MEASURING ACIDITY OR CONFINEMENT EFFECTS IN ZEOLITES? AN ANSWER FROM INTEGRATED SSNMR AND MODELING

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The nature, strength, and spatial distribution of acid sites in zeolites are central to their catalytic performance, yet their characterization remains a formidable challenge. Using trimethyl-phosphine oxide (TMPO) as a probe for acidity, we combined solid-state NMR and computational modeling to redefine the understanding of zeolite acidity. 2D ^{1}H-^{31}P HETCOR combined with ab initio molecular dynamics revealed that confinement effects and protonated TMPO dimers – not distinct Brønsted acid strengths – explain ^{31}P NMR resonances in HZSM-5.[1,2] An atomistic view of host–guest dynamics is provided by examining aluminum siting and guest–guest interactions. Extending this approach to external zeolite surfaces, we are able to identify unique SiOH species, pore-mouth Brønsted sites, and tricoordinate Al-Lewis sites, previously undetected.[3] This talk also demonstrates the importance of optimizing TMPO adsorption methods, showing how solvent choice and gas-phase loading influence dimer formation and acid site quantification.[4] Altogether, these insights bridge internal confinement effects and external surface chemistry, offering a unified framework for a better atomic-level understanding of acid site structures in zeolite catalysts.

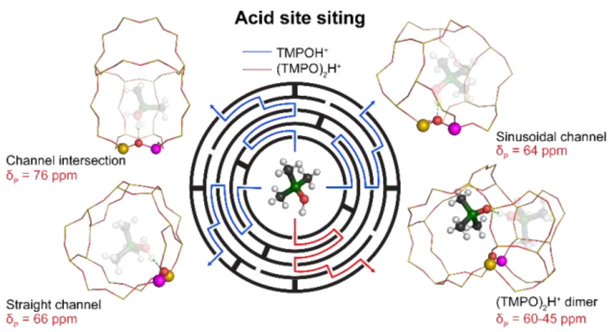

Figure 1. Structure and calculated δ ^{31}P of TMPO interacting with distinct Brønsted acid sites.

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