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

Marco Mais, Subhradip Paul, Nathan S. Barrow and Jeremy J. Titman

School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK

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

Johnson 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 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 μL 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 ±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 \( \varepsilon \). 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 x \( T_{DNP} \)). The contact time was 0.5 ms and the rf amplitudes for \(^1\text{H}\) and \(^{27}\text{Al} \) 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 SWF-TPPM sequence with a \(^1\text{H} \) 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 x T\text{DNP}).

Surface $^{27}$Al sites were resolved using a DNP-enhanced $^1$H – $^{27}$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 SW$_t$-TPPM sequence with a $^1$H 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**

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$-Al$_2$O$_3$</th>
<th>BaO/$\gamma$-Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{^1H}$</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>$\varepsilon_{^{27}Al}$</td>
<td>36</td>
<td>29</td>
</tr>
<tr>
<td>$T_{\text{DNP}}$</td>
<td>5.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>