# Enhancement of Brønsted Acidity in Zeolitic Catalysts due to Intermolecular Solvent Effect in Confined Micropores[†]

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## Supporting Informations:

### Experimental section

H-form Mordenite zeolite (Si/Al = 20) sample was obtained from Strem Chemical Inc. The integrity of its framework structure was confirmed by powdered XRD (Fig. S1). $^{27}$Al MAS NMR (Fig.2S) indicated that only tetrahedral framework Al was present. Prior to the adsorption of TMPO probe molecule, the H-MOR zeolite was subjected to dehydration under vacuum ($<10^{-3}$ Pa). This is done by increasing the sample temperature at a rate of 1 K/min till reaching 673 K, then, maintained at the same temperature for at least 5 h before it was cooled back to room temperature (295 K). Detailed procedures invoked for introducing the TMPO molecule onto the zeolite sample can be found elsewhere.[S1] In brief, a known amount of TMPO adsorbate dissolved in anhydrous $CH_2Cl_2$ was first added into a vessel containing the dehydrated H-MOR in a $N_2$ glovebox, followed by removal of the $CH_2Cl_2$ solvent by evacuation at 323 K. To ensure a uniform adsorption of adsorbates in the pores/channels of the microporous adsorbent, the sealed sample vessel was further subjected to a baking treatment at 453 K for 8 h. Prior to the NMR measurements, the adsorbate-loaded sample sealed in the sample vessel was transferred into a NMR rotor with a Kel-F endcap in a glovebox under dry nitrogen atmosphere.

$^{31}$P and $^{27}$Al NMR experiments were carried out on a Varian Infinityplus-400 and 300 spectrometers operating at a Larmor resonance frequency of 161.98 and 78.11 MHz for $^{31}$P and $^{27}$Al, respectively. A single pulse sequence with a $\pi/2$ pulse length of 4.4 and 2.25 μs and a recycle delay of 1 and 10 s were used for acquiring the   $^{31}$P and $^{27}$Al  MAS NMR spectra at a sample-spinning frequency of 9 and 10 kHz, using 85% $H_3PO_4$ and 1 M $Al(NO_3)_3$ aqueous solution as the chemical shift reference, respectively.

### Computational method

During the structure optimization and subsequent calculations of $^{31}$P NMR parameters, the electron correlation effects were modeled using the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE method).[S2] For structure optimization, the couplings between the core and valence electrons were described by ultrasoft pseudopotentials. In addition, a plane-wave cut-off energy of 300 eV and a default medium level Monkhorst-Pack K point grid $(1\times1\times3)$[S3] in the Dmol package were adopted to sample the Brillouin zone. Calculation of all NMR parameters were performed by the GIPAW method[S4-S6] using a $1\times1\times2$ Monkhorst-Pack K point grid and by expanding all wavefunctions in a plane-wave basis set at a definite cut-off energy of 550 ev. All $(\delta^{31}P)_{cal}$ were derived using the NMR module available in the CASTEP program package based on the optimized TMPO adsorbed structures in the H-MOR. Typically, to complete calculations of NMR parameters for each adsorption system, it requires a computation time of about 24 hours utilizing the parallel 128 cpu in an IBM-1350 cluster facilitated by the National Center for High-performance Computing (NCHC), Taiwan. The $^{31}$P calculated

shielding tensors were further converted to $(\delta^{31}P)_{cal}$ values, which were referred to the absolute shielding of crystalline TMPO, namely 39 and 229 ppm for the experiment and theoretical value, respectively.[S7]

**References:**
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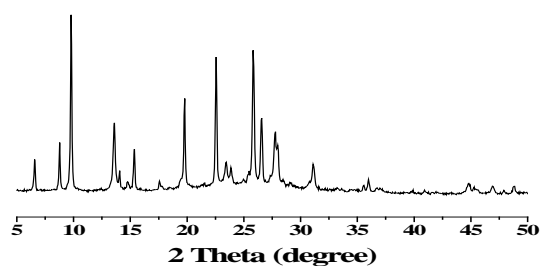
**Fig. S1.** Powdered XRD pattern of the H-Mordenite zeolite sample.
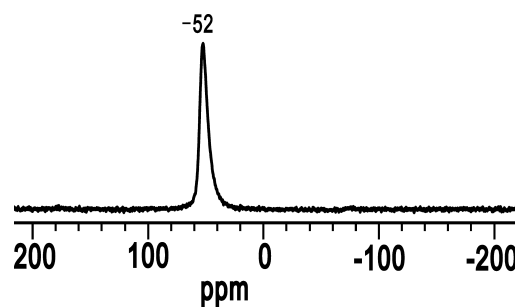


**Fig. S2.** $^{27}$Al MAS NMR spectrum of the H-Mordenite zeolite sample.
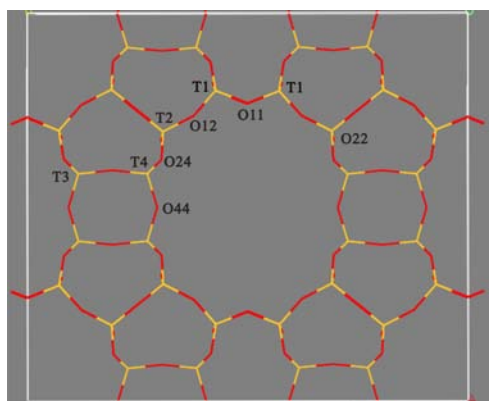


**Fig. S3.** Projection of the H-MOR topology indicating the four crystallographically unequivalent tetrahedral sites.