

Enhanced Solid-State NMR Correlation Spectroscopy of Quadrupolar Nuclei Using Dynamic Nuclear Polarization

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S Supporting Information

ABSTRACT: By means of a true sensitivity enhancement for a solid-state NMR spectroscopy (SSNMR) experiment performed under dynamic nuclear polarization (DNP) conditions, corresponding to 4–5 orders of magnitude of time savings compared with a conventional SSNMR experiment, it is shown that it is possible to record interface-selective ²⁷Al–²⁷Al two-dimensional dipolar correlation spectra on mesoporous alumina, an advanced material with potential industrial applications. The low efficiency of cross-polarization and dipolar recoupling for quadrupolar nuclei is completely negated using this technique. The important presence of pentacoordinated Al has not only been observed, but its role in bridging interfacial tetra- and hexacoordinated Al has been determined. Such structural information, collected at low temperature (~103 K) and 9.4 T with the use of DNP, would have been impossible to obtain under standard conditions, even using a higher magnetic field. However, here it is demonstrated that this information can be obtained in only 4 h. This work clearly opens a new avenue for the application of SSNMR to quadrupolar nuclei and notably the atomic-scale structure determination of catalysis materials such as mesoporous alumina.

Porous materials are a cornerstone of the chemical industry since they can be employed in heterogeneous catalysis, separation processes, sensors, photonics, biomaterials, etc. However, their rational design is currently limited by the lack of applicable atomic-resolution characterization methods. NMR spectroscopy can provide detailed information on the atomic-level structure and dynamics of these heterogeneous and often disordered systems. Unfortunately, the intrinsic insensitivity of NMR spectroscopy impedes the examination of interfaces, which are crucial to the properties of porous materials.

On the basis of the pioneering work of Griffin and co-workers,¹ recent developments in the combination of solid-state NMR spectroscopy (SSNMR) under magic-angle spinning (MAS) with dynamic nuclear polarization (DNP) at high magnetic field have facilitated the acquisition of high-resolution NMR spectra with greatly enhanced signal-to-noise ratios (S/N).² This heralds the imagination and implementation of previously unrealistic experiments. In this work, one such

experiment has been performed on technologically and catalytically important mesoporous alumina (Al₂O₃).³ This thermally stable (800 °C) and high-surface-area material (typically 200–400 m² g⁻¹) possessing ordered mesopores (Figure 1 a) has a high concentration of research interest due to

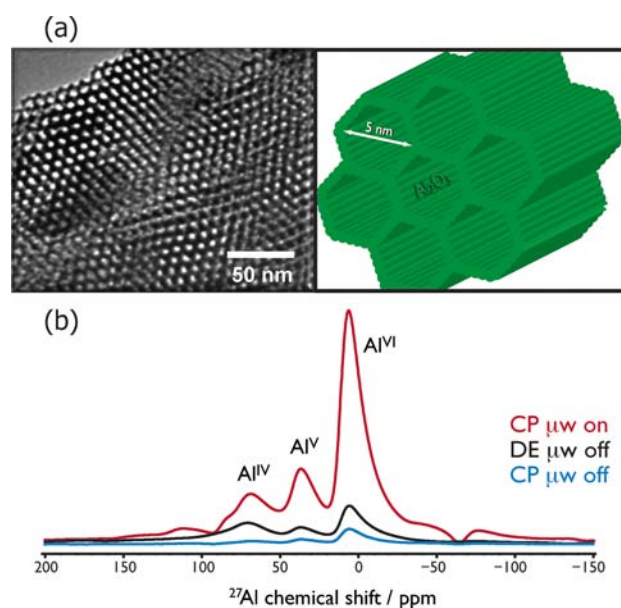


Figure 1. (a) Transmission electron micrograph (left) and associated schematic (right) showing the presence of ordered hexagonal mesopores throughout the alumina sample studied in this work. (b) ²⁷Al NMR spectra of this sample recorded with a MAS rate of 8 kHz and a sample temperature of ~103 K.

its catalytic significance in the production of biodiesel⁴ along with many other applications.⁵ Utilizing “green” and renewable fuels is forever becoming increasingly important, and understanding mesoporous alumina and its specific role in the catalysis of biodiesel production will lead to improved manufacturing methods and therefore increased system viability.

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A particular obstacle when knowledge of the local environment of ^{27}Al nuclei is desired is that conventional SSNMR radiofrequency (RF) irradiation sequences return very low efficiencies for quadrupolar nuclei. However, herein it is shown that in spite of the difficulties arising from the quadrupolar nature of ^{27}Al , DNP-enhanced SSNMR can be used to perform sophisticated yet fast interface-selective characterization measurements. Previous studies have shown that when protons are located only at the surface/interface of much larger systems, cross-polarization (CP) from protons to the nuclei of interest can result in a surface/interface-selective technique.⁶ This technique has been combined with DNP to study surfaces with greatly improved sensitivity⁷ as well as γ -alumina, where CP is very inefficient.⁸

In this work, the DNP is dominated by the cross-effect (CE)⁹ between two unpaired electrons in a biradical (TOTAPOL¹⁰) and protons in a glass-forming solvent matrix or at the interface in the mesoporous alumina. The experiments were performed on a Bruker BioSpin DNP-SSNMR spectrometer¹¹ equipped with a gyrotron and connecting transmission line that is able to provide microwave (μw) irradiation at 263 GHz and ~ 5 W at the sample, in combination with an AVANCE III 400 MHz wide-bore NMR system and a low-temperature MAS probe capable of achieving spinning rates of up to 17 kHz for 3.2 mm rotors at sample temperatures of ~ 100 K.

The "DNP-ready" sample was prepared by impregnation with an excess of solution.¹² The mesoporous alumina was first heated to 408 K for 6 h to ensure that the sample, including the pores, was dry. A 46 μL aliquot of TOTAPOL solution [20 mM in a glass-forming mixture of [$^2\text{H}_6$]DMSO, H_2O , and $^2\text{H}_2\text{O}$ (78, 8, 14 wt %, respectively)] was added to cover 28 mg of the mesoporous alumina powder. This mixture was stirred vigorously and then left to rest at room temperature for 24 h to allow time for the impregnation of the pores by the DNP chemical matrix. A repetition of centrifuging the mixture followed by pipetting any supernatant was employed to remove the excess liquid. The remaining wet powder was added to a thin-walled zirconia 3.2 mm MAS rotor. It must be stated that unlike other systems, here it was not necessary to dissolve/disperse¹ the impregnated mesoporous alumina in the DNP matrix, allowing this system to benefit from the ability to use the maximum possible amount of the sample of interest without compromising the DNP enhancement.

The NMR signal enhancement as a result of DNP in this system can be seen in Figure 1 b. With μw irradiation, the CE enhances the polarization of protons within the sample. This polarization is then transferred to the central transition (CT) of the ^{27}Al nuclei via low-power CP under MAS (CPMAS),¹³ and the resulting spectrum is recorded (red line). The experiment is repeated under the same conditions except without the μw irradiation (blue line). Here, the DNP enhancement, ϵ , is measured simply by comparing the intensities of the spectral peaks resulting from the CPMAS experiments with and without μw irradiation. For this system, ϵ was measured to be 15 for each of the ^{27}Al peaks. For comparison, the direct excitation under MAS (DEMAS) spectrum of ^{27}Al is also shown as the black line in Figure 1 b. As an aside, a similar DNP-ready sample that used an impregnation time of only 1 h was also tested and found to have $\epsilon = 11$. Thus, it appears that longer impregnation times are necessary to facilitate the penetration of the TOTAPOL solution into the pores.

In the spectra in Figure 1 b, three discrete ^{27}Al peaks can be seen. These correspond to hexacoordinated Al^{VI} ($\delta_{^{27}\text{Al}} = 5$

ppm), pentacoordinated Al^{V} ($\delta_{^{27}\text{Al}} = 36$ ppm), and tetraordinated Al^{IV} ($\delta_{^{27}\text{Al}} = 70$ ppm) sites. Contrary to the literature,⁸ the substantial presence of Al^{V} resonances observed here indicates that the water-based DNP matrix does not significantly coordinate to these sites, and thus, this solution is applicable for the study of Al^{V} sites using DNP-enhanced SSNMR measurements of similar systems. Furthermore, this abundance of Al^{V} sites at the interface demonstrates the industrial potential for this mesoporous alumina. Not only does this system exhibit greater surface area than the more commonly employed γ -alumina, but it also appears that these Al^{V} sites, which can act as binding sites for the active phase,¹⁴ are much more plentiful.

Not only does the impregnation solution provide the biradical necessary for DNP and the glass-forming solvents to best utilize this biradical, but this matrix also provides extra protons that enhance the CP signal, irrespective of DNP. Furthermore, the requirement of low temperatures for efficient DNP has the added advantage of increasing the nuclear relaxation times, whereas the usually fast relaxation of quadrupolar nuclei during spin-lock periods limits the success of CP for measurements at room temperature. The combination of low temperatures and the addition of these extra useful protons means that the time savings using this system for DNP-enhanced CPMAS experiments, relative to ubiquitous SSNMR systems, cannot be predicted by simply allowing for the DNP enhancement, the low-temperature gain (Boltzman factor and reduced thermal noise) while taking into account sample "bleaching",¹⁵ and the change in relaxation times due to the paramagnetic effects of the added biradical. The only true comparison in this (and similar) system(s) is to record spectra under specific DNP conditions and under normal SSNMR conditions and compare the S/N per unit time.¹⁶ It should be noted that resolution is also an extremely important factor, and the apparent line widths should also be taken into account. In this system, however, the line widths are dominated by disorder, and there are negligible changes between the two sets of experimental conditions. A similar CPMAS experiment was recorded under conventional SSNMR conditions (9.4 T, 298 K, 8 kHz MAS on a 3.2 mm rotor; data not shown). Comparing the S/N per unit time for the DNP-enhanced CPMAS spectrum with that for the conventional CPMAS spectrum showed that using DNP for this system gave $\epsilon = 184$, corresponding to a time-saving factor of ~ 34000 . This demonstrates the considerable advantage of using DNP in the study of this system.

A comparison of the DNP-enhanced CPMAS and the DEMAS NMR signal intensities for each Al coordination state can give only a very crude indication of the influence of protons on each state. The $^{27}\text{Al}^{\text{IV}}$, $^{27}\text{Al}^{\text{V}}$, and $^{27}\text{Al}^{\text{VI}}$ peaks were 2.4, 4.6, and 6.1 times larger in the DNP-enhanced CPMAS spectrum, respectively. Notably, the line widths (and thus the apparent transverse dephasing times, T_2^*) did not vary between the two spectra, and accordingly, proton couplings were not the limiting factor of these line widths. A more complete analysis of the relative influence of protons can be performed using measurements of T_2' , the time constant associated with the homogeneous contribution to the transverse dephasing, which cannot be refocused with a π pulse. T_2' values were measured using a pseudo-two-dimensional (pseudo-2D) spin-echo experiment with various rotor-synchronized echo times, the pulse sequence for which is given in Figure S1 in the Supporting Information. Figure 2 shows the results of such measurements for each of the Al peaks in the mesoporous

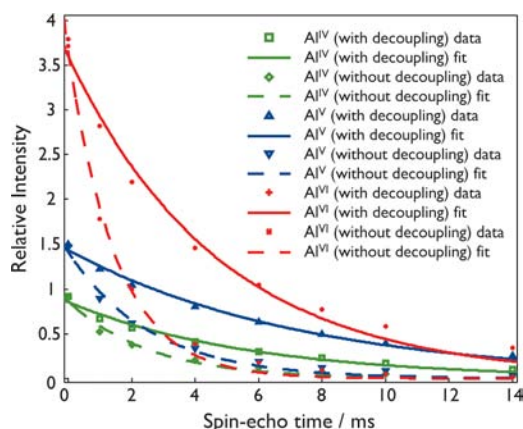


Figure 2. Normalized intensity decays for the ^{27}Al peaks with and without 100 kHz SPINAL-64 heteronuclear decoupling during a spin-echo period, as functions of the (rotor-synchronized) spin-echo time, from which T_2' values were determined. This DNP-enhanced experiment was performed using a MAS rate of 8 kHz, a sample temperature of ~ 103 K, and the pulse sequence shown in Figure S1.

alumina sample with and without heteronuclear decoupling. These data demonstrate the effect protons have on each T_2' value and thus on each Al site. Notably, the employed heteronuclear decoupling was deemed sufficient in that an increase in power did not affect the value of T_2' (this was observed for optimized SPINAL-64 decoupling¹⁷ with powers above 90 kHz; data not shown). The ratios of the T_2' value measured with decoupling to the value measured without decoupling were 2.3 for Al^{IV} , 2.9 for Al^{V} , and 3.2 for Al^{VI} . This is in agreement with the relative intensities of the CPMAS and DEMAS spectra. These corroborating observations indicate that the interfacial Al^{VI} sites are more heavily influenced by protons than the interfacial Al^{V} sites, which in turn are more heavily influenced by protons than the interfacial Al^{IV} sites. This is consistent with an increase in the number of hydroxo or aqua groups with increasing coordination number.

The lack of change in T_2^* for each spectral peak in the CPMAS and DEMAS experiments noted above could indicate that heteronuclear decoupling is not necessary. Nonetheless, as clearly shown in Figure 2, protons have a significant impact on the spin dynamics of ^{27}Al nuclei. Moreover, in this system the large influence of protons is not just limited to experiments that begin with a CP step. This realization is beyond the scope of the present work but will be discussed in detail in a future publication.

Figure 2 illustrates the importance of the heteronuclear decoupling during the spin-echo period; these periods (and thus the T_2' values) are vital in most SSNMR experiments involving J couplings.¹⁸ A further demonstration of its importance is given in Figure S2, which compares the spectral intensities of each ^{27}Al coordination state after CP and then a spin-echo period with a total duration of 4 ms with and without ^1H decoupling. Globally, the intensities without decoupling are reduced by 60% relative to those with decoupling. T_2' values are also important in SSNMR experiments involving dipolar couplings (REDOR-type experiments, etc.¹⁹). Furthermore, other dipolar recoupling sequences experience magnetization decay times on the order of T_2' that can also be heavily affected by proton couplings. Thus, heteronuclear decoupling during these sequences can also be highly beneficial, as long as interference effects are avoided.

The supercycled symmetry-based dipolar recoupling sequence $\text{BR}2_2^1$ has been shown to be of great utility when recording homonuclear correlation spectra.²⁰ However, the use of this and other²¹ sequences for ^{27}Al has been limited to bulk studies because of their low efficiency ($\sim 5\%$), which results from the intricate spin dynamics of quadrupolar nuclei in the presence of an RF field and MAS. The entirety of the adapted pulse sequence used here for interface-selective, DNP-enhanced correlation spectroscopy of quadrupolar nuclei is given in Figure S1. This pulse sequence first transfers hyperpolarized proton magnetization to nearby half-integer-spin quadrupolar nuclei via a CP step. Next, the sequence creates double-quantum (DQ) coherences between the CTs of dipolar-coupled quadrupolar nuclei while removing DQ coherence contributions involving satellite transitions of a single ^{27}Al nucleus. The spectra resulting from this sequence then give information about the spatial proximities between neighboring nuclei. The variables of this experiment can be optimized using a one-dimensional (1D) version (no indirect-dimension increments) that can also be used to demonstrate the importance of heteronuclear decoupling during the recoupling periods and also the whole sequence (Figure S2). Moreover, demanding experiments usually require careful calibrations of pulses and delays. Here, calibrations of the parameters required for maximum efficacy of the recoupling sequence could be performed on the sample of interest in <1 h because of the huge gain in S/N due to the DNP conditions. Under conventional SSNMR conditions, these calibrations would require much longer experimental times even with model samples.

Once calibrated, the 2D version of this pulse sequence was used to record the first correlation spectra of quadrupolar nuclei using DNP. Furthermore, since the sequence begins with a CP step, the only observed correlations would be between interfacial ^{27}Al nuclei. Spectra resulting from the implementation of this sequence on the mesoporous alumina sample are shown in Figure 3. It has been shown that the $\text{BR}2_2^1$ recoupling sequence has an offset dependence,^{20a} so three spectra with different offsets were recorded to remove any uncertainty in the data. Possibly the most striking point is that each spectrum took only ~ 4 h to acquire. Under conventional SSNMR conditions, the acquisition of equivalent data would require over 15 years for each spectrum! It can be seen that dipolar correlations between all sites are present (including same-site correlations between different nuclei, e.g., $\text{Al}^{\text{VI}}-\text{Al}^{\text{VI}}$ correlations), except for $\text{Al}^{\text{IV}}-\text{Al}^{\text{VI}}$ correlations. Therefore, at the interface of this material Al^{V} sites connect Al^{IV} and Al^{VI} sites.

To summarize, DNP enhancements (ϵ) of ~ 15 have been observed on an industrially important sample of mesoporous alumina using a 9.4 T DNP-SSNMR spectrometer. More importantly, this translates into a true sensitivity gain per unit time of 184 relative to equivalent room-temperature measurements. Transcending the sensitivity limitations of cross-polarization and also dipolar recoupling for quadrupolar nuclei, the corresponding 4–5 orders of magnitude of time savings allow not only very fast 1D CPMAS and pseudo-2D experiments but also interface-selective 2D homonuclear dipolar correlation experiments to be performed. These 1D and 2D experiments clearly demonstrate that spatial proximities involving quadrupolar nuclei can be probed using DNP-enhanced SSNMR with greatly reduced time scales. Moreover, the absence of $\text{Al}^{\text{IV}}-\text{Al}^{\text{VI}}$ correlations combined with the presence of $\text{Al}^{\text{IV}}-\text{Al}^{\text{V}}$ and $\text{Al}^{\text{V}}-\text{Al}^{\text{VI}}$ correlations shows that

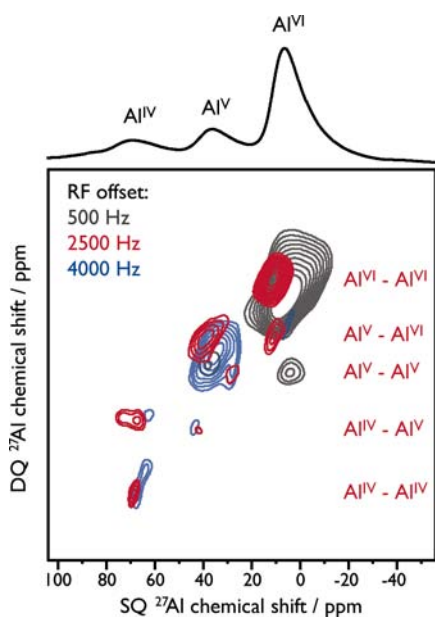


Figure 3. DNP-enhanced, interface-selective DQ–SQ ^{27}Al homo-nuclear dipolar correlation spectra of mesoporous alumina recorded using a MAS rate of 8 kHz, a sample temperature of ~ 103 K, and the pulse sequence shown in Figure S1. The total acquisition time for each spectrum was ~ 4 h. For illustrative purposes, the DNP-enhanced CPMAS spectrum (Figure 1 b), with the three different Al peaks labeled, is shown at the top.

interfacial Al^{IV} and Al^{VI} sites are bridged by interfacial Al^{V} . These structural data, together with the results of the influence of protons on the T_2' of each interfacial site, can be combined with ab initio calculations to help elucidate the surface structure of this amorphous material. This work is planned for a future publication.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, pulse sequence diagrams, and spectra demonstrating the importance of heteronuclear decoupling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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