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Oxidation resistivity of montmorillonite–α-naphthylamine complex heated under nitrogen

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A thin film of montmorillonite–α-naphthylamine complex (MNC) was heated to various temperatures below 1473 K for 5 min under nitrogen. The resulting samples were further heated to 1073 to 1473 K for 30 min or 5 h in air to examine their oxidation resistivities. A thin montmorillonite film was also treated in the same manner for reference purposes. The layered structure of MNC was retained up to 1273 K under nitrogen, although it changed gradually to an amorphous state with increase in temperature. MNCs after heating below 1073 K under nitrogen were changed to montmorillonite by subsequent heating to 1073 K for 30 min in air, whereas, MNCs heated to 1173 and 1273 K under nitrogen retained somewhat their layered structures, even after heating to 1173 K for 30 min in air. The causes for such differences are discussed on the basis of the results obtained from X-ray diffraction, thermogravimetry, FT–IR and SEM observation.

1. Introduction

It has been reported that the layered structure of montmorillonite–α-naphthylamine complex (MNC) film is more thermally stable than the montmorillonite (Mont) film under nitrogen, and that a fine and homogeneous porous structure resulted after heating to 1273 K for 1 h [1]. These results aroused our interest in examining the oxidation resistivities of MNCs heated to various temperatures under nitrogen, One reason is that such work may produce fundamental data for preparing a thermally stable layered or porous material which can be used in an oxidizing atmosphere. Another reason is that the study of the relation between MNC and the crystal phases derived from it through oxidation, may bring about some valuable information of the studies of crystal phases derived from Monts with various exchangeable metal ions [2].

In the present work, MNC was heated to various temperatures below 1473 K under nitrogen, followed by heating to 1073 to 1473 K in air to examine their oxidation resistivities. Mont was also heated in the same manner for reference purposes. This paper reports solely on the oxidation resistivities of MNC. The crystal phases derived from MNC through oxidation will be reported in detail in a future paper.

2. Experimental details

2.1. Materials and heat-treatments

The montmorillonite self-supporting film was reacted with α-naphthylamine hydrochloride aqueous solution (NA) to convert it to MNC film, details of which were reported previously [1]. The chemical formula of MNC is $(\mathrm{Mont})(\mathrm{NA})_{1.26}$. After sealing in pyrex glass tubing under vacuum, MNC was subjected to γ-ray radiation (12 Mrad) and subsequent heating to 473 K. The resulting MNC was heated to various temperatures (HTT) below 1473 K at a heating rate of $20\,\mathrm{K\,min^{-1}}$ under nitrogen and maintained for 5 min. Mont was also treated in the same manner for reference. In this paper, the samples thus prepared are denoted by fixing HTT ($\times 10^{2\circ}$ C) after Mont or MNC, e.g. Mont-0 and MNC-10 are Mont with no heat-treatment and MNC heated to 1273 K, respectively. These samples were subsequently heated to temperatures between 1073 and 1473 K at a heating rate of $20\,\mathrm{K\,min^{-1}}$ in air and maintained for 30 min or 5 h to examine their oxidation resistivities.

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TABLE I Crystal phases observed in this work and their abbreviations

Crystal phases	Abbreviations
Montmorillonite	Mont
Montmorillonite–α-naphtylamine complex	MNC
Lithium alumino silicate	LAS
Crystobalite	CB
Mullite	MU
Cordierite	CD

2.2. Measurements

MNC and Mont were subjected to X-ray diffraction by using the nickel-filtered CuK_α radiation. Thermogravimetry was carried out in air or in a stream of nitrogen. Here sample weight and the heating rate were 8 mg and 10 K min^{-1}, respectively. Some samples were measured by FT–IR. The fracture surface of the film was observed using scanning electron microscopy (SEM). These methods have been described elsewhere in detail [1].

3. Results

3.1. X-ray diffraction

TABLE II Changes of basal spacing d_{001} of Mont and MNC with HTT (heating rate: 20 K min^{-1}, residence time: 5 min. atm: N_2)

HTT(K)	Mont(nm)	MNC(nm)
473	1.15	1.64
773	0.96	1.25
1073	0.96	1.30
1273	*	1.34
1473	*	*

The crystal phases observed in this work were the six shown in Table I. which also gives their abbreviations. Figs. 1 and 2 show X-ray diffraction profiles of Mont and MNC after heating to various HTTs under nitrogen. The basal spacings, d_{001}, of these samples are summarized in Table II. Mont-0 decreased its d_{001} from 1.45 nm to 0.96 nm in Mont-5. Mont-8 has also 0.96 nm but the background in the X-ray diffraction profile is considerably high. LAS appeared in Mont-10, and CB and MU in addition to LAS were observed in Mont-12. The details of LAS derived from MNC will be discussed in our next paper. On the other hand, d_{001} of MNC decreased from 1.65 nm in MNC-0 to 1.25 nm in MNC-5. In MNC-8 and MNC-10, d_{001} increased slightly with a weakening of the diffraction peak. MNC-12 changed into an amorphous phase.

Figs. 3 and 4 show X-ray diffraction profiles of some of the samples summarized in Table II, after heating to 1073 and 1273 K for 30 min in air. The

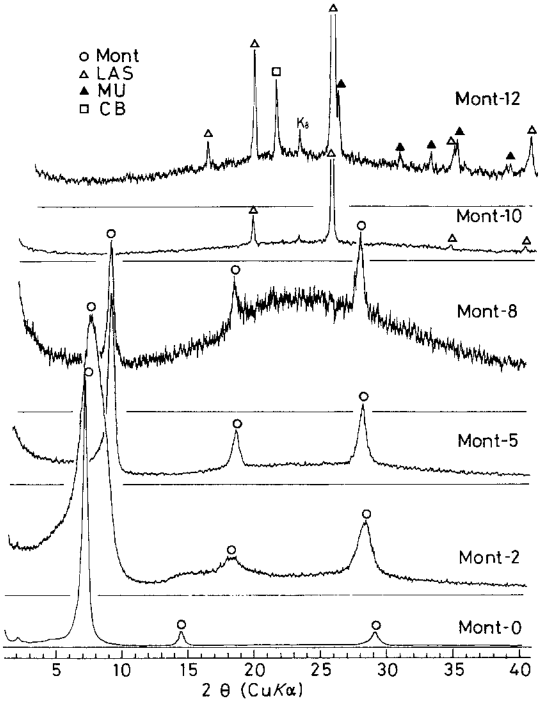

Figure 1 X-ray diffraction profiles of Monts after heating to various HTTs for 5 min under nitrogen.

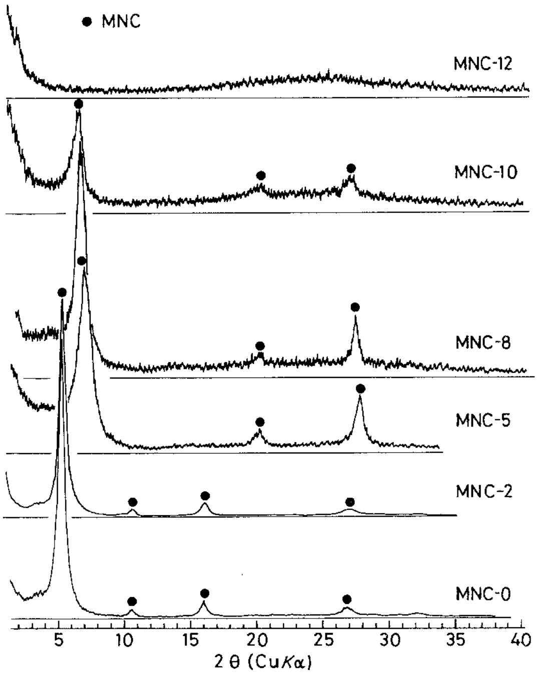

Figure 2 X-ray diffraction profiles of MNCs after heating to various HTTs for 5 min under nitrogen.

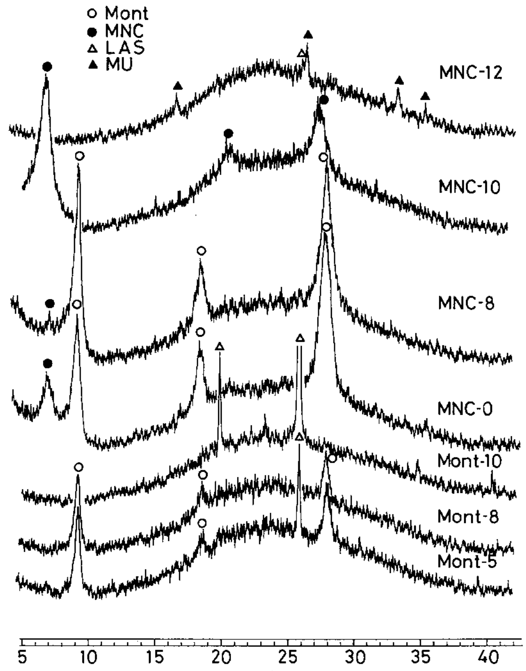

Figure 3 X-ray diffraction profiles of Monts and MNCs after heating to 1073 K for 30 min in air.

crystal phases observed in the samples are listed in Table II. After heating to 1073 K in air, LAS was observed in Mont-0, Mont-2 and Mont-5 together with the remaining Mont. No crystal phase, except for Mont, appeared in Mont-8, and on the contrary, Mont-10 converted into LAS with no remaining Mont. MNC-0, MNC-2 and MNC-5, as well as MNC-8, reverted to Mont, with an exception of slight amount of MNC remaining in MNC-0. After this treatment at 1073 K in air, MNC-10 remained almost unchanged, but MU and LAS only were formed slightly in MNC-12.

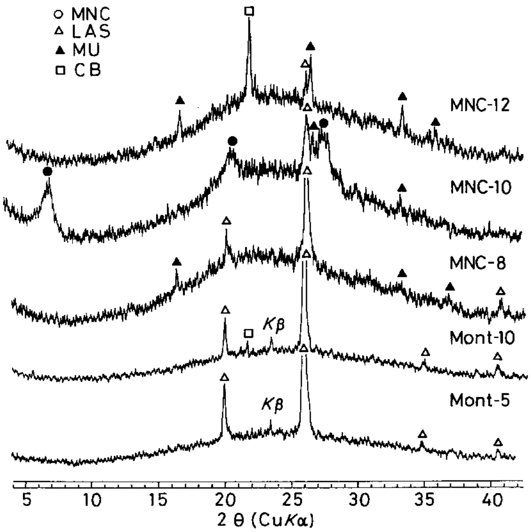

Figure 4 X-ray diffraction profiles of Monts and MNCs after heating to 1273 K for 30 min in air.

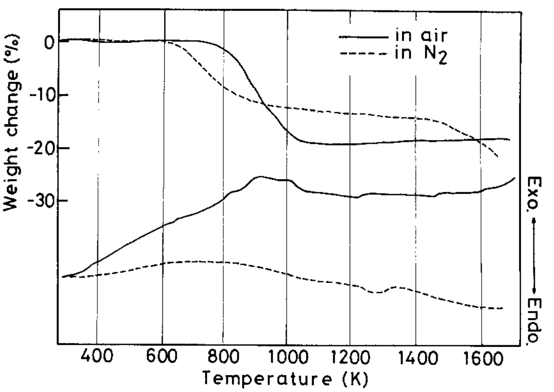

Figure 5 TG–DTA curves of MNC-2 in air and a stream of nitrogen.

Through heating to 1273 K in air (Fig. 4), Mont-0, Mont-2 and Mont-5 changed into LAS. A small amount of CB in addition to LAS appeared in Mont-8 and Mont-10. On the other hand, LAS and a small amount of MU formed in MNC-0, MNC-2, MNC-5 and MNC-8. MNC-10 retained its layered structure slightly even after heating to 1273 K in air. An amorphous phase of MNC-12 changed into CB, MU and a small amount of LAS. No effect of HTT under nitrogen appeared on the crystal phases formed from Mont or MNC after heating to 1473 K in air, as shown in Table III. MNC-9 and MNC-10 retained their structures even after heating to 1173 K and 1073 K for 5 h, respectively.

3.2. Thermogravimetry

TG–DTA curves of MNC-2 in air and under nitrogen are shown in Fig. 5. Weight decrease started at a lower temperature under nitrogen than in air, but between 1000 and 1400 K, the weight decrease in air was larger than that under nitrogen by about 5%. MNC-2 decreased remarkably in weight between 800 and 1000 K in air with a broad exothermic peak. A small endothermic peak around 1300 K under nitrogen must have resulted from the conversion of the crystalline phase to the amorphous phase [3].

Fig. 6 shows TG curves for MNCs in air. MNC, in general, exhibited two steps in the weight decrease. The first step starts at around 800 to 900 K. Here MNC heated to a higher HTT under

TABLE III Changes of Mont and MNC, after heating under N_2, through further heating in air (heating rate: 20 K min^{-1}, residence time: 30 min)

Original samples HTT(K)	No further heating		HTT(K)							
			973	1073		1173	1273		1473	
	Mont	MNC	MNC	Mont	MNC	MNC	Mont	MNC	Mont	MNC
No heating	Mont	MNC		Mont LAS	Mont MNC		LAS	LAS MU(vw)	LAS CB MU CD(vw)	CD CB MU(w) LAS(vw)
473	Mont	MNC		Mont LAS	Mont		LAS	LAS Mu(vw)	LAS CB(w) MU(w) CD(w)	CD CB MU(w) LAS(vw)
773	Mont	MNC		Mont LAS	Mont		LAS	LAS MU(vw)	LAS CB(w) MU(w) CD(w)	CB CD MU(w) LAS(vw)
1073	Mont	MNC	Mont	Mont	Mont		LAS CB(w)	LAS MU(vw)	LAS CB CD(w) MU(vw)	CD CB MU(w) LAS(w)
1173		MNC				MNC(w) MNC(vw)*				
1273	LAS	MNC		LAS	MNC MNC*	MNC	LAS CB(w)	MNC LAS MU(w)	LAS CB MU MU(vw)	CD CB MU(w) LAS(w)
1473	LAS MU CB	Amorphous			MU(w) LAS(vw)			MU CB LAS(w)		MU

*Residence time: 5 h, (w) and (vw) are small and very small amounts of formation.

nitrogen decreased in weight less remarkably. The second step was observed between ~1400 and 1500 K. After heating to a higher HTT under nitrogen, MNC exhibited a larger decrease in weight with the exceptions of MNC-2 and MNC-8. Weight decreases of the MNCs at 1600 K are smaller with increasing HTT under nitrogen.

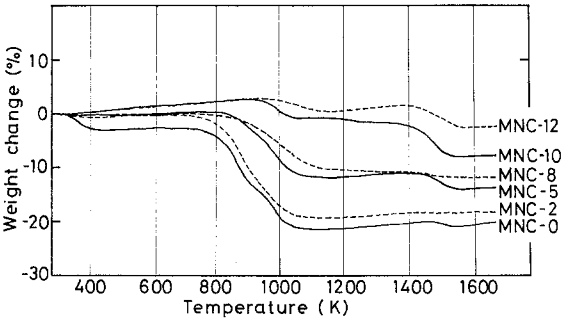

Figure 6 TG curves of MNCs in air.

3.3. FT–IR spectroscopy

Fig. 7 shows FT–IR spectra of MNC-8, MNC-10 and Mont-10. The spectrum of MNC-10, on the whole, is very similar to that of Mont-10. Absorption peaks between 1000 and 1200 cm^{-1} assigned to Si–O are clearer in MNC-8 than in the other two samples. MNC-8 exhibited some clear peaks below 900 cm^{-1}, which will be assigned to Si–O and Al–O [4].

3.4. SEM observation

Figs. 8 and 9 are scanning electron micrographs of the fracture surfaces of some films before and after heating in air. As can be seen from Fig. 8a and b, the layers seen in Mont-5 became slightly thicker by sintering through heating to 1073 K for 30 min in air. More serious sintering occurred in Mont-8, though with a clear memory of the layered structure. After heating to 1273 K for 30 min in air, such memory disappeared completely as

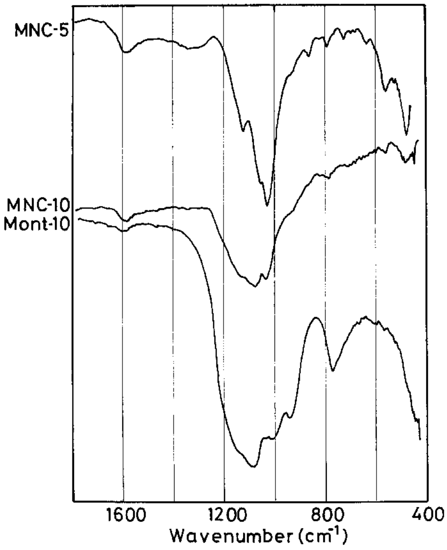

Figure 7 FT–IR spectra of MNC-8, MNC-10 and Mont-10.

shown in Fig. 8d. Similar structures were seen in Mont-10 before and after heating to 1273 K for 30 min in air.

On the other hand, MNC-0 and MNC-8, before and after heating to 1073 K for 30 min in air, showed layer stacking (Fig. 9a to d). MNC-10 resulted in a fine and homogeneous porous structure (Fig. 9e) which is superior to that reported elsewhere [1]. However, such a structure was destroyed after heating to 1273 K for 30 min in air, as indicated in Fig. 9f. The layered structure of MNC-10 sintered seriously resulting in a characteristic porous structure after heating to 1473 K for 30 min in air (Fig. 9g).

4. Discussion and conclusions

The following points should be noted:

1. heat-treatment around 1173 to 1273 K, under nitrogen is the most effective in preparing MNC with a high oxidation resistivity. MNC heated below 1073 K under nitrogen reverts to Mont on heating at 1073 K for 30 min in air;
2. a fine and porous structure was observed in MNC heated to 1273 K under nitrogen, but it changed to a layered less porous structure and a less fine characteristic porous structure after heating to 1273 K for 30 min in air, respectively.

The causes of these phenomena are discussed below.

As shown in Fig. 5, a weight decrease of MNC-2 around 1000 to 1400 K in air is larger than that found under nitrogen by ~ 5 %, which indicates the presence of some residue derived from NA between montmorillonite layers in MNC heated to this HTT range under nitrogen. Such a residue acts to maintain the layered structure of MNC up to higher HTT, a mechanism which has been discussed elsewhere [1].

MNC-0, MNC-5 and MNC-8 have layered structures, both microscopically and macroscopically, as indicated by X-ray diffraction profiles and SEM observations. In view of their low oxidation resistivities, the oxygen molecule can easily penetrate between the montmorillonite layers of MNCs to oxidize the residue from NA. The resulting Mont after oxidation also has a distinct layered structure (Fig. 9d), and has a higher thermal stability than the usual Mont, i.e. sintering of the latter results in a small amount of LAS, whereas no change in the former was observed after heating to 1073 K for 30 min in air (Figs. 3 and 9d). The layered structure of Mont is known to be destroyed through dehydroxylation at 800 to 1000 K [5]. Montmorillonite layers in MNC, however, were maintained by the inserted residue derived from NA even at the dehydroxylation stage. Through this process, the montmorillonite layers possibly become so thermally stable as to withstand even heating to 1073 K.

The next problem to be discussed is why the oxidation resistivity of MNC is changed so widely by HTT under nitrogen. The layered structure of MNC-10 was sintered, apparently because of its characteristic porous structure (Fig. 9e). The X-ray diffraction profile of this sample, however, exhibited small peaks from the MNC structure with high background. Two reasons are considered to account for the high oxidation resistivity of MNC-10.

1. The residue derived from NA in montmorillonite forms strong bonds with the montmorillonite layer, e.g. carbide-like bonding. No evidence supporting this theory, however, was obtained from FT–IR and X-ray diffraction.
2. The montmorillonite layers in MNC sinter to result in the inclusion of the residue derived from NA between them. Here an oxygen molecule cannot penetrate to oxidize the residue from NA. This theory will be reasonably explained below. The first step in weight decrease is attributable to oxidation of NA or its derived residue by the penetration of the oxygen molecule between the montmorillonite layers. This is supported by the exothermic peak, accompanied by a weight loss

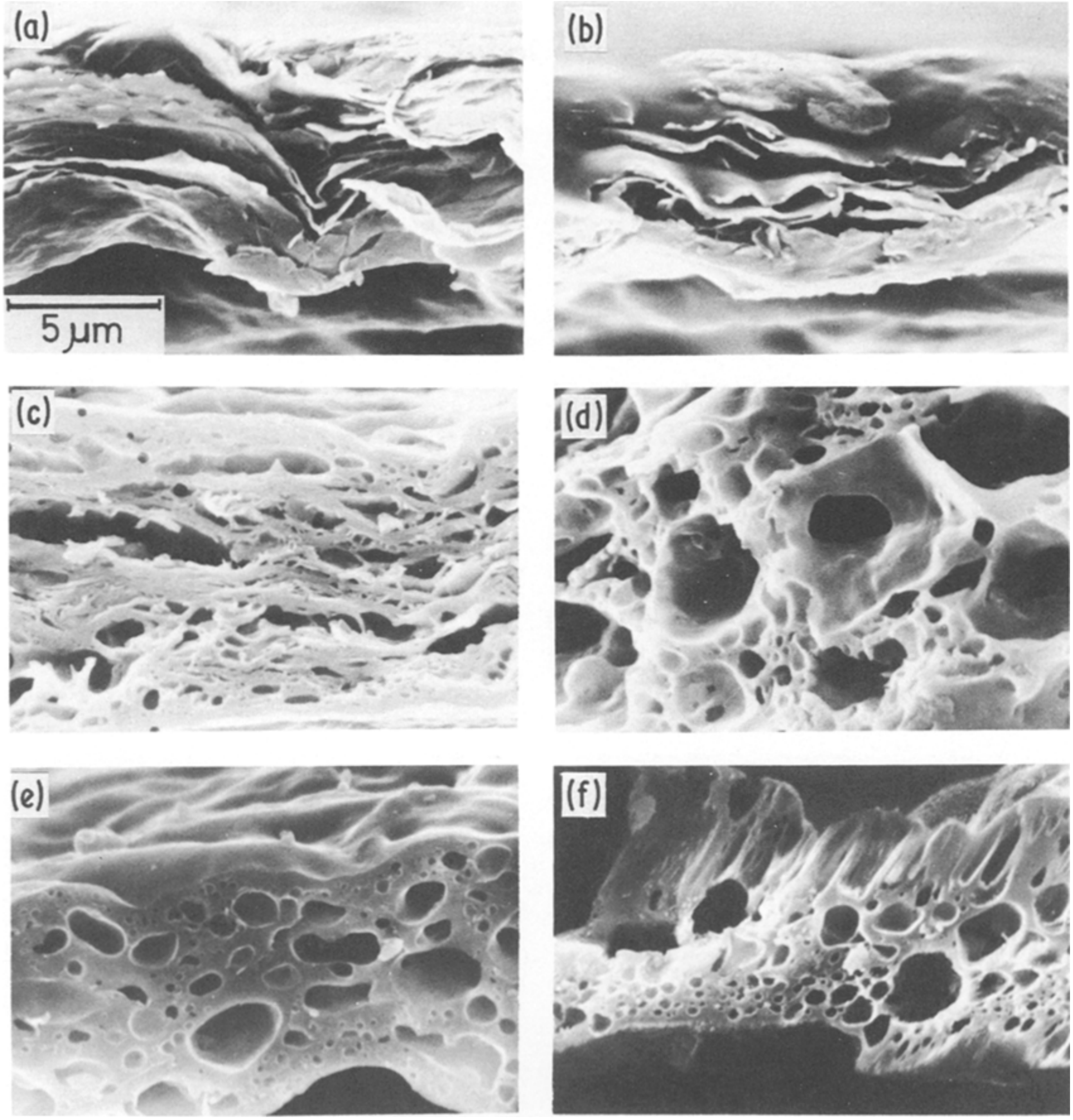

Figure 8 Scanning electron micrographs of the fracture surfaces of Monts. (a) Mont-5, (b) Mont-5 after heating to 1073 K for 30 min in air, (c) Mont-8, (d) Mont-8 after heating to 1273 K for 30 min in air, (e) Mont-10, and (f) Mont-10 after heating to 1273 K for 30 min in air.

(Fig. 5). When MNC is heated to a high HTT, e.g. 1400 to 1500 K, it becomes so fusible that the enclosed residue escapes as CO and CO_2 [1], as suggested by the porous structure. This is the second step in the weight loss which is not accompanied by an exothermic peak (Fig. 5). Therefore, MNC with a lower HTT under nitrogen exhibits a larger weight loss in the first step. MNC-10 and MNC-12, on the other hand, decrease in weight greatly at the second step. As a result, the high oxidation resistivity of MNC-10 depends on the inclusion of the residue derived from NA which acts to disturb the sintering of the montmorillonite layers in MNC.

The fine and homogeneous porous structure of MNC-10 (Fig. 9e) should also be noted here. This porous structure is superior to that reported previously [1]. In view of the remarkable change in the porous structure of the MNC resulting from the heat-treatment conditions, methods for preparing the finer and more homogeneous porous structure should be studied.

At present, as a result, it is possible to prepare

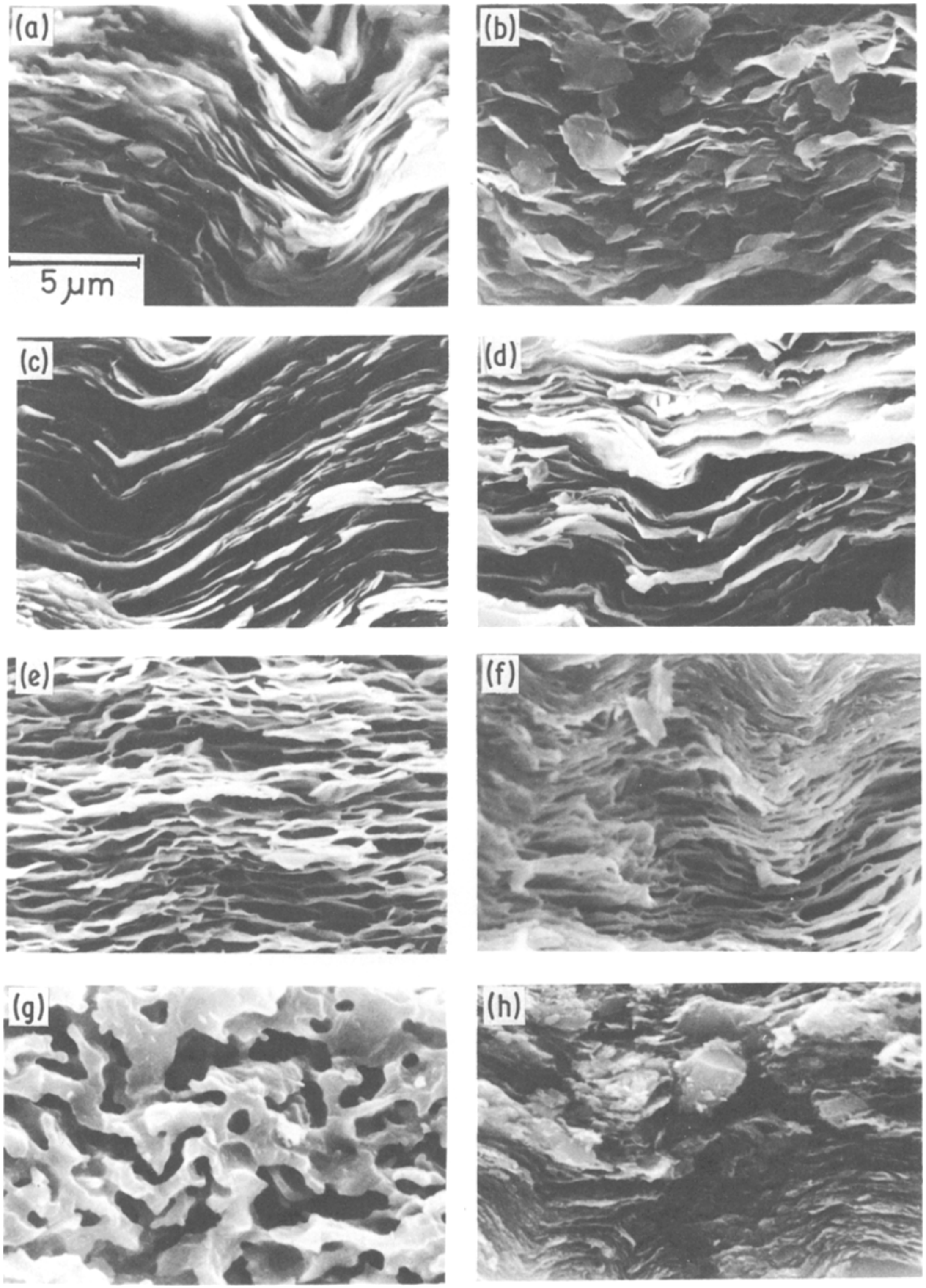

Figure 9 Scanning electron micrographs of the fracture surfaces of MNCs. (a) MNC-0, (b) MNC-0 after heating to 1073 K for 30 min in air, (c) MNC-8, (d) MNC-8 after heating to 1073 K for 30 min in air, (e) MNC-10, (f) MNC-10 after heating to 1273 K for 30 min in air, (g) MNC-10 after heating to 1473 K for 30 min in air, and (h) MNC-12.

a fine porous material which can withstand temperatures up to 1173 K in air. However, MNC exhibiting distinct layer stacking which can be prepared by heating below 1073 K under nitrogen reverts to Mont after heating to 1073 K for 30 min in air.

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