-on-stream because it condenses reaction conditions—bed loading, catalyst site density, inlet concentrations, and space velocity—into a single progress variable. At 623 K, the catalyst is completely deactivated, conversion of dimethyl ether to hydrocarbon products is zero, at $\sim 800 \text{ mol}_{\text{C}} \text{ mol}_{\text{H}^+}^{-1}$ catalyst turnovers (see Figure S4 in Supporting Information).

C_n -olefins and -paraffins for $n = 1 - 7$ and butadiene are the only observed effluent hydrocarbons; the paraffin fraction for each C_n grouping is between 0.5% and 3.5% for each n throughout the observed reaction period, and the butadiene fraction in the C_4 species is always less than 2%.

Figure 1: Effluent (*top*) and retained (*bottom*) hydrocarbon product selectivity versus time-on-stream during the reaction of 18 kPa dimethyl ether at 623 K and $210 \text{ g}_{\text{MeOH equiv}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ WHSV over HSAPO-34 ($4.3 \text{ mg}_{\text{cat}}$, $0.66 \text{ mmol}_{\text{H}^+} \text{ g}_{\text{cat}}^{-1}$). M_xB denotes toluene, xylenes, tri-, tetra-, penta-, and hexamethylbenzenes for $x = 1, 2, 3, 4, 5$, and 6 , respectively; polycyclic aromatic species heavier than hexamethylbenzene constitute the ‘others’ fraction. X_{DME} is the conversion of dimethyl ether to effluent hydrocarbons excluding methanol. Turnover numbers are reported in $\text{mol}_{\text{C}} \text{ mol}_{\text{H}^+}^{-1}$.

The ethylene selectivity in the effluent product monotonically increases while the retained hydrocarbon selectivities increasingly evolve towards higher methylbenzene homologues with catalyst turnover before stabilizing after $\sim 200 \text{ mol}_C \text{ mol}_{H^+}^{-1}$ TON—consistent with previous results from isotopic switching experiments that tetra-, penta- and hexamethylbenzenes are the primary precursors to light olefins over HSAPO-34 for mature hydrocarbon pools [24, 28]. The observed inverse relationship between the fraction of polycyclic aromatic species, denoted as ‘others’ in Figure 1, and dimethyl ether conversion is also consistent with previous reports characterizing these species as inactive coke precursors [27, 28, 41, 42]. The invariance in both effluent hydrocarbons and entrained polymethylbenzenes distributions at $>200 \text{ mol}_C \text{ mol}_{H^+}^{-1}$ TON provides evidence that the mechanistic origins of olefin products are independent of reaction progress for mature hydrocarbon pools.

Pentene and higher olefins selectivities monotonically decrease with TON indicating that pathways for C_{5+} olefins formations are available at low catalyst turnovers and sub-complete methanol conversions but become progressively unavailable with hydrocarbon pool maturation because of decreased propagation of a postulated olefins-based cycle, enhanced transport restrictions due to aromatics accumulation in chabazite cages, or coking of external surface sites which may have propensities for higher olefins methylation. We examined the role of olefins-based pathways for light olefins formation at early catalyst turnovers through isotopic tracing with $^{13}C_3$ -propylene co-feeds.

3.2. Mechanistic implications from reactions of $^{12}C_2$ -DME with $^{13}C_3$ -propylene co-feeds

The addition of 4 kPa of $^{13}C_3$ -propylene to 70 kPa of dimethyl ether in the feed for methanol conversion over HZSM-5 increased the relative propagation of the olefins-based cycle resulting in an increased steady-state production of C_4 – C_7 aliphatics compared to zero propylene co-feed at sub-complete and iso- conversion conditions (8.5 vs. 6.8 $\text{mol}_C \text{ mol}_{Al}^{-1} \text{ s}^{-1}$) [15]. We performed analogous experiments for MTO conversion over HSAPO-34 where incessant transients in methanol conversion and product selectivity, purportedly caused by chabazite-cage occupancy, pore blockage, and coke deposition [10, 28], prohibit the comparison between steady-state selectivities. Instead, we compared effluent hydrocarbon selectivities with and without $^{13}C_3$ -propylene co-feeds at identical conversions and TONs.

Figure 2 shows the effluent hydrocarbon selectivities versus feed concentration of $^{13}C_3$ -propylene at three stages of the reaction prior to $100 \text{ mol}_C \text{ mol}_{H^+}^{-1}$ turnovers with reaction conditions otherwise identical to those in Section 3.1. Effluent propylene with three ^{13}C atoms is considered as unreacted feed. The identity of the effluent hydrocarbons and the marked preponderance of olefins over paraffins for each carbon number in the product distribution were unaltered with $^{13}C_3$ -propylene co-feeds.

The product selectivities to ethylene decrease and butenes increase with increasing co-feed concentrations of $^{13}C_3$ -propylene at all TON considered. These trends reflect the increased relative propagation of an olefins-based cycle where butenes are predominantly products of olefins-based propylene methylation and higher olefins β -scission reactions and ethylene is a product unique to aromatics-based dealkylation events—demonstrated for methanol conversion over HZSM-5 [13, 16] and below for MTO conversion over HSAPO-34. The relative changes in butenes selectivity with propylene co-feeds compared to dimethyl ether only

Figure 2: Effluent hydrocarbon selectivity during the reaction of 18 kPa dimethyl ether with 0, 1.2, and 2.8 kPa $^{13}\text{C}_3$ -propylene at 623 K and $200\text{--}210 \text{ g}_{\text{MeOH equiv}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ WHSV over HSAPO-34 ($4.1\text{--}4.3 \text{ mg}_{\text{cat}}$, $0.66 \text{ mmol}_{\text{H}^+} \text{ g}_{\text{cat}}^{-1}$).

reactions decrease with catalyst turnover (58% at 20, 48% at 40, and 30% at $90 \text{ mol}_\text{C} \text{ mol}_\text{H}^+{}^{-1}$ when co-feeding 2.8 kPa $^{13}\text{C}_3$ -propylene) ostensibly because aromatics accumulate in the chabazite-cages with TON leaving those associated catalytic sites unavailable for olefins-based chemistries [43]. These results are consistent with the increased tendency for $^{13}\text{C}_3$ -propylene co-feeds to emerge unreacted with catalyst deactivation [9].

Figure 3 displays the observed and ‘methylation-predicted’ ^{13}C -contents of effluent olefins when co-feeding 1.2 kPa and 2.8 kPa $^{13}\text{C}_3$ -propylene with 18 kPa $^{12}\text{C}_2$ -dimethyl ether at 623 K and $\sim 92 \text{ mol}_\text{C} \text{ mol}_\text{H}^+{}^{-1}$ turnovers. The ‘methylation-predicted’ isotopic content for the n^{th} olefin is calculated by considering the ^{12}C -methylation of the $(n - 1)^{\text{th}}$ olefin, i.e.

$$\frac{n - 1}{n} \times \left[^{13}\text{C}\text{-content of } (n - 1)^{\text{th}} \text{ olefin} \right].$$

The observed ^{13}C -content of propylene is less than 100% and that of butenes is less than its methylation-predicted value because propylene and butenes form via β -scission of higher olefins and/or dealkylation of polymethylbenzenes in the autocatalytic MTO reaction network. In contrast, the agreements between observed and predicted ^{13}C -contents for pentenes and hexenes indicate that the prevailing pathway for higher olefins formation is methylation of their respective preceding homologues.

The observed ^{13}C -content of ethylene is distinct from other olefins but matches those of entrained tetra-, penta-, and hexamethylbenzenes ($\diamond$) suggesting that ethylene is predominantly a product of the aromatics-based cycle over HSAPO-34, similar to the find-

Figure 3: Observed (■) and methylation-predicted (○) ^{13}C -contents in effluent olefins and average observed ^{13}C -content of entrained tetra-, penta-, and hexamethylbenzenes (◇) at 90 mol_C mol_{H+}⁻¹ and 94 mol_C mol_{H+}⁻¹ catalyst turnovers during the reaction of 1.2 kPa (*left*) and 2.8 kPa (*right*) $^{13}\text{C}_3\text{-propylene}$, respectively, with 18 kPa $^{12}\text{C}_2\text{-dimethyl ether}$ over HSAPO-34 (4.1–4.3 mg_{cat}, 0.66 mmol_{H+} g_{cat}⁻¹) at 623 K and 200–210 g_{MeOH} equiv g_{cat}⁻¹ h⁻¹ WHSV.

ings for methanol-to-hydrocarbons conversion over HZSM-5 [13, 16] where the contributions of olefins-based β -scission events for ethylene formation were demonstrated as negligible compared to aromatics-based dealkylation events at reaction conditions for sub-complete methanol/dimethyl ether conversion [20]. Also, the ethylene selectivity during methanol (18 kPa CH_3OCH_3) conversion over HSAPO-34 at 623 K is at least five times larger than the ethylene selectivity during propylene (8.4 kPa C_3H_6) oligomerization and cracking over HSAPO-34 at 623 K when compared at similar catalyst turnovers and C_{6+} olefins partial pressures, indicating that indeed aromatics-based routes are the prevailing pathways for ethylene formation (see Section S3 of the Supporting Information for further discussion). This assessment of ethylene as a product unique to the aromatics-based cycle during MTO conversion over HSAPO-34 is consistent with previously reported findings of negligible changes to product distributions with and without ethylene co-feeds [7] and the tendency for ethylene to emerge from the catalyst bed unreacted [8].

These data establish the operation of both aromatics- and olefins-based cycles at early catalyst turnovers during MTO conversion over HSAPO-34 where ethylene and higher olefins formation pathways are mechanistically distinct, reminiscent of the dual catalytic cycles proposed for methanol-to-hydrocarbons conversion over HZSM-5 [13, 16]. The role of the olefins-based cycle remained inconspicuous when interpreting previously reported isotopic tracer studies because the reaction conditions were always such that either methanol was

completely converted where olefin interconversion reactions in the downstream portion of the catalytic bed [20] induce homogenization of isotopic contents in all effluent hydrocarbons or catalysts were deactivating ($\sim 300 \text{ mol}_C \text{ mol}_{H^+}^{-1}$, as calculated by assuming 1:1 stoichiometry between framework Si atoms and Brønsted acid sites) [28] where aromatics-cycle propagation is invariably overwhelming. The precursors and pathways to olefin products during MTO conversion over HSAPO-34 are necessarily dependent on catalyst turnover, and the conclusion that all olefins are exclusively formed from the same aromatics-based intermediates [28] is only valid provided sufficient catalyst turnovers for hydrocarbon pool maturation.

4. Conclusions

The mechanistic interpretation of product selectivities and isotopic contents during $^{13}\text{C}_3$ -propylene co-feed reactions with $^{12}\text{C}_2$ -dimethyl ether, at sub-complete conversions, elucidates the role of the olefins-based catalytic cycle during methanol-to-olefins conversion over HSAPO-34. The prevalence of olefins-based and aromatics-based pathways in light olefins production is necessarily dependent on hydrocarbon pool maturity which is succinctly and accurately captured by the number of catalyst turnovers. At early catalyst turnovers, ethylene is a product unique to aromatics-based dealkylation, butenes are products of both the olefins-based methylation and β -scission and/or aromatics dealkylation, and pentenes and higher olefins are products of olefins methylation events. The inevitable accumulation of aromatics in the small-pore chabazite cages impedes the olefins-based cycle while facilitating the relative propagation of the aromatics-based cycle with catalyst turnover. These results extend the concepts of the dual cycle mechanism for methanol conversion over solid acidic zeotype catalysts to HSAPO-34.

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