

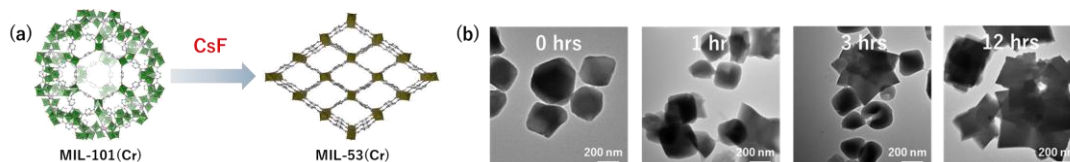
## Development of a New Structural Transformation Reaction with Cr-based MOFs Induced by Fluoride

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Metal-organic frameworks (MOFs), composed of metal ions and organic linkers, possess well-defined structures with permanent porosity, high specific surface areas and notable flexibility. These properties position MOFs as promising candidates for various applications. A distinguishing feature of MOFs is their ability to form various structures using the same metal ions and organic ligands and it is noteworthy that some MOFs could transform to other MOFs. However, the transformable MOFs were still very few especially in the case of kinetically inert MOFs, though they are promising for future sustainable applications. In this work, we focused on kinetically inert Cr-based MOFs, MIL-101(Cr) and MIL-53(Cr) to develop new structural transformation system. Both MOFs are composed of  $\text{Cr}^{3+}$  ions and terephthalate and have the same  $\text{Cr}^{3+}$ /terephthalate ratio, indicating that MIL-101(Cr) could be completely consumed to form MIL-53(Cr). In addition, we used fluoride as an additive to weaken the coordination bond between  $\text{Cr}^{3+}$  and terephthalate, inducing the structural transformation reaction. (**Figure a**).

By heating MIL-101(Cr) in 60 mM CsF (aq), MIL-53(Cr) was successfully obtained. From time-course TEM observations, the number of sphere-like MIL-101(Cr) crystals decreased while the number of large cubic-like MIL-53(Cr) increased. Additionally, the size of MIL-101(Cr) crystals has become gradually smaller as the transformation proceeded, indicating that the nucleation reaction of MIL-53(Cr) initiated from partially eluted metal ions and organic linkers (**Figure b**). These results suggest that the structural transformation reaction proceeded through a partial dissolution-recrystallization process. In addition, XPS measurements showed that the resulting MIL-53(Cr) has fewer defects than the one directly synthesized from  $\text{Cr}^{3+}$  ions and terephthalic acid, indicating that this transformation reaction is useful to generate highly crystalline MIL-53(Cr).



**Figure.** (a) Schematic of structural transformation from MIL-101(Cr) to MIL-53(Cr).  
(b) TEM images of the samples obtained with 60 mM CsF (aq) over different reaction times.