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Applications of a New CAVERN Design to the Study of Reactions on Catalysts Using *in Situ* Solid-State NMR

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A new approach to preparing samples for *in situ* magic-angle spinning (MAS) NMR studies of chemical reactions on catalysts that offers several significant improvements over existing methods is described. This contribution describes the design and use of a second-generation CAVERN apparatus that is easily fabricated from glass and other inexpensive materials. The success rate using this apparatus for preparing reactive catalyst-adsorbate samples for study by MAS NMR is nearly 100%. A second major advantage of this design is that it permits the MAS rotor to be returned to the vacuum line for the adsorption of additional reactants prior to resuming *in situ* NMR study. The use of the second-generation CAVERN apparatus is illustrated by demonstrating the sequential adsorption feature. The observed induction period in the conversion of methanol to gasoline on HZSM-5 is studied by sequential adsorption of methanol. Although the first aliquot of methanol exhibited a long induction period before hydrocarbon synthesis at 523 K, none was observed following adsorption of a second aliquot, showing that the products have an influence on the observed kinetics. © 1992 Academic Press, Inc.

INTRODUCTION

A major emphasis of our research group for the past several years has been the development of solid-state NMR methods for the study of chemical reactions on heterogeneous catalysts. Most of this work has been directed toward *in situ* methodologies in which the reactions are studied while in progress in the NMR probe at some appropriate temperature. Using such methods, we have studied catalytic reactions such as olefin oligomerization (*1, 2*), hydrocarbon cracking (*3*), and the methanol-to-gasoline process that is catalyzed by zeolite HZSM-5 (*4, 5*). All of these studies were carried out using the line-narrowing technique magic-angle spinning (MAS) to obtain high-resolution ^{13}C NMR spectra of the reacting systems.

In situ MAS NMR studies of catalytic reactions face several conflicting sample handling requirements. Most catalyst-adsorbate samples are air or moisture sensitive, and such samples generally require preparation on a vacuum line. The integrity of the sample must be maintained throughout all subsequent steps, including loading into the MAS rotor. This can be especially challenging if the adsorbate is only weakly adsorbed. Furthermore, some of the catalyst-adsorbate systems of interest are reactive at ambient or subambient temperature, and sample preparation and handling must then be carried out at cryogenic temperature to present the NMR experiment with an unreacted sample. Regardless of the preparation and handling requirements, the sample must end up inside an MAS rotor with a sample compartment that is ca. 1 cm in length by 4 to 6 mm in diameter. During spectral acquisition, the rotor spins at a rate of typically 3000 to 10,000 rotations per second while suspended on air bearings. In order to spin properly, the sample must be well balanced.

There are two general approaches to reconciling the conflicting requirements of

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maintaining sample integrity while loading it into an MAS rotor. One approach makes use of glass ampules prepared by flame sealing on the vacuum line (*6–8*). Although glass ampules are desirable when long-term sample storage is required, that approach has several disadvantages. Glass ampules can be difficult to spin, and sample heating during the flame sealing step can also be a concern. The most fundamental limitation of glass ampules, however, is that the adsorption of additional reagents is precluded once the sample is sealed. Recent *in situ* studies in our laboratory have required the adsorption of up to three reactants with NMR characterization following each step. Clearly, glass ampules would not be convenient for such experiments.

The second approach for preparing samples for *in situ* MAS NMR studies makes use of rotor caps with 10 to 15 deformable ridges that create an air-tight seal when the cap is driven into the rotor (*1, 9*). Using rotor designs based on that idea, we developed the CAVERN apparatus for preparing highly reactive catalyst-adsorbate samples for *in situ* MAS NMR studies (*1*). The somewhat contrived acronym originally stood for "cryogenic adsorption vessel enabling rotor nestling." We now use the term CAVERN to designate any device for sealing or unsealing an MAS rotor on a vacuum line. Indeed, the original CAVERN apparatus proved useful for general preparation of samples at room temperature for *in situ* studies at elevated temperatures. Using the CAVERN, adsorption onto the catalyst takes place inside the MAS rotor, which is then sealed prior to removal from the vacuum line and transfer to the NMR probe.

This contribution reports the development of a second-generation CAVERN apparatus and illustrates its use in various ways for *in situ* studies of reactions on heterogeneous catalysts. The new design is considerably easier to fabricate than the original, it is much more reliable, and it allows the sample to be returned to the vacuum line for the adsorption of other reagents prior to additional *in situ* NMR experiments. The induction period in the conversion of methanol to gasoline (*10, 11*) on HZSM-5 is probed to demonstrate the utility of a two-step adsorption protocol. The first aliquot of [^{13}C]methanol was adsorbed using the CAVERN and then converted into hydrocarbons and water in the NMR probe at 523 K. The *in situ* ^{13}C spectra revealed the expected induction period. The rotor was then returned to the CAVERN, and a second aliquot of [^{13}C]methanol was adsorbed. The reaction resumed at 523 K without an induction period, suggesting that the products have an effect on the reaction kinetics.

METHODS

Sample preparation. All results reported in this contribution were obtained on catalyst samples prepared from zeolite HZSM-5 (Si/Al = 38) provided by Union Carbide Corporation. Zeolite samples were activated to a final temperature of 673 K using a multistep activation procedure described elsewhere (*1*). [^{13}C]Methanol (99% ^{13}C) was obtained from Cambridge Isotopes and purified via several freeze–pump–thaw cycles. For each NMR experiment, approximately 0.2–0.3 g of activated catalyst was loaded into a zirconia rotor equipped with a grooved Kel-F cap and spacer (*1, 9*) in a glovebox containing a dry-nitrogen atmosphere. The rotor was placed into the new CAVERN apparatus and attached to the vacuum line, and the CAVERN was evacuated to a pressure of less than 10^{-5} Torr.

Description of the CAVERN. Figure 1 shows a drawing of the new CAVERN apparatus. The main body is constructed from 10-mm-i.d. glass, which is decreased to 8-mm-i.d. glass in the lower section of the CAVERN apparatus to hold a standard Chemagnetics pencil rotor, which has an o.d. of 7.5 mm. Two Teflon stopcocks (Ace Glass) are used in the CAVERN. The first stopcock is located beneath the 18/9 ball joint used to attach the apparatus to the vacuum line. The end of the second stopcock has been modified to firmly hold a $\frac{1}{8}$-in. alu-

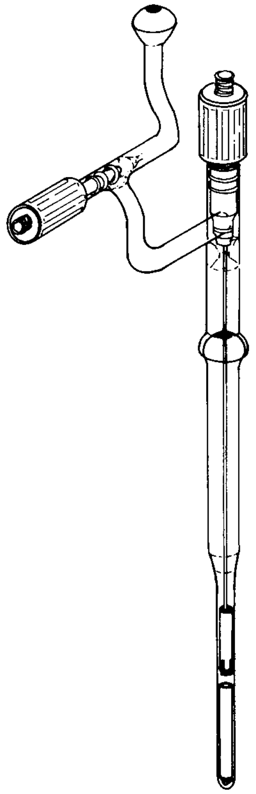

FIG. 1. Diagram of the second-generation CAVERN apparatus used for both capping rotors following adsorption of reactants and the capping and uncapping of rotors to allow the sequential adsorption of reactants onto catalysts. The Kel-F plunger mechanism used for the capping of rotors is shown in this diagram.

minum rod. A metal pin is used to hold the rod in place and to allow easy removal if necessary. Turning the second stopcock extends or retracts the aluminum rod, for capping or uncapping the rotor, respectively. An 18/9 ball and socket joint secured by a metal clip connects the upper and lower sections of the CAVERN. After the rotor is sealed, the lower section is removed and carried to the NMR probe. For experiments on highly reactive samples, the lower section (containing the rotor) is kept in a cryogen before adsorption and up to the moment of transfer to the precooled NMR probe. In our lab this transfer process is accomplished by first cooling the NMR probe to at least 20–30 K below the temperature at which the sample reacts. The lower section of the CAVERN containing the capped rotor is then separated from the vacuuum line and carried in a dewar containing cryogen to the NMR spectrometer. Spinning is stopped, and the probe is lowered to extract the rotor. At this point the probe is below the magnet and is separated from the variable-temperature (VT) accessory, which is mounted on top of the magnet and is no longer cooling the probe. After the rotor is extracted from the probe, the rotor containing the sample is quickly transferred to the probe (less than 5 s) and the probe is immediately raised into the magnet until it mates with the VT accessory, at which point the sample is cooled by the VT flow. Care must be taken to stop the flow of drive and bearing gas during the transfer process, as these gases are at room temperature and can prematurely warm the sample. We have found that the sample is not heated significantly during the transfer process using this protocol.

The close-up views in Fig. 2 illustrate the capping mechanism. Two Kel-F parts are mounted on the end of the aluminum rod (1). One of these, a solid cylinder 5.5 mm in diameter by 4 mm in length (2), is threaded onto the rod and serves as a plunger to drive the cap into place. A hollow Kel-F sleeve (3), which is 7.5 mm o.d., 30 mm long, and has a 6-mm-i.d. hole bored 25 mm in length, slides over the plunger and holds the cap (4, 6 mm o.d., 9 mm long) in place prior to sealing. Four small slits 5 mm in length have been cut into the bottom of the sleeve to allow easy separation of the capped rotor from the sleeve. In the diagram on the left in Fig. 2, the plunger is located inside the Kel-F sleeve and the cap is inserted into the sleeve. During the capping process, the Teflon stopcock is screwed down, forcing the plunger to push the Kel-F cap into the rotor (5). The sleeve aligns the cap into the rotor. After the rotor has been capped, the aluminum rod is retracted, lifting the plunger and sleeve away from the capped rotor (Fig. 2, right diagram). Since the new

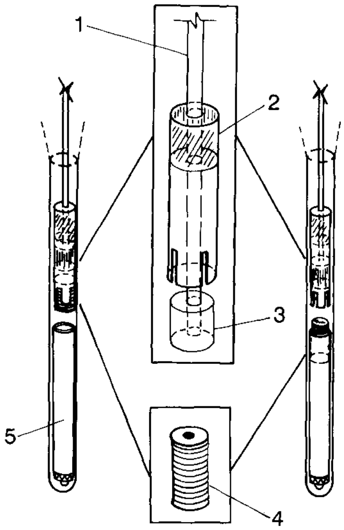

FIG. 2. Expanded views of the lower section of the CAVERN apparatus that depict the capping procedure. The parts are labeled as follows: (1) aluminum rod; (2) Kel-F sleeve; (3) plunger; (4) Kel-F cap; (5) zirconia rotor. The diagrams on the left and right show the lower section of the CAVERN prior to capping and immediately after capping, respectively, and the middle sections show enlarged views of the plunger mechanism and the Kel-F cap used.

design uses a glass body, the capping procedure can usually be observed, contributing to the reliability of the new design.

A different set of attachments is used for uncapping and recapping the rotor when adding additional reagents. In this case, instead of the plunger mechanism and sleeve, the aluminum rod is threaded 4 mm to screw into a hole tapped into the Kel-F rotor cap. A long Kel-F tube (4 mm i.d., 7.5 mm o.d.) fits over the aluminum rod and extends from the top of the inside of the CAVERN to the beginning of the threads of the aluminum rod when the rod is fully extended. The bottom 30 mm of the Kel-F tube has been drilled out to 6.2 mm i.d. to accommodate the rotor cap. The tube is designed so that the Kel-F cap of a sealed zirconia rotor is screwed into the aluminum rod until the rotor is touching the Kel-F tube. The function of these attachments are thus: when the aluminum rod is retracted, it pulls the rotor up against the Kel-F tube. The body of the rotor is held by the tube, but the cap is removed as the rod is fully retracted. Additional adsorbates are then admitted, and the rotor is resealed by extending the rods and reversing the process. The rotor is then returned to the NMR instrument for further *in situ* NMR studies.

NMR spectroscopy. All NMR experiments presented were performed on a modified Chemagnetics CMC-200 spectrometer operating at 50.06 MHz for ^{13}C. A standard Chemagnetics pencil probe equipped with a variable-temperature accessory was used to spin a zirconia rotor at 3.5–4 kHz. The Kel-F caps should (ideally) remain near room temperature with this spinning system design, but our experience has been that some modifications are prudent to prevent melting of the caps close to the sample chamber. The Kel-F caps were shortened, and macor spacers were used to separate the Kel-F caps from the heated sample region. Kel-F was chosen as the material for the caps because it has a high melting point (483 K) and produces no observable ^{13}C signal in our experiments. We have never observed any chemistry that we could attribute to the Kel-F interacting with the sample. Single-pulse excitation (Bloch decay) with proton decoupling (90° pulse width = 4.5 μs, pulse delay = 1 s, 100–400 transients) was used to acquire all spectra shown in this contribution.

RESULTS AND DISCUSSION

Several copies of the second-generation CAVERN apparatus are in use in our laboratory, and we have used these to prepare ca. 100 samples for *in situ* NMR study. The success rate with this apparatus is greater than 95% for adsorptions at room temperature, including sequential adsorptions, and greater than 90% for adsorptions at cryogenic temperatures. For comparison, our success rates with the original CAVERN design (*1*) were ca. 75% for room-temperature adsorptions and ca. 50% for low-temperature adsorptions. Sequential adsorptions were not possible with the pre-

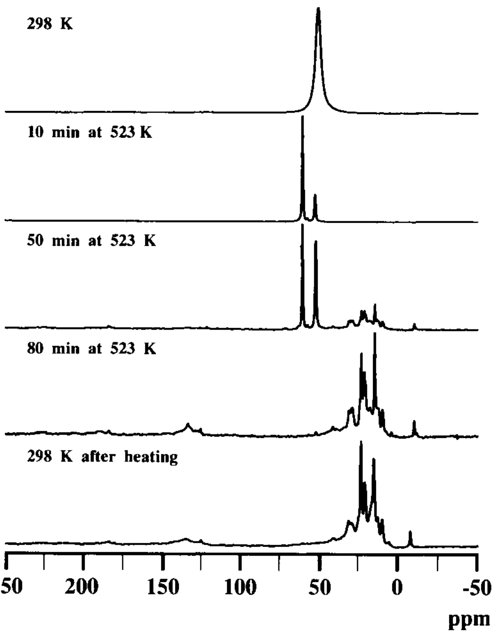

FIG. 3. *In situ* ^{13}C MAS NMR spectra showing the reactions of [^{13}C]methanol on zeolite HZSM-5. Methanol (50 ppm) was converted to dimethyl ether (60 ppm) upon heating to 523 K, and after an induction period of 40 min, hydrocarbons began to form (– 10 to 40 ppm).

vious design. The greater reliability of the new design has had a major impact on productivity, which can easily be appreciated if one considers the cost of custom-synthesized, stable-isotope chemicals and the sometimes lengthy catalyst activation procedures.

The new feature of the second-generation CAVERN apparatus, the sequential addition of reagents, is demonstrated by a study of a representative catalytic system, the conversion of methanol to gasoline on zeolite HZSM-5. The mechanism of the MTG process is controversial (*10, 11*) and we have performed a large number of *in situ* NMR experiments to better understand it (*4, 5*). One characteristic of the MTG reaction is the observation of an induction period prior to hydrocarbon synthesis (*10*). We report here a study of the induction period as an illustration of the sequential adsorption technique using the second-generation CAVERN apparatus. A sample of zeolite HZSM-5 was activated to a temperature of 673 K, and an aliquot of [^{13}C]methanol (1.6 mmol/g catalyst) was adsorbed on the catalyst at room temperature. The rotor was removed from the CAVERN and transferred to the MAS probe. As indicated in Fig. 3, the ^{13}C spectrum at room temperature revealed unreacted methanol at 50 ppm. As was observed previously, dimethyl ether (60 ppm) formed immediately after heating the rotor to 523 K in the NMR probe. After an induction period of 45 min, hydrocarbon synthesis (– 10 to 40 ppm) commenced and was complete after a total reaction time of 75 min. No methanol or dimethyl ether remained at this point, and none was reformed after the sample was cooled back to room temperature.

At this point, the rotor was returned to the CAVERN, which was set up for a sequential

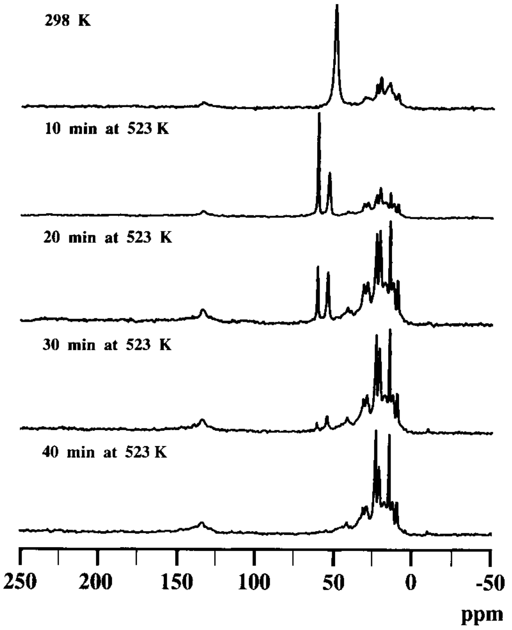

FIG. 4. *In situ* ^{13}C MAS NMR spectra showing the reactions of [^{13}C]methanol and hydrocarbon products on zeolite HZSM-5. A second aliquot of [^{13}C]methanol was sequentially adsorbed on the catalyst sample used in the experiment shown in Fig. 3. The sample temperature was returned to 523 K, and hydrocarbon synthesis resumed without an induction period.

adsorption experiment as described in the Experimental Section. The CAVERN was evacuated, the rotor uncapped, and a second aliquot of [^{13}C]methanol was added. The rotor was recapped, removed from the CAVERN, and returned to the NMR probe where the *in situ* procedure used for Fig. 3 was repeated. Figure 4 shows the result of the second *in situ* experiment. The second aliquot of methanol began to form hydrocarbons almost immediately after the probe equilibrated at 523 K; i.e., no induction period was observed. The methanol reacted at approximately the same rate as before. We conclude that the products of the MTG reaction, hydrocarbons and/or water, are responsible for the observed kinetic effect rather than a structural modification due to prolonged heating.

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