Proposed Models of Mesopore Structures in Sulfuric Acid-Treated Montmorillonites and K10

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The models of pore structures of commercially available K10 and sulfuric acid-treated montmorillonites are proposed on the basis of XRD, NMR, and N_2 adsorption-desorption isotherm measurements.

In the preceding paper, we revealed that montmorillonite K10 and sulfuric acid-treated montmorillonites (SA-Mont) are effective for *meso*-alkylsubstituted porphyrin synthesis from aliphatic aldehydes and pyrrole because the clays have appropriate mesopores fitting the dimension of porphyrins. Here we wish to propose the models of pore structures specific to the SA-Mont and K10, which are produced via transformations in structures from laminated to delaminated.

A parent sodium montmorillonite (Na-Mont) was treated with 30% sulfuric acid under reflux conditions.[1] Figure 1 shows the dependence of the N_2 BET surface area and the amount of acid sites with $H_0 \leq -5.6$ of the SA-Mont on sulfuric acid-treatment time. After short acid treatment within 1 h, both the BET surface area and the acid site amount of the SA-Mont drastically increased. Upon further acid treatment on the clay for more than 1 h, the gradual reduction of the acid site amount with a slight decrease in BET surface area was observed. The decrease in the acid site amount was caused by extraction of aluminum atoms from the clay on the acid treatment.[2]

Next, the structural transformation was followed by taking powder X-ray diffraction (XRD) and NMR analysis. Figure 2 shows XRD patterns, and ^{29}Si and ^{27}Al MAS NMR spectra of 1 h-, 3.5 h-, and 8 h-acid-treated clays and K10 as well as parent Na-Mont. The XRD patterns as well as ^{29}Si and ^{27}Al NMR spectra can be taken as indicators of remaining laminar montmorillonite structure. As shown in Figure 2(a), the presence of strong reflections from (001) planes centered at $2\theta=5.6^{\circ}$ on XRD of Na-Mont proved that Na-Mont has the ordered laminar structure. The resonances at -94 ppm in ^{29}Si NMR were assigned to silicon atoms in the two-dimensional silica network (Q^3 state),[3] and the two resonances at -4 and 56 ppm in ^{27}Al NMR were associated with aluminum atoms in octahedral and tetrahedral sites in the montmorillonite lattice, respectively.[3] The 1 h-sulfuric acid-treated montmorillonite (abbreviated as 1 h-SA-Mont) had weak XRD peaks at around $2\theta=6^{\circ}$, and in ^{29}Si NMR, besides the peaks at -97 ppm (characterized as Q^3-silicons), new resonances appeared at -109 ppm which can be assigned to silicon atoms in the three-dimensional silica network (Q^4 state)(Figure 2(b)).[3] It is reasonable to assume that the aluminum leaching process caused by the acid treatment accompanied the disorder of arranged laminar sheets of Na-Mont during the initial stage of acid treatment. In the 3.5 h-SA-Mont, the laminated structure slightly remained on XRD, and ^{29}Si resonances in the Q^4 state were predominant, while residual aluminum atoms in tetrahedral and octahedral sites were still observed in ^{27}Al NMR (Figure 2(c)). In contrast, no ^{27}Al resonances could be detected in the 8 h-SA-Mont sample, indicating that most of aluminum atoms were leached out from the clay lattice (Figure 2(d)). In this way, originally layered aluminosilicate, Na-Mont was

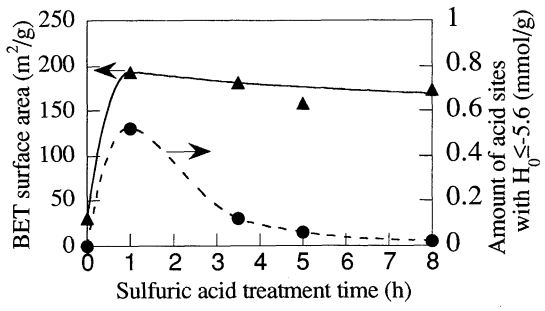

Figure 1. The dependence of the N_2 BET surface area (▲) and the amount of acid sites with $H_0 \leq -5.6$ (●) of the SA-Mont on sulfuric acid treatment time.

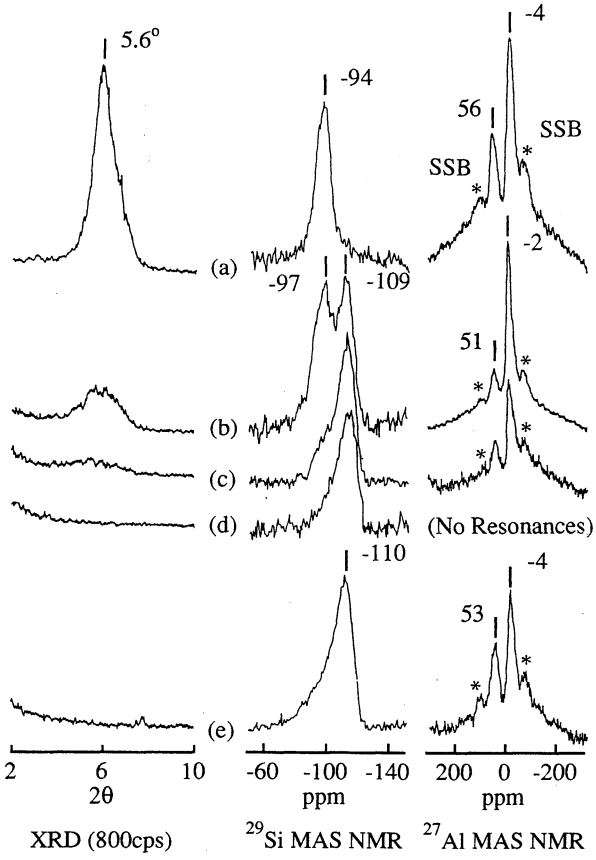

Figure 2. XRD patterns and ^{29}Si, ^{27}Al MAS NMR spectra of (a) Na-Mont, (b) 1 h-SA-Mont, (c) 3.5 h-SA-Mont, (d) 8 h-SA-Mont, and (e) montmorillonite K10.

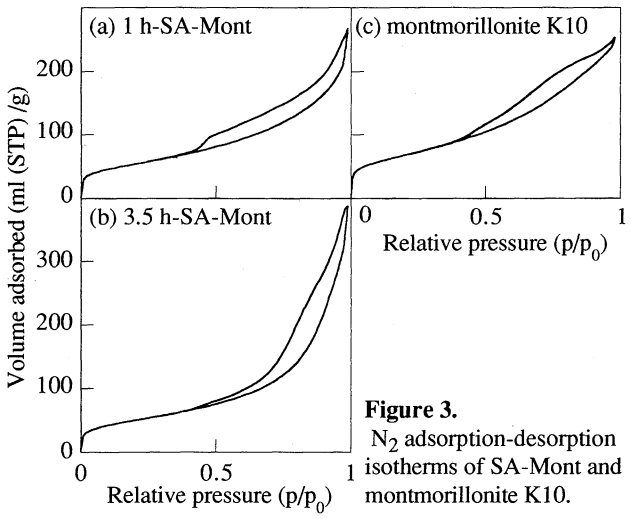

Figure 3. N_2 adsorption-desorption isotherms of SA-Mont and montmorillonite K10.

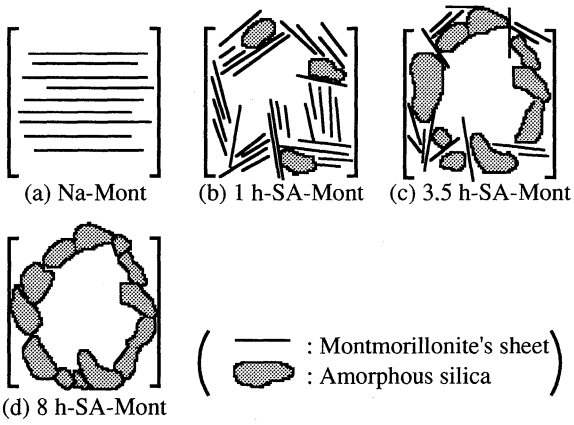

Figure 4. The transformation of laminated montmorillonite into mesoporous amorphous silica on progressive acid treatment.

converted into porous amorphous silica on the progressive acid treatment.

Figure 3 represents the N_2 adsorption-desorption isotherms of 1 h- and 3.5 h-SA-Mont as well as K10. The 1 h-SA-Mont has a hysteresis loop of the H3-type (Figure 3(a)),[4] which is typical of spaces between plate-like particles.[5] It is known that synthetic Laponite composed of small-sized layered sheets tends to adopt the "edge-to-face" association, which is called a "card-house" structure.[6] Therefore, a similar structural change would happen to SA-Mont; a card-house structure is constructed from the well-ordered layers of the parent Na-Mont on acid treatment. Based on the XRD patterns, ^{29}Si and ^{27}Al MAS NMR spectra, and the type of N_2 adsorption-desorption isotherms of 1 h-SA-Mont, mesopores of 1 h-SA-Mont are presumed to be mainly composed of delaminated sheets of montmorillonite with partially formed amorphous silica. In contrast, the 3.5 h-SA-Mont shows a hysteresis loop of H1-type (Figure 3(b)),[4] which is characteristic of cylindrical pores, suggesting that during the prolonged acid treatment a distinct change in structure from two-dimensional, delaminated aluminosilicate to porous amorphous silica occurred.

Based on these results, a possible scenario concerning the transformation from ordered laminar montmorillonite into mesoporous silica is presented in Figure 4: at the initial stage of acid treatment, the dimensions of laminar sheets of Na-Mont would be getting smaller as aluminum atoms in the clay are gradually extracted out, leading to the formation of delaminated card-house structure bearing mesopores. Thus, newly formed mesopores would cause a drastic increase in the BET surface area of SA-Mont. Upon extended exposure to sulfuric acid, remaining layered aluminosilicates would gradually be converted into amorphous silica with progress of aluminum extraction while the dimensions of mesopores are approximately maintained. The structure of 3.5 h-SA-Mont would be a hybrid of layered aluminosilicates and amorphous silica. In the 8 h-SA-Mont, the mesopores would be surrounded by amorphous silica.

In the preceding paper, we demonstrated in *meso*-tetrapentylporphyrin synthesis that 3.5 h-SA-Mont has the highest efficiency among various sulfuric acid-treated montmorillonites, of which the efficiency (39% yield) is comparable to that of K10 (46% yield). There is much similarity in composition between the 3.5 h-SA-Mont and K10 in terms of XRD patterns as well as ^{29}Si and ^{27}Al MAS NMR spectra (Figures 2(c) and (e)). The N_2 adsorption-desorption isotherms of K10 are associated with H1-type because of no sharp dip in the desorption isotherm at p/p_0 of around 0.5 (Figure 3(c)).[7] In addition, the pore size distribution of K10 is also in good agreement with that of 3.5 h-SA-Mont.[1] Therefore, the structure of K10 is assumed to be made of porous silica containing partly laminar aluminosilicates as represented in Figure 4(c).

Recently commercially available K10 has been often utilized in organic synthesis.[8] However, it has only been recognized as an acid-treated clay without any understanding of structural features on K10. Our proposed models for K10 as well as SA-Mont will help the clay-based acids much more accessible to synthetic organic chemists as practical solid acids in organic synthesis.

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