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Optimal topotactic conversion of layered octosilicate to RWR-type zeolite by separating the formation stages of interlayer condensation and elimination of organic guest molecules

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We demonstrate that the separation of two stages of interlayer condensation under refluxing and elimination of organic guests provides the optimal condition for the formation of RWR-type zeolite from layered octosilicate. The obtained RWR-type zeolite has higher quality than any other RWR-type zeolites reported previously.

Zeolites are applied for various fields including catalysis, adsorption, separation, and ion exchange.1 Recently, topotactic conversion of layered silicate through interlayer condensation has expanded synthetic chemistry of zeolites which are normally prepared under hydrothermal conditions.2 Layered silicates possess 2D layers composed of mainly SiO4 tetrahedral units and cations as a counterpart of the negatively charged layers in the interlayer spaces. Interlayer Si-O/Si-OH groups with ordered arrangement on the surfaces of layered silicates are reactive for covalent modifications,3 including interlayer condensation, silylation and esterification, while the resultants can reflect the original frameworks and crystal morphologies. Interlayer condensation has led to topotactic formation of zeolites.4 Topotactic conversion has advantages and disadvantages. The advantages are acquisition of unique frameworks,4a,c-g,i new compositions,4h and unconventional morphologies4h,j that have not yet been accessible under hydrothermal conditions. One of the disadvantages is the presence of larger amounts of defects due to incomplete condensation, stacking disorder of layers, and/or intra-layer condensation than those of hydrothermally obtained zeolites.1b Another one is the tendency to form more heterogeneous structures, judging from the broadness of signals in 29Si MAS NMR spectra.4c,h,i,j Such local structures largely influence the properties, such as catalysis, adsorption, and so on. Therefore, novel synthetic conditions for topotactic conversion of layered silicate to zeolite are needed in order to reduce structural defects and/or local heterogeneities of Si atoms in finally obtained zeolites.

RWR-type zeolite, RUB-24, is only obtained from layered octosilicate (Na-Oct: Na8[Si32O64(OH)8·32H2O], RUB-18, or Ilerite) by interlayer condensation after the control of the stacking sequence through intercalation with organic molecules.4c,i,j There are three reports for the synthesis of RUB-24. In the first report by Marler et al.,1b RUB-24 was obtained through intercalation of triethylenetetramine.1c Two other methods by Omi et al.4e and Ikeda et al.5b used intercalation of acetic acid. However, all three reports show obtained RUB-24s after calcination possess many defects (uncondensed =Si-O-Si sites) and low degree of homogeneity of Si environments in the local structure, judging from the existence of Si atoms with Q3 environment and broadness of the 29Si MAS NMR signals. In those methods for the synthesis of RUB-24, both interlayer condensation between neighboring layers and elimination of organic compounds simultaneously occur during calcination (Scheme 1a). Such simultaneous reactions probably affect the structure (the amount of defects and the degree of homogeneity of Si environments) of finally obtained RUB-24, because the interlayer environment constantly changes during the formation of Si-O-Si linkages between layers by burning the interlayer organic compounds. In order to circumvent such uncontrollable processes, we conceived that the separation of stages of interlayer condensation and removal of organic guest molecules should lead to the formation of more regulated structure under more controlled formation conditions. However, such processes have never been investigated in the field of topotactic conversion of layered silicates through interlayer condensation.

Scheme 1 Synthesis of RUB-24 from layered octosilicate through (a) the conventional approach and (b) the novel approach in this study.
Here we report a successful method for the separation of interlayer condensation and elimination of organic compounds in topotactic conversion of layered octosilicate for the first time (Scheme 1b). Protonated octosilicate (H-Oct) in N-methylformamide (NMF) was refluxed for intercalation of NMF, and more importantly this reaction resulted in interlayer condensation of neighboring silicate layers without elimination of NMF to retain the interlayer environments during the interlayer condensation. Then, the subsequent calcination leads to the formation of RUB-24. NMF was selected because of the following three reasons. (i) We have recently clarified amide molecule can be used for topotactic conversion of layered silicates. 5(ii) The boiling point of NMF is relatively high, which is preferable for condensation of Si-OH groups between neighboring layers. 9 (iii) The size of NMF is comparable to the pore size of RUB-24. Therefore, NMF is suitable for this concept.

Protonated H-Oct (characterization data of H-Oct: powder X-ray diffraction (XRD) pattern in Fig. 1a and the $^{29}$Si MAS NMR spectrum in Fig. 2a) with no Na ions (determined by the inductively coupled plasma analysis) was refluxed in neat NMF at 180 °C for 1 h to achieve only interlayer condensation (denoted as Reflux-NMF-Oct). The experimental details are described in ESI. 

The XRD pattern of H-Oct (Fig. 1a) shows the formation of framework of RUB-24. Although the ratio of integral intensity in the starting H-Oct of the $^{29}$Si MAS NMR spectrum (Fig. 2a) is $Q_3$:$Q_4 = 1:1$, the $^{29}$Si MAS NMR spectrum of Reflux-NMF-Oct (Fig. 2b) shows only $Q_4$ units with several environments, indicating almost all the interlayer Si-OH groups are condensed between the layers. Importantly, the $Q_3$ signals are well resolved and much sharper than those in the previous reports, implying several inequivalent Si environments in the framework of formed RUB-24. The C/N value of Reflux-NMF-Oct (Table S1, ESI†) is 2.5, and the value is higher than that of NMF (2.0), showing decomposition of NMF to some extent during refluxing. In addition, the $^{13}$C CP/MAS NMR spectrum of Reflux-NMF-Oct (Fig. S2, ESI†) shows the presence of small amounts of different species possibly arising from NMF. These results show interlayer condensation of H-Oct proceeds without elimination of organic compounds through refluxing in NMF to form RUB-24-type framework with higher quality than the previously reported RUB-24. 5

Next, Reflux-NMF-Oct was calcined in air at 550 °C to eliminate the interlayer organic compounds. The obtained sample is denoted as Cal-Reflux-NMF-Oct. The SEM image of Cal-Reflux-NMF-Oct (Fig. S1c) also shows plate-like particles, reflecting the morphology of H-Oct. The elemental analysis (Table S1, ESI†) shows no carbon and nitrogen species, indicating the elimination of organic compounds by calcination. The XRD pattern of Cal-Reflux-NMF-Oct (Fig.1c) is virtually the same as that of Reflux-NMF-Oct (Fig.1b), indicating no collapse of the framework of RUB-24. In addition, the $^{2}$Si MAS NMR spectrum of Cal-Reflux-NMF-Oct (Fig. 2c) shows nearly the same signals as that of Reflux-NMF-Oct, indicating no collapse of silica framework. Therefore, the high quality framework of Reflux-NMF-Oct was retained after calcination. The $^{29}$Si MAS NMR spectrum of Cal-Reflux-Oct shows at least six signals. However, the previously analyzed structure of RUB-24 is thought to consist of only two Si environments. 5 This discrepancy suggests that RUB-24 can possess more Si environments than recognized previously, though the two environments may be the major different ones.

In order to investigate the effect of the refluxing, an intercalation compound of H-Oct with NMF was formed at r.t. (NMF-Oct), avoiding interlayer condensation (the detailed procedures are shown in ESI†). The powder XRD pattern of NMF-Oct (Fig. S3, ESI†) shows higher basal spacing (1.2 nm) than that of H-Oct (0.75 nm). The $^{29}$Si MAS NMR spectrum of NMF-Oct (Fig. S4) shows the same value of $Q_3$:$Q_4$ as that of pristine Na-Oct and H-Oct. These results indicate the expansion of the interlayer spaces and no interlayer condensation after intercalation with NMF, although NMF in the interlayer spaces is slightly decomposed judging from the ratio of C/N by CHN analysis (Table S1).

We prepared another RUB-24 for comparison through calcination of NMF-Oct (denoted as Cal-NMF-Oct) at 550 °C in order to investigate the effect of the unseparated approach using the same organic species. The XRD pattern of Cal-NMF-Oct (Fig. 1d) also shows the formation of RUB-24, indicating NMF can be tuned the stacking sequence of layers without refluxing. However, the signals in the $^{29}$Si MAS NMR spectrum of Cal-NMF-Oct (Fig. 2d) is slightly broader than that of Cal-Reflux-NMF-Oct, although the chemical shifts are coincident each other. This indicates Cal-Reflux-NMF-Oct possesses the higher homogeneous Si environments than Cal-NMF-Oct. From another point of view, the quality of Cal-NMF-Oct is higher than that of RUB-24s reported previously, 4c,5 suggesting NMF can be a better controller of the stacking sequence than triethylenetetramine 4c and acetic acid. 5

Finally, Cal-Reflux-NMF-Oct and Cal-NMF-Oct were
calcined at higher temperature 900 °C (denoted as Cal-Reflux-NMF-Oct_900 and Cal-NMF-Oct_900, respectively) in order to compare their thermal stabilities. Both the samples after calcination possess some amounts of an amorphous phase, judging from a halo peak around 20-30° in addition to the peaks due to RUB-24 in the XRD patterns (Fig. 3). However, the degree of degradation of Cal-Reflux-NMF-Oct is lower than that of Cal-NMF-Oct, indicating the higher thermal stability of Cal-Reflux-NMF-Oct.

The reason for the higher thermal stability of Cal-Reflux-NMF-Oct is probably due to the difference in the local structures as shown by the degree of broadness in the $^{29}$Si MAS NMR spectra. Because it is known that the higher flexibility of zeolite framework leads the lower thermal stability, the framework flexibility of Cal-Reflux-NMF-Oct is probably lower than that of Cal-NMF-Oct. In addition, Gies et al. reported that thermal analysis of RUB-24 until 1000 °C leads to the formation of cristobalite. However, the TG-DTA measurement of Cal-Reflux-NMF-Oct in this study shows no exothermic peaks until 1000 °C, indicating the higher thermal stability of Cal-Reflux-NMF-Oct.

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Notes and references


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