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Thermal degradation behaviour of fluorosaponite–α-naphtylamine complex under nitrogen

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The layer-type complex of fluorosaponite and α-naphtylamine (F-SNC) was heat treated below 1473 K under nitrogen to investigate its thermal degradation behaviour. The most striking characteristic of the behaviour is that the layered structure of F-SNC remained considerably unchanged up to temperatures as high as 1273 K. In order to derive the clay–carbon layer-type complex from the clay–organic compound complex, the degradation behaviour of F-SNC was compared with those of other complexes reported previously. As a result, the most important factor to arise from this work is to use a layered-structural clay with high thermal stability and to intercalate organic compounds, with high carbon yield, as much as possible.

1. Introduction

The present authors have been studying the thermal degradation behaviour of the layer-type complex consisting of clay and α-naphtylamine with the ultimate purpose of preparing a layer-type complex consisting of clay and carbon [1–4]. In order to accomplish this, as described previously [4], the use of a clay mineral with as high a thermal stability as possible seems to be preferable, because saponite gave more favourable results than montmorillonite [1, 4]. Saponite, furthermore, is expected to become more stable thermally by substituting OH in saponite by fluorine. In this work, therefore, the thermal degradation behaviour of the complex consisting of fluorosaponite and α-naphtylamine was examined under nitrogen. Two points discussed here are: (a) the characteristics of the thermal degradation behaviour of fluorosaponite–α-naphtylamine complex in comparison with that of fluorosaponite and (b) the directions to prepare the clay–carbon layer-type complex by comparing the thermal degradation behaviour of three complexes consisting of clays and α-naphtylamine reported elsewhere [1, 4].

2. Experimental details

Saponite has the idealized chemical formula of $X_{2/3}Mg_6(Al_{2/3}Si_{22/3})O_{20}(OH)_4 \cdot nH_2O$ and is thought to become more thermally stable by substituting OH by F. Such fluorosaponite (F-Sap) was kindly supplied by Kunimine Ind Co. F-Sap has 84.2 meq $100g^{-1}$ in cation exchange capacity (CEC) and chemical composition as shown in Table I in which saponite (Sap) used in the previous previous work [4] was also shown for comparison. 3.5 wt% of F-Sap aqueous solution was spread out to prepare the self-supporting film of several 10 μm thickness. 1 g of the resultant film was soaked in 0.1 *N* α-naphtylamine hydrochloride ($C_{10}H_7NH_2 \cdot HCl$) aqueous solution at 353 K for 4 days to form the F-Sap–α-naphtylamine (NA) complex (F-SNC). After washing away any NA attached on the film surface with acetone, the film was sealed in glass tubing under vacuum for γ-ray radiation by 12 Mrad, followed by heating to 473 K to produce polymerization of NA. The film was subsequently heat treated from 673 to 1473 K for 1 h under nitrogen. The heating rate was 5 K min.$^{-1}$. For comparison, F-Sap film was also heated according to the procedures stated above.

X-ray diffraction and scanning electron microscope (SEM) observation methods have been described elsewhere [1]. Sap film after heating below 973 K rehydrates so readily that such film under dehydration was covered with paraffin to prevent rehydration and then used for X-ray diffraction. Thermogravimetric analysis (TGA) was carried out in a flow of nitrogen or air with a heating rate of 10 K min^{-1}. Carbon content in such a complex is usually so difficult to measure accurately by the conventional combustion method that tin metal was added into the complex film to combust NA completely.

3. Results

3.1. X-ray diffraction analysis

Figs. 1 and 2 shows changes of X-ray diffraction profiles of F-Sap and F-SNC with heat treatment temperature (HTT). The basal spacing (d_{001}) obtained from these profiles are shown in Table II. Paraffin in the 873 K-F-Sap was used to prevent rehydration as stated above. When paraffin was not used, the profile obtained was analogous to that of original F-Sap. F-Sap after heating above 1073 K did not rehydrate again. Through this dehydration, d_{001} of F-Sap decreased from 1.20 to 0.98 nm. The layered structure of F-Sap was observed clearly even after heating to 1273 K, that is, the layered structure is more thermally stable than those of montmorillonite [1] and saponite [4] used previously. Enstatite ($MgO \cdot SiO_2$) appeared at 1073 K and increased in amount at higher HTT.

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TABLE I Chemical compositions (wt%) and cation exchange capacities (meq 100 g^{-1}) of Sap and F-Sap

	Sap	F-Sap
SiO_2	54.71	53.34
Al_2O_3	5.02	4.88
Fe_2O_3	0.03	0.02
MgO	30.74	29.97
CaO	0.00	0.02
Na_2O	2.15	3.29
F	0.00	1.79
SO_3	0.67	0.65
NH_3	0.00	0.07
Ignition loss	6.67	6.64
Total	99.99	100.67
CEC*	71.2	84.2

*CEC: cation exchange capacity.

In F-SNCs after heating to 673 to 1273 K, on the other hand, (0 0 *l*) diffraction peaks of F-SNC were observed clearly at almost the same diffraction angle from which 1.3 nm of d_{001} was calculated. Enstatite in F-SNC appeared at higher HTT than in F-Sap. The 1473 K-F-SNC consists of large amount of enstatite and possibly a slight amount of quartz.

3.2. Carbon content

Table II shows carbon contents in F-SNC. 7.9 wt% at 473 K decreased gradually with increasing HTT and went down to 5 wt% at 1073 K and only 2.4 wt% at 1473 K.

3.3. Thermogravimetric analysis

Fig. 3 shows thermogravimetric analysis (TG-DTA) curves of original F-Sap and the 473 K-F-SNC films under nitrogen. F-Sap showed weight decreases around 350 and 1100 K. These are attributable to dehydration resulting from water between clay layers and OH constituting F-Sap, respectively. Because, as discussed later, the F-Sap used here contained OH in addition to fluorine.

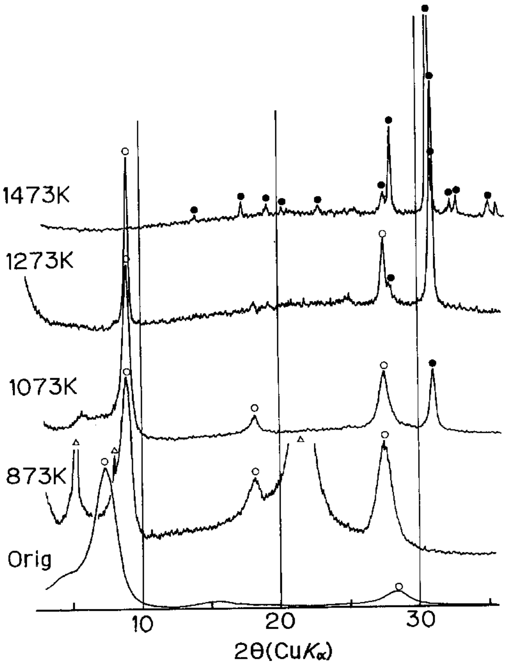


Figure 1 Changes of X-ray diffraction profiles of F-Sap with HTT. ○: F-Sap; ●: enstatite; △: paraffin.

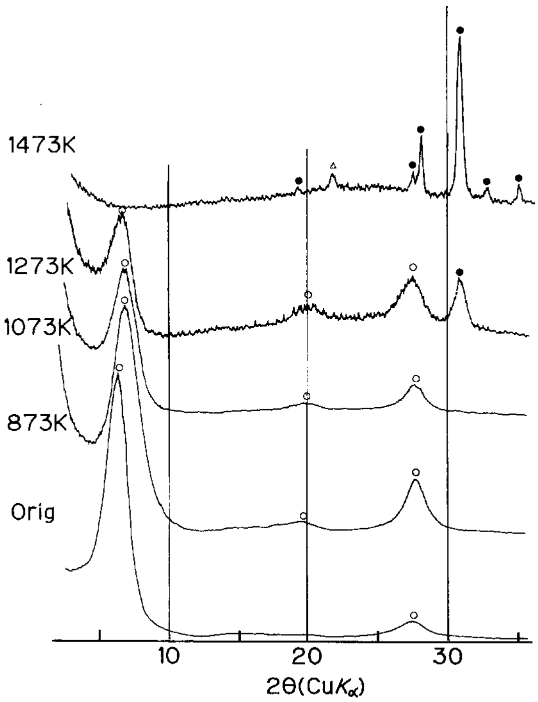


Figure 2 Changes of X-ray diffraction profiles of F-SNC with HTT. ○: F-SNC; ●: enstatite; △: quartz.

F-SNC after heating to 473 K showed a small and gradual weight decrease above ~300 K. Weight decreases resulting from OH in F-SNC were also mild but the ultimate weight decrease at 1473 K was almost equal in both F-SNC and F-Sap films.

Fig. 4 shows TG-DTA curves of F-SNC, after heating to various HTTs under nitrogen, in air. Original F-SNC showed larger weight decreases at a lower temperature range than the 873 K-F-SNC. It is interesting to see that the 1273 K-F-SNC showed no decrease up to ~1300 K and then large decreases at higher temperature. F-SNC after heating to 1473 K under nitrogen showed again the weight decrease around 900 K with no decrease at higher temperature. These weight decreases accompanied by exothermic reaction are possibly attributable to the combustion of NA or the derived residue.

3.4. SEM observation

The fracture surfaces of F-Sap and F-SNC films, with and without heating under nitrogen, are shown in Figs. 5 and 6. Both original films have a very dense layered structure which remained substantially after heating to 873 K. In both films after heating to 1073 K, the layered structure sintered somewhat, especially near the film surface. At these stages, F-Sap film cleaved into several pieces. Both films did not exhibit the dense and smooth surface observed in the saponite–α-naphtylamine complex (SNC) reported previously [4].

4. Discussion

4.1. Chemical compositions and thermal stability of F-Sap

Chemical composition of Sap is simplified as

TABLE II Changes of basal spacings (d_{001}) and carbon contents of clay minerals and their complexes with HTT

HTT (K)	F-Sap d_{001} (nm)	F-SNC		Sap, d_{001} (nm)	SNC		Mont, d_{001} (nm)	MNC[‡]	
		d_{001} (nm)	C (wt%)		d_{001} (nm)	C (wt%)		d_{001} (nm)	C (wt%)
Original	1.20	1.38	7.6	1.28	1.61	11.2	1.23	1.70	13.0
473	0.99	1.38	7.9	0.98	1.67	11.0	0.97	1.68	13.0
573							0.97	1.52	
673	0.99	1.30	7.0	0.98	1.43	10.2	0.96	1.26	12.0
773				0.98	1.34		0.95	1.28	
873	0.98	1.30	5.5	0.98	1.34	8.6	0.95	1.28	11.0
973				0.98	1.26		0.95	1.24	
1073	0.98	1.30	5.0	*	1.30	6.9	0.95	1.26	10.2
1173				*	1.52		*	1.28	
1273	0.97	1.32	5.8	*	1.52	6.0	*	1.30	7.3
1473	*	*	2.4	*	*	7.3		*	5.6
1673				*	*				

*: The layered structure was destroyed completely.

‡MNC is the complex consisting of montmorillonite and α-naphtylamine.

$Mg_6Si_8O_{20}(OH)_4$ of which chemical compositions are not so far from the analytical values shown in Table I. If OH in Sap is substituted by fluorine completely, its chemical composition is $Mg_6Si_8O_{20}F_4$ which contains 10 wt% fluorine. In view of the 1.79 wt% of F observed, therefore, only less than one-fifth of OH was substituted by fluorine. Nevertheless, the layered structure of F-Sap remained up to 1273 K in contrast to the complete disappearance of the layered structure of Sap at 1073 K [4]. F-Sap with higher thermal stability will be produced by further proceeding of such substitution.

4.2. Thermal degradation behaviour of F-Sap and F-SNC films

Water in F-Sap is removed below ~450 K, followed by a slight lowering of its crystallinity up to around 1073 K, in light of the strengthening of the background of the X-ray diffraction profile. Around 1100 K, dehydration from OH occurs and simultaneously, the layered structure begins to sinter, resulting in enstatite formation. This layered structure, however, remains considerably up to high temperatures such as 1273 K.

In the case of F-SNC, on the other hand, there is no weight decrease resulting from the inserted water around 400 K. d_{001} of the layered structure of F-SNC decreases gradually up to 1073 K by removal of NA, with or without thermal degradation [1], as suggested from carbon contents in Table II. According to SEM observation, the F-SNC film begins to sinter immediately after removal of OH around 1073 K, but enstatite appeared at 1273 K which is higher than that of F-Sap by 200 K. One point noted here is that peaks of F-SNC are observed considerably clearer even after heating to 1273 K. Such phenomenon was never observed in the cases of montmorillonite [1] and saponite [4]. At 1473 K, no F-SNC is observed completely. As a result, there is no difference in the thermal stabilities between F-Sap and F-SNC layer structures.

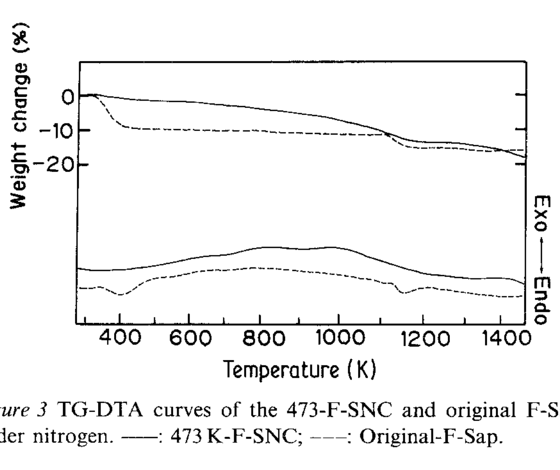


Figure 3 TG-DTA curves of the 473-F-SNC and original F-Sap under nitrogen. ——: 473 K-F-SNC; – – –: Original-F-Sap.

4.3. Some guidelines for preparing clay–carbon complex

The ultimate purpose of this series of works is to prepare the layer-type complex consisting of clay and carbon. This idealized complex has not been prepared yet but some guidelines to accomplish this work become clear through comparisons of the thermal degradation behaviours of montmorillonite, saponite, fluoro-saponite and their complexes [1, 4] of which data are summarized in Table II and Figs. 7 and 8. The carbon contents in MNCs, before and after heating, were reported previously [1] but the data in Table II are the values revised by using a tin addition method stated above.

According to X-ray diffraction profiles in Fig. 7, on the whole, the thermal stability of the layered structure of the clay minerals should be estimated to

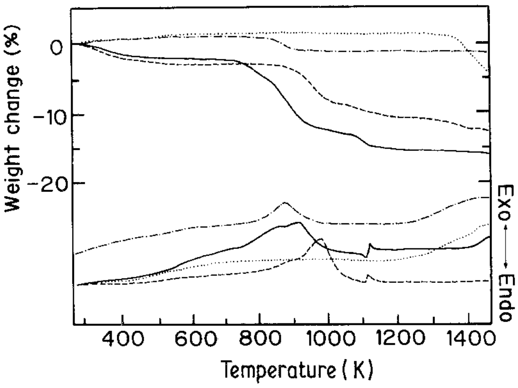


Figure 4 TG-DTA curves of F-SNCs, after heating to various HTTs under nitrogen, in air. ——: Original-F-SNC; – – –: 873 K-F-SNC; · · · · ·: 1273 K-F-SNC; ·–·–·: 1473 K-F-SNC.

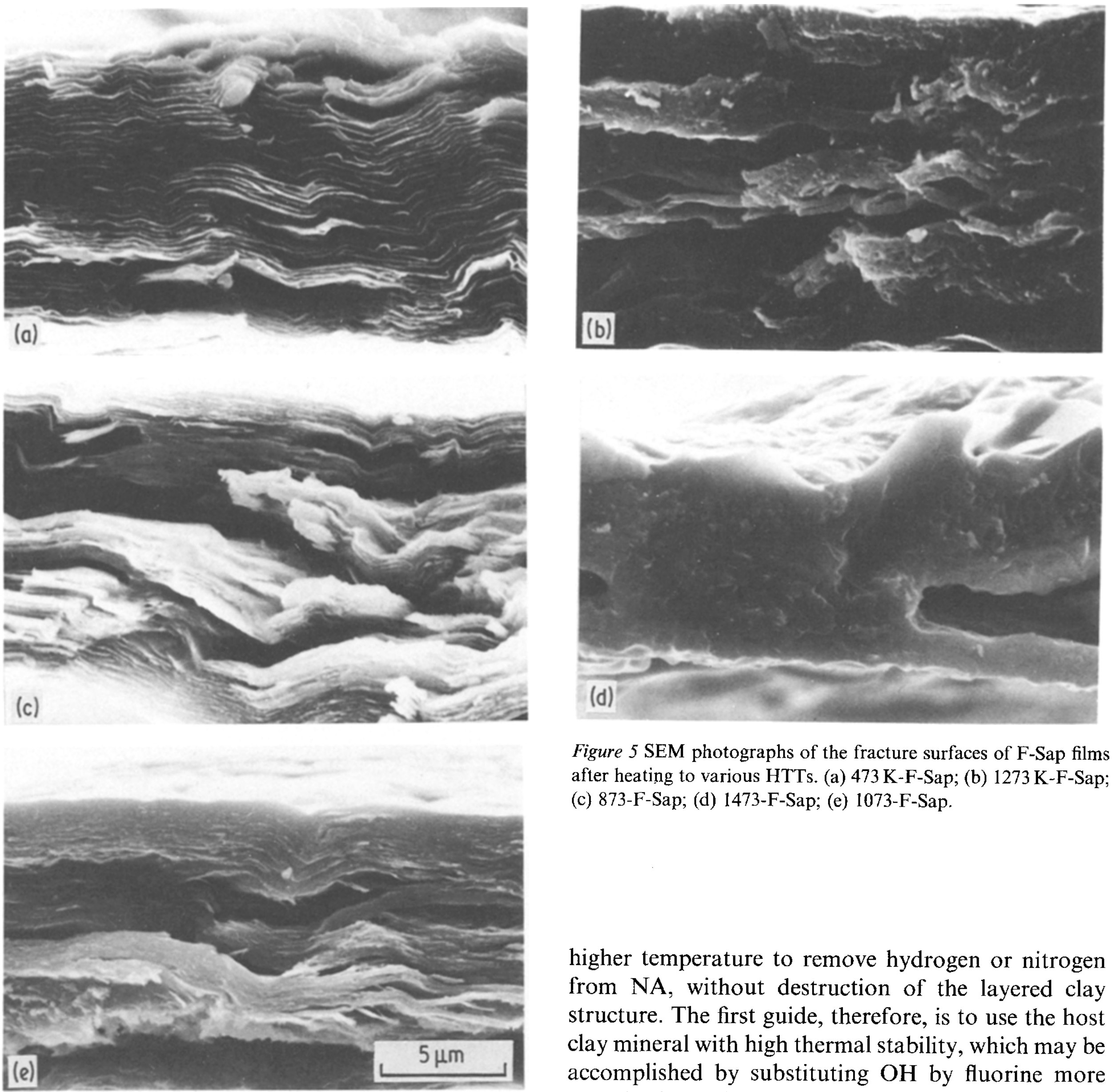


Figure 5 SEM photographs of the fracture surfaces of F-Sap films after heating to various HTTs. (a) 473 K-F-Sap; (b) 1273 K-F-Sap; (c) 873-F-Sap; (d) 1473-F-Sap; (e) 1073-F-Sap.

increase in the order of F-Sap > Sap > Mont, although this order is not necessarily explained reasonably in the 1073 K samples because of the slight residue of the layered structure of Mont. Such order is roughly in accord with that of the thermal stabilities of their complexes with NA (Fig. 8). In order to prepare the more complex carbon or graphite layer between clay layers, the complex must be heat treated to a higher temperature to remove hydrogen or nitrogen from NA, without destruction of the layered clay structure. The first guide, therefore, is to use the host clay mineral with high thermal stability, which may be accomplished by substituting OH by fluorine more completely.

It is also reasonable to conclude that the thermal stability of the layered clay structure is enhanced by intercalating NA which results in the carbon layer at high temperature [4]. Table II shows that the complex with lower carbon content exhibits higher thermal stability. This phenomenon, however, does not mean that the thermal stability of the complex is lowered by intercalating larger amounts of carbon, in other words, by the more complex carbon layer. Rather this

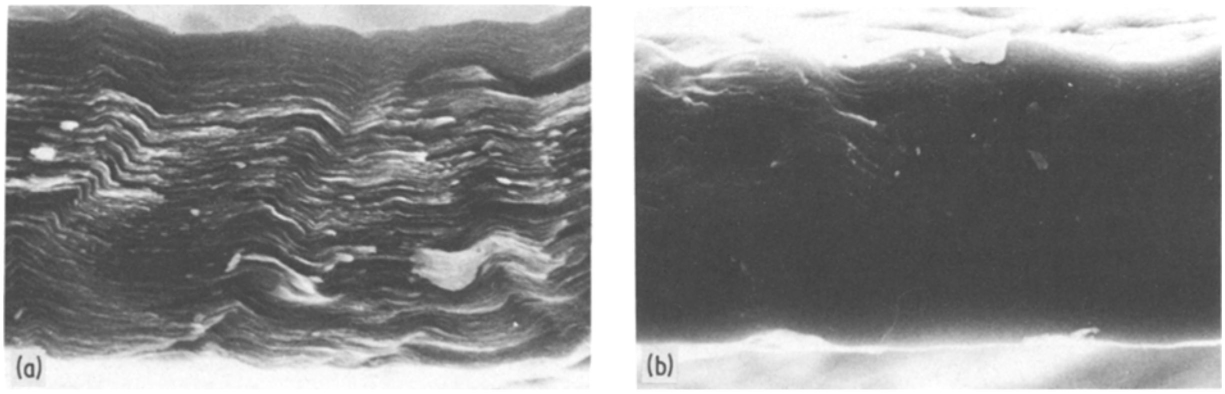
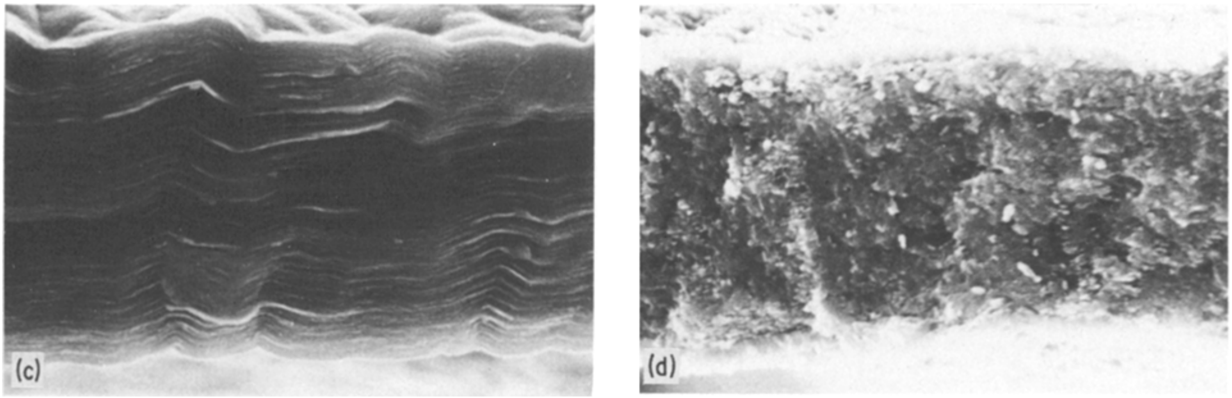


Figure 6 SEM photographs of the fracture surfaces of F-SNC films after heating to various HTTs. (a) 473 K-F-SNC; (b) 1273-F-SNC; (c) 873-F-SNC; (d) 1473-F-SNC; (e) 1073 K-F-SNC.



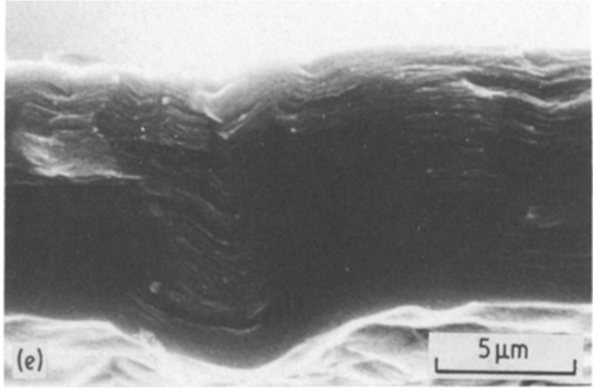


Figure 6 Continued

phenomenon should be explained as follows; as reported previously [4], the carbon layer in the 1073 K-SNC occupies less than one-third of Sap layer surface. A similar condition is also observed in the case of MNC or F-SNC. Therefore, the thermal stability of the complex with such a small carbon layer is mainly governed not by the carbon content but by the thermal stability of the layered clay structure. It should be also pointed as second factor that the more complex carbon layer increases the thermal stability of the layered structure of the complex. The second factor will be accomplished by the following: (a) an organic compound with high carbon yield must be used. Such material is usually polymerizable [5]. The increase of the carbon yield is also accomplished by polymerizing an organic compound sufficiently before heating; and (b) in order to intercalate larger amounts of an organic compound by an ion exchange technique, the clay with high cation exchange capacity should be used.

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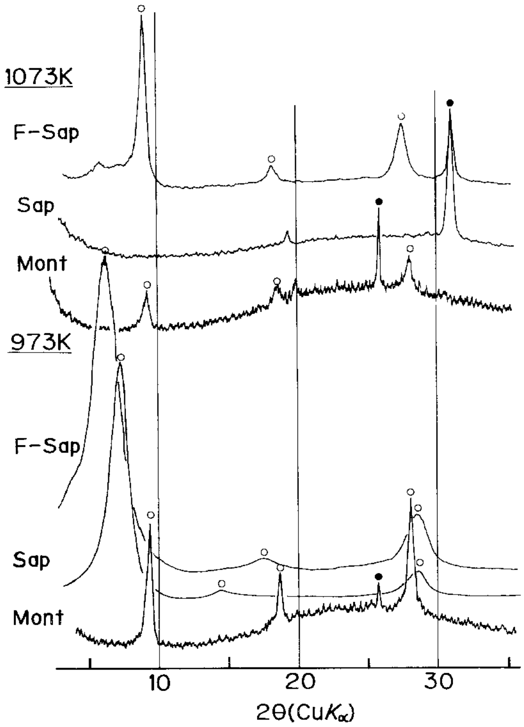

Figure 7 X-ray diffraction profiles of Mont, Sap and F-SNC after heating to 973 and 1073 K. ○: clay; ●: other componds.

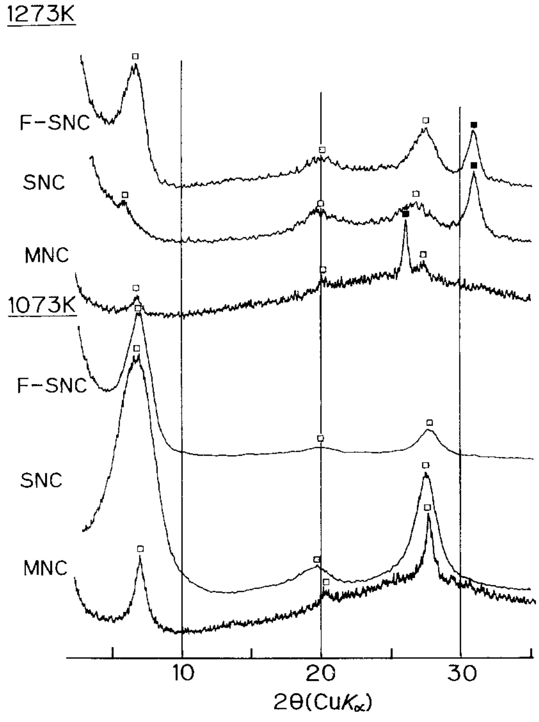

Figure 8 X-ray diffraction profiles of MNC, SNC and F-SNC after heating to 1073 and 1273 K. □: Complex; ■: other compounds.

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