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A novel high-temperature MAS probe with optimized temperature gradient across sample rotor for in-situ monitoring of high-temperature high-pressure chemical reactions

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A B S T R A C T

We present a novel nuclear magnetic resonance (NMR) probe design focused on optimizing the temperature gradient across the sample for high temperature magic angle spinning (MAS) experiments using standard rotors. Computational flow dynamics (CFD) simulations were used to assess and optimize the temperature gradient across the sample under MAS conditions. The chemical shift and linewidth of ^{207}Pb direct polarization in lead nitrate were used to calibrate the sample temperature and temperature gradient, respectively. A temperature gradient of less than 3 °C across the sample was obtained by heating bearing gas flows and adjusting its temperature and flow rate during variable temperature (VT) experiments. A maximum temperature of 350 °C was achieved in this probe using a Varian 5 mm MAS rotor with standard Vespel drive tips and end caps. Time-resolved ^{13}C and ^{1}H MAS NMR experiments were performed at 325 °C and 60 bar to monitor an in-situ mixed phase reverse water gas shift reaction, industrial synthesis of CH_3OH from a mixture of CO_2 and H_2 with a $Cu/ZnO/Al_2O_3$ catalyst, demonstrating the first in-situ NMR monitoring of a chemical system at temperatures higher than 250 °C in a pressurized environment. The combination of this high-temperature probe and high-pressure rotors will allow for in-situ NMR studies of a great variety of chemical reactions that are inaccessible to conventional NMR setup.

1. Introduction

Several key NMR parameters are impacted by sample temperature, as is overall molecular motion. Sensitivity and resolution are directly affected through temperature-dependent NMR parameters such as spin-lattice relaxation time constant T_1, spin-spin relaxation time constant T_2, and diffusion rates. A temperature gradient across the sample in a MAS probe may adversely affect the resolution and subsequent analysis, especially for critical temperature regimes where phase transitions or chemical reactions occur. Minimizing and controlling temperature gradients in a MAS rotor for high-resolution solid-state NMR experiments is usually challenging due to inhomogeneous heating, inefficient heat transfer, heating effects from high-power radiofrequency radiation, and high flow rates for the driving and bearing gas.

Commercial solids MAS NMR probes with a temperature range up to 250 °C are available from Bruker, Doty Scientific, Revolution NMR and Phoenix NMR. MAS Experiments above 250 °C can be achieved by three methods: laser heating, inductive heating, and hot gas heating. Bruker LASERMAS system utilizes a laser beam fed through an optical fiber to achieve a temperature jump up to 900 °C within several seconds, but the spatial temperature distribution across the sample is significant due to the intense laser heating [1,2]. Another way of reaching temperature jumps up to 700 °C is to perform radio frequency inductive heating on platinum layers coated outside MAS rotors [2,3] or on platinum metal inserts inside rotors [4], but the temperature obtained at each sample is dependent on the heat capacity of the materials. The Doty HT probe uses hot nitrogen gas streams to obtain a sample temperature of 700 °C, but requires a specialized high temperature stable MAS assembly to prevent heat transfer to the magnet [5–8]. Conventionally, Varian style housings rely on a heated VT gas stream which flows towards the center of the rotor to accomplish VT, while the bearing and drive gas streams are at room temperature. This results in a temperature gradient that runs from the center of the sample towards each end of the rotor [9,10]. Here we present a design that minimizes the temperature gradient across the sample for VT experiments up to 350 °C by heating both the VT and bearing gas streams (Fig. 1). Furthermore, no expensive specialized rotors or inserts are required and the probe design can be adapted to any rotor size and commensurate spin rate. More importantly, this probe can readily host our in-house designed pressurized MAS WHiMS rotors which hold pressures up to 400 bar [17] and enable in-situ NMR studies for

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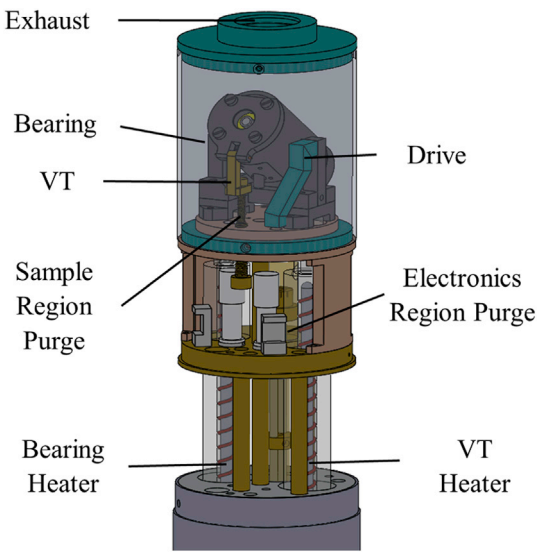

Fig. 1. Solidworks model of the probe showing the VT and Bearing heater/dewar assembly as well purge and exhaust design. The custom designed temperature controller uses 2 Ω CN8201 controllers, NI USB-6009 ADC and NI USB-9211A thermocouple reader. We control the VT and Bearing Temperature (BT) while monitoring the sample and electronics region temperature via custom Labview software. The temperature controllers are configured to provide a pulsed DC output for use with a solid state relay which regulates the 48VDC power supply to drive the heaters. Filter capacitors in front of the heaters and thermocouples improve the noise immunity of the probe.

mixed-phase reactions that are inaccessible to traditional NMR setups.

2. Probe Details

2.1. Design

The probe was designed for use with a 14.1 T wide-bore Bruker Avance III spectrometer, but can be used with most 70 mm bore shim sets with an appropriate mounting collar. The housing obtained from Revolution NMR is a 5 mm Varian Pencil 2 design crafted from high temperature plastic (Celazole PBI). Celazole PBI is a thermoplastic material rated for continuous operation at temperatures up to 420 °C when used with nitrogen gas. Two Inconel heater assemblies with nonmagnetic Type E thermocouples from ARI Heaters are housed inside triple walled Quartz dewars from Wilmad Labglass for heating the VT and bearing gas streams (as shown in Fig. 1). The dewars are silver plated, which reduces probe body heating caused by radiated heat. The thermocouples are welded to the heater assemblies which have helical heat exchangers made of Inconel welded to the heaters to increase surface area for better heat transfer. The dewars are mated to the housing using Celazole PBI parts. Springs are used to hold the heaters in place, and also allow for expansion and contraction as parts thermally cycle. The housing region is enclosed with a shield which directs all the heated gas as well the drive and sample region purge gas streams to the top of the probe to be exhausted into a thermally insulated line that vents outside the magnet. The shield is a 3D printed part by Cideas Inc., which can print parts for applications up to 290 °C. The electronics region purge follows around the shield and prevents the probe body from overheating the shims. We do not heat the drive gas stream as it only comes into contact with the drive tip. Since the drive gas stream is at room temperature standard Zirconia and Silicon Nitrite rotors with Vespel drive tips can be used. While the VT gas stream is heated to 350 °C, the bearing heating is limited to 180 °C to maintain a temperature well below the softening point temperature of end caps and drive tips.

The probe is a double resonance HX probe with a circuit where the proton side tuning is accomplished with an adjustable quarter wave resonator and the low frequency side is tuned via capacitors which have plug in attachments to cover different frequency ranges [11]. The sample coil is a 5 turn solenoid which is 15 mm long and has a 6 mm inner diameter. The coil wire is a gold flashed magnetic susceptibility matched wire designed for use at temperatures up to 500 °C, purchased from Doty Scientific Inc. This probe will be modified in the future for *in situ* constant flow experiments [12] for high temperature flow through experiments.

2.2. Simulation

Simulations were conducted using Solidworks Flow Simulation 2012 which is a computational fluid dynamics solver integrated within Solidworks for flow and heat transfer applications [13]. Simulations include the Celazole housing as well as the Zirconia rotor. The drive and bearing inlets are assigned boundary conditions of 10 psi and 15 psi, which correspond to a spinning speed of 5 kHz. The VT boundary is setup for a 40 L per minute (LPM) of nitrogen inlet. The generated mesh includes 376501 cells and the calculation converged in 326 iterations. For the first simulation VT gas temperature is set to 180 °C with bearing and drive gases are at 25 °C, and in the second simulation both the VT and bearing gas temperature are set to 180 °C, while the drive gas is at 25 °C. As shown in Fig. 2 the temperature gradient is much less when both the VT and bearing gas streams are heated to the same temperature.

3. NMR probe characterization

Experimental Details: MAS NMR experiments were performed on a 600 MHz Bruker Avance III spectrometer using 5 mm zirconia rotors spinning at 5000 ± 10 kHz. A series of experiments were conducted by increasing VT stepwise from 20 °C to 350 °C and varying BT in the range from 20 °C to 180 °C with an interval of ~20 °C. Boron nitride spacers were used instead of Teflon spacers. The gas flow rates were set to 40 LPM for VT, 60 LPM for sample region purge and 70 LPM for electronics region purge to maintain shim temperatures below 60 °C when the sample temperature is maintained at 350 °C for 8 h. The average drive and bearing pressure for 5 mm rotors spinning at 5 kHz is 10 and 16 psi, respectively. The sample was equilibrated at each temperature for at least 10 min before NMR measurements. The ^{207}Pb spectra were obtained with 8 scans at VT < 200 °C, 32 scans at 200 ≤ VT ≤ 250 °C, and 128 scans at VT > 250 °C, using a 90° pulse width of 5 μs (corresponding to an

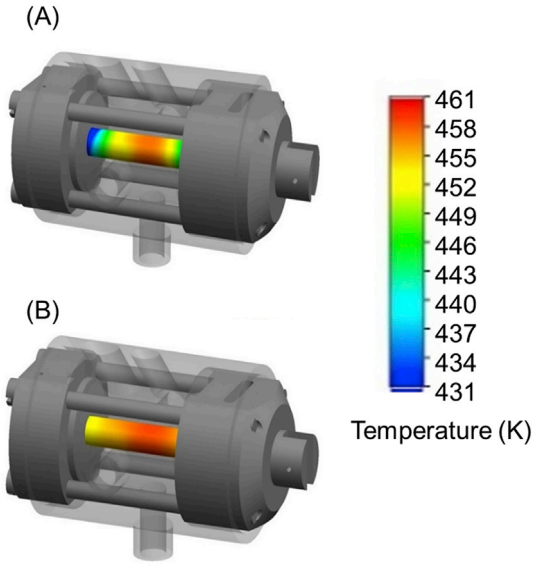

Fig. 2. Temperature gradient across MAS rotors obtained from Solidworks Flow Simulation 2012 using (A) driving gas at 25 °C, bearing gas at 25 °C and VT gas at 180 °C, and (B) driving gas at 25 °C, bearing gas at 180 °C and VT gas at 180 °C.

excitation bandwidth of 50 kHz) at 200 W and a recycle delay of 10 s.

Spinning stability: The maximum spinning speed for the probe is 12 kHz at room temperature, and we have reached up to 8 kHz with bearing heating at 200 °C. For most of our high-temperature high-pressure studies where samples usually turn into gas or liquid under these experimental conditions, MAS at 5 kHz is usually fast enough to produce a high-resolution NMR spectrum. We observed that spinning speed increases by a few percent when VT or bearing gas is heated, so we used Auto mode on a Varian MAS speed controller to regulate the spinning speed and we were able to control the spinning speed within 2% for days. To understand the influence of temperature on the magic-angle we obtained ^{79}Br spectra of KBr at varying temperatures. Fig. S2 shows ^{79}Br spectra and FIDs at varying temperatures with and without bearing heating. The ^{79}Br time domain rotational echoes extend to 10 ms at room temperature and decrease to 6 ms at 320 °C. Although this change is not insignificant, we have not seen the data quality and subsequent interpretation suffer."

Temperature Gradient: The chemical shift of ^{207}Pb in solid lead nitrate $Pb(NO_3)_2$ is sensitive to temperature variations and is commonly utilized as a temperature calibration standard up to 400 °C in MAS NMR [14–16]. Here we use ^{207}Pb direct polarization of $Pb(NO_3)_2$ to characterize the effect of bearing heating on the temperature gradient across the rotor with its entire length (12 mm) filled with sample.

The chemical shift of ^{207}Pb in lead nitrate was set to 0 ppm at 20.1 °C. The actual sample temperature T (℃) is related to ^{207}Pb chemical shift δ (ppm) using the equation:

$$T = \delta/0.725 + 20.1 \quad (1)$$

As shown in Fig. 3A the linewidth and shape of the ^{207}Pb spectrum are determined by the difference between BT and VT. When BT equals VT, a symmetric Lorenzian peak is obtained with the smallest linewidth, while a shoulder at lower (or higher) frequency is produced when BT is smaller (or greater) than VT. The temperature gradient across the sample, ΔT, is calculated from the linewidth at 5% peak height using $\Delta T = \Delta\delta/0.725$. At a sample temperature of T = 162 °C, temperature gradient ΔT is reduced dramatically from 26 °C without bearing heating to 2.8 °C with BT = VT (Fig. 3B).

Fig. 4 shows ΔT plotted against sample temperature T with and without bearing heating. $\Delta T < 4$ °C is achieved with BT = VT when VT ≤ 180 °C. Due to the upper limit of BT at 180 °C, ΔT increases with T when VT > 180 °C, but is still 2–3 times lower than with no bearing heating. For example, $\Delta T = 39$ °C at $T = 350$ °C with BT = 180 °C, while $\Delta T = 94$ °C at $T = 333$ °C with BT = 20 °C.

To further demonstrate the effect of temperature gradient in solid-state NMR spectra, Fig. 5 displays ^{13}C MAS spectra of hexamethylbenzene (HMB) at temperatures ranging from 25 °C to 166 °C. With

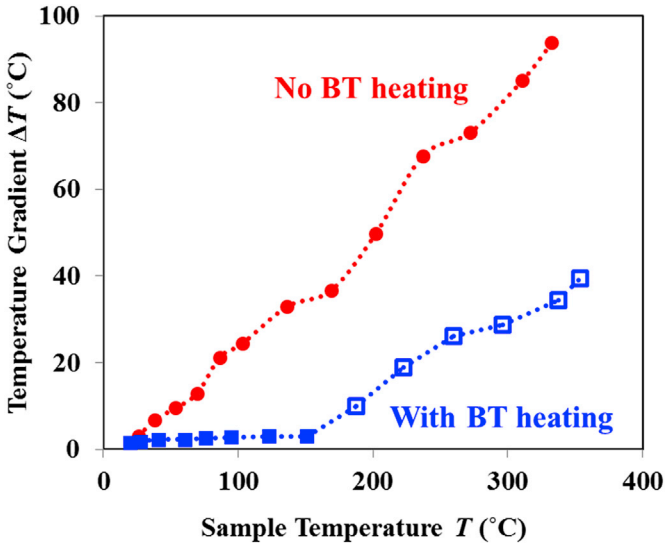

Fig. 4. Temperature gradient ΔT vs actual sample temperature T, with no bearing heating (red circle), and with bearing heating (filled blue square for BT = VT when VT ≤ 180 °C and empty blue square for BT = 180 °C when VT > 180 °C).

no bearing heating, ΔT ~26 °C at the melting point, leading to the coexistence of solid and liquid phases for more than an hour. With bearing heating, all solid HMB turns into liquid phase in 5 min due to a small temperature gradient of ~3 °C. To investigate in-situ chemical reactions that happen within a certain temperature range, a uniform temperature distribution across the rotor is especially important, making our probe design particularly suited for these measurements.

Applications: Compared to the Doty HT probe or the Bruker LASERMAS system, another advantage of our probe is its compatibility with our in-house developed pressurized MAS *WHiMS* rotors that can hold pressures up to 400 bar [17]. The combination of the high-temperature and high-pressure capacities allows for a great variety of in-situ solid-state MAS NMR investigations of materials and chemical reactions that are inaccessible to NMR studies in the absence of these hardware and component improvements. Here we use in-situ NMR monitoring of the industrial synthesis of CH_3OH from a mixture of CO_2 and H_2 based on a $Cu/ZnO/Al_2O_3$ heterogeneous catalyst [18] as an example. Fig. 6 displays the ^{13}C and ^{1}H MAS spectra of the reaction kinetics at 325 °C under a pressure of 60 bar 1:2 CO_2:H_2, with the

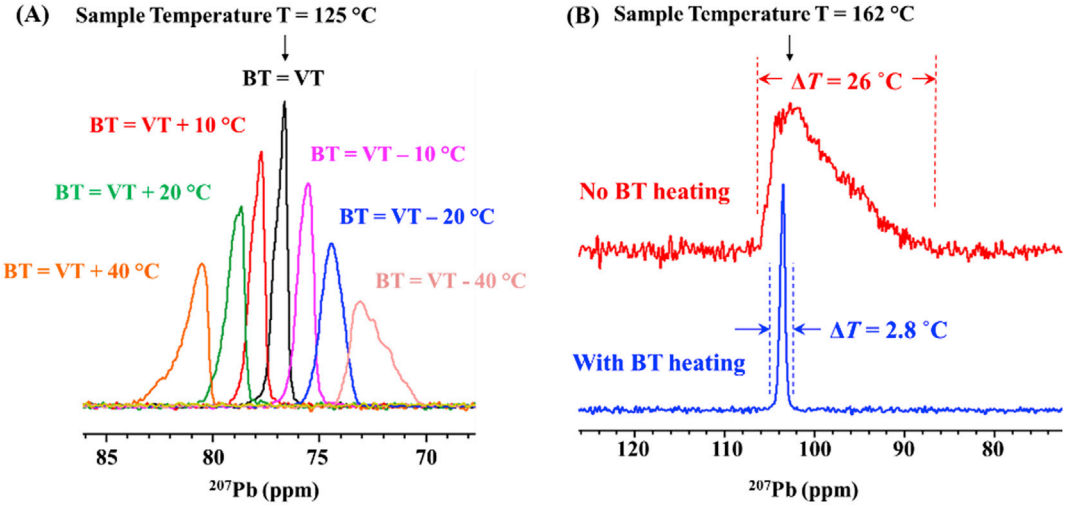

Fig. 3. (A) ^{207}Pb spectra obtained at varying BT. (B) The significant decrease in ΔT with BT heating at T = 162 °C.

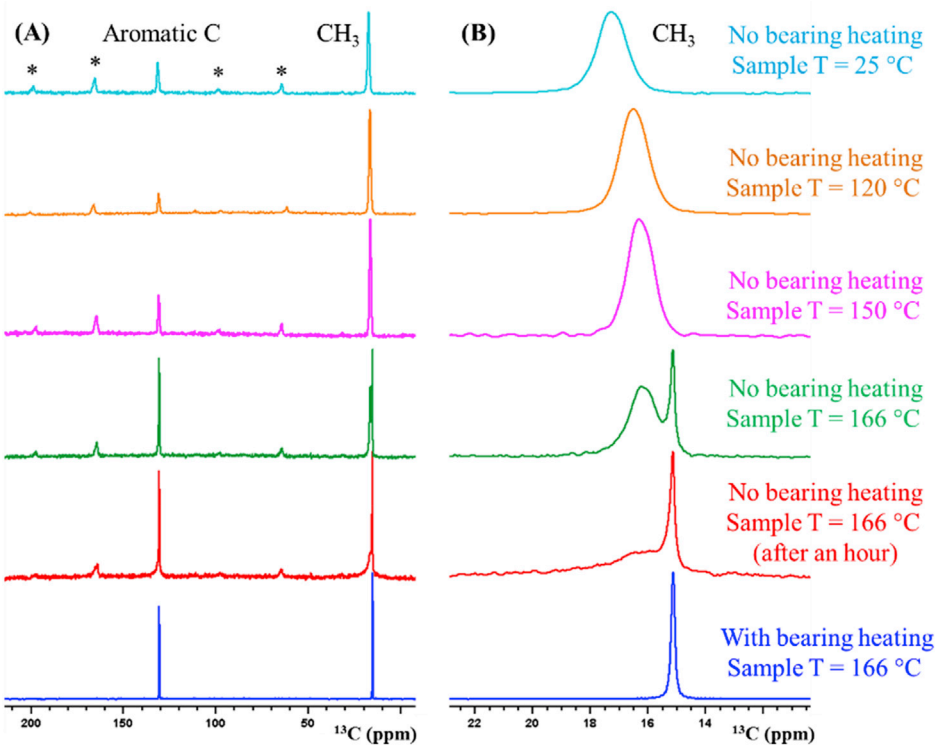

Fig. 5. ^{13}C MAS spectra of HMB at a spinning speed of 5 kHz, with spinning sidebands denoted with *. Solid HMB (the downfield broader peak) and liquid HMB (the upfield sharper peak) coexist for more than an hour at melting temperature with no bearing heating, but all sample inside the rotor turns into liquid phase in 5 min with bearing heating.

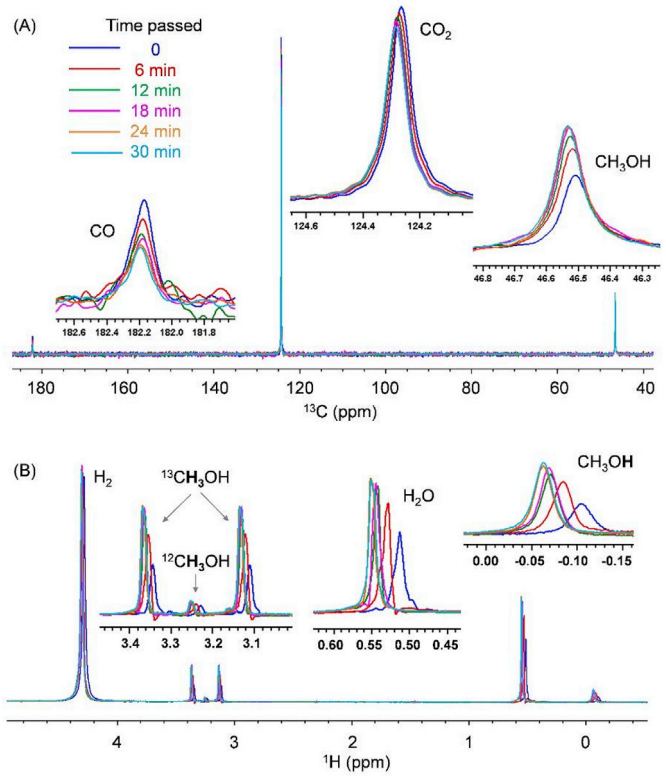

Fig. 6. ^{13}C and ^{1}H MAS NMR spectra collected every 6 min for a mixture of CO_2 and H_2 with a $Cu/ZnO/Al_2O_3$ catalyst at 325 °C under 60 bar 1:2 CO_2:H_2.

concentration of CH_3OH and H_2O quickly increasing and reaching equilibrium within 30 min while the concentration of CO decreases with time. In contrast to what was observed in our previous studies [19] where a significant amount of alkyl carbonate, ammonium formate and alkyl ester were involved in the reaction as the key intermediates in the presence of tertiary amines and alcohols at 120–170 °C, CH_3OH formation at 325 °C occurs via CO and CO_2 hydrogenation routes in the absence of the organic solvents (Eq. 2 and 3). More detailed analysis about the reaction will be the focus of the future studies.

4. Conclusions

A fairly simple probe design is presented that improves the temperature gradient across the sample during VT experiments by heating both the VT and bearing gas streams. Simulation results show diminished temperature gradients while using standard rotors, end caps and drive tips. Lead nitrate experiments show a maximum sample temperature of 350 °C is achievable and the temperature gradients across the sample ΔT is significantly reduced compared to conventional heating, and specifically ΔT can be maintained below 3 °C when sample temperature is under 180 °C. The small temperature gradient is especially important for monitoring in-situ phase transitions, as shown in the ^{13}C NMR spectra of HMB at 166 °C. Finally, we monitor the reaction kinetics of the industrial CH_3OH synthesis using ^{13}C and ^{1}H MAS NMR spectra for a mixture of CO_2 and H_2 with a $Cu/ZnO/Al_2O_3$ catalyst, demonstrating the first NMR spectra at temperatures higher than 250 °C using pressurized rotors. The combination of this high-temperature probe and the high-pressure rotors will allow in-situ NMR studies of a great variety of chemical reactions under these experimental conditions that are out of reach for conventional NMR setup.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ssnmr.2019.06.003.

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