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Structure-inheriting solid-state reactions under hydrothermal conditions

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Abstract

We have explored several structure-inheriting solid-state reactions (SISSRs) under hydrothermal conditions for syntheses in the Co–Mo–O system. And we found an interesting hydrothermal SISSR from $CoMoO_4 \cdot 3/4H_2O$ to high-pressure (hp-) phase of $CoMoO_4$, which enabled us to considerably reduce the severe conditions for the synthesis of hp-$CoMoO_4$. As similar hydrothermal SISSRs are expected to be useful tools for material syntheses, we also briefly discuss them as a means of developing novel material syntheses and designs.

Keywords: Hydrothermal synthesis; Solid-state reaction; Soft chemistry; Cobalt molybdate

1. Introduction

As is now well-known, hydrothermal syntheses can lead to the formation of materials at much lower temperatures than those necessary for conventional solid-state syntheses. Some of these low-temperature syntheses may lead to intermediate states, which maintain a structural resemblance to the starting compound, as shown in Fig. 1. Usually hydrothermal syntheses involve the dissolution of the starting compounds and thus the products may lose any structural resemblance to the reactants. However, when one of the reactants remains in the solid state under hydrothermal conditions it becomes possible to control the structure of the product by varying the structure of the insoluble reactant. Some such solid-state reactions (SSRs), such as ion-exchange and intercalation, under hydrothermal conditions are known [1–5]. However, further systematic research on SSRs under hydrothermal conditions is needed in order to apply them to the syntheses of new compounds with novel structures. We have been exploring, especially, the hydrothermal SSRs that lead to structural reconstruction while maintaining a structural resemblance between the starting and product compounds, and referred to them as structure-inheriting SSRs (SISSRs) under hydrothermal conditions [6–9].

Recently we have studied hydrothermal syntheses in the Co–Mo–O system and found an interesting hydrothermal SISSR, which enabled us to significantly reduce the severity of the synthesis from the prior work for the high-pressure (hp-) phase of $CoMoO_4$. In this paper, we report this SISSR and describe briefly SISSRs expected to be useful for designing novel materials.

2. Experimental

In order to investigate the effects of the solubility of the starting materials on the material formed, starting reagents consisting of various combinations of soluble and insoluble Mo and Co sources were studied (see Table 1). MoO_3 and CoO were used as the insoluble sources and were essentially insoluble in the solution before the hydrothermal treatment, whereas amorphous (am-) $MoO_3 \cdot nH_2O$ and $CoCl_2 \cdot 6H_2O$ were used as the soluble sources. Reagent grade MoO_3, CoO, and $CoCl_2 \cdot 6H_2O$ were purchased. The am-$MoO_3 \cdot nH_2O$ was prepared by

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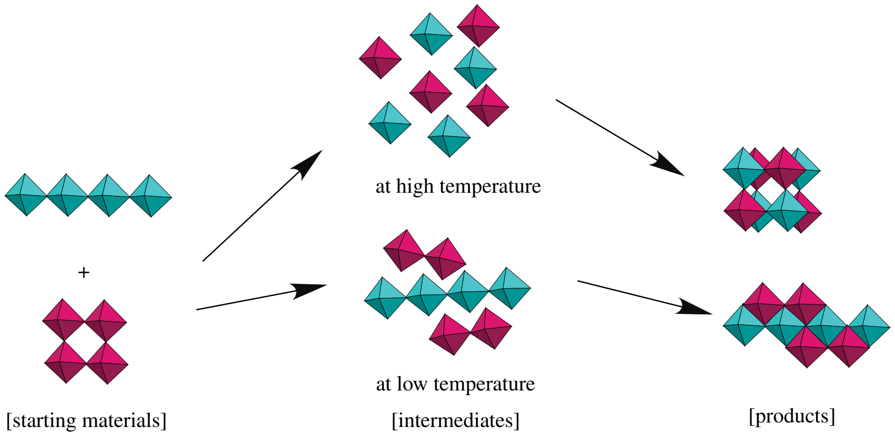


Fig. 1. Conceptual schemes of material formation.

Table 1
Co–Mo–O products obtained by the hydrothermal treatment of various starting materials at 453 K for 3 days

Run	Mo[a] source	Co[a] source	Additives	Initial state[b]	pH[c]	Products
1	$\underline{MoO_3}$	$\underline{CoO}$	—	Solid	4.1	hp-$CoMoO_4$
2	am-$MoO_3 \cdot nH_2O$	$\underline{CoO}$	—	Solid + solution	2.1	$CoMoO_4 \cdot 3/4H_2O$, hp-$CoMoO_4$, $CoMo_4O_{13} \cdot 2H_2O$
3	$\underline{MoO_3}$	$CoCl_2 \cdot 6H_2O$	—	Solid + solution	3.9	MoO_3
4	am-$MoO_3 \cdot nH_2O$	$CoCl_2 \cdot 6H_2O$	—	Solution	1.9	$CoMo_4O_{13} \cdot 2H_2O$, MoO_3
5	$\underline{MoO_3}$	$\underline{CoO}$	HCl	Solid	1.6	$CoMo_4O_{13} \cdot 2H_2O$, MoO_3
6	am-$MoO_3 \cdot nH_2O$	$\underline{CoO}$	HCl	Solid + solution	1.6	$CoMo_4O_{13} \cdot 2H_2O$, MoO_3
Ref. [13][d]	$Na_2MoO_4 \cdot 2H_2O$	$CoCl_2 \cdot 6H_2O$	Succinic acid, KOH	Solution	3	hp-$CoMoO_4$

[a] Underlined are the compounds that remain essentially in the solid state in the solutions before the hydrothermal treatment.
[b] The state of the solution before the hydrothermal treatment.
[c] pH value of the solution before the hydrothermal treatment.
[d] The product obtained by the hydrothermal treatment at 473 K for 3 days.

spray-drying a molybdic acid solution, obtained by passing a $Na_2MoO_4 \cdot 2H_2O$ solution through an acid ion-exchange resin (Dow Chemical Co. Dowex 50W-X8). The hydration number n of the am-$MoO_3 \cdot nH_2O$ was determined to be about 1.1 by thermogravimetric analysis (TG-DTA). The mixture of Mo and Co sources (2.4 mmol each) was suspended or dissolved in 40 mL of distilled water. For runs 5 and 6 (see Table 1), 4.8 mmol of HCl was also added to the solution to match its chlorine content to that of the solutions of runs 3 and 4. The resulting solution was put into a 60 mL Teflon-lined autoclave and heated in a forced convection oven at 453 K under autogenous pressure for the desired time. The resulting product was filtered, washed with distilled water, and dried in air at room temperature.

The pH value of the solution was measured before the hydrothermal treatment. The powder X-ray diffraction (XRD) patterns of the products were measured on a Mac Science MXP3VZ X-ray diffractometer with a graphite monochromator using Cu$K\alpha$ radiation. Thermal analysis was performed on a Mac Science TG-DTA 2010S system at a heating rate of $10\,K\,min^{-1}$ in air flow. The chemical compositions of the products were determined by a HITACHI 180-80 atomic absorption spectrometer.

3. Results and discussion

3.1. Products obtained by hydrothermal treatments of the starting materials consisting of various combinations of Mo and Co sources

Table 1 shows the products obtained in the hydrothermal syntheses consisting of various combinations of the Mo and Co sources. The formation of three kinds of cobalt molybdates was observed as shown in the table. They were hp-$CoMoO_4$, $CoMoO_4 \cdot 3/4H_2O$, and $CoMo_4O_{13} \cdot 2H_2O$ [10]. The last is apparently a new compound, while the first two are known [11–13]. The last compound has a triclinic cell with $a = 5.525(2)$ Å, $b = 7.058(2)$ Å, $c = 7.556(2)$ Å, $\alpha = 90.011(7)^\circ$, $\beta = 105.252(7)^\circ$, and $\gamma = 90.381(7)^\circ$. Recently we succeeded in determining it's crystal structure and that of an isotructural nickel molybdate; this work will be reported elsewhere.

The pH of the hydrothermal reaction medium has been shown previously to play a critical role in determining the product formed [14]. The products formed here, shown in Table 1, also depend on the pH of the initial solutions as well as on the specific starting materials. The specific reactants also play a role in determining the pH as shown in Fig. 2, which shows the pH change with time for MoO_3 as a function of time and temperature. The partial dissolution/hydrolysis of the molybdenum oxide creates an acidic medium, which increases at elevated temperatures where the solubility increases; as cobalt oxide is added there is a slight increase of the pH. Comparison of runs 3 and 4 with runs 5 and 6 in Table 1 proves the key role of pH. That is, the same products ($CoMo_4O_{13} \cdot 2H_2O + MoO_3$) are formed from the solutions with pH$<$ ca. 2 (runs 4–6), in spite of the differences in the initial state of the solution among runs 4–6. The crystal size and crystallinity of the $CoMo_4O_{13} \cdot 2H_2O$ were changed easily with the cooling rate after the hydrothermal treatment and the reactant concentrations of Mo and Co in the hydrothermal solution. This suggests that the $CoMo_4O_{13} \cdot 2H_2O$ is formed via a hydrothermal dissolution-precipitation process. On the other hand the crystal size and crystallinity of hp-$CoMoO_4$ and $CoMoO_4 \cdot 3/4H_2O$ did not change with the cooling rate and the concentrations. Therefore there is a possibility that they are formed by a solid-state process, although Livage et al. reported that hp-$CoMoO_4$ is formed via a hydrothermal solution process [13]. As mentioned by Livage et al., the formation at around 450 K of hp-$CoMoO_4$, which is usually prepared via a solid-state phase transition from α-$CoMoO_4$ or β-$CoMoO_4$ under very severe conditions (50 kbars and ca. 900 K [15]), is of great interest for materials scientists. Thus it is important to reveal its formation mechanism. For comparison the details of the Livage's synthesis of hp-$CoMoO_4$ are also presented in Table 1. In Livage's synthesis, the reactants are soluble thus the hp-$CoMoO_4$ must be formed via a solution process, but an intermediate product might be initially formed. In that synthesis, hp-$CoMoO_4$ and $CoMoO_4 \cdot 3/4H_2O$ are formed from the same starting solution, the former is formed at 473 K and the latter at 423 K. In our run 2 both compounds are present simultaneously in the product. Therefore we investigated the formation process of hp-$CoMoO_4$ and the relation between these compounds in the formation process. The results are described in the following section.

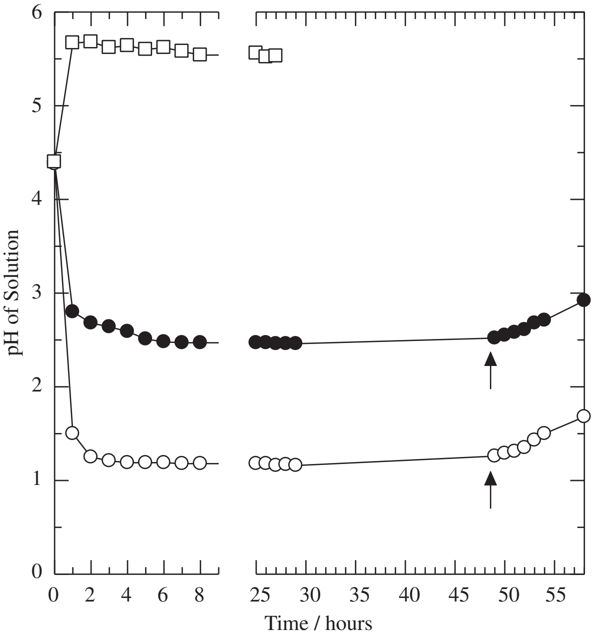


Fig. 2. The pH of solutions prior to hydrothermal synthesis for MoO_3 (0.01 mol in 100 mL water) at room temperature (●) and at 353 K (○), and the effect of adding CoO (0.01 mol). Arrows indicate the addition of CoO. After 1 week the pH values were 2.92 and 1.68 respectively. For comparison the data for ammonium molybdate is also presented (□).

3.2. *Formation mechanism of hp-$CoMoO_4$ and a SISSR under a hydrothermal condition*

In order to reveal the formation process, we investigated the changes of the products during the hydrothermal treatment as a function of reaction time. Fig. 3 shows the progression of the structural changes of the products during the treatment of MoO_3 and CoO at 453 K. According to this figure, the MoO_3 reactant is completely dissolved within the first 5 min of hydrothermal treatment. Subsequently $CoMoO_4 \cdot 3/4H_2O$ is formed probably via a

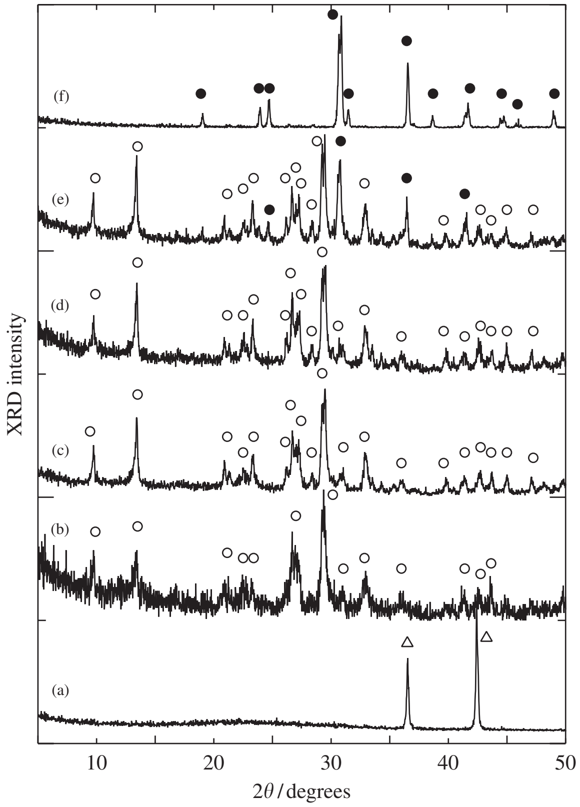


Fig. 3. The XRD patterns of the samples obtained by the hydrothermal treatments of $MoO_3 + CoO$ at 453 K for 5 min (a), 3 h (b), 12 h (c), 1 day (d), 2 days (e), and 3 days (f). Symbols △, ○, and ● indicate CoO, $CoMoO_4 \cdot 3/4H_2O$, and hp-$CoMoO_4$, respectively.

reaction between the Co and Mo species in the solution (i.e., by a hydrothermal solution process). The formation of hp-$CoMoO_4$, accompanied with the gradual disappearance of the $CoMoO_4 \cdot 3/4H_2O$, is found for the two or more day's treatment, and thus it is proposed that the initially formed $CoMoO_4 \cdot 3/4H_2O$ is converted gradually into hp-$CoMoO_4$. The yields of the solid products (81.6% for the 1-day treatment and 73.8% after 3-day treatment [16]) proved the formation of hp-$CoMoO_4$ via $CoMoO_4 \cdot 3/4H_2O$. The hydrothermal treatment of the same starting materials at 423 K provided $CoMoO_4 \cdot 3/4H_2O$, but not hp-$CoMoO_4$, like Livage's synthesis at 423 K. Moreover, in the case of the hydrothermal treatment of am-$MoO_3 \cdot nH_2O$ and CoO at 453 K it took a much longer time (about 6 days) for hp-$CoMoO_4$ to be completely formed from $CoMoO_4 \cdot 3/4H_2O$, compared to the hydrothermal treatment of MoO_3 and CoO. Thus the formation of hp-$CoMoO_4$ seems to be related to the treatment temperature and the pH value of the solution as well as the nature of starting materials.

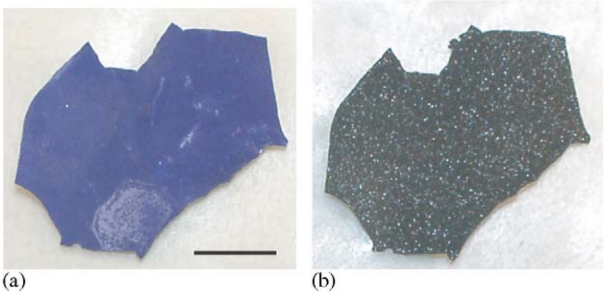


Fig. 4. Photographs of the samples: (a) before and (b) after the transformation from $CoMoO_4 \cdot 3/4H_2O$ to hp-$CoMoO_4$ by the hydrothermal treatment at 453 K. The scale bar indicates 5 mm.

According to the literature [11–13,17], three polymorphs of $CoMoO_4$ are known. The formation of hp-$CoMoO_4$ from $CoMoO_4 \cdot 3/4H_2O$ seems not to agree with the Ostwald step rule [18], because hp-$CoMoO_4$ is the densest of the three (4.78, 4.57, 5.58 g/cm^3 for α-, β-, and hp-$CoMoO_4$'s, respectively) and is much denser than $CoMoO_4 \cdot 3/4H_2O$ (3.76 g/cm^3). Thus we propose that the formation is related to a constrained process, that is, to a solid-state process rather than to a solution process. The fact, mentioned above, that the crystal size and crystallinity of $CoMoO_4 \cdot 3/4H_2O$ and hp-$CoMoO_4$ do not depend on the cooling rate and the concentrations of Mo and Co probably suggests a solid-state formation of hp-$CoMoO_4$ from $CoMoO_4 \cdot 3/4H_2O$. Because the $CoMoO_4 \cdot 3/4H_2O$ precipitates here tend to form a hard mass during the hydrothermal treatment, we checked to see if the morphology of the $CoMoO_4 \cdot 3/4H_2O$ sample is retained after the transformation into hp-$CoMoO_4$. The $CoMoO_4 \cdot 3/4H_2O$ product was removed from the hydrothermal solution after a 1-day treatment. Then a part of the product was changed into hp-$CoMoO_4$ by treating it in the same hydrothermal solution for a further 2 days. Fig. 4 shows that the

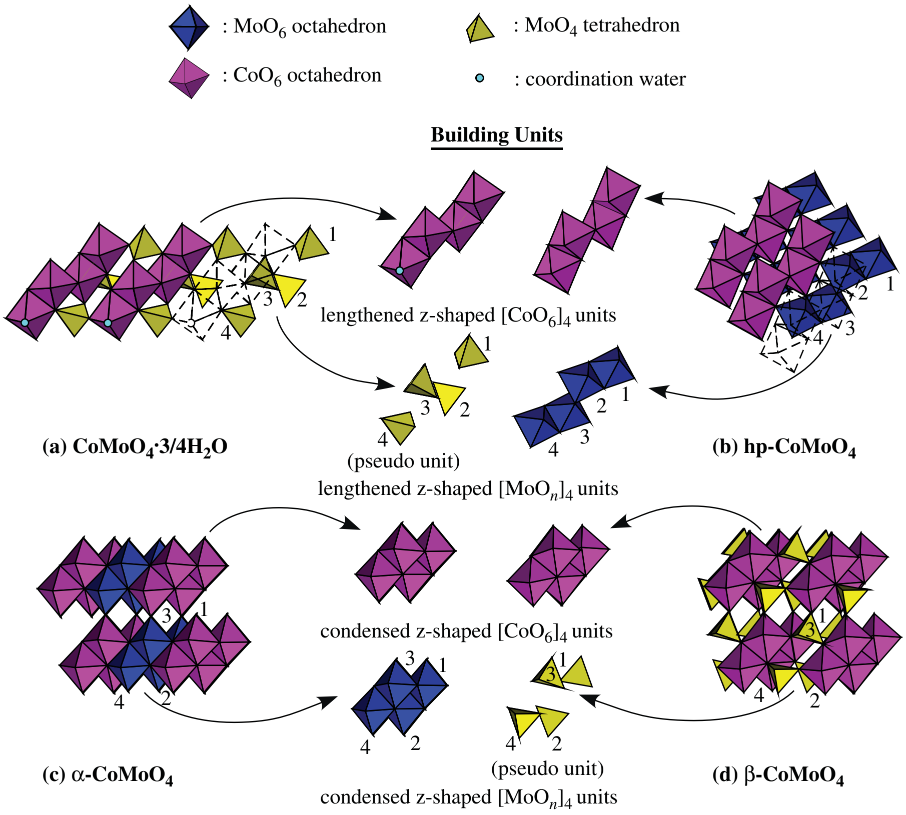


Fig. 5. Crystal structures and MO_n building units of $CoMoO_4 \cdot 3/4H_2O$ and the three $CoMoO_4$ polymorphs.

morphology of the $CoMoO_4 \cdot 3/4H_2O$ is retained after transforming into the hp-$CoMoO_4$, supporting the hypothesis that the transformation is a solid-state process.

This solid-state transformation occurs at temperature much lower than the usual solid-state transformation of hp-$CoMoO_4$ from α-$CoMoO_4$ or β-$CoMoO_4$ (50 kbars and ca. 900 K). Thus, it is expected that there is stronger affinity between the structures of $CoMoO_4 \cdot 3/4H_2O$ and hp-$CoMoO_4$ than between those of hp-$CoMoO_4$ and α-$CoMoO_4$/β-$CoMoO_4$. Although the crystal structure of $CoMoO_4 \cdot 3/4H_2O$ was not known until quite recently, we successfully determined its crystal structure and compared it to those of the three $CoMoO_4$ polymorphs [19]. This comparison revealed that $CoMoO_4 \cdot 3/4H_2O$ consists of structural building units (shown in Fig. 5) similar to those found in hp-$CoMoO_4$, and confirmed the strong structural affinity between $CoMoO_4 \cdot 3/4H_2O$ and hp-$CoMoO_4$. That is, these two phases consist of similar lengthened types of $[CoO_6]_4$ units, differing from α- and β-$CoMoO_4$'s that are composed of the condensed types. And the lengthened types of $[MoO_n]_4$ units in $CoMoO_4 \cdot 3/4H_2O$ and hp-$CoMoO_4$ have similar arrangements of the MoO_n polyhedra, so that the pseudo $[MoO_4]_4$ unit of $CoMoO_4 \cdot 3/4H_2O$ may turn easily into the $[MoO_6]_4$ unit of hp-$CoMoO_4$ by small translational and/or rotational displacements of corresponding MoO_n polyhedra. Thus we regard the formation reaction of hp-$CoMoO_4$ from $CoMoO_4 \cdot 3/4H_2O$ as a SISSR.

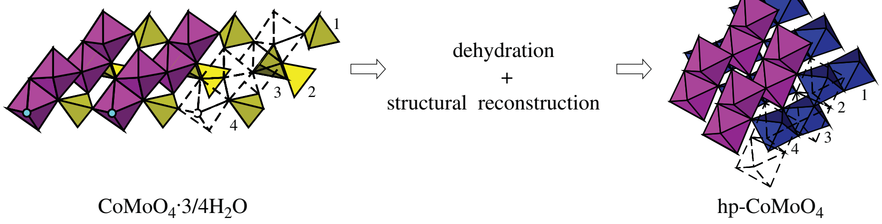
This SISSR under hydrothermal conditions enables us to markedly reduce the prior severe synthetic conditions of hp-$CoMoO_4$. Thus similar SISSRs under hydrothermal conditions are expected to be useful tools for material syntheses and designs. Therefore we discuss briefly below SISSRs under hydrothermal conditions, which are useful for material design.

3.3. *SISSRs under hydrothermal conditions for material design*

In order to synthesize materials with desired structures and/or compositions, we have often to add or remove some structural units or some constituting elements from the starting materials. There may be three types of SISSRs under hydrothermal conditions: (i) addition, (ii) elimination, and (iii) substitution ones.

As for the addition SISSRs under hydrothermal conditions we have not found any real examples yet. Structural reconstructions under hydrothermal conditions, which are induced by addition reactions such as insertion or intercalation, are related examples. As for the last two types of SISSRs under hydrothermal conditions we have found examples in hydrothermal syntheses of M–Mo–O system (M = Co, K), as shown in Fig. 6. The present SISSR from $CoMoO_4 \cdot 3/4H_2O$ to hp-$CoMoO_4$ is regarded as an elimination SISSR under the hydrothermal condition. In this reaction dehydration takes place with

(a) Elimination SISSR under hydrothermal condition



(b) Substitution SISSR under hydrothermal condition

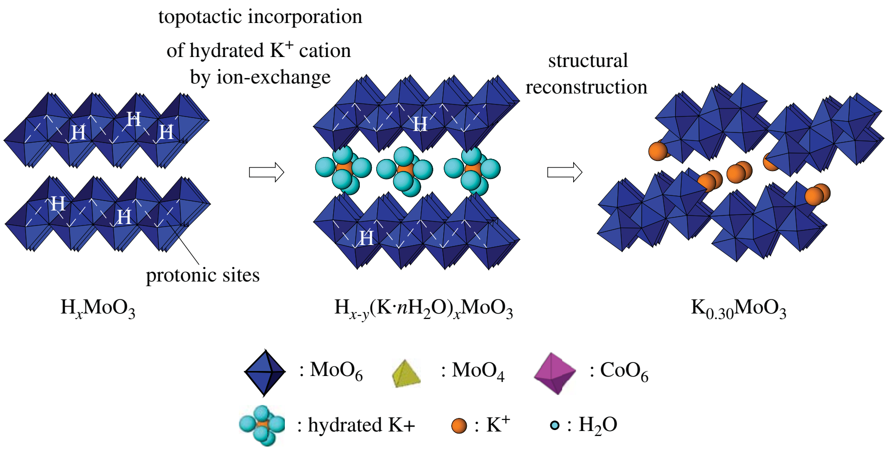


Fig. 6. Two types of SISSRs under hydrothermal conditions, found in the hydrothermal syntheses of M–Mo–O system (M = Co, K).

structural reconstruction. Other than dehydration, leaching [20,21] of the starting materials under hydrothermal conditions may lead to interesting elimination SISSRs. The formation of $K_{0.3}MoO_3$ from H_xMoO_3 (Fig. 6(b)), which we found earlier [9], is attributed to a substitution SISSR under a hydrothermal condition. Structural retention under solid-state ion-exchange reactions under hydrothermal conditions is now quite common, with one famous example being the hydrothermal synthesis of hydroapatite by Roy et al. [1].

All the SISSRs mentioned above are related to the reactions used in ordinary soft chemistry. Various SSRs concerning ordinary soft chemistry will provide many interesting SISSRs under hydrothermal conditions. Therefore, the presence of a large number of them is expected, although not so many SISSRs under hydrothermal conditions have been reported so far. Because many hydrates with a range of structures such as $CoMoO_4 \cdot 3/4H_2O$ can be prepared via solution reactions even under ambient conditions, exploring their hydrothermal treatment might lead to some interesting SISSRs and some new compounds with novel structures. We believe that some presently considered hydrothermal solution reactions might in fact be occurring in the solid state with partial structural retention. Searching various SISSRs under hydrothermal conditions and analyzing them systematically will provide novel soft chemical tools useful for material designs, and could lead to a more rational approach to the synthesis of new materials.

Acknowledgments

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