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Structure Determination of Molecular Sieve Nanoparticles with Electron Microscopy and Powder X-Ray Diffraction

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Molecular sieves are crystalline materials with ordered pores of molecular sizes. Zeolites and metal-organic frameworks (MOFs) are the most utilized molecular sieve materials. Zeolites are silicon dioxide with ordered micropores (0.5 nm – 2 nm), some of which have silicon substituted with metal atoms for added functionality. [1] MOFs are 3-D coordination networks composed of metal nodes and linkers, where the linkers create a 3-D scaffold that lead to ordered porosity. [2] These molecular cavities give molecular sieves the capability to recognize and manipulate molecules at microscale. For example, zeolite ZSM-5 is an important catalyst that can produce gasoline by catalytic cracking of heavy hydrocarbons, due to its special pore size and pore connections in the crystal structure. ZIF-8 and related materials are MOFs that can be used for CO_2/CH_4 separation, due to its chemical composition that results in selective adsorption and accelerated transport of CO_2 in its molecular cavities. In addition to the crystal structure that decides pore size and topology, the morphology of the crystals is also of great importance. For example, 2-D molecular sieve particles are beneficial for gas separation due to the shortened diffusion path that leads to higher gas permeance; catalyst nanoparticles with sub-100 nm size are beneficial for fully exploiting the reactive surface area of nanoparticles for catalytic reactions.

Studying the structures of these molecular sieve materials is crucial in elucidating their structure-property relationships, which is an avenue toward rational design of molecular sieve materials of industrial interests. This is especially important for materials "custom made" to specific applications, which is quite common in the synthesis of MOFs. Powder X-ray diffraction and single crystal X-ray diffraction are conventional and established methods in studying the structure of zeolites and MOFs. However, these methods usually require bulk phase materials, which in some cases is challenging for nanoparticles. The X-ray diffraction patterns also contain scattering information related to the size and shape of the nanoparticles, which could convolve with the crystal structure information in an X-ray diffraction pattern. Electron microscopy, as a complimentary technique, is capable to provide high-resolution local molecular-scale information that can be used to understand the structures of these materials. One major hurdle related to electron microscopy of molecular sieves, however, is their electron beam sensitivity.

In this study, we show our findings in performing high-resolution imaging and diffraction on zeolite and MOF nanoparticles of various morphologies (Fig. 1) with reduced electron dose, which is a necessary step in studying structures of molecular sieve nanoparticles. FEI Tecnai G^2 20 XTWIN and FEI Talos F200X were used for studying the materials. We then focus on 2-D zeolite [3] and 2-D MOF materials [4] prepared for gas separation, and report structural findings from high-resolution electron microscopy. Additionally, EELS was also performed on one of the MOF samples, MIL-101 (Cr), to demonstrate the possibility of studying molecular sieve local structures with electron microanalysis. (Fig. 2) We also show an investigation of powder X-ray diffraction patterns of these materials, and interpretation of powder X-ray diffraction patterns of nanoparticles with ultra-small dimensions, where the non-Bragg peaks were related to the size and shape of the nanoparticles. In addition to experimental findings, for 2-D zeolite and MOF nanoparticles, structural optimization using density functional theory (DFT)

methods was also performed to study the effects of small dimensions on the crystal and surface structures of zeolite and MOF nanoparticles. Based on the optimized structure, powder X-ray diffraction patterns of nanoparticles of finite size were simulated using a GPU-accelerated algorithm. [5, 6] Electron diffraction patterns were also simulated using Multislice method to investigate the effects of small size. [7]

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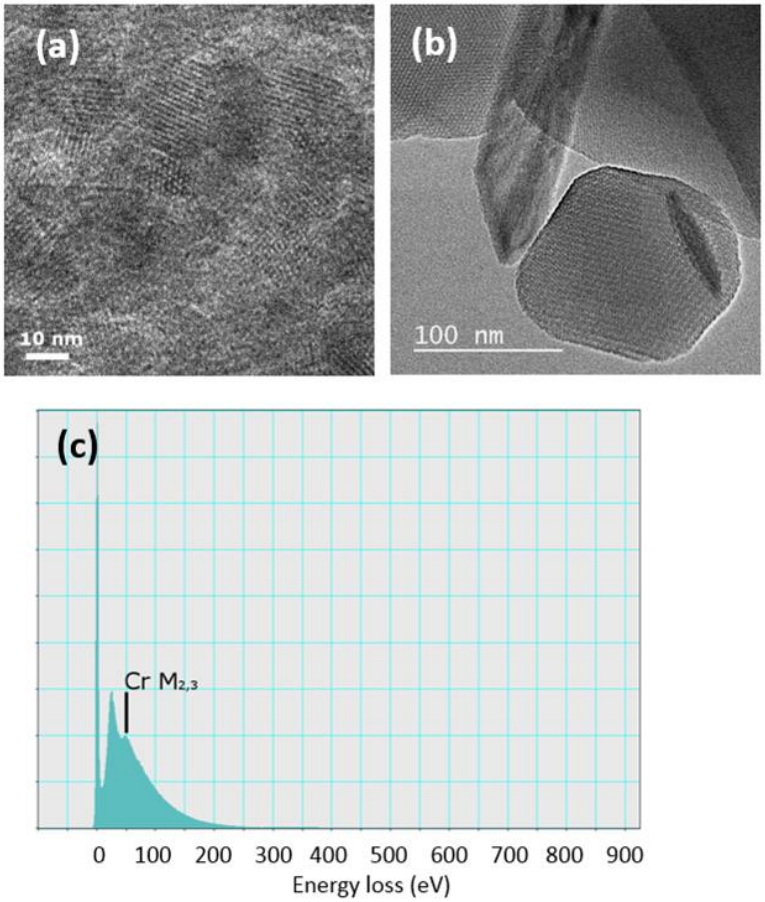

Figure 1. High-resolution TEM images of (a) Zn-MOF-74, (b) MIL-101 (Cr) and (c) EELS spectrum from a typical MIL-101(Cr) particle.

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