

Dynamic Nuclear Polarization Enhanced Solid-state NMR Studies of Surface**Modification of γ -Alumina: SUPPLEMENTARY INFORMATION**

Marco Mais,^a Subhradip Paul,^b Nathan S. Barrow^c and Jeremy J. Titman^{a*}

^aSchool of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK

^bNottingham DNP MAS NMR Facility, Sir Peter Mansfield Imaging Centre, University of Nottingham, NG7 2RD, UK

^cJohnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH, UK

Preparation of BaO-modified γ -alumina

BaO-modified γ -alumina samples were prepared by incipient wetness impregnation of γ -alumina with aqueous Ba(NO₃)₂ solution. After impregnation, the samples were dried at 378 K before being calcined for two hours at 773 K.

Conventional Solid-state NMR Experiments

Conventional ²⁷Al MAS experiments were performed were performed on a Bruker Avance III 600 MHz spectrometer, equipped with a triple resonance 2.5 mm CPMAS probe operating at ambient temperature.

DNP Sample Preparation

Sample preparation was found to be critical for optimizing the DNP enhancement, and the γ -alumina and BaO-modified γ -alumina were first dried in an oven overnight at 120 °C. Then 32 mg was wetness impregnated with 25 μ L of a 10 mM of the biradical TEKPol in the organic solvent 1,1,2,2-tetrachloroethane (TCE). The wetness impregnation was carried out in a glovebox under a N₂ atmosphere to avoid rehydration

of the γ -alumina surface. The wet solid was packed into a 3.2 mm zirconia MAS rotor for DNP experiments.

DNP Experiments

DNP-enhanced solid-state NMR experiments were performed on a Bruker Avance III HD 600 MHz spectrometer, equipped with a triple resonance low-temperature 3.2 mm CPMAS probe. DNP was achieved by irradiating the sample with high-power microwaves (10 W at the center of the waveguide) at a frequency of 395 GHz, generated by a gyrotron that operated continuously with a stability of better than $\pm 1\%$. Thin-walled 3.2 mm zirconia rotors were used for all DNP experiments, and the spinning frequency was 11.3 kHz regulated to ± 5 Hz. A constant sample temperature of 95 ± 3 K was used for all DNP experiments. Further parameters are given in the figure captions. Microwave on/off experiments were performed with a train of saturation pulses prior to a relaxation delay followed by signal excitation in order to measure the DNP enhancement ϵ . The DNP build-up time T_{DNP} was measured indirectly with a saturation recovery sequence followed by polarization transfer via $\{^1\text{H}\} - ^{27}\text{Al}$ CP before signal acquisition. The build-up time determines the rate at which scans can be repeated for signal averaging and hence the relaxation delay.

DNP-enhanced CPMAS spectra (Figure 3) were the result of 32 co-added scans separated by a relaxation delay of 7.1 s ($1.3 \times T_{\text{DNP}}$). The contact time was 0.5 ms and the rf amplitudes for ^1H and ^{27}Al were 72.7 and 84.0 kHz, respectively, and the ^1H amplitude was ramped between 70 and 100% of this value. The acquisition time was 16.4 ms with a dwell time of 8 μs giving a spectral width of 62.5 kHz. Heteronuclear decoupling was applied using the $\text{SW}_f\text{-TPPM}$ sequence with a ^1H rf amplitude of 90 kHz during

acquisition. For BaO-modified γ -alumina the corresponding spectra (Figure 6) are the result of 256 co-added scans separated by a relaxation delay of 5.1 s ($1.3 \times T_{\text{DNP}}$).

Surface ^{27}Al sites were resolved using a DNP-enhanced $\{^1\text{H}\} - ^{27}\text{Al}$ CP-MQMAS experiment. The MQMAS experiment correlates multiple- and single-quantum coherences across two frequency dimensions, in order to resolve resonances arising from half-integer quadrupolar nuclei that overlap because of second-order quadrupolar broadening. The variant of the CP-MQMAS experiment used here (S. E. Ashbrook and S. Wimperis, *J. Magn. Reson.*, 2000, **147**, 238–249) generates triple-quantum ^{27}Al coherence directly during the cross polarization step. After evolution during t_1 the triple-quantum ^{27}Al coherence is converted back to longitudinal magnetization which is passed through a z-filter prior to detection as transverse magnetization in t_2 . For the CP-MQMAS spectra recorded here (Figure 4) there were 100 t_1 increments with 120 co-added scans for each. Heteronuclear decoupling was applied using the $\text{SW}_f\text{-TPPM}$ sequence with a ^1H rf amplitude of 90 kHz during t_1 and t_2 . The z-filter delay was 20 μs . The non-selective ^{27}Al coherence transfer pulse after t_1 was 1.5 μs in duration with a rf amplitude of 88.6 kHz, and the selective ^{27}Al pulse before t_2 was 11.5 μs in duration with a rf amplitude of 7.0 kHz.

Table S1. DNP Enhancements and Build-up Times

	$\gamma\text{-Al}_2\text{O}_3$	BaO/ $\gamma\text{-Al}_2\text{O}_3$
$\epsilon_{1\text{H}}$	30	31
$\epsilon_{27\text{Al}}$	36	29
T_{DNP}	5.5	4.0