Angewandte
Highlights

Reaction Mechanisms

International Edition: DOI: 10.1002/anie.201504899
German Edition: DOI: 10.1002/ange.201504899

A Mousetrap for Carbenium Ions: NMR Detectives at Work

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density functional calculations ·
heterogeneous catalysis ·
solid-state NMR spectroscopy · surface species ·
zeolites

Despite the tremendous importance of heterogeneous catalysis[1] for large-scale industrial chemistry, there is still a huge gap in the detailed knowledge of the processes and reaction intermediates occurring on the surface of the catalyst. Understanding these processes in detail would pave the way to the rational, knowledge-driven design of novel catalytic materials, instead of the current design approach, which is still strongly based on empirical methods and chemical intuition.

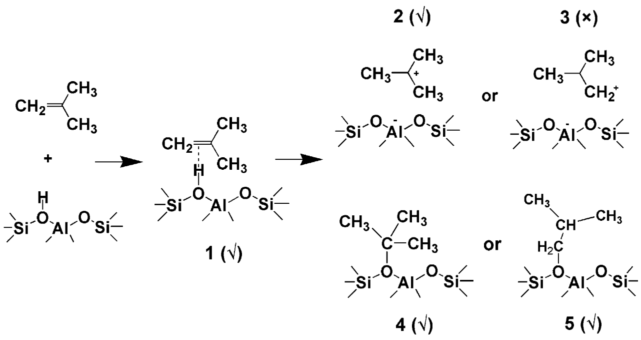
While surface-chemistry techniques can provide this knowledge for clean and well-defined model systems, for example clean metal surfaces, they are often ill suited for real-world systems, which therefore have to be investigated by other techniques. Multinuclear solid-state NMR spectroscopy can deliver a detailed atomistic picture of the local surface structures and reactive processes at the interface between surfaces. Although solid-state NMR techniques have been employed for many years for the investigation of zeolite-type alumosilicates with their large porosity and specific surface areas,[2] only in recent years techniques have been developed that are suitable for the investigation of many other types of heterogeneous catalysts with smaller specific surface areas.

Solid-state NMR spectroscopy in general delivers only a small number of spectroscopic parameters, for example chemical shifts, quadrupolar coupling constants, and dipolar interactions, and cannot provide a full picture of the processes on a complex surface. For this reason, the interpretation of the solid-state NMR spectra nearly always depends on model assumptions and necessitates detailed modeling of the involved species, usually by means of quantum chemical calculations, for example DFT calculations. This combination of DFT and solid-state NMR is currently one of the most powerful approaches for the spectroscopic characterization of "real-world" catalysts.

In a recent publication,[3] which reads like a detective novel, a consortium consisting of the Hunger group, the Xie group, and the Li group applied this combination successfully to a long-unanswered question in the area of zeolite catalysis concerning the existence and role of *tert*-butyl cations on solid acids.[4] The *tert*-butyl cation is a carbenium ion, which was proposed as a reaction intermediate in the butene/isobutene conversion on acidic zeolites. While various other carbenium ions have been identified on solid acids by NMR, UV/Vis, and IR spectroscopy, the shy tert-butyl cation has stayed hidden, despite considerable efforts to prove its presence inside the zeolites.

The major challenge in the detection of this carbenium ion is its transience and short lifetime, which renders it invisible to ^{1}H and ^{13}C MAS solid-state NMR spectroscopy. To address this challenge, the authors set out to stabilize the cation by trapping it with an ammonia molecule, resulting in a stable reaction intermediate that they could study by ^{1}H and ^{13}C MAS NMR spectroscopy.

In the first step of their study, the authors carefully modeled, based on quantum chemistry, the possible adsorption states (see Scheme 1) and surface species generated by the interaction of isobutene with the zeolite surface to elucidate their binding energies and the optimum temperature range for their formation. In the next step, the authors had to model the possible stable products arising from the coadsorption of isobutene and ammonia inside the zeolite and identify the catalyst that is most likely to contain/host the *tert*-butyl cation.



Scheme 1. Possible adsorption states and surface compounds formed by isobutene on acidic zeolites (√ and × mean the species are or are not stable on acidic zeolites, respectively.) Reproduced from Ref. [3].

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Based on their calculations, they identified H-ZMS-5 zeolites with a silicon/aluminum ratio of 12.5 as suitable candidates. These zeolites were filled with various amounts of isobutene and then heated to different reaction temperatures to identify the optimum temperature range for the identification of the *tert*-butyl cation. For this the formation of the different chemical species was monitored by ^{1}H MAS NMR spectroscopy. These studies indicated that the experiments should be performed at reaction temperatures below 473 K to prevent the formation of other products or cations that could prevent the detection of the *tert*-butyl cation.

The final step in setting up the trap for the cation was finding the best route for the insertion of ammonia into the zeolites, which is possible both ex situ and in situ. In the ex situ route first only isobutene is adsorbed and the zeolite is heated. Then ammonia is adsorbed in order to capture the cation. In the in situ route, a gaseous mixture of isobutene and ammonia is adsorbed and the zeolite is then heated. Studying these samples by ^{1}H MAS NMR spectroscopy reveals that only the in situ route is capable of trapping the *tert*-butyl cation through the formation of a stable *tert*-butylammonium cation. This result corroborated previous studies of Haw[5] and Sauer et al.,[6] who suggested that the very short lifetime of the *tert*-butyl cation prevents its capture by ammonia by means of the ex situ route. With this last step, the trap is set to capture the shy species by proton-decoupled ^{13}C MAS NMR spectroscopy.

Figure 1 compares the ^{13}C MAS NMR spectra after a) ex situ and b) in situ loading of the zeolite, and c) after thermal treatment. In spectrum (c) two new signals at $\delta = 62$ ppm and 53 ppm are visible that were not in spectra (a) and (b). While the signal at $\delta = 62$ ppm is caused by alkoxy species, created by reactions on the surface of the zeolite, the signal at $\delta = 53$ ppm is the spectroscopic signature of the quaternary carbon of the *tert*-butylammonium ions. To support this assignment, the authors performed ^{13}C chemical shift calculations employing DFT methods. Their results are in excellent agreement with the experimentally observed chemical shift value, proving it is indeed possible to capture the *tert*-butyl cation formed on zeolite H-ZSM-5 by conversion of isobutene by a combination of solid-state NMR spectroscopy, DFT calculations, and capturing with ammonia.

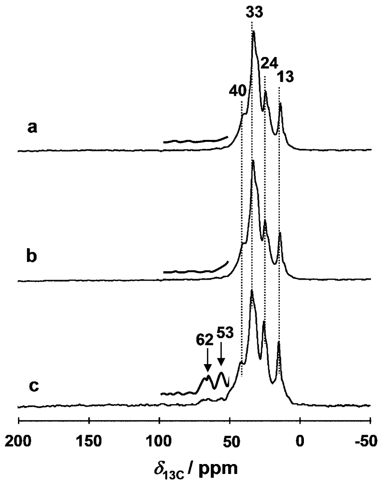

Figure 1. ^{13}C MAS NMR spectra of the HZSM-5 catalysts recorded after a) loading with isobutene loading and b) subsequent ex situ loading of ammonia, and c) after in situ loading of isobutene and ammonia, followed heating at 473 K for 5 min. Reproduced from Ref. [3].

However, the impact and importance of the present work is much greater. With their excellent piece of detective work, the consortium of Hunger, Xie, Li, and their co-workers has beautifully demonstrated the power of state-of-the art solid-state NMR spectroscopy, combined with careful chemical modeling and quantum chemical calculations for investigating the surface chemistry of real-world heterogeneous catalysts. If one considers the current developments in sensitivity enhancements in solid-state NMR spectroscopy via indirect detection,[7] dynamic nuclear polarization (DNP),[8] and deuteron MAS NMR,[9] which drastically reduce the required specific surface areas of the catalyst, and recent developments in the quantum chemical modeling of surface species (e.g. Ref. [10]), in the future many more chemical puzzles are expected to be solved by employing the strategy pioneered in the paper by Hunger et al.[3]

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9450–9451
Angew. Chem. **2015**, *127*, 9582–9584

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Received: May 29, 2015