

High-temperature MAS-NMR at high spinning speeds

1. Introduction

MAS NMR experiments at ambient temperature at high spinning speed have developed to a routine experiment available in many NMR laboratories. High temperature experiments at temperatures up to 300 °C and spinning speeds of 10 kHz are available from various manufacturers. However, the temperature range $300\text{ °C} < T < 800\text{ °C}$ is only accessible employing specialized hardware requiring quite an investment. In the LASERMAS system from Bruker Biospin, a 7 mm MAS assembly is used; the heating is accomplished via a laser beam from a 200 W diode laser operated at 986 nm, which is fed through an optical fiber [1]. Since the laser beam in principle is exclusively heating the AlN container inside the MAS spinner, the probe setup may rely on standardized hardware. In the setup by DOTY Sci., the sample is heated via conventional heating employing nitrogen gas, thus requiring a sophisticated, high temperature stable MAS assembly [2,3]. Both systems enable MAS NMR experiments at temperatures of up to 700 °C, however, the maximum achievable spinning frequencies for the two commercially available systems is restricted to approx. 5 kHz. This limitation poses a serious drawback, severely limiting the applicability of high temperature MAS NMR. In this contribution we will report on the attempts to achieve a stable, cost-effective hardware setup which allows high temperature MAS NMR at temperatures of up to 700 °C at spinning speeds of up to 10 kHz. We applied the inductive heating method [4–6] as originally introduced by Kendrick and Yannoni in 1990 [4] employing a standard 4mm Bruker MAS NMR probe.

2. Experimental

The experiments were performed on a Bruker Avance III spectrometer operating at 7 T, employing a standard 4 mm Bruker triple channel MAS NMR probe with resonance frequencies of 75.4 MHz and 121.5 MHz for ^{79}Br and ^{31}P , respectively. A standard 4 mm rotor with a zirconia cap was used for the experiments. For the inductive heating, an external amplifier (Amplifier Research 200 HA, 200–400 MHz, 100 W) was used. We note, however, that the Bruker ^1H amplifier may also be used for the inductive heating.

The chemical shift of the ^{79}Br signal of KBr was used as a chemical shift thermometer, as outlined in [1]. Inductive heating

was performed employing the ^1H -channel of the probe, using either cw or pulsed irradiation. In the latter case the heating efficiency can be adjusted via the rf power and the pulse width and spacing, whereas for the former the rf power marks the only adjustable parameter. A series of 32–128 dummy scans prior to data acquisition ensured thermal equilibration of the sample.

3. Results and discussion

3.1. Fabrication of rotor inserts

Sample containers fitting exactly within a standard 4mm rotor were machined from BN (cf. Fig. 1). These containers were then coated with a thin layer of platinum via physical vapor deposition employing a commercial, e-beam evaporating system (BOC Edwards, Auto 500). During this process, the specimen were continuously rotated around the long axis to ensure a maximum homogeneity of the coated metal layer. This layer is then acting as the cathode for the subsequent galvanization process. To galvanize the inserts, a platinum electrolyte solution was used as being supplied by METAKEM (Platinum-DNS, 6 g Pt/l). Before and after the galvanization, the inserts were weighed using a micro balance. Contacts were realized by fixing a copper wire to the top or bottom of the insert with silver paint and painting a thin conducting path to the vapor deposited metallic layer. After the galvanization process, these electrical contacts can simply be removed by rinsing the insert with acetone.

For the calculation of the thickness of the layer deposited on the surface, we determined the deposition rates for our experimental setup to 6 nm/min for the e-beam evaporation and 180 nm/min for the galvanization process (calculated from the determined mass of the deposited platinum). The thickness of the e-beam deposited layer on the specimen was determined by a standard quartz oscillator thickness monitor.

Using this approach, a series of platinum and silver coated inserts were produced to check the reproducibility of the resulting layer thickness and to study the effect of this parameter on spinning and rf performance of the inserts.



Fig. 1. Boron nitride insert used for the conductive heating: left: schematics; middle: insert after deposition of a thin Pt layer using physical vapor deposition. The contacting for the subsequent galvanization process is shown; right: final insert together with 4 mm spinner.

3.2. NMR experiments

The nature of the metal (or combination of metals) used as well as the applied layer thickness will affect the heating efficiency, effective rf power and spinning performance. In general, the larger the layer thickness, the more efficient will the rf waves from the ^1H channel (the heating channel) and from the X-channel (the observe channel) be absorbed, entailing effective heating, but on the other hand leading to a decrease in the signal to noise ratio, to longer $\pi/2$ pulse lengths and to a deterioration of the spinning performance due to the forces induced by Lenz's rule. Thus, achieving the right balance between effective heating and spinning performance/signal to noise ratio marks the crucial step of this work. As a general rule of thumb, inserts for which the $\pi/2$ pulse length is found to be roughly twice the value as compared to a rotor without any insert, show a quite decent spinning performance in combination with an acceptable signal to noise ratio. Inserts selected according to this recipe allowed spinning around 10 kHz and heating to $T > 600^\circ\text{C}$.

Fig. 2 shows the obtained chemical shifts for the ^{79}Br resonance in KBr and the temperatures achieved as a function of the power of the cw-irradiation for two inserts. The temperature was calculated as given in Refs. [1,7]. For the MAS NMR experiments we noted a sudden increase of the spinning speed by several 100 Hz when starting the heating. However, after this initial increase, the

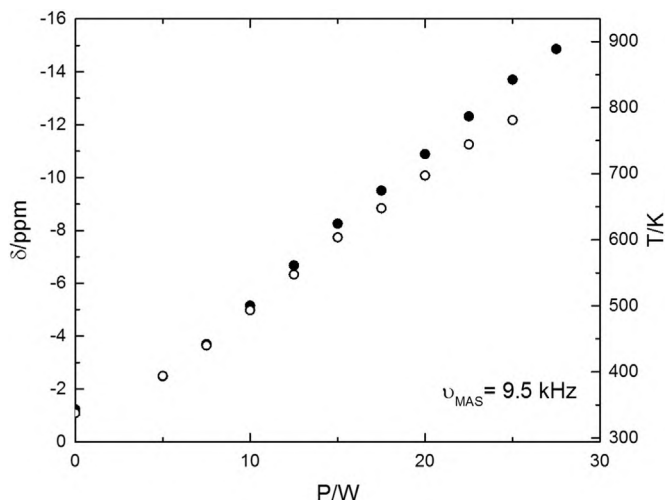


Fig. 2. Chemical shift position of the ^{79}Br line (left) and temperature (right) as a function of the cw-irradiation power. Closed symbols represent an insert with vapor deposited and galvanized Platinum. Open symbols show the results for an insert where an initial vapor deposited silver layer was galvanized with platinum. MAS was performed at 9.5 kHz.

spinning speed was found to remain constant within ± 2 Hz. The filled symbols were obtained employing an insert, with a platinum coating of 1 mg (closed symbols), which translates to an approximate layer thickness of $0.75\ \mu\text{m}$.

In an attempt to reduce the amount of platinum needed, inserts were also produced by depositing an initial layer of silver (300 nm), followed by a short galvanization with platinum (350 nm). Inserts manufactured this way showed the same properties as their pure platinum counterparts, but their long-term usability is limited to temperatures below 800 K, attributed to the much lower melting point of silver compared to platinum, which leads to a successive deterioration of the heating properties at high temperatures.

Using the pure platinum coated insert, we performed a temperature dependent ^{31}P MAS NMR experiment on a $\text{K}_2\text{O} \cdot 4\text{P}_2\text{O}_5$ glass in the temperature range $334\ \text{K} \leq T \leq 778\ \text{K}$ to follow the species exchange above the glass transition temperature. The glass was doped with 0.05% of MnCO_3 to cut down T_1 relaxation. For the glass composition, the local structure is dominated by Q^3 ($(\text{OP})_3\text{P}=\text{O}$) and Q^2 ($(\text{OP})_2(\text{O}-)\text{P}=\text{O}$) phosphate units. The resulting spectra as shown in **Fig. 3** were collected using 64 scans and a repetition time of 5 s. The coalescence of the two signals, observable at $T > 343\ \text{K}$ clearly indicates the species exchange between the Q^3 (-28 ppm) and Q^2 (-44 ppm) phosphate sites (for details, the reader is referred to Ref. [3]). The sidebands are clearly separated from the centerband, facilitating the analysis. At the B_0 field of 7 T, due to the chemical shift dispersion present in the amorphous sample, the sidebands and centerband are heavily overlapping at spinning speeds ≤ 4.5 kHz (cf. e.g. the spectra shown in Ref. [8]), which severely complicates the analysis of the spectra. Thus, the possibility to perform high temperature MAS NMR experiments at these spinning speeds can be considered a significant advancement in high temperature MAS NMR. The fact that conventional probes and spectrometer hardware without any mandatory modifications may be used makes this approach available to many NMR laboratories. Due to the limited heat transfer to the probe, shim coils etc., this setup also proves to be

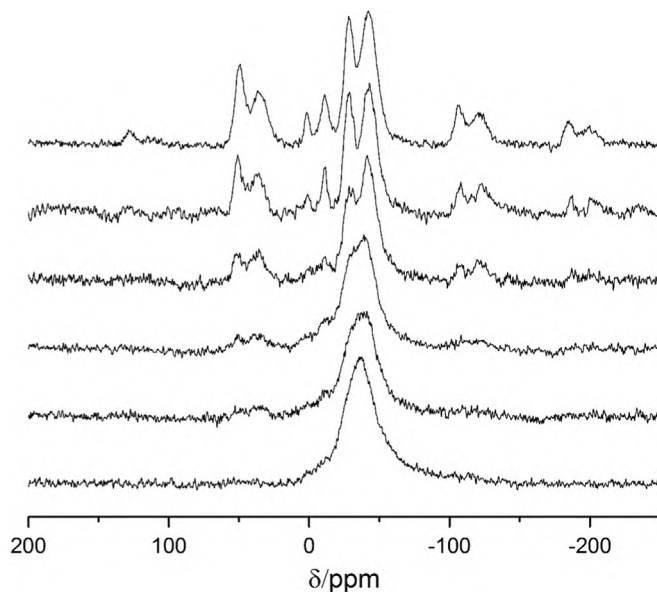


Fig. 3. ^{31}P -MAS NMR spectra of a $20\text{K}_2\text{O} \cdot 80\text{P}_2\text{O}_5$ glass as a function of temperature (from top to bottom: 334 K, 544 K, 605 K, 616 K, 649 K, 778 K). The two minor signals at 1.5 ppm and -10.8 ppm indicated the presence of small amounts of Q^1 and Q^0 units due to moisture attack to the sample.

stable for long term high temperature experiments, which are occasionally problematic with the conventional hardware described above.

4. Conclusions

A cost-efficient alternative to conventional high temperature MAS NMR which relies on inductive heating has been presented. Inserts manufactured from boron nitride are coated with thin metal layers employing a combined physical vapor deposition/galvanization process. Temperatures above 600 °C with spinning frequencies around 10 kHz have been achieved. The fact that with the exception of the metal coated BN inserts no specialized hardware is needed makes this approach transferable to many NMR laboratories.

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References

- [1] S. Venkatachalam, C. Schroeder, S. Wegner, L. van Wuelen, *Phys. Chem. Glas.-Eur. J. Glass Sci. Technol. Part B* 55 (2014) 280–287.
- [2] L. van Wuelen, S. Wegner, G. Tricot, *J. Phys. Chem. B* 111 (2007) 7529–7534.
- [3] S. Wegner, L. van Wuelen, G. Tricot, *J. Phys. Chem. B* 113 (2009) 416–425.
- [4] G.G. Maresch, R.D. Kendrick, C.S. Yannoni, *Rev. Sci. Instrum.* 61 (1990) 77–80.
- [5] D.B. Ferguson, J.F. Haw, *Anal. Chem.* 67 (1995) 3342–3348.
- [6] J. Rinnenthal, D. Wagner, T. Marquardsen, A. Krahn, F. Engelke, H. Schwalbe, *J. Magn. Reson.* 251 (2015) 84–93.
- [7] K.R. Thurber, R. Tycko, *J. Magn. Reson.* 196 (2009) 84–87.
- [8] L. Munoz-Senovilla, S. Venkatachalam, F. Munoz, L. Van Wuelen, *J. Non-Cryst. Solids* 428 (2015) 54–61.

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