ChemComm

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Dynamic nuclear polarization of quadrupolar nuclei using cross polarization from protons: surface-enhanced aluminium-27 NMR†

Veronika Vitzthum,[a] Pascal Miéville,*[a] Diego Carnevale,[a] Marc A. Caporini,[a] David Gajan,[b] Christophe Copéret,[b] Moreno Lelli,[c] Alexandre Zagdoun,[c] Aaron J. Rossini,[c] Anne Lesage,[c] Lyndon Emsley[c] and Geoffrey Bodenhausen[adef]

The surface of γ-alumina nanoparticles can be characterized by dynamic nuclear polarization (DNP) surface-enhanced NMR of ^{27}Al. DNP is combined with cross-polarization and MQ-MAS to determine local symmetries of ^{27}Al sites at the surface.

Aluminas and in particular γ-alumina are some of the most widely used high-surface-area oxides; they are applied in industry either directly as catalysts or as supports for single-site or nanoparticle-based catalysts.[1] In particular, the surface is key to the formation of reactive sites for supported catalysts in various applications such as alkene hydrogenation,[2] metathesis[3] and alkene polymerization.[4] Surface sites are also involved in the low temperature activation of hydrogen and alkanes,[5] in numerous catalytic dehydration processes,[1] and probably in the stabilization of supported metal nanoparticles.[6] Despite recent advances,[6,7] a detailed understanding of the surface structure of γ-alumina at a molecular level still requires refinement.

Solid-state NMR spectroscopy is one of the most powerful methods to probe atomic-level surface structures without requiring long-range order,[8] particularly for carbon-containing adsorbed or chemisorbed species, or for silicon-containing materials. Surface sites can be readily identified through differences in chemical shifts, provided the ^{13}C or ^{29}Si spins are sufficiently concentrated or isotopically enriched in a specific manner. Aluminium-27 magic angle spinning (MAS) solid-state NMR (^{27}Al has a spin $I = 5/2$ and a quadrupolar coupling constant C_Q between 0 and 16 MHz)[9] can also be used to probe the bulk structure of aluminas and aluminosilicates.[10] To obtain structural information about the surface of these materials one requires a method to discriminate between signals from the surface and the bulk. This can be achieved by cross-polarization (CP) from ^{1}H to ^{27}Al as protons can only be found near the surface of aluminas, either in hydroxyl groups or in solvent molecules close to the surface.[11] While CP is efficient for $I = 1/2$ nuclei such as ^{13}C or ^{29}Si, it is less popular for quadrupolar nuclei such as ^{27}Al because spin-locking is difficult under MAS as a result of the time-dependence of the quadrupolar splitting.[12] Since CP from ^{1}H to ^{27}Al is not very efficient[13] it has been used primarily to establish atomic connectivities, rather than to increase the sensitivity.

With the recent development of Dynamic Nuclear Polarization (DNP) combined with MAS,[14] NMR sensitivity can be greatly enhanced and experiments that were hitherto limited by low signal-to-noise ratios become feasible in a reasonable time frame. Recently, we have shown that it is possible to enhance the signals of ^{13}C of organic molecules grafted on surfaces.[15] We have also demonstrated that one can selectively enhance the signals of ^{29}Si sites on the surfaces of mesoporous and non-porous silicates.[16] To obtain good DNP signal enhancement we prepared the samples by 'incipient wetness impregnation' with an aqueous solution of stable biradicals such as TOTAPOL. Under MAS at temperatures of 100 K, saturating the EPR transitions of the radical with *ca.* 5 W continuous-wave microwave irradiation leads to enhanced polarization of the solvent protons, which is then transferred by CP from the ^{1}H nuclei to the ^{13}C or ^{29}Si nuclei on the surface.

Here, we show that a similar strategy can be used to selectively enhance the signals of ^{27}Al sites at the surface of γ-alumina. First, we optimize the sample preparation, which is the key to good DNP enhancements. Large variations of DNP enhancements are observed for different sample preparations; in our hands, the best ^{27}Al enhancement achieved was $\varepsilon_{DNP} \approx 20$. The enhancement reached on protons is the same as that for aluminium. The ^{1}H–^{27}Al CP efficiency is not affected by the polarization state of the protons. This corresponds to a 400-fold acceleration of signal acquisition, and as a result, we were able to record a DNP surface-enhanced CP-MQMAS spectrum of γ-alumina in less than 24 hours. This would have required a full year without DNP.

Most successful DNP experiments on small molecules and large biomolecules have relied on dissolving or suspending the target molecules in glycerol/water mixtures, which form glassy

[a] *Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, EPFL, Batochime, 1015 Lausanne, Switzerland. E-mail: pascal.mieville@epfl.ch*
[b] *Department of Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland*
[c] *Centre de RMN à Tres Hauts Champs, Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1), 69100 Villeurbanne, France*
[d] *Département de Chimie, Ecole Normale Supérieure, 24 Rue Lhomond, 75231, Paris Cedex 05, France*
[e] *Université Pierre-et-Marie Curie, Paris, France*
[f] *CNRS, UMR 7203, Paris, France*
† Electronic supplementary information (ESI) available: Detailed experimental procedures and additional data (Fig. S1 and S2). See DOI: 10.1039/c2cc15905h

matrices at 100 K[17]. Like in our recent DNP studies of ^{13}C and [29]Si in nanoporous materials,[15,16] we used water *without* glycerol as a solvent in this work, where γ-alumina powder was wetted with a H_2O/D_2O mixture containing TOTAPOL. For γ-alumina, it appears that only three parameters are relevant for the DNP enhancement factor ε_{DNP}: (i) the mole fraction x of H_2O in the H_2O/D_2O mixture (typically $0.1 < x < 0.2$) (ii) the TOTAPOL concentration c in the H_2O/D_2O mixture (typically $5 < c < 15$ mM), and (iii) the extent of wetting, expressed in terms of the ratio $r_{solvent}$ which is defined as the mass of the doped solvent divided by the total mass of the sample (typically $0.05 < r_{solvent} < 0.45$). For incipient wetness impregnation (IWI),[18] $r_{solvent} = r_{IWI}$ is such that any further added solvent will not be absorbed; if $r > r_{IWI}$, the sample has the appearance of a viscous paste. The dry powder obtained for $r < r_{IWI}$ is to be preferred, since it is easier to pack into the NMR rotor. As expected, the ratio $r_{IWI} = 0.45$ for γ-alumina corresponds to a fully impregnated sample and gives the best results (Fig. S1a in ESI†).

The radical concentration c has a pronounced effect on the DNP enhancement ε (Fig. S1b in ESI†). For γ-alumina ε is maximised at relatively low concentrations ($c = 4$ mM, $r = 0.45$). Note that the optimal c of TOTAPOL is lower here than in our work on mesoporous silicas.[15,16]

Finally, the mole fraction x of H_2O in the solvent mixture was optimized. Earlier DNP studies[19] have shown that x can have a significant effect on DNP enhancements, with optimal values between 0.05 and 0.10. Interestingly, in the ranges $0.025 < x < 0.25$ and $2 < c < 20$ mM there is little effect on the DNP enhancements here (Fig. S1c in ESI†), in contrast to the ratio r, for which a much stronger dependence is observed. The DNP enhancements varied in the range $0.2 < \varepsilon/\varepsilon_{opt} < 1.0$ for $0.05 \leq r \leq 0.5$.

Fig. 1 compares the [27]Al spectra obtained *via* direct excitation without DNP, CP without DNP, and CP with DNP. The reduced signal intensity of the CP spectra compared to direct excitation reflects the selectivity of CP for surface sites. The DNP enhancement here is $\varepsilon \approx 20$. In cases where only the surface is of interest, the DNP–CP approach leads to the suppression of bulk [27]Al sites as ^{1}H nuclei are only located near the surface of the material and affords a reduction in experimental time on the order of 400.

Multiple-quantum magic-angle spinning (MQMAS) experiments[20] offer a means to remove second-order quadrupolar broadening and, hence, obtain higher resolution NMR spectra of half-integer quadrupolar nuclei. The combination of CP with triple quantum TQ-MAS experiments has previously been accomplished by two different approaches: (i) by transferring polarization directly from protons to the TQ coherence[21], or (ii) by transferring magnetization from ^{1}H to [27]Al single-quantum (SQ) coherence *via* CP, then converting the SQ coherence to longitudinal magnetization of [27]Al, followed by conversion to TQ coherence.[22] These techniques tend to be rather inefficient, and their use to observe surface signals is challenging. Here, we used the second method in combination with DNP surface enhancement. We modified the phase-modulated z-filtered experiment[22] to obtain a phase-modulated shifted-echo split-t_1 version,[23,24] as shown in Fig. S2 (ESI†). One-dimensional experiments yielded similar enhancement factors as ordinary
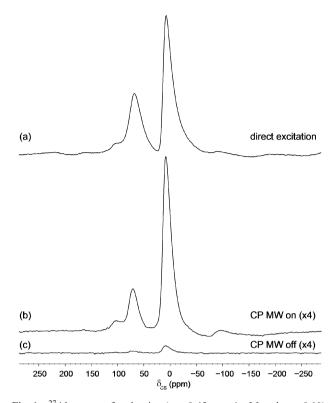

Fig. 1 [27]Al spectra of γ-alumina ($r = 0.45$, $c = 4$ mM and $x = 0.10$): (a) excited directly with a single *rf* pulse (signals from both surface *and* bulk); (b) excited by CP from protons with microwave saturation of the EPR transitions of the TOTAPOL radical (surface enhanced signals); and (c) CP without microwave irradiation (signals from surface only).

CP experiments, proving that the DNP-enhanced SQ coherence of [27]Al can be converted into TQ coherence without significant losses.

Fig. 2 shows a DNP surface-enhanced 2D-CP-MQMAS spectrum of γ-alumina. Two distinct [27]Al resonances associated with tetrahedral Al(IV) ($\delta_{iso} = 67$ ppm) and octahedral Al(VI) ($\delta_{iso} = 8$ ppm) alumina species are visible. A penta-coordinated aluminium species could not be identified in our spectra. It is worth bearing in mind that, in order to achieve a DNP enhancement, our wetted, glassy and frozen sample is observed under conditions that greatly differ from a dry powder at room temperature. This explains the absence of penta-coordinated surface sites that may be coordinated by H_2O or TOTAPOL in contrast to tetrahedral and octahedral sites. Hydrophobic preparation methods for DNP[25] should help to resolve water sensitive sites in the future.

In conclusion, we have shown that DNP can be used effectively to enhance [27]Al signals on surfaces with signal enhancements of up to a factor $\varepsilon \approx 20$, corresponding to time savings of a factor 400, and gave guidelines for preparing suitable samples by incipient wetness impregnation. We illustrated the approach with samples of γ-alumina, which offer good models for a large palette of materials. The approach could be extended to other quadrupolar nuclei and to solvents other than water, which would be of great interest for materials used in heterogeneous catalysis. Non-aqueous glass-forming solvents containing controlled concentrations of protons and radicals that can wet the surface of porous materials should lead to effective DNP enhancements.
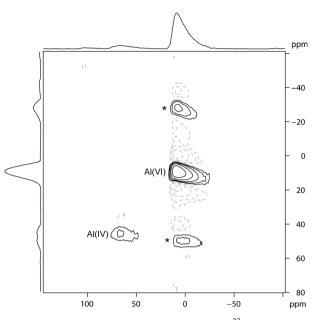
Fig. 2 DNP-enhanced CP-TQ-MAS spectrum of ^{27}Al in γ-alumina ($r = 0.45$, $c = 4$ mM and $x = 0.10$) recorded with the sequence of Fig. S2 in ESI† acquired in ~50 h. Octahedral, Al(VI), and tetrahedral, Al(IV), aluminium sites are clearly identified, but no pentacoordinated sites can be seen. The scale of the vertical isotropic dimension was plotted according to the conventions in ref. 24.

All DNP NMR spectra were recorded at EPFL on a 9.7 T (400 MHz for ^{1}H)/263 GHz (gyrotron frequency) solid-state DNP-MAS NMR spectrometer. Further experimental details are given in the ESI.†

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