Submission ID #: 61794
Scriptwriter Name: Bridget Colvin
Project Page Link: https://www.jove.com/account/file-uploader?src=18847218

Title: High-Temperature and High-Pressure In situ Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy

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Author Questionnaire

1. Microscopy: Does your protocol require the use of a dissecting or stereomicroscope for performing a complex dissection, microinjection technique, or similar? **N**

2. Software: Does the part of your protocol being filmed demonstrate software usage? **Y**

Videographer: All screen capture files provided, do not film

3. Interview statements: Considering the Covid-19-imposed mask-wearing and social distancing recommendations, which interview statement filming option is the most appropriate for your group? **Please select one**.

☒ Interview Statements are read by JoVE's voiceover talent.

4. Filming location: Will the filming need to take place in multiple locations (greater than walking distance)? **N**

Number of Shots: **0**

Introduction

1. Introductory Interview Statements

REQUIRED:

1.1. **JoVE's Voiceover Talent**: This non-destructive method can be used to analyze complex systems at controlled temperatures and pressures over time and is therefore highly useful for investigating key scientific questions **[1]**.

1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

REQUIRED:

1.2. **JoVE's Voiceover Talent**: These methods allow NMR experiments to be conducted under tightly controlled and specialized conditions to solve problems under environments relevant to the scientific hypothesis being explored **[1]**.

1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

OPTIONAL:

1.3. **JoVE's Voiceover Talent**: The multinuclear nature of NMR makes it suitable for numerous samples. Coupled with this method, it can provide insight into an array of systems, spanning fields such as catalysis, geochemistry, and biology **[1]**.

1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

Protocol

2. Solid Sample Pretreatment

2.1. For pretreatment of the sample solid, weigh approximately twice the mass of the solid sample that is desired for the NMR (N-M-R) experiment **[1]** and place the solid sample into a quartz sample tube plugged with quartz wool **[2]**.

2.1.1. LAB MEDIA: 1_1-takeE: 00:13-00:21
2.1.2. LAB MEDIA: 1_1takeC: 00:15-00:25

2.2. Connect the isolation valves to the tube for the pretreatment of interest **[1-TXT]** and fix the end of the tube onto the gas isolation valve in the open position **[2]**.

2.2.1. LAB MEDIA: 1_2-takeB: 00:04-00:12 **TEXT: *i.e.*, solids treatment, flow, or vacuum system**
2.2.2. LAB MEDIA: 1_2-takeB: 00:45-00:53

2.3. Then place the tube into the cool furnace **[1]** and begin the treatment **[2]**.

2.3.1. LAB MEDIA: 1_2takeB: 01:00-01:19
2.3.2. LAB MEDIA: 1_2takeB: 02:20-02:26

2.4. After the treatment, stop the flow and vacuum **[1]** and turn off the temperature controller **[2]**.

2.4.1. LAB MEDIA: 1_2-vaccum: 01:10-01:20
2.4.2. LAB MEDIA: 1_2-vacuum: 01:44-01:50

2.5. Disconnect the quartz tube from the treatment system **[1]** and quickly seal the sample with the isolation valves to maintain the desired sample environment **[2]**.

2.5.1. LAB MEDIA: 1_9 and 1_10-flow: 00:39-00:49
2.5.2. LAB MEDIA: 1_9 and 1_10-flow: 00:24-00:28

2.6. Then transfer the tubes and closed valves to the antechamber **[1]**.

2.6.1. LAB MEDIA: 1_11-takeA: 00:03-00:18

3. Solid Sample Loading

3.1. To load the samples into an NMR rotor, first place the rotor into the holder to maintain directionality **[1]** and place the sample funnel into the bore of the rotor **[2]**.

3.1.1. LAB MEDIA: 2_1 and 2_2 and 2_3 and 2_4 and 2_5: 00:41-00:48
3.1.2. LAB MEDIA: 2_1 and 2_2 and 2_3 and 2_4 and 2_5: 00:51-00:55

3.2. Remove the isolation valve from the sample tube **[1]** and pour a small quantity of solid material into the funnel **[2]**.

3.2.1. LAB MEDIA: 2_1 and 2_2 and 2_3 and 2_4 and 2_5: 01:01-01:04
3.2.2. LAB MEDIA: 2_1 and 2_2 and 2_3 and 2_4 and 2_5: 01:17-01:28

3.3. Tap the powder down into the funnel, using a packing rod to lightly direct the sample into the rotor as necessary **[1]**.

3.3.1. LAB MEDIA: 2_1 and 2_2 and 2_3 and 2_4 and 2_5: 01:45-01:55

3.4. When the desired quantity of sample has been loaded, a micro syringe can be used to slowly inject the desired volume of a liquid sample of into the center of the rotor **[1]** before placing the cap onto the top of the rotor **[2]** and turning the cap counterclockwise with the rotor cap bit to engage the O-ring between the rotor and cap **[3]**.

3.4.1. LAB MEDIA: 2_8 and 2-9 and 2_10: 00:09-00:20
3.4.2. LAB MEDIA: 2_8 and 2-9 and 2_10: 01:48-01:58
3.4.3. LAB MEDIA: 2_8 and 2-9 and 2_10: 02:01-02:10

4. NMR Rotor Charging

4.1. To charge the NMR rotor with the chemicals of interest, place the sealed rotor onto the rotor stage and tighten the nut by hand to secure the rotor in place **[1-TXT]**.

4.1.1. LAB MEDIA: 3_1 and 3_2 and 3_3: 00:15-00:21 **TEXT: Ensure stage insert compatibility with rotor size**

4.2. Lower the rotor stage into the lower section of the high-pressure exposure device **[1]** and use an Allen wrench to turn one of the screws 90 degrees to secure the rotor stage into the bottom of the exposure device **[2]**.

4.2.1. LAB MEDIA: 3_1 and 3_2 and 3_3: 00:27-00:34
4.2.2. LAB MEDIA: 3_1 and 3_2 and 3_3: 00:39-00:47

4.3. Place the top section of the NMR loading device into and on top of the bottom section

with the NMR cap bit aligned with the top of the cap head of the NMR rotor **[1]**.

4.3.1. LAB MEDIA: 3_4 and 3_5 and 3_6-takeA: 00:03-00:13

4.4. Place the two clamps over the top of the lip where the upper and lower sections of the exposure device meet and latch the clamps into place **[1]**.

4.4.1. LAB MEDIA: 3_4 and 3_5 and 3_6-takeA: 00:14-00:28

4.5. Tighten the six bolts on the top of the upper section of the exposure device to engage the sealing surface between the upper and lower sections **[1]** and connect the thermocouple on the upper section of the NMR exposure device to the gas line inlet and outlets **[2]**.

4.5.1. LAB MEDIA: 3_4 and 3_5 and 3_6-takeA: 00:39-00:49
4.5.2. LAB MEDIA: 3_8-takeA: 00:03-00:10

4.6. Apply vacuum to the system to purge the high pressure loading chamber of ambient gasses **[1]**.

4.6.1. LAB MEDIA: 3_10 and 3_12_1_4: 00:04-00:14

4.7. Open the gas source valves on the high-pressure syringe pump **[1]** and run the program set on the pump while monitoring the real pressure inside of the exposure device **[2]**.

4.7.1. LAB MEDIA: 3_11: 00:13-00:21
4.7.2. LAB MEDIA: 3_12_1_2 and 3_12_1_3: 00:12-00:20

4.8. To open the NMR rotor, rotate the external screw mechanism, which is coupled to the interior NMR cap bit, in the clockwise direction to allow the gas of the desired pressure to enter the NMR rotor and equilibrate **[1]**.

4.8.1. LAB MEDIA: 3_12_1_5 and 3_12_1_7 and 3_12_2_6 and 3_12_2_7 Macro view: 00:06-00:19

4.9. To reseal the NMR rotor, rotate the external screw mechanism counterclockwise **[1]**. A viewing window will assist in determining when the rotor is closed **[2]**.

4.9.1. LAB MEDIA: 3_12_1_5 and 3_12_1_7 and 3_12_2_6 and 3_12_2_7 Macro view: 00:25-00:34
4.9.2. LAB MEDIA: 3_12_1_5 and 3_12_1_7 and 3_12_2_6 and 3_12_2_7: 00:19-00:33

4.10. Then open the exposure device gas outlet valve to slowly depressurize the system **[1]**.

4.10.1. LAB MEDIA: 3_12_1_8: 00:01-00:11

5. Magic Angle Spinning (MAS) NMR Experiment

5.1. To conduct a magic angle spinning NMR experiment, place the NMR rotor into the NMR coil on the NMR probe **[1]** and raise and lock the probe into place in the magnet bore **[1]**.

5.1.1. LAB MEDIA: 4_1 and 4_2: 00:31-00:42
5.1.2. LAB MEDIA: 4_1 and 4_2: 00:48-00:55

5.2. Use the magic angle spinning control box to adjust the sample to the desired rotor spinning rate **[1]** and initiate sample spinning **[2]**.

5.2.1. LAB MEDIA: 4_3-control: 01:26-01:37
5.2.2. LAB MEDIA: 4_3-scopeB: 00:04-00:14

5.3. Use the computer to begin the tuning-match sequence on the desired channel **[1]** and adjust the tuning-match settings on the probe to optimize the probe electronics **[2]**.

5.3.1. SCREEN: 4_4-computer *Video Editor: please speed up*

5.4. Then collect the magic angle spinning NMR data **[1]**.

5.4.1. SCREEN: 4_6 and 4_7 *Video Editor: please speed up*

Results

6. Results: Representative In Situ ^{1}H and ^{13}C MAS NMR Analyses

6.1. In this representative analysis, some insight into the operational reaction mechanism for the conversion of ethanol to butenes can be observed **[1]**.

6.1.1. LAB MEDIA: Figure 4

6.2. The consumption of butyraldehyde **[1]**, coupled with the simultaneous appearance of peaks characteristic of n-butenes **[2]**, suggests that butyraldehyde is an intermediate in the formation of n-butene **[3]**.

6.2.1. LAB MEDIA: Figure 4 *Video Editor: please emphasize Butyraldehyde O+CH- section of data lines*
6.2.2. LAB MEDIA: Figure 4 *Video Editor: please emphasize peaks between Butyraldehyde O+CH- and 1-Butene*
6.2.3. LAB MEDIA: Figure 4 *Video Editor: please emphasize 1- and 2-Butene sections of data lines*

6.3. In situ, high-temperature, high-pressure magic angle spinning NMR can also be used to better understand the evolution of chemical species for biological applications **[1]**.

6.3.1. LAB MEDIA: Figure 5

6.4. For example, as this representative carbon-thirteen magic angle spinning NMR spectrum of vape juice solution shows, parent glycerol is present at 63 and 73 parts per million **[1]**.

6.4.1. LAB MEDIA: Figure 5 *Video Editor: please add/emphasize asterisks*

6.5. As time progresses at 130 degrees Celsius in an oxygen environment, the toxins acrylic acid **[1]** and formic acid with formaldehyde appear at 175 and 164 parts per million, respectively **[2]**.

6.5.1. LAB MEDIA: Figure 5 *Video Editor: please emphasize structure at about 175 ppm*
6.5.2. LAB MEDIA: Figure 5 *Video Editor: please emphasize structure at about 164 ppm*

6.6. The oxidation product carbon dioxide is observed at 125 parts per million **[1]** and, most importantly, even at such low temperatures, acetal-species of formaldehyde **[2]** and acetaldehyde are observed between 50 and 112 parts per million **[3]**.

6.6.1. LAB MEDIA: Figure 5 *Video Editor: please emphasize CO2 text at 125 ppm*
6.6.2. LAB MEDIA: Figure 5 *Video Editor: please emphasize structures at 50 ppm*
6.6.3. LAB MEDIA: Figure 5 *Video Editor: please emphasize structure at 112 ppm*

6.7. The addition of parent glycerol to formaldehyde and acetaldehyde generates new hemiacetal species at 105 and 112 parts per million, which act as aldehyde carriers and can self-interact and dehydrate to generate new acetal species **[1]**.

6.7.1. LAB MEDIA: Figure 5 *Video Editor: please emphasize structures at 105 and 112 ppm*

6.8. Numerous other peaks between 50 and 80 parts per million correspond to the many other chemical environments of the hemiacetals and acetals **[1]**.

6.8.1. LAB MEDIA: Figure 5 *Video Editor: please emphasize peaks/structure at 50 and 80 ppm*

Conclusion

7. Conclusion Interview Statements

7.1. **JoVE's Voiceover Talent**: In addition to working safely, it is important to maintain the environment within the rotor during transfers, particularly when removing the chamber top, as the rotor cap will still be engaged **[1]**.

7.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera (2.5., 2.6., 4.3., 4.10.)

7.2. **JoVE's Voiceover Talent**: Since NMR is non-destructive, additional characterizations, such x-ray diffraction, gas chromatography-mass spectrometry, and x-ray photoelectron spectroscopy, can be pursued, enabling comparison of the NMR results with complementary information on the same sample **[1]**.

7.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

7.3. **JoVE's Voiceover Talent**: These measurements, obtained at elevated temperatures and pressures, have enabled researchers to address challenging problems in a way not previously possible by looking at complex systems under relevant conditions **[1]**.

7.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera