

NOTE

An *in Situ* NMR Probe with Reagent Flow and Magic Angle Spinning

Two general kinds of NMR experiments are used for *in situ* studies in which the conditions of a catalytic reactor are simulated in the NMR probe (1). Most of the studies reported in the literature have used magic angle spinning (MAS) as a line narrowing technique to provide high resolution spectra of ^{13}C , ^1H , or other nuclei associated with the reactant and/or catalyst. Such an experiment typically requires sealed samples, and although spectra may be acquired at reaction temperature (2-4), reagent flow is not possible. This approach lends itself to spectral simplicity, especially when multiple adsorption sites or complex product distributions prevail. The second general *in situ* experiment, originally due to Reimer and Bell, sacrifices line narrowing by MAS for continuous or pulsed gas flow (5-7). The catalyst sample in such probes is contained in a quartz tube that is sealed to other components in the flow stream, and mechanical rotation is precluded. Such flow probes may be used to simulate the conditions of reagent flow and thus better approximate an actual reactor than previous MAS probes, but the interpretation of spectra dominated by overlapping powder patterns has limited the use of flow probes.

We report a novel *in situ* NMR probe that provides *in situ* MAS spectra with some degree of reagent flow over the catalyst. This design differs significantly from the alternative flow MAS probe recently reported by Hunger and Horvath (8). Figure 1 reports a diagram of our MAS spinning module and MAS rotor designed for flow MAS studies. The spinning module was fabricated from Vespel and is similar to that developed by Otsuka-Chemagnetics. The distinguishing feature of this design is the central chamber in which the sample region of the MAS rotor is bathed in hot or cold nitrogen gas to achieve temperature regulation between ca. 85 and 523 K. The radio frequency transmitter and receiver coil (not shown) are also in this region. This type of spinning module yields small background signals unless composite pulses are used for spatially selective background suppression (9); this was done in all work presented here. The MAS rotor was a 7.5-mm (o.d.) zirconia tube with a Kel-F drive tip and spacers drilled out to provide a pathway for reagent flow (vide infra).

During MAS, the rotor is stabilized by gas bearings top and bottom, and rotation is affected by drive gas directed against the flutes on the drive tip. The gas flow dynamics in essentially all MAS spinning systems creates a suction force

that holds the rotor near the drive stator; bench testing designs similar to Fig. 1 indicated that the pressure differential between the top of the rotor and the stator area was as large as 12 Torr, and this pressure differential was exploited for reagent flow over the catalyst bed.

The following modifications to the MAS rotor were made to provide for gas flow. Concentric holes 2.54 mm in diameter were drilled through the Kel-F endcaps. Three holes 0.78 mm in diameter were drilled through the drive tip, offset 0.89 mm from the center and spaced 120° apart. Catalyst samples were packed not overly tight such that the centripetal force of sample spinning would create a concentric passage over an annular catalyst bed. This catalyst was contained by Torlon disks 16.5 mm in thickness which had seven holes 0.89 mm in diameter drilled to allow passage of gas; small plugs of glass wool were placed over these to contain fine mesh catalysts.

Reagent gas is introduced into the MAS rotor through a Torlon needle 11.5 mm in length with an o.d. of 1.5 mm and i.d. of 0.75 mm. This needle is supported and positioned by a PVC cover plate that is firmly positioned onto the top of the spinning module by four 4-40 screws. As shown in Fig. 1, the needle is positioned inside the upper end cap along the spinning axis. Reagent gas is introduced through this needle onto the upper Torlon disk, and it must either pass through the rotor and over the sample bed, aided by the pressure differential, or flow back out of the top of the rotor where it mixes with nitrogen from the upper bearing and then vents from the module. The reagent gas that traverses the rotor mixes with gas from the drive system and lower bearing and exits the spinning module. All gases venting from the module were piped through the variable temperature stack and exhausted into a fume hood. We have not tested this design with explosive gas mixtures, and we recommend extreme caution when flowing flammable or toxic gases through any NMR probe design. Reagent gas flows were provided by two MKS 1159B mass flow controllers under the control of an MKS 247C. Typically, one of these was used to provide dry nitrogen and the second was directed through a microbubbler in order to equilibrate the nitrogen stream with a volatile organic. This bubbler could hold as little as 0.5 ml of reagent in order to facilitate the handling and introduction of ^{13}C -labeled adsorbates. The reagent gas stream could certainly be heated independently

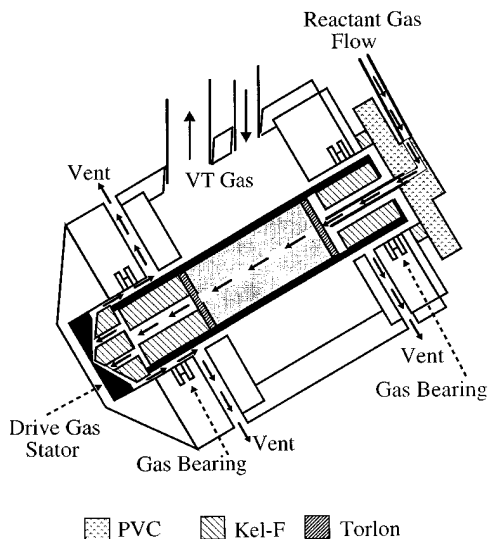


FIG. 1. Cut away view of the flow MAS spinning system and rotor, emphasizing modifications made to allow for reagent flow over the spinning catalyst bed.

to the temperature of the catalyst bed; in practice we kept the flow rate low enough that equilibration occurred on the Torlon disk and glass wool plug, and perturbation of the catalyst temperature was negligible.

Unactivated catalyst sample is packed into a flow rotor and placed into the flow MAS module, and the cover plate is secured with the flow needle inserted into the upper end cap. The spinning gases are turned on, and the rotor self-starts; spinning speeds of 2.0–2.5 kHz are typically used. The catalyst is activated in place by running a low flow of nitrogen through the rotor while heating the variable temperature chamber to 523 K. This process is very efficient as suggested by the ^1H spectra of zeolite HZSM-5 (UOP, Si/Al = 19) in Fig. 2. Prior to activation, the zeolite sample was wet, but the ^1H spectrum obtained at 298 K after 140 min at 523 K shows isotropic resonances at 2.0 ppm (silanols) and 4.7 ppm (Brønsted sites) as well as spinning sidebands; these spectra are similar to those obtained in standard MAS probes for zeolite samples activated off-line in the conventional manner and then loaded with nitrogen (10).

Figure 3 shows that organics can be adsorbed and desorbed from the catalyst bed using the flow MAS system. Benzene- $^{13}\text{C}_6$ (Cambridge Isotopes) was introduced into the nitrogen stream using the bubbler, and quantitative ^{13}C MAS spectra were acquired at 2-min intervals. In all cases studied, the integrated ^{13}C signal rose appreciably in the first 4 min and leveled off after approximately 10 min of exposure. This signal began to decrease immediately after the benzene stream was replaced with a pure nitrogen stream, and the rate of decrease was strongly temperature dependent, as expected for desorption from the catalyst. The ^{13}C MAS spectra from these experiments show very

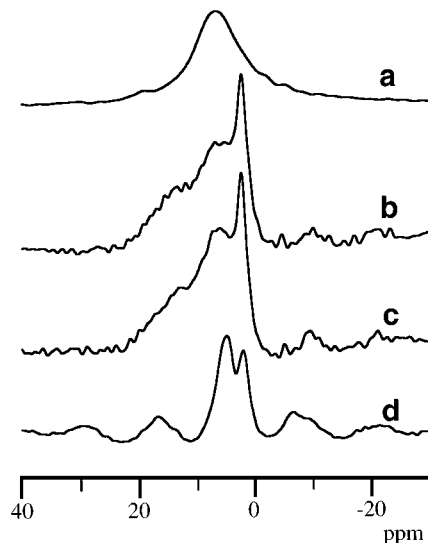


FIG. 2. 200 MHz ^1H NMR spectra showing activation of HZSM-5 in the flow probe. All spectra are the result of 32 signal averages, and nitrogen flowed over the catalyst for the duration of the experiment: (a) wet catalyst at 298 K (10° flip); (b) immediately after raising the temperature to 523 K; (c) after 140 min at 523 K; (d) after cooling to 298 K following heating.

clearly that the benzene was adsorbed into the channel system of the zeolite and exhibited temperature-dependent dynamics (spectra not shown). In particular, the spectra at lower temperatures exhibited appreciable spinning sidebands due to restricted reorientation, and cross-polarization was reasonably efficient; neither would be observed from gas phase benzene. At higher temperatures,

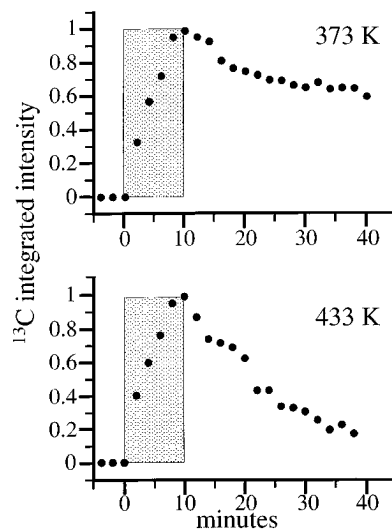


FIG. 3. Demonstration of the adsorption and desorption of benzene from a sample of HZSM-5 undergoing MAS in the flow probe. Nitrogen flow was continuous and was directed through a bubbler containing benzene- $^{13}\text{C}_6$ during the time indicated by shading. Experimental points are normalized integrated ^{13}C intensity for adsorbed benzene.

both the sidebands and the cross-polarization efficiency were attenuated, consistent with the onset of large amplitude reorientation. The ^{13}C MAS spectra obtained in the flow MAS probe were also very similar to those obtained for moderate loadings of benzene on HZSM-5 in a standard MAS probe.

We do not claim that the flow MAS system in Fig. 1 duplicates completely the conditions in a flow catalytic reactor, nor do we claim that this design is the best imaginable *in situ* NMR probe. It does combine some of the advantages of reagent flow and high-resolution MAS operation, and it is hoped that similar designs will find application for studies of processes that are not well modeled by batch reactor conditions but might be improved with some reagent flow.

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