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Syntheses and thermal degradation behaviours of saponite–α-naphthylamine complexes: effects of substitution of OH in saponite by fluorine

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Five saponites with various substitution degrees of the constituent OH by fluorine were subjected to complex formation with α-naphthylamine to examine the effect of substitution on the stabilities of the resulting complexes. Saponite with a larger substitution degree intercalated a lesser quantity of α-naphthylamine and was broken down more easily in the reaction process. The complexes were subsequently heated in nitrogen to examine their thermostabilities. The thermostability of saponite was enhanced with increasing degree of substitution. All saponite, especially those without substitution, enhanced their thermostabilities by intercalating with α-naphthylamine. The reasons for these phenomena are briefly discussed.

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1. Introduction

The authors have been studying the thermal degradation (carbonization) behaviours of a series of clay–organic layer-type complexes with the ultimate purpose of deriving a clay–carbon layer-type complex [1, 2]. These trials are not completed yet, but some requirements for this completion have been revealed. The requirements for the host clay mineral are; (i) to have a large cation exchange capacity (C.E.C.) to intercalate a large quantity of organic compound (as the carbon source) by ion-exchange reaction, and (ii) to have a high thermostability so that the carbonization of the guest organic compound proceeds more completely. The thermostabilities of clay minerals such as mica are enhanced by substituting the constituent OH by fluorine [3]. As far as we know, however, there is no work on the effects of substitution on the behaviour of the complex formation with an organic compound and the thermostability of the resulting complex. The present work, therefore, was carried out to examine such effects by using saponites with various degrees of substitution.

2. Experimental procedure

2.1. Raw materials and preparations of complexes

All saponites (abbreviation: Sap) were synthesized hydrothermally by Kunimine Industries Co. Ltd, Kuroiso, Tochigi, Japan. Table I shows abbreviations of Saps and the batch compositions of the starting raw materials. As sources of silicon, magnesium and aluminium we used water glass, $MgSO_4$ and $Al_2(SO_4)_3$, respectively. Substitution degrees of the constituent OH by fluorine were calculated and shown in Table I. Here, x corresponds to x in the chemical formula $[(OH)_{4-x}F_x(Si_{7.18}Al_{0.82})Mg_{6.0}O_{20}]^{-}_{0.82}Na^{+}_{0.82}$. After hydrothermal reactions, F(2)-, F(3)- and F(4)-Saps contained small amounts of analcime ($NaAlSi_2O_6 \cdot H_2O$) and NaF so these were washed away thoroughly by NaOH solution.

Sap film with thickness of several tens of micrometres was prepared from ≈ 5% aqueous sol of Sap [1, 2]. The film was soaked in 0.1 N α-naphthylamine aqueous solution at 353 K which included a far larger quantity of α-naphthylamine than the C.E.C. of Sap.

TABLE I Batch composition of raw materials, the substitution degree of the constituent OH by fluorine, and C.E.C. of saponites

Abbreviation	Batch composition				Substitution degree*	C.E.C.† (mEq per 100 g)
	Si	Mg	Al	Na		
F(0)-Sap	1.353	1.176	0.145	0.000	0.0	71.2
F(1)-Sap	1.353	1.176	0.145	0.176	1.0	94.9
F(2)-Sap	1.353	1.176	0.145	0.333	2.0	103.0
F(3)-Sap	1.353	1.176	0.145	0.500	3.0	97.5
F(4)-Sap	1.353	1.176	0.145	0.666	4.0	92.0

*Calculated values from batch compositions.
†Cation exchange capacity.

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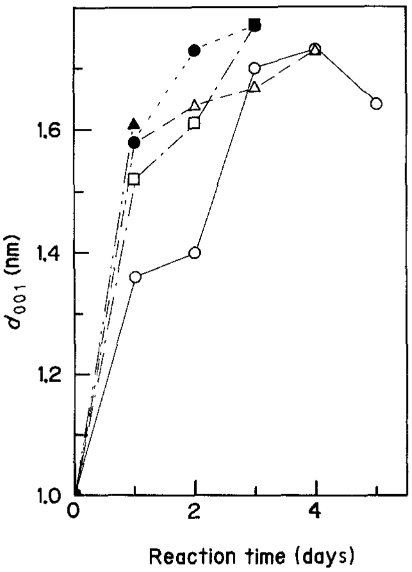

Figure 1 Changes of interlayer spacings of SNCs with reaction time. (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

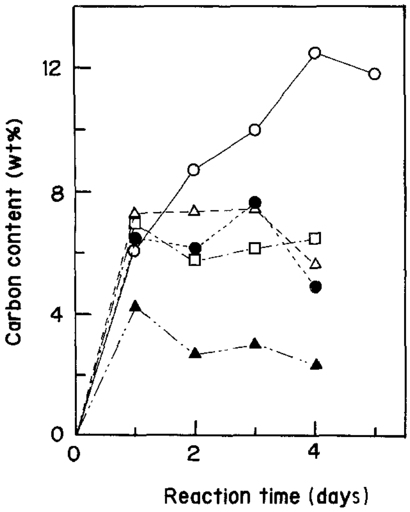

Figure 2 Changes of carbon contents of SNCs with reaction time. (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

In order to determine the optimum reaction time for complex formation, aliquots of the film were taken out occasionally for X-ray diffraction and carbon content measurement after washing with acetone. The complexes (abbreviation: SNC) synthesized under optimum conditions were heated (carbonized) below 1473 K in nitrogen. The heating rate and residence time were 5 K min^{-1} and 1 h, respectively.

2.2 Measurements

The films before and after heat-treatment were subjected to X-ray diffraction analysis, carbon content measurement, thermogravimetric analysis (TG) and SEM observation on the fracture surfaces of the films, of which details have been reported previously [1, 2]. Saps before heating are readily rehydrated so that their interlayer spacings (d_{001}) were measured under dehydration by use of the technique reported elsewhere [2].

3. Results

3.1. Formations of saponite–α-naphthylamine complexes

3.1.1. X-ray diffraction

Fig. 1 shows changes of d_{001} of SNCs with the reaction time. All raw Saps exhibited 1.0 nm under dehydration and 1.4 to 1.5 nm under hydration, though this is not shown in Fig. 1. After reaction for 1 day the d_{001} values of Saps, especially with large substitution degrees, were remarkably increased by intercalation, but the layer structure of F(4)-SNC with the largest substitution degree was destroyed after 2 days to change into an amorphous state. Both F(3)- and F(2)-SNCs lost their layer structures after 3 days. The layer structures of F(0)- and F(1)-SNCs were still stable even after reaction for 4 days.

3.1.2. Carbon content

Carbon contents in SNCs are shown in Fig. 2. F(1)-, F(2)- and F(3)-SNCs show a similar relation between the carbon content and reaction time. An analogous

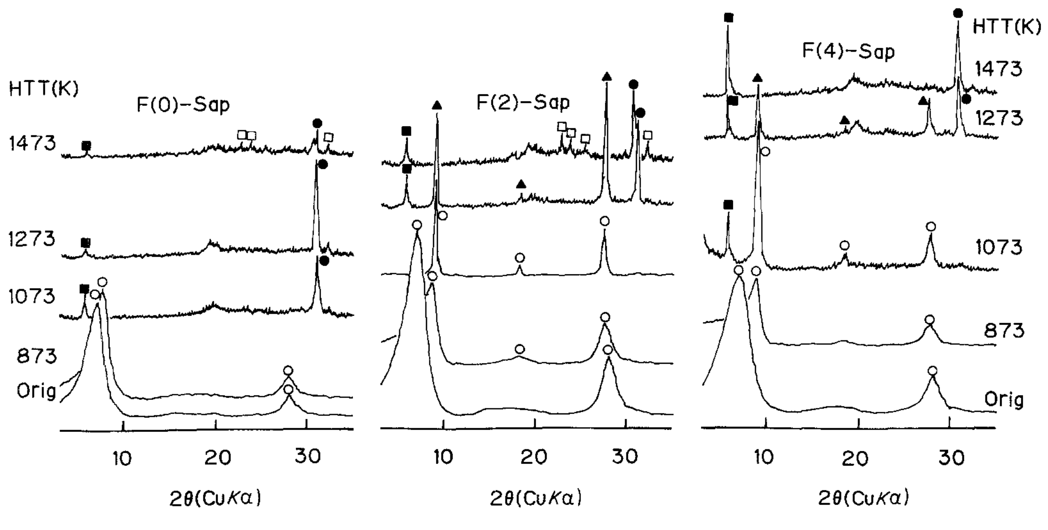

Figure 3 Changes of X-ray diffraction profiles of Saps with heat-treatment temperature. (○) Sap, (●) enstatite, (▲) $CaMg_6Al_2Si_6O_{20}F_4$, (□) forsterite, (■) Phase X.

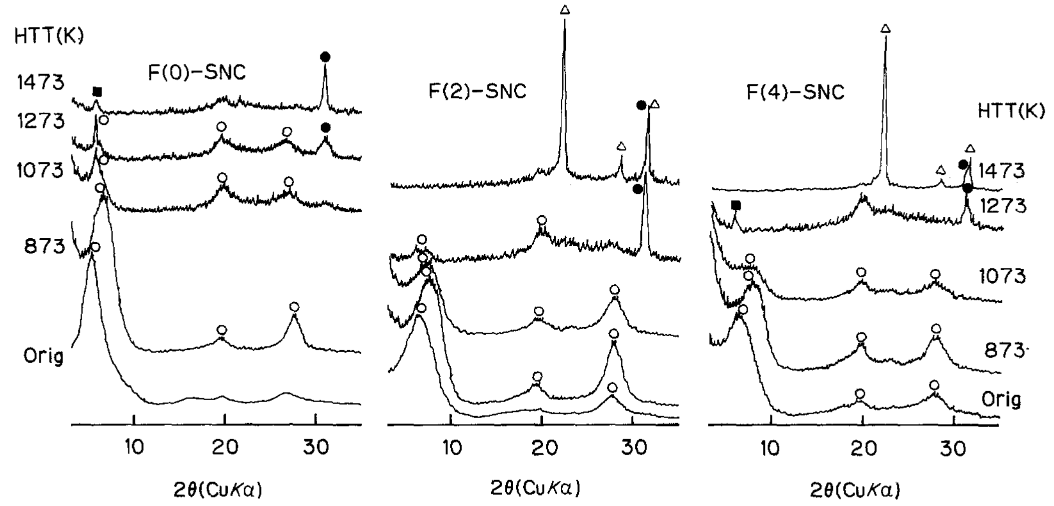

Figure 4 Changes of X-ray diffraction profiles of SNCs with heat-treatment temperature. (○) SNC, (●) enstatite, (△) α-cristobalite, (■) Phase X.

trend was also seen in F(4)-Sap, although the carbon contents were relatively small. The carbon content of F(0)-SNC continued to increase for 4 days, in contrast to saturation of the carbon content for other SNCs after just 1 day. An SNC with a smaller substitution degree had, on the whole, a larger carbon content. On the basis of these results, individual SNCs were synthesized by using the following reaction times and subjected to the subsequent heat-treatments; F(0)-SNC: 4 days, F(1)-SNC: 3 days, F(2) and F(3)-SNCs: 2 days, F(4)-SNC: 1 day.

3.2. Heat-treatment of Sap and SNC

3.2.1. X-ray diffraction

X-ray diffraction profiles of Saps before and after heating are shown in Fig. 3. The peaks of F(0)-Sap disappeared after heating to 1073 K, and enstatite together with a crystalline phase having a diffraction peak around 6° (2*θ*, Cu*K*α) appeared. This phase could not be firmly identified. It is referred to as Phase X in this paper. Such a profile was almost kept after heating to 1273 K. At 1473 K, in addition, forsterite appeared.

Diffraction peaks of F(2)-Sap were observed clearly after heating to 1073 K, indicating enhancement of the thermostability of Sap by substituting the constituent OH by fluorine. In F(2)-Sap heated to 1273 K, Phase X and enstatite existed together with $CaMg_6Al_2Si_6O_{20}F_4$ (ASTM 25-155 type crystal) of which the chemical composition is not clear. Forsterite appeared in F(2)-Sap after heating to 1473 K. F(4)-Sap heated to 1073 K showed sharp diffraction peaks together with a peak from Phase X. A larger amount of Phase X formed in Sap with a larger substitution degree. In F(4)-Sap, however, no forsterite was formed by heating to 1473 K.

Fig. 4 shows X-ray diffraction profiles of SNCs before and after heating. The (0 0 1) peak of F(0)-SNC around 5° weakened gradually with increasing temperature. Enstatite appeared at 1273 K and strengthened its diffraction peaks after heating to 1473 K. The behaviours of other SNCs were similar to that of F(0)-SNC, except for no formation of cristobalite. From a comparison between Figs 3 and 4, it is clear that the thermostabilities of all Saps are enhanced by intercalating with α-naphthyalmine.

Figs 5 and 6 show d_{001} of Saps and SNCs. All Saps, except for F(1)-Sap, under rehydration exhibited about 1.25 nm fat 400 K. The d_{001} values of Saps decreased remarkably after heating to 873 K. F(0)-

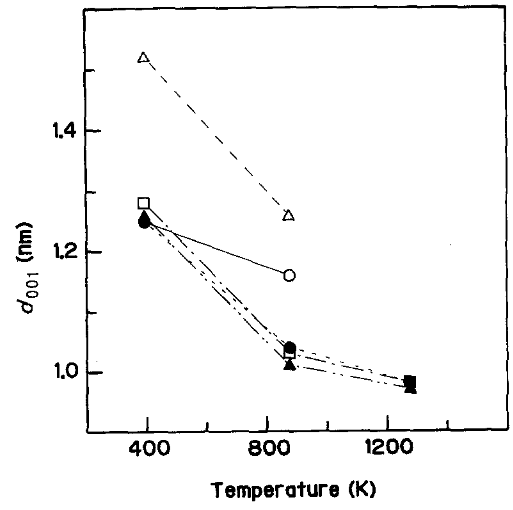

Figure 5 Changes of interlayer spacings of Saps with heat-treatment temperature. (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

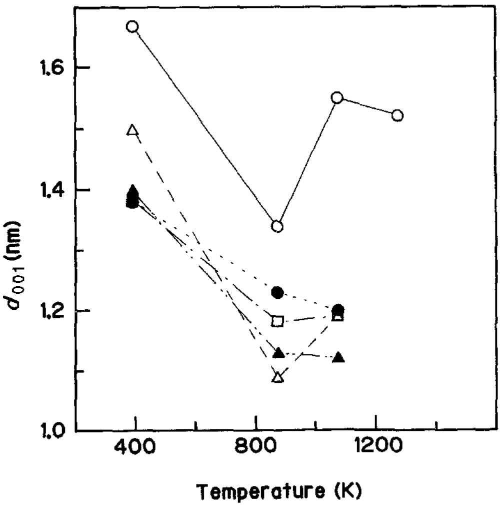

Figure 6 Changes of interlayer spacings of SNCs with heat-treatment temperature. (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

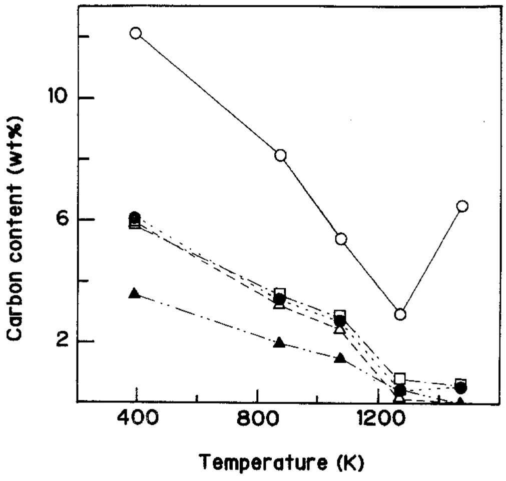

Figure 7 Changes of carbon contents of SNCs with heat-treatment temperature. (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

and F(1)-Saps exhibited somewhat different behaviours from others. Whereas d_{001} of SNC before heating is smaller for a larger substitution as shown in Fig. 6, large decreases in d_{001} of all SNCs were observed after heating to 873 K. Both F(0)- and F(1)-SNCs again increased their d_{001} after heating to 1073 K in contrast to no change in other SNCs.

3.2.2. Carbon content

Carbon content of SNCs are shown in Fig. 7. As was described in Fig. 2, an SNC with a smaller substitution degree included a larger amount of the guest α-naphthylamine. Such a trend was kept after heating to 1073 K. Above 1273 K, F(0)-SNC showed a larger carbon content than the other four SNCs.

3.2.3. Thermogravimetric analysis

Fig. 8 shows TG curves of Saps and SNCs in nitrogen. The differences between Saps and SNCs are: (i) final weight losses of SNCs, on the whole, were larger than those of Saps, (ii) Saps showed relatively sharp weight decreases around 1073 K, and (iii) the gradual weight decrease below 1100 K was slightly more clear in SNCs than in Saps.

4. Discussion and conclusions

4.1. Effects of fluorine on formations and stabilities of SNCs

As shown in Fig. 2, Saps, except for F(4)-Sap, exhibited nearly equal rates of initial intercalation, but the stabilities of the resulting SNCs were not equal. SNC derived from Sap with a lower substitution degree of fluorine, was in general more stable. This trend is completely opposite to that of the thermostabilities of Saps (Fig. 3).

Relations between d_{001} (Fig. 1) and carbon contents (Fig. 2) of SNCs in the intercalation process are summarized in Fig. 9. SNCs are classified in this figure into F(0)-SNC; the group of F(1)-, F(2)- and F(3)-SNCs; and F(4)-SNC. Comparing SNCs with a d_{001} of 1.6 nm, F(0)- and F(4)-SNCs have the largest and the smallest carbon contents, respectively. A guest species can take various conformations in the interlayer space, resulting in different values of d_{001} (e.g. [4]). To have an equal d_{001} indicates the same conformation of the guest species in an interlayer space. So, α-naphthylamine intercalacted more closely in an SNC with a larger carbon content (Fig. 9). If the ion-exchange reaction occurs completely, the quantity of the intercalated α-naphthylamine must be proportional to the extent of C.E.C.s of raw Saps, although such a relation was not observed. Percentages of ions exchanged were calculated on the basis of the maximum carbon contents of SNCs with a layer structure. Here, two assumptions were made: (i) the exchangeable cations in Saps are all Na^+ and (ii) the weight loss of SNC by heating is 5 wt % (Fig. 9). The results were: F(0)-SNC, 136%; F(1)-SNC, 61%; F(2)-SNC, 53%; F(3)-SNC, 61%; and F(4)-SNC, 36%. The value for F(0)-SNC is over 100%, which may be attributable to the extra surface cations on the Sap particle.

As a result, the substitution of the constituent OH by fluorine makes more difficult the ion-exchange by α-naphthylamine, and in addition makes the resulting complex unstable.

4.2. Effects of fluorine on thermostabilities of Saps and SNCs

Thermostabilities of micas were improved through substituting the constituent OH by F[3], which is consistent with the result shown in Fig. 3. However, the detailed effects of the substitution degree were not clear.

Thermostabilities of Saps were enhanced by intercalating α-naphthylamine irrespective of the substitution degree (Figs. 4 and 5). This effect was observed most remarkably in F(0)-Sap. It has been reported

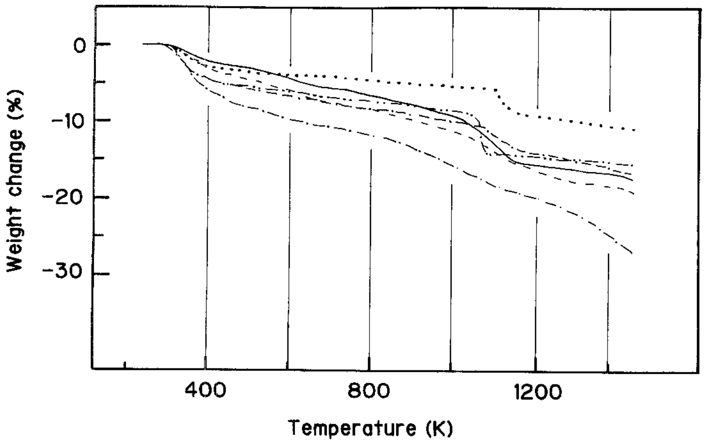

Figure 8 TG curves of Saps and SNCs under nitrogen. (——) F(0)-SNC, (– – –) F(2)-SNC, (–·–) F(4)-SNC; (—·—) F(0)-Sap, (· · ·) F(2)-Sap, (– – – – –) F(4)-Sap.

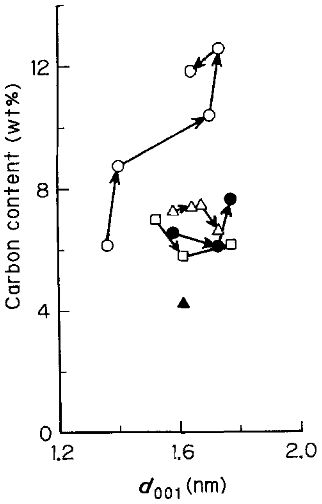

Figure 9 Relation between carbon contents and interlayer spacings of SNCs in the reaction process (arrows indicate the extension direction of reaction time). (○) F(0)-SNC, (△) F(1)-SNC, (□) F(2)-SNC, (●) F(3)-SNC, (▲) F(4)-SNC.

that the intercalated guest α-naphthylamine is converted to a carbon layer by heating and the resulting carbon layer interferes with sintering between clay layers, leading to enhancement of thermostabilities of the layer structures of clays [1, 2]. The carbon content of F(0)-SNC was so much larger than those of other SNCs (Fig. 8) that a more complete interference by the resulting carbon layer must occur. The next topic of interest is the effect of substitution upon the thermostability of SNC. Data on the reactivities of carbon with the constituent fluorine and OH in clays are not available as far as we know. However, all Saps enhanced their thermostabilities by intercalation, although further details of the effects of the substitution degree are not clear.

As a result, the effect of substitution on the thermostability of SNC is not so remarkable compared with that of the intercalated carbon layer.

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