Single Crystals as Reaction Vessels

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Japanese researchers from the University of Tokyo have made a complex that crystallizes as a porous solid. Common reagents, even bulky ones, can easily diffuse into these pores and are sufficiently mobile to react with embedded substrates. As they report in the journal *Angewandte Chemie*, the pores act as a sort of crystalline molecular test tube. The reaction products can then be directly examined by X-ray crystallographic methods.

Only single crystals can be examined by X-ray crystallography. The crystal's diffraction of X-rays can be used to determine its structure. Liquids are not so easy to analyze. In solid-state reactions, this technique is limited to cases in which the structural changes are very small. Bulky reactants cannot even get into an ordinary tightly packed crystal, and crystals often decompose in the course of the reaction.

A team led by Makoto Fujita has developed a complex of zinc ions and aromatic ring systems that crystallizes into a robust network with large pores. The compound is constructed so that reactive groups of atoms, such as amino groups, protrude into the pores.

Dipping the crystals into a solution containing common reactants brings these into contact with the embedded reaction partners. Even bulky molecules can get into the large pores. The researchers were thus able to react the amino groups with acetic anhydride or aniline. The reactivity of the reagents used and the course of the reaction are no different than if the reactants encountered each other freely in solution. The crystal changed color little by little, but remained intact in crystalline form

despite the reaction.

Because the final product of the reaction is still in the form of a single crystal, the course of the reaction can be followed by X-ray crystallographic methods. Labile reaction products and intermediates can thus be produced and detected in situ. The chemical reactions within the pores can also be used to modify the walls of the pores as needed. For example, they can be equipped with free acid groups.

Citation: Makoto Fujita, Title: Single-Crystalline Molecular Flasks: Chemical Transformation with Bulky Reagents in the Pores of Porous Coordination Networks; *Angewandte Chemie International Edition*, doi: 10.1002/anie.200802545

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