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A new in situ chemical reactor for studying heterogeneous catalysis by NMR: The GRASSHopper

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Abstract

A new device/technique, Gas Reactor And Solid Sample Hopper designated GRASSHopper II, is described as an alternative to magic-angle spinning (MAS) for in situ NMR experiments on reacting heterogeneous systems. It is capable of supporting NMR studies of heterogeneous catalysis in the batch mode, in the flow reactor mode and for measurements of chemical kinetics. This new approach is based on the technique of magic-angle hopping (MAH). Characteristics, advantages, limitations and potential areas of application are described. Preliminary results are shown on the formation, subsequent hydrolysis and then regeneration (via dehydration) of $(C_6H_5)_3C^+$ carbocations in zeolite HY cavities, and on the gas–solid polymerization of ethylene on a Cp_2ZrCl_2/MAO/SiO_2 'supported' catalyst. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclear magnetic resonance (NMR) techniques, especially the solid sample line-narrowing technique called magic-angle spinning (MAS) for averaging line-broadening effects due to chemical shift anistropy (CSA), have been playing important roles in heterogeneous catalysis research [1–13]. With regard to the in situ NMR examination of reacting systems based on heterogeneous catalysis, the following two approaches have been used successfully: (1) *flow* systems, in which a static sample cell serves as an in situ reactor [12]; and (2) *batch* systems, in which the reactants and products are sealed into the NMR sample cell (which can be a MAS rotor) [7–9]. Since industrial processes based on heterogeneous catalysis are often flow processes, it has long been recognized that a worthy technical goal would be to develop an in situ flow reactor in which the line-narrowing benefits of MAS could be achieved.

Achieving MAS line narrowing in a flow reactor has been extremely difficult because of the need to spin the sample/reactor at speeds of at least a few kHz, while simultaneously flowing a gas stream through the sample and maintaining the environmental integrity of the sample (vis-a-vis, e.g. contamination by air and/or other unwanted agents). In spite of these formidable technical difficulties, a few laboratories have developed flow MAS reactors that have yielded promising results [14–16]. Our approach to this problem has been to develop an in situ NMR reactor/cell around a line-narrowing technique, that is, in principle, an alternative to MAS. This approach is 'magic-angle hopping' (MAH), which was introduced and developed in our laboratory several years ago [17,18].

MAH is based on the idea that, for a specific crystallite or spin isochromat in a powdered or amor-

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phous sample, the average of three chemical shifts (δ_a, δ_b, δ_c) corresponding to three orientations that are related to each other by 120° rotations about the MAS axis is the isotropic chemical shift, $\delta_{iso} = (1/3)(\delta_a + \delta_b + \delta_c)$, given by a normal MAS experiment. In the MAH technique, originally developed as a 2D $\delta_{iso}/\delta_{CSA}$ experiment [17], the sample is stationary during three periods (each having duration $t_1/3$) between which it is 'hopped' by 120° about the MAH axis. The hopping is implemented by a suitably controlled step motor or servo motor, which drives a shaft that is coupled via a gear system to the sample cell. The physical arrangement is depicted in cartoon form in Fig. 1.

If one is willing to sacrifice the CSA dimension of the 2D format (which we are willing to do in the interest of time or signal-to-noise (S/N)), by repeatedly refocusing the magnetization during the detection period, then one can have a 1D technique that provides isotropic chemical shifts – an alternative to MAS [18].

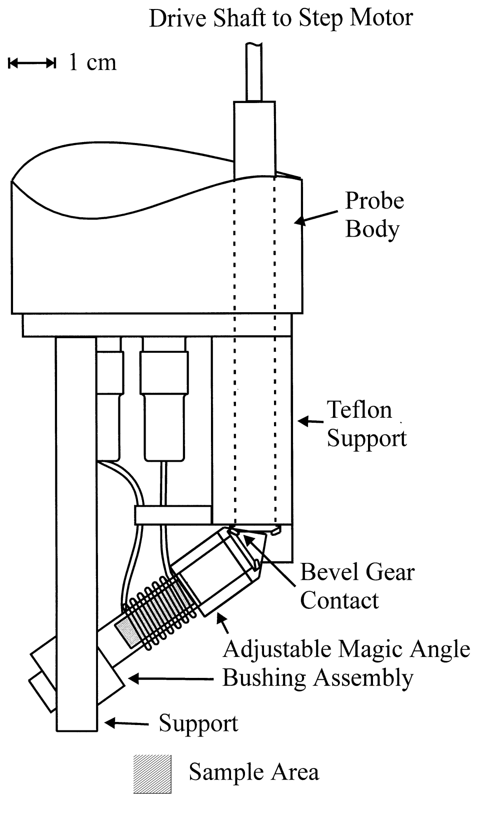

Fig. 1. Basic design of a GRASSHopper II probe.

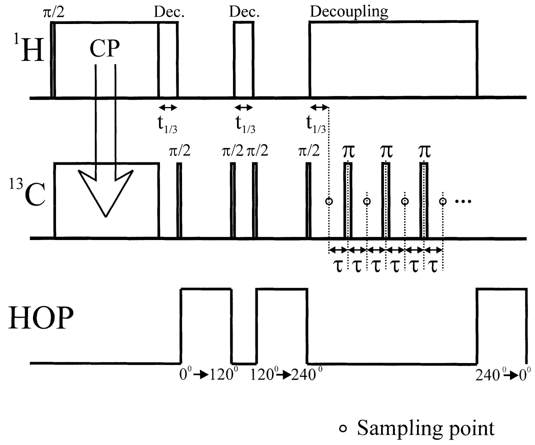

Fig. 2. Timing sequence of the 1D MAH technique, MAH-2.

Fig. 2 shows the timing sequence of a representative refocused 1D MAH technique (MAH-2). The optimization of these approaches is still the subject of continuing research, and the 1D MAH approach at this time still suffers somewhat in sensitivity (per g of sample) relative to the conventional MAS approach. However, even at its present stage of technical development, the MAH offers certain potential advantages that can compensate for this intristic sensitivity comparison; e.g. since there are no spinning sidebands, one can use a very large sample at very high field. In any case, the performance (resolution and sensitivity) of MAH is sufficiently good at this stage of its development that it is useful for a variety of chemical applications. It is the application of the MAH approach for the purpose of in situ examination of reactions proceeding by heterogeneous catalysis that is the subject of this paper. This application or, more specifically, the device adapted for this purpose, is referred to as the GRASSHopper, for Gas Reactor And Solid Sample Hopper.

There are at least two basic reasons why the MAH-GRASSHopper approach is, in principle, well suited to the study of heterogeneous catalysis. First, because one avoids the need to *spin* the sample rapidly, instead having only to *hop* it periodically, one can construct a GRASSHopper cell with gas-sealing bearings about which the sample hops, so one can introduce input/output lines for a flow system. This was the basis of the GRASSHopper I device built and tested in our laboratory during 1992. MacNamara and Raftery have recently described a preliminary 2D MAH ^{13}C spec-

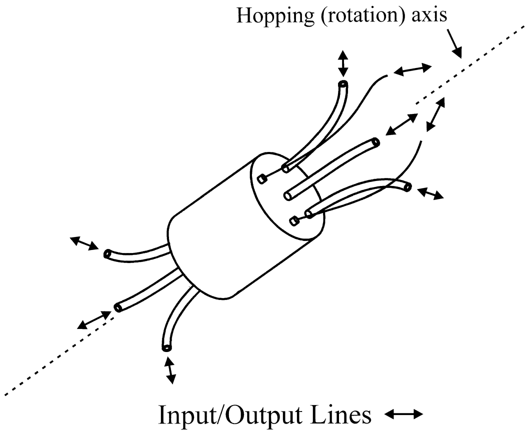

Fig. 3. Cartoon view of a GRASSHopper II cell, showing six 'input/output' lines.

trum obtained with a MAH device analogous to the GRASSHopper I [19].

The second, and *extremely important*, MAH-GRASSHopper advantage, which is the additional basis for the GRASSHopper II, is the fact that, after a complete MAH cycle of three orientations, the MAH device can be re-initialized by rotating *backward* to the initial orientation. For this reason, one can attach a number of input/output lines to the GRASSHopper cell, as long as they are sufficiently flexible to accommodate 240° of rotation of the sample cell about the MAH axis. The GRASSHopper II sample cell is represented in Fig. 3.

2. Experimental

^{13}C-enriched CCl_4 was obtained from Cambridge Isotopes. Natural-abundance ethylene (99.9% purity), hexamethylbenzene and benzene were obtained from Aldrich. The MAO (10% methylalumoxane in toluene), HY zeolite and zirconocene dichloride were obtained from Strem. Silica gel (S676) was obtained from Fisher.

All ^{13}C NMR spectra were obtained at 37.7 MHz, on a 3.5 T spectrometer, using a Chemagnetics CMX-II console and a home-built GRASSHopper probe. A significant improvement of the 120° hopping time (30 ms), relative to that of our earlier design (120 ms) [17,18], was achieved by choosing a more suitable (more expensive) step motor and by ramping the motor speed up and down using a quadratic speed/time profile, which was generated by a C program. In all of the experiments reported here, the 120° hop time (t_{hop}) was 30 ms. A requirement of the MAH technique is that $t_{\text{hop}} \ll T_1^{\text{C}}$. Also, the hopping must be accomplished in such a manner that it does not induce slippage of the particles in a powder sample.

A new 1D (refocused) MAH pulse sequence (Fig. 2), based on an 8-pulse refocusing cycle (to be described in detail elsewhere), each with 100–200 refocusing pulses, was employed in these experiments to obtain balanced refocusing of both the x and y components of ^{13}C magnetization. During the cross-polarization period, a spin-lock field of 41 kHz was used. The ^{1}H decoupling field strength was 45 kHz, and the width of each 180° refocusing pulse was 8.7 μs.

The current performance of the GRASSHopper II system in the 1D MAH experiment is shown in Fig. 4(A), a ^{13}C CP-MAH spectrum of hexamethyl-

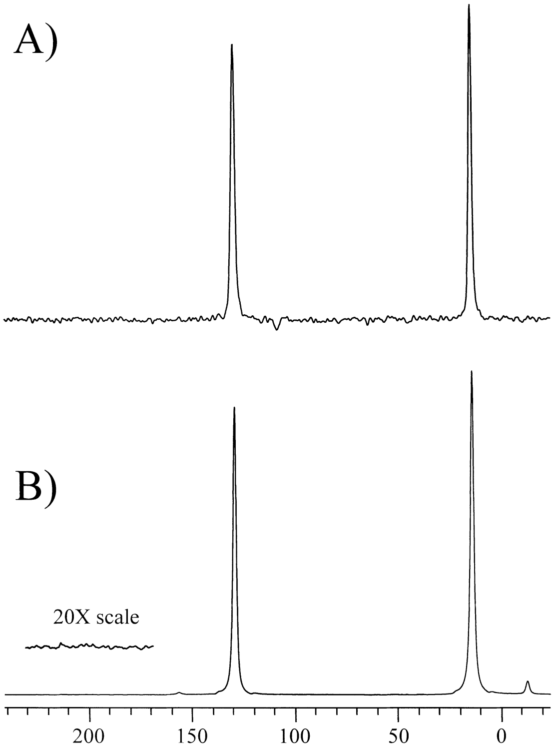

Fig. 4. ^{13}C CP spectra of hexamethylbenzene (HMB), obtained in 20 min (CP contact time = 5.0 ms) by MAH (A) and MAS (B).

benzene (HMB) obtained in 20 min. In a typical 1D MAH experiment, each complete cycle (for a given value of the parameter t_1) consisted, with appropriate phase cycling, of a sequence of eight 'experiments.' For each cycle, 200 values of t_1 were used, with an increment Δt_1 of 100 µs. In principle, these parameters yield a spectral range of 10 kHz and a resolution limit of 50 Hz. For comparison, Fig. 4(B) shows a CP-MAS spectrum of HMB obtained under similar CP conditions, on the same spectrometer in the same period of time.

3. Results

Fig. 5 shows a series of ^{13}C MAH-2 spectra obtained in the GRASSHopper II probe in a 'batch-type' experiment on a 0.727 g sample of zeolite HY (previously dried at 600°C and 10^{-3} Torr for 8 h) that has been loaded with 0.0714 g of $^{13}CCl_4$ (99% label) and 0.192 g of natural-abundance benzene. Initially one sees only weak signals due to natural-abundance C_6H_6 (~130 ppm) and $^{13}CCl_4$ (~96 ppm) because both are probably very mobile and the latter is too distant from protons, and/or too mobile, to yield substantial cross polarization signals. However, with increasing time one sees the growth of signals due to $(C_6H_5)_3\,^{13}C^+$ species (~210 ppm) that are formed in a 'ship-in-bottle' synthesis inside the zeolite cavities via reactions of the Friedel–Crafts type, as represented by the scheme shown in Fig. 6 [20]. It is interesting that as the consumption of $^{13}CCl_4$ proceeds, the 96 ppm CP signal due to residual $^{13}CCl_4$ increases, presumably because the transformations that occur inside the zeolite cavities enhance the proximity of residual $^{13}CCl_4$ carbons to protons and/or decrease the $^{13}CCl_4$ mobility.

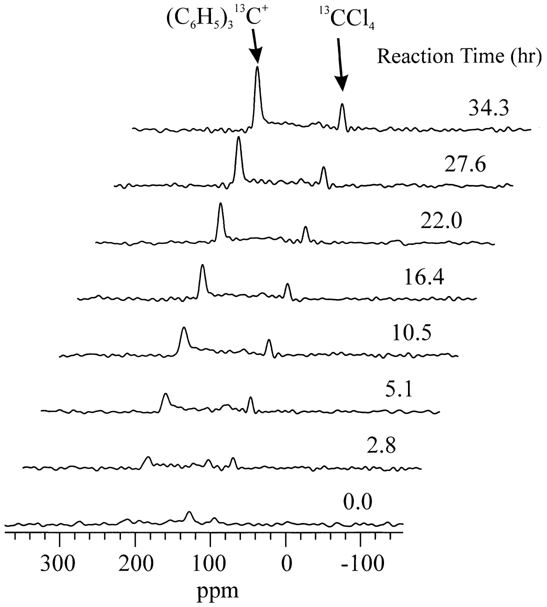

Fig. 5. ^{13}C MAH spectra, each obtained in 30 min by MAH-2 with cross polarization (CP contact time = 1 ms), on a reacting sample of benzene and $^{13}CCl_4$ adsorbed on a dried zeolite HY, as a function of time.

Fig. 7 shows the results of a related flow experiment in which a sample prepared by essentially the process depicted in Fig. 5 (except with complete conversion) was subjected to a flowing gas (air that included 8%

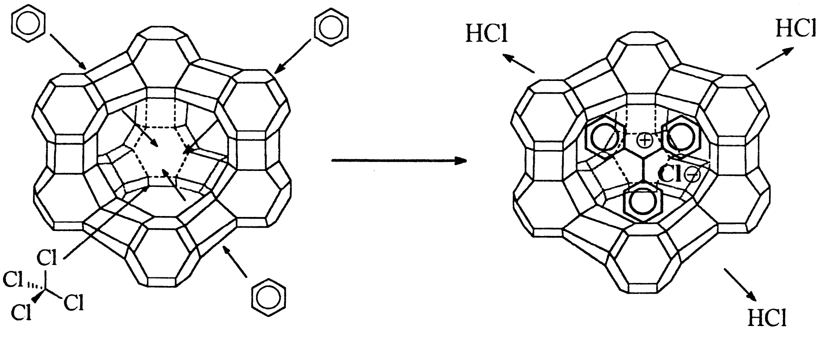

Fig. 6. The 'ship-in-a-bottle' synthesis of $(C_6H_5)_3C^+$, via reactions of the Friedel–Crafts variety, in a HY zeolite cavity.

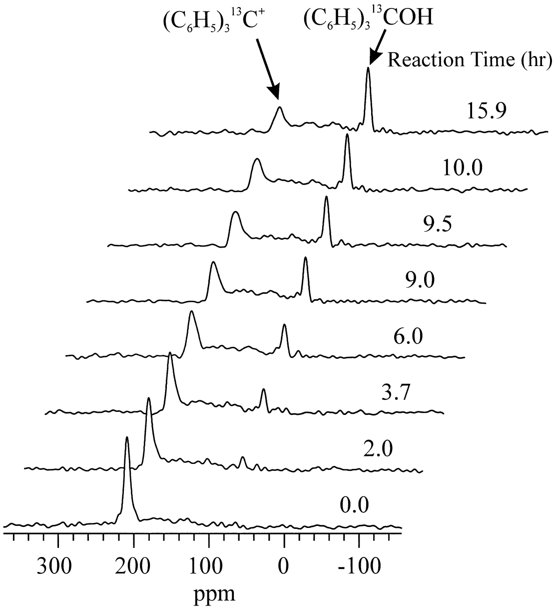

Fig. 7. ^{13}C MAH spectra, each obtained in 30 min by MAH-2 with cross polarization (CP contact time = 1 ms) on a sample that was initially the complete conversion product corresponding to the process depicted in Fig. 5, through which moist air was passed at a constant flow rate, as a function of flow time.

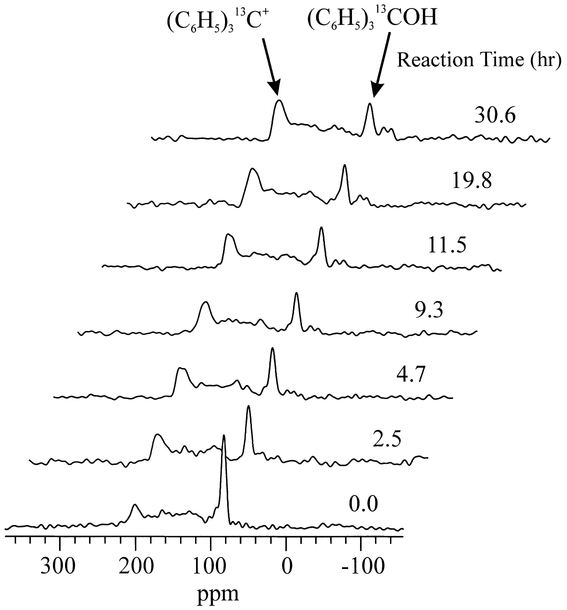

Fig. 8. ^{13}C MAH spectra, each obtained in 30 min by MAH-2 with cross polarization (CP contact time = 1 ms), of a sample that was initially the 15.9 h sample of Fig. 7, subjected to a continuous vacuum at 50°C, as a function of time.

H_2O) with a flow rate of about 75 ml/min. One sees that the $(C_6H_5)_3C^+$ signal at 210 ppm is in time replaced by a signal at 83 ppm due to the product, $(C_6H_5)_3COH$, of hydrolysis of the carbocation by water.

Fig. 8 shows a series of ^{13}C MAH spectra, based on the final sample shown in Fig. 7 (the most hydrolyzed sample) which was subjected to an active vacuum (about 0.1 Torr) at about 55°C. One sees a gradual conversion of the $(C_6H_5)_3COH$ back to $(C_6H_5)_3C^+$ as the sample undergoes dehydration under vacuum.

Fig. 9 shows a series of ^{13}C MAH-2 spectra obtained on a sample consisting of a metallocene-based polymerization catalyst, $Cp_2ZrCl_2/MAO/SiO_2$ (prepared according to the method described by Janiak and Reiger [21]), over which ethylene (diluted 80% by argon) was continuously passed. One sees in Fig. 9 that the polyethylene signal (~30 ppm) builds up with time. About 0.5 g of polyethylene (gravimetrically determined) was generated during the 30 h over which this experiment was conducted.

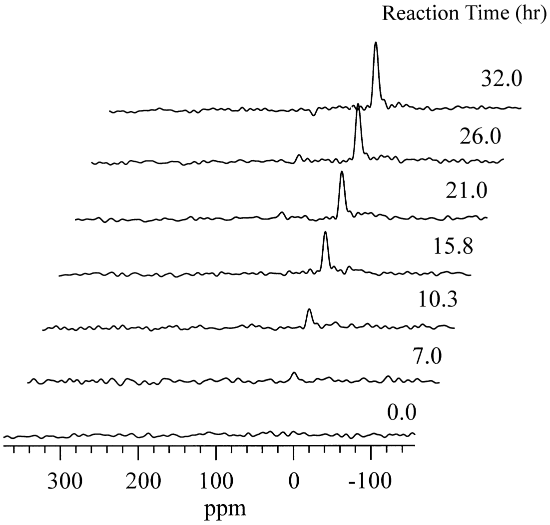

Fig. 9. ^{13}C MAH spectra, each obtained in 30 min by MAH-2 with cross polarization (CP contact time = 0.5 ms), on a sample in which natural-abundance ethylene is passed through a solid $Cp_2ZrCl_2/MAO/SiO_2$ polymerization catalyst, as a function of flow time.

4. Discussion

The results shown in Figs. 5–9 constitute a 'proof of principle' for the GRASSHopper approach, i.e. the GRASSHopper approach is viable as in situ, high-resolution NMR reactor that can be used in either batch or flow modes. Improvements are needed in the sensitivity of the MAH approach, and/or reducing the required experiment time (e.g. more efficient hardware and/or pulse sequence, larger samples, higher B_0 fields, more effective refocusing/data acquisition) and continuing efforts are underway in this direction.

These preliminary results (Fig. 8) also demonstrate that a dynamic vacuum can be applied to the reacting sample in a GRASSHopper cell. This may be important for examining the effects of removing certain agents from a reacting system. It is difficult to imagine how a dynamic vacuum can be applied to a MAS system.

A key capability that can readily be incorporated into the GRASSHopper approach is the 'pulse-quench' strategy that has recently been introduced into MAS NMR approach by Haw and co-workers [22,23]. Using a pulse-quench technique, one can essentially 'suspend in time' the reacting system, so that detailed NMR examination can be carried out. With the GRASSHopper device, one can subsequently 'unquench' the sample suddenly, by rapidly reheating it to the desired reaction temperature (e.g. by laser heating [24] or RF heating [24,25]) for further experiments, including a subsequent series of pulse-quench NMR examinations – without ever removing the sample from the intact GRASSHopper cell. Such techniques are now being explored.

Although not yet demonstrated in this paper, there are other potential advantages of the GRASSHopper approach that we are currently exploiting. One of these advantages is that the input/output lines depicted in Fig. 3 are not limited to just flow or vacuum lines. Within the context of gas lines, they can also be used to control the partial pressures of potentially relevant agents, e.g. O_2, ammonia, volatile reactant or volatile product; this should provide the basis for interesting and valuable kinetics studies of a variety of systems that undergo heterogeneous catalysis. Furthermore, the input/output lines need not be limited to gas lines for introducing reactants or removing products. An input line can also be used to introduce a bolus of a liquid agent for initiating a heterogeneous reaction. We have begun examining this approach in silylation reactions with silylating agents of relatively low volatility. These input/output lines can also equally well be optical fibres, either for introducing light into the sample for photochemical studies, or as interrogation lines for optical spectroscopy. The study of photo-induced decomposition of chlorohydrocarbons, based on this approach, have been initiated. In addition, the input/output lines can be electrical leads for in situ electrochemical studies; experiments based on this approach are planned.

Acknowledgements

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