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Surface Enhanced Dynamic Nuclear Polarization Solid-state NMR Spectroscopy Illuminates Brønsted-Lewis Acid Synergy During the Zeolite Catalyzed Methanol-to-Hydrocarbons Process

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S1. Experimental: Materials and Methods

S1.1. Catalyst Synthesis

The synthesis and detailed characterization of both zeolite catalysts along with their catalytic performances were included in our previous publications.[1,2] Ca-modified ZSM-5 was prepared *via* incipient wetness impregnation method using ZSM-5 (CBV 8014, Si/Al=40) purchased from Zeolyst International as a parent material. In a typical procedure, ZSM-5 was impregnated with 6.0 M aqueous solution of $Ca(NO_3)_2{\cdot}4H_2O$ aiming 6 wt. % Ca loading. The sample was subsequently dried in a desiccator followed by drying for 12 h at 80 °C and calcination at 550 °C.

High-silica ZSM-5 was hydrothermally synthesized aiming the same amount of Brønsted acid sites as Ca-modified sample. In a typical synthesis, 0.010 g $NaAlO_2$, 16.8 mL 1M tetrapropylammonium hydroxide, and 8.4 mL tetraethyl orthosilicate were mixed in 15.6 mL water, aged at 100 °C for 2 h and subsequently left for stirring for 16 h. The synthesis solutions were subjected to hydrothermal synthesis at 180 °C for 24 h. The as-synthesized material was calcined at 550 °C for 10 h in a static oven to remove the template. The calcined material was converted to the protonic form by triple ion-exchange with NH_4NO_3 (1 M, 80°C, 2 h, 100 mL per gram of zeolite) followed by calcination at 550 °C.

S1.2. Catalyst Characterization

N_2 adsorption at -196°C was carried out using a Tristar II 3020 analyzer (Micromeritics). Prior to the experiment, samples were outgassed under vacuum at 350 °C for 16 h. Transmission FT-IR spectroscopy using pyridine as a probe molecule was performed using a Nicolet 6700 spectrometer equipped with a MCT/B detector. Spectra were recorded in 1000-4000 cm^{-1} range at 4 cm^{-1} resolution and co-addition of 128 scans. The amount of Brønsted (BAS) and Lewis (LAS) acid sites was derived from the bands at 1545 and 1456 cm^{-1} as described elsewhere using extinction coefficients of 1.67 and 2.22, respectively.[3] Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart-Thornley detector (see Fig. S11). The XRD patterns of the materials were recorded in Bragg-Brentano geometry with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector (see Fig. S12). Measurements were performed at room temperature by using monochromatic CoKα (λ=1.788970 Å) radiation between 2Θ = 5° and 50°.

Textural and acidic properties of the catalysts under study are summarized in Table S1. As one can see from the table, both samples possess similar textural properties, therefore any possible effect evolving from this parameter can be excluded. Importantly, both samples are characterized with exactly the same amount of Brønsted acid sites and noticeably different amount of Lewis acidity.

In the present study, two samples, high silica ZSM-5 with Si/Al = 1280 and Ca-modified ZSM-5 (Si/Al=40) were taken as a representative specimens of unmodified and alkaline earth metal-modified zeolite, respectively. Two extreme choices, *i.e.* unmodified zeolite with lower acidity and its modified analogue with high Ca-content, have deliberately been considered here to understand their mechanistic differences as clearly as possible.

S1.3. Catalyst Testing

Catalytic experiments were carried out in a Microactivity Reference unit (PID Eng&Tech) at 500 °C and ambient pressure. Typically, the catalyst (pressed, crushed and sieved to particle sizes 250-420 μm) was mixed with SiC (6:1 wt%) and placed in a fixed-bed with an internal diameter of 9 mm for standard experiments. An ISCO pump was used to feed methanol to the reactor system. A weight-hourly space velocity (WHSV) of 8 $g_{MeOH}g_{cat}^{-1}h^{-1}$, an N_2: MeOH=1:1 molar feed composition and atmospheric pressure were utilized. Conversion, selectivities, and yields were calculated on a molar carbon basis (reported previously).[1] Both catalysts possessing the same amount of Brønsted acid sites were compared in methanol-to-hydrocarbon (MTH) process. While ZSM-5 shows no deactivation for 28 hours (corresponding to 224 g_{MeOH} converted per gram of catalyst), its Ca-modified counterpart is able to convert twice higher amount of methanol before deactivation starts. The stability towards deactivation is attributed to the presence of Lewis acidity generated *via* Ca incorporation and is discussed in detail in our previous manuscript (along with additional catalytic data).[1]

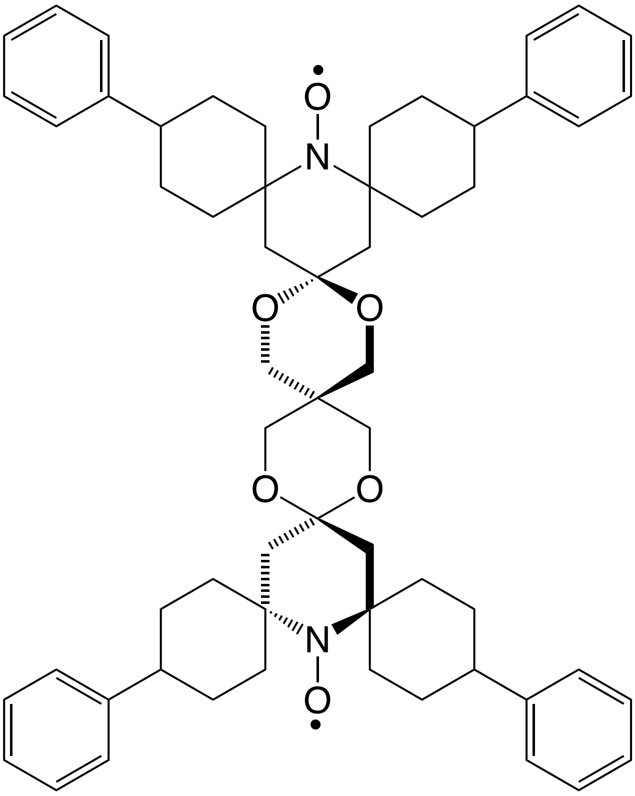
S2. Solid-state NMR Spectroscopy

One-dimensional ^{1}H magic angle spinning (MAS) and ^{1}H-^{13}C cross-polarization (CP) MAS solid-state NMR experiments were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequencies for ^{1}H employing a conventional double-resonance 3.2 mm CP-MAS probe. In all cases, the post-reacted zeolites were packed into zirconium rotors under an inert atmosphere inside gloveboxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external reference adamantane. Potassium bromide (KBr) was used to calibrate the magic angle for the MAS probes. For ^{1}H-^{13}C CP MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time of typically 2 ms, and finally acquisition of the ^{13}C NMR signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^{1}H nuclei, and the number of scans of 15000 - 30000 for ^{13}C. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. The 2D ^{1}H-^{13}C heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, CP to ^{13}C, and detection of the ^{13}C magnetization under TPPM (*i.e.*, a two-pulse phase modulation) decoupling. For the CP step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, while the ^{13}C channel RF field was matched to obtain an optimal signal. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination sphere to lead to correlations only between pairs of attached ^{1}H-^{13}C spins (C-H directly bonded).

S3. Dynamic Nuclear Polarization NMR spectroscopy (DNP SENS)

Sample Preparation: TEKPol (purchased from Cortecnet) was dried under high vacuum (10^{-4} mbar) and the solvents were stirred over calcium hydride and then distilled in vacuo. A radical solution consisting of 16 mM TEKPol (TEKPol, MW=905 g/mol) in 1,1,2,2-tetrachloroethane (TCE) was used. DNP samples were prepared by incipient wetness impregnation. As reported in the literature, the best enhancement for applications requiring organic solvents was obtained with TEKPol[4] in combination with organic solvents such as

1,1,2,2-tetrachloroethane (TCE) or dichlorobenzene.[5] TCE was preferred here, since its carbon resonances do not overlap with the expected ^{13}C chemical signal from both post-reacted zeolite materials. In a typical experiment, 20 mg of the samples was impregnated with the 20 µL volume of 16 mM solution of TEKPol (nTEKPol = 0.5 - 1.2 µmol/sample) and packed into a 3.2 mm o.d. sapphire rotor capped with a teflon plug under argon atmosphere. The packed samples were then immediately or after a defined time inserted into the pre-cooled DNP probe for experiments. All ^{13}C NMR spectra were referenced to adamantane with the higher frequency peak set to 38.48 ppm with respect to TMS (0 ppm).



TEKPol ($d_{molecule}$ = 2 nm)

Measurements: Data were acquired at the Core Labs of King Abdullah University of Science and Technology using 263 GHz/400 MHz Avance III Bruker DNP solid-state NMR spectrometer ($\nu_L(^{13}C)$ = 100.6 MHz) equipped with a 3.2 mm Bruker triple resonance low-temperature magic angle spinning (LTMAS) probe and the experiments were performed at *ca.* 100 K with a 263 GHz gyrotron microwave irradiation. The sweep coil of the main magnetic field was set for the microwave irradiation occurring at the ^{1}H positive enhancement maximum of the TEKPol biradical. For one-dimensional (1D) ^{13}C DNP SENS NMR experiments, the acquisition parameters used are 3 s repetition delay, a ^{1}H $\pi/2$ pulse length of 2.5 μs to afford 100 kHz ^{1}H decoupling using the SPINAL 64 decoupling method. The contact time was typically 3 ms for cross polarization experiments (unless specified otherwise) and the total number of scans was 10240 (both samples). The MAS frequency varied between 8 and 10 kHz. The two-dimensional (2D) ^{1}H-^{13}C heteronuclear correlation (HETCOR) spectra were acquired with 1024 scans per t1 increment, 48 (unmodified ZSM-5) or 64 (Ca-modified ZSM-5) individual increments and 2 ms contact time. 2D ^{13}C-^{13}C spectra were recorded using a 2 s recycle delay as well as 10 ms (F2) and 6 ms (F1) acquisition time with an accumulation of 512 scans. Herein, carbons were polarized *via* CP and ^{13}C-^{13}C mixing was achieved through proton-driven spin-diffusion using Phase-alternated-recoupling-irradiation-schemes (PARIS) for 30 ms.[6–9]

The ^{13}C DNP build up time with microwave irradiation (T_B) was measured by using a saturation recovery experiment $S(\tau) = A [1 - \exp(-(\tau / T_B)]$, where A is the equilibrium normalized signal intensity at μwave on, $S(\tau)$ is the integrated intensity of the signal at the polarization time/delay τ, and T_B value is the observed signal build-up time. Data are fit using a mono-exponential, which is analogous to that previously reported for porous solid materials, including metal-organic framework and mesoporous silica. [10–12]

S4. Supplementary Table

Table S1 Comparison of textural and acidic properties of catalysts under study.

Catalyst	**Si/Al**[a] (mol mol^{-1})	**V_{total}**[b,e] (cm^3 g^{-1})	**V_{micro}**[b,e] (cm^3 g^{-1})	**S_{BET}**[c,e] (m^2 g^{-1})	**n_{BAS}**[d,e] (µmol g^{-1})	**n_{LAS}**[d,e] (µmol g^{-1})
ZSM-5 (fresh)	1280	0.21	0.17	429	28	11
ZSM-5 (spent)	n.a.	0.18	0.12	300	n.a.	n.a.
Ca-ZSM-5 (fresh)	46	0.23	0.12	385	29	240
Ca-ZSM-5 (spent)	n.a.	0.17	0.10	262	n.a.	n.a.

[a] Molar ratio determined by ICP-OES.

[b] From N_2 adsorption isotherm using t-plot method.

[c] From N_2 adsorption isotherm using t-plot method.

[d] Concentration of Brønsted (BAS) and Lewis (LAS) acid sites derived from FT-IR spectroscopy with pyridine as a probe molecule.

[e] The standard measurement error is ~5% (n.a.=not applicable). Herein, we refer to our previous publication[1] for detailed/additional characterizations and corresponding spectra/isotherms.

S5. Supplementary Figures

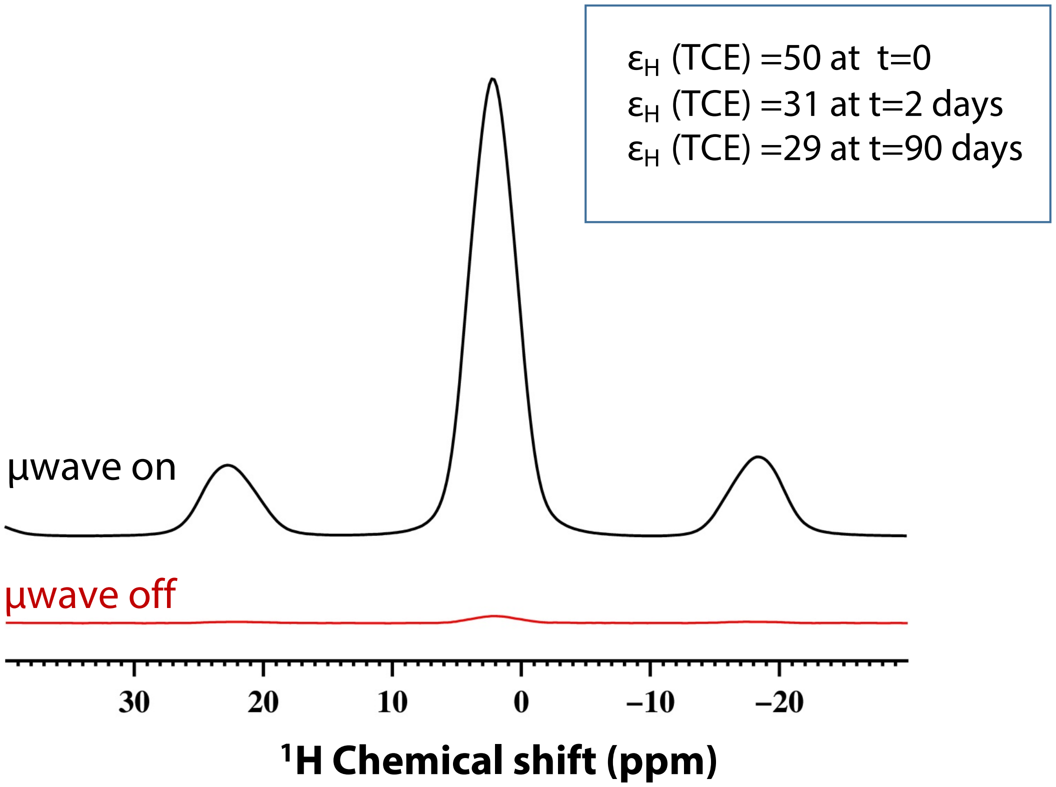


Fig. S1 ^{1}H MAS DNP SENS (100 K, 400 MHz / 263 GHz) of post-reacted unmodified zeolite ZSM-5 material in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE). The recycle delay was 3 s, and the MAS frequency was 8 kHz (ε = DNP enhancement factor, t=impregnation time). Herein, *t*=0 means immediately after the impregnation, and subsequently, the sample was stored in its rotor at -4˚C between each experiment at different time intervals (as indicated in the spectra). The red line represents the spectra without any microwave irradiation (16 scans), while the black line shows the experiment under microwave irradiation (16 scans).

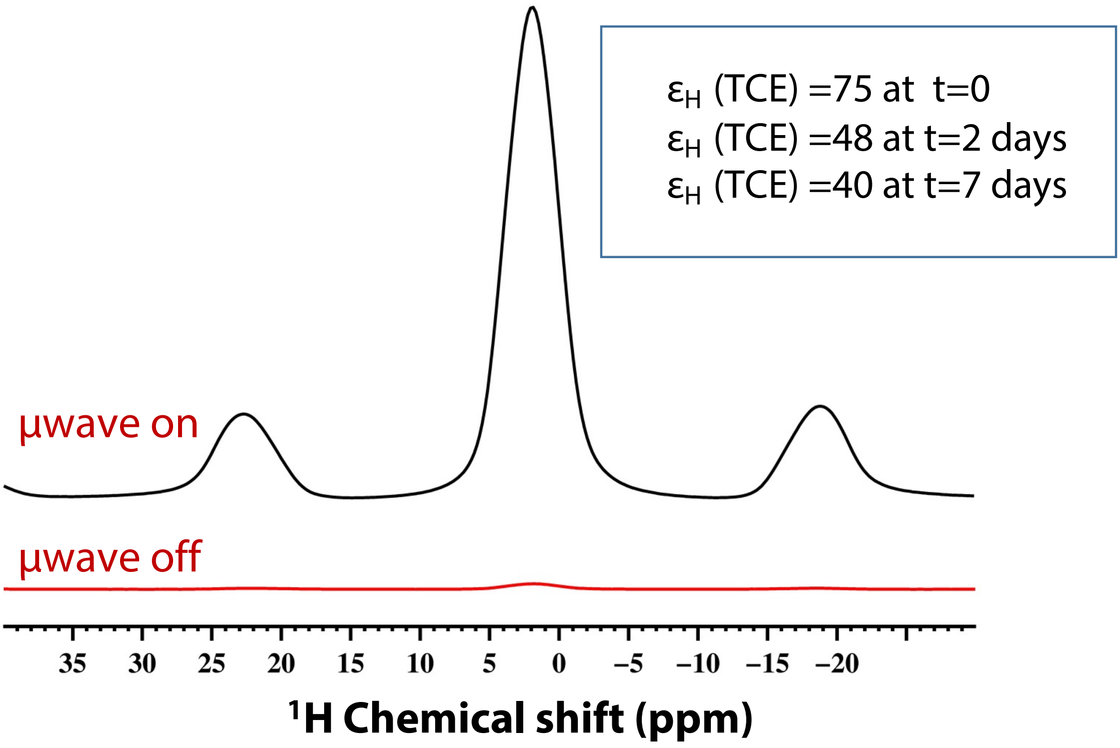


Fig. S2 ^{1}H MAS DNP SENS (100 K, 400 MHz / 263 GHz) of post-reacted calcium modified zeolite ZSM-5 in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE). The recycle delay was 3 s, and the MAS frequency was 8 kHz (ε = DNP enhancement factor, t=impregnation time). Herein, *t*=0 means immediately after the impregnation, and subsequently, the sample was stored in its rotor at -4˚C between each experiment at different time intervals (as indicated in the spectra). The red line represents the spectra without any microwave irradiation (16 scans), while the black line shows the experiment under microwave irradiation (16 scans).

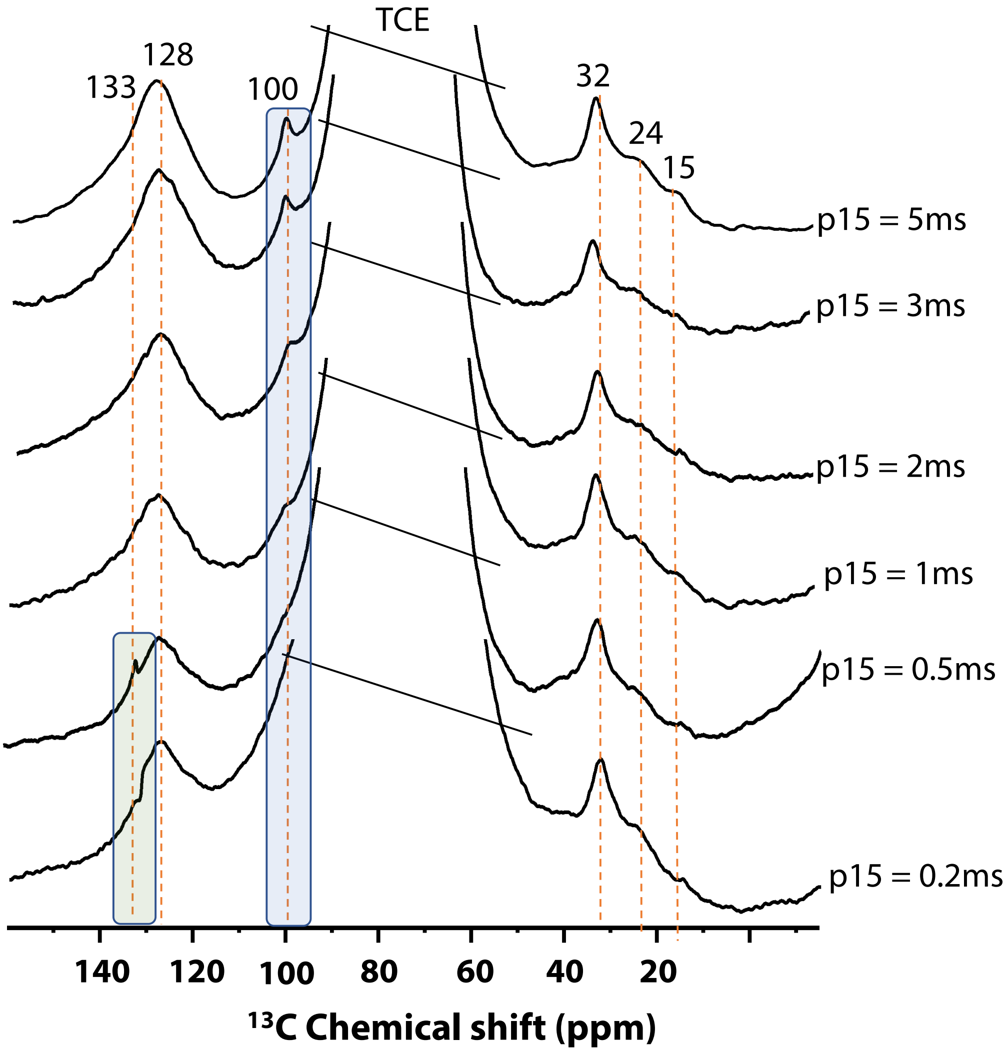


Fig. S3 1D ^{1}H-^{13}C MAS DNP SENS of post-MTH reacted zeolite ZSM-5 in a 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) at different CP contact times (p15). The strongest peak ~75 ppm belongs to solvent 1,1,2,2-tetracholoethane (TCE). The recycle delay was 3 s, and the MAS frequency was 8 kHz. The intensity of acetal peak (~100 ppm, blue-highlighted region) increases while increasing contact time, which means more efficient CP transfer at longer contact time. Considering that methylene of acetal (responsible for 100 ppm peak, -O-$\underline{C}H_2$-O-) is directly attached to hetero-atoms (*i.e.*, no proton containing atoms), the longer contact time is required for its better resolution. It also means that the acetal molecule is situated within the pores of a zeolite. Interestingly, an additional aromatic peak around 133 ppm (green highlighted region) is better resolved at shorter contact times due to its presence in the hydrogen-rich environment, which is exclusively situated on the surface of the zeolite. However, this peak is absent in the post-reacted Ca-modified ZSM-5 zeolite, as it does not contain any aromatic species (Fig. S4).

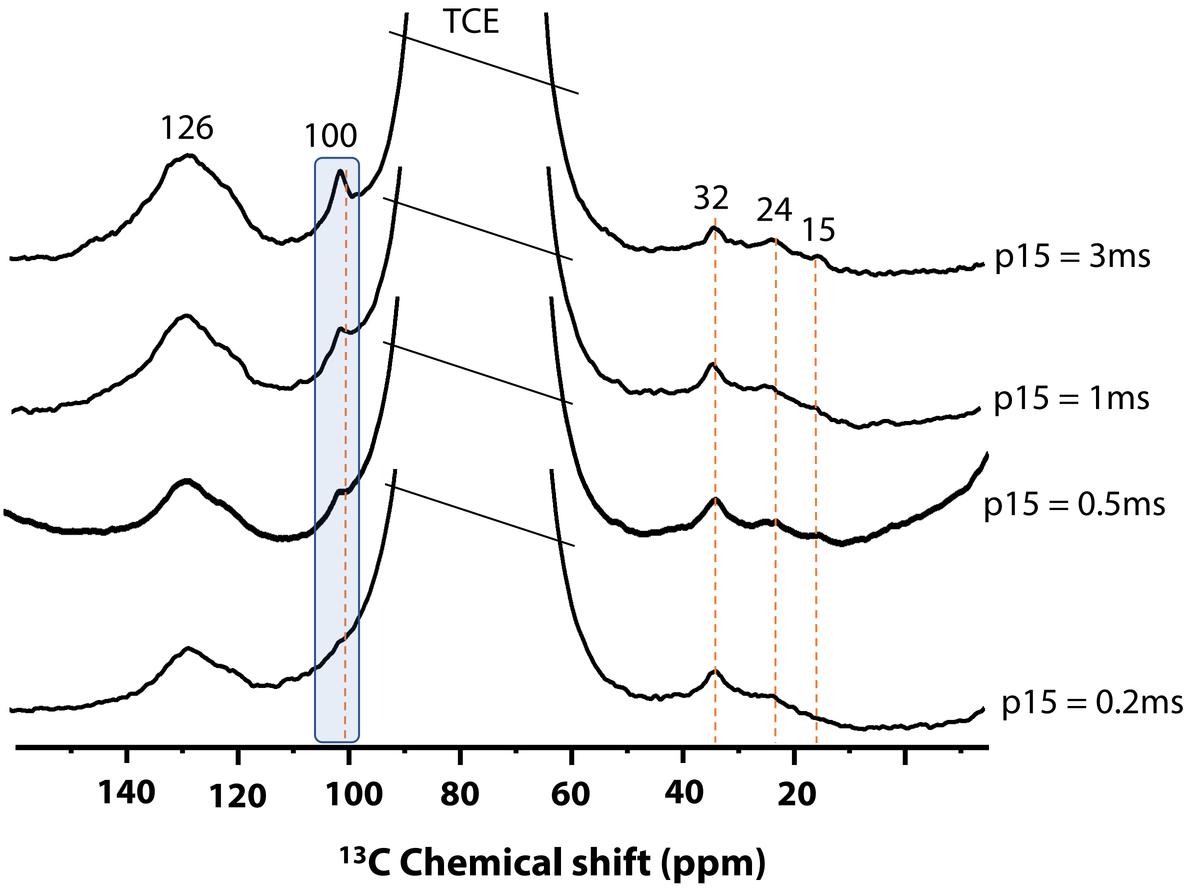


Fig. S4 1D ^{1}H-^{13}C MAS DNP SENS of post-MTH reacted zeolite Ca-ZSM-5 in a 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) at different CP contact time (p15). The strongest peak ~75 ppm belongs to solvent 1,1,2,2-tetracholoethane (TCE). The recycle delay was 3 s, and the MAS frequency was 8 kHz. The intensity of acetal peak (~100 ppm, blue-highlighted region) increases while increasing contact time (similar to post-reacted unmodified ZSM-5, see Fig. S3), which means more efficient CP transfer at longer contact times. It also means that the acetal molecule is situated within the pores of a zeolite. Since the methylene-group of acetals (responsible for ~100 ppm peak, -O-$\underline{C}H_2$-O-) is directly attached to hetero-atoms (*i.e.*, no proton containing atoms), the longer contact time is required for its better resolution. This sample does not contain any aromatic species, which could further be rationalized through the absence of the characteristic peak at 133 ppm (see the green highlighted region in Fig. S3 for comparison, unmodified post-MTH reacted H-ZSM-5 sample).

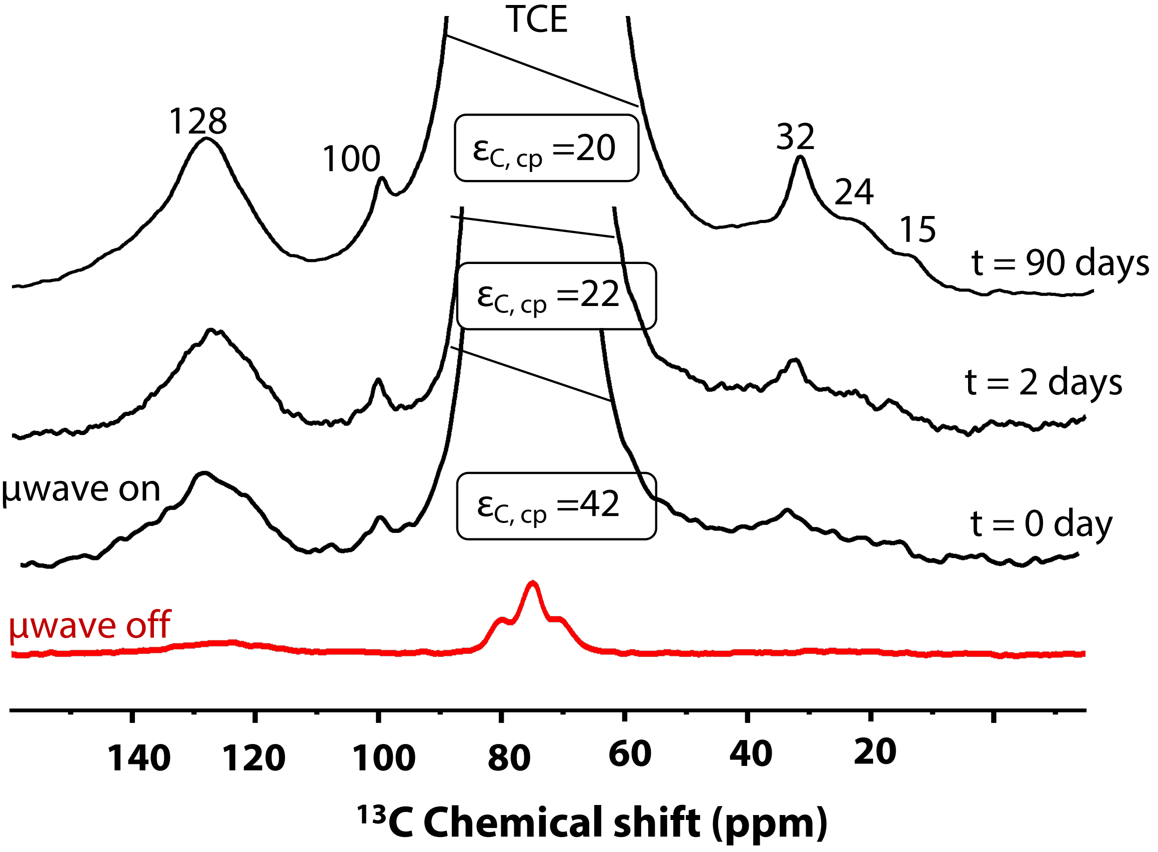


Fig. S5 ^{13}C CPMAS DNP SENS (100 K, 400 MHz / 263 GHz) of post-reacted unmodified zeolite ZSM-5 material (Si/Al=1280) in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE), acquired with the following parameters: a recycle delay of 3 s, a contact time of 3 ms, and 8 kHz MAS frequency. The red trace corresponds to the spectrum (1024 scans) without any microwave irradiation, the black traces with microwave irradiation (2048 scans) recorded after different impregnation time (t_{imp}). Herein, t_{imp}=0 means immediately after the impregnation, and subsequently, the sample was stored in its rotor at -4°C between each experiment at different time intervals (as indicated in the spectra). Herein, fast-solvent build-up times and a simultaneous high solvent enhancement were accompanied by the enhancement of aromatic peaks only at t_{imp}=0. Later, the enhancement of both aliphatic and acetal resonances was observed at the longer t_{imp}. It essentially means that the sample is overwhelmed by surface aromatics species and it takes a while to diffuse into the pores of the zeolite to enhance the signal originated from the species (like acetals and aliphatic groups) within the framework.

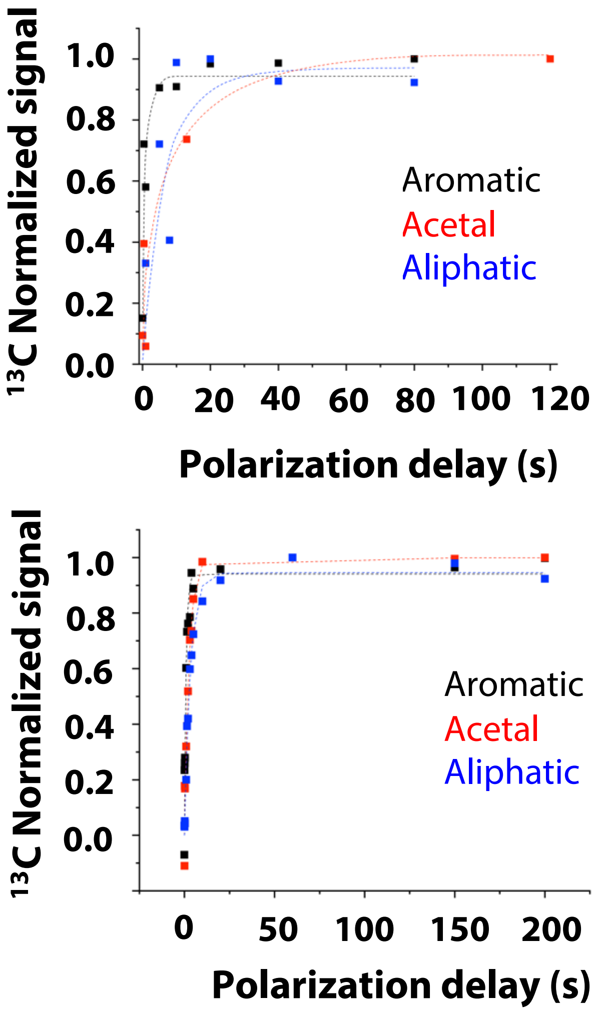


Fig. S6 ^{13}C normalized signal build-up curves of post-reacted unmodified zeolite ZSM-5 material (Si/Al=1280) in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) as a function of time acquired at various impregnation times, t_{imp}=0 (top) and t_{imp}=7 days (bottom), under microwave irradiation.

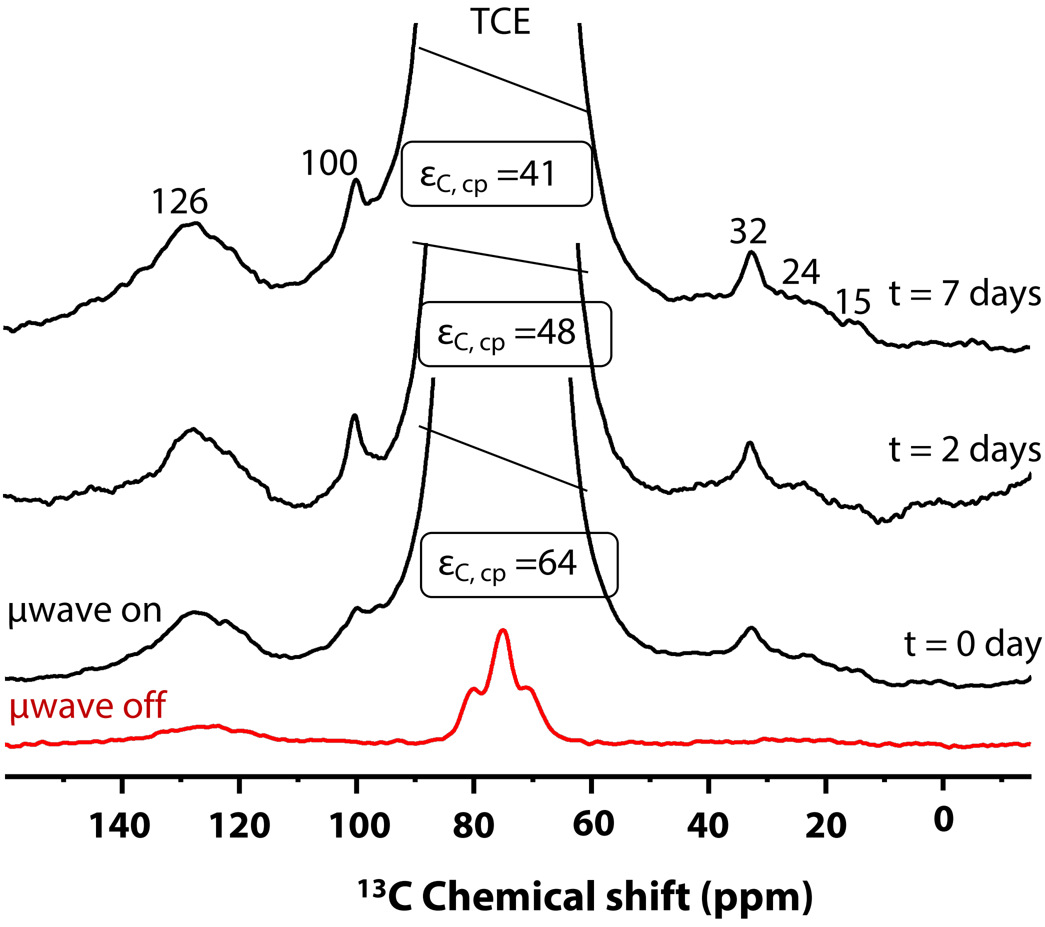


Fig. S7 ^{13}C CPMAS DNP SENS (100 K, 400 MHz / 263 GHz) of post-reacted Ca-modified zeolite ZSM-5 material (Si/Al=40) in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE), acquired with the following parameters: a recycle delay of 3 s, a contact time of 3 ms and 8 kHz MAS frequency. The red trace corresponds to the spectrum (1024 scans) without any microwave irradiation, the black traces with microwave irradiation (2048 scans) recorded after different impregnation time (t_{imp}). Herein, t_{imp}=0 means immediately after the impregnation, and subsequently, the sample was stored in its rotor at -4°C between each experiment at different time intervals (as indicated in the spectra). Contrary to Fig. S4, fast-solvent build-up times and a simultaneous high solvent enhancement were accompanied by the enhancement all peaks (aliphatic, olefinic, acetals) at t_{imp}=0 in this case. Later, the enhancement of all signals was observed at longer t_{imp}. It essentially means that in-situ formed hydrocarbon pool species were uniformly distributed across the sample, which is yet to be deactivated and shows resistive character towards coking/deactivation.

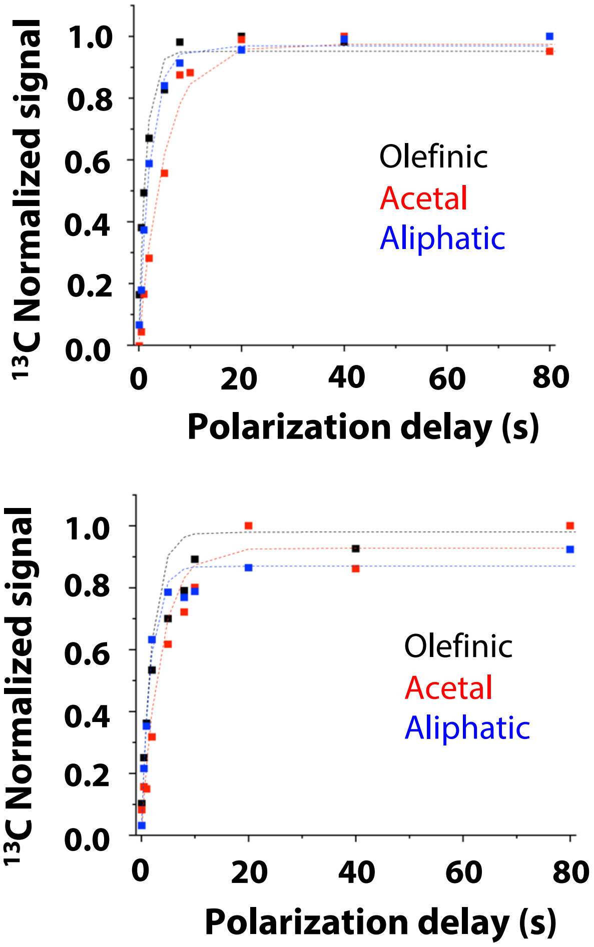


Fig. S8 ^{13}C normalized signal build-up curves of post-reacted zeolite Ca-modified ZSM-5 material (Si/Al=40) in 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) as a function of time acquired at various impregnation times, t_{imp}=0 (top) and t_{imp}=7 days (bottom), under microwave irradiation.

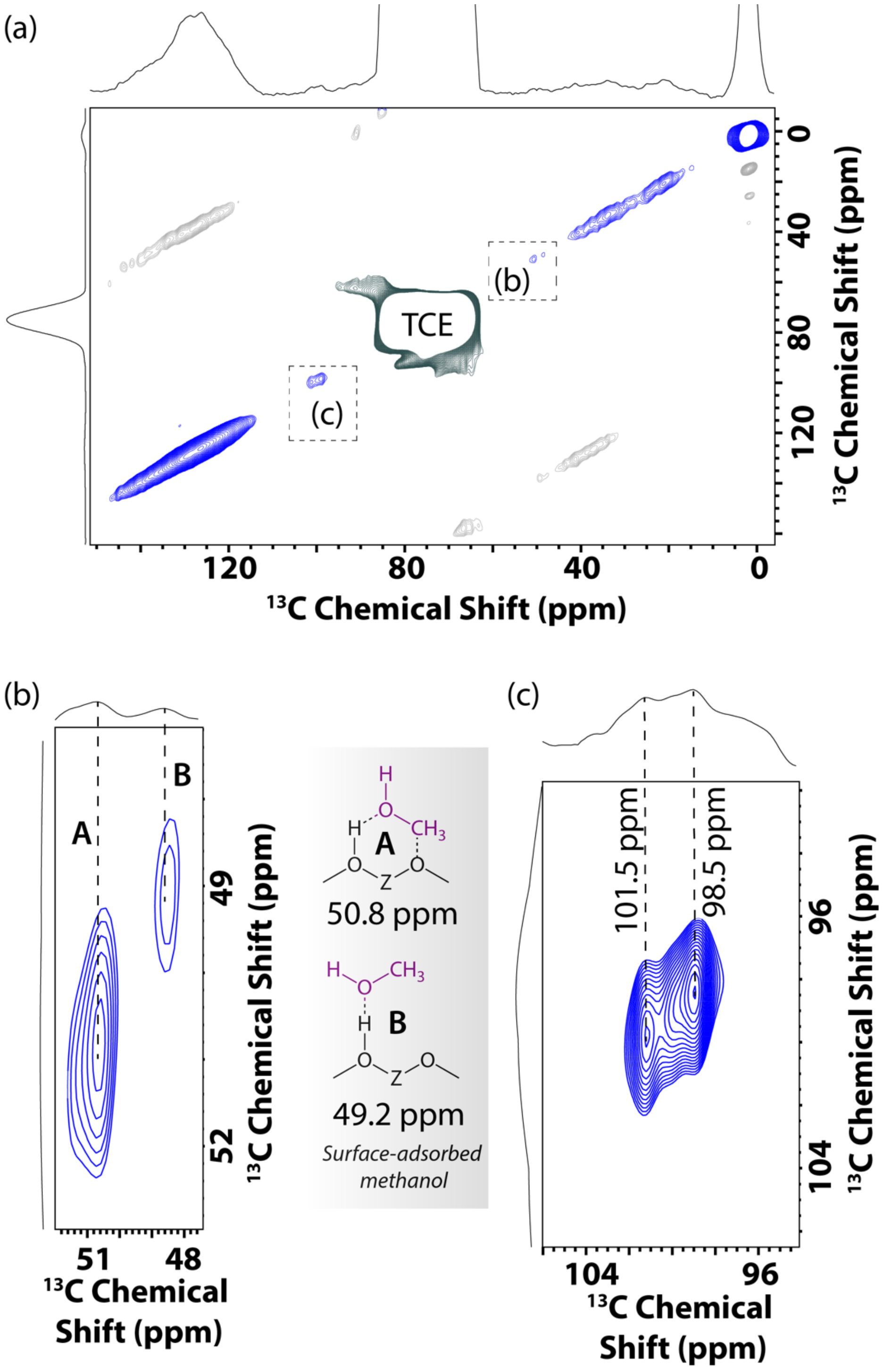


Fig. S9 DNP enhanced 2D ^{13}C-^{13}C MAS spin-diffusion solid-state NMR spectra of the post-MTH reacted zeolite (a) ZSM-5 in a 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) (spinning side bands and TCE are represented in light and slate-grey, respectively). Zooms of (b) methoxy and (c) acetal regions highlight the existence of surface-adsorbed methanol and dimethoxymethane, respectively.

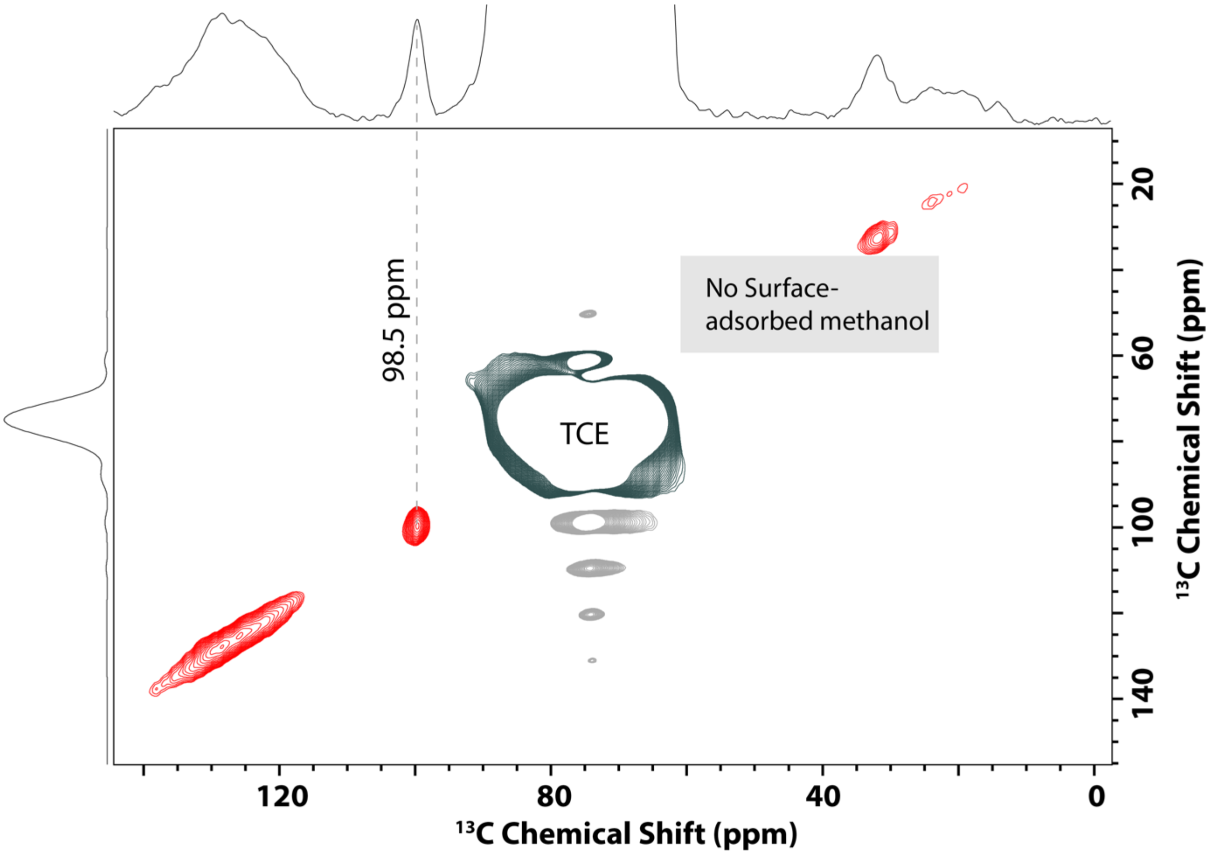


Fig. S10 DNP enhanced 2D ^{13}C-^{13}C MAS spin-diffusion solid-state NMR spectra of the post-MTH reacted zeolite Ca-ZSM-5 in a 16 mM TEKPol solution in 1,1,2,2-tetracholoethane (TCE) (spinning side bands and TCE are represented in light and slate-grey, respectively).

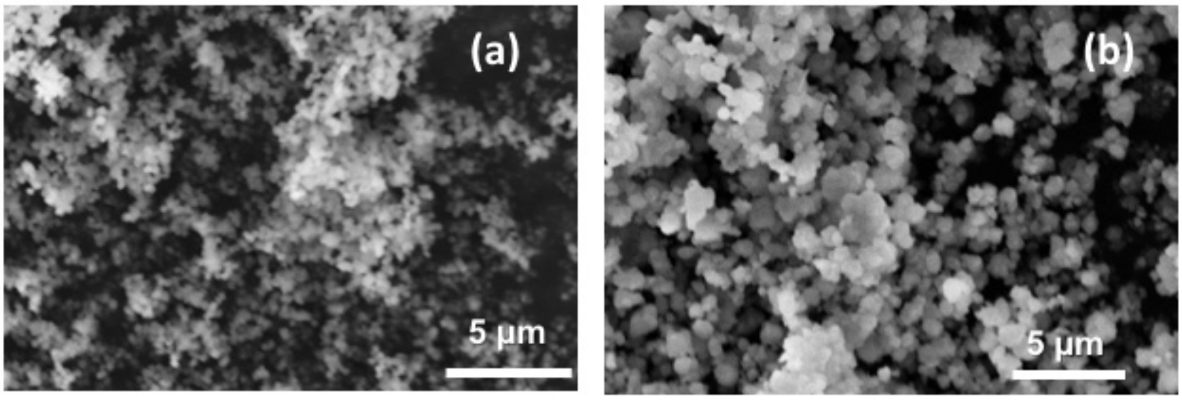


Fig. S11 SEM images of the (a) zeolite ZSM-5 material (Si/Al=1280) and (b) Ca-modified ZSM-5 material (Si/Al=40).

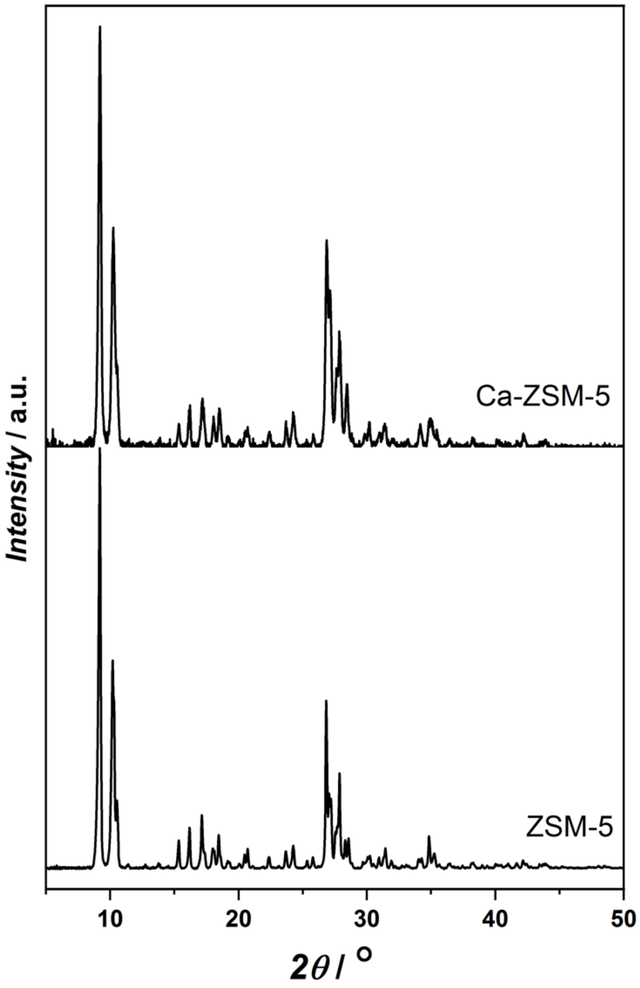


Fig. S12 X-Ray diffraction patterns of the (a) zeolite ZSM-5 material (Si/Al=1280) and (b) Ca-modified ZSM-5 material (Si/Al=40). The X-ray diffraction patterns confirm the single-phase crystalline MFI structure.

S6. Supplementary References

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