Direct ¹⁷O-isotopic labeling of oxides using mechanochemistry

Chia-Hsin Chen,¹ Emeline Gaillard,¹ Frédéric Mentink-Vigier,² Kuizhi Chen,² Zhehong Gan,² Philippe Gaveau,¹ Bertrand Rebière,¹ Romain Berthelot,¹ Pierre Florian,³ Christian Bonhomme,⁴ Mark E. Smith,⁵ Thomas-Xavier Métro,⁶ Bruno Alonso,¹ Danielle Laurencin^{1,*}

¹ ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

² National High Magnetic Field Laboratory (NHMFL), Florida State University, Tallahassee, FL, USA

³CEMHTI, UPR 3079 CNRS, Université d'Orléans, 45071 Orléans, France

⁴ Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), UMR 7574, Sorbonne Université, CNRS, 75005 Paris, France

⁵ Vice-Chancellor's Office, Highfield Campus, University of Southampton, University Road, Southampton, SO17 1BJ, and Department of

Chemistry, Lancaster University, Bailrigg, Lancaster, LA1 4YB, UK

⁶ IBMM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

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Supporting information S1. Preliminary study on the synthesis of ¹⁷O-enriched Li₂*O.

¹⁷O-enriched Li₂*O was synthesized using a similar approach as described in scheme 2 (main article).

The first step consisted in hydrolyzing 1 equivalent of Li₂O with 2 equivalents of H₂*O using mechanochemistry. After 30 minutes of BM, the crystalline phase identified by X-ray diffraction was LiOH.H₂O (Figure S1a, blue curve), which is the most stable form of lithium hydroxide at room temperature. ¹⁷O and ⁷Li MAS NMR analyses were consistent with the presence of the monohydrate (Figures S1b and S1c). In particular, the ¹⁷O NMR spectrum could be fitted considering 2 oxygen sites (see deconvolution in Figure S1c), with ¹⁷O quadrupolar coupling constants which are in agreement with those reported in the literature for the water molecule and hydroxyl in Li*OH.H₂*O.¹⁻² Based on the stoichiometry used between the reagents, the formation of LiOH.H₂O implies that an intermediate LiOH-like phase must also have formed during the LAG step. More complete analyses are still to be performed to fully characterize the nature and composition of the material recovered after LAG.

The second step of the procedure was nevertheless undertaken. It consisted in heat-treating the compound isolated after LAG at 650 °C under dynamic vacuum. The ¹⁷O NMR signature of the final product was found to be consistent with the formation of Li₂*O, based on previous ¹⁷O NMR studies of this phase.³⁻⁴

On a more general perspective, it is worth noting that this mode of production of Li_2*O is very convenient in comparison to previous protocols relying on the initial synthesis of Li*OH by hydrolysis of highly reactive organolithium precursors in dry tetrahydrofurane.⁵⁻⁶

Detailed synthetic procedure leading to Li*OH.H₂*O and Li₂*O

Non-labeled LiOH.H₂O was placed in a gold crucible and heat-treated to 650° C for 20h under dynamic vacuum to form Li₂O, and stored under inert atmosphere up until the LAG reaction. Li₂O (58 mg, 1.94 mmol, 1 eq) and 40%-enriched H₂¹⁷O (67 µL, 3.7 mmol, ~2 eq) were then introduced in a push-fit lid grinding jar (10 mL; stainless steel) with one stainless steel ball (10 mm diameter). The jar was closed and subjected to grinding for 30 minutes in the mixer mill operated at 25 Hz. The reactor was opened and the white powder was recovered by scraping the edges of the reactor and beads with a spatula (m = 114 mg), and immediately characterized by XRD, ¹⁷O, and ⁷Li solid state NMR (Figures S1a-c). ¹⁷O-enriched Li₂O was then produced by heat-treatment of this hydroxide intermediate in a gold crucible at 650°C for 20h under dynamic vacuum (Figure S1d), and kept under inert atmosphere prior to analysis.

Figure S1. a/XRD powder patterns of the commercial $Li(OH)_2$.H₂O precursor (top), the oxide obtained after heattreatment (middle), and the enriched phase recovered after LAG of this oxide in presence of H₂*O (bottom). The changes in relative intensity of the diffraction peaks between the non-labeled (black) and labeled (blue) forms is due to preferential orientation effects in the former case.

b/ ⁷Li MAS NMR spectra of the commercial Li(OH)₂.H₂O precursor (black), and the enriched phase recovered after LAG in presence of H₂*O (blue). Spectra recorded at 14.1 T, spinning at 20 kHz (D1 = 64 s, NS = 8).

c/ ¹⁷O MAS NMR spectrum of the enriched phase recovered after LAG in presence of H_2 *O (blue) (spectrum recorded at 14.1 T, spinning at 20 kHz). The spectrum could be fitted considering the presence of 2 oxygen environments (dashed red line), the parameters of which are consistent with those expected for Li*OH.H₂*O (green and purple lines).^{1,2} Acquisition parameters are in Table S1.

d/¹⁷O MAS NMR spectrum of the phase recovered after heat-treatment of the enriched intermediate under an inert atmosphere (spectrum recorded at 14.1T, spinning at 20 kHz). Acquisition parameters are in Table S1.





Figure S2. Characterization of SiO₂ before and after 1 h LAG, using a/ SEM, b/ N_2 adsorption/desorption analyses, and c/ EDXS. Traces of Fe and Cr were detected by EDXS after 1 h BM (but not after 1 min BM). These are due to contaminations from the milling jar and beads, and could be avoided by varying the milling conditions (e.g. reducing the milling time).



Figure S3. Characterization of Al_2O_3 before and after 1 h LAG, using a/ SEM, b/ N_2 adsorption/desorption analyses, and c/ EDXS. Traces of Si and Cl were detected by EDXS in both the starting material and final product (and related to the way in which this commercial alumina phase is prepared).



Figure S4. Characterization of TiO_2 before and after 1 h LAG, using a/SEM, b/N₂ adsorption/desorption analyses, and c/ EDXS. Traces of Si and S were detected by EDXS in both the starting material and final product (which are related to the way in which this commercial titania phase is prepared). In some cases, very small traces of Fe were detected by EDXS after 1h BM.



Figure S5. Characterization of ZrO_2 before and after LAG, using a/ SEM, b/ N_2 adsorption/desorption analyses, and c/ EDXS. Traces of Hf were detected by EDXS in both the starting material and final product (which are related to the way in which this commercial zirconia phase is prepared).



Figure S6. a/ ¹⁷O MAS NMR spectrum of a ZrO_2 phase recovered after 1h LAG in presence of H₂*O (blue), and the empty zirconia rotor (green). Both spectra were recorded in the exact same conditions and using the same rotor. b/ ¹⁷O MAS NMR spectrum of the non-labeled alumina precursor, after ~30 minutes acquisition (to be compared to the NMR spectrum of enriched alumina shown in Figure 2, obtained in less than 15 minutes). All acquisition parameters are in Table S1. The " \Diamond " symbol corresponds to the zirconia rotor.



Figure S7. Fit of the ¹⁷O MAS NMR spectrum of Si^*O_2 (recovered after 1h LAG in presence of H_2^*O and drying under vacuum at room temperature). The experimental spectrum is in blue and the fitted lineshape in dashed red. Acquisition parameters are in Table S1.



Figure S8. a/ ²⁷Al single-pulse MAS NMR spectra recorded at 14.1T for Al₂O₃ phases, before and after ¹⁷O enrichment by LAG (15 min and 1h BM). * symbols correspond to spinning sidebands. Acquisition conditions are in the main text.

b/ 27 Al{ 1 H} CPMAS NMR spectra recorded at 14.1T for Al₂O₃ phases, before and after 17 O enrichment by LAG (1h BM). The dashed red line indicates the position expected for Al^(V) sites. * symbols correspond to spinning sidebands. Acquisition conditions are in the main text.



Figure S9. Single-pulse ¹⁷O MAS NMR spectra recorded at 14.1 T for Al_2O_3 phases after different milling times, together with their deconvolution.

For each milling time, three independent fits were performed:

- by fitting all parameters,
- by using the full-width at half maximum (fwhm) value for zirconia and *OAl_x sites, as extracted from the fitting of the 1h BM spectrum, and then using these fixed values while fitting all other parameters at the different milling times (example provided below),
- by using the full-width at half maximum (fwhm) and δ_{iso} values for zirconia and *OAl_x sites, as extracted from the fitting of the 1h BM spectrum, and using these fixed values while fitting all other parameters at the different milling times.

When comparing the three different fits, the maximum deviations in δ_{iso} and fwhm values for zirconia and *OAl_x sites were 1.5 and 3.5 ppm, respectively.

For each type of fit, the integrated intensities for zirconia and $*OAl_x$ were then used to calculate an $**OAl_x$ relative intensity evolution. The three trends were then averaged, after correcting by the mass of sample analyzed, to produce Figure 3b (main text).



1h BM									
δ_{iso}/ppm	380	59	5.2						
Fwhm / ppm	15	37	57						
% intensity	4	40	56						
30 min BM									
δ_{iso}/ppm	379	59	5.7						
Fwhm / ppm	15	37	65						
% intensity	4	33	63						
15 min BM									
δ_{iso}/ppm	381	59	8.6						
Fwhm / ppm	15	37	53						
% intensity	6	35	59						
5 min BM									
δ_{iso}/ppm	378	58	2.6						
Fwhm / ppm	15	37	64						
% intensity	7	21	72						

Figure S10. Fast MAS ¹H solid state NMR spectra of an Al₂O₃ phase enriched in ¹⁷O by LAG (15 min BM), after drying under vacuum at room temperature, and comparison to the ¹H NMR spectrum of the rotor used for the analysis:

- The top two spectra correspond to analyses performed at 14.1T and 60 kHz MAS, using different ¹H echo delays. The sample spectrum is in blue, while the rotor spectrum is in grey. For each echo delay, both spectra were recorded here using the exact same acquisition conditions, and are here represented considering the absolute signal intensity.
- The bottom spectrum corresponds to the same phase, analyzed and 20.0T, at 60 kHz MAS (as also shown in the main text, Figure 4d).



Supporting Information S11. ¹⁷O DNP and ¹⁷O{¹H} CP-DNP MAS NMR experiments on alumina.

Two different impregnating solutions were tested in the DNP analyses of alumina: (*i*) TEKPol biradical⁷ in D₂-tetrachloroethane (Figure 5 in main text), and (*ii*) AsymPolPOK biradical⁸ in glycerol/D₂O/H₂O (Figure S10, below). No improvement in the DNP enhancement was observed in the latter case, despite that a higher affinity of the AsymPolPOK bi-radical for the alumina surface was expected (due to the presence of a chelating phosphate group). Indeed, as shown in Figure S11, for both types of DNP experiments tested, enhancements were of the same order of magnitude as those of the TEKPol/tetrachloroethane mixture. Moreover, the choice of a water-based impregnating solution is potentially problematic for alumina, as it may alter the nature of some surface sites by hydrolysis.

Figure S11. ¹⁷O DNP MAS NMR experiments carried out at 14.1 T on an Al₂O₃ phase enriched in ¹⁷O by 15 minutes LAG, and using as an impregnating solution the AsymPolPOK biradical in glycerol/D₂O/H₂O. (*a*) Direct-excitation ¹⁷O DNP NMR spectra (with a DFS enhancement), and (*b*) ¹H{¹⁷O} CPMAS DNP NMR spectra recorded at 50 µs contact time. Spectra recorded without (red) and with (blue) microwave irradiation are compared. Acquisition parameters are reported in Table S1.

a/ 17O DNP DFS (14.1T, 100 K)



b/ ¹⁷O{¹H} DNP-CPMAS (14.1T, 100 K)



Figure S12. ¹⁷O MAS DFS-single-pulse and ¹⁷O{¹H} CPMAS NMR spectra recorded at 14.1 T for an Al₂O₃ phase enriched in ¹⁷O by LAG (15 min BM), after drying under vacuum at room temperature. Different contact times were used in the CPMAS experiments. Acquisition parameters can be found in Table S1.

The lineshapes at these contact times are similar to those observed in the DNP-enhanced ¹⁷O{¹H} CPMAS experiments (see main text, Figure 5, for DNP data at 50 µs and 5 ms). At the shortest contact times ($\leq 200 \mu s$), only signals related to *OH groups are observed. The shift in the peak maximum is then observed at longer contact times, where resonances characteristic of *OAl_x sites become visible, meaning that these are also in close proximity to protons (as also shown by the ¹H{¹⁷O} D-HMQC study).



Figure S13. ¹⁷O MAS NMR spectrum of a SiO₂ phase, enriched by LAG (1 min BM), recorded at 14.1 T, and its fit considering the presence of enriched siloxane (green) and *OH groups (purple). For the *OH sites, a Gaussian-like lineshape was considered, using the same parameters as those extracted when fitting the ¹⁷O{¹H} CPMAS data (see insert, contact times of 100 μ s). Acquisition parameters can be found in Table S1.

<u>Fitting parameters:</u> Si-*O-Si (green): *O-H (purple):

 $\begin{array}{l} \delta_{iso}=42\pm1\ ppm;\ C_Q=5.2\pm0.1\ MHz;\ \eta_Q=0.25\pm0.10\\ \delta=4\pm2\ ppm;\ fwhm=42\pm8\ ppm \end{array}$



Figure S14. Siloxane region of the ¹⁷O MAS NMR spectra recorded at 20 T on SiO₂/TiO₂ mixtures labeled using the 2 procedures described in the main text, and comparison to the ¹⁷O-labeled silica phase recovered after 1 min LAG. Acquisition parameters can be found in Table S1.



Figure S15. XRD powder patterns of two monoclinic zirconia precursors of different crystallinity (a) and ¹⁷O MAS NMR spectra after 1h LAG (b), showing the importance of the initial crystalline state of the oxide precursor on the efficiency of the enrichment. Both ¹⁷O MAS NMR spectra were recorded in the same conditions, using the acquisition parameters reported in Table S1. The " \Diamond " symbol corresponds to the zirconia rotor.





b/ ¹⁷O MAS NMR after 1h BM

Figure S16. ¹⁷O MAS NMR spectra of ¹⁷O-labeled alumina (a) and titania (b) phases, as recovered after LAG (blue spectra), or after further heat-treatment at 900°C under Ar atmosphere (brown spectra). In the case of alumina, this leads to a complete loss of the *OH resonances. In the case of titania, the rutile form was found to be predominant after this treatment (as also shown by PXRD in the insert). Acquisition parameters for ¹⁷O NMR analyses can be found in Table S1.



Table S1.	¹⁷ O NMR	parameters use	d for the	acquisition	of the	NMR	spectra	shown	in the	main	text	and	in the
supporting	; informatio	on.											

Sample	Field	Probe	MAS speed	Pulse sequence	Recycle delay	Number of	Experimental	Figure
					(D1)	scans (NS)	Time	
Main text								
Ca(OH) ₂	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	20 s	360	~ 2 h	Figure 1b
CaO	14.1T	3.2 mm	16 kHz	Single pulse ^b	600 s	48	~ 8 h	Figure 1b
SiO ₂ (1 h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	0.5 s	2200	~ 18 min	Figure 2
Al_2O_3 (1 h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	2 s	400	~ 13 min	Figure 2
TiO_2 (1h BM)	14.1T	3.2 mm	20 kHz	DFS-1pulse ^a	5 s	1000	~ 1.5 h	Figure 2
ZrO_2 (1h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	6.5	4600	~ 8 h	Figure 2
Al_2O_3 (5min-1h BM)	14.1T	3.2 mm	16 kHz	Single pulse ^b	16 s	4096	~ 18 h	Figure 3a
Al_2O_3 (15 min BM)	35.2T	3.2 mm	18 kHz	WURST-echo ^c	15	512	~ 8 min	Figure 3c
Al_2O_3 (15 min BM)	35.2T	3.2 mm	16 kHz	30MAS ^d	0.2 s	240/slice	~30 min	Figure 3d
Al_2O_3 (15 min BM)	20.0T	1.3 mm	60 kHz	¹ HU ¹⁷ OLLHMOC ^d	0.5 s	480/slice	~ 9 h	Figure 4a
Al_2O_3 (15 min BM) Al_2O_2 (15 min BM)	20.0T	1.3 mm	60 kHz		0.5 s	96 384/slice	~ 9 H	Figure 4b
Al_2O_3 (15 min BM) Al_2O_2 (15 min BM)	20.0T	3.2 mm	24 kHz	27 AU 17 O) L HMOC $^{\circ}$	0.5 \$	10000/slice	~ 2-5 h	Figure 40
Al_2O_3 (15 min BM) Al_2O_2 (15 min PM)	20.01 DNB/14_1T	2.2 mm	24 KHZ	DES coho ^f	2.0 c	512	~ 50 li	Figure 40
$A1_{2}O_{3} (15 \text{ min BM})$	DNP/14.11	2.2 mm	13 KHZ		5.0 \$	512 10240	~ 50 mm	Figure 5
Al_2O_3 (15 IIIII BM)	DNP/14.11	2.2	13 KHZ	DEC 1 miles	1.5 8	312-10240	~ 10 1111-41	Figure 5
TiO_2 (1 min BM)	14.11	3.2 mm	20 KHZ	DFS-1pulse"	1 s	4000	~ 1 h	Figure 6a
T_1O_2 (15 min BM)	14.11	3.2 mm	16 kHz	DFS-1pulse ^a	2 s	2200	~ l h	Figure 6a
T_1O_2 (1 h BM)	14.11	3.2 mm	20 kHz	DFS-Ipulse ^a	8 s	1300	~ 3 h	Figure 6a
T_1O_2 (15 min BM)	35.21	3.2 mm	18 kHz	WURST-echo	2 s	512	~ 15 min	Figure 6b
T_1O_2 (15 min BM)	DNP/14.11	3.2 mm	13 kHz	DFS-echo ¹	2 s	4096	~2 h	Figure 6c
TiO_2 (15 min BM)	DNP/14.1T	3.2 mm	13 kHz	¹ 'O{ ¹ H} CPMAS ^g	2.3s	4096-10240	~2.5-6.5h	Figure 6d
SiO ₂ (1 min BM)	20.0T	1.3 mm	60 kHz	WURST-echo ⁿ	0.5s	9324	~1.5h	Figure 7a
ZrO ₂ (15 min BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	3.5 s	13000	~ 13 h	Figure 7b
ZrO_2 (1 h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	3.5 s	13000	~ 13 h	Figure 7b
SiO2-Ti*O2 (3min BM)	20.0T	1.3 mm	55 kHz	WURST-echo ^h	0.5 s	110000	~ 15 h	Figure 8c
SiO ₂ -TiO ₂ -H ₂ *O (3min BM)	20.0T	1.3 mm	50 kHz	WURST-echo ^h	0.5 s	113800	~ 16 h	Figure 8c
Supporting Information	tion							
LiOH.H ₂ O	14.1T	3.2 mm	20 kHz	DFS-echo ^a	16 s	4096	~ 18 h	Figure S1c
Li ₂ O	14.1T	3.2 mm	20 kHz	DFS-1pulse ^a	20 s	2230	~ 12 h	Figure S1d
ZrO2 (1h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	6 s	4600	~ 8 h	Figure S6a
Empty rotor (1h BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	6 s	4600	~ 8 h	Figure S6a
Non-labeled Al ₂ O ₃	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	1 s	1600	~30 min	Figure S6b
SiO ₂ (1 h BM)	14.1T	3.2 mm	16 kHz	Single pulse ^b	16 s	3530	~ 16 h	Figure S7
Al ₂ O ₃ (5min-1h BM)	14.1T	3.2 mm	16 kHz	Single pulse b	16 s	4096	~ 18 h	Figure S9
Al ₂ O ₃ (15 min BM)	DNP/14.1T	3.2 mm	13 kHz	DFS-echo ^f	1.2 s	164	~ 3 min	Figure S11
Al ₂ O ₃ (15 min BM)	DNP/14.1T	3.2 mm	13 kHz	¹⁷ O{ ¹ H} CPMAS ^g	1.2 s	128	~ 2.5 min	Figure S11
Al ₂ O ₃ (1 h BM)	14.1T	3.2 mm	16 kHz	¹⁷ O{ ¹ H} CPMAS ⁱ	1 s	2000 to 8000	up to ~2h	Figure S12
SiO ₂ (1 min BM)	14.1T	3.2 mm	16 kHz	DFS-1pulse ^a	2 s	2200	~ 1 h	Figure S13
SiO_2 (1 min BM)	14.1T	3.2 mm	16 kHz	¹⁷ O{ ¹ H} CPMAS ⁱ	0.5 s	80000	~11 h	Figure S13
SiO_2 (1 min BM)	20.0T	1.3 mm	60 kHz	WURST-echo ^h	0.5 s	9324	~ 1 h	Figure S14
SiQ2-Ti*Q2 (3min BM)	20.0T	3.2 mm	24 kHz	DFS-echo ^j	0.5 s	1800	~ 15 min	Figure S14
SiO ₂ -TiO ₂ -H ₂ *O (3min BM)	20.0T	3.2 mm	24 kHz	DFS-echo ^j	0.5 s	5186	~ 45 min	Figure S14
ZrO2 Aldrich (1 h BM)	14.1T	3.2 mm	24 kHz	DFS-1pulse ^a	35 \$	13000	~13 h	Figure \$15b
ZrO_2 Normo (1 h RM)	14.1T	3.2 mm	16 kHz	DES-1pulse ^a	350	13000	~13 h	Figure \$15b
$\Delta l_{2}\Omega_{2}$ (1 h RM)	14.11 14.1T	3.2 mm	16 1-112	DFS-1pulse ^a	J.J 5	140	~10 min	Figure \$160
$A_{12}O_{3} (1 \text{ II DW})$	14.11 14.1T	3.2 mm	16 1/11/2	DFS 1pulse ^a	+ 5	800		Figure \$160
T_{10} (1 h DM α linght tellip)	14.11 14.1T	3.2 11111	10 KHZ	DES 1 pulse	10.5	1300	~3.5 11	Figure \$164
$TO_{2} (1 \text{ II DW})$	14.11	2.2	20 KHZ	DEC 11	o s	1000	~ 5 11	Figure S10D
$11O_2$ (1 n BNI & high temp)	14.11	3.2 mm	20 KHZ	DFS-1pulse"	2 S	1020	~ 50 min	Figure S16b

(a) The typical DFS-single pulse conditions used were the following: DFS pulse of 500 μ s ($\nu_{rf}(^{17}O) \sim 10$ kHz), with a sweep between 80 and 200 kHz, followed by a ^{17}O excitation pulse of 1 μ s. Spinal-64 ¹H decoupling was applied in most cases (though no difference was observed for some samples in absence of decoupling). For the DFS-echo experiments, a rotor-synchronized echo delay corresponding to 1 rotor period was used. (b) Single pulse experiments were performed using a ^{17}O excitation pulse of 1 μ s ($\pi/12$ tip angle).

(c) WURST-echo spectra recorded using a WURST pulse for satellite-transition inversion/saturation (1ms pulse, set at 150 kHz offset), followed by solid $\pi/2$ and π pulses of 4.4 and 8.8 µs, and with the echo delay set to 1 rotor period.

(d) Details on the acquisition conditions are provided in the main text.

(e) Full acquisition conditions are provided in the main text. The sample characterized by ${}^{27}Al{}^{17}O$ J-HMQC came from a different synthetic batch than the one studied by ${}^{11}H{}^{17}O$ J- and J- HMQC.

(f) For the DNP-DFS-echo experiments, $\nu_{rf}({}^{17}O)$ was set to 100 kHz for the echo and the DFS was set to 30 kHz. Spinal-64 ¹H decoupling was applied (with $\nu_{rf}({}^{1}H) = 83$ kHz).

(g) For the DNP-CP experiments, the ramped CP conditions were $v_{rf}(^{17}O) = 37$ kHz with a ramp of 20% on the proton channel for which $v_{rf}(^{1}H) = 50$ kHz. The $\pi/2$ pulse on the protons was set to 2.5 µs. A proton presaturation consisting a 300 $\pi/2$ pulse train spaced by 50 µs was applied (with $v_{rf}(^{1}H) = 100$ kHz on for the $\pi/2$ ¹H pulses). Spinal-64 ¹H decoupling was applied during acquisition (with $v_{rf}(^{1}H) = 83$ kHz).

(h) WURST-echo experiments were performed spinning at 50-60 kHz, using a 600-720 μ s WURST pulse (1W power), applied at an offset of twice the spinning speed (100 to 120 kHz), and followed by solid $\pi/2$ and π pulses of 4 and 8 μ s, with the echo delay set to 1 rotor period.

(i) For ¹⁷O{¹H} CPMAS, the ramped CP conditions at 16 kHz MAS were ν_{rf} (¹⁷O) ~ 37 kHz and ν_{rf} (¹H) ~ 51 kHz, and the contact times were varied from 50 µs to 5 ms. The $\pi/2$ excitation pulse on the protons was set to 6.6µs.

(j) DFS-echo experiments were performed spinning at 24 kHz, using a 1 ms DFS pulse (17W power), with a frequency sweep from 800 to 125 kHz, followed by solid $\pi/2$ and π pulses of 2.5 and 5 μ s, with the echo delay set to 1 rotor period.

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