Mechanisms of Alkene and Diene Hydrogenation Reactions in H-MFI and H-CHA Zeolite Frameworks during MTO

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Abstract

Co-feeding H₂ at high pressures increases zeolite catalyst lifetimes during methanol-to-olefin (MTO) reactions while maintaining high alkene-to-alkane ratios; however, the mechanisms and species hydrogenated by H₂ co-feeds to prevent catalyst deactivation remain unknown. This study uses periodic density functional theory (DFT) to examine hydrogenation mechanisms of MTO product C₂–C₄ alkenes, as well as species related to the deactivation of MTO catalysts such as C₄ and C₆ dienes, benzene, and formaldehyde in H-MFI and H-CHA zeolite catalysts. Results show that dienes and formaldehyde are selectively hydrogenated in both frameworks at MTO conditions because their hydrogenation transition states proceed via allylic and oxocarbenium cations which are more stable than alkylcarbenium ions which mediate alkene hydrogenation. Diene hydrogenation is further stabilized by protonation and hydridation at α,δ positioned C-atoms to form 2-butene from butadiene and 3-hexene from hexadiene as primary hydrogenation products. This α,δ-hydrogenation directly leads to selective hydrogenation of dienes; pathways which hydrogenate dienes at the α,β-position (e.g., forming 1-butene from butadiene) proceed with barriers 20 kJ mol⁻¹ higher than α,δ-hydrogenation and with barriers nearly equivalent to butene hydrogenation, despite α,β-hydrogenation of butadiene also occurring through allylic carbocations. Hydrogenation of formaldehyde, a diene precursor, occurs with barriers that are within 15 kJ mol⁻¹ of diene hydrogenation barriers, indicating that it may also contribute to increasing catalyst lifetimes by preventing diene formation. Benzene, in contrast to dienes and formaldehyde, is hydrogenated with higher barriers than C₂–C₄ alkenes despite proceeding via stable benzenium cations because of the thermodynamic instability of the product which has lost aromaticity. Carbocation stabilities predict the relative rates of alkene hydrogenation and in some cases shed insights into the hydrogenation of benzene, dienes, and formaldehyde, but cation stabilities alone cannot account for the poor hydrogenation of benzene or the facile hydrogenation of dienes, boosted by stabilization conferred by α,δ-hydrogenation. This work suggests that the main mechanisms of catalyst lifetime improvement with high H₂ co-feeds is reduction of diene concentrations through both their selective hydrogenation and hydrogenation of their precursors to prevent formation of deactivating polyaromatic species.
1. Introduction

Zeolite-catalyzed conversion of methanol to C2–C4 alkenes is a widely studied1–7 alternative route for producing light olefins. Zeolite catalysts, however, are susceptible to deactivation via the formation of large, polyaromatic species thus limiting their efficiency and requiring the use of recirculating fluidized bed reactors in industrial applications.8–13 Two complementary cycles form C2–C4 alkenes in methanol-to-olefins (MTO) processes.14–19 Olefins methylate and grow to a size capable of cracking into C3–C5 compounds in the olefin cycle.1,17,20,21 These olefins can undergo hydride transfer reactions to form alkanes and dienes—either via formaldehyde-assisted routes22–24 or through alkene disproportionation25,26—which can cyclize to form aromatic species.27–29 Aromatics can further co-catalyze the formation of alkenes in the aromatics cycle.1,16,30–32 Alternatively, aromatic species can react with dienes to form site-blocking polyaromatic species,11,33–36 which ultimately deactivate the catalyst.12 Therefore, CH2O and dienes play an important role in the formation of aromatic co-catalysts and deactivating polyaromatic molecules.13

High H2 pressures significantly improve catalyst lifetime in common MTO zeolites such as H-SAPO-34, H-ZSM-5, and H-SSZ-13.37,38 Co-feeding H2 at high partial pressures (4–30 bar H2, 0.13 bar CH3OH, 673 K) improved catalyst lifetime, as measured by turnover number, by a factor of 2.8–70 in H-SAPO-34. Similarly, H2 co-feeds at pressures of 0.4 bar in H-SSZ-13 (CHA framework) and 16 bar in H-ZSM-5 (MFI framework), H-SSZ-39 (AEI framework), H-FER, and H-BEA improved catalyst lifetime by factors of 3–15 by measured turnovers. These extensions in catalyst lifetime did not result in dramatic changes in selectivity; while the alkane:alkene ratios generally increase, the predominant C2–C3 products remain olefins. Observed increases in C1–C3 alkane ratios are dependent on zeolite topology. For instance, C2–C4 alkane selectivity increases equally in H-SSZ-13, H-BEA, and H-FER (16 bar H2); however, in H-SSZ-39 C3 selectivity is higher than that of C2 and C4 alkanes, indicating that zeolite topology plays a role in hydrogenation selectivities. Increases in catalyst lifetime likely occur because H2 selectively hydrogenates reactive species, such as polyaromatics or polyaromatic precursors (e.g., dienes and formaldehyde), thereby limiting the amount of polyaromatic species formed via diene cyclization. Kinetic studies in CHA, FER, BEA, and AEI (0.1–1 mbar hydrocarbon, 1–16 bar H2, 623 K) corroborate the selective hydrogenation of dienes over alkenes by demonstrating that rate constants of butadiene (C4H6) hydrogenation are > 103 times higher than ethene (C2H4) and propene (C3H6).

Catalyst lifetimes can be further improved by combining high-pressure co-feeds of H2 and H2O, which prolong the lifetime of H-SAPO-34 from 75 hours measured by turnover number with H2 cofed with CH3OH (35.7 bar H2, 4.2 bar CH3OH, 673 K) to 118 hours with both H2 and H2O cofed (22.8 bar H2, 12.8 bar H2O, 4.2 bar CH3OH, 673 K).38 H2O can assist in mitigating deactivation by either dealkylating methylolated acid sites through hydration (reforming protons necessary for hydrogenation reactions) or by facilitating the protonation of dienes or formaldehyde by directly participating in hydrogenation steps.

There are two proposed mechanisms of Brønsted-acid catalyzed double-bond hydrogenation39,40 (Scheme 1): a concerted mechanism in which protonation of the double bond and cleavage of the H–H bond occur simultaneously:

$$C_2H_2 + H_2 + Z\text{-}H \rightarrow C_3H_2 + Z\text{-}H$$  \hspace{1cm} (1)

and a sequential mechanism in which a surface-bound species is formed:

$$C_3H_2 + Z\text{-}H \rightarrow Z\text{-}C_3H_2$$  \hspace{1cm} (2)

followed by subsequent hydridation by H2:40,41

$$Z\text{-}C_3H_2 + H_2 \rightarrow C_3H_4$$  \hspace{1cm} (3)
Both mechanisms involve the heterolytic splitting of H₂ to transfer a hydride to an organic cation and a proton back to the catalyst surface; thus, isotopic tracer experiments are incapable of distinguishing these mechanisms. Moreover, both mechanisms may have similar kinetic isotope effects, depending on the kinetically relevant step of the sequential pathway. Previous density functional theory (DFT) calculations on 3T cluster models examining hydrogenation of C₂H₄ and CH₂O suggest that in the sequential mechanism, barriers of Z–C₂H₅ formation (Eq. 2) are facile compared to its hydridation—indicating that the second step (heterolytic H₂ cleavage, Eq. 3) is kinetically relevant in the sequential mechanism. Overall barriers (relative to the Z–H state) of concerted and sequential hydrogenation are less than 10 kJ mol⁻¹ different for C₂H₄, indicating that the two mechanisms are likely competitive. Additionally, overall potential energy barriers of CH₂O hydrogenation are facile (60 kJ mol⁻¹) and are over 100 kJ mol⁻¹ lower than those of ethene, indicating that hydrogenation of CH₂O, a diene precursor, may contribute to the experimentally observed increases in catalyst lifetime.

Scheme 1. Brønsted-acid catalyzed double-bond hydrogenation can occur via a concerted single-step pathway or via a two-step sequential pathway, both of which effectively exchange a surface proton with a proton atom derived from H₂, indicating that these pathways cannot be distinguished by isotopic tracer studies.

The increases in catalyst lifetime observed by the previously discussed kinetic studies have demonstrated that hydrogenation reactions play an important role in increasing catalyst lifetime in zeolites of varying topologies. No theoretical study, however, has investigated and compared hydrogenation mechanisms across multiple alkenes, dienes, aldehydes, and arenes. Such theoretical analysis can provide insight inaccessible by experiment into preferred hydrogenation mechanisms and understanding of how H₂ improves lifetimes and alters the hydrocarbon pool or product selectivity in MTO reactions. Here, we use density functional theory (DFT) to examine concerted and sequential (Scheme 1) hydrogenation schemes of C₂–C₄ alkenes, C₄ and C₆ dienes, CH₂O, and benzene in two common MTO zeolite frameworks: MFI and CHA. We show hydrogenation of dienes and CH₂O are kinetically favored over alkene and benzene hydrogenation in CHA and MFI, suggesting that decreases in deactivation can be attributed to elimination of dienes. Furthermore, these results indicate that diene hydrogenation preferentially occurs through protonation and hydridation of α,δ (1,4) C-atoms to form 2-butene from butadiene and 3-hexene from 2,4-hexadiene. This α,δ reaction mechanism is novel and more facile than other reactions that similarly proceed through an allylic carbocation, such as α,β hydrogenation of butadiene, indicating that the kinetic benefit of diene hydrogenation is not solely attributable to carbocation stability.

2. Methods

2.1 Computational Methods
Periodic, dispersion-corrected density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP) as implemented in the Computational Catalysis Interface (CCI). Planewaves were constructed using the projector augmented-wave (PAW) potentials with an energy cutoff of 400 eV. The Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies. The DFT-D3 method with Becke and Johnson damping accounted for dispersive interactions. The Brillouin zone was sampled at the Γ-point for all calculations.

The MFI structure obtained from the experimental results of van Koningsveld et al. is used in all MFI-calculations because restructuring artifacts are minimized in this zeolite form. The lattice parameters (a = 20.090 Å, b = 19.738 Å, c = 13.142 Å) and orthorhombic shape were fixed in all calculations. All calculations in MFI were performed with a single Bronsted acid site at the T11 tetrahedral site (T-site), which has been predicted to have lower Z–CH₃ formation barriers than other T-sites residing in the channel intersection (T3, T10, and T12). There are four O-sites surrounding T11: O14, O16, O24, and O25. Previous work has demonstrated that O24 is inaccessible to species larger than CH₃–Z, because of confinement by the surrounding framework; therefore, reactions were investigated at O14, O16, and O25, and their respective combinations for reactions involving two O atoms. The CHA structure was obtained from the International Zeolite Association (IZA) database—no significant restructuring artifacts are observed upon annealing or optimization of the CHA structure. The lattice parameters (a = b = 13.675 Å, c = 16.675 Å and α = β = 90°, γ = 120°) were fixed in all calculations. All reactions in CHA were performed with a single Bronsted acid site at the single cryptographically unique T-site of CHA. All four O-sites surrounding that T-site were considered for all reactions (and in all combinations for sites which directly interact with a pair of O atoms).

Reactants, products, and adsorbed intermediates were optimized until the maximum force on any atom was < 0.05 eV Å⁻¹ in a two-step convergence procedure as implemented in CCI. In the first step, wavefunctions were converged to within 10⁻⁴ eV and forces were computed using a fast Fourier transform (FFT) grid with a cutoff 1.5× the planewave cutoff. In the second step, accuracy was improved by converging wavefunctions to within 10⁻⁶ eV and using an FFT grid 2× the planewave cutoff. No atoms were constrained in any DFT optimization, pathway, or transition state calculations. Minimum energy pathways were estimated using the nudged elastic band (NEB) method using 12–16 images and wavefunctions converged to 10⁻⁴ eV with an FFT grid 1.5 times the size of the plane-wave cutoff. The maximum force on each atom in all images were converged to < 0.5 eV Å⁻¹ for NEB calculations. This estimate of the minimum energy pathway was used to generate initial transition state structures and reaction modes for the Dimer method, which optimizes a pair of structures to determine the local curvature of the potential energy surface until ultimately converging on a saddle point. Dimer calculations were done in an analogous two-step optimization procedure using the same convergence criteria as reactant, product, and intermediate optimizations. All DFT-optimized reactant, product, and transition states were modeled at all possible O-sites and O-site pairs (if the species interacted with a pair of O atoms) associated with T11 of MFI and T1 of CHA. Furthermore, all structures were systematically reoriented (Section 2.2), to increase the likelihood that global minima and optimum transition state structures were obtained via static (non-dynamic) DFT calculations.

Frequencies were calculated for all reactant, product, and transition states using a fixed displacement method where the adsorbates (e.g., CH₃OH and benzene) and AlO₄ of the acid site are displaced while all other framework atoms are fixed. Low-frequency modes (< 60 cm⁻¹) were replaced with 60 cm⁻¹, similar to previous work, because low frequencies are inaccurate and contribute significantly to vibrational entropy terms. These frequency calculations are used to determine zero-point vibrational energies and vibrational enthalpies and entropies which can be combined with ideal gas treatments of rotational and translational modes (for bulk gas species) to determine
temperature-corrected (353–673 K) enthalpies and free energies using equations given in Section S1 of the supporting information (SI).

2.2 Reorientation of Reactant, Product, and Transition State Species

All reactant, product, and transition state structures were modeled on the three accessible O-sites of T11 in MFI (O14, O16, and O24) and at all four unique O-sites in CHA (O1, O2, O3, and O4). Each reactant, product, and transition state structure was systematically reoriented as implemented in CCI\(^{48}\) in an attempt to identify the global minimum, rather than local minima. These reorientations can find configurations of guest species with energies as much as 50 kJ mol\(^{-1}\), as discussed in previous work.\(^{63}\)

Reorientation schemes are based upon how an adsorbate interacts with the zeolite. States that interact non-specifically with the Brønsted acid site (e.g., adsorbed alkenes, dienes, and protonated states) are reoriented in space about the axes defined by the a-, b-, and c-vectors of the unit cell around their centers of mass (Fig. 1a). The orientation of each state was varied in 30° increments from 30–330° around each of these rotational axes individually and subsequently optimized with the parameters discussed in Section 2.1 to identify the lowest energy orientation.

![Spatial Reorientations: around the a, b, and c vectors](image1)

**Figure 1.** a) Spatial reorientations of butadiene about the a-, b-, and c-axes of the unit cell and b) acid site reorientations of the hydrogenation of C\(_4\)H\(_6\) (transition state) about the Al–O\(_a\)–A\(_1\) angle (green), O\(_t\)–Al–Si–O\(_a\) angle (cyan), and O\(_t\)–O\(_a\)–A\(_1\)–A\(_2\) (blue).

States that interact strongly with the framework—via covalent, incipient, or hydrogen bonds—are reoriented about the acid site. Three types of acid site reorientations are used here: O\(_t\)–Al–Si–O\(_a\) (Fig. 1b), Al–O\(_a\)–A\(_1\), and O\(_t\)–O\(_a\)–A\(_1\)–A\(_2\), which have been described in previous literature.\(^{59}\) Reorientations about the O\(_t\)–Al–Si–O\(_a\) dihedral angle sweep the adsorbate around the Brønsted acid site (Fig. 1b). The orientations of these states were varied in 30° increments from 30–330° and all converged states were subsequently optimized. Altering the Al–O\(_a\)–A\(_1\) angle moves the adsorbed state parallel to the acid site through the zeolite void (Fig. 1b). Each state was reoriented in 15° increments between −30° and 30°, and the four resulting states were reoptimized using the parameters discussed in Section 2.1. Finally, O\(_t\)–O\(_a\)–A\(_1\)–A\(_2\) reorientations result in guest species spun about their interaction with the O atom with which they interact on the acid site or its conjugate base (Fig. 1b). These O\(_t\)–O\(_a\)–A\(_1\)–A\(_2\) reorientations were done in 30° increments from 30–330°. Reactant and product states that are covalently bound to the zeolite surface (e.g., C\(_2\)H\(_5\)–Z) are reoriented with O\(_t\)–Al–Si–O\(_a\) and O\(_t\)–Al–Si–O\(_a\) reorientations (covalently bound states are ineligible for Al–O\(_a\)–A\(_1\) reorientations) to probe the potential energy surface. States that are not covalently bound but strongly interact with the surface through either hydrogen bonding (e.g., CH\(_2\)O) or nascent bonds (e.g., sequential hydrogenation) are rotated through all acid site reorientation schemes.

The alkoxide-forming transition state (Eq. 2) and the concerted hydrogenation transition state (Eq. 1) strongly interact with two O-sites simultaneously. Therefore, reorientations of these states would significantly change the transition state structure and, as such, these states were not systematically reoriented. However, each transition
state was examined between all possible O-site combinations among the 3 accessible O-sites in MFI and 4 accessible O-sites in CHA, resulting in 6 optimized transition state structures for these transition states in MFI and 10 optimized transition states in CHA.

3. Results and Discussion

3.1 Hydrogenation Thermodynamics

Hydrogenation reactions were investigated for all possible hydrogenation products of ethene, propene, 1-butene, 2-butene, butadiene, 2,4-hexadiene, formaldehyde, and benzene (Fig. 2). Gas phase reaction energies (Fig. 2) indicate that there is no significant thermodynamic preference to hydrogenate species involved in polyaromatic formation (aromatics, dienes, and formaldehyde) compared to alkenes, and that C=C bond stability increases with C-atom substitution. This indicates that the tendency for dienes to be hydrogenated over alkenes—as shown experimentally—arises from a kinetic preference, likely because of the increased stability of allylic carbocations caused by resonance. A preference for formaldehyde hydrogenation over alkene hydrogenation has not been directly observed, but has been predicted by DFT calculations contrasting formaldehyde and ethene hydrogenation. The reaction free energy of $-24 \text{ kJ mol}^{-1}$, however, indicates less favorable hydrogenation than that of ethene $(-63 \text{ kJ mol}^{-1})$ or other alkenes $(-33 \text{ to } -54 \text{ kJ mol}^{-1})$, suggesting that the increased stability of the oxocarbenium ion formed during formaldehyde hydrogenation decreases the overall barriers. Despite the stability of the benzenium ($\text{C}_6\text{H}_7^+$) cation, the disruption of the aromaticity results in a large reaction free energy ($+94 \text{ kJ mol}^{-1}$) and the instability of the cyclohexadiene product is likely to limit benzene hydrogenation rates. Direct analysis of both hydrogenation mechanisms (sequential and concerted) and altering which carbon is protonated and which is hydridated during these reactions will give additional insights.

![Figure 2](image)

Figure 2. Gas phase reaction energies of a) alkene hydrogenation, b) diene hydrogenation, c) aromatic hydrogenation, and d) formaldehyde hydrogenation.

3.2 Hydrogenation in H-MFI

Two hydrogenation schemes were considered in this work: a concerted mechanism in which protonation and hydridation occur simultaneously and a sequential mechanism in which the alkene is protonated and forms a zeolite-bound intermediate followed by hydridation by $\text{H}_2$. These mechanisms were investigated for C$_2$–C$_4$ alkenes, C$_4$ and C$_6$ dienes, benzene, and a diene precursor species, CH$_2$O.
Sequential hydrogenation generally involves the formation of a surface-bound Z–C₆H₅ species followed by subsequent hydridation by H₂. Formation of Z–C₆H₅ involves simultaneous protonation from of the α carbon and C–O bond formation with the β carbon (Fig. 3). The transition state with the lowest energy among all six distinct O-site pair possibilities is shown in Fig. 3b, and the effective free energy barrier to form this transition state (relative to gas-phase species and a bare proton) is 118 kJ mol⁻¹ with an intrinsic barrier of 92 kJ mol⁻¹ (Fig. 4). The second step of the sequential mechanism involves detachment and rotation of C₆H₅⁺ so that heterolytic H₂ dissociation can occur (Fig. 3c) to transfer a hydride to the carbocation and a proton to the zeolite surface and occurs with an effective free energy barrier of 216 kJ mol⁻¹. The free energy barriers of the two sequential hydrogenation steps (118 and 216 kJ mol⁻¹) cannot be directly compared to evaluate their relative rates because the second step requires H₂ adsorption as such the pressure dependences in their respective rate equations differ:

\[
\frac{r_{s1}}{[L]} = K_{C_6H_4} k_{S1} (C_2H_4)[\bullet]^{-1}
\]

(4)

\[
\frac{r_{s2}}{[L]} = K_{C_6H_4} K_{C_2H_4 \cdots H_2} k_{S2} (C_2H_4)(H_2)[\bullet]^{-1}
\]

(5)

with rate and equilibrium constants defined in Section S1 of the SI and [\bullet] indicating a bare proton on the zeolite surface. Bare protons will not be abundant at MTO conditions, however, surface methoxies or other species will equally inhibit the rates of both steps (and equally inhibit all reactions studied in this work). To determine which step in this sequence is the rate determining step, the sequential mechanism is analyzed using maximum rate analysis (described in Section S1 of the SI) to determine the kinetically relevant step by comparing the maximum rates of alkoxide formation and H₂ splitting. Protonated benzene and hexadienes cations are too stable and sterically hindered to form bound alkoxides, so these species were only investigated by the concerted hydrogenation mechanism. For formaldehyde, butadiene, and all alkenes studied here, alkoxide hydridation (Eq. 3) had maximum rates over 1000× lower than alkoxide formation (Eq. 2) at all relevant conditions (553–723 K, 1–20 bar H₂, 0.01–0.15 bar reactant, Fig. S1 of the SI); therefore, subsequent discussion will focus on alkoxide hydridation as it is the kinetically relevant step of the sequential mechanism.

Figure 3. Transition state structures of a) Z–C₆H₅ formation, b) sequential hydrogenation, c) concerted hydrogenation in MFI. Enthalpy (H, kJ mol⁻¹), entropy (S, J mol⁻¹ K⁻¹) and free energy (G, kJ mol⁻¹) barriers are reported at 623 K and 1 bar. Effective barriers (referenced to gas-phase species and a bare proton, ΔGeff) and intrinsic barriers (in parentheses, ΔGa) are both listed.
The most facile concerted ethene hydrogenation transition state involves simultaneous protonation from O14 and heterolytic H2 splitting to re-form a proton at O16 with the organic compound residing in the straight channel (Fig. 3c), rather than the channel intersection. Exploring the effects of transition state confinement is crucial to understanding the effects of topology on zeolite catalyzed reactions, as such each of the reactions in this work was investigated at all possible O-site combinations within MFI. Generally, aliphatic compounds, such as C2H4, reside in the straight channel of MFI as it is appropriately sized for small, aliphatic transition states, where dispersive interactions between transition state and the framework are most favorable. This reaction occurs with an identical $\Delta G^\ddagger$ (216 kJ mol$^{-1}$) to that of ethoxide hydrogenation (Fig. 3b), indicating that these mechanisms compete at 623 K, while having slightly different $\Delta H^\ddagger$ (73 and 55 kJ mol$^{-1}$ for alkoxide hydridation and concerted hydrogenation, respectively) indicate that other temperatures may lead to a single dominant mechanism but precise predictions are not within the accuracy of these DFT methods. Generally, concerted and sequential free energy barriers tend to be similar as the transition state for both structures primarily involve a carbocation (fully or partially formed) interacting with a cleaving H2 molecule which is also interacting with the zeolite framework. Moreover, their rate equations reflect identical pressure dependences and, thus, these data yield identical predicted rates for each pathway in ethene hydrogenation at 623 K—making them indistinguishable by kinetic studies.

DFT-predicted kinetic isotope effects (KIE) for the concerted and sequential mechanisms are 3.2 and 1.5, respectively, for C2D4–D2 reactions over D-MFI. The slightly higher KIE for concerted is likely because that transition state (Fig. 3c) involves the transfer of three H-atoms (two to C2H4 and one to the zeolite) whereas the alkene hydridation transition state (Fig. 3b) only involves the transfer of two H-atoms as the protonation has already occurred in the previous step. These KIE values, however, are likely too close to one another to provide an effective experimental discrimination between these two reaction mechanisms.

Effective free energy barriers for ethene hydrogenation are at least 40 kJ mol$^{-1}$ higher than all other alkene species (Fig. 4), because the short-lived primary carbenium ion (C2H5$^+$) is unstable relative to the secondary carbenium ions that can be formed from larger alkenes. Kinetic studies in H-ZSM-5 (MFI) indicate that there are not significant changes in C2H4 selectivity (16 bar H2, 0.13 bar CH3OH, 723 K),$^{37}$ which is consistent with the DFT-derived free energy barriers that indicate ethane is not a predominant hydrogenation product. Additionally, rate constants of ethene hydrogenation in H-CHA (H-SSZ-13), H-SSZ-39, H-FER, and H-BEA suggest that rate constants of ethene hydrogenation are 1.5–16× lower than rate constants of propene hydrogenation.$^{43}$

Unlike ethene, which involves a single unique hydrogenation scheme, there are two unique hydrogenation schemes for propene: formation of a primary carbocation by protonation the secondary (\(\beta\)) carbon (Fig. 5a) or formation of a secondary carbocation by protonation of the primary (\(\alpha\)) carbon (Fig. 5b). Secondary carbenium ions are significantly more stable than primary carbenium ions, leading to lower hydrogenation barriers ($\Delta G^\ddagger$, by 45–75

Figure 4. Reaction coordinate diagram of ethene (red), propene (green), 1-butene (purple), and 2-butene (pink) concerted (dashed) and sequential (solid) hydrogenation routes. Free energies (kJ mol$^{-1}$) are reported at 623 K and 1 bar of each alkene and 1 bar H2.
kJ mol\(^{-1}\), Fig. 5). This trend is consistent across all aliphatic species investigated (Fig. S5), indicating that carboxation stability is a good predictor of aliphatic hydrogenation barriers among similar reactants (such as alkenes). The \(\Delta G^\ddagger\) for propene hydrogenation (171 and 167 kJ mol\(^{-1}\)) are lower than those of ethene (216 kJ mol\(^{-1}\)) as shown in Fig. 4. This is corroborated by experimental results that indicate very small increases in \(\text{C}_3\) alkane selectivity (16 bar H\(_2\), 1.3 bar CH\(_3\)OH, 723 K).\(^{37}\)

Figure 5. a) Primary and b) secondary hydrogenation schemes and potential energies (kJ mol\(^{-1}\)) to form primary and allylic carboxations via concerted hydrogenation of \(\text{C}_3\text{H}_6\).

Concerted hydrogenation of 1-butene, like propene, also occurs by protonation of the primary \(\alpha\)-C and hydridation of the secondary \(\beta\)-C (Fig. 6c). Routes via secondary carbenium ions have \(\Delta G^\ddagger\) that are 10–60 kJ mol\(^{-1}\) lower than routes proceeding via primary carbenium ions (Table S1, SI). Similarly, in the sequential mechanism, 1-butene preferentially forms \(\beta\)-bound alkoxide species via protonation of \(\alpha\)-C (rather than \(\alpha\)-bound, shown in Fig. S6). The effective free energy barriers for hydrogenating 1-butene and 2-butene are nearly identical 162 and 161 kJ mol\(^{-1}\) (Fig. 4)—indicating that hydrogenation is equally as likely to occur regardless of the \(\text{n}\)-butene isomer present in the hydrocarbon pool. Additionally, butene hydrogenation barriers are significantly lower than those of ethene but within 5 kJ mol\(^{-1}\) of propene suggesting that longer carbon chains do not significantly impact hydrogenation barriers. Rather, barriers of alkene hydrogenation are most dependent on alkylcarbeniums stability which follows as \(1^\circ < 2^\circ < 3^\circ\) indicating that branched alkenes such as isobutene would be most readily hydrogenated, followed by \(\text{n}\)-alkenes (\(n > 2\)), and then ethene.

Figure 6. Most favorable transition state structures of hydridating a) \(\alpha\)-bound alkoxide from 1-butene, b) \(\beta\)-bound alkoxide from 1-butene, c) \(\beta\)-bound alkoxide from 2-butene, d) hydridation of the \(\beta\)-bound alkoxide and the concerted hydrogenation transition states for d) 1-butene, and e) 2-butene. Enthalpy (\(H\), kJ mol\(^{-1}\)), entropy (\(S\), J mol\(^{-1}\) K\(^{-1}\)) and free energy (\(G\), kJ mol\(^{-1}\)) barriers are reported at 623 K and 1 bar. Effective barriers (referenced to gas-phase species, \(\Delta G^\ddagger\)) and intrinsic barriers (in parentheses, \(\Delta G^\text{act}\)) are both listed. Yellow and blue shaded H-atoms represent those from the zeolite and H\(_2\), respectively.

Butadiene can react with aromatics to form large, polyaromatic species that deactivate zeolite catalysts; therefore, elimination of butadiene species through hydrogenation is one possible mechanism through which H\(_2\) co-feeds elongate catalyst lifetime. Measured second order rate constants of butadiene hydrogenation in H-CHA
(H-SSZ-13), H-SSZ-39, H-FER, and H-BEA are 7–318 times higher than rate constants of ethene and propene hydrogenation, suggesting that butadiene is selectively hydrogenated regardless of zeolite topology. This selectivity, however, is not because of a thermodynamic preference as reaction free energies for diene hydrogenation (−33 to −50 kJ mol⁻¹) are similar to those of alkene hydrogenation (−33 to −63 kJ mol⁻¹) (Fig. 2). Butadiene can be hydrogenated to form 1-butene (via α,β attack) and 2-butene (via α,δ attack) leading to four unique alkoxide hydridation reactions (Eq. 3, Figs. 8a–d) and two unique concerted hydrogenation routes (Fig. 8e, f). The alkoxide hydridation transition states depicted in Figs. 8a–c involve formation of a carbenium followed by rotation to reach the orientation in which hydridation occurs, as such the transition state for these species involves both rotation and H₂ stretching. The transition state shown in Fig. 8d represents alkoxide hydridation; however, unlike Figs. 8a–c, this route does not require rotation of C₄H₇⁺ because the δ-carbon is being hydridated (rather than the surface-bound carbon). Alkoxide hydridation transition state barriers tend to reflect the stability of carbenium formed; barriers among transition states with secondary, allylic carbeniums (Figs. 8b–d) are remain between 150–154 kJ mol⁻¹ and are 70 kJ mol⁻¹ lower in ΔG° than non-allylic transition states (Fig. 8a). Furthermore, the formation of secondary, allylic carbocations results in transition states ~10 kJ mol⁻¹ lower than secondary, alkylcarbenium transition states (161–167 kJ mol⁻¹, Fig. 7), consistent with increased stabilities of allylic carbeniums. Concerted protonation and hydridation of the α,δ C-atoms in butadiene forms 2-butene and has a ΔG° that is 14 kJ mol⁻¹ lower than the most favorable α,β-attack (Fig. 8b, which forms 1-butene) transition state, despite both reactions proceeding via an allylic carbocation. Furthermore, barriers of α,β-butadiene hydrogenation (ΔG° of 154–164 kJ mol⁻¹, Fig. 8b and e) are essentially identical propene and butene hydrogenation barriers (ΔG° of 161–167 kJ mol⁻¹, Fig. 4), demonstrating the importance of the α,δ-attack to explain experimentally observed differences in alkene and diene rate constants. The direct formation of 2-butene from butadiene, however, cannot be experimentally verified as n-butene double bond isomerization and skeletal isomerization are facile resulting in an equilibrated mixture of isobutene, 1-butene, and 2-butene at MTO and hydrogenation conditions. This inability of experiments to determine the primary butadiene hydrogenation product further motivates our theoretical studies. Moreover the similar barriers between butadiene to 1-butene (via α,β attack and aliphatic carbocations) and propene hydrogenation indicates that carbocation stabilities cannot, as previously suggested, fully explain why butadiene hydrogenation rate constants are 7–185× larger than those of propene.⁴³

![Reaction coordinate diagram of butadiene hydrogenation](image)

**Figure 7.** Reaction coordinate diagram of butadiene hydrogenation to 1-butene (brown) and 2-butene (orange), hexadiene hydrogenation to 2-hexene (dark blue) and 3-hexene (light blue), benzene (gray), and formaldehyde (black) via concerted (dashed) and sequential (solid) mechanisms. Free energies (kJ mol⁻¹) are reported at 623 K.
Figure 8. Most favorable transition state structures of a) sequential butadiene to 1-butene via a β-bound surface intermediate, b) sequential butadiene to 1-butene via an α-bound surface intermediate, c) sequential butadiene to 2-butene via an α-bound surface intermediate, d) sequential butadiene to 2-butene via a β-bound surface intermediate, e) concerted hydrogenation of butadiene to 2-butene, f) concerted hydrogenation of butadiene to 1-butene. Effective and intrinsic (italics, parentheses) free energy barriers are reported in kJ mol\(^{-1}\) at 623 K. Yellow and blue shaded H-atoms represent those from the zeolite and H\(_2\), respectively.

Hexadiene can hydrogenate to form 2-hexene via α,β-attack or 3-hexene via α,δ-attack. As previously discussed, both transition states only involve heterolytic cleavage of H\(_2\) (Figs. 9a and b), rather than simultaneous protonation and hydridation as seen in C\(_2–C_4\) aliphatics. Protonated hexadiene is relatively stable (ΔG of 9 kJ mol\(^{-1}\) relative to gas phase species) because it forms an allylic carbocation coupled with long C\(_6\) aliphatic chain; C\(_2–C_4\) aliphatic carbenium ions, in contrast, are unstable when protonated. Moreover, the Z–C\(_6\)H\(_{11}\) species are unstable compared to the protonated state (ΔG of 46 kJ mol\(^{-1}\) relative to gas phase species), as such only the concerted mechanism was investigated for hexadiene species. Hexadiene hydrogenation does not benefit from α,δ hydrogenation as much as butadiene, likely because the hexadiene transition state does not involve simultaneous protonation and hydridation. α,δ hydrogenation of 2,4-hexadiene is 20 kJ mol\(^{-1}\) more/less favorable than α,β hydrogenation; this contrasts with these reactions on butadiene, where concerted α,δ hydrogenation is favored over α,β hydrogenation by 20 kJ mol\(^{-1}\). The energetic consistency between these two different mechanisms in 2,4-hexadiene arises because the larger hexadiene protonates easily and does not need to be concurrently hydridated in the transition state, which butadiene does.

Figure 9. Most favorable transition states of hexadiene hydrogenation to a) 2-hexene and b) 3-hexene, c) Z–CH\(_2\)OH hydridation, d) concerted CH\(_2\)O hydrogenation, and e) benzene hydridation. Effective and intrinsic
(italics, parentheses) enthalpies (kJ mol\(^{-1}\)), entropies (J K\(^{-1}\) mol\(^{-1}\)), and free energies (kJ mol\(^{-1}\)) are reported at 623 K.

Previous literature has implicated CH\(_2\)O as a precursor to dienes and aromatics and as a significant contributor to catalyst deactivation.\(^{24,42,64-66}\) Kinetic studies have demonstrated that co-feeding H\(_2\) and CH\(_2\)O (4 bar H\(_2\), 0.13 mbar CH\(_2\)O, 1.3 bar CH\(_3\)OH, 673 K) increases catalyst lifetimes by 2.1-fold compared to identical co-feeds of He and CH\(_2\)O. This indicates that H\(_2\) may limit polyaromatic formation by intercepting CH\(_2\)O diene precursors. Therefore, we investigate CH\(_2\)O hydrogenation and compare it to diene hydrogenation reactions to determine if deactivation was limited by direct hydrogenation of dienic species (i.e., arene precursors) or hydrogenation of diene precursors to prevent the initial formation of dienes. Concerted CH\(_2\)O hydrogenation to form oxocarbeniums (CH\(_2\)OH\(^+\), Fig. 9d) via O-protonation is >100 kJ mol\(^{-1}\) more favorable than C-protonation to form CH\(_3\)O\(^+\). Similarly, the sequential mechanism involves formation and hydridation of a hydroxyalkoxide (HOH\(_2\)C–Z) (Fig. 9c). Concerted and sequential transition states are remarkably similar for formaldehyde hydridation (Figs. 9c and d), and both are stabilized by hydrogen-bonding between the framework and –OH group. Hydrogenation of CH\(_2\)O occurs with identical ΔG\(^\ddagger\) to butadiene at 623 K (140 kJ mol\(^{-1}\), Fig. 7) and close in value to that of hexadiene (115 kJ mol\(^{-1}\)), consistent with previous studies suggesting that barriers of CH\(_2\)O hydrogenation are low compared to those of ethene hydrogenation.\(^{41}\) This suggests that polyaromatic formation during MTO is limited by both direct diene hydrogenation and hydrogenation of diene precursor species.

The benzene hydrogenation transition state involves a fully protonated species and the heterolytic cleavage of H\(_2\) because protonated benzenium cations are relatively stable compared aliphatic carbenium ions. Moreover, C\(_6\)H\(_7\)+ (ΔG of 87 kJ mol\(^{-1}\) relative to gas phase species, Table S2) is significantly more stable than Z–C\(_6\)H\(_7\) species (ΔG of 341 kJ mol\(^{-1}\) relative to gas phase species, Table S2); therefore, alkoxide-formation and alkoxide-hydridation pathways were not considered for benzene. The benzene hydridation transition state Free energy barriers associated benzene hydridation (239 kJ mol\(^{-1}\), Fig. 7) are significantly higher than all investigated alkenes and dienes, because breaking the aromaticity of the benzene ring results in unstable states. This is consistent with previous experimental studies suggesting that benzene does not react with hydrogen unless there are tertiary hydride sources present.\(^{39}\) Benzene hydrogenation routes are insignificant at high H\(_2\) MTO conditions, so arene hydrogenation does not contribute to decreases in deactivation rates in MFI.\(^{37,38}\) Rather, the formation of polyaromatics is limited through elimination of CH\(_2\)O and dienes.

### 3.3 Hydrogenation in H-CHA

Concerted and sequential hydrogenation reactions were also investigated in CHA zeolites, which is topologically distinct from MFI. MFI contains straight and sinusoidal channels that intersect to form the channel intersection, where T11 is situated, and the three accessible O-sites of T11 reside in the straight channel (O14) or bridge straight channel and channel intersection (O16 and O25). This work, and previous work,\(^{59}\) have demonstrated that the straight channel of MFI offers confinement for smaller transition states, such as those associated with aliphatic hydrogenation. Conversely, the O-sites of CHA each have different chemical environments: O1 bridges a 6 membered-ring (6-MR) and two 4-MRs, O2 spans two 8-MRs, O3 spans the 6-MR and 8-MR, and O4 spans the 8-MR and 4-MR (Fig. S1). Similar to MFI, hydrogenation of C\(_2–C_4\) alkenes, C\(_4\) and C\(_6\) dienes, benzene, and CH\(_2\)O was investigated at all O-site combinations within CHA.

Alkene hydrogenation in CHA (Fig. 10) occurs with similar trends as observed in MFI. Maximum rate analysis is used to identify the rate-determining step of the sequential mechanism and rates of alkoxide hydridation are >1000× lower (553–723 K, 1–20 bar H\(_2\), 0.01–0.15 bar reactant, Fig. S1 of the SI) than rates of alkoxide formation; therefore, alkoxide hydridation is kinetically relevant (as observed for MFI) and the remainder of this discussion will focus on comparing concerted and alkoxide hydridation. There are two distinct alkoxide hydrogenation transition states: heterolytic H\(_2\) cleavage (Figs. 11b and d, bottom) or alkoxide rotation (Figs. 11a
and c, bottom). The instability of primary carbocations causes an earlier transition state that includes rotation whereas transition states of secondary carbocations primarily involve heterolytic cleavage of H\textsubscript{2}. The trends observed in alkene hydrogenation agree with experimentally predicted rate-constants suggesting that rates of propene hydrogenation are \(1.5\times\) higher than those of ethene hydrogenation (H-CHA, 1–16 bar H\textsubscript{2}, 0.1–1 mbar C\textsubscript{2}H\textsubscript{4} or C\textsubscript{3}H\textsubscript{6}, 673 K)\textsuperscript{43} whereas DFT-predicted propene rate constants are \(~14\times\) higher than those of ethene hydrogenation (Fig. S3). Alkene hydrogenation barriers in CHA (Fig. 10) are consistently 5–15 kJ mol\(^{-1}\) lower than those in MFI (Fig. 4), indicating that the topology of CHA stabilizes alkylcarbeniums slightly better than MFI. This is corroborated by experimental results showing that H\textsubscript{2} co-feeds (16 bar H\textsubscript{2}, 0.13 bar CH\textsubscript{3}OH, 673 K) increase turnover by \(4.5\times\) in H-CHA (H-SSZ-13) and \(3\times\) in H-MFI (H-ZSM-5) catalysts.\textsuperscript{37}

**Figure 10.** Free energy barriers of ethene (red), propene (green), 1-butene (purple), and 2-butene (pink) concerted (dashed) and sequential (solid) hydrogenation barriers in CHA. Free energies (kJ mol\(^{-1}\)) are reported at 623 K and 1 bar of each species (alkene and H\textsubscript{2}).

**Figure 11.** Most favorable concerted (top) and sequential (bottom) transition states of a) ethene, b) propene, c) 1-butene, and d) 2-butene. Enthalpies (kJ mol\(^{-1}\)), entropies (J K\(^{-1}\) mol\(^{-1}\)), and free energies (kJ mol\(^{-1}\)) are reported relative to the gas phase energies at 623 K.
Barriers of butadiene hydrogenation (149 and 122 kJ mol\(^{-1}\), Fig. 12) are lower than those of alkene hydrogenation (158–189 kJ mol\(^{-1}\))—indicating that butadiene hydrogenation occurs preferentially over alkene hydrogenation in CHA. Similar to MFI, the \(\alpha,\delta\) attack of butadiene to form 2-butene occurs with \(\Delta G\#\) significantly lower than \(\alpha,\beta\) attacks—further demonstrating the importance of this \(\alpha,\delta\) attack mechanism. DFT-predicted rate constants predict that rates of butadiene hydrogenation are \(\sim 76 \times\) those of propene hydrogenation and \(1000 \times\) higher than ethene hydrogenation (Fig. S5). Kinetic studies co-feeding 1,3-butadiene (H-CHA (H-SSZ-13), 1–16 bar \(H_2\), 0.1–1 mbar \(C_2H_4\) or \(C_3H_6\) or \(C_4H_6\), 673 K) predict that butadiene hydrogenation rates are 185-fold higher than propene hydrogenation and 263-fold higher than ethene hydrogenation.\(^{43}\) There is a larger discrepancy between predicted and observed rate constants in the case of butadiene hydrogenation; however, the DFT-predicted trends agree well with those experimentally indicating that rates of butadiene hydrogenation are significantly higher than those of ethene and propene. Butadiene hydrogenation in CHA also occurs with barriers \(\sim 5 \text{ kJ mol}\(^{-1}\) lower than those in MFI, further supporting that the CHA topology facilitates hydrogenation of \(C_2\)–\(C_4\) aliphatic compounds slightly better than MFI.

Unlike MFI, hexadiene hydrogenation barriers in CHA are higher than those of butadiene hydrogenation—likely because CHA does not offer the same confinement as the straight channel of MFI for the longer \(C_6\) chain. Like in MFI, benzene hydrogenation is unfavorable. Barriers associated with \(CH_2O\) hydrogenation (\(\Delta G\#\) of 142 kJ mol\(^{-1}\) and 150 kJ mol\(^{-1}\), Fig. 12) are lower than those of alkene hydrogenation (\(\Delta G\#\) of 158 kJ mol\(^{-1}\)–189 kJ mol\(^{-1}\)), consistent with previous DFT-predictions\(^{41}\), and comparable to those of diene hydrogenation (\(\Delta G\#\) of 122 kJ mol\(^{-1}\)). Therefore, similar to conclusions in H-MFI, deactivation is likely prevented through both direct hydrogenation of dienes and hydrogenation of \(CH_2O\) to prevent diene formation, rather than elimination of aromatic species.

Figure 12. Reaction coordinate diagram of butadiene hydrogenation to 1-butene (brown) and 2-butene (orange), hexadiene hydrogenation to 2-hexene (dark blue) and 3-hexene (light blue), benzene (gray), and formaldehyde (black) via concerted (dashed) and sequential (solid) mechanisms. Free energies (kJ mol\(^{-1}\)) are reported at 623 K.

4. Conclusions

Here, we investigate concerted and sequential diene hydrogenation schemes for \(C_2\)–\(C_4\) \(n\)-alkenes, \(C_4\) and \(C_6\) dienes, benzene, and \(CH_2O\) to determine the mechanism by which high pressure \(H_2\) co-feeds improve catalyst lifetime. Gas phase reaction energies suggest that dienes, \(CH_2O\), and \(C_6H_6\) hydrogenation are not thermodynamically preferred over \(C_2\)–\(C_4\) alkene hydrogenation, indicating that any preferential hydrogenation of those deactivation-related compounds is kinetically derived. Each hydrogenation mechanism was compared in two common MTO zeolite catalysts, CHA and MFI. Generally, hydrogenation barriers in the two frameworks are within 20 kJ mol\(^{-1}\) of one another and hydrogenation barriers follow nearly identical trends between the two frameworks, despite the different confining void topologies.
Transition states which limit the rates of sequential and concerted hydrogenation routes are formed effective free energy barriers generally within 10 kJ mol\(^{-1}\) of each other, indicating that both routes compete at MTO and hydrogenation conditions (623 K). Asymmetric species, such as propene and 1-butene, and species with multiple double bonds, such as butadiene, have multiple hydrogenation schemes in which primary or secondary carbocation intermediates are formed during hydrogenation. Transition states with secondary carbocations results in free energy barriers > 20 kJ mol\(^{-1}\) more favorable than formation of primary carbocations, as expected. Oxocarbenium ions formed in CH\(_2\)O hydrogenation are also stable and result in low hydrogenation barriers, however, stable benzenium carbocations cannot overcome the thermodynamic instability of benzene hydrogenation, resulting in large benzene hydrogenation barriers. Allyclic carbocations are formed during diene hydrogenations and are more stable than alkylcarbenium cations (formed in alkene hydrogenations). However, the extra stability of allylic carbocations does not fully account for the preferential hydrogenation of dienes over alkenes. Diene hydrogenation is further accelerated by the protonation and hydridation at \(\alpha,\delta\) positions (a route only available to conjugated dienes) as demonstrated by effective free energy barriers 10–30 kJ mol\(^{-1}\) lower to form 2-butene than 1-butene from butadiene (and similarly it is easier to form 3-hexene than 2-hexene from 2,4-hexadiene).

Hydrogenation barriers of C\(_4\) and C\(_6\) dienes, diene precursor species CH\(_2\)O, and aromatic species C\(_6\)H\(_6\) were investigated to determine causes of catalyst lifetime improvement. The main mechanism of lifetime improvement is through limiting the formation of deactivation precursors—dienes and CH\(_2\)O—as C\(_6\)H\(_6\) hydrogenation occurs with high barriers (> 200 kJ mol\(^{-1}\) in MFI and CHA) because breaking aromaticity of these species is unfavorable. Direct hydrogenation barriers of butadiene are relatively low (140 kJ mol\(^{-1}\) in MFI and 122 kJ mol\(^{-1}\) in CHA), as are those of hydrogenation of CH\(_2\)O, which plays a role in diene formation\(^{24,42}\) (140 kJ mol\(^{-1}\) in MFI and 142 kJ mol\(^{-1}\) in CHA). The limited hydrogenation of alkenes with dramatic increases in catalyst lifetime in MTO studies suggest that deactivation precursors must be selectively hydrogenated (i.e., hydrogenated at a higher rate) than the desired alkene products, and this is proven here as diene and formaldehyde hydrogenation occurs with barriers 20–30 kJ mol\(^{-1}\) lower than those for propene or butene hydrogenation and 60–70 kJ mol\(^{-1}\) lower than those for ethene hydrogenation. Furthermore, hydrogenation of dienes and CH\(_2\)O is facile compared C\(_2–C_4\) alkene hydrogenation, indicating that dienes are also selectively hydrogenated over alkenes, consistent with previous kinetic studies suggesting that rate constants of butadiene hydrogenation are higher than those of C\(_2\) and C\(_3\) alkene hydrogenation.\(^{43}\) Overall, hydrogenation of dienes and CH\(_2\)O is relatively facile compared alkenes in MFI and CHA zeolite frameworks demonstrating that diene elimination is the primary mechanism of catalyst lifetime improvement with high-pressure H\(_2\) co-feeds.
References


