Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for **"Sealed Rotors for *In Situ* High Temperature High Pressure MAS NMR"**

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Experimental Section

Chemicals

Aluminum isopropoxide ($Al(OiP)_3$, Sigma-Aldrich, >98%), H_3PO_4 (Fisher Scientific, 85%), Triethylamine (TEA, Sigma-Aldrich, >99.5%), ^{13}C-labeled cyclohexanol-1-^{13}C (Sigma-Aldrich, 99 atom % ^{13}C), H-Beta (HBEA150, Si/Al = 75) were obtained by the same procedures as those we reported earlier.[1]

Sample preparation

$AlPO_4$-5 molecular sieves were synthesized with the gel composition of Al_2O_3:P_2O_5:TEA:H_2O as 1:1.32:1.2:46. Typically, 0.627 g H_3PO_4 was diluted by 2.0 g H_2O, and 0.837 g $Al(OiP)_3$ was added under magnetic stirring. After stirring for 3 h, 0.239 g TEA was dropwise added, and the mixture was stirred for another 3 h to get a homogeneous gel. Part of the gel was transferred into the Teflon-lined stainless steel autoclave, and part (typically 250-280 mg) was loaded in the high temperature and high pressure (HTHP) MAS rotor for *in situ* experiment. Both gels were crystallized at 150 °C for 12 h, and after crystallization, the solid powders were obtained by repeated centrifugation and washing with deionized water. Both the crystallized powders show characteristic AFI phase in XRD patterns (Figure S1).

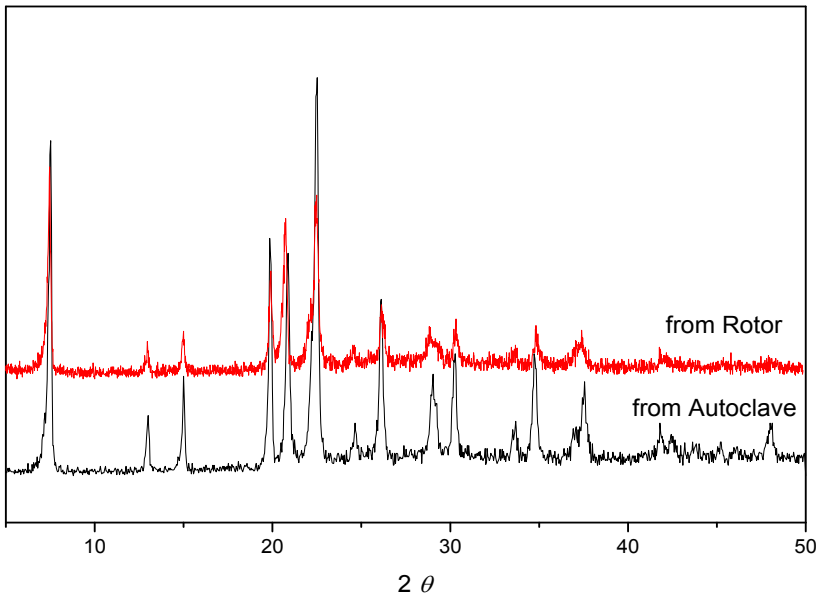

Figure S1. XRD patterns of samples crystallized in autoclave and HTHP MAS NMR rotor at 150 °C for 12 h. The lower intensity of the samples from the MAS rotor was due to the fact that only a small amount of powders (about 10 mg) can be collected from the rotor using Q-tips as tools. Also, minor differences in diffraction peak positions and broadened peaks are resulted from different contents of orthorhombic and hexagonal phases in the samples synthesized in the rotor and autoclave.[2, 3]

Catalytic Reaction

Cyclohexanol dehydration reactions catalyzed by H_3PO_4 and H-Beta zeolite were conducted

as model reaction. For H_3PO_4 catalyst, a mixture of 210 mg 0.02 M H_3PO_4 and 8 mg 1-^{13}C-cyclohexanol was loaded in the 7.5 mm rotor for *in situ* NMR investigation. For H-Beta catalyst, a mixture containing 6.6 mg H-Beta (HBEA150, Si/Al=75), 211 mg H_2O and 6.6 mg 1-^{13}C-cyclohexanol was loaded in the 7.5 mm rotor. The reaction was also performed at 160-190 °C in a 300 mL Parr autoclave reactor, using aqueous solution (0.33 M) of cyclohexanol. For a typical batch experiment using H-Beta: 170 mg HBEA150 and 80 mL 0.33 M cyclohexanol were sealed in a Hastelloy PARR reactor, pressurized to 50 bar using H_2 and stirred vigorously while heated to the set temperature. For a typical H_3PO_4–catalyzed experiment: 100 mL 0.02 M phosphoric acid and 3.3 g cyclohexanol were sealed in a Hastelloy PARR reactor, pressurized to 50 bar using H_2 and stirred vigorously while heated to the set temperature. The charge H_2 would not participate in the acid-catalyzed dehydration, but was introduced to reduce the time spent on reaching a set temperature and to maintain identical environments as in hydrodeoxygenation reactions. Preliminary tests show the same kinetics in N_2. The reaction time was reported counting from the point when the set temperature was reached (~12 min). After reacting at a certain temperature for a controlled amount of time, the reactor was cooled using ice/water and the contents were extracted using dichloromethane (25 ml, 4 times). The organic phase was analyzed on an Agilent 7890A GC equipped with HP–5MS 25 m 0.25 μm i.d. column, coupled with Agilent 5975C MS. 1, 3-dimethoxybenzene was used as internal standard for quantification.

Characterization

All the X-ray diffraction patterns were collected at a Philip PW3040/00 X′Pert powder X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å), in the 2θ range of 5-50° and scan rate of 1°/min.

In situ ^{31}P, ^{27}Al, ^{13}C MAS NMR measurements were carried out on a Varian 300 MHz NMR spectrometer using a 7.5 mm HX MAS probe with a spinning rate of 3.7- 3.9 kHz at resonance frequencies of 121.4, 78.1, 75.4 MHz respectively. The varying temperature experiments were conducted by the commercially available heating stack provided by Varian company, and the real temperature in the HTHP MAS rotor was calibrated by ethylene glycol.[4]

^{13}C MAS NMR spectra were recorded using a pulse width 3 μs for a π/4 pulse with ^{1}H TPPM decoupling, and 128 scans were accumulated with 5 s recycle delay. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. ^{31}P MAS NMR spectra were recorded using a pulse width 6 μs for a π/2 pulse with ^{1}H TPPM decoupling, and 128 scans were accumulated with 2 s recycle delay. The chemical shifts were externally referenced to 85% H_3PO_4 at 0 ppm. ^{27}Al MAS NMR experiments were acquired using a pulse width 2.25 μs for a π/4 pulse, 64 scans, and a 1 s recycle delay. The spectra were externally referenced (*i.e.*, the 0 ppm position) to 1 M $Al(NO_3)_3$ aqueous solution. Nuts program was used to simulate the spectra, and integrate the peak areas. For ^{27}Al MAS NMR spectra, we fitted the tetrahedral and octahedral coordinated ^{27}Al sites in series of spectra, and they both have the identical quadrupole interaction constants ranging from 0.3 to 0.4 MHz, and η_Q=0. There relative quantification can be approximatively carried out by the ratio of individual

peak area in total area (the signals of spinning sidebands were excluded),[5] and the relative total signal intensities were normalized by the maximum total signal intensity. The representative deconvoluted ^{27}Al and ^{31}P spectra are shown in Figure S2.

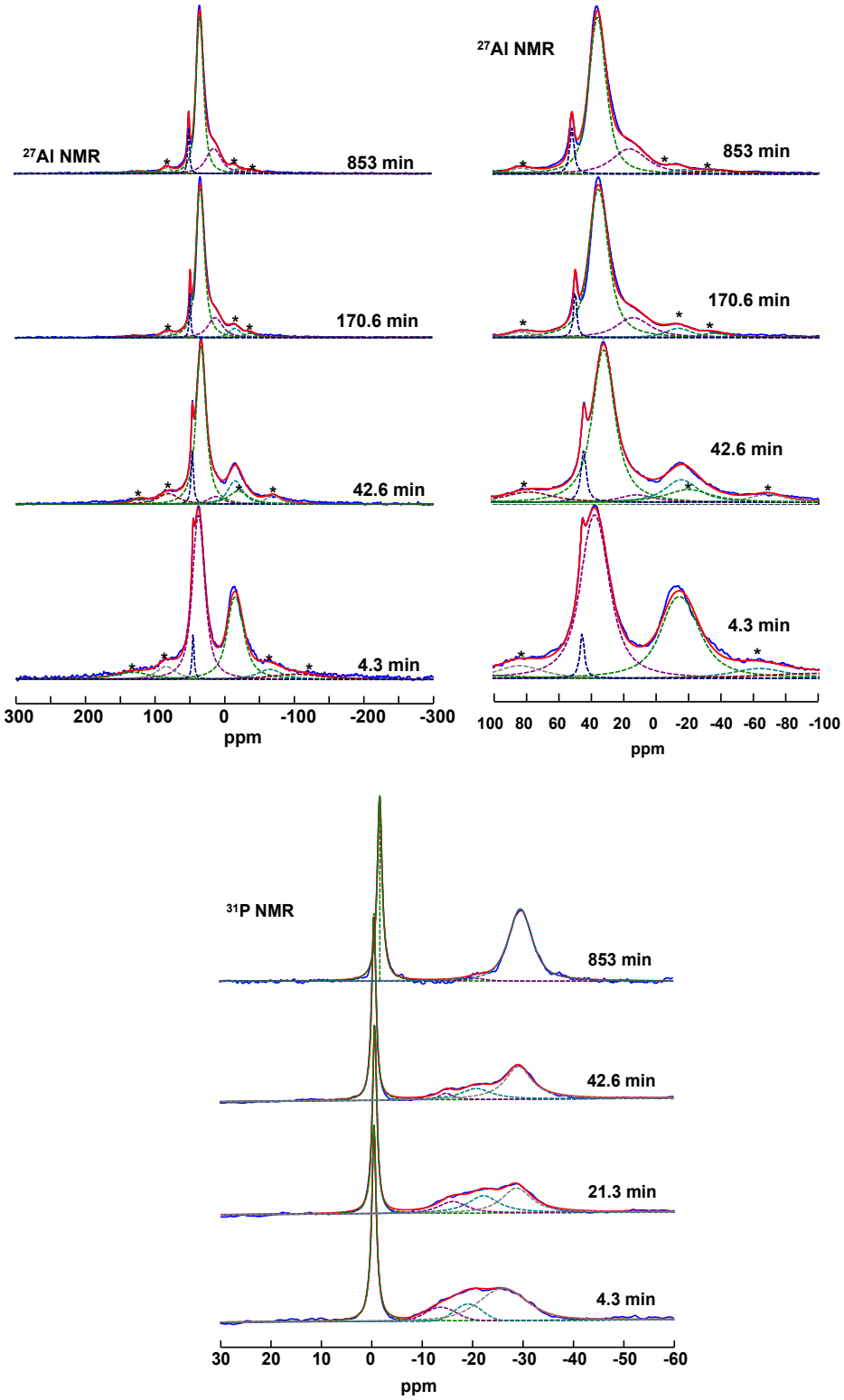

Figure S2. Representative deconvoluted *in situ* ^{27}Al and ^{31}P spectra of $AlPO_4$-5 synthesized at 150 °C. asterisks denote spinning sidebands.

Data analysis

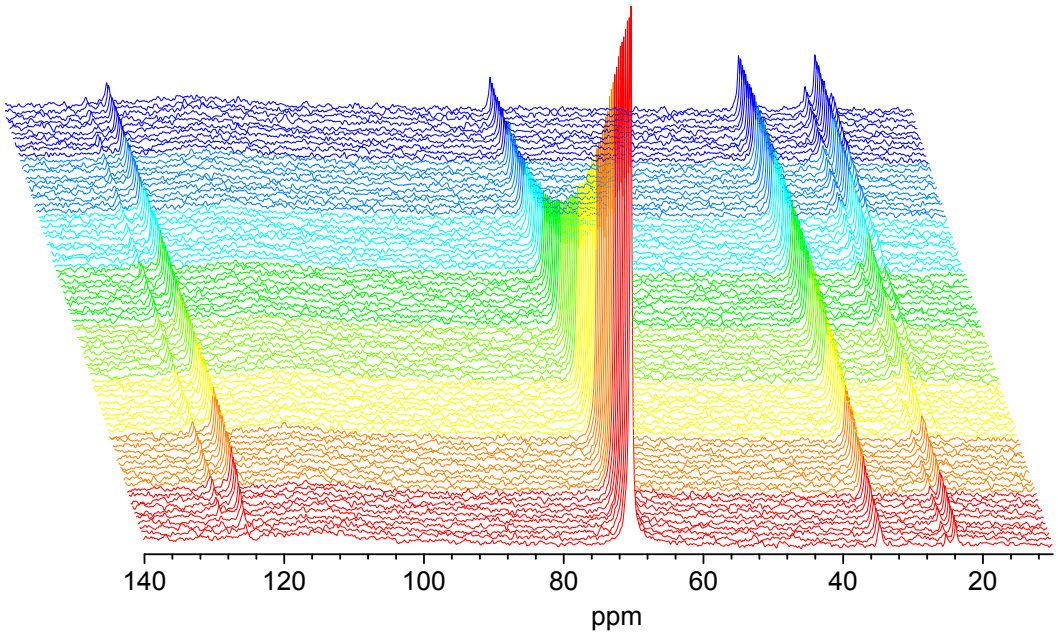

Figure S3. Stacked plot of in situ ^{13}C MAS NMR spectrum of 1-^{13}C-cyclohexanol dehydration for H-beta at 140 °C

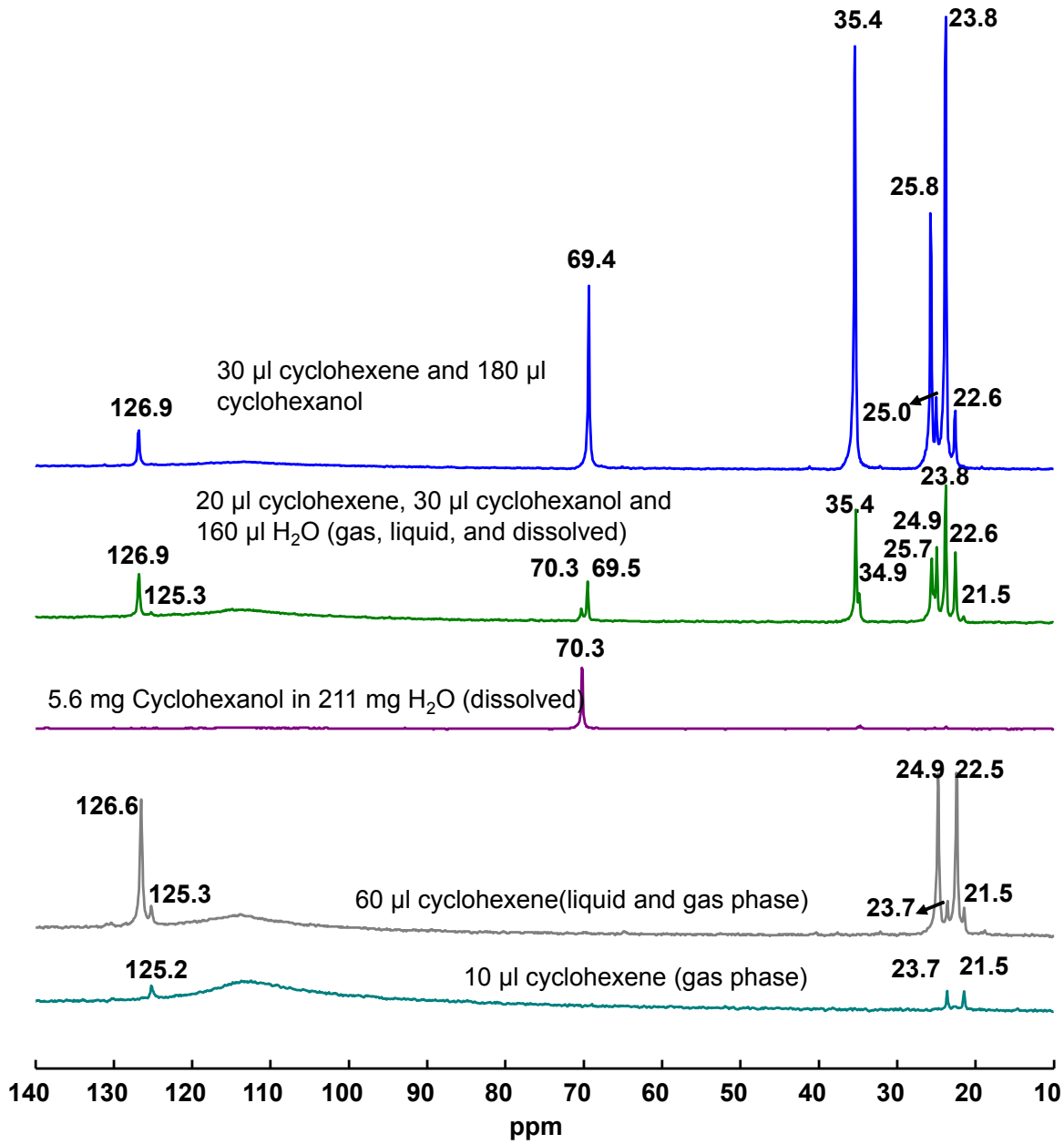

Figure S4. Stacked plot of ^{13}C MAS NMR spectra of cyclohexanol, cyclohexene, H_2O, and their mixtures in the MAS rotor at 150 °C.

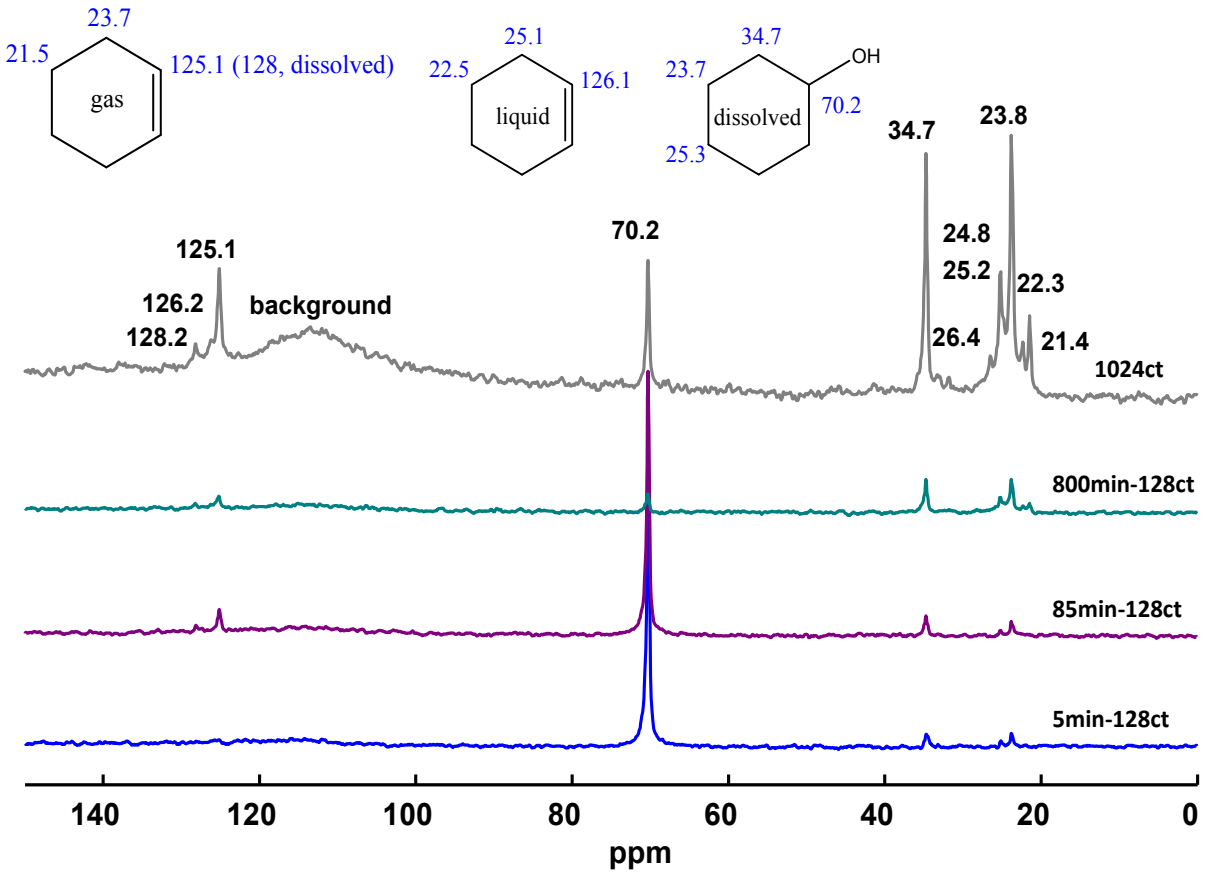

Figure S5 Typical stack plots of *in situ* ^{13}C MAS NMR spectra for H-Beta catalysts conducted at 140 °C: 1st spectrum 5 min, 128 scans; 8th spectrum, 85 min, 128 scans; 80th spectrum, 800 min, 128 scans; and after 80th spectrum, 1024 scans.

Figure S4 and S5 shows typical stack plots of *in situ* ^{13}C MAS NMR spectra, where the assignment of each peak is indicated in the molecular structure. The area of each peak can be obtained by fitting the spectrum. To avoid the back reaction, ^{13}C-isotope scrambling, and diffusion that all would affect the forward reaction rate, the reaction rates were determined at conversion lower than 10%. So, at the initial reaction stage only cyclohexanol dehydration to cyclohexene was considered. It is worth noting that as the reaction progresses, the total ^{13}C signal intensities decrease by about 5% at the time point of the first 50 minute reaction, which may result from a combination of (i) a part of the cyclohexene gas, initially generated at reaction temperature, is outside sensitivity region of the RF coil; and (ii) the fact that part of the reaction products, i.e., cyclohexene, is NMR invisible due to the currently available sensitivity of the NMR set-up on our 300 MHz NMR for detecting the species that are absorbed onto the HBEA catalyst surface, where broader NMR peaks are generally expected that may be buried into the noise of the baseline. To confirm that the rotor is 100% sealed and the total carbon loss is resulted from the catalytic reaction, a control experiment was carried out using a mixture of water and cyclohexanol without H_3PO_4 or H-Beta catalysts. The normalized total ^{13}C signal intensities as a function of reaction time is shown in figure S6. As

is expected, the total ^{13}C signal intensity is essentially constant over the course of the experiment, only with small fluctuations from 97% to 100% during the whole reaction time.

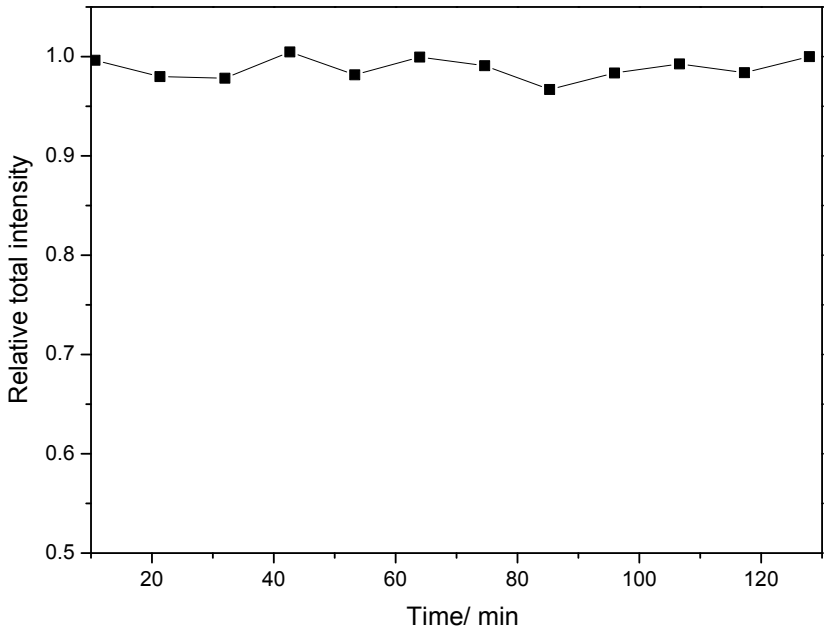

Figure S6 Normalized total ^{13}C signal intensities as a function of time for cyclohexanol and water mixture in the MAS rotor spinning at 3 kHz at 150 °C.

The reaction rates are calculated as follows:
The real time concentration of cyclohexene:
$[cyclohexene](t) = A_{cyclohexene}(t)[cyclohexanol](0)/A_{cyclohexanol}(0)$
$A_{cyclohexene}(t)$: real time NMR signal intensity of cyclohexene.
$[cyclohexanol](0)$, $A_{cyclohexanol}(0)$: initial concentration and NMR signal intensity of cyclohexanol.

Reaction rate: According carbon balance，$A_{cyclohexanol}(0) = A_{[cyclohexene]}(t) + A_{cyclohexanol}(t)$

$$r = \frac{d[cyclohexene](t)}{dt} = -\frac{[cyclohexanol](0)}{A_{cyclohexanol}(0)} \times \frac{dA_{cyclohexanol}(t)}{dt}$$

Note: above reaction rate calculation is based on the fact that no side reaction happens and the ^{13}C-isotope scrambling of cyclohexene at initial reaction stage can be ignored (no more than 1%).

The reaction rates for H_3PO_4 and H-Beta catalyst are listed in Table S1

Table S1. TOF and activation energy of cyclohexanol dehydration catalyzed by H-Beta and H_3PO_4 catalyst.

Reaction condition	TOF/s^{-1}*	Ea/kJ·mol^{-1}
H_3PO_4, 424.7K	0.00129	148±15
H_3PO_4, 428.1K	0.00185	
H_3PO_4, 433.1K	0.00287	
H_3PO_4, 438.2K	0.00470	
H-Beta, 403.1K	0.00039	164±15
H-Beta, 408.1K	0.00076	
H-Beta, 413.1K	0.00136	
H-Beta, 418.1K	0.00226	
H_3PO_4, batch,**	0.0021(**438K**)	155±5
H-Beta,batch,**	0.0037(**418.1K**)	169±10

*TOF calculated based on the concentration of H_3O^+ (for H_3PO_4, it was estimated using the dissociation equilibrium constants of H_3PO_4 in water at elevated temperatures; for zeolites, it was the concentration of Brønsted acid sites determined by pyridine IR)

**For batch reactions, the TOFs at 438 (H_3PO_4) and 418 K (H-Beta) were reported as extrapolated or interpolated values from the Arrhenius plot with measured TOFs and activation energies (433−473 K).

^{1}H HR-MAS NMR metabolomics

Varying temperature ^{1}H HR-MAS NMR metabolomics measurements were carried out on a Varian 500 MHz NMR spectrometer using a 7.5 mm HX MAS probe with a spinning rate of 3.7 kHz at resonance frequencies of 500.18 MHz. The real temperature in the rotor was calibrated by methanol.[4] To avoid tissue degradation, the sample was packed in the dry ice box. 280 mg mouse-liver tissue was loaded and sealed in the rotor. ^{1}H MAS NMR was conducted varying temperature from 0 °C to 25 °C, and at each temperature the spectrum was acquired using a CPMG pulse sequence with 5 π pulses that were synchronized to the rotor period with accumulation number of 384. The representative spectrum with the corresponding peak attributions are shown in figure S7.[6]

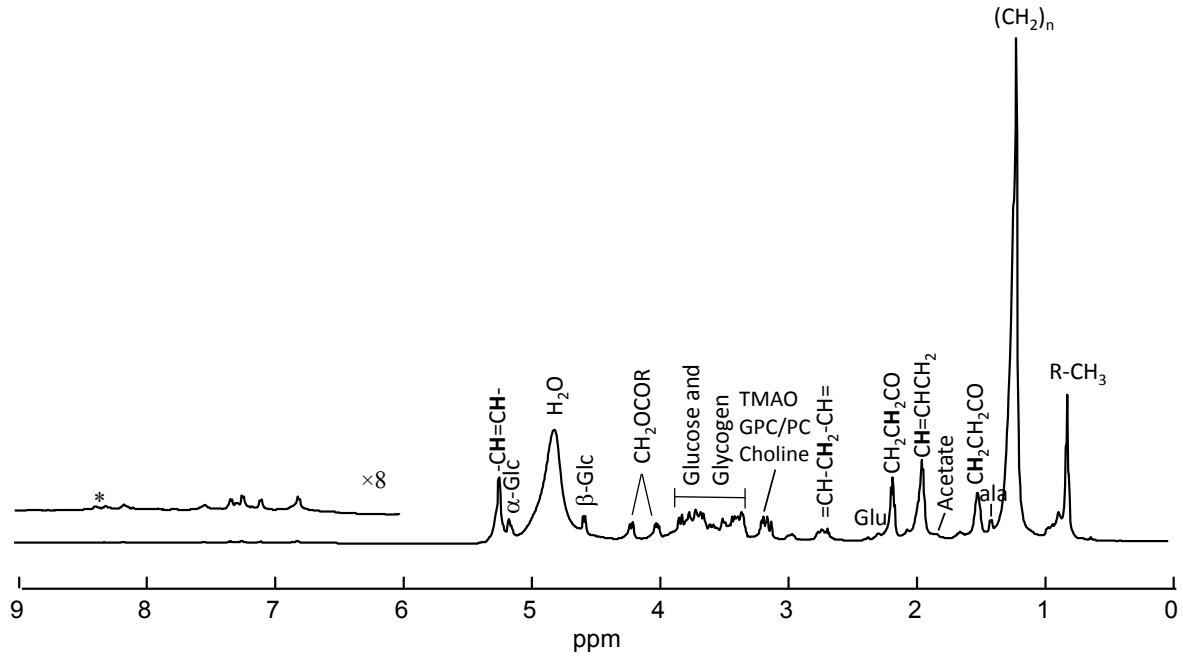

Figure S7. Representative ^{1}H MAS NMR spectrum of mouse-liver acquired at 25 °C with 384 scans. Glc, glucose; GPC, glycerophosphorylcholine; and TMAO, trimethylamine-*N*-oxide.

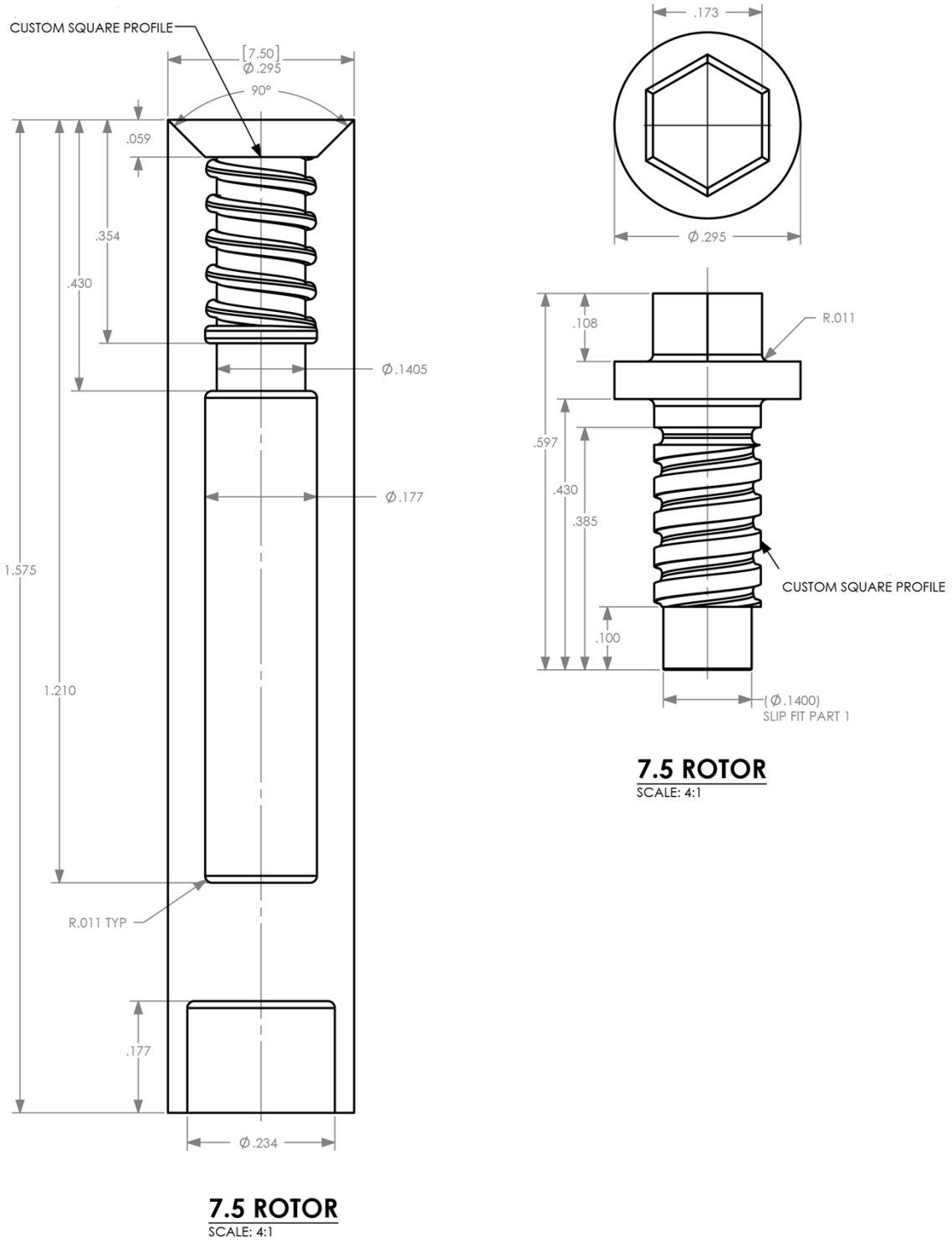

Figure S8. Detailed dimensions of a representative 7.5 mm zirconia MAS rotor, where the O-ring (not shown) is a general purpose high temperature O-ring, the spin-tip is a commercial 7.5 mm Kel-F pencil-type spin tip, the screw and the rotor body in this study are made of magnesia partially stabilized zirconia with constituent (weight percentage) as ZrO_2 (94.8%), HfO_2 (1.8%), MgO (3.25%) and other (0.15%).

References

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