

EMSL Research and Capability Development Proposals

High Temperature, Large Sample Volume, Constant Flow Magic Angle Spinning NMR Probe for a 11.7 T Magnetic Field for *In Situ* Catalytic Reaction Characterization

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Detailed understanding of the mechanisms involved in a catalytic reaction requires identification of the nature of the active sites and the temporal evolution of reaction intermediates. Although optical methods such as UV-visible and infrared (IR) spectroscopies can be used for some types of reactions, these do not provide the sensitivity or information needed for many complex reactions. For these reactions, especially selective oxidations of alkanes or alcohols, reaction products and intermediates are complex and difficult to identify using a single spectroscopic tool. Nuclear magnetic resonance (NMR) spectroscopy under reaction conditions can contribute to the required analysis provided that some typical problems are circumvented.

Several technological- and technique-related issues had to be addressed in the development of an *in situ* NMR probe. The first prototype probe (Hu et al. 2009)¹ developed in EMSL is based on both magic angle turning (MAT) and magic angle hopping (MAH) strategies. This approach realizes the high spectral resolution associated with traditional magic angle spinning (MAS). Using a method called “discrete magic angle turning,” or DMAT, the sample is rotated back and forth as in a MAH experiment, albeit by less than 360 degrees. In this way, the continuous introduction of reactants and removal of products does not interfere with the mechanics required for the discrete sample rotation. Consequently, precise control over reaction conditions, such as temperature, pressure, flow conditions, and feed composition, are possible, and the reaction mechanisms can be studied *in situ*. The prototype DMAT probe without pressure control has been successfully tested, and the technology will be further developed so that pressure control is realized.

One issue with the DMAT method is that the required measuring time can be relatively long because it is a true two-dimensional NMR technique. A method developed earlier by Hunger and Horvath (1995)² addressed this challenge using constant fast magic angle spinning of several kHz or more. Nitrogen carrier gas loaded with reactants was constantly injected into the bottom of a MAS NMR rotor through an axially placed hole in the rotor cap, which leads into sample volume. The sample is formed into a hollow cylinder to accommodate the injection. The advantage of Hunger and Horvath’s (1995) approach is high NMR sensitivity (because it is essentially an MAS experiment). However, pressure control is impossible, and there are concerns with the inhomogeneous penetration of the reactants inside the catalyst bed due to the use of a hollow, cylinder-shaped sample, e.g., only one opening that is connected to the sample for

¹ Hu J.Z., J.A. Sears, J.H. Kwak, D.W. Hoyt, Y. Wang, and C.H.F. Peden. 2009. “An isotropic chemical shift–chemical shift anisotropic correlation experiment using discrete magic angle turning.” *Journal of Magnetic Resonance* 198(1):105-110. DOI: 10.1016/j.jmr.2009.01.027.

² Hunger M. and T. Horvath. 1995. “A new MAS NMR probe for *in situ* investigations of hydrocarbon conversion on solid catalysts under continuous-flow conditions.” *Journal of the Chemical Society, Chemical Communications* (14):1423-1424. DOI: 10.1039/C39950001423.

both delivering the reactants to the catalysts bed and eluting the products. However, this method is attractive for studying a range of reactions, where reaction is at atmospheric pressure and pressure control is not required.

We have developed a modified *in situ* constant flow (CF) MAS probe of Hunger and Horvath's (1995) type. The MAS rotor system in our design is illustrated in Figure 1. In our modification, the concern with the inhomogeneous penetration of the reactants associated with the original report has been addressed by minimizing the center hole inside the sample volume and using two openings at the opposite sides of the sample rotor—with one opening used for delivering the reactants to the catalyst bed while the other is used for eluting the products. Furthermore, a large sample volume with an outer diameter of 9.5 mm and height of 5 to 10 mm is used to increase the NMR sensitivity so that shorter time scale dynamic processes may be studied. The sensitivity associated with using the large sample volume affords detection using natural ^{13}C abundance compounds as the reactants that have never been achieved previously. To date, we have reached the following operating conditions: sample spinning rate of 3.5 kHz, ^1H and ^{13}C 90-degree pulse width of 8 μs , constant flow control at 1.0 atmospheric pressure, and temperature control up to $\sim 250^\circ\text{C}$. This probe is at its working stage for application by users.

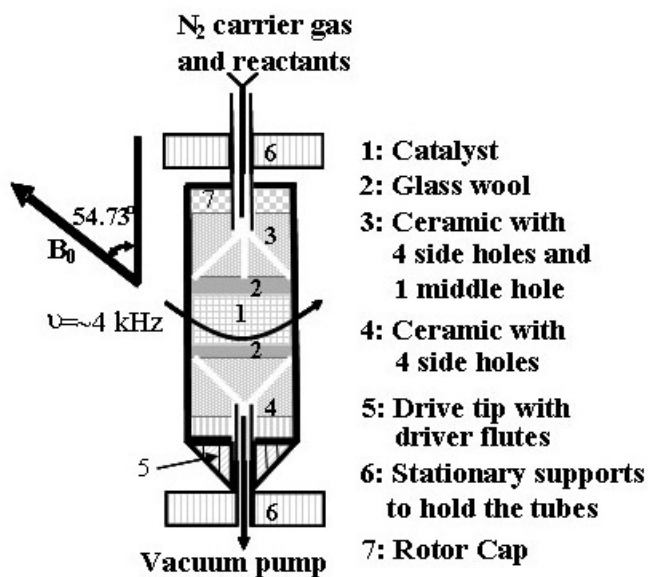


Figure 1. Rotor design for the 500-MHz Constant Flow MAS NMR Probe.

It is expected that the combination of DMAT and CF-MAS approaches will provide a powerful tool for *in situ* investigations. Implementation of the aforementioned *in situ* NMR capabilities will allow the first dynamic studies of the structural transformations of supported polyoxometalate (POM) clusters during treatment and catalysis. In addition, such NMR studies during catalysis will be essential to our mechanistic studies by allowing the dynamic detection of reaction intermediates during chemical transformations of molecules selectively labeled with ^{13}C and ^2H , addressing the type and nature of the catalytic reactions of interest on a wide range of catalyst materials.

Products and Output

New Capability for EMSL Users

The 9.5mm CF-MAS probe on the wide-bore Varian 500-MHz NMR spectrometer is now available for EMSL users through the user proposal system.

Publications

Hu J.Z., J.A. Sears, J.H. Kwak, D.W. Hoyt, Y. Wang, and C.H.F. Peden. 2009. "An isotropic chemical shift–chemical shift anisotropic correlation experiment using discrete magic angle turning." *Journal of Magnetic Resonance* 198(1):105-110. DOI: 10.1016/j.jmr.2009.01.027.

Baer D.R., M.H. Engelhard, A.R. Felmy, J.J. Ford, J.Z. Hu, A.S. Lea, P. Nachimuthu, L. Saraf, J.A. Sears, and S. Thevuthasan. 2009. "New approaches for characterizing sensor and other modern complex materials." *ECS Transactions* 19(6):137-148. DOI: 10.1149/1.3118546.

Presentations

Ford J.J., J.Z. Hu, J.A. Sears, J.H. Kwak, and D.W. Hoyt. 2008. "Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems." presented at the *American Vacuum Society 55th International Symposium & Exhibition*, October 21-23, 2008, Boston, Massachusetts.

Hoyt D.W., J.A. Sears, N.G. Isern, S.D. Burton, J. Ford, D.N. Rommereim, M.J. Froehlke, H.M. Cho, J.Z. Hu, A.S. Lipton, and P.D. Ellis. 2008. "Unique Capabilities at a User Facility to Support the Study of Biosystems/Materials in Solid- and Liquid-State Spectroscopy." abstract submitted to the *Experimental Nuclear Magnetic Resonance Conference (49th ENC)*, March 9-14, 2008, Pacific Grove, California.

Ford J.J., J.Z. Hu, J.A. Sears, J.H. Kwak, and D.W. Hoyt. 2008. "Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems." presented at the *Experimental Nuclear Magnetic Resonance Conference (50th ENC)*, March 29-April 3, 2009, Pacific Grove, California.