RESEARCH NOTE

A High-Resolution Solid-State NMR Probe for *in-Situ* Studies of Heterogeneous Catalysis under Flowing Conditions

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Solid-state nuclear magnetic resonance (SSNMR) constitutes a powerful tool for the investigation of heterogeneous catalysis. Some of the principal advantages include its ability to perform atom-specific studies, to quantitatively identify species in both the gas phase and at the surface, and to measure atomic distances and connectivities. A broad range of studies have been performed which provide important information on reaction mechanisms, transport and diffusion, intermediate formation, and catalyst structure (1). A number of researchers have used *in-situ* methods to observe reactions under realistic catalytic conditions and have made significant progress in understanding fundamental mechanistic details through the identification of long-lived intermediates and products (2–7). One of the current challenges in analyzing catalytic processes is the development of *in-situ* probes that can characterize reactions while under conditions that closely mimic reactor systems prevalent in industrial practice. Currently, the majority of *in-situ* SSNMR experiments are run under static batch conditions, i.e., the catalyst and reactant are loaded outside of the NMR probe in a sealed tube. The sample is then inserted into the NMR probe, spun at the magic angle to improve the spectral resolution, and brought to temperature to initiate the reaction. Spectra are acquired as a function of time to follow the progress of the reaction, while the identification of important intermediates is facilitated by the high resolution conditions afforded by magic angle spinning (MAS). Although simple and effective, this method can suffer from an inability to replenish reactant during the course of the reaction, which may have important effects on the kinetics and mechanism of the reaction (8). In other cases, reaction kinetics and/or pathways may be modified by the presence of high concentrations of intermediates or products which would not accumulate under flowing conditions.

In this communication, we describe a novel approach to the design of high resolution *in-situ* solid-state NMR probes

that provides reactant flow over a sealed sample. Sealed in this case refers to the fact that the sample is isolated from the atmosphere. Until recently, *in-situ* NMR methods that have incorporated flow were limited to static samples (4, 9, 8) and although useful, were unable to produce high-resolution spectra of strongly adsorbed or solid species. Several groups (11–13) have recently introduced probe designs which allow for reactant flow during MAS. These designs are limited, however, by the difficulty of sealing a rotating sample that is turning at approximately 180,000 rpm. Because the sample chambers are not sealed, flow over the catalyst can be challenging, particularly at high pressure, and the effluent gas cannot be collected quantitatively for further analysis. In particular, the interpretation of kinetic data is challenging when unsealed probes are used because the material balances cannot be determined.

Our design, shown in Fig. 1, is based on the incorporation of commercially available Variseal seals (American Variseal Corp., Broomfield, CO) specifically designed to seal rotating shafts. The seals contain a nonmagnetic steel spring that provides a gas-tight connection between the rotor and the housing. The seals can operate over a temperature range from −196 to 300°C and pressures up to 13.8 MPa. Although Variseals provide low friction compared to elastomeric seals, the residual frictional force is still too large to turn the rotor with conventional air-based drive mechanisms. Instead, we use a stepper motor to turn the rotor and make use of three helical aluminum gears to couple the motor to the sample rotor. A number of high-resolution methods are available to acquire the data in a situation where the sample is slowly rotating (14, 15) or hopping in discreet jumps around the magic angle (16, 17). We currently use the magic angle hopping (MAH) pulse sequence designed by Bax and co-workers (16). During the experiment, the rotor hops to three positions spaced 120° apart around the magic angle (54.7°), which produces the desired line narrowing as similarly obtained under MAS conditions. The rotor remains static during the acquisition period, which occurs between a set of three hops. Bax and
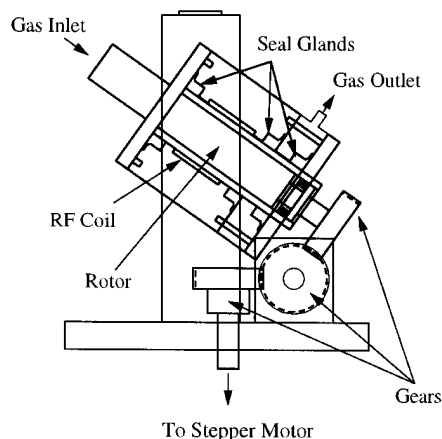
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FIG. 1. Cutaway view of the top portion of the flowing magic angle hopping (FLOWMAH) probe showing the rotor housing, rotor, seal glands, and gear assembly.

co-workers showed that the resulting data could be combined to yield a two-dimensional (2D) spectrum where the projection along ω_1 gives purely isotropic chemical shift (i.e., high-resolution) information and the ω_2 projection contains the full chemical shift anisotropy (CSA) information in the form of powder patterns for the individual carbon atoms. Our design takes advantage of the slow (compared to MAS) turning speeds that are sufficient to perform the MAH experiment and are advantageous for maintaining a gas-tight seal for catalytic studies. Typical hopping rates are 3–5 Hz. As shown in Fig. 1, the seals sit in three glands machined into the rotor housing. This allows a flow path for reactants and products in the experiment and prevents reactant gas from flowing back into the region occupied by the RF coil. A hole on the top of the rotor housing allows for the introduction of heated nitrogen gas to provide temperature control. The sample is contained in a 1.27 cm diameter, 7.6 cm long ceramic rotor which has a small hole toward the bottom of the tube to allow an exit path for effluent gases. The hole is aligned with a shallow channel that has been turned into a brass plate which forms part of the rotor housing. Gas flows through the hole in the rotor, into the channel and through an outlet tube that has been soldered onto the brass plate. Glass wool loaded into the bottom of the rotor centers the sample in the RF coil region. The sample chamber volume is 1.9 cc. Small tubes are used to introduce the reactant gas to the sample and to remove the effluent gas, which can be analyzed downstream by gas chromatography, for example.

In our preliminary experiments, we have studied the absorption of methanol and ethanol on HY zeolite. The zeolite was dehydrated at 140°C for 4 h at 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) and subsequently calcined at 500°C for 5 h. Approximately 400 mg of zeolite powder was loaded into the probe in a dry box, transferred to the NMR magnet,

and kept under a N$_2$ stream to prevent rehydration. Approximately 50 μL each of ^{13}C enriched methanol and C-1 ^{13}C-enriched ethanol (Cambridge Isotope Laboratories) were loaded into a small gas bubbler and delivered to the sample by a flow of N$_2$ at $\sim$2 L min^{-1}. After all the reactant mixture had been transferred, the flow was shut off and the temperature increased to 110°C for 6 h. The probe temperature reached 110° within 10 min. Spectra shown in Fig. 2 allow us to monitor the adsorption process during heating. In Fig. 2a, the Bloch decay spectrum is liquid-like due the effective removal of the CSA by fast molecular motions. The chemical shifts for the two methyl groups are 49.7 ppm for methanol and 58.1 ppm for ethanol (referenced to TMS), in agreement with liquid-state chemical shift values. A spectrum (Fig. 2b) acquired with cross polarization (CP) shows a similar result. CP is effective here evidently because the molecular tumbling is not sufficient to completely average the dipolar couplings to zero. After heating, the two peaks broaden to form one peak with a width of approximately 30 ppm centered around 56 ppm (Figs. 2c–e). We assign this peak to the adsorption of the corresponding alcohols onto the zeolite framework in accordance with previous experimental and theoretical work done on these or similar systems (18, 19). Additional heating did not affect the spectrum. The MAH experiment was then started immediately after heating. Figure 2f shows the resulting spectrum acquired using the MAH experiment and indicates the presence of the two species. It is clear that we can resolve two peaks due to the adsorbed methanol and ethanol species that results from the increased resolution of the experiment.
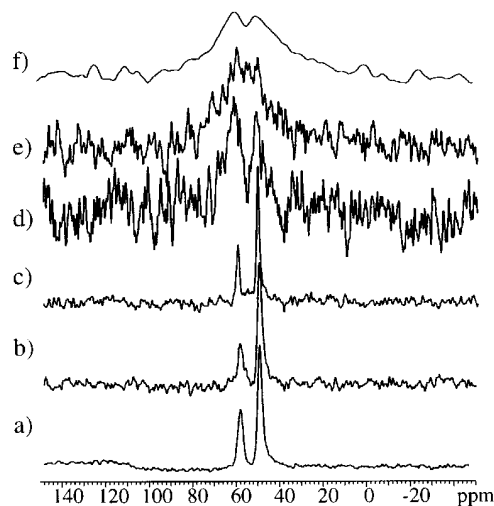

FIG. 2. 75 MHz ^{13}C NMR spectra showing the time course of the reaction of MeOH and EtOH on HY zeolite. (a) Bloch decay spectrum acquired before heating. (b) CP spectrum before heating. (c–e) CP spectra after 20, 40, and 60 min of heating at 110°C. (f) Isotropic 1D projection from the 2D MAH spectrum.
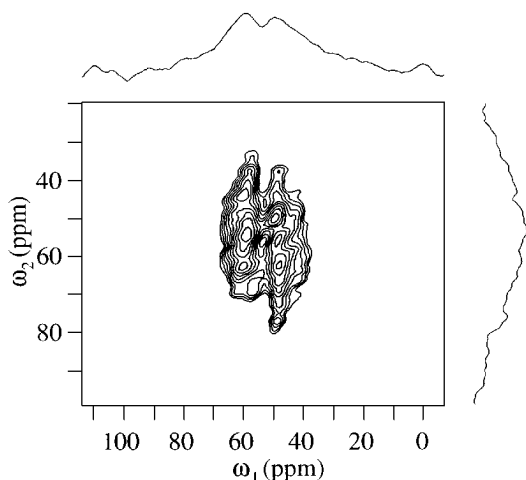
FIG. 3. 2D MAH spectrum of a mixture of MeOH and EtOH coadsorbed on to zeolite HY. 32 t_1 increments were used with an indirect dimension sweep width of 10 kHz. The recycle delay time was 3 s, and 156 transients were collected per increment. The spectrum is presented in absolute value mode. The pulse sequence used in this experiment is described in detail in Ref. (16).

The full 2D MAH spectrum is shown in Fig. 3. The projection of the data along the ω_2 axis contains the sum of the CSA powder patterns and is equivalent to a 1D static spectrum, i.e., without any line narrowing. The ω_1 projection shows the isotropic shifts due to both types of carbon atoms. The linewidth is reduced by more than a factor of 2. The residual line width is mainly the result of adsorption site heterogeneity (18) although the resolution may also be somewhat compromised by the limited number of increments in the 2D experiment. As the ω_2 projection shows, we would be unable to resolve the individual resonances without the line narrowing provided by the MAH pulse sequence.

We conducted leak tests to determine the efficacy of the sealing system. The tests were performed while the rotor was turning to simulate experimental conditions. Acetone was bubbled through with N_2 gas and collected in a liquid nitrogen condenser. We were able to collect 100% of the acetone when the seals were fully assembled. For the initial heated adsorption experiment, we replaced the steel springs in the seals with o-rings because our stepper motor could not reliably generate enough torque to turn the rotor over the course of the 2D experiment. Using the o-ring-loaded seals, we collected 85% of the acetone. With a more powerful stepper motor, we will be able to run the experiment with the fully assembled seals.

In conclusion, we have presented preliminary data from our new flowing, magic angle hopping probe. This probe is designed to perform sealed, high-resolution *in-situ* solid-state NMR experiments under flowing conditions with a full capture of effluent streams. We should emphasize that

in this preliminary experiment we acquired the 2D (i.e., high-resolution) data after stopping the flow (i.e., under quenched conditions) due to the prohibitively long time required to run the MAH experiment (~4 h) with our current sensitivity. The ultimate goal of this work is, of course, to acquire the high-resolution data under flowing conditions. To this end we are working on methods to reduce the experimental time by introducing a series of 180° pulses during acquisition to collapse the CSA into a 1D experiment (20). More advanced MAH experiments will be implemented to further increase resolution (17). By using smaller diameter rotors and seals we will be able to study reactions under high-pressure flowing conditions. Although there are a number of refinements that can be made, we believe this design will further studies of catalytic reactions under industrially relevant conditions.

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