COMMENTARY

Unraveling the hidden world of perplexing inhomogeneous zeolite structures by electron ptychography

Xiaona Liu[1,2] and Peng Guo[1,2,*]

[1]National Engineering Research Center of Lower Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[2]University of Chinese Academy of Sciences, Beijing 100049, China

*Correspondence: pguo@dicp.ac.cn

Received: May 30, 2023; Accepted: July 15, 2023; Published Online: August 3, 2023; https://doi.org/10.59717/j.xinn-mater.2023.100019

Citation: Liu X. and Guo P. (2023). Unraveling the hidden world of perplexing inhomogeneous zeolite structures by electron ptychography. The Innovation Materials 1(2), 100019.

Zeolites are commonly known as crystalline porous aluminosilicates with highly organized and regular arrangements of cavities and channels with molecular size pore openings. They are constructed by basic building units TO_4 (T=Al or Si) through corner-sharing oxygens. They have been extensively utilized as the industrial adsorbents and catalysts. Such unique and significant properties are closely associated with their crystallographic structures at the atomic structure. Initially, structural investigations primarily were focused on the diversity of intriguing zeolite frameworks, including pore openings, channel dimensionalities, unique composite building units, etc. Traditionally, such crucial structural information can be extracted from three-dimensional (3D) diffraction data in reciprocal space (such as X-ray diffraction and electron diffraction). The average information is then manifested in one single unit cell. However, in real cases, variations in the composite contents and fine structures within one single unit cell can be observed. When these inhomogeneities are present in the small quantities, they are challenging to detect using the conventional diffraction methods. Furthermore, these inhomo-

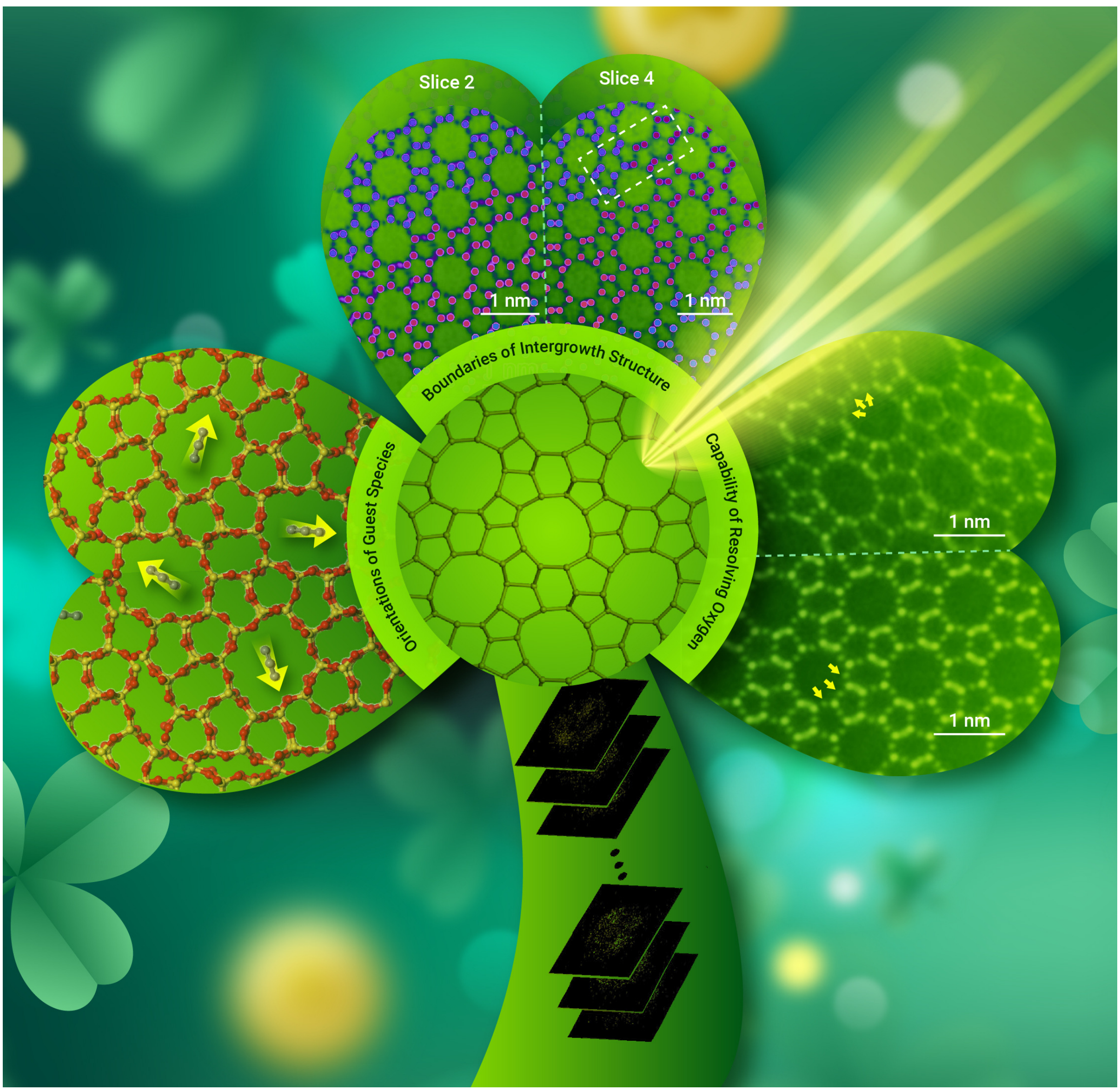

Figure 1. Schematic illustration of inhomogeneous zeolite structure revealed by electron ptychography.

geneities have a significant impact on the specific properties of zeolites.[1] For instance, the intergrowth of multiple polymorphs, where two-dimensional zeolite layers stack disorderly in the third dimension, can greatly influence the catalytic performance. Another important type of inhomogeneity is reflected in the presence of extra-framework Al atoms generated during post-synthesis calcination, resulting in the formation of Lewis acid sites.

The emerging integrated differential phase-contrast scanning transmission electron microscopy (iDPC-STEM) is considered as the state-of-the-art imaging technique for zeolites and other beam-sensitive materials. Utilizing this unique technique, complex stacking disorders of zeolites, fine structures at the zeolite boundary, guest species within zeolite channels, and the evolution of structural dynamics in zeolite frameworks can be visualized at the low-electron dose condition.[1,2] However, this technique still suffers from a requirement for precise electron beam focusing, limited image lateral resolution due to specimen thickness, and a lack of resolving power along the projection direction. Therefore, it will lead to a reduced success rate of imaging, the challenges in detecting oxygens within the zeolite framework, and unsuccessful capture of structural features along the projection direction using the iDPC-STEM technique, respectively.

Very recently, a research work published in the journal Science, led by Prof. Zhang and Prof. Han, has revealed that the hidden world of perplexing inhomogeneities in zeolite structures can be unraveled using low-dose electron ptychography based on four-dimensional (4D) STEM data.[3] Although the concept of ptychography emerged in 1969 for tackling the crystallographic phase problem, electron ptychography was hindered by the hardware and the computing ability. The advent of innovative TEM infrastructures, high-performance pixelated electron detectors, and significant advances in computing power enables researchers to acquire the high-quality 4D STEM data for the further utilization in the electron ptychography. The Science work conducted by Prof. Zhang and Han demonstrates that ptychography reconstructed by maximum likelihood (ML) method combined with multislice and mixed-state algorithms enables the sub-angstrom resolution with the excellent tolerance of specimen thickness and defocus values, while also achieving resolving power along the projection direction, even for the beam-sensitive zeolite materials. Therefore, inhomogeneities of composite contents and fine structures in zeolites including orientations of guest species, the deviation of framework oxygens (O) from the crystallographic sites, and 3D boundaries of complex intergrowth structure can be visualized through multislice ptychography. We would like to highlight three specific applications illustrated in their work:

1) Due to its remarkable tolerance to specimen thickness and focusing conditions, multislice ptychography offers ultrahigh lateral resolutions, which enables the precise determination of orientations of guest species within zeolite channels (Figure 1). Three orientations (pointing to the T atoms, O atoms, and middle of the T-O bonds) of *p*-xylene (PX) were identified in ~40-nm-thick PX-adsorbed **MFI**-type zeolite ZSM-5, implying the inhomogeneous chemical environments in this sample. In addition, the inhomogeneous channel shape in PX-adsorbed and pristine ZSM-5 was also observed.

2) The capability to resolve O atoms within the zeolite framework allows for analysis of the intensity of O columns (Figure 1). The observed abnormal intensity fluctuation of O columns suggests that certain O atoms deviate from their average crystallographic positions. The deviation is likely associated with the generation of extra-framework Al atoms during the calcination process. It is important to note that while the term "oxygen vacancy" was used to describe this deviation in the original contribution, it does not necessarily mean the complete removal of O atoms from the zeolite framework. Benefiting from the depth resolution, the O vacancies and their distributions throughout a zeolite were directly observed.

3) ZSM-5 (**MFI**) and ZSM-11 (**MEL**) share an identical pentasil 2D layer, but they stack in a different manner along the third direction. The mirror symmetry applied to this layer generates ZSM-11, while the inversion center yields ZSM-5. They frequently exhibit the complex intergrowth within a nanodomain. Hence, understanding the spatial distribution of ZSM-5 and ZSM-11 has become an important research topic. Using multislice ptychography, the intergrowth manner of ZSM-5 and ZSM-11 along the *b*-axis was revealed and the interfaces between ZSM-5 and ZSM-11 in the *ac*-plane were also identified at the atomic level. As illustrated in Figure 1, **MEL**-type zeolite ZSM-11 domain consisting of only two pentasil chains presents in slice 2, while such domain expands, generating a new ZSM-5/11 interfaces in slice 4. Based on the observed information, a structure model with dangling silanol groups was built to explain the intergrowth of ZSM-5 and ZSM-11.

The groundbreaking research conducted by Prof. Zhang and Han demonstrates that multislice ptychography is an efficient low-dose 3D imaging approach for the atomic-resolution structural characterization of beam-sensitive zeolite materials. It has been successfully utilized to investigate the inhomogeneity of composite contents and fine structures in zeolites. Notably, two additional independent studies on this topic were coincidentally published around the same time.[4,5] The further structural explorations by multislice ptychography of higher beam-sensitive materials, such as metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and hybrid perovskites, will hold promise. Moreover, with the continuous development of related algorithms and hardware, the improved depth resolution along the projection is also expected, which would enable the discovery of even finer structural features in 3D. Furthermore, While the present time-consuming electron ptychography is unsuitable for in-situ studies of dynamic processes, it is anticipated that this limitation will be overcome as data acquisition and processing capabilities continue to improve.

REFERENCES

1. Shen, B., Chen, X., Fan, X., et al. (2021). Resolving atomic SAPO-34/18 intergrowth architectures for methanol conversion by identifying light atoms and bonds. Nat. Commun. *12*, 2212.
2. Liu, X., Liu, L., Pan, T., et al. (2021). The Complex Crystal Structure and Abundant Local Defects of Zeolite EMM - 17 Unraveled by Combined Electron Crystallography and Microscopy. Angew. Chem. Int. Ed. *60*, 24227–24233.
3. Zhang, H., Li, G., Zhang, J., et al. (2023). Three-dimensional inhomogeneity of zeolite structure and composition revealed by electron ptychography. Science *380*, 633–638.
4. Dong, Z., Zhang, E., Jiang, Y., et al. (2023). Atomic-Level Imaging of Zeolite Local Structures Using Electron Ptychography. J. Am. Chem. Soc. *145*, 6628–6632.
5. Sha, H., Cui, J., Li, J., et al. (2023). Ptychographic measurements of varying size and shape along zeolite channels. Sci. Adv. *9*, eadf1151.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 22288101 and 21972136).

DECLARATION OF INTERESTS

The authors declare no competing interests.