Unraveling the Homologation Reaction Sequence of the Zeolite-Catalyzed Ethanol-to-Hydrocarbons Process

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Abstract: Although industrialized, the mechanism for catalytic upgrading of bioethanol over solid-acid catalysts (that is, the ethanol-to-hydrocarbons (ETH) reaction) has not yet been fully resolved. Moreover, mechanistic understanding of the ETH reaction relies heavily on its well-known “sister-reaction” the methanol-to-hydrocarbons (MTH) process. However, the MTH process possesses a Cn-entity reactant and cannot, therefore, shed any light on the homologation reaction sequence. The reaction and deactivation mechanism of the zeolite II-ZSM-5-catalyzed ETH process was elucidated using a combination of complementary solid-state NMR and operating UV/Vis diffuse reflectance spectroscopy, coupled with online mass spectrometry. This approach establishes the existence of a homologation reaction sequence through analysis of the pattern of the identified reactive and deactivated species. Furthermore, in contrast to the MTH process, the deficiency of any olefinic-hydrocarbon pool species (that is, the olefin cycle) during the ETH process is also noted. The production of (C3-Cn) olefins is still primarily based on the cracking of natural gas and naphtha. Since the direct carbon emissions from fossil feedstocks are considerably higher than for renewables, the economic and environmental motivations for replacement with renewables is steadily increasing every year. For instance, ethylene is also currently manufactured from bioethanol-derived sugary and starchy feedstocks. In fact, the ethanol-to-hydrocarbons (ETH) process carried out by catalytic upgrading over solid-acid catalysts has recently captured a lot of attention in academia and industry. The ETH reaction was first commercialized by Elektrochemische Werke GmbH in Germany in 1913. The supported phosphoric acid and activated alumina were used as a catalyst until the 1980s. Zeolites were then introduced to achieve superior product selectivity and better environmental tolerance. Despite these industrial advancements, the reaction and deactivation mechanisms of the ETH reaction are yet to be established. Moreover, mechanistic insights that are available to date are principally built on the understanding of the well-studied methanol-to-hydrocarbons (MTH) process. This is because both ETH and MTH processes give similar product distributions. However, it is not reasonable to assume that all zeolite-catalyzed conversion processes of alcohols would have an identical mechanism. A few exemplary characteristic differences are: 1) the MTH process requires a Koch-carbonylation-based direct mechanistic route to form the initial C2-Cn bonds from Cn-methanol to produce (≥Cn) products, which is apparently not needed from C2-ethanol in the ETH process (Figure 1). It is impossible to evaluate the homologation reaction sequence during the MTH process, as all reaction products/intermediates are integers of its reactant C2-methanol. Importantly, the ETH process offers us a unique possibility to investigate the homologation reaction in zeolite catalysis as it involves a C2 reactant (Figure 1).
These arguments collectively hint at the plausible existence of a different reaction mechanism occurring in the ETH process.

Only the first step of the ETH reaction (that is, dehydration) is relatively better understood in the literature.\[^{[8,22–25]}\] Unfortunately, the rest of the reaction sequences (that is, homologation, cyclization, aromatization, and cracking) have yet to be unraveled. In particular, the exact mechanistic routes to the origin of $>C_2$ even-numbered products (such as $C_2$-butene) and $>C_2$ odd-numbered products (that is, non-homologated products such as $C_3$-propylene) carbon-containing hydrocarbon pool (HCP) species from $C_2$-ethane are still under scrutiny within the ETH process. The importance of the mechanistic understanding of this industrial reaction should not be underestimated; as such, information is crucial to maximizing yields and developing new and/or improved heterogeneous catalysts.\[^{[26]}\]

Aiming to dispel the ambiguity surrounding the zeolite-catalyzed ETH process, we have now established an in-depth fundamental mechanistic understanding of its complete reaction sequence—primarily by identification of multiple surface-adsorbed active catalytic species (that is, surface alkoxo and carbonylated species), $C_2$–$C_4$ olefins, homologated HCP (that is, hydrogen-transferred alkylated aromatics and smaller paraffin), and deactivated polyaromatic “coke” species. These new insights were obtained using advanced multidimensional magic angle spinning (MAS) solid-state NMR (ssNMR) spectroscopy, and corroborated with operando UV/Vis diffuse reflectance spectroscopy (DRS) coupled with on-line mass spectrometry (MS). In addition to the elucidation of the (homologation-dominated) reaction and deactivation mechanism, the mobility-dependent, distinctive host-guest chemistry between the zeolite and the trapped hydrocarbons during catalysis were also identified.\[^{[19,27,28]}\]

Initially, operando UV/Vis DRS with on-line MS was used to identify and differentiate between neutral and carbocationic zeolite-trapped organic species, as well as gas-phase products, formed during an ETH reaction conducted at 573 K over millimeter-sized alumina-bound H-ZSM-5 extrudates (Figure 2; Supporting Information, Figure S1).\[^{[27]}\] Figure 2a shows spectral features during the first 10 minutes of the reaction, as the absorption bands at $\leq 300, 336, 355, 421,$ and 576 nm increase in intensity as a function of reaction time (Figures 2b and 2c). The observed absorption bands at $\leq 300, 330–375, 421,$ and $\geq 575$ nm are attributed to $\pi\rightarrow\pi^*$ transitions associated with neutral alkylbenzene molecules, carbenium ions with alkyl side chain carbocations (up to four alkyl groups)/neutral polyaromatics, alkylated areneum molecules, and poly-areneum species/complexes between the zeolite and aromatic species, respectively (Supporting Information, Scheme S1).\[^{[19,27,28]}\] Leveling off of the intensity of bands in the UV region after 7 minutes of reaction is indicative of the autocatalytic part of the reaction, whereas a continuous increase in the intensity of bands in the visible region indicates the formation of larger sized poly/fused aromatics (Figure 2c) during the deactivation of the catalyst.

The simultaneously measured on-line MS data reveal the predominant existence of diethyl ether and $C_2$–$C_4$ olefins (Figure S2d), along with $C_3$–$C_7$ hydrocarbon species in relatively lower quantities (Figure S1b). Interestingly, no traces of $>C_4$ HCP species were detected in the effluent gas phase, whereas NMR could easily distinguish trapped $>C_4$ aromatic HCP species (see proceeding text). The simultaneous decrease and increase of ion current of ethylene and butylene (10 min, Figure 2d), respectively, essentially demonstrates the ethylene-assisted dimerization of ethylene to butylene,\[^{[30]}\] and hence, the existence of a homologation-reaction-mediated C–C bond-coupling sequence.

Advanced ssNMR was performed on the post-reacted material using $^{13}$C$_2$-labeled ethanol. The use of isotope-enriched ethanol not only significantly increased the NMR sensitivity, but also allowed us to perform multidimensional NMR correlation experiments for accurate structural determination of the homologation products. $^1$H–$^1$C cross-polarization (CP),\[^{[30]}\] $^1$H–$^1$C insensitive nuclei enhanced by polarization transfer (INEPPT),\[^{[31]}\] and $^1$C direct excitation (DE) ssNMR spectra show the following five features: 1) $7–37$ ppm aliphatic groups, 2) $58–70$ ppm alkoy groups, 3) $125–160$ ppm aromatic moieties, 4) $180–187$ ppm carboxyl groups, and 5) additional peaks at approximately $227$ ppm corresponding to carboclastic carbon nuclei (Supporting Information, Figure S2, Table S1). The strongest aliphatic and aromatic signals at $20–32$ and $129–144$ ppm, respectively, are mostly from the zeolite-trapped ethylated benzene molecules. This is consistent with the concept of both HCP species formation and the homologation reaction. The applied different NMR magnetization transfer techniques also allowed us to distinguish their spectral appearance on the basis of mobility.\[^{[19,27,28,32–33]}\] As a result, both rigid (that is, physisorbed in/on zeolite; Figures 3 and 4; Figures S2–S9) and mobile (that is, with fast tumbling or local rotation; Figure S10) species of zeolite-trapped organics could be distinguished.

To probe the rigid molecules, 2D $^1$H–$^1$C dipolar-based correlation spectra were acquired (Figures 3 and 4; Figures S2–S9).\[^{[34]}\] In Figure 3a, we identified two non-identical

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Operando UV/Vis DRS measurements during the ETH reaction over alumina-bound H-ZSM-5 extrudates at 573 K for a) 0–10 and b) 10–30 min. Time-resolved changes of c) absorbance bands and d) mass spectral profiles for diethyl ether and $C_2$–$C_4$ olefins as a function of reaction time.
Moreover, we detected broader resonances for the aliphatic region (Figure S7), indicating the formation of hydrocarbons (that is, hexamethylbenzene (2d, Figure S4), multiple isomers of tetra-methylbenzenes (3a; that is, isomerized from 2a; Figure S7), and the two polyaromatic species tetraethylphthalalene (4a) and hexahydropyrene (4b) (Figure S8). The identification of such homologated hydrocarbons (that is, 2a/2b/3a/4a/4b) is further confirmed by so-called Guinset’s method of zeolite-material dissolution (Figure S11, Section S1.5).[36]

Subsequently, weak signals at approximately 227 ppm in the 1D DE (Figure S2), and their cross-peaks with $^{13}$C-methylene carbon atoms at 32–37 ppm in the $^{12}$C–$^{13}$C correlation spectra (Figure S9), indicate the formation of alkylated carbenium species or a $\pi$-complex within a six-membered ring framework.[16,27] Moreover, we detected mobile molecules (that is, ethanol and hydrogen-transferred C$_2$-C$_3$ alkanes; Figure S10) in 2D ssNMR experiments probing through-bond connectivities.[25]

Finally, a catalytic (homologation-dominated) reaction pathway for the ETH process is proposed in Scheme 1 (Scheme S2, Section S2). The first step involves dehydration of ethanol into ethylene, via a mono- or bimolecular pathway (with diethyl ether as an intermediate).[23] First, ethanol is adsorbed on the zeolite through a H-bonding interaction with its Brønsted acid site (1a) with two binding motifs; that is, end-on (ν$_1$-ν) and side-on (ν$_1$-ν) conformations (Figure 3). Subsequently, 1a undergoes dehydration over the zeolite to form SES (1b), followed by decomposition to eliminate

To identify unique spin systems in the aromatic regions of rigid molecules, we collected $^{13}$C–$^{13}$C correlation spectra using different mixing times (Figure S3). In the $^{13}$C–$^{13}$C correlation spectrum with a short mixing time (30 ms), an intense cross-peak correlated a methyl resonance at 10.4 ppm with a resonance at 37 ppm (green cross in Figure 4). These
ethylenes and regenerate OH groups on zeolite via a concerted mechanism (monomolecular pathway, loop 1 in Scheme S2). The formation of ethylene from SES is concluded as the rate-determining step of the ETH process by Potter et al.[25] In a bimolecular pathway, the adsorption of another ethanol molecule on 1a leads to the formation of a dimeric ethanol adduct on the surface of zeolite (1c), which is further decomposed/dehydrated to form diethyl ether and regenerates the zeolites in the process.[22]

Once the first ethylene forms from SES (1b), the homologation reaction is promptly initiated. Subsequently, ethanol undergoes the first homologation-reaction-mediated C–C bond coupling to form zeolite–butylene species (1d)—either directly from 1c or when 1b reacts with another ethanol molecule (Scheme 1). Species 1d then directly generates either butylene and zeolite or propylene and surface-methoxy species (1e, as a result of cracking in Scheme 1). The first non-homologated product, propylene, is formed from surface-propylene species (1f) as a result of interaction between 1e and ethanol. In the next stage, the homologation-reaction-mediated C–C bond-coupling route continues to dominate the ETH process. The species 1d could undergo further alkylation by ethanol and is followed by cyclization to form cyclic ethylated carbonium species (1g, Scheme 1). The cyclic 1g species first led to a stable/neutral counterpart, diethylbenzene (2a) by dehydrocyclization, which reacts with ethanol/ethylene successively to produce a series of homologated products; that is, tri-/tetra-/hexa-ethylbenzenes (2b–2d, Scheme 1). Interestingly, most identified rigid ethylated aromatics have an even number of carbon atoms, which essentially advocates for the domination of the homologation-reaction-mediated C–C coupling routes during the ETH process.

The oligomerization/cyclization and isomerization of ethylated benzenes are two major deactivation pathways in the ETH process. The poly/fused-aromatic-based bulkier “coke” species (that is, 4a and 4b in Figure S8), are the primary deactivated species, which formed from ethylated benzenes through oligomerization via sequential C–H activation steps and followed by ring-closure (Scheme S2). These polyaromatic species are the precursors of pyrene (4c), which is a well-established, infamous coke/deactivated species in zeolite catalysis.[15,16,29,37,38] The methylated aromatics (that is, 3a in Figure S7) were formed by cracking of bulkier species (compare 2d/4c) and by isomerization from the ethylated aromatics (that is, 2a) to tetramethylbenzene/durene (3a). Durene is an undesired side-product because of its high freezing point, and was not detected until now during the zeolite-catalyzed ETH process.[7] Simultaneously, Koch-carbonylated species (that is, surface-propionate (1’I) and surface acetate (1’)) are independently capable of producing several methylated aromatic-based HCP species and C–C olefins (Scheme S3).[19–21,28] Concurrently, C3–C4 alkanes (5a–5c; Figure S9) are formed as a result of the “concomitantly operating” hydrogen-transfer reactions from the corresponding olefins.[26]

In conclusion, our combined spectroscopic approach validates the hypothesis that the homologation-reaction-mediated C–C bond coupling is indeed responsible for the formation of olefins and its higher homologues during the zeolite-catalyzed ETH process. The “mechanistically decoupled” formation of ethylene from ethanol,[28] and its subsequent involvement in the formation of C3–C4 HCP species (aromatics/alkanes) as a result of homologation reaction, govern both autocatalytic and deactivation segments of the reaction. Although the homologation-reaction-dominated HCP mechanism is found to be influential,[34] characteristically it is quite different from the MTH process because of the deficiency of its olefin cycle owing to its higher reactivity. The HCP species in the ETH process typically constitute multiple (m)ethylated aromatics (Table S3). Therefore, the acquired knowledge from this work will not only be useful for the development of superior materials for the catalytic upgrading of ethanol, but also contribute to the understanding of zeolite-catalyzed hydrocarbon conversion chemistry.

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Conflict of interest

The authors declare no conflict of interest.

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