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Shallow-Bed CAVERN Design for *in Situ* Solid-State NMR Studies of Catalytic Reactions

In a recent series of papers, this laboratory has described *in situ* magic-angle spinning (MAS) solid-state NMR studies of the reactions of various adsorbates on zeolites and other catalysts (*1–7*). Most of those studies used one form or another of the CAVERN apparatus (*1*, *2*, *5*) for adsorption of one or more reagents onto a catalyst bed packed into an MAS sample rotor. As originally formulated, the contrived acronym stood for "Cryogenic Adsorption Vessel Enabling Rotor Nestling," reflecting the fact that the earliest work focused on subambient studies of highly reactive systems which necessarily required sample preparation at cryogenic temperatures. As those investigations were extended to include high-temperature studies of less reactive systems, the operational definition of a CAVERN apparatus became any device for manipulating an MAS rotor inside of a vacuum line.

Until recently, all CAVERN experiments in our laboratory were performed with devices based on one of two designs. The first design was difficult to build and awkward in use (*1*). The second design, which remains very useful, was described in a paper in this journal (*5*). A common feature and sometimes disadvantage of both designs is that they result in deep-bed adsorptions and hence, if the adsorbate does not readily diffuse at the temperature of adsorption, there is an inhomogeneous distribution of adsorbate over the sample. In those designs, the catalyst is packed into the MAS rotor before adsorption, and it therefore presents a bed of 20 mm depth to the reagent gas. Since the catalyst is usually tightly packed for maximum sample payload, mass transfer over the dimensions of the catalyst bed may be restricted. Thus deep-bed adsorption can result in samples in which the top of the catalyst bed is nearly saturated with reagent while the bottom of the bed is unexposed. This can complicate the study of phenomena that vary with adsorbate loading. Even with systems in which diffusion is fairly rapid at the temperature of adsorption, the preparation of a sample with a high coverage on a deep catalyst bed can require prolonged exposure times.

In this contribution we report a new CAVERN design which facilitates shallow-bed adsorption of reagents while retaining most of the advantages of the previous design. This design, which is useful for adsorptions at room temperature, also permits the catalyst to be activated under shallow-bed conditions at temperatures up to at least 773 K prior to adsorption. This is a very significant advantage in that it eliminates the need to handle activated catalyst in a glove box in order to transfer it into the MAS rotor. In addition to greatly simplifying and speeding up sample preparation, use of this device precludes any possibility of contamination from the glove box atmosphere.

Operation of this device and the advantages of shallow-bed adsorption for *in situ* MAS NMR experiments are illustrated by ^{133}Cs spectra of samples of zeolite CsZSM-5 loaded with methanol. Following deep-bed adsorption in a previously-described CAVERN device (*5*), two well-resolved ^{133}Cs resonances were observed with chemical shifts corresponding to near-saturation coverage and unexposed catalyst, respectively. Although it was possible to obtain a

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near-uniform loading of methanol by heating the sample in the NMR probe, this would not have been possible with a more reactive adsorbate. In contrast, the ^{133}Cs MAS spectrum of the sample prepared in the shallow-bed CAVERN had the single, very narrow signal characteristic of a uniform loading, and a chemical shift intermediate between the unloaded and saturation values.

Figure 1 shows an "activation CAVERN" (1–5) positioned near the induction tube furnace (6) used for catalyst activation prior to adsorption. Only the central region of the CAVERN is heated during the activation step of an experiment. The connection to the vacuum line is made in the upper right of the photograph. Two Teflon stopcocks (Ace Glass) are used in the CAVERN. One isolates the device from the vacuum line upon completion of adsorption, while to the other stopcock (1) is attached a stainless-steel rod (3-mm diameter) which extends the length of the CAVERN. Rotation of this stopcock either extends or retracts the rod. A 35/25 ball-and-socket joint (2) secured with a metal clamp is used to connect the upper assembly containing the stopcocks to the lower section. The catalyst bed (3) is located in the activation section (ca. 10-cm long, 28-mm o.d.) of the CAVERN. A small bell-shaped piece of glass prevents the catalyst from falling down into the lower section (ca. 20-cm long, 14-mm o.d.). The zirconia MAS rotor (7.5-mm o.d.) is located in a 5-cm length of 10-mm o.d. glass tubing sealed at the bottom of the CAVERN (4). During activation, temperature is measured via a thermocouple wire (5) that is inserted into a glass well. The well extends into the vicinity of the catalyst bed, and is constructed of 3-mm glass tubing. The heater (6) (4-cm i.d.) surrounds the activation chamber and part of the capping section. Quartz wool is used at the top and bottom of the heater to seal the area between the heater and the CAVERN. The temperature of the glass surrounding the MAS rotor does not exceed 310 K during activation at 673 K.

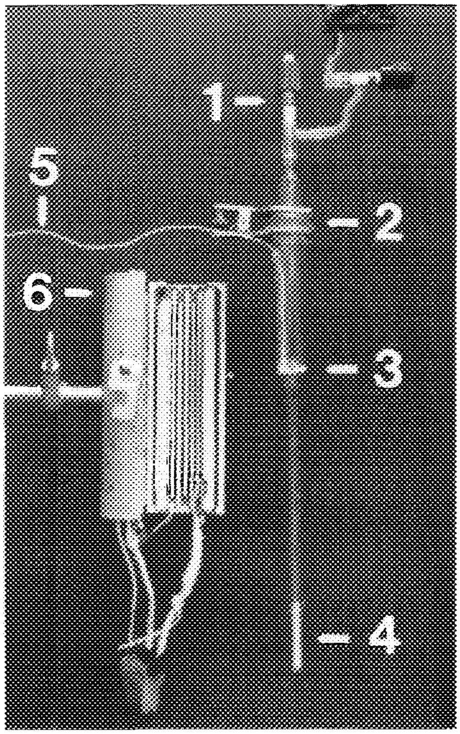

FIG. 1. Photograph of the shallow-bed CAVERN apparatus that permits catalyst activation at high temperature before adsorption at room temperature or above: (1) Teflon stopcock for extending and retracting stainless-steel rod; (2) 35/25 ball-and-socket joint secured with a metal clamp; (3) activation chamber and catalyst bed; (4) Kel-F cap and zirconia MAS rotor; (5) thermocouple wire for monitoring catalyst temperature during activation; and (6) heater used to activate catalyst. The operation of this device is explained in the text.

A close-up view of the inner workings of the activation chamber and capping section of the activation CAVERN is shown in Fig. 2. Two pieces of 3-mm i.d. glass tubing slide over the stainless steel rod (1). The first piece (2), which is 3-cm long and bell-shaped at one end, sits flush with the bottom of the activation chamber and serves as a trap door to prevent the catalyst from falling into the rotor during activation. The second piece of glass tubing (3) is normally the length of the capping section, but has been shortened by ca. 3 cm to aid the reader in distinguishing it from metal rod and trap door. This piece sits against the Kel-F cap (*8*) (4) and the trap door (2). After the reac-

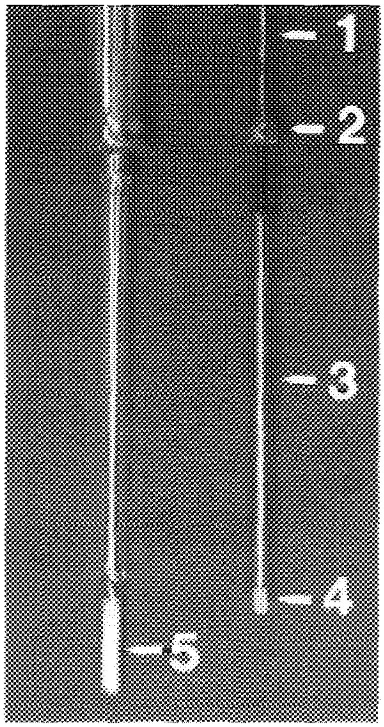

FIG. 2. An enlarged view of the internal components of the activation CAVERN: (1) stainless-steel rod; (2) bell-shaped glass trap door to prevent catalyst from falling into rotor during activation; (3) glass tubing that lifts trap door when the rod is retracted; (4) Kel-F cap; and (5) zirconia MAS rotor.

tant has been adsorbed onto the catalyst, the rod (1) is retracted, and the glass tubing (3) raises the trap door (2) above the bottom of the activation chamber and allows the catalyst to fall into the rotor (5). The rotor is secured in the bottom of the CAVERN by a Kel-F ring which also serves to guide the catalyst into the rotor. After the trap door is raised, the CAVERN is gently tapped if necessary to encourage any remaining catalyst to drop. The rotor is sealed by turning the Teflon stopcock (Fig. 1, (1)), which extends the metal rod and forces the grooved Kel-F cap into the rotor. This sealing mechanism is essentially identical to that described in the design of the deep-bed CAVERN as well as elsewhere. Because the bearing gas streams are kept near room temperature in the Chemagnetics "pencil module" probe design, this Kel-F seal is effective up to a temperature of 523 K. In our experience, these seals do not leak, except that after prolonged use at 523 K, the Kel-F can shrink when cooled back to 298 K.

Zeolite HZSM-5 (Si/Al = 20) was obtained from UOP Corp. and ion exchanged three times with 1 M NH_4Cl (30 ml per g zeolite) for 24 h at 298 K to generate the ammonium form. The procedure was repeated with 1 *M* CsCl (Aldrich) to obtain CsZSM-5. The catalyst was activated to 673 K using a multistep activation procedure described previously (*1*).

All ^{133}Cs NMR spectra were acquired at 47.2 MHz on a Chemagnetics CMX-360 spectrometer equipped with an Oxford wide bore 8.45-Tesla magnet. ^{133}Cs chemical shifts were referenced externally to 0.5 M CsCl aqueous solution. Single-pulse excitation with proton decoupling was used to obtain all spectra shown (300 transients, 1-s repetition delay, 5.6-μs 90° pulse width).

Several copies of the activation CAVERN (Fig. 1) have been in use for several months. The success rate with this device is nearly 100%. The elimination of the need to pack activated catalyst into the MAS rotor in a glove box has proven to be a major advantage of this device both in terms of time savings and confidence in sample integrity. This design has all of the advantages of the deep-bed CAVERN previously reported in this journal (5), with the exception that glove box manipulations would be required in order to return the sample to a CAVERN for a second shallow-bed reagent addition following *in situ* study. Alternatively, a deep-bed CAVERN could be used for further reagent addition without exposing the sample to the glove box.

The problem of shallow-bed vs deep-bed adsorptions, and the solution provided by the activation CAVERN are illustrated by the ^{133}Cs MAS spectra in Fig. 3. In the course of some unrelated work on the interactions of alkali metal cations in zeolites with adsorbates, it was noted that the chemical shift of ^{133}Cs in CsZSM-5 was

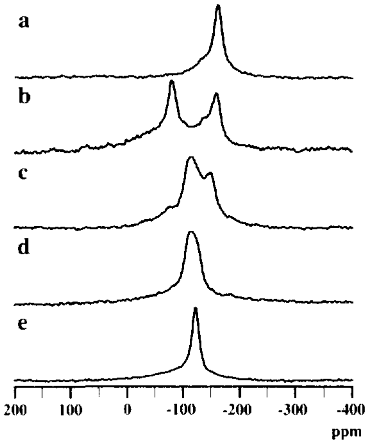

FIG. 3. ^{133}Cs MAS NMR spectra of zeolite CsZSM-5 comparing the effects of sample preparation using a deep-bed CAVERN and a shallow-bed CAVERN: (a) zeolite without adsorbate; (b) zeolite after deep-bed adsorption of methanol at 298 K; (c) the above sample after heating at 423 K for 15 min; (d) after 30 min at 423 K; and (e) a second sample prepared by shallow-bed adsorption using the activation CAVERN. See text for details.

strongly dependent on adsorbate loading. Figure 3a shows the spectrum obtained in the absence of adsorbate: 0.63 mmol of methanol/g catalyst was adsorbed at 298 K using the deep-bed cavern design, and the ^{133}Cs MAS spectrum in Figure 3b was acquired. This spectrum clearly reveals a bimodal sample loading; about one-half of the zeolite exhibited a chemical shift identical to that of the unexposed sample, while the remainder showed a resonance at a position characteristic of near-saturation coverage of methanol. The methanol/CsZSM-5 system is relatively unreactive, and it was possible to obtain a more homogeneous adsorbate loading by gentle heating in the NMR probe. Figure 3c shows the spectrum obtained after 15 min at 433 K, and Fig. 3d shows the result after 30 min at that temperature. These results show that the methanol slowly diffuses through the catalyst bed at elevated temperature, and the uniformity of the adsorbate loading is reflected in the spectral profile.

A second sample was prepared in an identical manner except that the activation CAVERN was used. The ^{133}Cs MAS spectrum of that sample obtained without any sample heating is reported in Fig. 3e. This spectrum clearly shows that a very homogeneous adsorbate loading is achieved with the shallow-bed CAVERN.

The methanol/CsZSM-5 system is convenient for demonstrating the difference between shallow- and deep-bed adsorptions. A more general test of whether or not any given system has nonuniform distributions of adsorbate would be to make use of ^{129}Xe spectroscopy (*9*).

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ERIC J. MUNSON
DAVID K. MURRAY
JAMES F. HAW[1]

Department of Chemistry
Texas A&M University
College Station, Texas 77843

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[1] To whom correspondence should be addressed.