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On the impact of co-feeding aromatics and olefins for the methanol-to-olefins reaction on HZSM-5

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ABSTRACT

The impact of adding various aromatic molecules (benzene, toluene, and xylenes) or olefins (ethene, propene, 1-butene, 1-pentene, and 1-hexene) to methanol over a HZSM-5 catalyst on activity and selectivity was systematically studied. Addition of a low concentration of aromatic molecules (16–32 C%), which are free of diffusion constraints, significantly enhanced the aromatics-based catalytic cycle and greatly suppressed the olefin-based cycle. This led to enhanced methane and ethene formation and methylation of aromatic rings at the expense of propene and C_{4+} higher olefins. The ratio of propene to ethene is controlled by the concentration of the aromatic molecules added. Co-feeding the same molar concentration of benzene, toluene and *p*-xylene influenced the methanol conversion to a nearly identical extent, as none of them experience transport constraints and the methylation rapidly equilibrates the aromatic molecules retained in the pores. In stark contrast, addition of small concentrations (10–40 C%) of C_{3-6} olefins with 100 C% methanol does not selectively suppress the catalytic cycle based on aromatic molecules. This led to unchanged selectivities to ethene and higher olefins (C_{3+}). Within the C_{3+} fraction, the selectivity to propene decreased and the selectivity to butenes were enhanced with increasing concentration of the co-fed olefin. Because of the relatively fast rates in methylation and cracking of C_{3-6} olefins in the olefin-based cycle, the product distributions at high methanol conversion were identical when co-feeding C_{3-6} olefins with the same carbon concentrations. This work provides further insights into the two distinct catalytic cycles operating for the methanol conversion to produce ethene and propene over HZSM-5 catalysts.

1. Introduction

Methanol-to-hydrocarbon processes using microporous zeolites or zeo-type catalysts are regarded as a vital family of conversion technologies to bypass petroleum-based routes for the production of specific fuels and platform petrochemicals [1–6]. Methanol can be readily produced by proven technologies via synthesis gas, which in turn is generated by reforming carbon resources including coal, natural gas, and biomass. On the other hand, special significance of the methanol chemistry originates from its versatility of enabling selective transformations toward various products by proper choice of catalysts and reaction conditions [1–6]. Successfully implemented processes include Methanol-To-Gasoline [7,8], Methanol-To-Propene (both based on HZSM-5) [9–12], and Methanol-To-Olefins (based on SAPO-34, producing both ethene and propene) [13–15]. However, the typical single-pass selectivity for many of these commercialized processes has remained limited since their inception, and substantial recycling is required.

Fundamental insights into the reaction mechanism play a vital role in achieving selectivity control. Ever since the first report by Chang and Silvestri [16], three decades of considerable experimental and computational research efforts have been dedicated to unraveling the complex reaction mechanism. Instead of the direct mechanisms, which involve the initial C–C bond formation directly from C_1 entities, the indirect “hydrocarbon pool” mechanism [17–19] is generally accepted for explaining the formation of light (C_2–C_4) olefins from methanol during steady-state operation. In the original “hydrocarbon pool” concept, the active site has been proposed to be located in the pores or cages of a microporous solid, comprised of an hydrocarbon species (organic part) and a proximate Brønsted acid site (inorganic part) [17–19]. It is described to act as a virtual scaffold for the assembly of light olefins and avoids unstable and high-energy intermediate species required for the direct C–C coupling mechanisms [17–23]. In a proposed cycle, methanol successively reacts with the hydrocarbon species via

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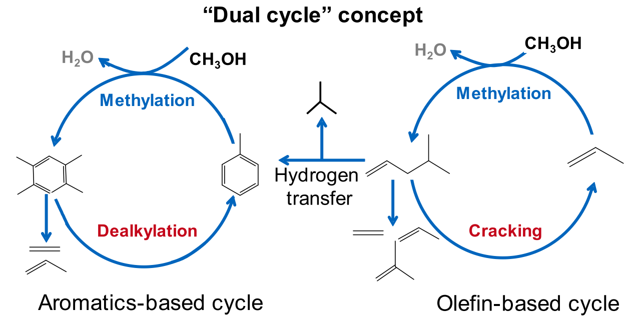
methylation, and subsequently elimination of light olefin products such as ethene and propene regenerates the initial hydrocarbon species [17–23].

Recent experimental and theoretical work demonstrated that focusing on polymethylbenzenes as the sole active species would cause a biased understanding on the MTO mechanism, and olefins may act as another kind of active "hydrocarbon pool" species in zeolites such as the medium-pore ZSM-5 zeolite with 3-D 10-ring channels, while aromatic intermediates seem to be kinetically-relevant for catalysts with large pores or voids [24,25]. This leads to the proposal and establishment of the "dual-cycle" mechanism [24,25], as shown in Scheme 1. Thus, considering that both aromatics and olefins exist in the zeolite pores, the corresponding olefin- and methylbenzene-mediated routes operate on a competing basis. Taking advantage of the different activities and selectivities of olefin- and aromatics-populated cycles toward ethene and propene formation, it has been hypothesized that one could optimize the product distribution through selectively propagating or suppressing one of the two (aromatics- and olefin-based) catalytic cycles.

Three potential strategies can be conceived for achieving selectivity control. Given that turnover of the aromatics-based cycle demands generally a larger space for the transition states than the olefin-based cycle, one approach is to adjust the pores by varying zeolite topologies [26,27]. Indeed, very recent experiments on methanol conversion over the one-dimensional 10-MR H-ZSM-22 zeolite without intersections showed that the sterically restricted topology suppressed selectively the reactions via the aromatics-based cycle and secondary aromatization via hydrogen transfer which would require larger transition states and reaction intermediates [28–31]. Thus, methanol conversion at 673 K proceeded exclusively via the olefin-based cycle, leading to a product mixture rich in C_{3+} branched alkenes, very low in ethene and almost negligible in aromatics [28–31]. The second strategy is to tune the inorganic part, i.e., the Brønsted acidity, through zeolite synthesis or post-synthetic anion or cation modifications, which have been documented in a large body of literature [2]. The third approach for selective propagation of a catalytic cycle is to influence the organic part, i.e., the concentration of olefin or aromatic species, by adding specific hydrocarbons together with methanol.

In this contribution, we explore this third approach by varying the nature and concentration of the co-processed hydrocarbons, to adjust the product selectivity under industrially relevant reaction conditions. Several reports on co-reacting hydrocarbons with methanol including various olefins and aromatics have appeared, but their main intentions were to elucidate the mechanistic features via isotopic labeling under conditions far away from realistic MTO(P) operations, and the impacts of co-feeding on product distributions is largely lacking [32–41]. Most recently, Ilias and Bhan reported in an elegant paper the impact on the product distributions by co-processing low concentrations of toluene and/or propene with dimethylether, but the experiments were mainly performed at reaction temperatures as low as 548 K and a dimethyl ether pressure of 70 kPa [40]. To simulate industrial process conditions, experiments were performed with methanol pressure fixed at 10 kPa on a highly siliceous HZSM5 catalyst at 723 K. Various aromatic co-feeds including benzene, toluene and xylenes, and olefins including ethene, propene, 1-butene, 1-pentene, and 1-hexene were evaluated.



Scheme 1. Proposed "dual-cycle" mechanism in methanol-to-olefins conversion over HZSM-5 [24,25].

2. Experimental

2.1. Catalyst and reagents

The specific synthesis method of the HZSM-5 (Si/Al = 90) was reported previously [42]. The as-synthesized material has a crystal size of 500 nm. The zeolite powder was pressed into a wafer, crushed, and sieved to a fraction of particle size in the range of 200–280 μm. Methanol (99.93%), 1-hexene, 1-heptene, benzene, toluene, *para*- and *meta*-xylenes (99.0%) were supplied by Sigma–Aldrich. Gases of C_{2-5} olefins (5% or 10% in volume diluted in N_2) were supplied by Westfalen GmbH.

2.2. Catalytic testing

All catalytic tests were performed on a bench-scale plug flow reaction unit. The catalyst pellets were homogeneously diluted with silicon carbide (ESK-SIC, 1:15 wt:wt) with a comparable particle size to ensure temperature uniformity. Catalysts were placed in a quartz tube (26 cm in length, 6.0 mm i.d.) and supported between two quartz wool plugs. The samples were activated at 753 K with the temperature control at the external surface of the quartz tube with 50 ml min^{-1} N_2 for 2 h prior to switching to feed. The reaction temperature was held at 723 K, and the total pressure was 108 kPa. The methanol partial pressure was maintained at 10 kPa. The total flow rate was held at 55 ml min^{-1}. Methanol vapor was fed by passing dry N_2 flow (29 ml min^{-1}) through the methanol-containing saturator which was thermo-stated at 298 K. Flow rates of gaseous olefin co-feeds (C_{2-5}) were controlled by mass flow controllers (Bronkhorst). For aromatics, 1-hexene or 1-heptene, the co-fed vapor was introduced by passing dry N_2 flow through a saturator containing the liquid reactant. Catalyst loading (2–100 mg) and reactant flow velocity were varied to achieve a wide range of contact time and methanol conversion. Here the contact time is defined as the ratio of catalyst mass to the molar flow rate of methanol. The reactor effluent was kept at 393 K and transferred via a heated line into a gas chromatograph (HP 5890) equipped with a HP PLOT-Q column (30 m × 0.32 mm × 0.5 μm) connected to a flame ionization detector for on-line analysis. Product analysis was performed at steady-state conversions.

Both methanol and dimethyl ether were treated as reactants. The concentration of a co-feed is given as a molar ratio of its partial pressure to methanol partial pressure (10 kPa). The product distributions (concentration and yield) were given on a carbon basis, and the carbon in the methanol feed with a partial pressure of 10 kPa was defined as 100%. For instance, a feed of 0.4 kPa toluene and 10 kPa methanol is depicted as co-feeding 4 mol.% toluene. As one toluene molecule has seven carbon atoms, 28% toluene with 100% methanol in carbon, the feed was referred to as containing a total carbon concentration of 128% (28 C% from toluene with 100 C% from methanol) in the feed.

In the experiments of methanol conversion with aromatic co-feeds, the final aromatics increment after reaction is defined as the aromatics concentration (in C%) from which the initial concentration of the aromatics co-feed (in C%) is subtracted.