^{13}C NMR Observation of the Triphenylmethyl Cation Imprisoned inside the Zeolite HY Supercage

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The adsorption of triphenylmethyl cation precursors, $(C_6H_5)_3CX$ (X = Cl, OH, H), on amorphous solid catalyst surfaces has been investigated by such spectroscopic methods as UV,[1] IR,[2] and NMR,[3−5] which have shown that a cationic species, $(C_6H_5)_3C^+$, can be formed. High-resolution solid-state ^{13}C NMR,[6] based on the techniques of magic-angle spinning (MAS) and high-power dipolar decoupling,[7] often combined with cross-polarization (CP),[8] has recently figured prominently among the host of investigative methods used in solid-adsorbent catalyst research.[3−5,9,10]

An approach that has attracted our attention recently explores the possibility of generating the triphenylmethyl cation in the supercage of zeolite HY, which has uniform intracrystalline pore networks that provide a favorable microenvironment for trapping ionic intermediates. It is well known[11] that the framework structure of zeolite Y, which is the basis for some of the most important catalysts used in petroleum processing, consists of a three-dimensional array of fairly large sorption supercages, each of which can be approximated by a sphere with a diameter of about 12 Å. The openings into the supercage are formed by 24-membered $(Si-O)_{12}$ rings having a diameter of 7.4 Å. According to molecular modeling calculations,[12] the triphenylmethyl cation has a diameter of about 9 Å. Hence, the three-dimensional supercage structure is perhaps large enough to admit, via fluctuating geometrical distortions, one guest like the triphenylmethyl cation or a simple precursor, but the 7.4 Å openings are still somewhat too small for facile cation diffusion.

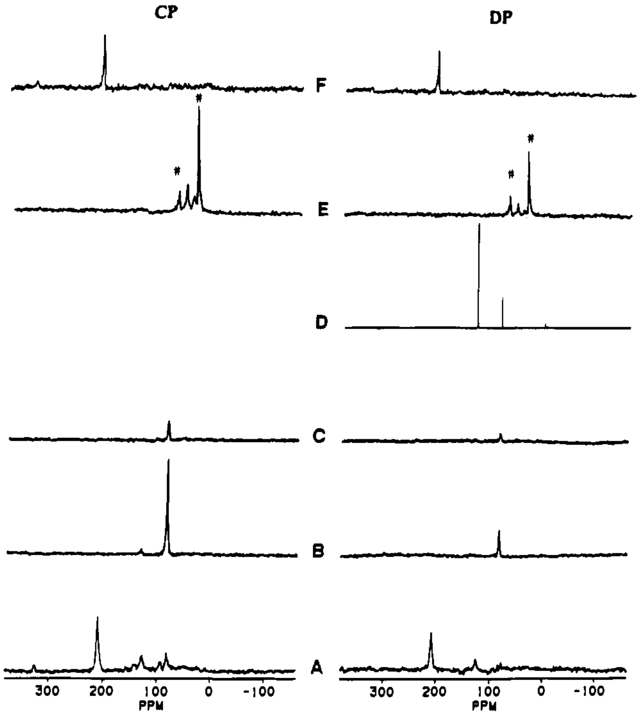

Figure 1. ^{13}C MAS NMR spectra of the products of reaction of $(C_6H_5)_3{}^{13}CCl$ with HY and related samples. Both CP and DP spectra are shown. (A) $(C_6H_5)_3{}^{13}CCl$ mixed with preheated HY; (B) sample 1A open to ambient moisture; (C) solid residue of sample 1B washed with C_6D_6; (D) liquid extract from C_6D_6 extraction of sample 1B (75.47 MHz); (E) product of reaction of sample 1A with $LiAl[OC(CH_3)_3]_3H$ (peaks marked with # at top correspond to the signals from the reducing agent); (F) product of reaction of $(C_6H_5)_3{}^{13}CCl$ with solid $AlCl_3$.

Figure 1A shows ^{13}C MAS spectra obtained by both CP and DP (direct polarization, i.e., via direct ^{13}C spin−lattice relaxation) techniques[13] on a sample prepared by reaction of $(C_6H_5)_3{}^{13}CCl$ with pretreated zeolite HY.[14,15] Both the CP-MAS and DP-MAS spectra show a characteristic $(C_6H_5)_3{}^{13}C^+$ peak at 210 ppm. This chemical shift value is in good agreement with that obtained previously on solid surfaces,[3−5] in the liquid phase in superacid media,[16] and in reaction with solid $AlCl_3$ (Figure 1F). To examine the structural environment of the triphenylmethyl cation, e.g., whether it is imprisoned inside the HY supercage, the sample represented in Figure 1A was subjected to a series of interrogating treatments.

Figure 1B shows the ^{13}C spectra obtained from the powder produced when the sample of Figure 1A was exposed to atmospheric moisture; in these spectra the 210 ppm peak is missing, and the dominant peak is at 82 ppm, which is identified with $(C_6H_5)_3{}^{13}COH$, formed by reaction of the cation with water in air. After the spectrum of Figure 1B was obtained, the sample was subjected to extraction by deuterated benzene (C_6D_6), using a Soxhlet extractor, for 24 h. The resulting solid residue was stripped of solvent under vacuum, yielding a solid for which the ^{13}C MAS spectra, shown in Figure 1C, indicate that most of the $(C_6H_5)_3{}^{13}COH$ can be washed out by C_6D_6. The C_6D_6 extract was analyzed by liquid−solution ^{13}C NMR (Figure 1D), and the only nonsolvent component detected was triphenylmethanol. These results imply that the $(C_6H_5)_3{}^{13}C^+$ cation formed from $(C_6H_5)_3{}^{13}CCl$ is not imprisoned in the zeolite supercage and suggest the possibility that $(C_6H_5)_3{}^{13}CCl$ or $(C_6H_5)_3{}^{13}C^+$ may be unable to pass into or out of the HY supercage through the 7.4 Å openings.

To produce a cation that is obviously trapped inside the supercages, we tried to prepare $(C_6H_5)_3{}^{13}C^+$ directly inside the cavity by a so-called "ship-in-a-bottle synthesis".[17] In this case, $^{13}CCl_4$ and benzene were used as reactants in a reaction of the

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(13) All solid-state ^{13}C MAS NMR spectra shown were obtained at 22.71 MHz at room temperature on a Chemagnetics M-90S spectrometer. Kel-F rotors were used at a spinning speed of about 2.5 kHz. For CP experiments: ^{1}H decoupling, 50 kHz; CP contact time, 2 ms; delay between scans, 1 s. For DP experiments: a 45° pulse of 2.5 ms length, with 50 kHz ^{1}H decoupling; repetition time, 5 s.

(14) Zeolite HY was generated from NH_4Y (Strem Chemical, Inc., Si/Al = 2.5) by (i) first slowly heating the HN_4Y to 600 °C in 1 °C/min increments, (ii) maintaining that temperature for 10 h, and then (iii) gradually cooling back to room temperature; all steps at a pressure less than 10^{-3} Torr.

(15) A 150 mg portion of $(C_6H_5)_3{}^{13}CCl$ and a 1.0 g portion of the activated HY were weighed out in a 25 mL flask in a dry glovebox. A 4 mL portion of sodium-dried benzene was then transferred into the flask. The resulting mixture was stirred for 5−6 h under N_2 protection; after removal of the benzene solvent under vacuum at 10^{-3} Torr, the resulting residual solid appeared yellow in color. The solid sample was packed into MAS rotors in a glovebox.

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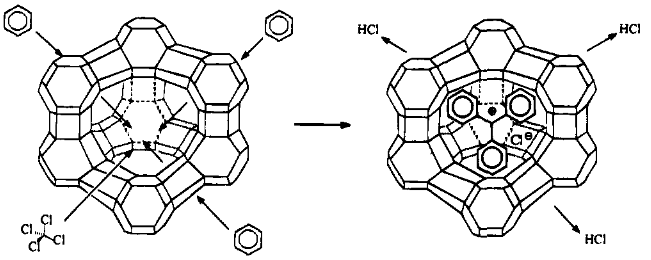

Figure 2. "Ship-in-a-bottle" synthesis of $(C_6H_5)_3{}^{13}C^+$ from $^{13}CCl_4$ and benzene inside the HY supercage.

Friedel–Crafts type.[18] Since both reactants are small enough to enter the supercages through the 7.4 Å openings, the acid sites in HY can play a catalytic role, and one hopes that the Friedel–Crafts reaction would occur inside the supercage, generating caged $(C_6H_5)_3{}^{13}C^+$ as a major product (Figure 2).

Figure 3A,B shows ^{13}C MAS spectra of individual mixtures of $^{13}CCl_4$ (Figure 3A) with preheated HY and benzene (Figure 3B) with preheated HY. The spectra show that both species are just physically adsorbed on HY; no significant chemical interactions were detected. However, when *both* $^{13}CCl_4$ and benzene were added together to HY, the resulting sample produced the spectra shown in Figure 3C, which display the anticipated signal at 212 ppm.[19] When the sample represented in Figure 3C was opened to air, the resulting moisture-contacted solid produced the ^{13}C MAS NMR spectra shown in Figure 3D, which display the dominant $(C_6H_5)_3{}^{13}COH$ peak. The residual solid generated by C_6D_6 Soxhlet extraction of the sample of Figure 3D produced the spectra in Figure 3E, which show that almost all of the triphenylmethanol represented in Figure 3D still remains in the extracted zeolite. The liquid–sample ^{13}C spectrum of the C_6D_6 extract (Figure 3F) shows no evidence of triphenylmethanol in the liquid phase after exhaustive extraction.

To explore further the $(C_6H_5)_3{}^{13}C^+$ cation's location and accessibility, we tried using an organic hydride donor to react with cations prepared by each of the two different pathways represented above. Lithium tri-*tert*-butoxyaluminum hydride, $LiAl[OC(CH_3)_3]_3H$, was chosen for reducing $(C_6H_5)_3{}^{13}C^+$ to $(C_6H_5)_3{}^{13}CH$.[20] Figure 1E shows the ^{13}C MAS spectra obtained for the product of reaction of $LiAl[OC(CH_3)_3]_3H$ with the carbocation sample prepared by mixing $(C_6H_5)_3{}^{13}CCl$ with HY; in these spectra one can see that the carbocation signal at 210 ppm is gone and a new peak corresponding to $(C_6H_5)_3{}^{13}CH$ has appeared at 56 ppm. Figure 3G shows the ^{13}C MAS spectra obtained on the product of reaction between the hydride and the carbocation sample prepared by the $^{13}CCl_4/C_6H_6/HY$ route. In contrast to Figure 1E, Figure 3G shows that much of the original carbocation signal is still present, and the $(C_6H_5)_3{}^{13}CH$ peak is very small. These results indicate that the bulky reagent, $LiAl[OC(CH_3)_3]_3H$, cannot easily access the carbocations synthesized from $^{13}CCl_4/C_6H_6/HY$, which are apparently formed and largely remain inside the zeolite cavity.

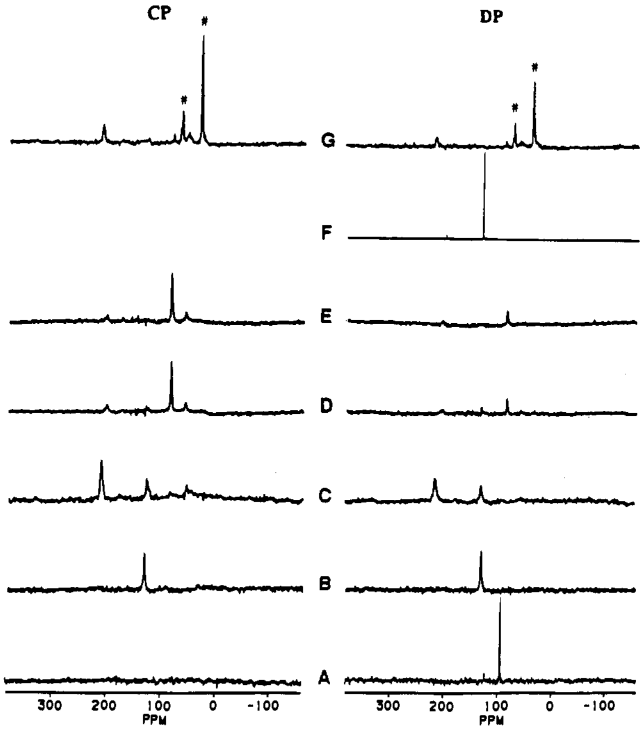

Figure 3. ^{13}C MAS NMR spectra of the reaction product of $^{13}CCl_4$ with benzene in HY and related samples. Both CP and DP spectra are shown. (A) $^{13}CCl_4$ mixed with preheated HY; (B) benzene mixed with preheated HY; (C) $^{13}CCl_4$ and benzene mixed with preheated HY; (D) sample 3C exposed to ambient moisture; (E) solid residue of sample 3D washed with C_6D_6; (F) liquid extract from C_6D_6 extraction of sample 3D (75.47 MHz); (G) product of reaction of sample 3C with $LiAl[OC(CH_3)_3]_3H$ (peaks marked with # at top correspond to the signals from the reducing agent).

In summary, we have described an example of generating a bulky, moderately unstable intermediate (triphenylmethyl cation), which can be entrapped in the zeolite supercage by ship-in-a-bottle synthesis. The nature and location of the cation have been well-characterized by solid-state ^{13}C MAS NMR. This kind of "cavity isolation" may be applicable to other types of carbocations and other classes of unstable intermediates, which can then be subjected to systematic studies of chemical and physical properties that would otherwise be difficult or impossible. Such possibilities are being explored.

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(18) A mixture of 0.10 g of $^{13}CCl_4$, 4 mL of sodium-dried benzene, and 1.0 g of preheated[14] (600 °C) HY in a 10 mL round-bottom flask was stirred at room temperature for 2 days under a dry N_2 atmosphere. The flask was then connected to a vacuum line (10^{-3} Torr) for removal of excess benzene. The resulting solid was packed into a rotor in a glovebox and was analyzed by ^{13}C MAS NMR.

(19) We do not yet know exactly why this chemical shift is about 2 ppm different from that of the sample prepared by mixing $(C_6H_5)_3{}^{13}CCl$ with HY; it might be rationalized in terms of a small geometry change of the cation due to its adaptation to the supercage microenvironment, or to differences in the specific electrical microenvironments of different "surfaces" of the zeolite.

(20) Samples of 0.25 g of the $(C_6H_5)_3{}^{13}C^+/HY$ from notes 15 and 18 were individually stirred with 0.10 g of $LiAl[OC(CH_3)_3]_3H$ (obtained from Aldrich) in 3 mL of benzene for 6 h under a dry N_2 (g) atmosphere. After removal of benzene under vacuum, the residual solid was packed into a MAS rotor for NMR measurement.