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Identification of *tert*-Butyl Cations in Zeolite H-ZSM-5: Evidence from NMR Spectroscopy and DFT Calculations**

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Abstract: *Experimental evidence for the presence of tert-butyl cations, which are important intermediates in acid-catalyzed heterogeneous reactions, on solid acids has still not been provided to date. By combining density functional theory (DFT) calculations with $^{1}H/^{13}C$ magic-angle-spinning NMR spectroscopy, the tert-butyl cation was successfully identified on zeolite H-ZSM-5 upon conversion of isobutene by capturing this intermediate with ammonia.*

Analogous to reactions in superacidic media, it is generally accepted that hydrocarbon conversion on solid acids involves carbenium ions as important reaction intermediates, which are formed by the protonation of hydrocarbons on strongly Brønsted acidic sites.[1,2] In contrast to superacidic solutions, where carbenium ions can be clearly identified and well characterized,[3] providing evidence for the existence of carbenium ions on solid acids is not straightforward, mostly because of their short lifetimes. Previously, several types of persistent carbenium ions, for example, cyclic alkenyl or aromatic carbenium ions, have been identified on solid acids by NMR, UV/Vis, and IR spectroscopy.[4–6] Nevertheless, the identification of carbenium ions derived from small alkenes still remains challenging.

The *tert*-butyl cation has attracted special interest, and strong efforts have been made to characterize the *tert*-butyl cation as an intermediate of butene/isobutene conversion on acidic zeolites.[7–9] Unfortunately, all experimental attempts have appeared to be unsuccessful thus far, and the presence of *tert*-butyl cations on acidic zeolites remains controversial. Recently, it was theoretically predicted that the *tert*-butyl cation should be stable and detectable in H-FER and H-MOR zeolites. However, the corresponding experimental evidence was not available until now.[10,11] Considering the successful application of the zeolite H-ZSM-5 as a commercial catalyst for the cracking of C_4 alkenes,[12] the existence of *tert*-butyl cations as possible reaction intermediates is of great significance, from both theoretical and experimental points of view, for understanding the reaction mechanism.

Herein, the *tert*-butyl cation was successfully identified on the zeolite H-ZSM-5 by capturing these reaction intermediates with an ammonia molecule and investigating these stable surface compounds by $^{1}H/^{13}C$ magic angle spinning (MAS) NMR spectroscopy and density functional theory (DFT) calculations. All intermediates that are possibly formed during the reaction of isobutene on zeolites with Brønsted acidic sites that feature bridging OH groups (Scheme 1), for example, the π complex of adsorbed isobutene (**1**), the *tert*-butyl cation (**2**, **3**), and the *tert*-butoxide (*tert*-C_4Z, **4**) and primary butoxide (pri-C_4Z, **5**) adducts, were first investigated by theoretical calculations using the BEEF-vdW functional with the van der Waals (vdW) interaction correction.[11]

Table 1 summarizes the adsorption and formation energies of C_4 species on selected aluminosilicates, namely H-CHA, H-MFI, H-FER, and H-MOR. The physisorption energy of isobutene on H-FER was calculated to be $-77\ \mathrm{kJ\,mol^{-1}}$, which is identical to that determined by the hybrid MP2:DFT method in a previous study ($-77\ \mathrm{kJ\,mol^{-1}}$).[11c] The formation energy of the butoxides depends more strongly on the zeolite structure than on the physisorption energy of isobutene [isobutene (**1**) + HZ]. The primary butyl cation (**3**) is extremely unstable and was therefore not included in our study. Considering the stability

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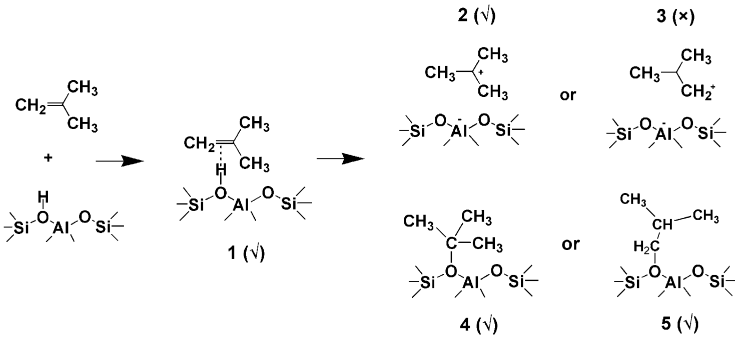

Scheme 1. Possible adsorption states and surface compounds formed from isobutene on acidic zeolites (√ and × indicate species that can or cannot exist in a stable form on acidic zeolites, respectively.)

Table 1: Calculated formation energies (in kJ mol^{-1}) of C_4 species without or with the co-adsorption of NH_3 on different acidic zeolites (HZ) from gaseous isobutene and NH_3.

Zeolite	H-CHA	H-MFI	H-FER	H-MOR
C_4 species				
isobutene (**1**) + HZ	−71	−84	−77	−83
tert-butyl cation (**2**) + Z^-	−45	−44	−40	−45
tert-butoxide (**4**) C_4Z	1	−59	−22	−47
primary butoxide (**5**) C_4Z	−38	−87	−73	−64
C_4 species and NH_3				
Ammonium **I** + Z^-	−265	−261	−199	−255
Ammonium **II** + Z^-	−243	−244	−201	−243
C_4 (HZ) + NH_3 (pore)	−104	−118	−120	−107
C_4 (pore) + NH_4^+ (Z^-)	−226	−205	−185	−203

of the *tert*-butyl cation (**2**), its formation energy is similar in different zeolites. This intermediate is approximately 40 kJ mol^{-1} less stable than physisorbed isobutene (**1**).

The stability dependences of the C_4 species on the temperature were found to be different when entropy contributions were included (Figure 1). This finding is in agreement with a previous report by Sauer et al. for the zeolite H-FER.[11a] Physisorbed isobutene (**1**) is the most stable C_4 species in H-ZSM-5. With an increase in temperature, the absolute Gibbs free formation energies of the C_4 species gradually decrease. However, the entropy loss associated with the generation of physisorbed isobutene (**1**) seems to be larger than for the generation of the *tert*-butyl cation (**2**), and the energy difference gradually decreases. The lifetime of the *tert*-butyl cation (**2**) increases with temperature before the Gibbs formation energies become positive (e.g., >500 K). Therefore, the *tert*-butyl cation (**2**) can only be observed in a specific temperature range during isobutene conversion on H-ZSM-5 zeolite. This sheds new light on the identification of the *tert*-butyl cation by spectroscopic methods.

The adsorption of ammonia as a basic probe molecule is a well-known approach to titrate the acidic sites in zeolites.[13] More interestingly, the nucleophilic addition of ammonia to cyclic carbenium ions to produce onium ions has been revealed and successfully applied to the capture of carbenium ions.[14,15] Herein, the possible structures resulting from co-adsorption of isobutene and NH_3 were theoretically investigated. The formation energies and optimized structures in H-ZSM-5 are listed in Table 1 and Figure 2. For the four different structures, two *tert*-butyl ammonium structures were calculated to be more stable than the other two. The formation of butyl cations is a prerequisite to produce these ammonium structures. We failed to locate the structures of zwitterions in H-ZSM-5 by the direct nucleophilic addition of NH_3 to isobutene. The competitive adsorption of ammonia and isobutene leads to the co-adsorption of isobutene in the pores and of ammonia at Brønsted acidic sites [C_4(pore) + NH_4^+(Z-)]. Nevertheless, this arrangement is less stable than the ammonium structure by approximately 20–40 kJ mol^{-1}. Theoretically, the *tert*-butyl cation (**2**) in acidic zeolites can be fixed after the loading of ammonia to form stable ammonium cations, and therefore, ammonia is a good probe molecule to detect carbenium ions.

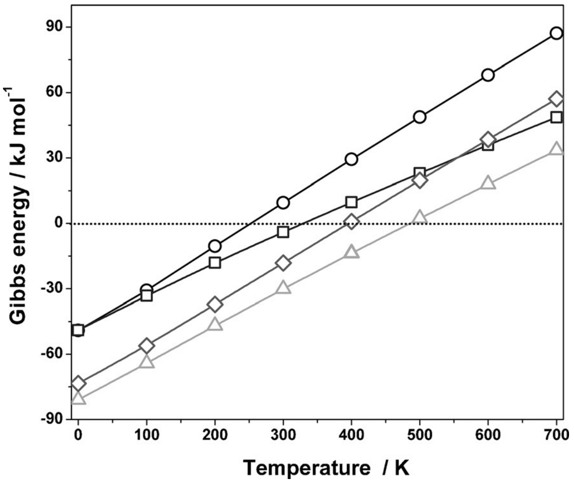

Figure 1. Gibbs formation energies of different C_4 species on H-ZSM-5 (at 1 atm) plotted as a function of the temperature. All energies are given relative to gaseous isobutene. △: isobutene (**1**) + HZ; ○: *tert*-butoxide (**4**) C_4Z; □: *tert*-butyl cation (**2**) + Z^-; ◇: primary butoxide (**5**) C_4Z.

On the basis of the above-mentioned calculations, zeolite H-ZSM-5 with a n_{Si}/n_{Al} ratio of 12.5 was employed as a model catalyst to investigate the possible existence of *tert*-butyl cations during isobutene conversion. First, different amounts of isobutene were introduced into H-ZSM-5 zeolites to confirm the saturated adsorption capacity (Supporting Information, Figure S4). Thereafter, a surplus of isobutene was introduced into the zeolite H-ZSM-5 and heated to different temperatures to generate *tert*-butyl cations. Aside from the signals of the freshly dehydrated H-ZSM-5 catalyst (Figure S4, top), new signals occurred at $\delta = 0.7$, 2.8, and 4.8 ppm in the ^{1}H NMR spectrum upon subjecting zeolite H-ZSM-5 to isobutene at 298 K (Figure S5, top left). The latter one can be attributed to the olefinic $=CH_2$ groups of isobutene or its dimers and oligomers, while the signals at $\delta = 0.7$ and 2.8 ppm are due to CH_3 or CH_2 groups of alkenes.[16,17] Furthermore, a weak ^{1}H MAS NMR signal corresponding to non-covered Brønsted acidic sites could also be observed at $\delta = 3.8$ ppm.[18] With an increase in temperature from 298 to 473 K, the signal of the Brønsted acidic sites (3.8 ppm) gradually decreased in

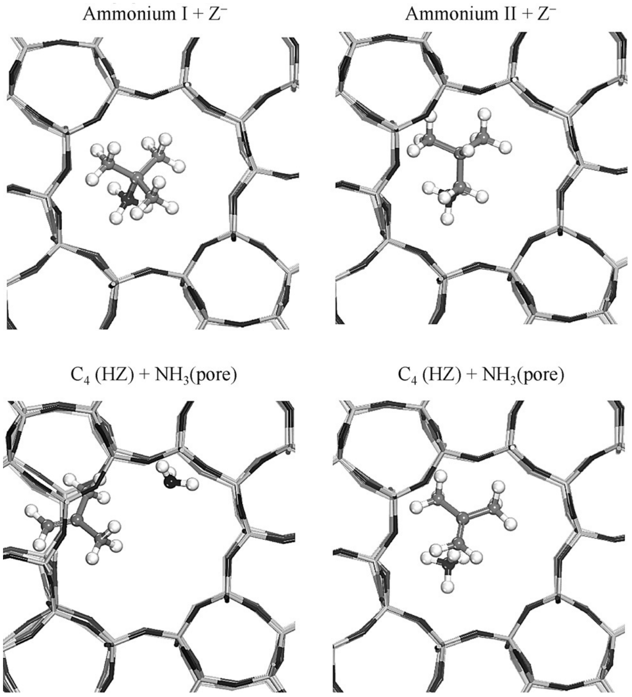

Figure 2. Structures of C_4 species after the loading of ammonia in H-ZSM-5.

intensity, while the signal of isobutene or its oligomers (4.8 ppm) gradually increased. Upon further increasing the reaction temperature ($T > 473$ K), the alkene signal (4.8 ppm) became less intense, and a new signal at $\delta = 7.2$ ppm, which is due to aromatic species, was observed.[19] These results indicate that the oligomerization (dimerization) of isobutene plays a dominant role at treatment temperatures below 473 K and that polymerization occurs at temperatures above 473 K to produce aromatic compounds, which is in line with the results of previous studies by Stepanov and co-workers.[20] Furthermore, according to previous studies,[21,22] cyclopentenyl cations (CPCs) could be formed and may serve as intermediates in polymerization reactions. To increase the chances of observing the *tert*-butyl cation (see Figure S2) and to avoid the puzzling observation of CPCs, relatively low treatment temperatures ($T \leq 473$ K) were selected for investigating the existence of the *tert*-butyl cation by NMR spectroscopy.

For effectively capturing and identifying the *tert*-butyl cation on zeolite H-ZSM-5, ammonia was introduced by two different routes: 1) Following the ex situ route, isobutene was first adsorbed onto zeolite H-ZSM-5 and heated to different temperatures before ammonia was adsorbed to capture the *tert*-butyl cation. 2) In the in situ route, ammonia and isobutene (as a gas mixture) were simultaneously adsorbed onto the catalyst, and the resulting system heated to different temperatures. The ^{1}H MAS NMR spectra of H-ZSM-5 catalysts processed according to these two routes are shown in Figures S6–S8. After ex situ ammonia loading according to route 1 at 298 K, a new ^{1}H MAS NMR signal was observed at $\delta = 6.4$ ppm (Figure S6, left). This signal indicates the formation of NH_4^+ ions at bridging OH groups. With an increase in ammonia loading, the relative intensity of this signal gradually increased, whereas that of the signal of the bridging OH groups gradually decreased, indicating that the introduced ammonia mainly covered the residual Brønsted acidic sites in zeolite H-ZSM-5. On the other hand, nearly no changes and a similar variation trend could be observed in the ^{1}H MAS NMR spectra when the ammonia was adsorbed according to the in situ route at 298 K (Figure S6, right) or even at temperatures of up to 423 K (Figures S7 and S8).

When the temperature was increased to 473 K, a new signal occurred at $\delta = 7.8$ ppm when ammonia was introduced in situ (Figure 3, right). Based on ^{1}H chemical shift calculations (Figure S3, left), this signal can be attributed to the *tert*-butylammonium ions **I** ($\delta = 7.6$ ppm), which are formed by the reaction of ammonia with *tert*-butyl carbenium ions. These experimental observations fit well with the results of the above-mentioned calculations and confirm that *tert*-butyl cations formed on zeolite H-ZSM-5 are effectively captured by ammonia. With increasing ammonia loading, the relative intensity of the *tert*-butylammonium ion signal also increased slightly. It is worth mentioning that the ^{1}H MAS NMR signals corresponding to the *tert*-butylammonium ions could not be observed in the spectra recorded upon ex situ ammonia loading (Figure 3, left). According to the previous studies of the groups of Haw[8] and Sauer,[11c] this may be due to the very short lifetime of the *tert*-butyl cation, which is not long enough to allow for its capturing by ammonia along the ex situ route. Furthermore, no reaction between ammonia and isobutene occurred in the absence of Brønsted acidic sites, for example, on Na-ZSM-5.

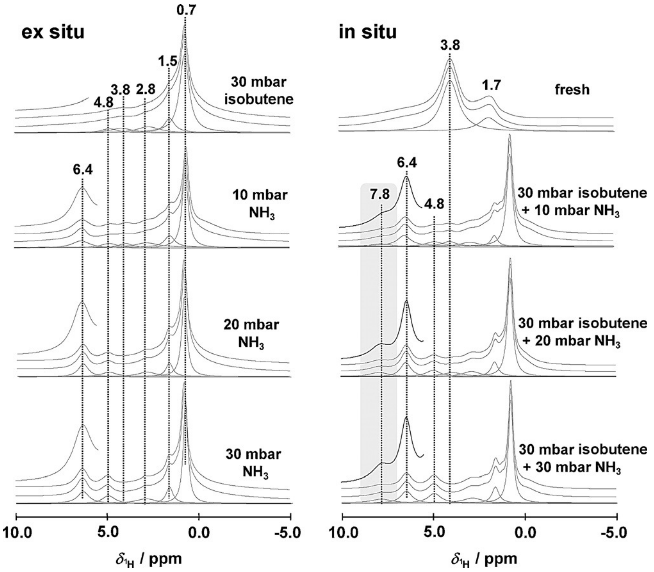

Figure 3. ^{1}H MAS NMR spectra of the H-ZSM-5 catalysts recorded after ex situ or in situ loading of isobutene and ammonia according to route 1 (left) and route 1 (right), respectively, and heating to 473 K for 5 minutes. From top to bottom, the experimental spectra, the simulated spectra, and the signal components utilized for the simulation are shown.

To confirm the assignments of the ^{1}H MAS NMR signals of the *tert*-butylammonium ions formed on zeolite H-ZSM-5, ^{13}C MAS NMR spectroscopy was performed. After loading of isobutene and heating to 473 K for five minutes, the predominant ^{13}C MAS NMR signals were observed $\delta = 13$,

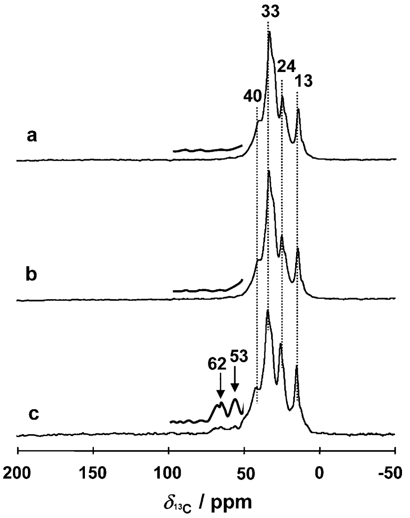

Figure 4. ^{13}C MAS NMR spectra of the H-ZSM-5 catalysts recorded after isobutene loading (a) and subsequent ex situ loading of ammonia (b), and after in situ loading of isobutene and ammonia, followed by heating at 473 K for 5 minutes (c).

24, 33, and 40 ppm, which are due to isobutene oligomers (Figure 4 a).[7c,19] This observation indicates that the oligomerization of isobutene is the predominant reaction at 473 K, which is in agreement with the results obtained by ^{1}H MAS NMR spectroscopy (Figure S6). The absence of any changes in the ^{13}C MAS NMR spectra of zeolite H-ZSM-5 when ammonia was introduced by the ex situ route (Route 1; Figure 4 b) is also in agreement with the ^{1}H MAS NMR studies (see Figure 2). However, a new signal, which was attributed to the *tert*-butylammonium ions **I** ($\delta = 53$ ppm), appeared when ammonia was loaded by the in situ route (Route 2; Figure 4 c). New signals at approximately $\delta =$ 62 ppm may be due to alkoxy species of oligomers or cracking products.[23] These species are probably formed at terminal Si–OH groups ($\delta = 1.7$ ppm), which exist on H-ZSM-5 zeolites in a relatively high concentration (Figure 2, top right). The above-mentioned signal assignments were supported by ^{13}C chemical shift calculations (Figure S3, right). Again, the ^{13}C and ^{1}H MAS NMR studies as well as the theoretical calculations are in good agreement, indicating that the *tert*-butyl cation formed on zeolite H-ZSM-5 by conversion of isobutene can be captured with ammonia.

In summary, the formation of the *tert*-butyl cation during isobutene conversion on zeolite H-ZSM-5 has been undoubtedly confirmed for the first time by NMR spectroscopy after capturing with ammonia, which was supported by theoretical calculations. The chances of observing *tert*-butyl cations on zeolite H-ZSM-5 strongly depend on the experimental conditions employed. Future studies should clarify whether the simple and efficient method can be extended to the identification and monitoring of carbenium ions formed on a larger variety of solid catalysts that are used for acid-catalyzed heterogeneous reactions.

Keywords: adsorption · density functional calculations · heterogeneous catalysis · NMR spectroscopy · zeolites

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