



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



Andrew Hwang¹, Dario Prieto-Centurion¹, Aditya Bhan^{*}

Department of Chemical Engineering and Materials Science, University of Minnesota – Twin Cities, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

ARTICLE INFO

Article history:

Received 19 September 2015

Revised 27 December 2015

Accepted 24 January 2016

Keywords:

Methanol-to-olefins

HSAPO-34

Hydrocarbon pool

Dual cycle

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 ¹³C₃-propylene/¹²C₂-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 hydrocarbon pool maturity and reaction progress. The distinct ¹³C-content of ethylene from other effluent products and its agreement with the ¹³C-content of entrained polymethylbenzenes indicate that ethylene is a product of aromatics-based dealkylation events while the match between methylation-predicted and experimentally observed ¹³C-contents for C₅₊ 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 >~200 mol_C mol_H⁻¹ catalyst turnovers.

© 2016 Elsevier Inc. All rights reserved.

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 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] (~80% carbon basis [25]) compared to methanol conversion with HZSM-5 (~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 ¹²C₂-ethylene to emerge unreacted when co-fed (introduced into the reactor as ¹²C₂-ethanol) with ¹³C-methanol [8] and demonstrated the enhanced reactivity of co-fed propylene (introduced as ¹²C₃-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 yield and entrained polymethylbenzenes concentrations, qualitatively evaluated via ¹³C 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

* Corresponding author.

E-mail address: abhan@umn.edu (A. Bhan).

¹ These authors contributed equally to this work.

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 ($\sim 10\text{ kJ mol}^{-1}$ 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 a rationale 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 Fig. 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 $<6\text{ }\mu\text{m Hg}$, 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 $\sim 1\text{ }\mu\text{m}$ in size from micrographs taken via scanning electron microscopy (JEOL JSM-6700F; see Fig. 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 $180\text{--}400\text{ }\mu\text{m}$ 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, $50\text{ m} \times 320\text{ }\mu\text{m} \times 0.52\text{ }\mu\text{m}$) 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 by the following techniques introduced by Arstad and Kolboe [27] and Magnoux et al. [40]: rapidly quenching the catalyst bed in an ambient temperature water bath (623 K to 300 K at $\sim(-20\text{ K s}^{-1})$), dissolving the spent catalyst in hydrochloric acid (37 wt% HCl in water, Sigma–Aldrich), extracting the organics into dichloromethane (99.5%, Sigma–Aldrich), and quantification using the aforementioned chromatographic techniques.

3. Results and discussion

3.1. Transient evolution of effluent product and retained hydrocarbons selectivities

Fig. 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 Fig. 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

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

Download English Version:

<https://daneshyari.com/en/article/6526967>

Download Persian Version:

<https://daneshyari.com/article/6526967>

[Daneshyari.com](https://daneshyari.com)