Electronic Supplemental Information (ESI)

Spatial distribution of organic functional groups supported on mesoporous silica nanoparticles (2): a study by \(^1\)H triple-quantum fast-MAS solid-state NMR

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S1. \(^{29}\)Si DPMAS NMR

The \(^{29}\)Si direct polarization magic-angle spinning (DPMAS) experiment was performed on an Agilent NMR spectrometer, equipped with a 5-mm double-resonance magic-angle spinning (MAS) probe and operated at 9.4 T. The AP-1.2 was packed in the MAS zirconia rotor and spun at 8 kHz. The spectrum was taken with the RF magnetic field \(v_{RF}(^{29}\text{Si}) = 50 \text{ kHz}\) for a \(\pi/2\) pulse, \(v_{RF}(^{1}\text{H}) = 50 \text{ kHz}\) for a SPINAL-64 \(^1\)H decoupling during the acquisition, recycle delay \(\tau_{RD} = 300 \text{ s}\), and the number of scans \(NS = 296\). The \(^{29}\)Si chemical shift was referenced with respect to tetramethylsilane (TMS) at 0 ppm. Based on the integration of silicon sites, we estimated that 8.7 \% of Si atoms in this sample were bound to carbon, corresponding to an aminopropyl concentration of 1.2 mmol/g.

Figure S1. \(^{29}\)Si DPMAS spectrum of AP-1.2.
S2. DNP-enhanced $^{13}$C{$^{1}$H} CPMAS NMR
The DNP-enhanced $^{13}$C{$^{1}$H} cross-polarization (CP)MAS experiment was carried out on a Bruker Biospin DNP NMR spectrometer, operated at 9.4 T, equipped with a gyrotron generating microwaves at 264 GHz. Samples were impregnated with 10 mM AMUPol [1] dissolved in water, packed in 3.2-mm sapphire rotors and spun at a 10 kHz at a temperature of ~110 K. The spectra were taken with the RF magnetic field $\nu_{RF}(^{13}$C) $\sim$ 70 kHz during cross-polarization, $\nu_{RF}(^{1}$H) = 100 kHz during short pulse and SPINAL-64 decoupling, $\nu_{RF}(^{1}$H) = 80 kHz during CP, contact time $\tau_{CP}$ = 2 ms, recycle delay $\tau_{RD}$ = 3 s, and the number of scans $NS$ = 256. The $^{13}$C chemical shifts were referenced with respect to tetramethylsilane (TMS) at 0 ppm.

Figure S2. DNP-enhanced $^{13}$C{$^{1}$H} CPMAS spectra of AP-MSNs samples.
S3. 2D $^1$H TQ/SQ correlation spectrum of L-alanine·HCl.

The pulse sequence for the TQ/SQ correlation experiment was tested on L-alanine·HCl and verified by comparing the spectrum with that shown in an earlier paper by Spiess et al.[2]

Figure S3. 2D $^1$H TQ/SQ correlation spectrum of L-alanine·HCl. The spectrum was obtained using $\nu_R = 36$ kHz, $\nu_{RF}(^1H) = 100$ kHz, $\tau_{exc/rec} = 4\tau_R (111.1 \mu s)$, $\tau_{z-fil} = 0.5$ ms, $\tau_{RD} = 1.0$ s, 160 rows with $\Delta t_1 = 27.778$ $\mu$s, NS = 24, AT = 2.1 h.

References