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Effects of oxidation on the structure of porous material prepared from a montmorillonite–α-naphthylamine complex

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A porous material was prepared by carbonizing the layer-type complex of montmorillonite–α-naphthylamine at 873 to 1273 K and it was then subjected to heat-treatment in air to examine the effects of oxidation on the porous structure. After oxidation at 1273 K for 10 h the pore volume decreased remarkably, with a broadening of the pore size distribution. Oxidation at 873 or 1073 K, on the contrary, increased the pore volume with a small increase in pore size. The mechanisms of these oxidation behaviours are discussed.

1. Introduction

The present authors have reported [1] that the carbonization of a montmorillonite–α-naphthylamine complex results in a homogeneous porous material (pore radius: several tens of nanometres) of which the maximum pore volume was obtained by carbonization at 873 to 1073 K. This porous material, in addition, is characterized by a wrinkled paper-like structure and by containing about 10 wt % of intercalated carbon which is readily oxidized at high temperature [2]. If the porous structure is changed by oxidation unfavourably, therefore, its application field may be limited. In the present work, from such a practical point of view, the porous material was heated below 1273 K in air to examine the effects of oxidation on its porous structure.

2. Experimental details

The porous material was prepared as follows, of which further details have been reported elsewhere [1]. α-naphthylamine hydrochloride ($C_{10}H_7NH_2 \cdot HCl$) was dissolved into about 3 wt % of an aqueous sol of purified montmorillonite (particle size: smaller than 2 to 3 μm, cation exchange capacity (CEC): 108 meq per 100 g) by 1.1 times the CEC, followed by maintaining for 4 days at 353 K. The resulting montomorillonite–α-naphthylamine complex was dried in a 300 ml beaker at 333 K in air. Montmorillonite and the complex are abbreviated at Mont and MNC, respectively. Two series of experiments were carried out by use of the MNC thus prepared:

(i) After being crushed to particles of several millimetres in size, it was carbonized at 873, 1073 and 1273 K for 1 h under nitrogen. The MNC porous materials obtained were oxidized at 873, 1073 and 1273 K for 10 h in air. In this paper, the specimen with carbonization and subsequent oxidation is shown by adding (N) and (A) after the heat-treatment temperature (HTT), e.g. 873 K (N) → 1073 K (A) means the specimen oxidized at 1073 K after carbonization at 873 K.

X-ray diffraction analysis, thermogravimetric analysis (TG-DTA) and SEM observation were carried out according to conventional procedures. Pore size distribution was measured by a mercury penetration porosimeter.

(ii) Some MNC porous materials (ca. 2 mm × 5 mm × 30 mm) were heat-treated as follows to measure weight loss and linear shrinkage. The raw porous material (N) without any treatment was first carbonized at 473 K for 1 h under nitrogen and then subjected successively to further carbonization at higher temperatures for 1 h. Two other specimens, (A) without treatment and (N) → (A) after carbonization at 1073 K, were oxidized successively to higher temperatures in air as analogous to the (N) specimen; here the residence time at fixed temperature was 10 h.

3. Results

3.1. X-ray diffraction analysis

As shown in Fig. 1, MNC exhibited a (0 0 1) diffraction peak at 5° (2θ, Cu$K\alpha$) which corresponds to 1.67 nm of the interlayer distance (d_{001}), whereas d_{001} of raw Mont under dehydration was 0.97 nm. MNC decreased its d_{001} to 1.47 nm after carbonization at 873 K. At higher HTT, the (0 0 1) diffraction peak became very weak but the layered structure remained faintly even after carbonization at 1273 K.

Fig. 2 shows X-ray diffraction profiles of the 1073 K (N) specimens before and after oxidation. The specimen before oxidation showed no clear (0 0 1) diffraction peak. In view of the appearance of a small but sharp (0 0 1) peak corresponding to 0.97 nm after oxidation at 873 and 1073 K, this specimen must be the transition

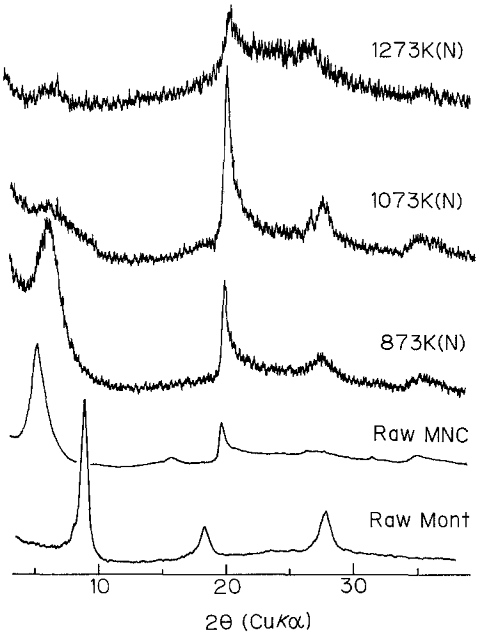

Figure 1 X-ray diffraction profiles of raw Mont and MNCs before and after carbonization.

state between the layered structures with d_{001} of 1.47 nm and 0.97 nm. The layered structure was destroyed by oxidation at 1273 K to change into mullite and cristobalite. Quite analogous phenomena were observed in the 873 K (N) specimen. The layered structure of the 1273 K (N) specimen also remained faintly after oxidation to 1073 K.

3.2. TG-DTA

Fig. 3 shows TG-DTA curves in air for MNCs before and after carbonization. Raw MNC before carbonization exhibited two weight losses at 400 K and 800 to 1100 K. The former is attributable to the removal of adsorbed water. The latter must have mainly resulted from combustion of the intercalant in view of its exothermic reaction. Dehydration from OH in the Mont layer may possibly somewhat contribute to this weight loss around 400 K and the other weight loss became smaller.

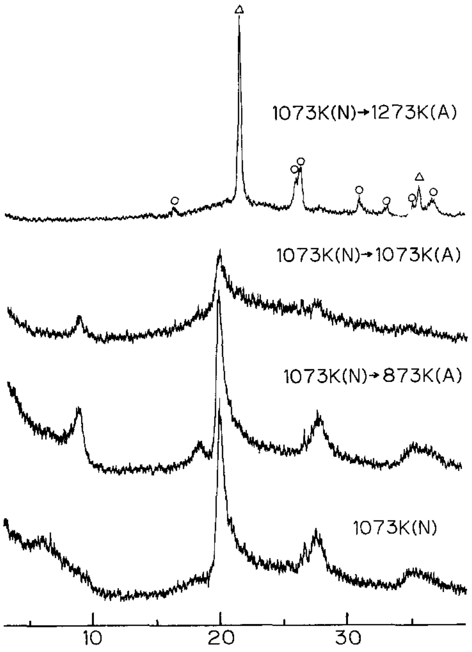

Figure 2 X-ray diffraction profiles of 1073 K (N) specimens before and after oxidation. (○) Mullite, (△) cristobalite.

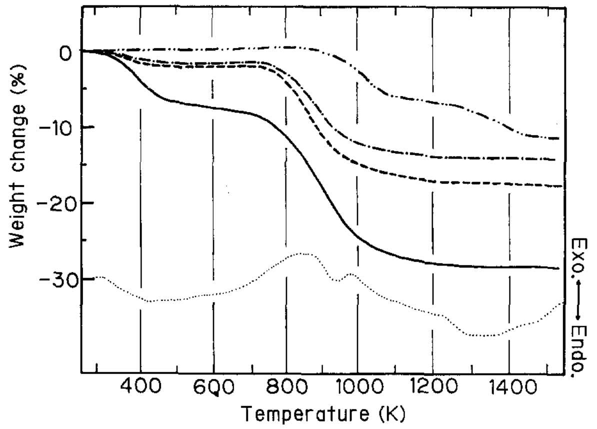

Figure 3 TG-DTA curves of MNCs before and after carbonization (in air, heating rate: 10 K min^{-1}). TG: (——) raw, (– – –) 873 K (N), (–·–) 1073 K (N), (–··–) 1273 K (N). DTA: (···) raw.

3.3. SEM observations

SEM photographs of the fractured surfaces of the 1073 K (N) specimens before and after oxidation are shown in Figs 4 and 5. As shown in Fig. 4, the porous structure of the 1073 K (N) specimen consists of wrinkled paper-like thin flakes. It is clear under higher magnification that individual thin flakes further cleaved and curved to form pores among them. This material seems to include heterogeneous pores from this photograph but, in fact, exhibited quite a uniform

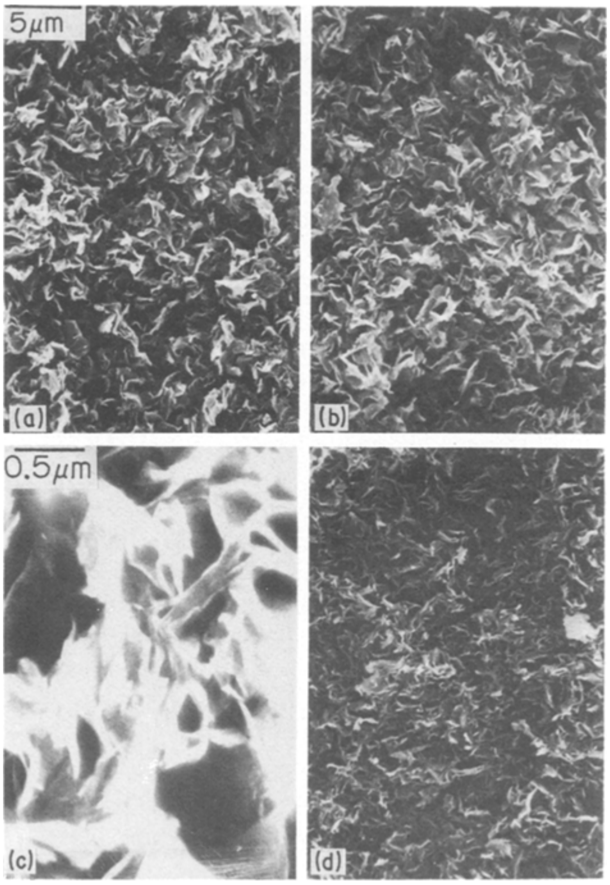

Figure 4 SEM photographs of the fractured surfaces of MNCs before and after oxidation: (a) 1073 K (N), (b) 1073 K (N) → 873 K (A), (c) 1073 K (N), (d) 1073 K (N) → 1073 K (A).

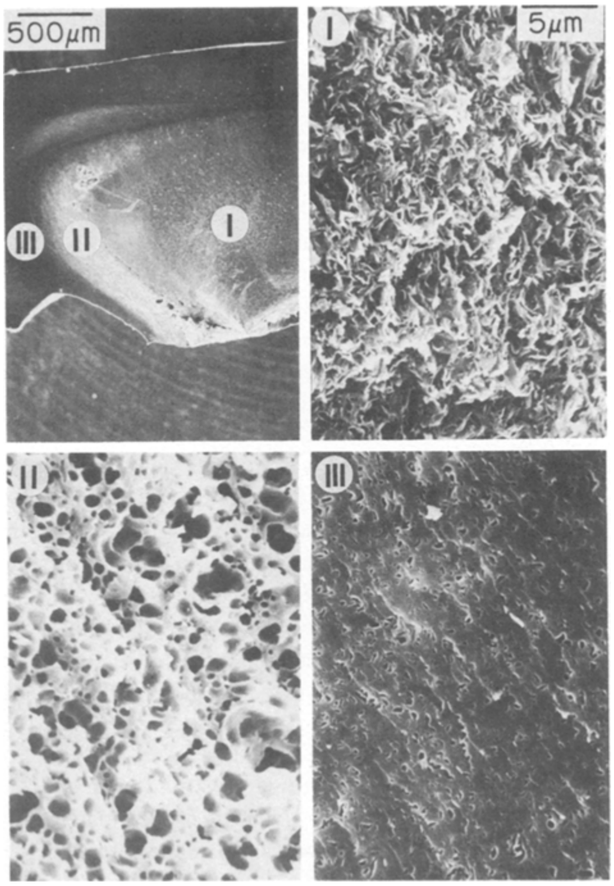

Figure 5 SEM photographs of the fractured surfaces of 1073 K (N) specimen after oxidation at 1273 K: three resultant regions.

pore size distribution as described later. This structure scarcely changed after oxidation at 873 K but became more dense through oxidation at 1073 K. Fig. 5 shows the fractured surface of the relatively large 1073 K (N) specimen after oxidation at 1273 K, in which three regions are clearly observed, i.e. the inner black region (I), the outer white region (III) and the intermediate grey region (II) between the two. Region I seems to be similar to that before oxidation. Region III must sinter via the state of Region II. These phenomena were also observed in specimens oxidized at 1273 K.

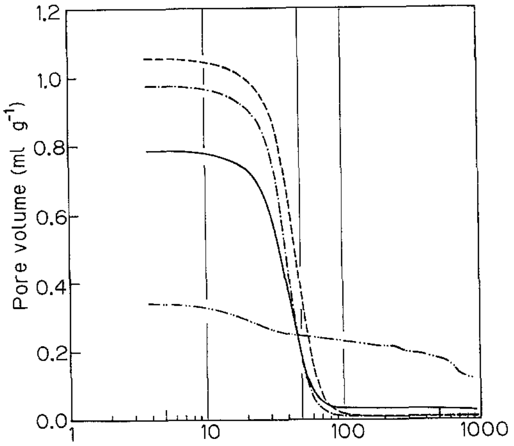

Figure 6 Pore size distribution diagrams of 1073 K (A) and 1073 K (N) before and after oxidation: (——) 1073 K (N), (– – –) 1073 K (N) → 873 K (A), (–·–) 1073 K (N) → 1073 K (A), (–··–) 1073 K (N) → 1273 K (A).

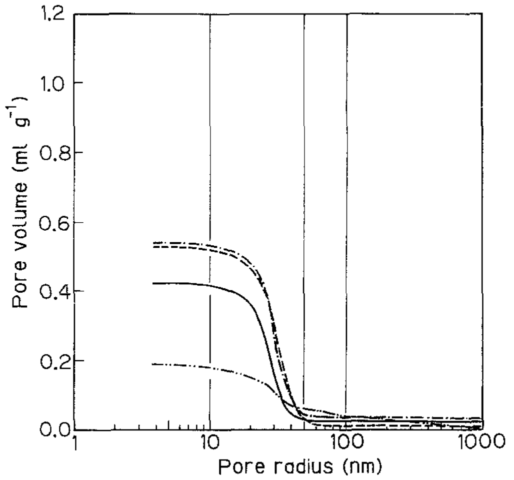

Figure 7 Pore size distribution diagrams of 1273 K (N) before and after oxidation: (——) 1273 K (N), (– – –) 1273 K (N) → 873 K (A), (–·–) 1273 K (N) → 1073 K (A), (–··) 1273 K (N) → 1273 K (A).

3.4. Pore size distribution

Figs 6 and 7 show the pore size distribution diagrams for the specimens before and after oxidation. As shown in Fig. 6, the 1073 K (N) specimen increased its pore volume remarkably after oxidation at 873 K, with a small increase in pore size, but its pore volume decreased slightly after oxidation at 1073 K. Oxidation at 1273 K decreased the pore volume remarkably with a broadening in the pore size distribution.

As can be seen from Fig. 7, when the carbonization temperature was raised to 1273 K the resulting specimen gave a far smaller pore volume consisting of smaller pores by sintering. However, the effects of oxidation are very similar to those shown in Fig. 6. The 873 K (N) specimen, though not presented here, exhibited very similar phenomena to those of the 1073 K (N) specimen, though its pore volume was slightly smaller.

3.5. Linear shrinkage and weight loss

Fig. 8 shows changes of linear shrinkage and weight

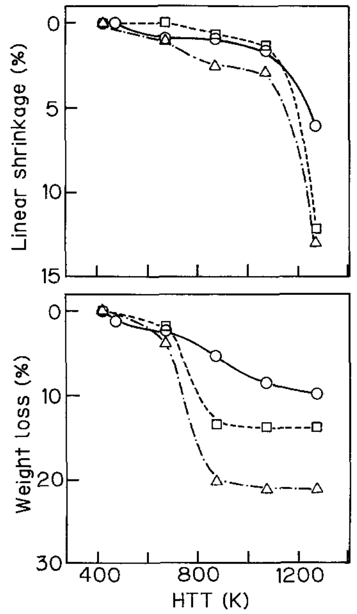

Figure 8 Changes of weight loss and linear shrinkage with HTT. (○): (N), (□): (N) → (A), (△): (A).

loss of the specimens by heat-treatment. Remarkable shrinkage was observed for all specimens, especially those heated in air, at 1073 to 1273 K. By heating in air, both specimens (A) and (N) → (A) showed large and small weight losses at 673 to 873 K and at higher temperature, respectively, whereas a nitrogen atmosphere brought about a gradual increase of weight loss for the (N) specimen.

4. Discussion

As stated above, oxidation at 1273 K and below 1073 K gave different effects on the porous structure, i.e. the former decreased the pore volume with a broadening of the pore size distribution but the latter increased the pore volume with a small increase in pore size.

It has been reported that destruction of the Mont layered structure begins around 673 K and accelerates at 900 K [2]. In the case of MNC, the intercalant disturbs sintering between the Mont layers to enhance the thermal stability of the layered structure, which also means that a shaped body of MNC does not sinter or deform up to a higher temperature than that of Mont. Based on the TG curve with a heating rate of $5\,\mathrm{K\,min^{-1}}$ (Fig. 3), however, the combustion of the intercalant except for the 1273 K (N) specimen, begins at 800 K and completes at 1100 K to return into the Mont layered structure. Of course, when the specimen is held for 1 h at the fixed temperature, the intercalant is removed completely at a lower temperature (Fig. 8). This is the cause of the destruction of the MNC porous structure after oxidation at 1273 K. In the oxidation process at 1273 K, large pores are first formed, followed by sintering (Fig. 5). For the relatively large MNC specimen, the outer region alone is oxidized to sinter and hinders further diffusion of oxygen into the interior. It is also interesting to know that the Mont layered structure derived from MNC remained up to above 1073 K (Fig. 2), because this temperature is far higher than the destruction temperature of the original Mont layered structure [1], of which further details are not clear at present.

The next point to be noted is why oxidation below 1073 K increases the pore volume with a small increase in pore size. The most substantial reason is derived from Fig. 8, i.e. oxidation at 873 to 1073 K brings about a small shrinkage in spite of the large weight loss. Since the (N) → (A) specimen was carbonized at 1073 K before oxidation, weight loss and shrinkage at this stage were used to correct those after oxidation in order to compare with the (A) specimen oxidized without carbonization. After this correction, there were no differences in weight loss and shrinkage between the (A) and the (N) → (A) specimens oxidized above 873 K. As far as the porous material without carbon is concerned, therefore, the carbonization process of MNC is substantially meaningless. The removal of the intercalant decreases the interlayer distance (d_{001}) of the layered structure constituting the porous structure; in other words, the pore wall becomes thin. This is the cause of the small increase of pore size after oxidation at 873 and 1073 K.

According to the phenomena stated above, the porous structure depends strongly on the carbonization and oxidation processes which, in turn, relate intimately with the kind of intercalant. Therefore, the porous structure may be controlled by selecting the organic compound intercalated.

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