Supporting Information

Directing the Rate-Enhancement for Hydronium Ion Catalyzed Dehydration via Organization of Alkanols in Nanoscopic Confinements

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1. Methods

1.1 Chemicals and Catalysts

**Chemicals**: 3-heptanol (Sigma-Aldrich, 99%), 2-methyl-3-hexanol (TCI America, minimum 96%), 2-methyl-2-hexanol (Sigma-Aldrich, 97%), dichloromethane (HPLC grade), and sodium sulfate (99%, anhydrous) were purchased and used without purification. In addition to the substrates used in the main text, 3-ethyl-3-pentanol (>98%, Sigma-Aldrich), 2-heptanol (>98%, Sigma-Aldrich), 4-methylcyclohexanol (mixture of cis and trans, 98%) and 4-heptanol (>97%, TCI Chemicals) were used. Water (H$_2^{16}$O) was used from an ultrapure (resistivity 18.2 MΩ cm) water dispenser system. H$_2^{18}$O (97% purity) was purchased from Medical Isotopes. Phosphoric acid, H$_3$PO$_4$, ($\geq$99.999% trace metals basis) was purchased from Sigma-Aldrich.

Deuterated 2-methyl (d3), 3-hexanol (1,1,1,2,3,4,4 d7), and 2-methyl (d3) -2-hexanol (1,1,1,3,3 d5) were purchased from CDN isotopes. 3-heptanol (2,2,3,4,4 d5) was synthesized in our laboratory with 99.1% purity. β hydrogens from 3-heptanone were exchanged with deuterium by stirring 3-heptanone with D$_2$O at least seven times for 24 h each, separating the organic layer each time. The deuterated substrate is reduced with NaBD$_4$ to form 3-heptanol (2,2,3,4,4 d5) and then distilled. The purity of the substrate is quantified with $^1$H nuclear magnetic resonance (NMR).

**Catalysts**: Zeolite HBEA (Si/Al = 75) was obtained from Clariant in H-form. Zeolite HMFI (CBV 8014, Si/Al = 40) was obtained from Zeolyst International. HFAU (CBV 760, Si/Al = 30) also from Zeolyst International was used in addition to the catalysts used for the study in the main text. The catalysts were activated in a muffle furnace at 450°C for 6 h (ramp 2°C/min) under flowing air prior to catalytic measurement.
S.1.2 Catalyst Characterization

**BET Surface Area:** The BET surface area and the pore volume (BJH method) were determined after activation in vacuum at 200°C for 2 h in a Micromeritics automatic Sorptometer. The results of the studied zeolites are summarized in Supplementary Table S1.

**Pyridine infrared spectrum (IR) and Brønsted acid site density (BAS):** The IR spectra of the sample and of adsorbed pyridine were recorded with a Perkin–Elmer 2000 spectrometer at a resolution of 4 cm⁻¹. The catalyst samples were prepared as self-supporting wafers and activated under vacuum (p = 10⁻⁶ mbar) at 450°C for 1 h at a heating rate of 10°C min⁻¹. After cooling to 150°C, the sample was equilibrated with 0.1 mbar pyridine for 0.5 h followed by outgassing for 1 h and acquisition of the spectrum. Finally, a desorption program (up to 450°C with 10°C min⁻¹ and 0.5 h at 450°C) was initiated, and spectra were recorded until equilibrium was achieved. The concentrations of BAS and Lewis acid sites were quantified using the integrated areas of peaks at 1540 cm⁻¹ and 1450 cm⁻¹. For quantification, molar extinction coefficients of 0.73 cm μmol⁻¹ and 0.96 cm μmol⁻¹ were used for Brønsted and Lewis acid sites, respectively. The OH stretching vibration region of the IR spectrum for the zeolites is shown in Figure S1.

**Powder X-ray diffraction (PXRD) patterns:** PXRD patterns were collected using a Phillips X’pert Pro System, with Cu-Kα radiation source operating at 45 kV and 40 mA. The sample was measured at a scanning rate of 0.02° s⁻¹ in 5-70° 2θ range. The PXRD patterns of the studied zeolites are shown in Figure S2.

**Nuclear Magnetic Resonance:** ²⁷Al solid-state NMR spectra were obtained on a Bruker 600M instrument by a 3.2 mm probe. Single-pulse experiments were measured with a short pulse width (0.5 μs, 33° for solid; the power was 100 W and 90° pulse width is 4 μs for liquid) and without decoupling on the H channel. The number of scans was 16,384. The spinning speed was 20 kHz, and recycle delay was optimized. ²⁹Si solid-state NMR spectra were obtained on a Varian 300M instrument by a 5.0 mm probe. Single-pulse experiments were measured with a short pulse width (15°). The recycle delay was 60 s, and the spinning speed was 5 kHz. The ²⁷Al and ²⁹Si NMR spectra were shown in Figure S3 and S4, respectively.
**Supplementary Table S1:** Textural properties and Brønsted/Lewis acid site concentrations of BEA (Si/Al = 75) and MFI (Si/Al = 40). Textural properties of samples measured by N$_2$ adsorption and Brønsted/Lewis acid site concentrations measured by pyridine adsorption$^a$.

| Catalysts | Si/Al ratio | N$_2$ physisorption | Acidity (μmol/g)$^a$ |
|-----------|-------------|----------------------|----------------------|
|           |             | BET surface area (m$^2$/g) | $V_{\text{micro}}$ (cm$^3$/g) | $V_{\text{meso}}$ (cm$^3$/g) | Brønsted acidity | Lewis acidity |
| H-BEA     | 75          | 600                  | 0.17                 | 0.20                         | 167             | 43            |
| H-MFI     | 40          | 430                  | 0.18                 | 0.07                         | 367             | 45            |
| H-FAU     | 30          | 850                  | 0.32                 | 0.10                         | 140             | 49            |

$^a$Values represent concentrations of Brønsted (1540 cm$^{-1}$, molar integral extinction coefficients of 0.73 cm μmol$^{-1}$) and Lewis (1450 cm$^{-1}$, molar integral extinction coefficients of 0.96 cm μmol$^{-1}$) acid sites from gas-phase IR measurements at 423 K.

**Figure S1:** OH stretching vibration region of the IR spectrum of HBEA (Si/Al = 75) and HMFI (Si/Al = 40). The band at 3740 cm$^{-1}$ is attributed to terminal and internal Si–OH (non-acidic) groups, while the band at 3605 cm$^{-1}$ is attributed to the Brønsted acidic bridging hydroxyl groups associated with Al T sites.
Figure S2: Powder X-ray diffraction (PXRD) patterns of studied zeolites pre-reaction. HBEA (Si/Al = 75), HMFI (Si/Al = 40) and HFAU (Si/Al = 30) are the three zeolites.

$^{27}$Al NMR

Figure S3: $^{27}$Al solid-state nuclear magnitude resonance (NMR) spectra of studied zeolites. HBEA (Si/Al = 75), HMFI (Si/Al = 40) and HFAU (Si/Al = 30) are the three zeolites.
Figure S4: $^{29}\text{Si}$ solid-state nuclear magnitude resonance (NMR) spectra of studied zeolites. HBEA (Si/Al = 75), HMFI (Si/Al = 40) and HFAU (Si/Al = 30) are the three zeolites.
S.1.3 Alkanol dehydration kinetic measurements

**Experimental methods**

Kinetic measurements were performed at temperatures ranging from 80–180°C using a 300 mL Hastelloy PARR reactor. A typical reaction involved loading 2 g alkanol in 100 mL water and 0.02 M H₃PO₄ or 100 mg HBEA zeolite. In all cases, the reactor was pressurized with 40 bar H₂ at room temperature and heated to the reaction temperature while stirring vigorously at 700 rpm. The reaction rate is reported from the time the reaction temperature was reached. When the reaction was completed, the reactor was quenched in an ice/water mixture till the temperature dropped below 5°C. The organic phase was extracted with 100 mL dichloromethane (20 mL per extraction and five extractions). The carbon balance typically was more than 97%. The organic phase was dried over sodium sulfate and quantified with an Agilent 7890A GC equipped with a HP-5MS (25 × 0.25 μm inner diameter column). An Agilent 5975C MS was used to identify the products. Dodecane was used as an internal standard for the measurements.

**Turn over frequency (TOF) determination**

As noted in the main text, we correct for volumetric expansion, loss of alcohol, and water to the gas phase to obtain accurate values of alcohol and water concentrations in solution under reaction conditions. The extent of volume expansion is calculated based on the decrease in the density of water (see Supplementary Table S6). In the absence of reliable data on the density changes of alcohol with temperature, we ignore any changes in the density of alcohol. The loss of water to the gas phase is estimated using Antoine equation, which considers vapor pressure in the gas phase.

\[
\log_{10} P_{vap}(\text{mm Hg}) = 10^{\left(8.14019 - 1810.94/(T(\text{K}) + 244.485)\right)}
\]  

(1)

The loss of alcohol is estimated by considering Henry’s constant of the alcohols under reaction temperature. The Henry’s constant for 3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol are 21.273, 58.754, and 64.432 mol l⁻¹ bar⁻¹ at 298 K.[²] The temperature dependence of the Henry’s constant was considered to be 3500 K⁻¹ based on previous work on the temperature dependence of Henry’s constant on aliphatic alcohols and chemical structure, from the following equation:[³]

\[
H_{cp}(T) = H_{cp}(298 \text{ K}) \times \exp\left(-B(T(K) - 298)/(T(K) \times 298)\right)
\]

(2)

The Henry’s constant under reaction conditions are tabulated in Supplementary Tables S8–S10. Derivation of rate expressions for hydronium-ion catalyzed alcohol dehydration in water has been described in detail in previous reports.[⁴] We briefly describe the methodology below. As shown
in previous reports,[4] we can consider that the reaction starts with an association of an alcohol molecule with a hydronium ion, which is the displacement of a water molecule by an alcohol molecule in the first solvation shell of the hydronium ion.

\[ ROH(aq) + H^+(H_2O)_n(aq) \]

\[ \rightleftharpoons H^+(H_2O)_{n-1}(ROH)(aq) + H_2O(l) \]

(3)

We can consider this step to be quasi-equilibrated with an equilibrium constant \( K_{L,a} \) where \( L \) stands for liquid phase and \( a \) for association. We can express this relationship by the following equation:

\[
\frac{[H_2O(l)][H^+(H_2O)_{n-1}(ROH)(aq)]}{[ROH(aq)][[H^+]_0 - H^+(H_2O)_{n-1}(ROH)(aq)]} = K_{L,a}
\]

(4)

Solving the equation gives:

\[
\frac{[H^+(H_2O)_{n-1}(ROH)(aq)]}{[H^+]_0} = \frac{K_{L,a} [ROH(aq)]}{1 + K_{L,a} [ROH(aq)]}
\]

(5)

The next step is the proton transfer to the alcohol to form protonated alcohol before their C-O and C-H bond cleavage.

\[ H^+(H_2O)_{n-1}(ROH)(aq) \rightleftharpoons (H_2O)_{n-1}(ROH^+)(aq) \]

(6)

For this equilibrated step, we consider the following:

\[
\frac{[(H_2O)_{n-1}(ROH^+)(aq)]}{[H^+(H_2O)_{n-1}(ROH)(aq)]} = K_{prot}
\]

(7)

Combining Equations 5 and 7, we get the following:

\[
\frac{[(H_2O)_{n-1}(ROH^+)(aq)]}{[H^+]_0} = K_{prot} \frac{K_{L,a} [ROH(aq)]}{1 + K_{L,a} [ROH(aq)]}
\]

(8)

For an E1-type mechanism with sequential C-O and C-H bond cleavage, we apply steady-state assumption to the solvated carbenium-ion intermediate, \((H_2O)_{n-1}(R^+)(aq)\) and considering the formation of the olefin.

\[ (H_2O)_{n-1}(ROH^+)(aq) \sto{k_r} (H_2O)_{n-1}(R^+)(aq) + H_2O(l) \]

(9)

\[ (H_2O)_{n-1}(R^+)(aq) + H_2O(l) \rightarrow R(-H) + H^+(H_2O)_n(aq) \]

(10)

The expression for \( \text{TOF}_L \) (i.e., turnover frequency) can be expressed as given below:
Because of the relevance of both C-O and C-H bond cleavage in the rate expression, the analysis of H/D KIE is complex. In an extreme where the C-O bond is equilibrated, the primary KIEs of a higher value would be observed. In the other extreme in which the C-O bond cleavage is the rate-determining step, secondary KIEs would be observed. In a scenario in which both C-O and C-H bond cleavage are important, intermediate KIE values would be observed as in our current study. The TOF also can be expressed as an effective rate constant and fractional association of alcohol with hydronium ion as given below:

\[
\text{TOF}_L = k_{C-H} \frac{[(H_2O)_{n-1}(R^+)(aq)] [H_2O(l)]}{[H^+]} 
\]

\[
k_f [(H_2O)_{n-1}(ROH^+)(aq)] - k_r [(H_2O)_{n-1}(ROH^+)(aq)] [H_2O(l)] = k_{C-H} [(H_2O)_{n-1}(R^+)(aq)] [H_2O(l)]
\]

\[
[(H_2O)_{n-1}(ROH^+)(aq)] = \frac{k_f [(H_2O)_{n-1}(ROH^+)(aq)]}{(k_r + k_{C-H}) [H_2O(l)]}
\]

\[
\text{TOF}_L = k_{C-H} \frac{k_f}{(k_r + k_{C-H})} \frac{[ROH(aq)]}{[H_2O(l)]}
\]

\[
\text{TOF}_L = k_{C-H} \frac{k_f}{(k_r + k_{C-H})} K_{prot} \frac{K_{L,a} [ROH(aq)]}{1 + K_{L,a} [ROH(aq)]}
\]

The measurement of TOF values at two different concentrations allow the value of \( K_{L,a} \) to be calculated as shown below. The rate constants can then be determined based on TOF and the association constants.
Determination of hydronium-ion concentration for \( H_3PO_4 \) as a weak acid

Because \( H_3PO_4 \) is a weak acid, the hydronium-ion concentration in the aqueous phase will be affected by the temperature-dependent dissociation constant, total acid concentration, and the association of the hydronium-ion with alcohol molecules. The mathematical approach outlined in previous reports is briefly shown below. First, we consider the dissociation of acid:

\[
H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+
\]  

(20)

\[
K_{a,1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}
\]  

(21)

The equilibrium constant, \( K_{a,1} \), is tabulated in Supplementary Table S7 at the reaction conditions. The hydronium ion is associated with alcohol (Equation 3, Supplementary Information). This step will shift the acid-dissociation equilibrium. The concentration of dissociated proton can be considered as \([a]\). Consequently, \([H_2PO_4^-] = [a]\), \([H^+(H_2O)_{n-1}(ROH)(aq)] = [a] \times \theta_{L,a}\), \([H^+(H_2O)_n] = [a](1 - \theta_{L,a})\), and \([H_3PO_4] = [H_3PO_4]_0 - [a]\). We can have \( K_{a,1} \) expressed as:

\[
K_{a,1} = \frac{[a][a](1 - \theta_{L,a})}{[H_3PO_4]_0 - [a]}
\]  

(22)

We solve Equation 22 to get a quadratic expression for \([a]\).

\[
[a] = \frac{-K_{a,1} + \sqrt{K_{a,1}^2 + 4 \times K_{a,1} \times (1 - \theta_{L,a})[H_3PO_4]_0}}{2 \times (1 - \theta_{L,a})}
\]  

(23)

Once we have obtained volumetric reaction rates at two different concentrations, we can solve Equations 19 and 23 together to estimate \( K_{L,a} \) which enables us to estimate the concentrations of hydronium ions and association of alcohol with hydronium ion (refer to Supplementary Tables S3-S5).

If the association constant values are the same across the catalyst systems because of the high ratio of alcohol/water inside zeolite pores as compared to water, the association of alcohol to hydronium
ion is nearly complete. For example, at an alcohol/ratio of 0.1–0.2 inside MFI pores, with $K_{L,a}$ value of $\sim 230$, the $\theta_{z,a}$ value can be estimated to be around 0.96–0.98, which is consistent with the zero-order dependence on alcohol concentration observed inside zeolites.

**Figure S5**: Association constants ($K_{L,a}$) for the different alcohols with inverse of temperature (Van’t Hoff plot). The enthalpy and entropy of association are estimated from the slope and intercept of the Van’t Hoff plot for (a) 3-heptanol, (b) 2-methyl-3-hexanol, and (c) 2-methyl-2-hexanol. Reaction conditions: Temperature = 413–443 K for 3-heptanol, 423–453 K for 2-methyl-3-hexanol, and 343–373 K for 2-methyl-2-hexanol. Refer to notes above for the calculations and Supplementary Tables S8-10. The volumetric rates normalized to the acid site concentration given in Supplementary Table S2.
**Figure S6**: Olefin formation rates for 3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol for hydronium ions in solution (via H$_3$PO$_4$) with varying concentration of alkanol in the liquid phase (measured at room temperature). Reaction conditions: temperature = 443, 423, and 363 K for 3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol, respectively. Conversions less than 20%.

**Figure S7**: Natural logarithm of the olefin formation rates with varying nature logarithm of the hydronium ion concentration shown in Figure S6 for 3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol. Reaction conditions: temperature = 443, 423, and 363 K for 3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol, respectively. Conversions less than 20%.
Figure S8: Olefin formation rates with varying alcohol concentration (measured at room temperature) for (a) 3-heptanol, (b) 2-methyl-3-hexanol, and (c) 2-methyl-2-hexanol. Reaction conditions: Temperature = 433 K for 3-heptanol, 423 K for 2-methyl-3-hexanol, and 373 K for 2-methyl-2-hexanol. HBEA (Si/Al = 75) and HMFI (Si/Al = 40) are the studied zeolites.
**Supplementary Table S2**: Reaction rates and activation energies for dehydration of alkanols (3-heptanol, 2-methyl-3-hexanol, and 2-methyl-2-hexanol)*

| Catalyst | TOF (mol_{alcohol} mol_{acid sites}^{-1} s^{-1}) |
|----------|--------------------------------------------------|
|          | 3-heptanol                                       |
|          | Reaction temperature (°C)                        |
|          | 130  | 140  | 150  | 160  | 170  | 180  |
| H_{3}PO_{4} | 0.0001 | 0.0002 | 0.0008 | 0.0021 |
| MFI      | 0.009  | 0.029  | 0.086  | 0.168  | 0.459 |
| BEA      | 0.005  | 0.017  | 0.056  | 0.149  | 0.309 |
|          | 2-methyl-3-hexanol                               |
|          | Reaction temperature (°C)                        |
|          | 70   | 80   | 90   | 100  | 110  |
| H_{3}PO_{4} | 0.0002 | 0.0009 | 0.0030 | 0.0101 |
| MFI      | 0.008  | 0.025  | 0.090  | 0.247  |
| BEA      | 0.007  | 0.021  | 0.074  | 0.271  |
|          | 2-methyl-2-hexanol                               |
|          | Reaction temperature (°C)                        |
|          | 70   | 80   | 90   | 100  | 110  |
| H_{3}PO_{4} | 0.0002 | 0.0009 | 0.0030 | 0.0101 |
| MFI      | 0.008  | 0.025  | 0.090  | 0.247  |
| BEA      | 0.007  | 0.021  | 0.074  | 0.271  |

* Reaction conditions: Reactor was pressurized with 40 bar H\textsubscript{2} at ambient temperature and stirred vigorously at 700 r.p.m. Concentration of ~0.2–0.3 M based on density of water at room temperature. The rates were determined from the formation of olefin after the set temperature was reached. Turnover frequency (TOF) is determined as olefin formation rate (mol l\textsuperscript{-1} s\textsuperscript{-1}) normalized to the concentration of hydronium ions (H\textsubscript{3}PO\textsubscript{4}) or total BAS (zeolite). The concentration of hydronium ions in water depends on temperature and alcohol concentration.
**Supplementary Table S3**: Concentration of 3-heptanol, hydronium ion and [ROH]/[H$_2$O] ratio in the starting reaction mixture under reaction temperatures. The physical properties used for the calculation are given in Supplementary Table S6.

| Temperature (°C) | [ROH] (M) | [ROH]/[H$_2$O] ($10^{-3}$) | [H$_3$O$^+$] ($10^{-3}$ M) |
|-----------------|-----------|-----------------------------|-----------------------------|
| 140             | I: 0.09   | I: 1.78                     | I: 5.30                     |
|                 | II: 0.17  | II: 3.26                    | II: 5.37                    |
| 150             | I: 0.09   | I: 1.67                     | I: 4.61                     |
|                 | II: 0.17  | II: 3.29                    | II: 5.02                    |
| 160             | I: 0.09   | I: 1.67                     | I: 4.21                     |
|                 | II: 0.17  | II: 3.33                    | II: 4.72                    |
| 170             | I: 0.09   | I: 1.73                     | I: 3.94                     |
|                 | II: 0.16  | II: 3.16                    | II: 4.20                    |

**Supplementary Table S4**: Concentration of 2-methyl-3-hexanol, hydronium ion and [ROH]/[H$_2$O] ratio in the starting reaction mixture under reaction temperatures. The physical properties used for the calculation are given in Supplementary Table S6.

| Temperature (°C) | [ROH] (M) | [ROH]/[H$_2$O] ($10^{-3}$) | [H$_3$O$^+$] ($10^{-3}$ M) |
|-----------------|-----------|-----------------------------|-----------------------------|
| 150             | I: 0.29   | I: 5.81                     | I: 5.82                     |
|                 | II: 0.09  | II: 1.71                    | II: 4.70                    |
| 160             | I: 0.31   | I: 6.14                     | I: 5.49                     |
|                 | II: 0.09  | II: 1.74                    | II: 4.24                    |
| 170             | I: 0.29   | I: 5.77                     | I: 4.70                     |
|                 | II: 0.14  | II: 2.80                    | II: 4.11                    |
| 180             | I: 0.30   | I: 6.01                     | I: 4.33                     |
|                 | II: 0.13  | II: 2.69                    | II: 3.65                    |
**Supplementary Table S5:** Concentration of 2-methyl-2-hexanol, hydronium ion and [ROH]/[H$_2$O] ratio in the starting reaction mixture under reaction temperatures. The physical properties used for the calculation are given in Supplementary Table S6.

| Temperature (°C) | [ROH] (M) | [ROH]/[H$_2$O] (10$^{-3}$) | [H$_3$O$^+$] (10$^{-3}$ M) |
|----------------|-----------|---------------------------|---------------------------|
| 90             | I: 0.24   | I: 4.40                   | I: 6.60                   |
|                | II: 0.16  | II: 2.98                  | II: 5.39                  |
| 100            | I: 0.24   | I: 4.54                   | I: 5.56                   |
|                | II: 0.16  | II: 2.92                  | II: 5.22                  |
| 110            | I: 0.23   | I: 4.40                   | I: 4.89                   |
|                | II: 0.15  | II: 2.84                  | II: 4.67                  |
| 90             | I: 0.24   | I: 4.40                   | I: 6.48                   |
|                | II: 0.16  | II: 2.99                  | II: 5.34                  |
| 80             | I: 0.24   | I: 4.40                   | I: 8.48                   |
|                | II: 0.10  | II: 1.77                  | II: 7.60                  |

**Supplementary Table S6:** Physical properties of water under reaction conditions.

| Temperature (°C) | Density of water (g cm$^{-3}$) | Vapor pressure of water (bar) | Concentration of water (mol l$^{-1}$) |
|----------------|---------------------------------|-------------------------------|--------------------------------------|
| 80             | 0.974                           | 0.48                          | 54.1                                 |
| 90             | 0.967                           | 0.70                          | 53.7                                 |
| 100            | 0.960                           | 1.00                          | 53.3                                 |
| 110            | 0.955                           | 1.42                          | 53.1                                 |
| 140            | 0.920                           | 3.54                          | 51.1                                 |
| 150            | 0.91                            | 4.66                          | 50.6                                 |
| 160            | 0.90                            | 6.06                          | 50.1                                 |
| 170            | 0.89                            | 7.77                          | 49.6                                 |
| 180            | 0.88                            | 9.84                          | 49.1                                 |
Supplementary Table S7: Dissociation equilibrium constants ($K_{a,1}$) for the first proton of H$_3$PO$_4$ at reaction temperature.

| Temperature ($^\circ$C) | $K_{a,1} (10^{-4})$ |
|-------------------------|---------------------|
| 70                      | 42.84               |
| 80                      | 37.19               |
| 90                      | 32.02               |
| 100                     | 27.37               |
| 110                     | 23.24               |
| 120                     | 19.62               |
| 130                     | 16.46               |
| 140                     | 13.74               |
| 150                     | 11.41               |
| 160                     | 9.43                |
| 170                     | 7.76                |
| 180                     | 6.36                |

The equilibrium constant $K_{a,1}$ for aqueous H$_3$PO$_4$ solutions at elevated temperatures is given by

$$pK_{a,1} = 756.26/T - 4.0886 + 0.012396T.$$ [7]

Supplementary Table S8: Equilibrium constants ($K_{L,a}$) for association between hydronium ion and 3-heptanol, the extent of association $\theta_{L,a}$ for aqueous solution of 3-heptanol and rate constants ($k_{L,D}$) for H$_3$PO$_4$-catalyzed dehydration reactivity at different temperatures. The corrected molar concentrations are compiled in Supplementary Table S3.* The concentrations are reported at room temperature.

| Temperature ($^\circ$C) | Henry’s constant (mol l$^{-1}$ bar$^{-1}$) | $K_{L,a}$ (dimensionless) | Conc. ($\theta_{L,a}$) | Conc. ($\theta_{L,a}$) | $k_{L,D}$ (x 10$^{-3}$ s$^{-1}$) |
|-------------------------|------------------------------------------|---------------------------|-------------------------|-------------------------|---------------------------------|
| 140                     | 0.81                                      | 246.9                     | 0.11                    | 0.31                    | 0.19                            |
|                         |                                          |                           |                         |                         | 0.44                            |
|                         |                                          |                           |                         |                         | 0.20                            |
| 150                     | 0.66                                      | 234.9                     | 0.10                    | 0.28                    | 0.20                            |
|                         |                                          |                           |                         |                         | 0.44                            |
|                         |                                          |                           |                         |                         | 0.56                            |
| 160                     | 0.55                                      | 231.7                     | 0.10                    | 0.28                    | 0.2                            |
|                         |                                          |                           |                         |                         | 0.44                            |
|                         |                                          |                           |                         |                         | 1.80                            |
| 170                     | 0.46                                      | 231.5                     | 0.11                    | 0.29                    | 0.19                            |
|                         |                                          |                           |                         |                         | 0.42                            |
|                         |                                          |                           |                         |                         | 5.08                            |

*The $K_{L,a}$ were calculated from the fitting to Equations 19 and 23.
**Supplementary Table S9**: Equilibrium constants ($K_{L,a}$) for association between hydronium ion and 2-methyl-3-hexanol, the extent of association $\theta_{L,a}$ for aqueous solution of 2-methyl-3-hexanol and rate constants ($k_{L,D}$) for H$_3$PO$_4$-catalyzed dehydration reactivity at different temperatures. The corrected molar concentrations are compiled in Supplementary Table S4.* The concentrations are reported at room temperature.

| Temperature (°C) | Henry’s constant (mol l$^{-1}$ bar$^{-1}$) | $K_{L,a}$ (dimensionless) | Conc. ($\theta_{L,a}$) (M) | Conc. ($\theta_{L,a}$) (M) | $k_{L,D}$ (x 10$^{-3}$ s$^{-1}$) |
|----------------|-------------------------------------------|---------------------------|-----------------------------|-----------------------------|-------------------------------|
| 150            | 1.83                                      | 266.3                     | 0.33                        | 0.61                        | 0.10                          | 0.31                          | 1.3                           |
| 160            | 1.52                                      | 250.0                     | 0.35                        | 0.61                        | 0.10                          | 0.30                          | 3.5                           |
| 170            | 1.26                                      | 244.8                     | 0.33                        | 0.59                        | 0.16                          | 0.41                          | 11.0                          |
| 180            | 1.06                                      | 235.5                     | 0.35                        | 0.59                        | 0.15                          | 0.39                          | 23.0                          |

*The $K_{L,a}$ were calculated from the fitting to Equations 19 and 23.

**Supplementary Table S10**: Equilibrium constants ($K_{L,a}$) for association between hydronium ion and 2-methyl-2-hexanol, the extent of association $\theta_{L,a}$ for aqueous solution of 2-methyl-2-hexanol and rate constants ($k_{L,D}$) for H$_3$PO$_4$-catalyzed dehydration reactivity at different temperatures. The corrected molar concentrations are compiled in Supplementary Table S5.* The concentrations are reported at room temperature.

| Temperature (°C) | Henry’s constant (mol l$^{-1}$ bar$^{-1}$) | $K_{L,a}$ (dimensionless) | Conc. ($\theta_{L,a}$) (M) | Conc. ($\theta_{L,a}$) (M) | $k_{L,D}$ (x 10$^{-3}$ s$^{-1}$) |
|----------------|-------------------------------------------|---------------------------|-----------------------------|-----------------------------|-------------------------------|
| 90             | 8.0                                       | 269.0                     | 0.25                        | 0.54                        | 0.17                          | 0.44                          | 1.6                           |
| 100            | 6.1                                       | 220.8                     | 0.25                        | 0.50                        | 0.16                          | 0.40                          | 6.0                           |
| 110            | 4.8                                       | 225.7                     | 0.25                        | 0.50                        | 0.16                          | 0.39                          | 20.4                          |
| 90             | 8.0                                       | 242.8                     | 0.25                        | 0.52                        | 0.15                          | 0.42                          | 1.7                           |
| 80             | 10.5                                      | 217.3                     | 0.25                        | 0.49                        | 0.10                          | 0.28                          | 0.5                           |

*The $K_{L,a}$ were calculated from the fitting to Equations 19 and 23.
S.1.4. Calculation of activation enthalpies and entropies based on TS formalism and error analysis

Transition state theory assumes that a hypothetical TS (activated complex) exists between reactants and products and quasi-equilibrium is established between the reactant and the TS. If the rate constant has been experimentally determined, the theory can be used to calculate the Gibbs free energy, activation enthalpy, and entropy by employing the Eyring equation given below. The results are compiled in Figure 2 of the main text. The approach is briefly summarized below:

\[
k_{\text{rxn}} = \frac{k_B T}{\hbar} e^{\Delta S^\dagger} e^{-\Delta H^\dagger/RT}
\]  

(24)

Rearranging the Supplementary equation 24 in the logarithmic form:

\[
\ln \left( \frac{k_{\text{rxn}}}{T} \right) = \left( \ln \frac{k_B}{\hbar} + \frac{\Delta S^\dagger}{R} \right) - \frac{\Delta H^\dagger}{R} \frac{1}{T}
\]  

(25)

The activation enthalpy and entropy can be determined using Eyring plots \( \ln \left( \frac{k_{\text{rxn}}}{T} \right) \) vs \( \frac{1}{T} \) from the slope and intercept of the Eyring plot.

The activation free energy can be determined from the activation enthalpy and entropy.

\[
\Delta G^\dagger = \Delta H^\dagger - T \Delta S^\dagger
\]  

(26)

With respect to the error analysis, the standard error in activation enthalpy and entropy are determined from the standard error of the intercept and slope of the Eyring plot. The standard error in the activation energy is determined from errors in the experimentally measured intrinsic rate constants. Specifically, for zeolite, \( \text{TOF}_z = k_z \). According to the Eyring equation,

\[
\Delta G^\dagger = RT \left( \ln \frac{k_B}{\hbar} - \ln \frac{\text{TOF}_z}{T} \right)
\]  

(27)

As \( \ln \frac{k_B}{\hbar} \) is a constant, the error source in \( \Delta G^\dagger \) is only the errors in the measurement of \( \ln \frac{\text{TOF}_z}{T} \). We will have the following equation:

\[
\Delta \Delta G^\dagger = RT \Delta \ln \frac{\text{TOF}_z}{T}
\]  

(28)
**Supplementary Table S11**: Apparent activation parameters aqueous-phase hydronium catalyzed alkanol dehydration.*

| Catalyst | 3-heptanol | 2-methyl-3-hexanol | 2-methyl-2-hexanol |
|----------|------------|--------------------|--------------------|
|          | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ ($J$ mol$^{-1}$ K$^{-1}$) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ ($J$ mol$^{-1}$ K$^{-1}$) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ ($J$ mol$^{-1}$ K$^{-1}$) | $\Delta G^\circ$ (kJ mol$^{-1}$) |
| HMFI     | 140 ±6     | 61 ±14             | 114 ±1             | 138 ±4     | 64 ±9             | 110 ±1             | 126 ±4     | 70 ±11             | 101 ±1             |
| HBEA     | 159 ±4     | 94 ±10             | 118 ±1             | 153 ±2     | 96 ±3             | 111 ±1             | 128 ±5     | 86 ±13             | 97 ±1             |
| $H_3$PO$_4$ | 161 ±4     | 71 ±9              | 130 ±1             | 153 ±8     | 60 ±18            | 127 ±1             | 137 ±2     | 80 ±5              | 108 ±1             |

*Standard enthalpies, entropies and free energies of activation calculated from kinetic measurements and TS formalism. The error bars on enthalpies and entropies represent the standard errors from the Eyring plot while the error bars for standard free energies represents maximum error rounded up to the nearest integer.
S.1.5 Alkanol dehydration H/D kinetic isotope effects (KIE) and $^{18}$O tracer experiments

Rates of dehydration of deuterated substrates (~0.05–0.1 M) were carried out in the 300 mL Hastelloy PARR with similar procedures as to those used for non-labeled substrates. Experiments with unlabeled substrates (~0.25 M) and $^{18}$O-labeled water were carried out in a ~ 1 mL batch reactor constructed from a stainless steel “tee” (HiP) to ensure a similar headspace-to-solution ratio as in the PARR reactor. The organic components were extracted with dichloromethane, and the conversion was quantified with Agilent 7890A GC. The ratio between the two O-containing fragments were quantified as mentioned below ($^{18}$O tracer experiments).

Measurement of H/D kinetic isotopic effects (KIEs)

For dehydration of heptanols, the measured KIEs on the reaction rates reflect the effects of H/D identity on the individual rate and equilibrium constants, as shown below:

$$\frac{r_H}{r_D} = \frac{k_{3,H}K_{1,H}K_{2,H}}{k_{3,D}K_{1,D}K_{2,D}} \times \frac{1 + k_{3,D}/k_{-2,D}}{1 + k_{3,H}/k_{-2,H}} \times \frac{[\text{Non-deuterated}]_1}{[\text{Deuterated}]_1}$$  \( \text{(29)} \)

where $K_{1,H(D)}$ is the equilibrium constant for protonation of the alcohol, $K_{2,H(D)}$ is the equilibrium constant for C–O bond cleavage in the protonated alcohol (forming nondeuterated (perdeuterated) carbenium-ion intermediate), $k_{-2,H(D)}$ is the rate constant for the C–O bond recombination between $\text{H}_2\text{O}$ and the nondeuterated (perdeuterated) carbenium-ion intermediate, and $k_{3,H(D)}$ is the rate constant for the C$\beta$–H(D) bond cleavage in the nondeuterated (perdeuterated) carbenium-ion intermediate. The concentrations of the nondeuterated and the deuterated alcohols are similar and should not be different because alcohol-hydronium ion association is not anticipated to change with H/D isotopic substitution at C–H bonds. There should be only a negligible effect of H/D isotopic substitution on the equilibrium constant $K_1$ for protonation of the alcohol because isotopic substitution also should hardly affect the thermodynamics of protonation of alcohol by hydronium ions. We note that this analysis holds for applying a pseudo steady-state hypothesis on intermediates on the intermediates following C–O bond cleavage.

According to Lowry and Richardson,[5] for a step involving the re-hybridization of α carbon from sp$^3$ to sp$^2$ in the transition state (TS), the KIE value can be estimated by the following equation for $K_2$:

$$\frac{K_{2,H}}{K_{2,D}} = \exp \left( -\frac{0.1865}{T} \times (\nu_p - \nu_R) \right)$$  \( \text{(30)} \)
where $\nu_P$ is the vibrational frequency of a C–H bond of the product state (carbenium ion) and $\nu_R$ is the vibrational frequency of the corresponding C–H bond of the reactant state (protonated alcohol). For $sp^3$ hybridization on the $\alpha$ carbon of the protonated alcohol and $sp^2$ hybridization on $\alpha$ carbon of the carbenium ion, the $\nu_R$ is $\sim1350$ cm$^{-1}$ and the $\nu_P$ is $\sim800$ cm$^{-1}$, so the estimated KIE value is $\sim1.35$ at 343 K and $\sim1.25$ at 453 K. This value is far lower than the KIE value of 2.1–2.4 for 3-heptanol and 2.6–3.2 observed for 2-methyl-2-hexanol on all catalysts. The KIE value suggests that C–H bond cleavage has a higher degree of kinetic control over the reaction. To further investigate this effect, we consider the KIE value for an elementary step involving complete cleavage of C–H bond by the following equation:

$$\frac{k_{3,H}}{k_{3,D}} = \exp\left(-\frac{0.1865}{T} \times \nu_H\right)$$

where $T$ is the absolute temperature and $\nu_H$ is the vibrational frequency of the C–H bond (~2985 cm$^{-1}$). Thus, the estimated KIE value involving the cleavage of a C–H bond is 3.4-5.1 at 343–453 K. This value is often attenuated from its theoretical maximum (in the absence of tunneling effect) as the C–H bond is often not fully broken at the TS.

The measured KIEs (Table 2) are smaller than the theoretical maximum values (3.4–5.1). This may be explained by a less than fully broken C–H bond at the TS in the deprotonation step of the carbenium-ion intermediate. In addition, we note that $\frac{1+k_{3,D}/k_{-2,D}}{1+k_{3,H}/k_{-2,H}}$ should be strictly smaller than 1, because $k_{3,D} < k_{3,H}$ while $k_{-2,D} \approx k_{-2,H}$. The ratio of $k_3/k_2$ reflects the free energy difference between TS3 and TS2; that is, TSs for deprotonation of carbenium ion and for C–O bond cleavage of protonated alcohol, respectively.

Next, we consider three scenarios:

If $k_{3,H} = 0.1 \times k_{-2,H}$ (the subscript “H” means nondeuterated reactant), the free energy difference between TS3 and TS2 would be $+8$ kJ mol$^{-1}$ and $\frac{1+k_{3,D}/k_{-2,D}}{1+k_{3,H}/k_{-2,H}}$ would be close to 1. In this case (or more generally, $k_{3,H} << k_{-2,H}$), the measured KIE has to be reconciled by less complete C–H bond cleavage at TS3 or that C–O bond cleavage has the higher degree of rate control.

If $k_{3,H} = k_{-2,H}$, $\Delta G^{\circ}_{TS3,H} - \Delta G^{\circ}_{TS2,H}$ would be zero. $k_{3,H}/k_{3,D}$ is 3.4–5.1 at 343–453 K (full C–H bond breaking at TS3) and $k_{-2,H} \approx k_{-2,D}$. $\frac{1+k_{3,D}/k_{-2,D}}{1+k_{3,H}/k_{-2,H}}$ would be 0.60–0.65 in the same temperature range.

The overall KIE predicted from the above theoretical analysis would be 2.2–3.0, which is within
the range of observed values in the current study. It may imply that C–O and C–H bond cleavage TS have comparable energies.

If \( k_{3,H} = 10k_{2,H} \), \( \Delta G_{TS3,H}^o - \Delta G_{TS2,H}^o \) would be -8 kJ mol\(^{-1}\), and \( \frac{1+k_{3,D}/k_{2,D}}{1+k_{3,H}/k_{2,H}} \) would be 0.28–0.36 at 343–453 K. The overall KIE would be 1.2–1.4, which is far less than that observed for all substrates. Therefore, we can certainly rule out the possibility of C–O bond cleavage having the highest degree of rate control in the mechanism. Taken together, our measured KIEs would be consistent with a mechanism in which the C–H bond cleavage has likely a higher degree of rate control with less than complete cleavage of C–H bond in the TS or both C–O and C–H bond cleavage TS having comparable energies with respect to the ground state. We note that even in the extreme scenarios considered in scenarios 1) and 3) described above, the differences in the \( \Delta G_{TS3,H}^o - \Delta G_{TS2,H}^o \), varied from +8 kJ mol\(^{-1}\) to -8 kJ mol\(^{-1}\), which is small compared to the overall free energy of activation implying that the relative differences in the energies between TS2 and TS3 likely are small compared to the reaction energetics.

**Supplementary Table S12**: H/D kinetic isotope effect measured over HBEA, HMFI and \( \text{H}_3\text{PO}_4 \) for 3-heptanol

| Reactant                  | TOF \((10^{-3} \text{ s}^{-1})\) |
|---------------------------|----------------------------------|
|                           | HBEA     | HMFI     | \( \text{H}_3\text{PO}_4 \) |
| 3-heptanol                | 35.8     | 16.1     | 1.3                     |
| 3-heptanol (2,2,3,4,4 d5) | 17.2     | 7.2      | 0.6                     |
| KIE                       | 2.08     | 2.25     | 2.07                    |

Reactant conversion less than 20% at 433 K over HBEA, 413 K over HMFI, and 443 K over \( \text{H}_3\text{PO}_4 \). Concentration = 0.05 M over HMFI and HBEA and 0.1 M over \( \text{H}_3\text{PO}_4 \). 99.1% isotopic purity of deuterated alcohol.
Supplementary Table S13: H/D kinetic isotope effect measured over HBEA, HMFI, and H$_3$PO$_4$ for 2-methyl-3-hexanol

| Reactant                        | TOF ($10^{-3}$ s$^{-1}$) |
|--------------------------------|--------------------------|
|                                | HBEA  | HMFI | H$_3$PO$_4$ |
| 2-methyl-3-hexanol             | 96.3  | 68.4 | 0.89        |
| 2-methyl (d$_3$), 3-hexanol    | 35.0  | 28.9 | 0.29        |
| (1,1,1,2,3,4,4 d$_7$)          |       |      |             |
| KIE                            | 2.75  | 2.37 | 3.05        |

Reactant conversion less than 20% at 423 K over HBEA and 413 K over HMFI and 443 K over H$_3$PO$_4$. Concentration = 0.04 M over HMFI and 0.09 M over HBEA and 0.1 M over H$_3$PO$_4$. 99.7% isotopic purity of deuterated alcohol.

Supplementary Table S14: H/D kinetic isotope effect measured over HBEA, HMFI and H$_3$PO$_4$ for 2-methyl-2-hexanol

| Reactant                        | TOF ($10^{-3}$ s$^{-1}$) |
|--------------------------------|--------------------------|
|                                | HBEA  | HMFI | H$_3$PO$_4$ |
| 2-methyl-2-hexanol             | 4.5   | 23.9 | 0.07        |
| 2-methyl (1,1,1 d$_3$) 2-hexanol (d$_5$, 1,1,1,3,3) | 1.9   | 10.1 | 0.02        |
| KIE                            | 2.61  | 2.36 | 3.12        |

Reactant conversion less than 20%. Temperature = 353 K on HBEA, 373 K on HMFI, and 363 K on H$_3$PO$_4$. Concentration = 0.05 M. 99.4% isotopic purity of deuterated alcohol.

$^{18}$O tracer experiments

For 2-methyl-2-hexanol, considering that $^{18}$O incorporation in recovered alcohol with unlabeled alcohol and H$_2^{18}$O shows that C-O bond cleavage approaches reversibility, it is likely that C–H bond cleavage has the highest degree of rate control.

The understanding of $^{18}$O incorporation is done by looking at MS fragmentation patterns of the recovered alcohol. In an E1-type pathway in which a carbenium ion is formed after C–O bond cleavage, the $^{18}$O incorporation when H$_2^{18}$O is used as a solvent can occur from the recombination of the carbenium ion and H$_2^{18}$O that follows from the reversibility of C–O bond cleavage. Using
3-heptanol as an example, we look at the intensities of m/z 87 (M-C\textsubscript{2}H\textsubscript{5}) and 89 ions to estimate the $^{18}$O incorporation (Supplementary Table S15). For 2-methyl-2-hexanol, we look at the intensities of m/z 59 (M-C\textsubscript{4}H\textsubscript{9}) and 61 ions (Supplementary Table S16). If the reaction were to occur via an E2-type elimination pathway, no significant $^{18}$O incorporation should be observed. From our analysis, we can see that at a minimum, olefin formation and recombination occur at comparable yields, which provides evidence for the existence of an E1 mechanism.

**Supplementary Table S15**: Single peak ion intensity of m/z 89 and 87 ion (normalized to m/z 87 ion fragment) in the mass fragmentation pattern for the recovered reaction mixture from 3-heptanol on HMFI, HBEA and H\textsubscript{3}PO\textsubscript{4}.

| m/z | No reaction | MFI | BEA  | H\textsubscript{3}PO\textsubscript{4} |
|-----|-------------|-----|------|---------------------------------|
| Conversion (mol%) | 0 | 24.3 | 38.1 | 14.2 |
| 87  | 1.000       | 1.000 | 1.000 | 1.000 |
| 89  | 0.003       | 0.084 | 0.266 | 0.084 |

**Supplementary Table S16**: Single peak ion intensity of m/z 61 and 59 ion (normalized to m/z 59 ion fragment) in the mass fragmentation pattern for the recovered reaction mixture from 2-methyl-2-hexanol on HMFI, HBEA, and H\textsubscript{3}PO\textsubscript{4}.

| m/z | No reaction | MFI | BEA  | H\textsubscript{3}PO\textsubscript{4} |
|-----|-------------|-----|------|---------------------------------|
| Conversion (mol%) | 0 | 1.2  | 24.6 | 8.4 |
| 59  | 1.000       | 1.000 | 1.000 | 1.000 |
| 61  | 0.003       | 0.044 | 4.724 | 0.669 |
S.1.6 Adsorption of alkanols in zeolite in liquid phase: adsorption capacity and adsorption constant

**Liquid phase adsorption:** Adsorption isotherms were obtained by immersing 20–100 mg zeolite in a substrate solution at a given concentration for 24 h. The zeolite was filtered from the liquid, and the residual concentration was obtained with an Agilent 7890A GC after extraction of the organic phase with dichloromethane. Quantification was done using dodecane as an internal standard. The uptake was determined by the change in bulk concentration, volume of the solution, and mass of the solid sample. High temperature adsorption uptakes were measured by equilibrating the solution in an oven for 24 h.

**Figure S9:** Adsorption isotherm of alkanols in zeolite pores. Adsorption of (a) 3-heptanol, (b) 2-methyl-3-hexanol, and (c) 2-methyl-2-hexanol into BEA and MFI zeolites at 298 K. The x-axis refers to equilibrium bulk liquid concentration and y-axis refers to alkanol uptake in the zeolite pore.

**Estimation of adsorption capacity and adsorption constant under reaction conditions**

The adsorption isotherms of the alcohols from aqueous solutions into MFI and BEA zeolites have been measured at 280–313 K. A Langmuir-type adsorption model has been fit to the measured isotherms to obtain the adsorption constant ($K_{ad}$) and saturation uptake ($q_{max}$) at each temperature. The saturation uptake on BEA was ~1.8–2 times more than on MFI for all three alcohols. To estimate the pore environment around the active site under reaction conditions, the saturation uptake was estimated under reaction conditions. Because of the decreased density of the adsorbed
alcohol with temperature, the saturation uptake decreased as temperature increased as shown in Table S17. This takes the functional form:

$$\frac{1}{q_{\text{max}}} \frac{dq_{\text{max}}}{dT} = -\delta$$ \hspace{1cm} (32)

By plotting the measured uptakes with temperature yielded slopes as given in Supplementary Table S17. The extrapolation of these uptakes at reaction temperatures gives a saturation uptake of the alcohols under the reaction conditions given in the main text.

The adsorption constants were measured at each temperature. The enthalpy and entropy of adsorption were estimated from the slope and intercept of the Van’t Hoff plot. The lower adsorption constant for 2-methyl-2-hexanol and 2-methyl-3-hexanol as compared to 3-heptanol adsorption into MFI is likely due to repulsion of the branched hydrocarbon structure with MFI voids. The drop in adsorption constants in BEA is not as drastic because of the larger void size that minimizes the interaction of the alcohols with the pores.

**Supplementary Table S17**: Saturation uptake with temperature for alcohols on BEA and MFI zeolites

| Temperature \(^{\circ}C\) | Saturation uptake \((q_{\text{max}}), \text{mmol g}^{-1}\) |
|--------------------------|-------------------------------------------------|
|                          | 3-heptanol | 2-methyl-3-hexanol | 2-methyl-2-hexanol |
|                          | MFI | BEA | MFI | BEA | MFI | BEA |
| 7                        | 1.19 | 1.64 | 1.06 | 1.71 | 1.03 | 1.95 |
| 25                       | 1.09 | 1.51 | 1.01 | 1.64 | 0.95 | 1.77 |
| 35                       | 1.05 | n.d  | n.d  | n.d  | n.d  | n.d  |
| 40                       | n.d  | 1.45 | 0.92 | 1.53 | 0.88 | 1.60 |
| \(\delta\) \((\text{mmol g}^{-1} \text{K}^{-1})\) | 0.0042 | 0.0038 | 0.0042 | 0.0032 | 0.0049 | 0.0057 |
S.2. Supplementary Notes

S.2.1 Product selectivity

The product selectivity from 3-heptanol dehydration marginally favors 3-heptene over 2-heptene over all three catalysts as seen from the higher selectivity toward 3-heptene at ~65%. The product selectivity from 2-methyl-3-hexanol dehydration unsurprisingly favors the highly substituted 2-methyl-2-hexene (65–80%) over all the catalysts. This is because of the higher stability of 2-methyl-2-hexene due to higher number of β-hydrogens available for hyperconjugation. In addition, 2-methyl-1-hexene shows a product selectivity between ~15–18% that forms from the Cβ-H bond cleavage of the primary carbon atoms of 2-methyl-2-hexyl carbenium ion, showing that 1) dehydration occurs through an E1 mechanism and 2) the 1,2-hydride shift of 2-methyl-3-hexyl carbenium ion to form 2-methyl-2-hexyl carbenium ion occurs at rates comparable to Cβ-H bond cleavage. The product selectivity from 2-methyl-2-hexanol dehydration leads to 2-methyl-2-hexene as the majority product (65–70%) on HMFI and H₃PO₄ in aqueous solution. Although 2-methyl-2-hexene is the most stable product for the previously discussed reasons, 2-methyl-1-hexene is formed at significant selectivities (30–35% on HMFI and ~50% on HBEA). During the Cβ-H bond cleavage step, 6 β hydrogens can be eliminated in the path to form 2-methyl-1-hexene as compared to 2 β hydrogens in the path to form 2-methyl-2-hexene, which explains the higher selectivity toward 2-methyl-1-hexene. In addition, possible steric effects in BEA confinement pockets due to higher alcohol concentration in BEA pores also might contribute to the higher selectivity toward 2-methyl-1-hexene.

Figure S10: Olefin product selectivity values with varying conversion levels of alcohols (a) 2-methyl-2-hexanol, (b) 3-heptanol, and (c) 2-methyl-3-hexanol in HBEA and HMFI zeolites. HBEA (Si/Al = 75) and HMFI (Si/Al = 40) are the studied zeolites.
**S.2.2 The choice of 3-heptanol as a substrate with reactivity on 2-heptanol and 4-heptanol on BEA**

We explored dehydration reactivity for 2-heptanol and 4-heptanol to investigate the influence of the location of alcohol (–OH) functional group at the 2, 3, or 4 position. Specifically, we compared the activation parameters of 2, 3, and 4-heptanol on BEA. As seen in Supplementary Table 18, the activation enthalpy and entropy of the reaction path are within experimental error similar across the three alcohols. The free energy of activation at 433 K decreases from 2 to 3 to 4-heptanol, which shows that the intrinsic reactivity of the hydronium ion in BEA increases as the alcohol (–OH) functional group from the 2 position toward the 4 position. The formation of 3-heptene from 2-heptanol and 2-heptene from 4-heptanol is additional evidence that the reaction pathway goes through a carbenium-ion intermediate (Supplementary Table S19). Further, the low selectivity toward minor products from 2 and 4-heptanol away from statistical distributions that may be expected if the 1,2-hydride shift is facile to form statistical distributions of carbenium ions following C-O bond cleavage shows that 1,2 hydride shift occurs at much lower rates as compared to Cβ-H bond cleavage. This also can be seen from no detectable yield of 1-heptene from the dehydration of 3- and 4-heptanol and a relatively high selectivity of ~18% toward 1-heptene from the dehydration of 2-heptanol. The slightly higher mean activation entropy of 4-heptanol dehydration seems to be due to possible cleavage of 4 Cβ-H bonds from 4-heptyl carbenium ion to yield 3-heptene as compared 2 Cβ-H bonds from 3-heptyl carbenium and 2 Cβ-H bonds from 2-heptyl carbenium ions to form 2-heptene.

As seen from the similar activation parameters that were obtained for the dehydration of 2, 3, and 4 heptanol over BEA, we surmise that the position of the functional group (–OH) would lead to activation parameters within experimental uncertainties over other catalysts, specifically MFI and H₃PO₄.
**Figure S11**: Olefin formation rates for 2, 3, and 4-heptanol dehydration over HBEA (Si/Al = 75). Reaction conditions: 0.2–0.25 M concentration, temperature = 413–453 K. Conversions less than 20%. The activation parameters are given in Supplementary Table S18.

**Supplementary Table S18**: Apparent activation parameters for dehydration reactivity of 2, 3, and 4-heptanol over BEA catalyst.

| Substrate    | Apparent activation energy, E_{app} (kJ mol\(^{-1}\)) | Activation enthalpy, ΔH_{o}^‡ (kJ mol\(^{-1}\)) | Activation entropy, ΔS_{o}^‡ (J mol\(^{-1}\) K\(^{-1}\)) | Free energy of activation, ΔG_{o}^{o,433K} (kJ mol\(^{-1}\)) |
|--------------|------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 2-heptanol   | 165 ±3                                               | 161 ±3                                          | 90 ±6                                           | 122 ±1                                          |
| 3-heptanol   | 163 ±5                                               | 159 ±5                                          | 94 ±10                                          | 118 ±1                                          |
| 4-heptanol   | 162 ±7                                               | 158 ±7                                          | 99 ±15                                          | 115 ±1                                          |
**Supplementary Table S19:** Product selectivity for dehydration reactivity of 2, 3, and 4-heptanol over BEA catalyst. The selectivity is reported at conversion values 10-15%.

| Substrate     | Product selectivity (mol%) |
|---------------|----------------------------|
|               | 1-heptene      | 2-heptene      | 3-heptene      |
| 2-heptanol    | 17.4           | 79.4           | 3.2            |
| 3-heptanol    | -              | 29.1           | 70.9           |
| 4-heptanol    | -              | 2.2            | 97.8           |

**S.2.3 Additional data on the higher reactivity on BEA in tertiary alcohols**

In addition to the data reported in the main text, Figure S12 shows that the reactivity toward dehydration of 1-heptanol, a primary alcohol (~50 % selectivity to ether) has a similar trend as 3-heptanol. Specifically, a medium-size MFI pore is the most reactive among MFI and the larger-pore BEA and FAU zeolites. 3-ethyl-3-pentanol shows a trend similar to 2-methyl-2-hexanol. Specifically, BEA is the most reactive for dehydration reactivity of 3-ethyl-3-pentanol among BEA, MFI, and FAU. MFI exhibits diffusion limitations whereby the reaction rate follows a first-order rate dependence with concentration of alcohol while BEA shows a zero-order dependence. In addition, the reaction rate is similar in value to the reaction rate in water. More details will be given in a manuscript that is in preparation. FAU shows lower reactivity than BEA (Figure S12). This may be attributed to the lower van der Waals contact stabilization of the TS along with a lower intraporous alcohol concentration, as reported by Shi et al. that limits the stabilization of the TS by intraporous alcohol molecules.[4]
Figure S12: Olefin formation rates on HZSM5, HBEA and HFAU zeolites from (a) 1-heptanol at 513 K, (b) 3-heptanol at 433 K, and (c) 3-ethyl-3-pentanol at 373 K. Concentration of the alcohols was 0.25 M. HBEA (Si/Al = 75), HMFI (Si/Al = 40) and HFAU (Si/Al = 30) are the three zeolites.

S.2.4 Influence of ionic strength on measured turnover frequency
Zeolites provide “quasi-solid electrolyte” environment inside the zeolite pores. The charged hydronium ions provide a specific ionic strength in the pores.[6] A salting-out model for uncharged molecules can be used to estimate activity coefficients for adsorbed alcohols inside the pores. The increasing charge density (increasing ionic strength) that accompanies an increasing concentration of hydronium ions was shown to increase the activity coefficient of the adsorbed cyclohexanol inside the zeolite pore. These specific interactions influence the adsorption of the cyclohexanol inside the pores through the reduction in the adsorption constant of the cyclohexanol inside the zeolite pore. This change in the activity coefficient is expected to influence the observed TOF toward olefin formation. The detailed investigation of these effects on reactivity inside zeolite pores will be the focus of another manuscript. We note that a higher activity coefficient should lead to higher reactivity. We estimate the activity coefficient of the alcohol molecules inside the pore in order to rule out activity coefficient differences being the cause of reactivity differences between BEA and MFI zeolites. We used the following equations to estimate the activity coefficients. The varying activity coefficient of the alcohol molecule with ionic strength can be written as:

\[
\log_{10} \gamma_{\text{alcohol, pore}} = K_s I_{\text{zeo}}
\]  

(33)

where \(\gamma_{\text{alcohol, pore}}\) is the activity coefficient of the alcohol inside the zeolite pore, \(K_s\) is the Setschenow constant, and \(I_{\text{zeo}}\) is the ionic strength.
\[ I_{\text{zeo}} = \frac{1}{2} [H_3O^+] + \frac{1}{2} [Z^-] \]  

where \([H_3O^+]\) and \([Z^-]\) are the concentrations of hydronium ions and negatively charged framework anions. The concentration of both \([H_3O^+]\) and \([Z^-]\) is the BAS density as measured by pyridine IR (Table S1). For the purpose of our analysis, we assume the same Setschenow constant (0.27) in BEA and MFI as determined by Eckstein et al.\(^7\) The calculated activity coefficients were 1.5 and 1.2 for MFI and BEA zeolite, respectively (Table S20). The value for BEA is within 80\% of the value for MFI, which cannot explain the multifold differences in dehydration reactivity between MFI and BEA.

**Supplementary Table S20:** Properties of zeolite acting as a “quasi-solid electrolyte”

| Catalyst | Framework density \((\text{g cm}^{-3})^a\) | Conc. of anions and cations \((\text{mol l}^{-1})^b\) | Ionic strength, \(I_{\text{zeo}}\) \((\text{mol l}^{-1})^d\) | Activity coefficient in the pore,\(^e\) γ_{alcohol, pore} |
|----------|-----------------------------------------|----------------------------------------|-------------------------------|-------------------------------------|
| MFI      | 1.8                                     | 0.67                                   | 0.67                          | 1.5                                 |
| BEA      | 1.5                                     | 0.17                                   | 0.26                          | 1.2                                 |

\(^a\) Calculated based on framework density of 18.4 and 15.3 T site per 1000Å\(^3\) on MFI and BEA zeolite  
\(^b\) Hydronium ion  
\(^c\) Negatively charged framework  
\(^d\) Calculated by multiplying BAS concentration per unit volume with framework density  
\(^e\) Calculated assuming Setschenow constant value of 0.27.

**S.2.5 Analysis of transition state activation parameters with respect to alcohol molecules in the liquid phase**

We consider the alcohol in the liquid phase to investigate the role of stabilization or destabilization of the ground state on the measured activation parameters. We note that the measured activation parameters refer to the relative differences in the enthalpies, entropies, and free energies of the \(C_\beta\)-H TS with reference to the ground state. The ground state is adsorbed alcohol molecules in the pore loosely bound to the hydronium-ion cluster inside the zeolite pores.
We consider a scheme (Scheme S1) where 1) alcohol molecules in the liquid phase in the zeolite pores, which is the ground state, followed by 2) conversion of the adsorbed molecules to olefin. The measured activation parameters are calculated from the ground state energy to the TS energy. The standard states for the gas phase, liquid phase, and adsorbed phase are 1 bar, 1 mol l⁻¹, and intrazeolite occupancy of 1. Our analysis shows that the enthalpy of TS with respect to alcohol molecules in the liquid phase is the lowest for 2-methyl-2-hexanol and highest for 3-heptanol (Table S22). Overall, minor changes in the stabilization/destabilization of the ground state of adsorbed alcohols do not significantly affect the enthalpic difference between the TS, and the presence of alcohol molecules in the liquid phase is consistent with the trends in the activation parameters across zeolites and alcohol molecules. The nanoscopic confinements provide for an inherent reduction in the enthalpic barriers of the TS and observed reactivity differences are not due to any preferential stabilization or destabilization of the ground state.

![Figure S13](image)

**Figure S13:** Apparent activation enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) with alkanol molecules in the liquid state as a reference state. Data for H₃PO₄, MFI, and BEA are shown in black, blue, and red, respectively. The activation enthalpies and entropies are derived from kinetic measurements and corrected for adsorption inside the zeolites and association with hydronium ion in solution. The secondary alcohols and tertiary alcohol follow different isokinetic temperatures.
Scheme S1: Energetics of conversion of alcohols from the gas phase to the $C_\beta$-H TS.
**Supplementary Table S21**: Enthalpy of desorption, activation enthalpy, van der Waals and intraporous intermolecular stabilization of TSs on homogeneous acids, MFI and BEA catalyst.

| Substrate         | \(\Delta H^0_{\text{des, alcohol}}\) (kJ mol\(^{-1}\))\(^a\) | \(\Delta H^0\) (kJ mol\(^{-1}\))\(^b\) | \(\Delta H^0_{\text{vdW, pore}}\)\(^+\) | \(\Delta H^0_{\text{intermolecular, pore}}\)\(^+\) | \(\Delta H^0_{\text{Des, (H2O)n}}\) \(\Delta H^0_{\text{Deprotonation, H+ (H2O)n}}\) | \(\Delta H^0_{\text{PPE}}\) \(\Delta H^0_{\text{Protonation, (H2O)n}}\) (kJ mol\(^{-1}\))\(^d\) |
|-------------------|-------------------------------------------------|---------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| 3-heptanol        | 27                                              | 140                             | 159                              | 161                              | 48                               | 23                               | 25                               |
| 2-methyl-3-hexanol| 24                                              | 138                             | 153                              | 153                              | 39                               | 19                               | 20                               |
| 2-methyl-2-hexanol| 22                                              | 126                             | 128                              | 137                              | 33                               | 28                               | 5                                |

\(^a\)The enthalpies of desorption are estimated from the negative of the adsorption enthalpies in Table 1 of the main text.

\(^b\)The apparent activation enthalpy of dehydration on MFI, BEA and \(\text{H}_3\text{PO}_4\) are computed from kinetic experiments and given in Table S11.

\(^c\)The value calculated from Equation 1 of the main text for MFI and BEA from the desorption and activation enthalpies for zeolites and in solution.

\(^d\)The difference between MFI and BEA of the vdW and intermolecular stabilization of the TS along with desorption enthalpies of water cluster \((\Delta H^0_{\text{vdW, pore}} + \Delta H^0_{\text{intermolecular, pore}} - \Delta H^0_{\text{Des, (H2O)n}})\) estimated from Equation 2 of the main text.
**Supplementary Table S22**: Apparent activation enthalpy of TS with respect to alcohol molecules in the liquid phase. Calculations performed at 298 K (Scheme S1).

| Substrate       | $\Delta H^o_{\text{adsorption}}$ (kJ mol$^{-1}$) | $\Delta H^o_{\text{TS}}$ (kJ mol$^{-1}$) | $H^o_{\text{TS}} - H^o_{\text{alcohol}}$ (kJ mol$^{-1}$) |
|-----------------|-----------------------------------------------|-----------------------------------------|------------------------------------------------------|
|                 | MFI | BEA | MFI | BEA | MFI | BEA |
| 3-heptanol      | -27 | -21 | 140 | 159 | 113 | 138 |
| 2-methyl-3-hexanol | -24 | -19 | 138 | 153 | 114 | 134 |
| 2-methyl-2-hexanol | -22 | -19 | 126 | 128 | 104 | 107 |
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