

Imaging of Acid Site in H-Mordenites with Stimulated Raman Scattering Microscopy

Liu Kuan-Lin¹, Alexey Kubarev², Johan Hofkens¹, Maarten Roeffaers²

¹Department of Chemistry, KU Leuven, B3001, Heverlee, Belgium

²Center for Surface Science and Catalysis, KU Leuven, B3001, Heverlee, Belgium

Mordenites are important acid catalysts both in research and in large scale industrial process, e.g. hydrocarbon cracking reaction. The main active site in protonic mordenite (H-MOR) is the strongly acidic bridging Si–(OH)–Al group located in the internal 3-dimensional micropore networks. A comprehensive knowledge on the acidity, distribution, and accessibility of the acid sites is crucial for the rational design of efficient heterogeneous catalysts. However, most of the characterization work was done on bulk H-MOR samples, and less is known at the single crystal level: the spatial distribution and accessibility of acid sites.^[1]

We report the imaging of distribution and accessibility acid sites in commercial H-MOR ZM101 (Si/Al = 6), ZM510 (Si/Al = 11), and ZM980 (Si/Al:70) using stimulated Raman scattering (SRS) microscopy in combination with nitrile probes.^[2] Nitriles are small and weak base, they can form hydrogen bonding with the acid sites in H-MOR framework. Upon adsorption of deuterated acetonitrile (CD₃CN) on acid site, CN stretch shifts to higher frequency, whose magnitude ($\Delta\omega_{\text{CN}}$) depends on the acidic strength. CD₃CN is able to access all acid sites in H-MOR and thus chemical mapping of adsorbed CD₃CN effectively reveals the distribution of acid sites. Furthermore, the availability of acid site to larger molecules can be visualized by adsorbing larger nitrile probe—benzonitrile.

Homogeneous distribution of acid site is observed in the parent ZM101 and severely dealuminated ZM980 samples. Polarization measurement reveal the orientation of C≡N bond is symmetrically aligned to the crystal b axis for CD₃CN adsorbed in ZM101. Diverse distributions of acid site, however, appear in ZM510 samples after mild dealumination. Polarization measurements further imply acid site in the large channel are preferentially removed during dealumination. Accessibility of acid site is found to be strongly dependent on dealumination. Benzonitrile probes are only found in dealuminated region inside the crystal.

References

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