Gas Adsorption Crystallography via in Situ Transmission Electron Microscopy

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Porous crystals, like zeolites, metal organic-frameworks (MOFs) and covalent-organic frameworks (COFs), have well-defined nanopores and large surface areas. They can serve as adsorbents for gas adsorption and separation, which have gained many interests from chemists and industries. Therefore, the study of mechanisms behind host-guest interactions of porous crystals are necessary for developing more excellent functional porous materials. Many techniques, such as XRD, NMR, electron microscopy, have been playing important roles in explaining related mechanisms and effects.

In 2015, Terasaki \textit{et al.} developed a new method that combined a SAXS instrument and a gas adsorption instrument, to in situ study the structural transformation during adsorption process in a MOF \cite{1}. Later they called it gas adsorption crystallography, which can precisely control temperature and adsorbate pressure, follow the change of frameworks, map the adsorbate distribution during different adsorption stages.

Transmission Electron microscopy (TEM) is also a powerful tool in elucidating adsorption mechanisms of porous crystals, since TEM can obtain both high-resolution images and structure information by electron diffraction. Wei \textit{et al.} used the iDPC-STEM imaging to directly observe para-xylene molecules adsorbed inside the channels of the zeolite MFI at atomic resolution \cite{2, 3}, allowing us better understand the location sites where host-guest interactions occur. Three-dimensional electron diffraction (3D ED) has been developed for \textit{ab initio} structure solution of sub-micron crystals in recent decades. Our group has reported a method, called environmental 3D ED, which can track the stimuli-responsive structures of a MOF crystal at the atomic-level under various environmental conditions, including cryogenic, heating, gas and liquid \cite{4}.

Here, we put forward a method of gas adsorption crystallography via in situ TEM, which can real-time reveal 3D structure changes of porous crystals by environmental 3D ED as the atmosphere (0-1bar) or temperature (77K-1200K) change. It can track the expand-shrink of frameworks, size of pores, distortion of chemical bonds and atomic sites or concentrations of adsorbate during the entire adsorption process. Compared with gas adsorption crystallography realized by in situ SAXS mentioned above, in situ TEM has advantages that 3D ED can obtain 3D structure information rather than 1D SAXS results, and image information can be compensated by high-resolution (S)TEM imaging. We believe this method can strengthen our understanding of host-guest interactions in porous materials, which guide us to optimize adsorbents with better selectivity and efficiency.