

## Observation of rapid lift-up behavior of acetate-intercalated layered yttrium hydroxide interlayer in water: Application for heterogeneous Brønsted base catalysts

Due to their unique characteristics combined with their host–guest properties and rare-earth cations, layered rare-earth hydroxides (LRHs) are receiving much attention as a new type of anionic layered compound [1]. The general formula of LRHs is  $\text{Ln}_2(\text{OH})_5\text{X}\cdot n\text{H}_2\text{O}$ , where Ln and X are a trivalent rare-earth metal cations and anions, respectively. There are two kinds of coordination polyhedra, such as a dodecahedron and a monocapped square antiprism, linked through  $\mu^3$ -hydroxy groups in the cationic layer of LRHs,  $[\text{Ln}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]^{2+}$ . Numerous studies by use of various types of LRHs applied as the functional materials have been reported, however, there are few examples of the application of LRHs as catalyst materials.

We have reported successful Knoevenagel condensation with various anion-exchanged layered yttrium hydroxides (Y-LRHs) as solid base catalysts [2]. Catalytic condensation in water proceeded efficiently in the presence of acetate-intercalated Y-LRH ( $\text{CH}_3\text{COO}^-/\text{Y-LRH}$ ). In this catalysis, the specific lift-up behavior of the basal spacing of  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  in the presence of excess water was confirmed by time-resolved synchrotron-radiation X-ray diffraction (*t*-SXR) profiles.

A novel *t*-SXR measurement system was developed at SPring-8 BL02B2 [3]. The measurement system consisted of a diffractometer equipped with a sample stage, an auto-titrator, and multiple MYTHEN detectors at room temperature. The sample stage contained a glass tube holder ( $\phi 10$  mm) was set with

a magnetic stirrer. A constant solution volume was remotely and promptly transferred from the auto-titrator to the sample glass tube through a fluorinated ethylene propylene (FEP) tube. The *t*-SXR patterns were acquired over 360 s with accumulation time of 0.5 s per diffraction pattern and an X-ray wavelength of 0.08 nm (15.5 keV) was selected.

According to the report by Sasaki *et al.* [4], the parent chloride-intercalated Y-LRH ( $\text{Cl}^-/\text{Y-LRH}$ ;  $\text{Y}_2(\text{OH})_5\text{Cl}\cdot 1.43\text{H}_2\text{O}$ ) was synthesized by the homogeneous precipitation method. The treatment of  $\text{Cl}^-/\text{Y-LRH}$  with various sodium acetate yielded  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst in the form of white powders. The  $\text{Cl}^-/\text{Y-LRH}$  was dispersed in water set on the glass tube with vigorous stirring, and then the SXR pattern of the aqueous dispersion of the sample was collected. The aqueous sodium acetate solution was immediately added at once using the auto-titrator.

Figure 1(a) shows the 2D maps of the *t*-SXR profiles for Y-LRH during the anion exchange reaction from chloride into acetate. This anion-exchange reaction rapidly occurred. After the addition of aqueous sodium acetate into the solution of  $\text{Cl}^-/\text{Y-LRH}$  dispersed in water, the  $d_{001}$  peak at  $5.51^\circ$  ( $0.85$  nm) disappeared immediately, a new peak based on the formation of  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  in water appeared at  $3.45^\circ$  ( $1.33$  nm), and the FWHM value of the newly appeared peak was constant. From the time profile of the peak area at  $3.45^\circ$  (Fig. 1(b)), two steps, fast and slow increment behavior, were clearly observed. In contrast, anion-exchange ratio of 91 and 93%,

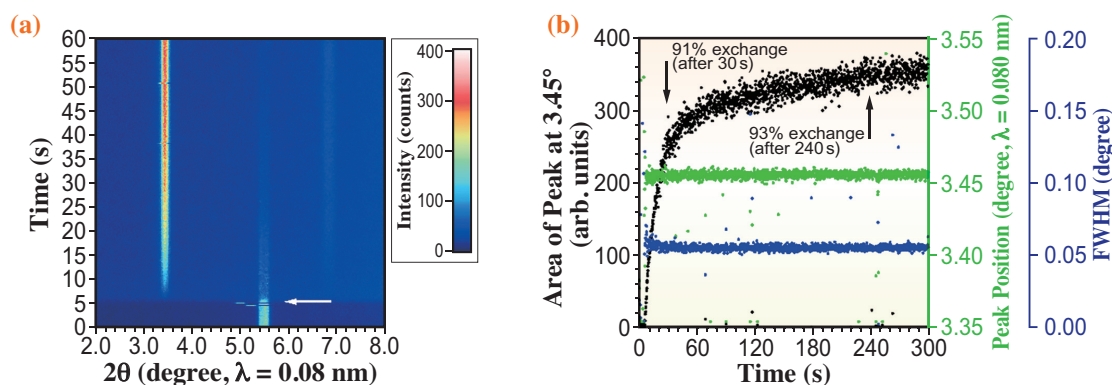


Fig. 1. (a) 2D mapping plots of the *t*-SXR patterns of Y-LRH during the anion-exchange reaction from chloride into acetate. The arrow indicates the starting point of the addition of aqueous sodium acetate solution. (b) Time profile of the newly appeared peak area at  $3.45^\circ$ , peak position, and FWHM value in *t*-SXR.

confirmed by ion chromatography of the liquid phase, were obtained after 30 and 240 s, respectively. From these results indicate, it can be speculated that anion-exchange from  $\text{Cl}^-$  into  $\text{CH}_3\text{COO}^-$  occurred rapidly and that diffusion and rearrangement of the anion species in the Y-LRH interlayer space took place relatively slowly, accompanied by the formation of a stacked structure. In the previous studies of ion exchange behavior, the structures after ion exchange reaction, i.e., after an ion exchange equilibrium, have been discussed. By use of this measurement technique in liquid phase, the structural change of solid materials until reaching ion exchange equilibrium was able to be discovered.

Interestingly, the basal spacing of the  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst increased from 1.00 nm to 1.35 nm only in the addition of water. The isolated interlayer acetate by electrostatic interaction between the layered host might interact with *ca.* four water molecules by hydrogen bonds to form acetate–water composites in the interlayer. To the best of our knowledge, this is the first example showing the lift-up behavior of LRH interlayers in aqueous media. During the water-swelling process of the  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst, the  $d_{001}$  peaks of the nonhydrated

matrix, observed at  $4.70^\circ$  (1.00 nm), immediately disappeared, and new peaks based on the lifted-up  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  were appeared at  $3.47^\circ$  (1.32 nm), shown in Fig. 2(a). The *t*-SXR measurement was conducted with the addition of water into nonswelling  $\text{CH}_3\text{CN}$  in the presence of the  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst. From the time profile of the peak area at  $3.47^\circ$ , the expanded layered structure increased rapidly, and a newly arranged interlayer was formed within a minute (Fig. 2(b)). The time scale of the expansion of the interlayer spacing due to the formation rate of the acetate–water composite in the Y-LRH interlayer was faster than that of the catalytic Knoevenagel condensation.

The  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst was able to be applied for gram-scale Knoevenagel reaction, and an almost quantitative amount of corresponding analytically pure grade product was obtained. The  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  catalyst was reusable without any loss of its catalytic activity and selectivity. We expect that the proposed characterization method will contribute to the understanding the relationship between dynamical structural change of layered compounds as a catalyst material and their catalytic properties.

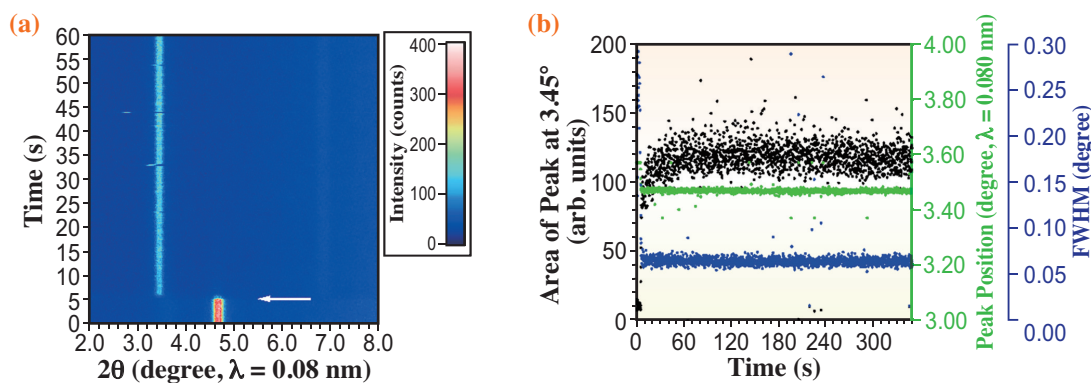


Fig. 2. (a) 2D mapping plots of the *t*-SXR patterns of  $\text{CH}_3\text{COO}^-/\text{Y-LRH}$  during the interlayer lift-up process. The arrows indicate the starting point of the addition of water into a solid dispersion in acetonitrile solution. (b) Time profile of the newly appearing peak area at  $3.45^\circ$ , peak position, and FWHM value in *t*-SXR.

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## References

- [1] J.-G. Li *et al.*: J. Adv. Ceram. **6** (2017) 177.
- [2] T. Hara, M. Habe, H. Nakanishi, T. Fujimura, R. Sasai, C. Moriyoshi, S. Kawaguchi, N. Ichikuni and S. Shimazu: Catal. Sci. Technol. **12** (2022) 2061.
- [3] K. Sugimoto *et al.*: Rev. Sci. Instrum. **88** (2017) 085111.
- [4] T. Sasaki *et al.*: J. Am. Chem. Soc. **130** (2008) 16344.