Design of organic structure-directing agents for the synthesis of zeolites with controlled active sites

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Syntheses of materials need to involve trial-and-error in time-consuming wet experiments. We have been working on the syntheses of zeolites with the aid of computational techniques to accelerate the speed of the material design. Zeolite is a class of crystalline microporous materials composed of tetrahedral atoms and oxygen atoms. Especially we focus on the crystal structures, chemical compositions, and atomic locations that are critical factors in the syntheses and applications of zeolites.

The site of Al in zeolite frameworks can influence the physicochemical properties of zeolites. It is of great interest to develop synthetic methods that allow for the siting Al into the specific tetrahedral sites (T-sites) within zeolite frameworks. The synthesis of zeolites with desired sites of Al, however, is very challenging mainly because of the unclarified formation mechanisms of zeolites and the limitation of analytical techniques. Thus far, some successes in controlling over the Al distribution in zeolite frameworks have been reported, but they have mainly relied on a trial-and-error approach by alteration of synthesis parameters such as types of organic structure-directing agents (OSDAs) and sources of Si and Al. Recently, computational calculations suggested that the placement of Al into the specific T-sites is not restricted as there exist thermodynamically favorable sites for Al in some zeolite frameworks[1, 2].

We synthesized IFR-type zeolite with controlled Al locations. The effects of OSDAs on the Al distribution were clarified by combining computational and experimental techniques. The molecular dynamics simulations on GULP suggested that the OSDAs are likely to be tightly fitted inside the zeolite cavities and can alter the relative stability of Al sites. IFR-type zeolites synthesized under an identical condition but with three different OSDAs were characterized by ^{27}Al solid-state NMR with the aid of DFT calculations using Quantum ESPRESSO. The results showed that the Al distribution of IFR-type zeolites can be tuned in accordance with energies derived from the zeolite–OSDA complexes. This combined computational and experimental approach provide a paramount step forward the rational synthesis of zeolites with controlled Al locations[3].

References

[1] K. Muraoka, W. Chaikittisilp, T. Okubo, Journal of the American Chemical Society, 2016, 51, 10718.

[2] M. D. Oleksiak, K. Muraoka, M.-F. Hsieh, M. T. Conato, A. Shimojima, T. Okubo, W. Chaikittisilp, J. D. Rimer, Angewandte Chemie International Edition, 2017, 56, 13366.

[3] K. Muraoka, W. Chaikittisilp, Y. Yanaba, T. Yoshikawa, T. Okubo, Angewandte Chemie International Edition, 2018, 57, 3742.