We have been focusing on expanding our high temperature $^1$H CRAMPS capability to a temperature range from 250 °C to 500 °C, using a RF heating technique. As described in the last report, we have constructed another RF channel for RF heating. We also found the proper procedure for plating a platinum coating on both Pyrex and quartz NMR sample tubes for RF heating. To get a better control on the thickness of the platinum coating, we found that dilution of the original platinum suspension (Standard Ceramic Supply, Bright Platinum for Glass #S-2) with a solvent (Hannovia, Gold Essence) is very helpful. Dilution also helps make a more homogeneous layer of coating, which is critical for obtaining high RF heating efficiency. In RF heating experiments, we can now achieve a temperature of 650-700 °C for static samples, using a RF power of about 16W with 80% duty cycle.

For magic-angle spinning (MAS) experiments, we found that the room-temperature driving and bearing gases can significantly reduce the highest temperature achievable for RF heating. For example, for a given RF power setting, the equilibrium temperature for a static sample subject to RF heating was 460 °C, while the temperature for a spinning sample was only about 250 °C, using our VT CRAMPS probe. The temperature difference between a static sample and a spinning sample depends on many factors, including the driving and bearing gas pressures, the spinning system used, and RF power level for RF heating. To compensate the cooling effect caused by the room-temperature driving and bearing gas, we combined the RF
heating with regular hot-gas heating. With 20-Watt RF heating combined with a nominal 250°C hot gas heating, we can achieve a temperature of about 400°C for a spinning sample. The temperature achievable with RF heating certainly depends also on the thermal conductivity and heat capacity of rotor materials. Quartz tubes seem to be better than Pyrex in this respect. Although we have so far used thick-wall sample tubes (5mm O.D., 2.16 mm I.D.) in all our experiments, we expect that thin-wall tubes may be more efficient for RF heating.

Temperature calibration is very important and non-trivial for VT NMR experiments. For RF heating experiments on a spinning sample, the sample temperature is very different from that of its environment and a temperature sensor cannot be attached directly to the sample. A remote IR temperature sensor may be used for detecting the sample temperature, but its accuracy is affected by many factors and it requires a NMR probe specially designed for using this kind of temperature sensor. It would be better to use some NMR parameters of a sample for temperature calibration.

Many compounds have been used for NMR chemical shift thermometry. However, calibration of temperatures beyond 350 °C using ¹H NMR is very challenging. Very few materials that contain hydrogen are thermally stable beyond 350 °C. For solid samples, the ¹H NMR resolution is limited even with multiple-pulse experiments, and the chemical-shift range of ¹H NMR is also limited. Relaxation parameters, especially T₁, may be good for temperature calibration, since the high sensitivity of ¹H NMR makes a relaxation experiment fast enough for the calibration purpose. We have spent quite a lot of time searching for proper materials for high-temperature calibration by ¹H NMR signals. So far, we have not found the right material for this purpose, except for several compounds that can be used for calibrating the temperature at one value, using their melting points.

The multiple-pulses of ¹H CRAMPS experiments are required for obtaining complete chemical information on the structural changes that occur in coal at high temperature. Multiple-pulse experiments coupled with RF heating have never been demonstrated previously. There are quite a few factors that make this combination quite challenging. The platinum coating will reduce the RF power applied to the sample. A compromise in coating thickness must be found to retain enough heating capacity, yet realize a short enough 90 degree pulse length for CRAMPS experiments. The proton power amplifier must have enough dynamic range to deliver low CW
RF power (10-50W) for RF heating and high power (200-600W) RF pulses for the CRAMPS technique. A proper way must be found to check and readjust the tuning of the probe under RF heating condition, in order to minimize phase transients and to maintain accurate pulse widths and phase settings for the RF pulses. To our surprise, one factor that makes this combination extremely difficult is that, as we discovered after numerous experiments, intense RF pulses of CRAMPS destroy the heating capability of the platinum film coated on the NMR sample tubes. It was reported by James Haw’s group that the platinum coating on a ceramic spinner tends to lose its heating capacity after repeated use; the reason was unclear. We have observed the same phenomenon for platinum coatings on Pyrex and quartz NMR tubes. We found that the loss of heating capacity was directly related to applying a series of intense RF pulses (200W or more) to the platinum coating.

A platinum coating that has lost most of its heating capacity may have a very similar appearance to that of the original coating. However, a dramatic change of tuning and matching of the NMR probe with the sample tube placed inside the sample coil can be observed from a RF sweeper. The impedance of the probe with a platinum coated sample tube that has lost its heating capacity is very close to the probe with a uncoated sample tube in it. The resistance per unit length of the coating was also dramatically increased when the heating capacity is lost. The resistance of the film can be easily measured with a multimeter. Based on the resistance per centimeter measured from the coating, we estimated that the thickness of platinum coating is on the order of 0.01 micron.

Intense RF pulses can generate extremely high currents in the film. This may result in extremely high local temperatures that can destroy interconnections between metal particles in the film. Especially for tubes with very thin platinum coating, intense RF pulses can destroy the conductivity of the film completely.

In summary, CRAMPS experiments under RF heating conditions are much more difficult than what we expected. We are currently exploring other ways to solve this problem.

Reference:
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