Advanced nuclear magnetic resonance technique reveals precise structural, dynamical details in zeolites

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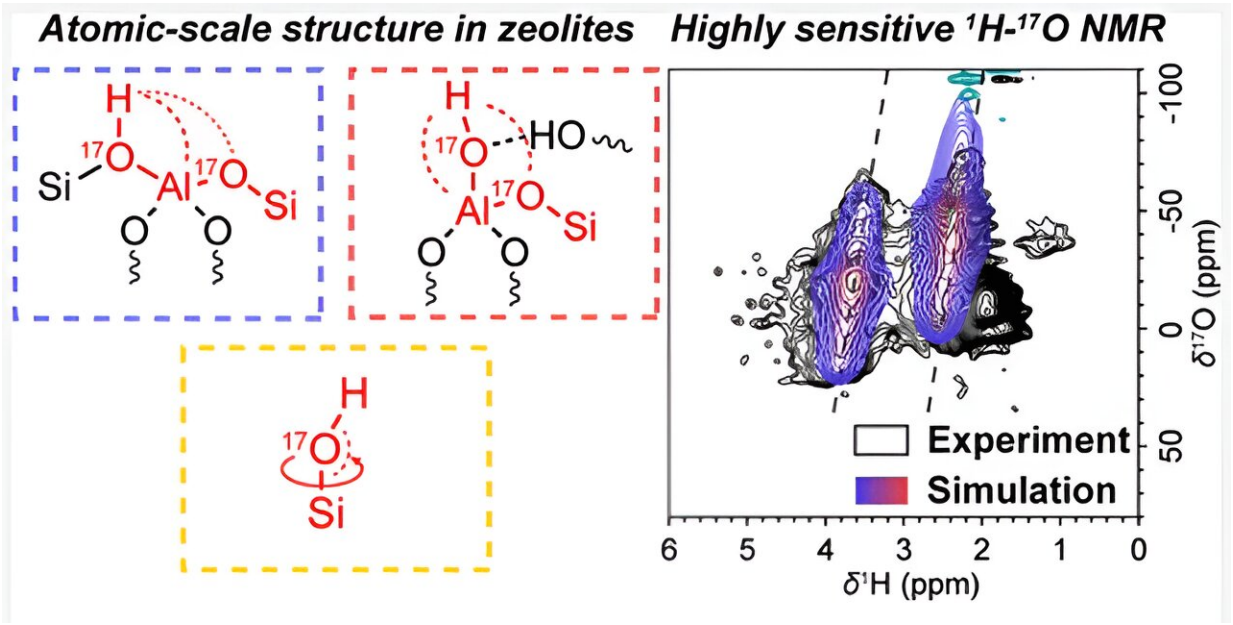

Credit: *Journal of the American Chemical Society* (2024). DOI: 10.1021/jacs.3c14787

Zeolites are widely used in many industries, yet their intrinsic catalytic nature is not completely understood, due to the complexity of the hydroxyl-aluminum moieties.

Atomic-scale analysis of local environments for the hydroxyl species is

essential for revealing the intrinsic catalytic activity of zeolites and guiding the design of high-performance catalysts. However, many unfavorable factors prohibit the elucidation of their fine structures such as low quantity, meta-stable property, structural similarity, hydrogen-bonding environment, and long-range disordered nature.

Recently, a research team led by Prof. Hou Guangjin and Prof. Chen Kuizhi from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS) unraveled the precise structure of complex hydroxyl groups in zeolites with a comprehensive set of self-developed coupling-edited ^{1}H-^{17}O solid-state nuclear magnetic resonance (NMR) methods. The study was published in the *Journal of the American Chemical Society*.

The ^{17}O solid-state NMR would be a candidate to improve the analytical precision of zeolites if it could overcome the technical difficulties related to the extremely low natural abundance, low gyromagnetic ratio, and quadrupolar nature of the ^{17}O isotope. Therefore, researchers employed a novel ^{17}O-enrichment method and developed a series of ^{17}O-NMR-based spectral editing pulse sequences, allowing them to improve the spectral resolution and address the subtle protonic structures within zeolites.

The precise and high-resolution species identification was attributed to comprehensively addressing an often-neglected and undesired NMR interaction, namely, the 2nd-order quadrupolar-dipolar cross-term interaction (2nd-QD interaction), which was indeed helpful in gaining invaluable information on zeolite structures.

In addition, researchers quantitatively probed Al···H, O···H proximities within both one-bond and multi-bond ranges, and semi-quantitatively realized the dissociation rates of hydroxyl protons such as BrØnsted acid site. They revealed the atomic-scale local environment of the

catalytically important Al-OH and Si-OH moieties.

The NMR techniques developed in this study might be further applied in providing high-resolution analysis of subtle protonic structures in other circumstances such as metal-oxide surfaces, metal-organic frameworks, and biomaterials. "Our study may provide a generic strategy for high-resolution analysis of the subtle protonic structures in zeolites with ^{17}O solid-state NMR," said Prof. Hou.

More information: Yi Ji et al, Precise Structural and Dynamical Details in Zeolites Revealed by Coupling-Edited ^{1}H–^{17}O Double Resonance NMR Spectroscopy, *Journal of the American Chemical Society* (2024). DOI: 10.1021/jacs.3c14787