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Supporting information

Insight into the formation of tert-butyl cation confined inside H-ZSM-5 zeolite from NMR Spectroscopy and DFT calculations

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1. Experimental Section

1.1 Sample preparation

0.1g H-ZSM-5 zeolite samples (Si/Al_2O_3=38, NanKai University) were dehydrated in glass tubes on a vacuum line at 673K with a pressure below 10^{-3} Pa for 12h. After cooling to the room temperature, 0.5 kPa $^{13}C_4H_{10}O$ (^{13}C, 99 %, Cambridge Isotope Laboratories, Inc.) and 0.5, 1, 3, 6 kPa NH_3 (99%) were co-fed onto the dehydrated H-ZSM-5 zeolites, respectively. The glass tubes were flame-sealed, heated at 200 °C for 60 min and then the reactions were suddenly quenched by liquid nitrogen. Thereafter, the catalysts were transferred into 4 mm ZrO_2 rotors under a dry nitrogen atmosphere in a glove box for subsequent NMR measurements.

2. Solid-State NMR experiments

All solid-state NMR characterizations were performed at 11.7 T on a Bruker-Avance III-500 spectrometer, equipped with a 4 mm probe, with resonance frequencies of 500.57, 130.42 and 125.87 MHz for ^{1}H, ^{27}Al and ^{13}C, respectively. The magic angle spinning rates were set to 10 kHz for all the experiments.

2.1 $^{1}H \rightarrow ^{13}C$ CP/MAS NMR experiments

The $^{1}H \rightarrow ^{13}C$ CP/MAS NMR experiments were carried out with a contact time of 4.8 ms and with a repetition time of 2 s. The Hartmann–Hahn condition was optimized by using hexamethylbenzene. High-power broad band ^{1}H decoupling, using the pulse scheme TPPM-13 with the amplitude of 62.5 kHz, was applied during ^{13}C signal acquisition to enhance spectral resolution and sensitivity. The ^{13}C chemical shifts were referenced to adamantine (a second reference to TMS).

2.2 ^{13}C-^{13}C CP MAS PDSD NMR experiment

2D ^{13}C-^{13}C CP MAS proton-driven spin diffusion experiments were performed to determine the correlations between ^{13}C signals. $^{1}H \rightarrow ^{13}C$ cross polarization with a contact time of 4.8 ms was used to prepare the initial ^{13}C signal. The $\pi/2$ pulse width of ^{13}C is 4.9 μs and the mixing time was set to 100 ms. A TPPM-13 ^{1}H decoupling at 62.5kHz was applied to the acquisition time t2. The experiments were acquired with 64 scans per experiment and 360 experiments in the State-TPPI scheme.

2.3 ^{13}C-{^{27}Al} S-RESPDOR NMR experiment

To perform the ^{13}C-{^{27}Al} S-RESPDOR experiments, a special frequency splitter (REDOR-BOX) was used, which enables tuning and matching to the Larmor frequencies of the ^{13}C and ^{27}Al nuclei on the X channel of 4mm HXY MAS NMR probe at the same time.

The pulse sequence of ^{13}C-{^{27}Al} S-RESPDOR is shown in Figure S1. The initial ^{13}C signal was prepared by $^{1}H \rightarrow ^{13}C$ cross polarization (same condition as the previous $^{1}H \rightarrow ^{13}C$

CP/MAS experiments). SR4 dipolar recoupling was used on the ^{13}C channel with $\nu_{nut,13C}$ =20 kHz. Continuous-wave ^{1}H decoupling with the amplitude of 62.5 kHz was used during SR4, while a SPINAL-64 (small-phase incremental alternation with 64 steps) ^{1}H decoupling with the amplitude of 62.5 kHz was used during acquisition. A π pulse length of 8 μs was used on the ^{13}C channel. The saturation pulse on the ^{27}Al channel with an amplitude of 53.8 kHz and the length of 100 μs = TR was irradiated at the 54 ppm ^{27}Al signal to transfer ^{13}C-^{27}Al interactions. The 54 ppm ^{27}Al signal corresponds to the tetrahedral framework Al (associated with the Brønsted acid site) of the HZSM-5 zeolite. The recycle delay was set to 3 s.

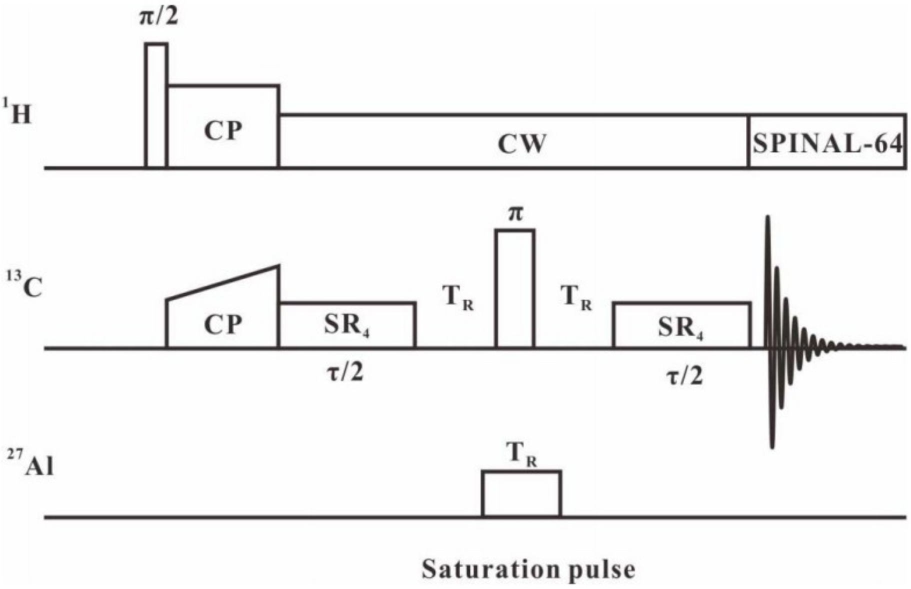

Figure S1. Pulse sequence for ^{13}C-{^{27}Al} S-RESPDOR experiment. Two experiments must be done: with(S) or without (S_0) the ^{27}Al saturation pulses.

3. Computational methods and modeling

Beyond the experimental evidence, we adopt the theoretical calculations to confirm the chemical shifts of tert-butylamine ions adsorbed in the zeolite channel.

A 72T cluster model that extracted from the crystallographic data was applied to represent the H-ZSM-5 zeolite, which contains the intersection of 10-membered ring straight and zigzag pore channels. On the basis of the accessibility of adsorbed molecules toward H-ZSM-5 zeolite, the Si12-O24(H)-Al12 site in the intersection channel was chosen as the Brønsted acid site. All the terminal Si atoms were capped with H atoms at a Si-H bond length of 1.47 Å, orienting along the direction of the corresponding Si-O bond.

The geometries of tert-butanol co-adsorbed with ammonia and tert-butylamine ions over the 72T cluster model were optimized by the combined theoretical ONIOM (Our-own-N-layered Integrated molecular Orbital & molecular Mechanics) method, where the (SiO)3-Si-OH-Al-(SiO)3 acid site and adsorbed organic molecules were considered as the high-level layer while the rest as the low level. In the calculations, the high layer atoms were allowed to fully relax with the latest ωB97XD functional with 6-31G(d,p) basis set, whereas the rest atoms were fixed at their crystallographic positions using the MNDO method. The ωB97XD method was a recently developed long-range-corrected hybrid functional by Chai and Head-

Gordon[1], which implicitly accounted for empirical dispersion and could describe long-range dispersion interactions well with respect to the traditional density functional theory methods. This functional was also recently found to perform very well for the description of adsorption and reactions on zeolites[2,3]. Based on the optimized structures, the ^{13}C NMR chemical shifts were then calculated at the ωB97XD/6-31G(d,p) level by GIAO method. All the geometry optimizations and NMR calculations were performed using the Gaussian 09 package.[4]

To visualize the noncovalent interactions between the adsorbed organic fragment and the zeolite channel, the noncovalent interaction index approach, which was developed by Yang et al., was also utilized in this work. [5] In this method, the reduced density gradient (RDG), defined as $s = (1/(2(3\pi 2)1/3))((|\Delta\rho(r)|)/(\rho(r)4/3))$, together with the electron density ρ, was used to distinguish the covalent and noncovalent interactions. In principle, the noncovalent interactions locate in the regions with low density and low RDG. The sign of the second largest eigenvalue ($\lambda 2$) of the electron density Hessian can be used to distinguish bonded ($\lambda 2 < 0$) from nonbonded ($\lambda 2 > 0$) interactions. Generally, the analysis of the sign of $\lambda 2$ can help to discern different types of noncovalent interactions: ($\mathrm{sign}(\lambda 2)\rho < 0$, H-bonding interactions; $\mathrm{sign}(\lambda 2)\rho \approx 0$, weak van der Waals interactions and $\mathrm{sign}(\lambda 2)\rho > 0$, strong repulsive interaction). To exhibit the intermolecular noncovalent interactions between the adsorbed organic species and the zeolite framework more obviously, the intramolecular interactions were eliminated for the calculated RDG function. All the functions RDG and $\mathrm{sign}(\lambda 2)\rho$ were calculated with the Multiwfn Software.[6]

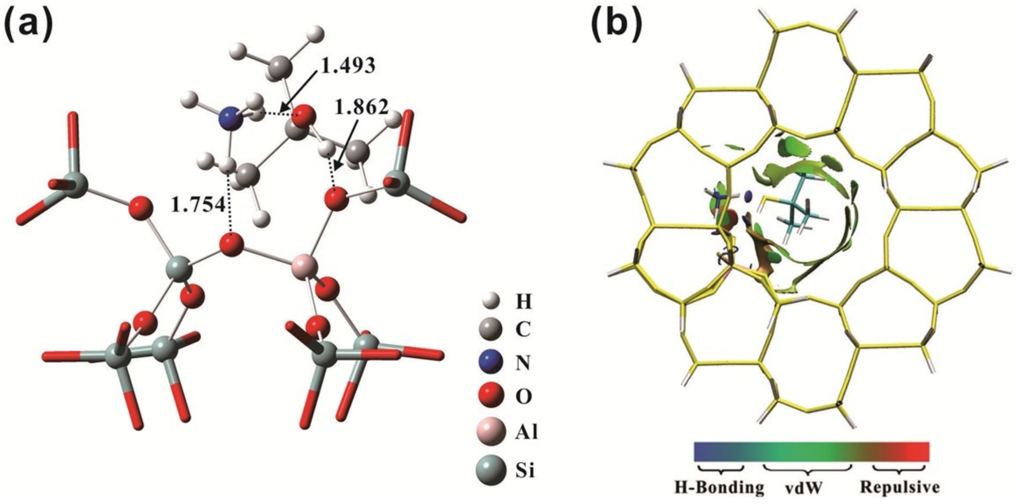

Figure S2. (a) The local structure of tert-butanol and ammonia confined in the 72T cluster model of H-ZSM-5 zeolite, in which selected distances (Å) are given. (b) Isosurface plots of reduced density gradient (s = 0.500 au) for tert-butanol co-adsorbed with ammonia confined in H-ZSM-5 zeolite.

References:

[1] J.D. Chai, M. HeadGordon, Phys. Chem. Chem. Phys. 2008, 10, 6615.

[2] X. Yi,Y. Byun,Y. Chu,A. Zheng, S.B. Hong,and F. Deng, J. Phys. Chem. C 2013, 117,23626-23637.

[3] W. Dai, C. Wang, X. Yi, A. Zheng, L. Li, G. Wu,N. Guan, Z. Xie, M. Dyballa, and M. Hunger, Angew. Chem. 2015, 127, 8907-8910.

[4] M. Frisch, et al. Gaussian 09, Revision B.01; Gaussian Inc.:Wallingford, CT, 2010.

[5] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, J. Am. Chem. Soc.,2010, 132, 6498-6506.31

[6]T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580-592.