SUPPORTING INFORMATION

Non-oxidative dehydrogenation of isobutane over supported vanadium oxide: nature of the active sites and coke formation

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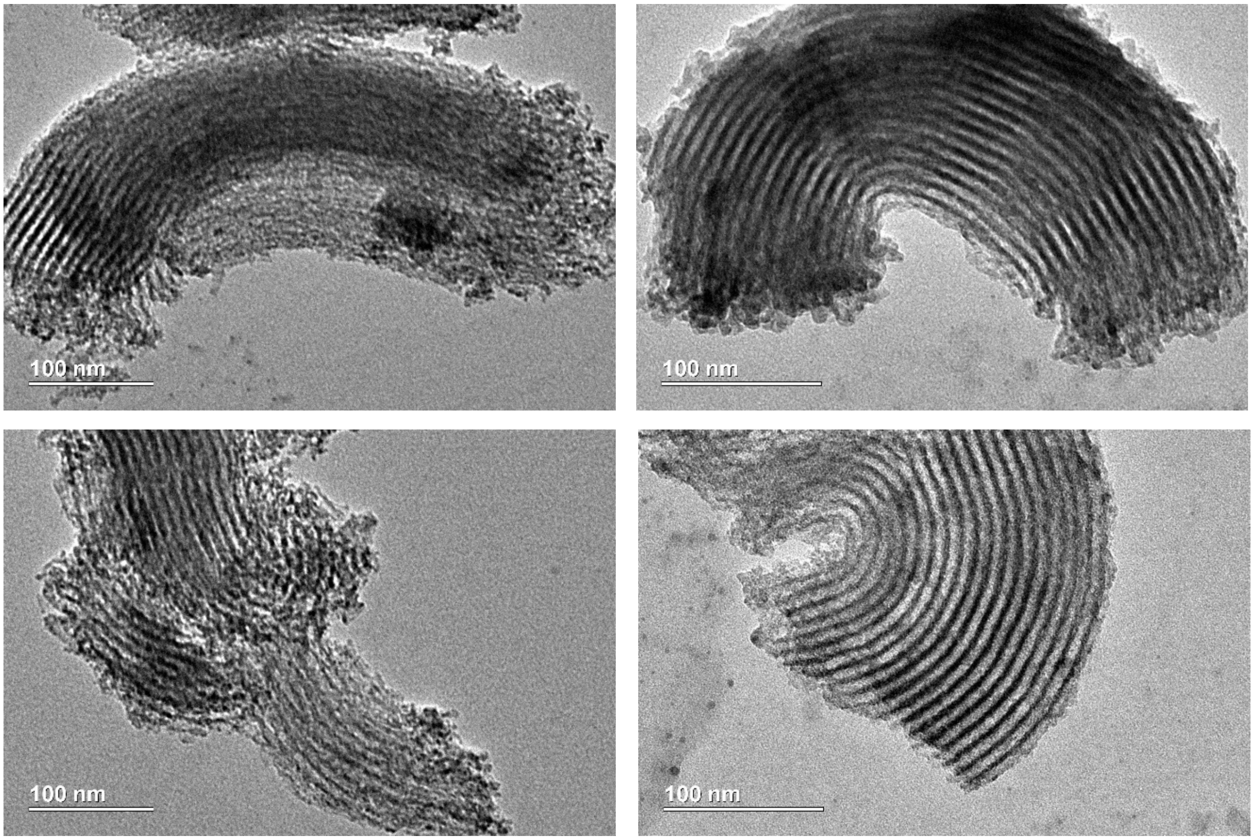

Fig. S1 Transmission Electron Microscopy (TEM) images of pristine V/SBA-15.

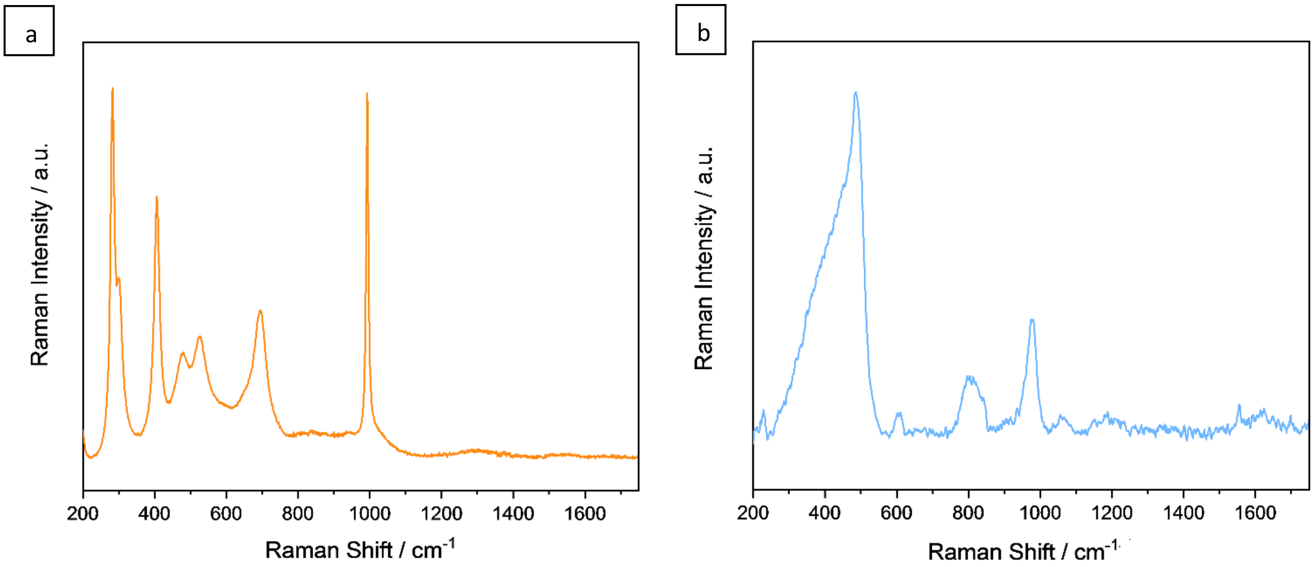

Fig. S2 Raman spectra of commercially available V_2O_5 (a) and pristine SBA-15 (b).

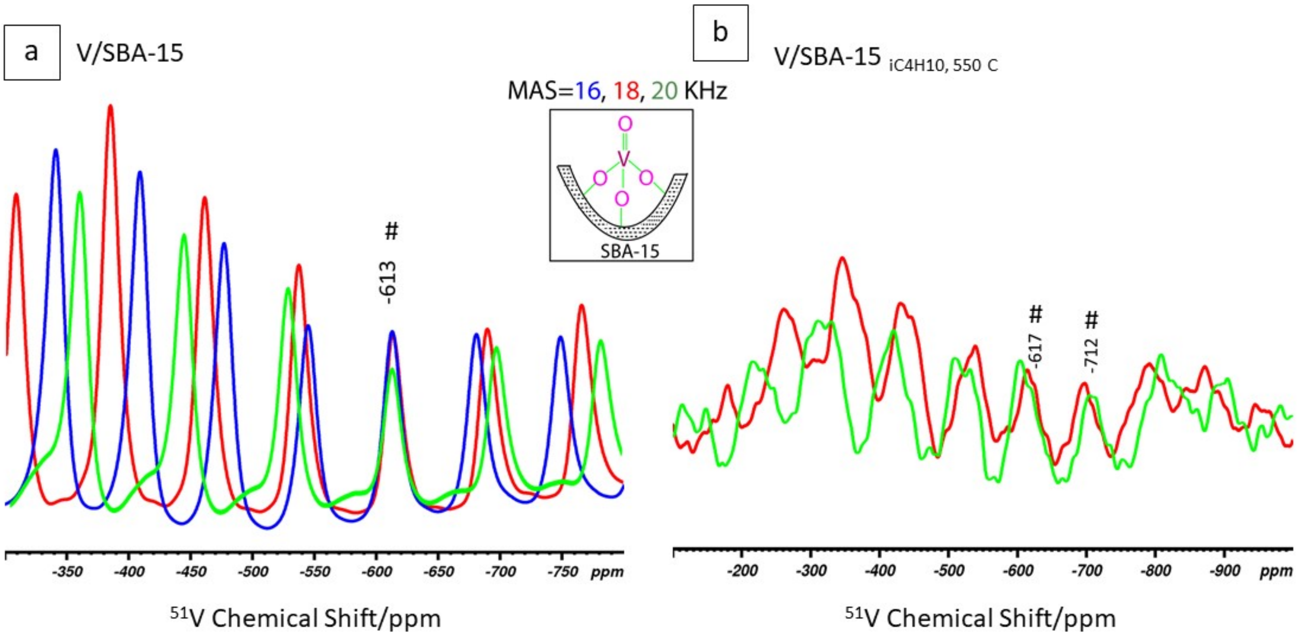

Fig. S3. 1D ^{51}V magic angle spinning (MAS) solid-state NMR spectra of (a) calcined catalyst and (b) spent catalyst. The peak(s) represented by '#' is the real peak, rest are spinning side-bands (recycle delay=1 sec). The poor signal-to-noise (S/N) ratio is due to change of oxidation state and the existence of paramagnetic species (see Figure 4) in a greater quantity.

Table S1 Raman band assignments for V_2O_5 [1].

Peak Position (cm^{-1})	Assignment
282	bending of V=O
300	bending of V_3-O
406	bending of V=O
480	bending of V-O-V
525	stretching of V_3-O
694	stretching of V-O-V
993	stretching of V=O

Table S2 Raman band assignments for SBA-15 [2], [3].

Peak Position (cm^{-1})	Assignment
430	6-membered rings
486	D1, 4-membered silaxone rings
609	D2, 4-membered silaxone rings
803	symmetric Transverse Optical (TO)/Longitudinal Optical(LO) stretching of Si-O-Si
981	stretching vibration of silanols
1055	asymmetric TO stretching of Si-O-Si
1188	asymmetric LO stretching of Si-O-Si

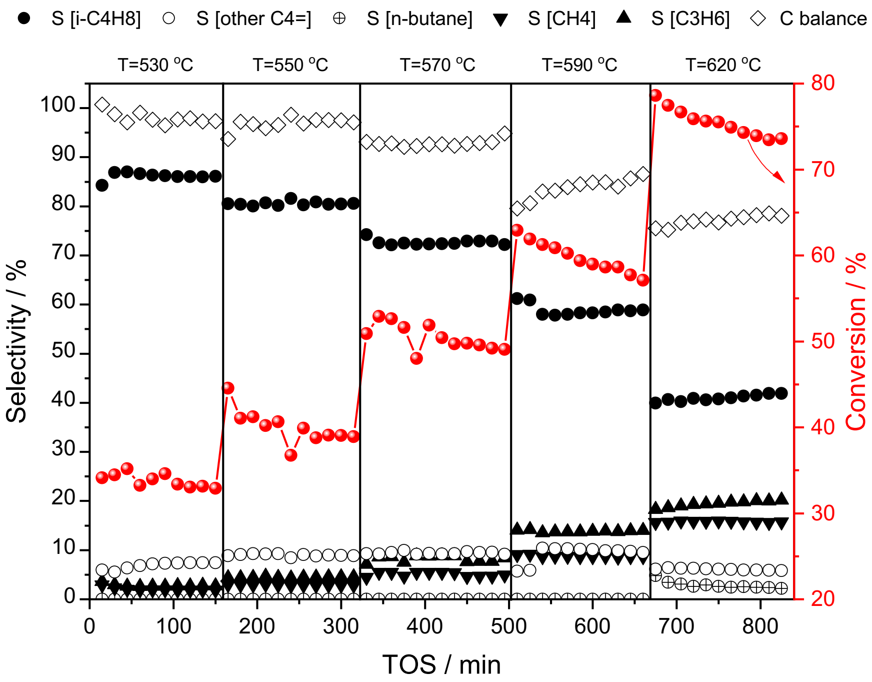

Fig. S4 Catalytic performance of V/SBA-15 in the non-oxidative dehydrogenation of isobutane. Conversion and selectivity to different products at different temperatures and WHSV=240 mL·min^{-1}·g$_{cat}$$^{-1}$.

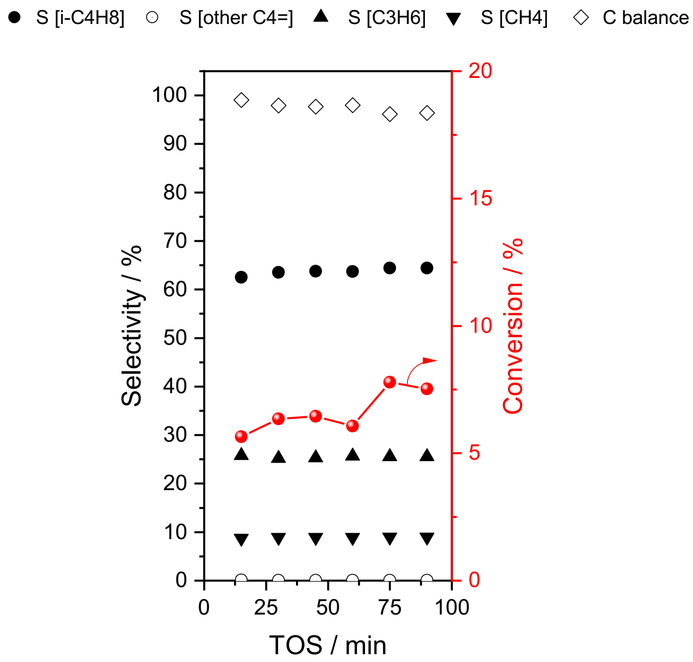

Fig. S5 Catalytic performance of a blank experiment with SiC at 550 °C and WHSV=240 mL·min^{-1}·g$_{cat}$$^{-1}$.

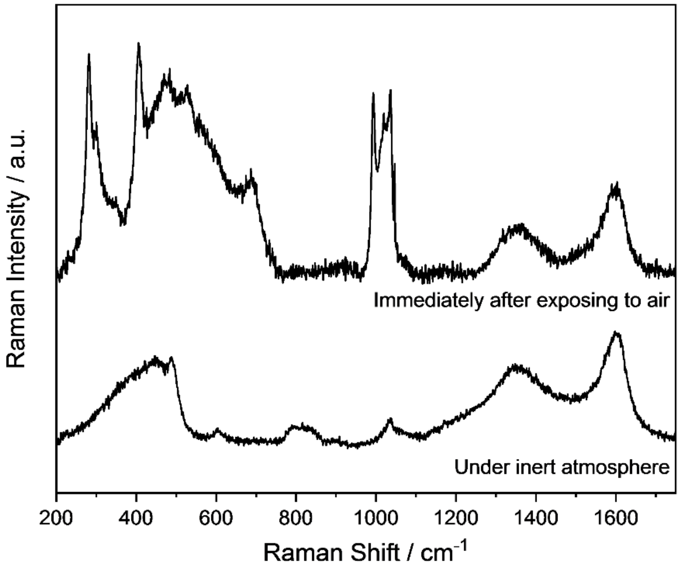

Fig. S6 Raman spectra of spent catalyst under inert (Ar) atmosphere and immediately after it is exposed to ambient air.

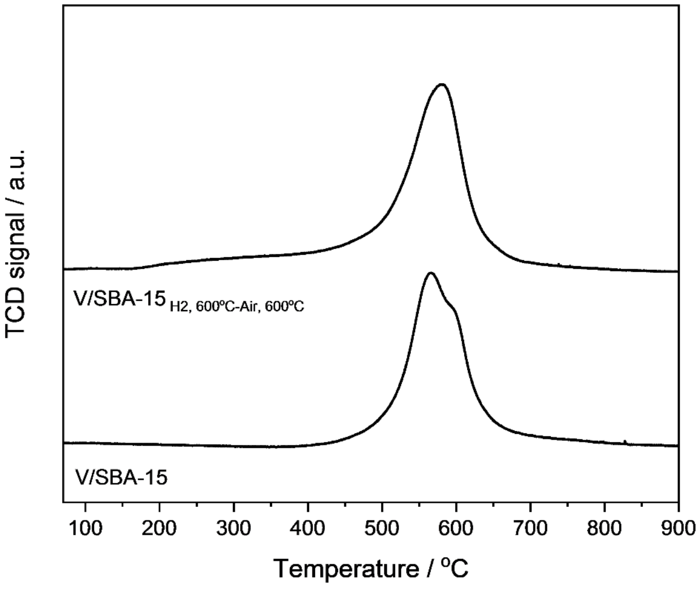

Fig. S7 Temperature programmed reduction profile of pristine V/SBA-15 and pre-treated in hydrogen and re-oxidized in air at 600 °C.

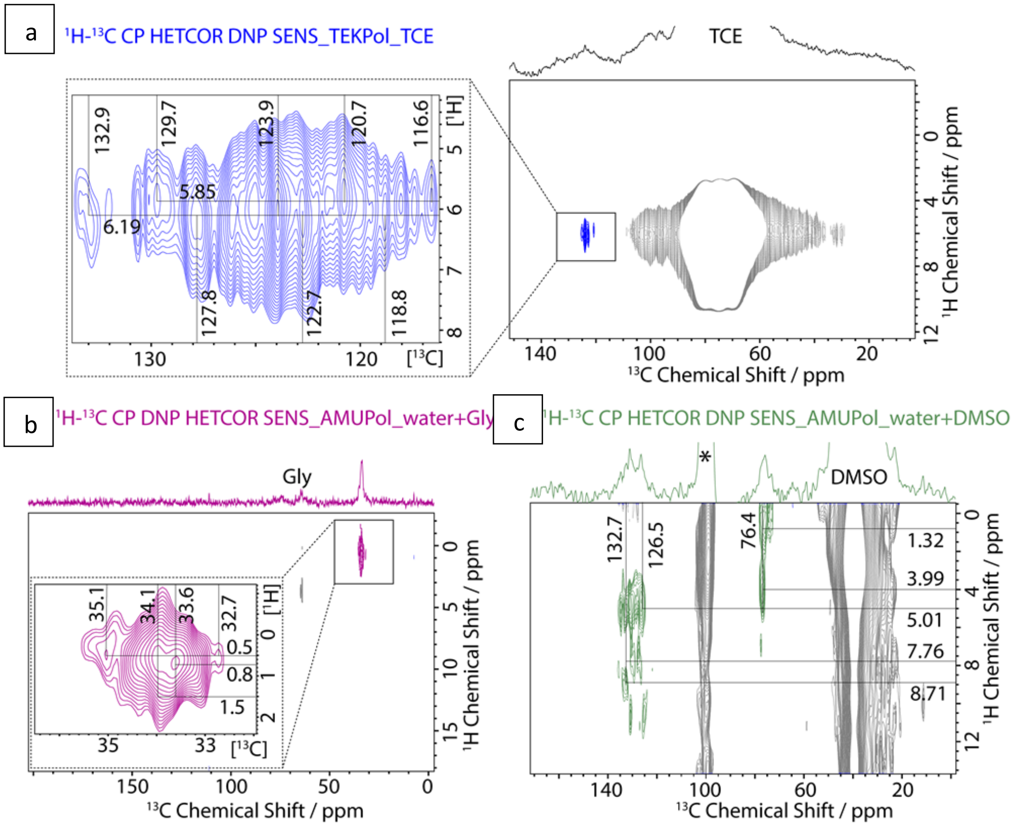

Fig. S8 2D ^{1}H-^{13}C cross-polarization (CP) magic angle spinning (MAS) DNP HETCOR solid-state NMR spectra (including 1D ^{1}H-^{13}C CPMAS) of post-reacted catalytic material (a) in TEKPol solution in 1,1,2,2-tetrachloroethane (TCE) as well as in AMUPol solution (aromatic region is in the zoom at left, ct=0.5 ms, d1=5 sec), (b) in water+ glycerol (water+Gly) (ct=1 ms, d1=3 sec), and (c) in water+dimethyl sulfoxide (water+DMSO) (ct=0.5 ms, d1=3.5 sec) (* = spinning side-bands, 8 kHz MAS, d1=recycle delay, ct=CP contact time).

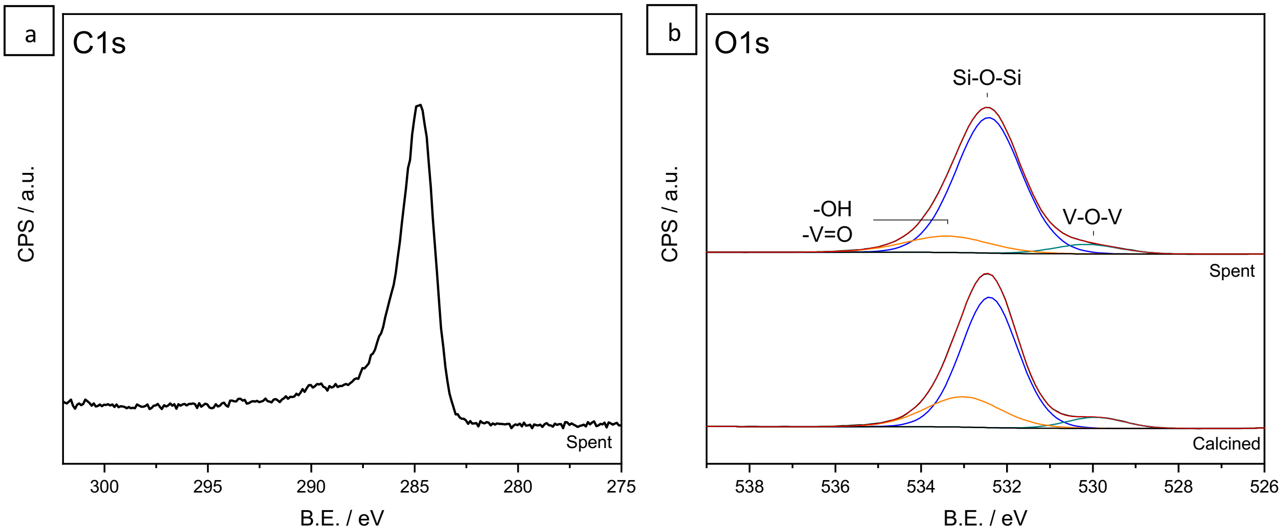

Fig. S9 XPS spectra of the V/SBA-15 sample in the C1s (a) and O1s (b) regions.

Additional experimental details for Dynamic Nuclear Polarization NMR spectroscopy (DNP SENS)

Sample Preparation:

Three set of samples were prepared using incipient wetness impregnation with a solution of 16mM of (i) TEKPol in TCE, (ii) AMUPol in glycine/water (60/40 ratio), and (iii) AMUPol in DMSO/water (60/40 ratio), where the water was also a mixture of D_2O/H_2O (90:10). Both DNP agents were dried under high vacuum (10^{-4} mbar) and the solvents were stirred and then distilled in vacuo. Usually, the best enhancement for applications requiring organic solvents was obtained with TEKPol in combination with organic solvents such as 1,1,2,2-tetrachloroethane (TCE). TCE was preferred here for the initial optimization purposes, since its carbon resonances do not overlap with the expected ^{13}C chemical signal from both post-reacted zeolite materials. Next, both DNP agents and solvent matrix were varied to eliminate the overlapping signals. In a typical experiment, 20 mg of the samples was impregnated with the appropriate volume of 16 mM solution of DNP agents (nTEKPol = 0.5 - 1.2 µmol/sample, nAMUPol= 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. DNP samples were prepared by incipient wetness impregnation 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).

Measurements:

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 specific contact time (typically from 0.05 ms to 2.0 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. 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, t1 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 (for instance, 0.5-1.0 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). In all 2D HETCOR, SPINAL-64 decoupling was applied during acquisition and were recorded with eDUMBO-1_{22} homonuclear decoupling in t_1 and a scaling factor of 0.56 was applied to correct the ^{1}H chemical shift scale. The eDUMBO-1_{22} scheme [4] was used for ^{1}H homonuclear decoupling during the indirect evolution time with ν1 = 100 kHz (and a basic eDUMBO cycle of 32 μs). For one-dimensional (1D) ^{13}C DNP SENS NMR experiments, the acquisition parameters used are 5 s repetition delay, a 1H π/2 pulse length of 2.5 μs to afford 100 kHz 1H decoupling using the SPINAL 64 decoupling method. The contact time and MAS frequency in each case have been mentioned in the respective figure captions. The total number of scans (usually between 5k and 10k) has been flexible to achieve the expected or good signal-to-noise ratio. The two-dimensional (2D) ^{1}H-^{13}C heteronuclear correlation (HETCOR) spectra were acquired with 2048 scans per t1 increment, 48 individual increments along with varying contact time, as mentioned in the figure captions.

References

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3. S. Chytil, L. Haugland, and E. A. Blekkan, *Micropor. Mesopor. Mater.*, 2008, **111**, 134–142.
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