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The critical role of methanol pressure in controlling its transfer dehydrogenation and the corresponding effect on propylene-to-ethylene ratio during methanol-to-hydrocarbons catalysis on H-ZSM-5

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ABSTRACT

A monotonic increase (2–18) in the effluent propylene-to-ethylene molar ratio as inlet methanol pressure is varied from 52.5 to 0.6 kPa during methanol-to-hydrocarbons catalysis (~30%C conversion) on H-ZSM-5 at 673 K reveals methanol pressure as the salient process parameter that allows control over the relative rates of propagation of the olefins- and aromatics-based methylation/cracking events. The enhanced propagation of the olefins-based cycle over its aromatics-based counterpart and consequently, decoupling of the two catalytic cycles at low influent methanol pressures is observed to persist irrespective of the reaction temperature (623–773 K). Reactions involving formaldehyde co-feeds (3–20 Pa or 0.5–5%C) with low-pressure (0.6 kPa) methanol at 623 K result in a monotonically decreasing trend in propylene-to-ethylene molar ratio from 24.7 in the absence of formaldehyde to 0.8 in the presence of 20 Pa formaldehyde implicating suppressed formaldehyde production from methanol transfer dehydrogenation events at low methanol pressures as the mechanistic basis for the observed effect of enhanced olefin cycle propagation. Co-reacting formaldehyde (11 Pa or 3%C) with propylene (0.1 kPa) on H-ZSM-5 at 623 K results in a 5.5-fold increase in aromatics selectivity suggesting Prins condensation reactions between formaldehyde and olefins are likely involved in aromatics production during methanol-to-hydrocarbons catalysis over H-ZSM-5.

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1. Introduction

The dehydrative conversion of methanol-to-hydrocarbons (MTH) over zeolite or zeotype solid acids is industrially utilized for the selective production of ethylene and propylene [1–5]. Hydrocarbon and oxygenate co-feed, chemical transient, isotopic, and spectroscopic experimental studies [6–19] and density functional theory (DFT) based computational studies [20–23] note the stability and unreactive nature of methyl groups formed upon methanol dehydration in the absence of a primordial "hydrocarbon pool" comprised of olefins and aromatics contained within the microporous environment of the zeolite or zeotype catalyst. The hydrocarbon pool mechanism is summarized by a dual-cycle description where olefinic chemistries of methylation and β-scission (referred to as the olefins-based catalytic cycle) are interconnected with aromatic chemistries of methylation and dealkylation to form light olefins (referred to as the aromatics-based catalytic cycle) via hydrogen transfer and cyclization reactions [9,17,24–32]. Isotopic switching experiments, where ^{12}C-methanol feed was switched with its ^{13}C-labeled counterpart during steady-state conversion on H-ZSM-5 at 623 K, showed ^{13}C content in ethylene to closely match that of aromatics and disparate from that of C_{3+} olefins following the switch, thereby implicating aromatic-dealkylation as the predominant route for ethylene production and evidencing that its production is mechanistically delinked from C_{3+} olefins [17,30]. The description of propagation events during MTH based on separate but linked olefins- and aromatics-based methylation/cracking cycles has been exploited to modulate the molar ratio of propylene and ethylene (P/E) by changes in feed identity [33–37], operating conditions [38–41], topology [1,31,42–45] and textural properties [39,40,46–50] of the zeolite or zeotype catalyst formulations. Here, we report that methanol pressure is the salient experimental parameter in controlling P/E and establish methanol transfer dehydrogenation to produce formaldehyde and olefin-formaldehyde alkylation reactions as the mechanistic basis for this behavior.

The early and seminal work of Langner [24] noted that the addition of cyclic compounds to methanol feed resulted in an 18-fold reduction in the time required to achieve 50% methanol conversion

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and devoid of any description based on the hydrocarbon pool mechanism, postulated that methanol dehydrogenation produces formaldehyde which may be involved in Prins-type condensation reactions with olefins and aromatics during MTH. The observation of high methane selectivities in the effluent during the induction period led researchers to postulate the existence of methanol disproportionation and dehydrogenation events [51–53] during MTH. This postulate is in agreement with theoretical treatments that followed these experimental demonstrations and mechanistic interpretations [54,55]. The observation of longer catalyst lifetimes when using (i) dimethyl ether versus methanol as feedstock over different zeolite or zeotype catalysts [35,37,56], (ii) continuous stirred tank versus packed bed reactors for methanol conversion on H-ZSM-5 [57], and (iii) low inlet methanol pressures or high contact times on CHA framework catalysts [58] can be rationalized as an effect of local methanol pressure on preferentially mediating methanol transfer dehydrogenation events in reference to methylation events involved in carbon chain-growth. Recent reports by Müller et al. [59], Hwang et al. [58], and Olsbye and co-workers [37,56] have clearly explicated the role of formaldehyde, a product of methanol dehydrogenation, in terminating propagation reaction sequences in MTH catalysis. The investigators purport formaldehyde to alkylate aromatics resulting in the transformation of active organic co-catalysts to inactive polycyclic species that occlude zeolite void spaces. Müller et al. [59] observed higher sensitivity of aromatic site-time yield to contact time at sub-complete versus complete methanol conversion, and higher aromatics selectivity utilizing methanol instead of dimethyl ether as feedstock on H-ZSM-5 leading the authors to suggest methanol as a prolific hydride donor during MTH.

We demonstrate the critical role of formaldehyde in initiating the aromatics-based catalytic cycle, and in effect modulating P/E by noting a systematic increase in the selectivity of aromatics and ethylene with increasing methanol concentration in the influent or with increasing formaldehyde co-feed concentration in formaldehyde-methanol co-feed experiments with a fixed inlet pressure of methanol. The likely involvement of Prins condensation reactions between formaldehyde and olefins at pressure and temperature conditions prevalent during MTH in forming aromatic co-catalysts is evidenced by the observation of a 5.5-fold increase in aromatics selectivity when co-processing formaldehyde (11 Pa or 3%C) with propylene (0.1 kPa) versus propylene-only feed. We propose a revised version of the dual-cycle schematic describing propagation in MTH catalysis that includes formaldehyde-mediated C_1 chain-growth steps in addition to methylation.

2. Materials and methods

2.1. Catalyst characterization

The ZSM-5 sample used in this study was obtained from Zeolyst Inc. (CBV8014) in ammonium form and converted to proton form by thermal treatment in flowing dry air (1.67 $cm^3\ s^{-1}$; Minneapolis Oxygen) at 823 K (0.018 $K\ s^{-1}$ ramp rate) for 4 h. X-ray diffraction patterns of H-ZSM-5 were recorded using a Brüker microdiffractometer with Cu-K_α (λ = 1.54 Å) as the radiation source to confirm its crystalline nature. N_2 adsorption isotherms were obtained at 77 K using a Micromeritics surface area and porosity analyzer (ASAP 2020) after an initial degas (evacuation to $\leqslant$ 6 μm Hg at 363 K) followed by thermal treatment in vacuo at 673 K (0.167 $K\ s^{-1}$ ramp rate) for 4 h and used to calculate the BET surface area (386 $m^2\ g^{-1}$) and micropore volume (0.12 $cm^3\ g^{-1}$) of the zeolite sample to confirm its microporous nature. The acid site density (0.39 mmol g^{-1}; 1:1 with Al content measured from inductively coupled plasma-optical emission spectroscopy) was measured from NH_3 temperature programmed desorption performed by saturating ~56 mg of H-ZSM-5 with flowing 500 ppm NH_3 (1.67 $cm^3\ s^{-1}$; Praxair, 1.01% NH_3/balance He) at 323 K followed by a He purge (1.67 $cm^3\ s^{-1}$; Minneapolis Oxygen, 99.997%) for 8 h at 323 K, and ramping the temperature at 0.083 $K\ s^{-1}$ ramp rate to 823 K during which the effluent stream was monitored via mass spectrometry (MKS Cirrus) for signals corresponding to m/z = 16 (for NH_3) and 40 (for Ar [0.083 $cm^3\ s^{-1}$; Matheson, 99.9995%] used as an internal standard) (Fig. S1).

2.2. Catalytic testing

Experiments were carried out in a borosilicate glass-lined stainless steel tube (SGE Analytical Science, 6.35 mm O.D. and 4 mm I.D.) reactor. 180–420 μm aggregates of H-ZSM-5 (ca. 3–30 mg) diluted (ca. 1:35) with 150–420 μm particles of quartz sand (Acros Organics; washed with 2 M HNO_3, rinsed with deionized water, and thermally treated in flowing dry air [1.67 $cm^3\ s^{-1}$] at 1273 K for 16 h) were packed between quartz wool plugs in the middle of reactor tube. The reactor was placed inside a resistively heated furnace (Applied Test Systems, Model 3210). The reaction temperature was measured using a K-type thermocouple (Omega, KMTXL-020U-12) wrapped around the reactor periphery with the tip placed near the axial-center and was regulated with an electronic controller (Watlow 96). The catalyst bed was thermally treated in flowing He (1.67 $cm^3\ s^{-1}$; Minneapolis Oxygen, 99.997%) at 823 K (0.0167 $K\ s^{-1}$ ramp rate) for 4 h prior to reaction. Liquid reagents (methanol [Fluka, $\geqslant$99.9%], formaldehyde [16% w/v in water; Pierce], and deionized water) were delivered using a syringe pump (KD Scientific), vaporized in heat traced lines (~353 K), and swept by a flowing gas stream comprised of diluent (He) and internal standard (Ar). Propylene (Liquid Tech, 999.2 ppm balance Ar), He, and Ar flows were metered using mass flow controllers (Brooks 5850E). The total gas-phase pressure during all experiments was ~1 atm. Reactor influent and effluent stream compositions were quantified using a gas chromatograph (Agilent GC 7890A) equipped with a dimethylpolysiloxane HP-1 column (50 m × 320 μm × 0.52 μm) connected in parallel to a flame ionization detector and a mass spectrometer (Agilent MSD 5975C) for detection of hydrocarbons, and a GS-GasPro column (60 m × 320 μm) connected to a thermal conductivity detector for detection of permanent gases (Ar and CO).

3. Results and discussions

Trends in steady-state selectivity during MTH catalysis on H-ZSM-5 reflect trends in the relative propagation of the aromatics-versus olefins-based catalytic cycle. Larger ethylene and aromatics selectivities reflect enhanced propagation of the aromatics-based cycle while larger propylene and longer-chain aliphatic hydrocarbon selectivities reflect enhanced propagation of the olefins-based cycle [33,34]. Moreover, kinetic studies of ethylene and propylene methylation with methanol or dimethyl ether over H-ZSM-5 have shown ethylene to be relatively inert towards methylation compared to propylene, thereby rendering ethylene as a termination product of the aromatics-based catalytic cycle during MTH [60–62]. Accordingly, Ilias et al. [63] proposed Ethylene/2MBu—defined as the ratio of carbon selectivity of ethylene and the combined selectivity of 2-methyl-2-butene and 2-methylbutane (collectively termed as '2MBu'; representative of products originating from the olefins-based catalytic cycle)—as a semi-quantitative indicator to assess the relative rates of propagation of aromatics- and olefins-based catalytic cycles during MTH on H-ZSM-5. The fact that ethylene is produced exclusively from the aromatics-based cycle proffers a strategy to modulate the molar ratio of propylene-to-ethylene (P/E) by operating under conditions where propagation of this cycle is either suppressed or enhanced.

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