Mechanistic origins of the high-pressure inhibition of methanol dehydration rates in small-pore acidic zeolites

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ABSTRACT

Turnover rates of Brønsted acid-catalyzed methanol dehydration to dimethyl ether become inhibited at high methanol pressures (>10 kPa, 415 K) on small-pore zeolites (CHA, AEI, LTA, LEV), irrespective of the distribution of framework Al and their attendant H⁺ sites, but not on medium-pore or large-pore zeolites. High-pressure kinetic inhibition occurs concomitantly with the stabilization of higher-order methanol clusters (e.g., trimers, tetramers) observed experimentally by physisorption of liquid-like methanol and the appearance of vibrational modes for methanol clusters in IR spectra, consistent with the attenuation of such inhibition at higher temperatures (>450 K) that result in decreased methanol coverage. DFT-predicted methanol coverage phase diagrams confirm that higher-order methanol clusters form in pressure and temperature ranges corresponding to the onset of kinetic inhibition observed experimentally, and that higher-order methanol clusters are reactive but that excess methanol increases the apparent barriers to form kinetically relevant transition states that eliminate dimethyl ether and thus inhibit turnover rates. This combined experimental and theoretical investigation provides precise mechanistic interpretation of the high-pressure inhibition of methanol dehydration turnover rates on small-pore Brønsted acid zeolites. This rigorous analysis enables the development of kinetic models to account for the diverse structures of methanol precursors that dehydrate to form dimethyl ether, and methods to assess the prevalence of higher-order clusters that serve as reactive and inhibitory intermediates within small-pore zeolites during methanol conversion.

Keywords:
Methanol dehydration
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1. Introduction

Methanol is a promising carbon source for producing light olefins (e.g., ethene, propene) and aromatics over acidic zeolite catalysts at elevated temperatures (>453 K) via the methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) processes [1,2], in which product selectivities can be tuned via judicious choice of reaction conditions (e.g., temperature, methanol pressure) [3] and zeolite framework [3–5]. The conversion of methanol into olefins proceeds through a “hydrocarbon pool” mechanism, wherein methanol is dehydrated at Brønsted acid sites to form methoxy intermediates that subsequently react with confined polymethylated aromatics to generate new C–C bonds [3,4,6]. Surface-bound methoxy groups (CH₂–Z), formed via methanol dehydration, have also been implicated in the initiation of C–C bond formation, at low turnover numbers, via carbonylation with either carbon monoxide or formaldehyde present either as impurities or formed during reaction [6–8]. Methanol dehydration to dimethyl ether (DME) occurs selectively without olefin formation at low-temperatures (<453 K) [9,10], and measurement of methanol dehydration rate constants has enabled investigating the individual effects of confinement and acid strength in zeolite acid catalysis [10–12].

Methanol dehydration to DME on solid Brønsted acids can proceed via two different mechanisms, referred to as the associative (concerted) or dissociative (sequential) mechanisms (Scheme 1) [10–14]. The first step in both mechanisms is quasi-equilibrated adsorption of a gas-phase methanol at a bare proton. In the associative mechanism, protonated methanol dimers form via quasi-equilibrated adsorption of a second gas-phase methanol, and then eliminate DME and water in a kinetically relevant dehydration step (Scheme 1, top). The dissociative mechanism (Scheme 1, bottom), in contrast, involves kinetically relevant dehydration of methanol monomers to eliminate water and form a surface-bound methoxy
intermediate. Surface methoxy intermediates then undergo nucleophilic attack by a second gas-phase methanol in a quasi-equilibrated step to form DME. DME formation rates via the dissociative mechanism are thus inhibited by the formation of protonated methanol dimers [10], while methanol-water complexes can inhibit both pathways (Scheme 1).

Measured reaction kinetics (433 K) and DFT calculations indicate that methanol dehydration to DME proceeds via the associative mechanism at Bronsted acid sites (H⁺ sites) of polyoxometalate clusters (POM) supported on amorphous SiO₂ [10], and at such sites confined within medium-pore and large-pore zeolites (FAU, SFH, BEA, MOR, MTW, MFI, and MTT; 0.5–1.2 nm diameter voids) [11–13,15]. Turnover rates of methanol dehydration (433 K, per H⁺) on these catalysts follow a Langmuirian dependence on methanol partial pressure (0.05–20 kPa), transitioning from a first-order to zero-order kinetic regime at high methanol pressures. Additionally, in situ IR spectra measured on MFI zeolites (433 K, 0.1–16 kPa CH₃OH) do not show bare protons or surface methoxy intermediates, consistent with the associative mechanism [13] and suggesting that all sites are covered by methanol monomers or higher order clusters during reaction. Turnover rates (per H⁺, 415 K) measured on small-pore CHA zeolites (Si/Al = 15) containing isolated H⁺ sites also appear to proceed via the associative mechanism, based on analogous observations from kinetic and in situ IR data (0.05–20 kPa CH₃OH, 415 K) [16]. In situ IR spectra (0.05–20 kPa CH₃OH, 415 K) of CHA zeolites of similar composition (Si/Al = 15) containing paired H⁺ sites (2 Al per 6-MR), however, show surface methoxy present at coverages that increase with the fraction of paired H⁺ sites [16], suggesting that the dissociative dehydration mechanism may proceed at paired H⁺ sites in CHA.

Furthermore, turnover rates (per H⁺) on CHA increase with the fraction of H⁺ sites in paired configurations [16,17], and density functional theory (DFT) calculations suggest that interactions between proximal Bronsted acid sites may alter the stability of the deprotonated conjugate base and lead to an increase in acid strength [18]. The precise mechanistic roles of paired and isolated H⁺ site ensembles in CHA, however, are convoluted by inhibition of methanol dehydration rates at high methanol pressures (415 K, >10 kPa CH₃OH) [16], a phenomenon not observed on medium-pore and large-pore zeolites [11,13].

The inhibition of certain alkane dehydration mechanisms has been previously reported for C₂–C₄ alkanols over solid acid catalysts. Bimolecular dehydration rates of ethanol to form diethyl ether (MFI, FER, MOR; 388–409 K, >6 kPa C₂H₅OH) [19] and propa
gol dehydration to dipropyl ether (MFI, 413–443 K, <4 kPa C₃H₆OH) [20] asymptotically approach a zero-order dependence and are not inhibited at higher alkane partial pressures, similar to reports of methanol dehydration rates on medium-pore and large-pore zeolites [11]. Ethanol and propanol, unlike methanol, are also able to undergo unimolecular dehydration to form the corresponding alkene. Ethanol dehydration to ethene is inhibited on MOR zeolites (368–409 K, <6 kPa C₂H₅OH) because additional ethanol molecules adsorb at ethanol monomers and must desorb prior to ethene formation transition states [19]. Similar observations have also been reported for unimolecular dehydration of propa
gol to propanol (MFI, 413–443 K, <4 kPa C₂H₅OH) [20] and butanol to butene (W-POM/SiO₂, 343 K, <1 kPa C₄H₁₀OH) [21].

Thus, the high-pressure inhibition of bimolecular methanol dehydration rates (415 K) in small-pore CHA zeolites presents a sharp contrast to the inhibition of only unimolecular alkane dehydration in medium-pore and large-pore zeolites, and the precise mechanistic origin of this inhibition has remained imprecisely understood. In our prior work, such high-pressure rate inhibition was accounted for by including an elementary step for the formation of an unreactive methanol trimer via quasi-equilibrated adsorption of a methanol at a protonated dimer, to derive an ad hoc rate equation that allowed estimating first-order and zero-order rate constants from experimentally measured rate data on CHA zeolites [16]. Here, we further investigate the formation and stability of different methanol species at isolated H⁺ sites in CHA zeolites during methanol dehydration catalysis using a combination of kinetic, spectroscopic, and theoretical probes. High-pressure inhibition of methanol dehydration rates (per H⁺) becomes attenuated at elevated reaction temperatures (>450 K), which coincides with the disappearance of IR vibrational bands characteristic of methanol trimers and larger clusters (~3770 cm⁻¹) detected by in situ IR spectroscopy (343–473 K, 10 kPa CH₃OH). Methanol adsorption isotherms indicate that the onset of dehydration rate inhibition (415 K, per H⁺) occurs at coverages corresponding to >2 CH₃OH per H⁺ site, consistent with IR spectra (0.01–3 CH₃OH/H⁺; 293 K) that show the appearance of methanol clusters at coverages of >0.7 CH₃OH per H⁺ site and that increase in intensity with increasing methanol coverage. DFT is used to calculate the Gibbs free energies of various methanol complexes (1–12 CH₃OH per proton) confined within CHA as a function of temperature and methanol pressure, which indicate that methanol trimers are preferentially stabilized in CHA at methanol pressures corresponding to the onset of kinetic inhibition observed experimentally (>10 kPa, 415 K). Apparent free energy barriers for methanol dehydration are calculated considering up to four methanol-derived species at an H⁺ site, in which spectating methanol species are found to insert between reacting species and framework O atoms. DFT-predicted methanol dehydration rates (415 K) are compared with experimental data to determine plausible reaction mechanisms and highlight the critical influence of the zeolite framework on stabilizing reactive and inhibitory intermediates in methanol conversion pathways.

2. Methods and materials

2.1. Catalyst synthesis and characterization

2.1.1. Synthesis of different small-pore zeolites

The full synthesis procedure of CHA zeolites containing isolated H⁺ sites is described in detail elsewhere [17]. In brief, CHA was syn-

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thesized using N,N,N-trimethyl-1-adamantylammonium hydroxide as the structure directing agent (SDA) with a molar ratio in the crystallization medium of 1 SiO₂/0.033 Al₂O₃/0.5 TMAOH/44 H₂O. In a typical synthesis, deionized water and an aqueous solution of TMAOH were mixed and stirred for 15 min under ambient conditions in a perfluoroalkoxy alkane (PFA) jar. Next, aluminum hydroxide powder was added and stirred for 15 min under ambient conditions. Finally, an aqueous colloidal silica solution was added and the contents were covered and stirred for 2 h under ambient conditions. The resulting mixture was transferred to a PTFE-lined stainless-steel autoclave and heated to 433 K under rotation at 40 RPM for 6 days.

The full synthesis procedure of AEI zeolites and the organic SDA, cis-2,6-dimethylpiperidinium hydroxide (DMPOH), are described in detail elsewhere [22,23]. Briefly, AEI was synthesized using a molar composition of 1 SiO₂/0.017 Al₂O₃/0.07 DMPOH/0.58 NaOH/12.3 H₂O. The resulting solution was transferred to a PTFE-lined stainless-steel autoclave and heated to 413 K under rotation for 4 days.

LEV zeolites were synthesized following a reported procedure using a mixture of 1-adamantylamine (AdaNH₂) and sodium fluoride [24]. A molar ratio of 1 SiO₂/0.024 Al₂O₃/0.3 AdaNH₂/0.05 NaF/10 H₂O was used in the crystallization medium. In a PFA jar, 4.455 g of AdaNH₂ (Sigma-Aldrich, 97 wt%) were added to 17.081 g of deionized water (18.2 MΩ) and stirred until fully dissolved. 6 g of FAU zeolite (CDV720, Si/Al = 21, Zeolyst) were added and stirred for 10 min until a uniform slurry was obtained. Finally, 0.237 g of NaF (Sigma-Aldrich, 99 wt%) were added and the mixture was covered and stirred for 2 h at ambient temperature. The resulting mixture was then loaded into a 45 cm³ PTFE-lined stainless-steel autoclave and placed in a static oven at 423 K for 10 days.

LTA zeolites and the required organic SDA, 1,2-dimethyl-3-(4-methylbenzyl)imidazolium hydroxide (DMMBI-OH) were synthesized according to previous reports [25]. The synthesis of DMMBI-CI was carried out in a two-neck 500 cm³ round-bottom flask attached to a water-cooled condenser to minimize solvent evaporation. In the round-bottom flask, a 0.1 M solution of 1,2-dimethylimidazole (Sigma-Aldrich, 98 wt%) was first prepared by dissolving 0.48 g of 1,2-dimethylimidazole in 50 cm³ of chloroform (Sigma-Aldrich, 99.8 wt%) and stirring for 15 min to homogenize the contents. In a separate 100 cm³ pear-shaped flask, a 0.1 M solution of 4-methylbenzyl chloride (Sigma-Aldrich, 98 wt%) was prepared by adding 0.7 g of 4-methylbenzyl chloride to 50 cm³ of chloroform and stirring until homogenous. The 0.1 M solution of 4-methylbenzyl chloride was then added to the 0.1 M solution of 1,2-dimethylimidazole, the second-neck of the round-bottom flask capped with a Viton septum, and stirred for two days at 303 K. After two days, the solution was evaporated, dissolved in a minimum amount of chloroform, and then recrystallized with diethyl ether (Sigma-Aldrich, 99 wt%). A portion of the crystalline product was dissolved in D₂O (Cambridge Isotope Laboratories, 99.9%) and a ¹H NMR spectrum was recorded and was consistent with reported ¹H chemical shifts for DMMBI-CI (details in Supp. Info.) [25]. The resulting Cl⁻ form of the SDA salt was then converted to its OH⁻ form by ion-exchange with a Dowex Marathon A (Sigma-Aldrich) using a mass ratio of 1 SDA/3 resin/H₂O and repeated thrice with fresh resin. A final purity of ~80% DMBMI-OH was confirmed by titration with a 0.1 M HCl solution.

The synthesis of high-silica LTA zeolites was performed using a mixture of DMBMI-OH and tetramethylammonium hydroxide (TMAOH) as the SDAs with a molar composition of 1 SiO₂/0.025 Al₂O₃/0.45 DMBMI-OH/0.05 TMAOH/0.49 HF/5 H₂O in the synthesis medium. In a PFA jar, 11.040 g of an aqueous DMBMI-OH solution (20 wt%) were added to 0.253 g of an aqueous TMAOH solution (Sigma-Aldrich, 25 wt%) and stirred for five minutes. Next, 0.032 g of Al(OH)₃ powder (SPI Pharma) were added to the SDA solution and stirred until fully dissolved. 1.746 g of tetraethyl-lorthiosilicate (TEOS, Sigma-Aldrich, 98 wt%) were then added and the resulting mixture was capped and stirred for two hours under ambient conditions. After two hours, the mixture was uncapped and excess water and ethanol, formed upon hydrolysis of TEOS, was allowed to evaporate under ambient conditions until the target H₂O/SiO₂ ratio was obtained. 5 g of additional water were then added and the mixture was again dehydrated to reach the target H₂O/SiO₂ ratio. After this second dehydration step, 0.160 g of hydrofluoric acid (Sigma-Aldrich, 48 wt%, 99.999% trace metals basis) were added dropwise and stirred with a PTFE spatula for 15 min. The synthesis mixture was then transferred to a 23 cm³ PTFE-lined stainless-steel autoclave and heated to 448 K under rotation (60 RPM) for 7 days.

After crystallization of each zeolite, the solid products were washed repeatedly with acetone (Sigma-Aldrich, 99.9 wt%) and deionized water (35 cm³ g⁻¹) until the pH of the supernatant remained constant between washes, recovered via centrifugation, and dried at 373 K overnight under stagnant air. The dried, as-synthesized zeolites were then heated to 853 K (0.0167 K s⁻¹) under flowing air (1.67 cm³ gcat⁻¹ s⁻¹) for 10 h to remove the occluded organic SDA.

2.1.1. ¹H NMR of 1,2-Dimethyl-3-(4-methylbenzyl)imidazolium chloride. After crystallization of DMMBI-CI, approximately 0.5 g of the recovered solid was dissolved in 0.5 cm³ of D₂O and a portion of this solution was placed inside an NMR tube (Wilmsad Lab-Glass, 5 mm thin wall, 7 in., 500 MHz) for ¹H NMR analysis. NMR spectra were collected on a Bruker ARX500 spectrometer equipped with a 5 mm BBFO Z-gradient probe at ambient temperature and represent the average of 128 scans. The measured spectrum is shown in Fig. S.9 of the Supp. Info. ¹H NMR (D₂O, 500 MHz): δ 7.31 (s, 2H), 7.27 (d, 2H), 7.18 (d, 2H), 5.27 (s, 2H), 3.74 (s, 3H), 2.54 (s, 3H), 2.31 (s, 3H).

2.1.2. Structural characterization of zeolite topology and porosity

The crystal topology of all synthesized zeolites was determined from powder X-ray diffraction (XRD) patterns measured on a Rigaku Smartlab X-ray diffractometer equipped with a Cu Kα radiation source (λ = 0.154 nm) operated at 1.76 kW. Samples were loaded onto zero-background sample holders (Rigaku) and pressed flat using a microscope slide prior to collecting diffraction patterns from 2θ = 4–40° at a rate of 0.04° s⁻¹ and a step size of 0.01°. Crystal topologies were confirmed by comparison of experimental diffraction patterns with those reported in the International Zeolite Association (IZA) structure database [26]. XRD patterns are shown in Fig. S.10 of the Supp. Info.

Zeolite micropore volumes were determined from Ar adsorption isotherms measured in a liquid Ar bath (87 K) on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Typically, 0.03–0.05 g of sieved zeolite (nominal diameter of 180–250 μm) were degassed by first heating to 393 K (0.167 K s⁻¹) under vacuum (<5 × 10⁻⁶ torr) for 2 h before further heating to 623 K (0.167 K s⁻¹) under vacuum (<5 × 10⁻⁶ torr) and holding for 9 h. The volume of gas adsorbed (cm³ g⁻¹) at STP was estimated from a semi-log derivative plot of the adsorption isotherm ((Q_ads)/((Q_ads/P_0))) vs. ln(P/P_0)). Ar adsorption isotherms are shown in Fig. S.11 and micropore volumes are tabulated in Table S.1 of the Supp. Info.

2.1.3. Elemental analysis and titration of H⁺ sites using NH₃

Total Al and H⁺ site contents are tabulated in Table S.1 of the Supp. Info. The total Al content of each zeolite was determined from atomic absorption spectroscopy (AAS) using a Perkin Elmer Analyst 300 Atomic Absorption Spectrometer. After removal of
occluded organic SDA molecules by oxidative treatment (853 K, 0.02 g) were digested in 3 g of HF acid (48 wt%, Sigma-Aldrich) overnight (at least 8 h) and then diluted with 50 g of deionized water (18.2 MΩ). Aqueous solutions were nebulized into an acetylene/nitrous oxide flame and Al absorbances were measured at a wavelength of 309.3 nm. Al concentrations were determined from calibration curves generated from solutions of known composition prepared by dilution of a 1000 ppm Al standard (Sigma-Aldrich, TraceCERT).

The number of H⁺ sites on each zeolite catalyst was measured by temperature programmed desorption (TPD) of NH₃ using reported procedures [27]. After organic removal, zeolite samples were exposed to a 1 M aqueous NH₄NO₃ (Sigma-Aldrich, 99 wt%) solution (150 cm³ g⁻¹) and stirred under ambient conditions for 24 h. Solids were then washed six times with deionized water (35 cm³ g⁻¹), recovered via centrifugation, and dried overnight at 373 K under stagnant air. NH₄-exchanged zeolite samples were then pelletized and sieved (nominal diameter of 180–250 μm) and suspended between two quartz wool plugs in a quartz U-tube reactor. The quartz reactor was then loaded into a Micromeritics Autochem II 2920 Chemisorption analyzer and heated to 873 K (0.167 K s⁻¹) under flowing He (50 cm³ g⁻¹ s⁻¹, 99.999%, Indiana Oxygen). The total amount of NH₃ desorbed was then quantified using an Agilent 5973 N mass selective detector (MSD).

2.2. Methanol dehydration kinetics and reactor configuration

Methanol dehydration kinetics were measured in a tubular packed-bed quartz reactor (7 mm inner diameter) with plug-flow hydrodynamics as described previously [16]. Zeolite samples were pelleted and sieved (nominal diameter between 180 and 250 μm) and supported between two quartz wool plugs in the reactor. The total amount of catalyst loaded into the reactor was varied between 0.005 and 0.030 g to maintain differential conversions. The total mass of zeolite charged to the reactor was maintained at a minimum of 0.025 g by dilution with Si-CHA. Dilutions (2–10 × dilution ratio) were prepared by grinding together both powders in a mortar and pestle, pelletizing, and then crushing to retain particles between 180 and 250 μm. Reactors were placed inside a three-zone furnace (Series 3210, Applied Test Systems) with a K-type thermocouple placed in direct contact with the external surface of reactor at the center of the catalyst bed and the temperature of the catalyst bed was controlled by Watlow controllers (EZ-Zone Series). Prior to contact with reactant mixtures, zeolite catalysts were heated to 773 K (0.033 K s⁻¹) and held for 4 h under a 5% O₂/He flow (50 cm³ g⁻¹ s⁻¹, 99.999%, Indiana Oxygen). Upon cooling to the desired reaction temperature, samples were flushed with He (150 cm³ g⁻¹ s⁻¹, 99.999%, Indiana Oxygen) for 0.5 h to remove residual O₂. Methanol (99.9 wt%, Sigma-Aldrich) was introduced into the He gas stream using a syringe pump (Legato 100, KD Scientific) and sent to the reactor through heated stainless-steel lines maintained at > 373 K using resistive heating tape (Brisk Heat Co.) and insulating wrap. Concentrations of reactants and products were measured using an Agilent 6890 gas chromatograph equipped with a flame ionization detector and an HP Plot-Q column (0.53 mm ID × 30 m × 0.4 μm film, Agilent). Methane (25% CH₄/Ar, 99.999%, Indiana Oxygen) was used as an internal standard and introduced into the reactor effluent at a constant rate (0.083 cm³ s⁻¹).

First apparent-order and zero-order methanol dehydration free energy barriers were measured on CHA zeolites with isolated H⁺ sites from DME formation rates (per H⁺) measured as a function of methanol pressure (0.05–50 kPa) at temperatures varied non-systematically between 383 and 415 K. Apparent first and zero-order methanol dehydration rate constants (per H⁺) were determined from a least squares regression of Eq. (4) to the rate data and the Eyring-Polanyi equation was used to extract first and zero-order apparent activation enthalpies and entropies. These data and calculations are shown in Section S.10 of the Supp. Info.

2.3. Measurement of IR spectra

2.3.1. Steady-state methanol dehydration

IR spectra collected under steady-state methanol dehydration catalysis were measured on a Nicolet 4700 spectrometer with an HgCdTe detector (MCT, cooled to 77 K by liquid N₂). Spectra were collected between 4000 and 400 cm⁻¹ and averaged over 64 scans at a 2 cm⁻¹ resolution and referenced to an empty cell background collected under He flow (0.33 cm³ s⁻¹, 99.999%, Indiana Oxygen) at 415 K. Zeolite catalysts were pressed into self-supporting wafers (0.01–0.02 g cm⁻²) and placed within a custom-built quartz IR cell sealed with CaF₂ windows [16,28,29]. Temperatures were measured by K-type thermocouples (Omega) held ~2 mm from each side of the zeolite wafer. Prior to each measurement, the zeolite wafer was heated to 773 K (0.083 K s⁻¹) for 4 h under flowing air (13.3 cm³ g⁻¹ s⁻¹) purified by a purge gas generator (Parker Balston, <1 ppm of CO₂, 200 K H₂O dew point), and then cooled under flowing He (13.3 cm³ g⁻¹ s⁻¹) to the analysis temperature. Methanol (Sigma-Aldrich, 99.9 wt%) was introduced to the quartz IR cell (0.1–22 kPa) by a syringe pump (Legato 100, KD Scientific) connected to a stainless-steel transfer lines maintained >353 K using resistive heating tape (Brisk Heat Co.) and insulating wrap. IR spectra were recorded as a function of time until peak intensities remained constant for >0.25 h. All spectra were baseline corrected and normalized to the zeolite combination and overtone T-O-T vibrational modes (1750–2100 cm⁻¹) of the freshly dehydrated zeolite spectrum.

2.3.2. IR spectra measured at known methanol coverages

Methanol adsorption isotherms were measured on the same IR apparatus as described in Section 2.3.1, except a custom-built glass vacuum manifold was used to introduce small amounts (<1 torr doses) of methanol onto dehydrated CHA zeolites [28,29]. IR spectra taken during methanol adsorption isotherms were referenced to an empty cell background taken under dynamic vacuum at 293 K. Prior to methanol dosing experiments, zeolite self-supporting wafers were heated to 773 K (0.083 K s⁻¹) under dynamic vacuum (<0.1 torr) for 2 h before cooling to room temperature. The adsorption temperature was maintained below room temperature (293 K) using a closed-loop chiller that recirculated chilled water (288 K) through cooling coils encircling the quartz IR cell [28]. Methanol was loaded into a glass ampule (1/4in OD) and purified on the vacuum manifold via successive freeze-pump-thaw cycles until dissolved gases were no longer observed bubbling out upon thawing. Zeolite samples were exposed to small amounts of methanol (2.5 × 10⁻⁵ mol per dose) and allowed to equilibrate for two minutes prior to measurement of an IR spectrum. Methanol coverages were calculated as the total number of moles of methanol that disappeared from the gas phase during each dose by taking the difference in the initial and final number of moles in the gas phase.

2.4. Measurement of methanol adsorption isotherms

High-resolution methanol adsorption isotherms were measured at 293 K using the same gas adsorption apparatus as described in Section 2.1.2. Methanol adsorbrates (Sigma-Aldrich, 99.9%) were degassed by successive freeze-pump-thaw cycles and supplied at their respective vapor pressures at 293 K. Adequate resolution at low pressures was achieved by holding samples under dynamic vacuum (<5 × 10⁻⁶ torr) on the analysis port during the prepara-
tion sequence until the dosing manifold was charged with adsor- 
bate prior to collection of the first data point. Methanol was then 
dosed onto the evacuated zeolite sample in equilibrated incre- 
mants of 1 cm$^3$ g$^{-1}$ (gas volume adsorbed at STP per gram) until 
a final relative pressure of P/P$_0$ = 0.6 was reached. This procedure 
was previously found necessary for obtaining accurate ethanol and 
water adsorption isotherms on siliceous BEA zeolites [30]. The full 
adsorption isotherm is shown in Fig. 5.16 in the Supp. Info.

2.5. Computational methods

Fully periodic density functional theory (DFT) calculations were 
performed using the Vienna ab initio software package (VASP) [31– 
34] and implemented in the Computational Catalysis Interface 
(CCI) [35]. Planewaves were constructed using the projector aug- 
mented wave method (PAW) with an energy cutoff of 400 eV 
[36,37]. The Brillouin zone was sampled at the Γ-point for all 
calculations. The Perdew-Burke-Ernzerhof (PBE) form of the general- 
ized gradient approximation (GGA) was used for all calculations 
[38]. Dispersive interactions were accounted for by including the 
DFT-D3 empirical correction with Becke and Johnson damping 
[39,40]. Structures were optimized in two steps to improve 
computational efficiency. Structures were optimized in the first 
step using a wavefunction convergence criteria such that energy 
variations between iterations were <10$^{-4}$ eV and forces were 
computed with a fast Fourier transform (FFT) grid of 1.5 × the energy 
cutoff (PREC = NORMAL in VASP); structures were relaxed until 
the maximum force on any atom was <0.05 eV Å$^{-1}$. These settings 
may result in inaccurate forces near the minimum; as such, struc- 
tures are then re-optimized with wavefunctions converged to 
within 10$^{-6}$ eV and forces computed with an FFT grid 2× the 
energy cutoff (PREC = ACCURATE in VASP). This two-step opti- 
mization scheme has been shown to increase computational effi- 
ciency by a factor of −3 for zeolite-based calculations that are 
sampled at the Γ point [35].

Transition state searches were initiated using the nudged elastic 
band (NEB) method with 16 intermediate images for each elemen- 
tary step and converged such that the forces on each atom were 
<0.5 eV Å$^{-1}$ [41,42]. Transition states were then refined starting 
from these NEB results using the Dimer method [43], where struc- 
tures were converged using the same criteria as those used for 
 optimizations (energy variation between iterations <10$^{-6}$ eV, 
max force per atom <0.05 eV Å$^{-1}$).

The CHA structure was obtained from the database of the inter- 
national zeolite association (IZA), with unit cell parameters 
a = b = 13.675 Å, c = 14.767 Å, α = β = 90.0$^\circ$, and γ = 120.0$^\circ$ [26]. 
The CHA structure is comprised of stacked six-member ring 
(6-MR) structures with adjacent eight-member ring (8-MR) windows 
leading into larger cage voids. CHA has one symmetrically 
unique T-site surrounded by four unique O atoms. One of the 36 
Si atoms in the CHA unit cell was replaced by an Al atom (Si/ 
Al = 35) and balanced by a proton to form a Brønsted acid site 
(Fig. S.1, Supporting Information). Previous work has shown that 
protons associated with Brønsted acid sites prefer to bind to O1 
or O4 atoms and are solvated by 6-MR or 8-MR motifs [18,44]. 
Zeoites are flexible materials and are prone to restructuring 
during DFT calculations, as recently emphasized for the MFI frame- 
work [45]. Therefore, the unit cell parameters of the CHA unit cell 
were optimized with an energy cutoff of 800 eV without con- 
straints (ISIF = 3 in VASP) to ensure that these initial unit cell 
parameters would not result in restructuring. These unit cell 
parameter optimizations yielded a <1% change in each unit cell 
parameter; therefore, the initial IZA structure was used in all sub- 
sequent calculations. Furthermore, annealing of the CHA structure 
was simulated with ab initio molecular dynamics (AIMD) in VASP 
to confirm that restructuring does not occur with the PBE 
exchange-correlation functional and D3BJ correction. The CHA 
structure was heated from 200 K to 800 K over 3 ps, held at 
800 K for 3 ps, and cooled from 800 K to 100 K over 15 ps, each with a timestep of 3 fs. The resulting annealed CHA structure 
was subsequently optimized using the same convergence criteria 
described above. This annealed and optimized CHA structure dif- 
fered by <1 kJ mol$^{-1}$ in energy from the directly optimized CHA 
structure from the IZA database. Moreover, the two structures dif- 
f ered by a negligible distance. These negligible changes in energy 
and structure indicate that the CHA structure supplied by IZA is 
sufficiently stable for kinetic studies.

Vibrational frequency calculations were used to approximate 
zero-point vibrational energies (ZPEVs), vibrational, rotational, 
and translational enthalpies (H) and free energies (G) using a fixed 
placement method (n = 2) for all gas-phase and adsorbed spe- 
cies. Framework Si and O atoms that were not bound to the Al 
atom were fixed during frequency calculations within the zeolite 
framework. These values were used to approximate total enthalpies 
in conjunction with VASP-derived electronic energies ($E_0$):

$$H = E_0 + ZPVE + H_{\text{ vib}} + H_{\text{ rot}} + H_{\text{ trans}}$$

(1)

and free energies

$$G = E_0 + ZPVE + G_{\text{ vib}} + G_{\text{ rot}} + G_{\text{ trans}}$$

(2)

at 415 K and 1 bar CH$_3$OH (standard pressure), the formulas for 
which are derived from statistical mechanics formalisms (see Sec- 
tion S.1 in the Supp. Info. for details) [46]. All motions for guest 
species within the zeolite framework are considered vibrations, 
such that translational and rotational $H$ and $G$ are zero for non-gas phase 
species, which are treated as ideal gases with appropriate equations 
from statistical mechanics. Enthalpies and entropies ($S$) derived 
from calculations were used to predict equilibrium constants of 
adsorption ($K$) from 300 to 500 K, in order to predict adsorption 
behavior of methanol in CHA and to predict equilibrium and rate 
constants for DFT-predicted rates. Low-frequency vibrational 
 modes disproportionately contribute to entropy estimates; as such, 
 frequencies below 60 cm$^{-1}$ were replaced by 60 cm$^{-1}$ (with the 
 exception of the negative frequency in transition states), as in pre- 
vious work [47,48].

The diverse confining voids within single zeolite frameworks 
affect the energies of guest species differently depending on the 
orientation and location of those species [48–50]. Therefore, a sys- 
tematic method of probing the configurational space of zeolites is 
critical to find favorable configurations of these intermediates [48]. 
Here, we perform systematic reorientations on adsorbates and 
 transition states interacting with each O atom of the CHA frame- 
work to ensure comprehensive probing of the confining space of 
the CHA voids. Adsorbates and transition states that strongly inter- 
act with framework O atoms (e.g., surface methoxy, transition 
states forming or breaking C−O bonds, and species H-bonding) 
were (1) reoriented about the axis formed by the Si and Al bond 
to the O atom; (2) rotated about their interactions with the frame- 
work O above the acid site by changing the adsorbate–O dihedral 
angle; and (3) moved by altering the angle between the Al, O, 
and adsorbate. Transition states were rotated about internal bonds 
and incipient bonds and adsorbates that did not interact strongly 
with the surrounding framework were rotated about the x-, y-, 
and z-axes (the y- and z-axes are the same as the b- and c- 
 vectors of the CHA unit cell, respectively). These reorientations 
yielded structures with large ranges of energies, while preserving 
strong interactions with the surrounding framework. This further 
indicates that there are diverse void environments around a single 
acid site within a zeolite framework, which can be probed using 
these systematic reorientations [48].
3. Results and discussion

3.1. Inhibition of methanol dehydration rates on small-pore zeolites

Methanol dehydration turnover rates (415 K, per H\(^+\)) on CHA zeolites containing predominantly isolated H\(^+\) sites increase linearly with methanol partial pressure (P\(_{\text{CH3OH}}\)) at low partial pressures (<1 kPa), before reaching a maximum and transitioning to a kinetic regime reflecting inhibition at high partial pressures (>10 kPa) (Fig. 1). This behavior is not captured by the form of the associative dehydration rate law derived assuming H\(^+\) sites are covered by methanol monomers and protonated dimers as most abundant surface intermediates (MASI) (Eq. (3)) [10].

\[
r_{A} = \frac{k_{\text{DME},A}K_{D}P_{\text{CH3OH}}}{1 + K_{D}P_{\text{CH3OH}}}
\]

In Eq. (3), \(k_{\text{DME},A}\) is the rate constant for DME formation via the associative mechanism, \(K_{D}\) is the equilibrium constant for forming a protonated dimer from a gaseous methanol and adsorbed methanol monomer, and \(P_{\text{CH3OH}}\) is partial pressure of methanol. \textit{In situ} IR spectra measured under conditions of methanol dehydration catalysis (415 K, 0.05–20 kPa) detected methanol monomers (2400 cm\(^{-1}\)) and dimers (2600 cm\(^{-1}\)) [13], and vibrational modes for methanol clusters (3370 cm\(^{-1}\)) [51] at high methanol partial pressures (>10 kPa) [16]. Including methanol trimers as a MASI introduces a second-order methanol pressure term in the denominator of the associative dehydration rate law (Eq. (4)), which is able to describe the rate inhibition measured at high methanol partial pressures (Fig. 1, solid line) [16].

\[
r_{A} = \frac{k_{\text{DME},A}K_{D}P_{\text{CH3OH}}}{1 + K_{D}P_{\text{CH3OH}} + K_{D}K_{P}P_{\text{CH2OH}}}
\]

In Eq. (4), \(K_{P}\) is the equilibrium constant for forming a methanol trimer from a gaseous methanol and adsorbed protonated dimer. Before using Eq. (4) to describe methanol dehydration rates on CHA zeolites, we first examine and discard other mechanistic assumptions that would also predict high-pressure kinetic inhibition, by considering other plausible intermediates and rate laws derived from the dissociative mechanism that do not consider surface methoxy as a MASI, since such species are not detected by \textit{in situ} IR spectra of CHA zeolites (Si/Al = 15) containing isolated H\(^+\) sites [16].

An alternate rate law can be derived for the dissociative mechanism, assuming methanol monomer dehydration to form methoxy intermediates is the kinetically relevant step, and that H\(^+\) sites, methanol monomers, and protonated dimers are the MASI (\(r_{D1}\); derivation in Section S.13.1 of the Supp. Info.):

\[
r_{D1} = \frac{k_{\text{Me}}K_{M}K_{M}P_{\text{CH3OH}}}{1 + K_{M}P_{\text{CH3OH}} + K_{M}K_{P}P_{\text{CH2OH}}}
\]

In Eq. (5), \(k_{\text{Me}}\) is the methoxy formation rate constant, and \(K_{M}\) is the equilibrium constant for forming a methanol monomer from gaseous methanol and a vacant H\(^+\) site. This expression predicts inhibition at high methanol partial pressures because protonated dimers are spectator species in the dissociative mechanism (Scheme 1). This rate expression would require vacant H\(^+\) sites to be a MASI, however, which is inconsistent with \textit{in situ} IR spectra that show complete perturbation of bridging OH stretching vibrations (~3608 cm\(^{-1}\)) by adsorbates at low methanol partial pressures corresponding to the first-order kinetic regime (~<1 kPa CH\(_{3}\)OH, 415 K) [16]. The removal of vacant H\(^+\) sites as a MASI causes Eq. (5) to predict between zero-order and negative-order dependences on methanol pressure, resulting in a rate law (Eq. (6)) that does not describe the first-order dependence of methanol dehydration rates at low pressures (Fig. 1, dotted line):

\[
r_{D2} = \frac{k_{\text{DME},A}K_{M}K_{M}K_{M}P_{\text{CH3OH}}P_{\text{CH2OH}}^{1/2}}{1 + K_{D}P_{\text{CH3OH}}}
\]

In Eq. (7), \(k_{\text{DME},A}\) is the DME formation rate constant for the dissociative mechanism, \(K_{M}\) is the equilibrium constant for forming a methoxy-methanol pair from a surface methoxy and gaseous methanol, and \(P_{\text{H2O}}\) is the gas-phase partial pressure of water, which is generated via methanol monomer dehydration to form a surface methoxy. This rate law predicts a first-order kinetic regime at low methanol pressures and a transition to a zero-order kinetic regime at higher pressures, but also predicts rate inhibition caused by hydration of surface methoxy intermediates. Eq. (7) was regressed to methanol dehydration rates (per H\(^+\), 415 K) measured on CHA zeolites containing isolated H\(^+\) sites, assuming the gaseous water partial pressure is equal to that of DME formed from reaction (Fig. 1, dashed line). The high-pressure inhibition observed experimentally causes methanol conversion to decrease (Fig. 2a) faster than Eq. (7) would predict, indicating that the product water formed via methanol dehydration is unable to account for the measured inhibition (Fig. 1, dashed line). Moreover, methanol dehydration rates do not depend on space velocity at fixed methanol pressure (per H\(^+\), 1 kPa CH\(_{3}\)OH, 5–30% conv.; Fig. 2b), as would be predicted by Eq. (7) because of the inverse dependence of methanol dehydration rates on water pressure (solid line, Fig. 2b; derivation in Section S.12 of Supp. Info.). Methanol dehydration rates (415 K, per H\(^+\)) were also measured after treating methanol reactants to remove any residual moisture and contaminants (purification procedure in Section S.4, Supp. Info.), and were
identical to those measured using unpurified methanol (Fig. S.9, Supp. Info.). Thus, any adventitious water present in the reactant methanol feed, or generated in situ as a reaction product, is not responsible for the observed inhibition at high methanol pressures.

### 3.2. DFT assessments of prevalent methanol dehydration reaction pathways

Prior to interpreting the mechanistic origin of high-pressure inhibition of methanol dehydration rates, we first use DFT to predict the free energy landscapes (Fig. 3) of both the associative and dissociative mechanism at isolated H⁺ sites in CHA (1 bar, 415 K). For the associative mechanism, DME formation from a protonated dimer intermediate is the kinetically relevant (i.e., rate-determining) step, and DFT estimates a zero-order free energy barrier \( \Delta G_{\text{zero}} = \Delta G_{\text{dimer}} \) of 137 kJ mol\(^{-1}\) and first-order free energy barrier \( \Delta G_{\text{first}} = \Delta G_{\text{dimer}} - \Delta G_{\text{monomer}} - \Delta G_{\text{CH₃OH}} \) of 123 kJ mol\(^{-1}\) (Fig. 3). For the dissociative mechanism, the first step methylates the zeolite surface with an intrinsic and overall barrier of 135 kJ mol\(^{-1}\), while the second step involves methylating methanol to form DME with an intrinsic barrier of 77 kJ mol\(^{-1}\) and an overall barrier of 130 kJ mol\(^{-1}\) (Fig. 3). Either of these steps could be kinetically relevant should DME form via the dissociative mechanism. Therefore, the kinetic fates of surface methoxy intermediates were determined by calculating ratio of the reverse rate of the first step \( r_{\text{D1}} \) to the forward rate of the second step \( r_{\text{D2}} \) as a function of conversion (details in Section S.3 in Supp. Info.). The forward rate of the second step is >10× faster than the reverse rate of the first step below 30% conversion, corresponding to the highest value tested in this work (Fig. S.7, Supp. Info.), and thus the first step is kinetically relevant at these conditions.

The reaction coordinate diagram in Fig. 3 was constructed after carefully examining each intermediate and transition state structure to identify their most stable configurations, using systematic reorientations of initially converged structures to more comprehensively probe the configurational space accessible within zeolite voids [48]. The first step of the dissociative mechanism involves surface methylolation transition states that are stabilized by 8-MR structures, in which H atoms of hydroxyl groups form H-bonds to lattice O atoms (Fig. 4a). Surface methylolation transition states preferentially interact with O3 of the conjugate base and form two H-bonds to O atoms in the 8-MR, in which O3 is located...
The framework O atom with which the methyl group interacts in (a) and (b) is labeled. Incipient bonds (black) and H-bonds (navy) are labeled in pm. Apparent ($\Delta G_{app}$) and intrinsic free energy ($\Delta G_{intr}$) and apparent enthalpy ($\Delta H_{app}$) barriers in kJ mol$^{-1}$, and apparent entropies ($\Delta S_{app}$) in J mol$^{-1}$ K$^{-1}$, are shown relative to an adsorbed methanol. The 8-MR (orange, green) and 6-MR (light blue) adjacent to each transition state are highlighted.

The most favorable transition state found in CHA for (a) surface methylation (the first step of the dissociative mechanism), (b) methanol methylation (the second step of the dissociative mechanism), and (c) associative dimethyl ether formation. The framework O atom with which the methyl group interacts in (a) and (b) is labeled. Incipient bonds (black) and H-bonds (navy) are labeled in pm. Apparent ($\Delta G_{app}$) and intrinsic free energy ($\Delta G_{intr}$) and apparent enthalpy ($\Delta H_{app}$) barriers in kJ mol$^{-1}$, and apparent entropies ($\Delta S_{app}$) in J mol$^{-1}$ K$^{-1}$, are shown relative to an adsorbed methanol. The 8-MR (orange, green) and 6-MR (light blue) adjacent to each transition state are highlighted.

The second step of the dissociative mechanism, in which another methanol accepts the surface methyl group, also occurs most easily in the 8-MR; however, this transition state forms preferentially at O4 of the conjugate base rather than at O3 (Fig. 4b). The methanol that accepts the surface methyl group forms one H-bond to another O atom in the 8-MR that contains O4 of the active site. The reacting oxygenate species (CH$_3$OH) contains only one polar O–H bond instead of two (H$_2$O), resulting in less H-bonding capacity in this transition state than in the other two possible transition states that occur during methanol dehydration (Fig. 4). Moreover, this H-bond is longer (196 pm; Fig. 4b) and weaker than the H-bonds formed in surface methylation (192 and 194 pm; Fig. 4a) and associative DME formation (179 and 201 pm; Fig. 4c) transition states.

The associative transition state (Fig. 4c) is stabilized by 8-MR structures similarly to surface methylation transition states (Fig. 4a). The water leaving group in this transition state forms two H-bonds to framework O atoms in the 8-MR, one of which is O4 of the conjugate base and stabilizes partial charges of the transition state structure. Furthermore, the methanol that accepts the methyl group forms another H-bond to O3 of the conjugate base, again stabilizing the transition state and allowing for rapid surface protonation after DME is formed. These concerted H-bonding motifs form a ring of interactions as the methyl group is transferred from one oxygenate to another (Fig. 4c, inset), allowing for more effective charge distribution than is possible in either of the dissociative transition states. Moreover, H-bonding in the associative transition state occurs predominantly with O atoms of the conjugate base, which harbor more negative partial charge, resulting in shorter (181 pm on average in Fig. 4c; 193 and 196 pm in Fig. 4) and stronger stabilizing interactions between reacting species and the zeolite surface.

Maximum rate analysis was then used to predict rates of competing reaction pathways using these DFT-predicted free energy barriers, which are taken together with statistical mechanics formalisms (see Section S.1 of the Supp. Info. for relevant formulas) to calculate rate ($k$) and equilibrium constants ($K$), as described in previous work [48,52]. The overall rate of a reaction pathway is taken as the rate of the slowest elementary step, identified from rates calculated by separately considering each elementary step to be the sole rate-limiting step. The fastest overall rates among different competing reaction pathways are used to identify prevailing reaction routes. Although the associative route occurs with an overall barrier 12 kJ mol$^{-1}$ lower than that of the dissociative route at 415 K (123 kJ mol$^{-1}$ overall; Fig. 3), the resulting larger rate constant does not account for pressure effects on rates, requiring maximum rate analysis to assess competing dehydration pathways.

The results of maximum rate analysis at 415 K and 0.1% conversion are shown in Fig. 5, with rates of the associative pathway and of the first and second steps of the dissociative pathway shown as a function of methanol pressure. The second step of the dissociative pathway occurs at faster rates than the associative mechanism at all pressures considered here (0.01–100 kPa) (Fig. 5), consistent with analysis of the reversibility of the first step that indicates it is the sole kinetically relevant step of the dissociative mechanism (Section S.3, Supp. Info.). The dissociative pathway dominates at pressures below 4 kPa at 415 K, which reflects the relative pressure dependences of rates for the associative and dissociative routes:

$$\frac{r_0}{r_1} = \frac{k_0}{k_1} K_D P_{CH_3OH}$$

(8)

This equation indicates that the dissociative route will dominate at sufficiently low methanol pressures, and that the prevailing reaction mechanism will shift to the associative route at higher pressures. Rates estimated by DFT predict this transition occurs at 4, 10, 23, and 63 kPa at 415, 433, 450, and 473 K, respectively (Fig. S6b). This shift reflects entropic and enthalpic preferences for these routes, in which the adsorption of a second methanol in the associative route confers enthalpic gains but concomitant entropic losses that preferentially benefit the dissociative mechanism at high temperatures and low pressures. This is consistent
with prior work on MFI zeolites [12,13,15] and POM catalysts [10], which indicate similar behavior for these mechanisms with different kinetic conditions.

3.3. Generality of high-pressure kinetic inhibition on small-pore zeolites and its dependence on temperature

Taken together, the experimental data in Section 3.1 provide strong evidence that methanol dehydration proceeds via the associative dehydration mechanism at isolated H⁺ sites in CHA zeolites. These findings are consistent with previous investigations of methanol dehydrogenation on microporous (medium-pore, large-pore) and mesoporous solid Brønsted acid catalysts that have compared both dehydration mechanisms under conditions where sites are covered by methanol monomers and dimers (433 K, 0.2–16 kPa CH₃OH) [10,12,13,53,54]. In Section 3.2, the DFT-calculated free energy barriers (415 K) on isolated H⁺ sites in CHA zeolites in both the first-order and zero-order regime for the associative mechanism show closer agreement with values measured experimentally (Table 1). Moreover, maximum rate analysis indicates that the associative mechanism prevails at sufficiently high methanol pressures (>4 kPa) in CHA containing only isolated H⁺ sites.

We next experimentally probed whether high-pressure inhibition is a general feature of small-pore microporous acids, given that such high-pressure inhibition of methanol dehydration rates was also observed in our prior studies of CHA zeolites with different fractions of paired H⁺ sites [16]. Methanol dehydration rates (415 K, per H⁺) were measured as a function of methanol pressure on other small-pore zeolite frameworks including AEL, LEV, and LTA, and the data are shown in Fig. 6. Methanol dehydration rates on all small-pore zeolites show a first-order kinetic regime at low methanol pressures, before reaching a maximum and then decreasing with increasing methanol pressure. These data suggest that small-pore zeolite framework topologies, in general, assist in stabilizing inhibitory methanol species at sufficiently high methanol partial pressures.

CHA zeolites (Si/Al = 15) containing predominantly isolated H⁺ sites were chosen as representative samples to further study the mechanistic origin of the high-pressure inhibition of methanol dehydration rates in small-pore zeolites. High-pressure inhibition becomes attenuated in CHA containing only isolated H⁺ sites (Fig. 7a), and in CHA containing paired H⁺ sites (Fig. S.15, Supp. Info.), with increasing reaction temperature (398–473 K). This behavior is inconsistent with that expected if inhibition were to reflect intracrystalline transport restrictions of larger DME products, which would cause inhibition to become more severe with increasing temperature. Light olefins (e.g., ethene and propene) were observed in the reactor effluent at low methanol partial pressures at temperatures >433 K, and decreased in concentration with increasing methanol partial pressures, consistent with previous reports of methanol-to-olefins in H-MFI (623 K) [4].

First-order rate constants (per H⁺), extracted from linear regression of Eq. (3) to the data in Fig. 7a, initially increase exponentially with temperature (398–415 K), but begin to deviate from this exponential dependence at elevated temperatures (433–473 K; Fig. 7b), in part reflecting scavenging of C₁ intermediates and DME products to produce olefins under first-order methanol dehydration conditions (<1 kPa). In contrast, zero-order rate constants (per H⁺) increase exponentially with temperature in the range studied (398–473 K), suggesting that any olefin formation does not significantly influence DME formation rates at high methanol pressures (>10 kPa CH₃OH) [4]. These results suggest that methanol dehydration rates are not inhibited by intracrystalline transport of DME products and instead may reflect inhibition by absorption of excess methanol molecules as proposed previously [17], as would be expected from the decrease in methanol coverage with increasing temperature at fixed methanol pressure.

The adsorbed methanol structures on CHA zeolites containing isolated H⁺ sites at varying temperatures (343–473 K) were assessed from in situ IR spectra measured at 10 kPa CH₃OH, which coincides with the onset of inhibition in CHA zeolites (Fig. 1). CH₃OH cluster (~3370 cm⁻¹) [51] formation is a strong function of temperature (Fig. 8), evident by IR peaks that decrease in intensity at faster rates than those for protonated methanol dimers (2620 cm⁻¹; Fig. 8, inset) [13], suggesting that methanol adsorbs in clusters (e.g., trimers, tetramers) [51] more weakly than in protonated dimer structures. These findings are consistent with the adsorption of excess methanol at protonated methanol dimers, and with the attenuated inhibition of methanol dehydration rates at higher reaction temperatures (398–473 K; Fig. 7).

### Table 1

Measured and calculated first-order and zero-order free energy barriers (ΔGₐ₁ (kJ mol⁻¹) at 415 K for the associative and dissociative dehydration mechanisms at isolated H⁺ sites in CHA zeolites.

<table>
<thead>
<tr>
<th></th>
<th>ΔG₁ (kJ mol⁻¹)</th>
<th>ΔG₀ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>100</td>
<td>117</td>
</tr>
<tr>
<td>Associative</td>
<td>123</td>
<td>137</td>
</tr>
<tr>
<td>Dissociative</td>
<td>135</td>
<td>77</td>
</tr>
</tbody>
</table>

* Calculated from rate data measured between 383 and 415 K.
* Calculated from DFT (PBE-D3BJ, PAW).

3.4. Adsorbed methanol structures as a function of coverage assessed from in situ IR spectra, equilibrium adsorption isotherms, and DFT-calculated free energies

Methanol adsorption isotherms (293 K; full isotherm shown in Fig. S.16 of Supp. Info.), normalized to the number of H⁺ sites, were used to determine methanol coverage (Θ₉CH₃OH, per H⁺ site; Fig. 8a) on isolated H⁺ sites in CHA zeolites as a function of methanol relative pressure (P/Pₛₐₜ; Pₛₐₜ is the saturated methanol vapor pressure).
Differential changes in methanol coverage (α) were calculated from the derivative of the methanol coverage isotherm (Fig. 9a) with respect to the logarithmic change in reduced pressure, according to the following equation:

$$\alpha = \frac{\partial \theta_{CH_3OH}}{\partial \ln \left( \frac{P}{P_{sat}} \right)}$$  \hspace{1cm} (9)

Values of α are plotted as the secondary abscissa in Fig. 9a, and used to assess the rate of change of methanol coverage as a function of relative pressure in order to identify transitions in methanol chemisorption regimes, as typically done to identify transitions in physisorption regimes of non-interacting adsorbates (e.g., N₂, Ar) caused by the filling of pores of different characteristic size [55,56].

At low methanol coverages (<1 CH₃OH per H⁺ site), adsorption is characterized by an initial maximum (~0.6 CH₃OH per H⁺) in the differential methanol coverage isotherm, followed by a local minimum at ~1 CH₃OH (per H⁺) (Fig. 9a). This adsorption behavior is characteristic of pore filling in the case of non-interacting adsorbates (e.g., Ar, N₂) within microporous voids [57], but in the case of
methanol reflects the selective adsorption at H⁺ sites to form methanol monomers at coverages <1 CH₃OH (per H⁺). Continued adsorption of methanol results in a second maximum and subsequent local minimum in the differential isotherm at ~1.7 CH₃OH (per H⁺), which reflects the adsorption of a second methanol to form protonated dimers. This local minimum is then followed by the continuous adsorption of additional methanol with increasing methanol pressure until saturation of the CHA pore volume is achieved at a value corresponding to ≥6 CH₃OH (~0.20 cm³ g⁻¹ CH₃OH adsorbed at STP).

Methanol coverages (per H⁺) at the temperatures of catalysis cannot be measured directly, and were instead estimated from equilibrium methanol adsorption data measured at 293 K by first transforming methanol relative pressure into an equivalent methanol Gibbs free energy (ΔGCH₃OH) according to the following equation (derivation in Section S.16 of the Supp. Info.):

\[ \Delta G_{\text{CH}_3\text{OH}} = R T \ln \left( \frac{P}{P_{\text{sat}}} \right) \]

where \( R \) is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) is the temperature (K), \( P \) is the absolute methanol pressure, and \( P_{\text{sat}} \) is the methanol vapor pressure (at T). The value of ΔGCH₃OH reflects equilibrium between gaseous and liquid-like intrazeolitic methanol species as a function of methanol pressure and temperature. Methanol coverages are plotted as a function of the methanol vapor pressure (at 415 K) according to Eq. (10), calculated from adsorption isotherm data (Fig. 9b) and Eq. (10). DME formation rates (415 K, per H⁺) are also plotted as a function of ΔGCH₃OH (Fig. 9b), after normalizing the methanol partial pressures at which rates were measured (0.05–50 kPa) by the vapor pressure of methanol at 415 K according to Eq. (10). DME formation rates show a first-order dependence on ΔGCH₃OH values corresponding to methanol coverages of ~1 CH₃OH (per H⁺), and begin to transition towards a zero-order kinetic regime for ΔGCH₃OH values corresponding to methanol coverages exceeding ~2 CH₃OH (per H⁺). The onset of inhibition coincides with ΔGCH₃OH values of ~0.7 CH₃OH (per H⁺), which reflects the adsorption of a second methanol to form protonated dimer structures, and that such inhibition becomes more severe as additional methanol adsorbs within microporous voids at higher methanol partial pressures.

The structures of adsorbed methanol were also monitored by in situ IR spectra (293 K) collected upon dosing methanol in fractional quantities (~0.05–50 kPa CH₃OH per H⁺ per dose), as shown in Fig. 10. Only bare H⁺ sites (~3605 cm⁻¹) and methanol monomers (~2380 cm⁻¹) are detected at low coverages of <0.3 CH₃OH (per H⁺). Protonated methanol dimers (~2600 cm⁻¹) begin to appear beyond a coverage of ~0.3 CH₃OH (per H⁺), and increase in intensity to saturation at ~2.3 CH₃OH (per H⁺). At methanol coverages >0.7 CH₃OH (per H⁺), peaks characteristic of methanol clusters (>2 CH₃OH per H⁺ site) at gas-phase methanol free energies that correspond to the onset of inhibition of methanol dehydration rates (415 K, per H⁺) in CHA zeolites.

Adsorption free energy values are calculated using DFT to estimate equilibrium constants, and thus most stable methanol cluster size (per H⁺) at an isolated H⁺ site in CHA as a function of methanol partial pressure and temperature. Free energies of adsorption of methanol clusters ranging in size from 0 to 12 methanol molecules were computed to estimate the most stable species at an isolated H⁺ site in CHA over a wide range of methanol pressures (10⁻³–10⁻¹ kPa CH₃OH) and temperatures (300–500 K), as shown in Fig. 11. Methanol clusters deprotonate H⁺ sites and form extended cationic networks with each other, in which methanol molecules link two O atoms of the AlO₄ conjugate base through a series of H-bonds (additional details and data in Section S.15, Supp. Info.). At low temperatures and high methanol pressures (<350 K, >50 kPa CH₃OH), the most stable methanol cluster rapidly
shifts from a pentamer to a dodecamer (12 CH$_3$OH$^+$; Fig. 11). The predicted formation of these dodecamers is analogous to capillary condensation, when enthalpic stabilization conferred by adsorption of large quantities of methanol (or another adsorbate) leads to rapid filling of zeolite pores. Notably, these dodecamers have approximately the same density (12 CH$_3$OH$^+$ per unit cell) as the methanol-saturated CHA samples measured experimentally (Fig. 9a). These CHA samples (Si/Al = 15) contain 2.25 H$^+$ per unit cell, while the DFT model (Si/Al = 35) contains 1 H$^+$ per unit cell; therefore, these DFT calculations reflect the pore-filling behavior observed experimentally.

The area enclosed by the dashed lines in Fig. 11 corresponds to the reaction conditions studied here, and methanol monomers and dimers dominate the surface of CHA at pressures below 3 kPa CH$_3$OH at 415 K. At high temperatures (>450 K) and low methanol pressures (<10$^{-2}$ kPa CH$_3$OH) at 415 K, which coincides with the onset of inhibition in experimentally measured DME formation rates (415 K, Fig. 1). DFT predicts that isolated H$^+$ sites in CHA are covered with a mixture of methanol tetramers and pentamers (~4.5 CH$_3$OH per H$^+$) at 50 kPa, the highest partial pressure where DME formation rates were measured. These results are consistent with experimentally measured methanol adsorption isotherms that indicate favor desorption into the gas-phase, assuming adsorbed methanol molecules do not react (Fig. 11). Methanol trimers become the most prevalent cluster size at higher methanol pressures (3–13 kPa CH$_3$OH) at 415 K, which coincides with the onset of inhibition in experimentally measured DME formation rates (415 K, Fig. 1). DFT predicts that isolated H$^+$ sites in CHA are covered with a mixture of methanol tetramers and pentamers (~4.5 CH$_3$OH per H$^+$) at 50 kPa, the highest partial pressure where DME formation rates were measured. These results are consistent with experimentally measured methanol adsorption isotherms that indicate favor desorption into the gas-phase, assuming adsorbed methanol molecules do not react (Fig. 11). Methanol trimers become the most prevalent cluster size at higher methanol pressures (3–13 kPa CH$_3$OH) at 415 K, which coincides with the onset of inhibition in experimentally measured DME formation rates (415 K, Fig. 1). DFT predicts that isolated H$^+$ sites in CHA are covered with a mixture of methanol tetramers and pentamers (~4.5 CH$_3$OH per H$^+$) at 50 kPa, the highest partial pressure where DME formation rates were measured. These results are consistent with experimentally measured methanol adsorption isotherms that indicate favor desorption into the gas-phase, assuming adsorbed methanol molecules do not react (Fig. 11). Methanol trimers become the most prevalent cluster size at higher methanol pressures (3–13 kPa CH$_3$OH) at 415 K, which coincides with the onset of inhibition in experimentally measured DME formation rates (415 K, Fig. 1).

Methanol clusters around Brønsted acid sites form extended networks with each other, in which methanol molecules link two O atoms of the acid site through a series of H-bonds (Fig. 12). The methanol monomer prefers to adsorb to O4 in CHA and interact with another O atom in the associated 8-MR (Fig. 12a). Monomers interact with only a proton bound to one O atom of the Brønsted acid site; however, as more methanol adsorbs, the site deprotonates to form protonated clusters that interact with multiple O atoms of the conjugate base. This multisite interaction has been shown in previous theoretical studies of methanol dehydration on CHA zeolites. This set of kinetic, spectroscopic, and theoretical data indicates that the low-temperature (415 K) dehydration of methanol to DME proceeds via the associative dehydration mechanism in CHA zeolites containing predominantly isolated H$^+$ sites and is inhibited by the formation of methanol clusters at high methanol partial pressures (>10 kPa). Although formation of these higher-order clusters can be included as separate elementary steps in a more comprehensive reaction mechanism, deriving a rate law to describe high-pressure inhibition becomes convoluted by the inability to distinguish whether a specific methanol cluster is solely responsible for inhibition, or whether parallel DME formation routes from higher-order clusters proceed at different rates via interactions of additional methanol with the relevant precursor and transition states. Perturbation of methanol dehydration turnover rates (per H$^+$, 473 K) by the presence of neighboring Na$^+$ atoms on partially-exchanged POM clusters [59] further suggests that the presence of excess methanol may alter the free energy landscape for DME formation in CHA zeolites. These different possibilities can be described by a generalized rate law accounting for the superposition of parallel DME formation routes at H$^+$ sites covered with different methanol cluster sizes:

$$r_A = \frac{\sum_{m=1}^{k} z_m P_{CH_3OH}^m}{\sum_{m=1}^{k} \beta_m P_{CH_3OH}^m}$$

(11)

Fig. 12. The most stable methanol clusters comprised of (a) a methanol monomer (CH$_3$OH$^+$), (b) a methanol dimer (2 CH$_3$OH$^+$), (c) a methanol trimer (3 CH$_3$OH$^+$), (d) a methanol tetramer (4 CH$_3$OH$^+$), and (e) a methanol pentamer (5 CH$_3$OH$^+$). Free energies ($\Delta G$) and enthalpies ($\Delta H$) in kJ mol$^{-1}$, and entropies ($\Delta S$) in J mol$^{-1}$ K$^{-1}$, are shown relative to the methanol monomer at 415 K and 1 bar CH$_3$OH. The 8-MR (orange, green) and 6-MR (blue) adjacent to each structure are highlighted. H-bonds are indicated with dashed lines (navy) and are all 170–250 pm.
cules) involved in the transition state, \( \alpha \) represents the apparent rate constants for DME formation when \( j \) methanol are involved in the transition state, \( m \) represents the number of methanol (i.e., 1 through \( n \) molecules) in the various MASI species (e.g., monomers, dimers, higher-order clusters), and \( \beta_m \) represents the apparent equilibrium constants to form a methanol cluster containing \( m \) molecules from a gaseous methanol and an adsorbed cluster containing \( m-1 \) methanol molecules. While this rate law (Eq. (11)) describes all possible DME formation routes and surface coverages, it does not provide additional mechanistic insight into the nature of high-pressure inhibition in small-pore zeolites. In the following section, we thus use DFT to investigate various DME formation routes via intermediates and transition states at different coverage, pressures, and temperatures in at isolated H\(^{+}\) sites in CHA zeolites.

3.5. DFT-predicted DME formation rates at different methanol coverages

DME formation can occur after desorption of excess methanol to form the kinetically relevant transition state, or in the presence of adsorbed spectating methanol molecules, which can influence the stabilities of the dehydration transition state and its relevant precursor state. Here, we calculate the Gibbs free energy barrier of each methanol dehydration transition state with up to four \( \text{CH}_3\text{OH} \) molecules. While this rate law (Eq. (11)) describes all possible DME formation routes and surface coverages, it does not provide additional mechanistic insight into the nature of high-pressure inhibition in small-pore zeolites. In the following section, we thus use DFT to investigate various DME formation routes via intermediates and transition states at different coverage, pressures, and temperatures in at isolated H\(^{+}\) sites in CHA zeolites.

Surface methylation transition states prefer to form H-bonds with spectating \( \text{CH}_3\text{OH} \) species rather than with framework O atoms (Fig. 13), because the methanol O–H bond is more polar than framework Si–O bonds, enhancing H-bonding between these hydroxyl moieties. Therefore, spectating methanol species prefer to insert themselves where H-bonds between transition states and framework O atoms are otherwise located in the absence of spectating adsorbates (Fig. 4a). Intrinsic reaction free energy barriers (\( \Delta G_{\text{int}} \)) are essentially unaffected by the insertion of one spectating species into transition states (135 kJ mol\(^{-1}\) without spectator to 134 kJ mol\(^{-1}\) with one spectator), but increase upon insertion of multiple spectating species (155 and 143 kJ mol\(^{-1}\) for two and three spectating methanol molecules, respectively) as they crowd the transition state and inhibit its formation (Fig. 13).

In contrast, apparent barriers (\( \Delta G_{\text{app}} \)) for surface methylation transition states remain similar (130–135 kJ mol\(^{-1}\)), except for that with one spectating methanol (121 kJ mol\(^{-1}\)), as larger methanol clusters become favored at the conditions at which free energies are approximated (415 K, 1 bar). Despite higher \( \Delta G_{\text{int}} \) values with additional spectating molecules, \( \Delta G_{\text{app}} \) values remain essentially unchanged because enthalpic stabilization conferred by H-bonding with additional methanol compensates for the entropic losses to form larger clusters. These data indicate that the first step of the dissociative dehydration mechanism occurs with lower standard state (1 bar) free energy barriers in the presence of a spectating methanol at isolated H\(^{+}\) sites in CHA (415 K).

Similarly, the second step of the dissociative route can occur in the presence of spectating methanol (Fig. 14). The intrinsic barriers for this second step decrease in the presence of additional spectating methanol molecules from 78 to 35–36 kJ mol\(^{-1}\) (Fig. 14). The methanol accepting the surface methoxy group forms additional H-bonds to spectating methanol in the most stable transition states identified, because framework Si–O bonds are less polar than hydroxyl O–H bonds of spectating methanol, which favors H-bonding between methanol species during reaction as in the case of surface methylation reactions. The insertion of these co-adsorbed methanol molecules into the transition states also overcomes strain in forming H-bonding networks between the cationic transition state and the zeolite framework. The stronger H-bonds provided by co-adsorbed methanol molecules stabilize dissociative DME formation transition states more than the precursor state, \( \text{CH}_3\text{Z} \), leading to decreases in intrinsic barriers with spectating methanol species.
methanol present. These decreases in the intrinsic barriers propag- 
ate to apparent free energy barriers (1 bar, 415 K) for this reac- 
tion, indicating that this reaction is more facile at high methanol 
coverages.

The associative route can also occur in the presence of spectat- 
ing methanol molecules (Fig. 15). One spectating methanol mole- 
cule at these conditions reduces both the overall (95 kJ mol
1
/C0 (b) one and (c) two spectating CH3OH molecules. Incipient and 
breaking bonds of the transition state are shown with black lines and H-bonds in 
navy. The O atom with which the methyl group is interacting is labeled. Apparent 
free energies (ΔGapp) and enthalpies (ΔHapp) in kJ mol
1
, and entropies (ΔSapp) in 
J mol
1
K
−1
, are shown relative to an adsorbed methanol. Intrinsic free energy 
barriers (ΔGint) are shown in kJ mol
1
. The 8-MR (orange, green) and 6-MR (blue) 
adjacent to each transition state are highlighted.

![Fig. 14](image1)

Fig. 14. The most favorable transition states for the second step of the dissociative 
route with (a) zero, (b) one and (c) two spectating CH3OH molecules. Incipient and 
breaking bonds of the transition state are shown with black lines and H-bonds in 
navy. The O atom with which the methyl group is interacting is labeled. Apparent 
free energies (ΔGapp) and enthalpies (ΔHapp) in kJ mol
1
, and entropies (ΔSapp) in 
J mol
1
K
−1
, are shown relative to an adsorbed methanol. Intrinsic free energy 
barriers (ΔGint) are shown in kJ mol
1
. The 8-MR (orange, green) and 6-MR (blue) 
adjacent to each transition state are highlighted.

![Fig. 15](image2)

Fig. 15. The most favorable transition states for the associative route with (a) zero, 
(b) one and (c) two spectating CH3OH molecules. Incipient and breaking bonds of 
the transition state are shown with black lines and H-bonds in navy. Overall free 
energies (ΔGapp) and enthalpies (ΔHapp) in kJ mol
1
, and entropies (ΔSapp) in 
J mol
1
K
−1
, are shown relative to an adsorbed methanol. Intrinsic free energy 
barriers (ΔGint) are shown in kJ mol
1
. The 8-MR (orange, green) and 6-MR (blue) 
adjacent to each transition state are highlighted.
low pressures, reach a maximum corresponding to the zero-order regime, and then become inhibited at higher pressures.

This theoretical evidence in conjunction with spectroscopic and adsorption data (Sections 3.3 and 3.4) indicates that associative methanol dehydration is inhibited at high pressures when trimers, tetramers, and pentamers form in small-pore zeolites. Methanol dehydration preferentially occurs from a trimer containing one spectating methanol at intermediate pressures. Tetramers and pentamers form at higher methanol pressures, but their dehydration transition states are crowded by spectating species and associative routes with only one spectator continue to prevail. Thus, desorption precedes DME formation to yield more favorable transition states and rates are inhibited at high methanol partial pressures. Given that DME formation proceeds predominantly via the associative route with one spectating methanol at relevant pressures (>0.3 kPa CH₃OH) and larger clusters can form within the CHA pores, DME formation rates can be described as

\[
T_{\text{DME}} = \frac{k_{\text{DME}}}{K_{\text{DME}} + K_{\text{DME}}P_{\text{OCH}_3}} + \frac{k_{\text{DME}}}{K_{\text{DME}} + K_{\text{DME}}P_{\text{OCH}_3}} + \frac{k_{\text{DME}}}{K_{\text{DME}} + K_{\text{DME}}P_{\text{OCH}_3}} + \frac{k_{\text{DME}}}{K_{\text{DME}} + K_{\text{DME}}P_{\text{OCH}_3}} + \frac{k_{\text{DME}}}{K_{\text{DME}} + K_{\text{DME}}P_{\text{OCH}_3}}
\]

(12)

This rate law reflects the dominance of the associative route with one spectating methanol, and up to a methanol pentamer as potential MASI, and accurately predicts the kinetic behavior measured experimentally (dashed line in Fig. 17).

4. Conclusions

A combined experimental and computational approach was used to investigate the mechanistic origin of the high-pressure inhibition of rates of methanol dehydration to dimethyl ether (DME) in small-pore zeolites (CHA, AEL, LEV, LTA), which occurs irrespective of the framework Al or extraframework H⁺ site distribution. CHA zeolites containing isolated H⁺ sites were chosen as the exemplar case in order to simplify mechanistic interpretation of experimentally measured data and to connect experimental data more faithfully to the low Al-content structures modeled by theory (Si/Al = 35). Identifying the mechanistic origins of high-pressure inhibition first required knowledge of the prevalent reaction mechanisms and kinetically relevant steps for methanol conversion to DME. Experimental measurements of methanol dehydration turnover rate dependences on pressure (0.05–50 kPa) and temperature (403–473 K), and in situ IR spectra that monitor prevalent surface intermediates as a function of reaction conditions, provide evidence that methanol dehydration proceeds via the associative mechanism on isolated H⁺ sites in CHA zeolites. These observations were corroborated by DFT calculations that enabled discriminating candidate parallel dehydration pathways from different surface intermediates. Reaction and activation free energies were calculated for the associative and dissociative dehydration mechanisms after systematically identifying the most energetically favorable adsorbate and transition state configurations by reorienting transition states and intermediates around framework binding sites and...
within adjacent voids. The most stable transition state structures were those that maximized the number of hydrogen bonds made with framework O atoms, leading to more effective charge distribution and stronger stabilizing interactions between reacting species and the zeolite framework. A maximum rate analysis of the most favorable routes for the associative and dissociative pathways showed that the dissociative mechanism prevails at isolated H⁺ sites in CHA at sufficiently low methanol pressures (e.g., <4 kPa at 415 K), but that the associative mechanism dominates at higher pressures, especially those corresponding to the onset of experimentally observed high-pressure inhibition (>10 kPa CH₃OH, 415 K).

Methanol adsorption equilibrium isotherms (10⁻⁴–10 kPa, 293 K) were used to estimate the methanol coverages (per H⁺ site) present during catalysis (0.05–50 kPa, 415 K), by comparing data at equivalent gaseous methanol free energy. This analysis suggests that inhibition of methanol dehydration rates (415 K) occurs at coverages exceeding 2 CH₃OH per H⁺ site. Methanol dehydration rates measured as a function of temperature (403–473 K) reveal that high-pressure inhibition disappears at elevated temperatures (>450 K), concomitant with the disappearance of methanol clusters in IR spectra measured under equivalent conditions. These experimental data indicate that the associative dehydration mechanism becomes inhibited by the adsorption of excess methanol, but these data alone are unable to distinguish between parallel dehydration pathways that may proceed through different methanol intermediates at different rates.

DFT-predicted methanol coverages agree with those estimated experimentally and indicate that inhibition of methanol dehydration occurs in the presence of methanol trimers and tetramers, with pentamers ultimately forming at the highest of experimental pressures studied (>40 kPa, 415 K). Methanol coverages calculated at high pressures and elevated temperatures (up to 473 K) show that the surface shifts to being covered primarily by methanol dimers, consistent with the disappearance of high-pressure inhibition at temperatures >450 K. Free energies for DME formation transition states were calculated for the associative and dissociative pathways, and a maximum rate analysis was used to predict DME formation rates as a function of methanol pressure and coverage. This analysis indicates that the associative dehydration pathway prevails under the experimental conditions tested here (0.1–50 kPa CH₃OH, 415 K), but that the most favorable dehydration route occurs via a methanol trimer and that inhibition reflects the formation of methanol tetramers, from which methanol must first desorb to form transition states of sufficient stability. Applying observations from both experiment and theory, a rate expression was derived for the associative dehydration mechanism wherein DME is formed via methanol trimers and becomes inhibited by methanol tetramers, which describes DME formation rates measured experimentally on isolated H⁺ sites in CHA. This kinetic model allows for the quantitative description of methanol inhibition in CHA zeolites, and extension of this analysis to better understand the mechanistic differences between isolated and paired H⁺ sites in small-pore zeolites. These findings highlight how modeling interactions between transition states and the zeolite framework with different reactant coverages can be used to clarify and extend insights gained from measurements of kinetic inhibition. This work highlights methods for handling the complexity that arises when zeolites turn over catalytic cycles under conditions wherein molecules are present in extended complexes and approach condensation regimes.

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Appendix A. Supplementary material

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References
