

PREPARATION OF DELAMINATED CLAY HAVING A NARROW MICROPORE DISTRIBUTION IN THE PRESENCE OF HYDROXYALUMINUM CATIONS AND POLYVINYL ALCOHOL

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Abstract—The pillaring of Na-montmorillonite with cationic oligomers of hydroxyaluminum (COHA) in the presence of an aqueous solution of polyvinyl alcohol resulted in the formation of a clay having a large surface area and pore volume. The pore-size distribution determined from a N_2 adsorption/desorption hysteresis was narrow and centered at about 25 Å. The peak width at half height in the distribution curve was <5 Å. As a result of delamination, the layer structure of the prepared clay was found from X-ray powder diffraction measurements to be lost. Short-range ordering, however, still existed in this delaminated clay, because exchangeable cations in the montmorillonite completely exchanged with Al^{3+} , a requisite step for pillaring.

The order of adding the starting materials (Na-montmorillonite, polyvinyl alcohol, and COHA) greatly affected the surface area and the pore volume of the delaminated clay. Two orders of addition (Na-montmorillonite, then COHA, then polyvinyl alcohol; and COHA, then Na-montmorillonite, then polyvinyl alcohol) gave no measurable surface area and pore volume. Two other orders of addition (polyvinyl alcohol, then COHA, then Na-montmorillonite; and polyvinyl alcohol, then Na-montmorillonite, then COHA) gave surface areas of 107 and 160 m^2/g and pore volumes of 0.13 and 0.29 cm^3/g , respectively. The amounts of the COHA solution and polyvinyl alcohol added greatly influenced the surface area and pore volume of the delaminated clay. Both properties increased monotonically with increasing amount of added polyvinyl alcohol, and increased to a maximum and then decreased with increasing amount of added COHA solution. The maximum surface area of the prepared delaminated clay was 330 m^2/g .

Key Words—Delaminated clay, Hydroxy aluminum, Montmorillonite, Ordering, Pillaring, Polyvinyl alcohol, Pore size, Surface area.

INTRODUCTION

Since the mid-1970s, new families of zeolite-like materials have been prepared by introducing various inorganic pillars into expandable clay minerals (Brindley and Sempels, 1977; Yamanaka and Brindley, 1978, 1979; Lahav *et al.*, 1978; Brindley and Kao, 1980; Vaughan and Lussier, 1980; Occelli and Tindwa, 1983; Shabtai *et al.*, 1984; Pinnavaia *et al.*, 1985; Occelli and Finseth, 1986). The production of such pillared clays is typically initiated by an ion-exchange process involving the exchangeable cations of the clay. Na-montmorillonite, for example, can be pillared by exchanging interlayer Na^+ cations with polyoxymetal cations, which, on dehydration, remain as pillars propping the clay laminae apart. Usually, the resultant pillared clay has a basal spacing of 18–20 Å, yielding interlayer space having pore openings of ~9 Å. The polyoxymetal cations apparently aggregate to form cationic oligomers in solution (Johansson, 1960; Muha and Vaughan, 1960). The size of these oligomers appears to control the size of the pore openings in the pillared clays. Cationic polyoxy oligomers of aluminum or zirconium, for example, are considered to have a dimension about 9–11 Å (Brindley and Sempels, 1977; Lahav *et al.*, 1978; Yamanaka and Brindley, 1979).

The pillared clay usually gives an X-ray powder dif-

fraction (XRD) typical of the layered structures; however, the XRD patterns of some pillared clays show no 001 reflections. Pinnavaia *et al.* (1984) first reported the synthesis of this kind of clay ("delaminated" clay), and its cracking activity was investigated by Occelli *et al.* (1984). From similarities in cracking selectivities for delaminated and pillared clay catalysts, they concluded that, in addition to macroporosity due to delamination, their delaminated clay had two-dimensional microporosity; its layer stacking was short-range, accounting for the absence of XRD reflections.

In the present study, we have prepared microporous delaminated clay by pillaring Na-montmorillonite with a basic aluminum hydroxychloride salt in the presence of an aqueous solution of polyvinyl alcohol. The preparation of such a delaminated clay is described below.

EXPERIMENTAL

Materials

The clay used was high-purity montmorillonite fractionated from bentonite produced in Tohoku, Japan. This clay (particle size <0.2 μm) is commercially available as KUNIPIA-F from Kunimine Industries Co., Ltd. The cation-exchange capacity (CEC) of the montmorillonite and the exchangeable cation content were reported by Kunimine Industries (1978) to be 119 meq/

100 g and Na⁺ (87%), Ca²⁺ (10%), and K⁺ (3%), respectively. This natural, Na-rich montmorillonite is referred to as Na-montmorillonite in this paper. The cationic oligomer of hydroxy aluminum (COHA) used was a basic aluminum hydroxychloride salt marketed by the Taki Chemical Co., Ltd. under the tradename of Takibine-powder. This chloride salt has the formula Al₂(OH)₅Cl·2.4H₂O and a chemical composition of Al₂O₃ (49.5 ± 1.5 wt. %), Cl (17 ± 1.0 wt. %), and Fe (<0.1 wt. %) (Taki Chemical company, 1974). In the present study, the Takibine-powder was used as a 10 wt. % aqueous solution. The polyvinyl alcohol used was Gohsenol NH-20, a commercial product of The Nippon Synthetic Chemical Industry Co., Ltd. The extent of polymerization was 2000. AlCl₃ (reagent grade), obtained from Wako Pure Chemical Industries, Ltd., was used to measure the cation exchange of Na-montmorillonite. The concentration of AlCl₃ was 0.12 N.

Preparation of alumina-pillared and delaminated clay

A typical procedure for the preparation of alumina-pillared delaminated clay is as follows: Na-montmorillonite (1.0 g) was added to the polyvinyl alcohol solution (10 wt. %, 10 ml) followed by stirring; the Takibine (cationic oligomer of hydroxy aluminum = COHA) solution (2.0 ml) was then added to the resultant mixture, followed by more stirring. The obtained paste was aged at room temperature for 1 day, dried at 60°C for an additional day, and then calcined at 500°C for 1 hr. Different preparation methods were also used in which the order of adding the starting materials was altered.

Using the method described by Lahav *et al.* (1978), the alumina-pillared Na-montmorillonite was also prepared in the absence of polyvinyl alcohol by exchanging cations in the clay with the cationic oligomers of hydroxyaluminum in the COHA solution.

Exchange of cations in Na-montmorillonite with Al³⁺

To confirm cation exchange in the presence of polyvinyl alcohol, the exchange reaction was performed as follows: First, 1.0 g of Na-montmorillonite was added to the polyvinyl alcohol solution (10 wt. %, 10 ml) followed by the addition of the AlCl₃ solution to the resultant mixture. Then the paste obtained in this manner was suspended in water (200 ml), followed by centrifugation. The amounts of cations in the supernatant was determined by atomic absorption spectrometry (Shimadzu AA-650N).

In the absence of polyvinyl alcohol, the cation exchange was examined in a manner similar to that described above.

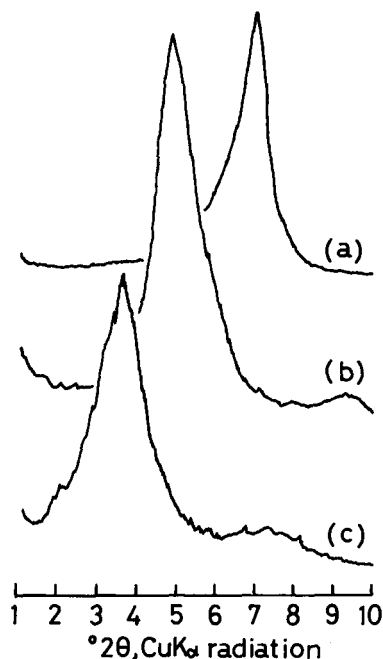


Figure 1. X-ray powder diffraction patterns of Na-montmorillonite and the mixtures of polyvinyl alcohol and Na-montmorillonite. Weight ratio of alcohol to clay = 0 (a), 0.25 (b), and 1.0 (c).

Characterization of delaminated clay

X-ray powder diffraction (XRD) measurements were made using a Rigaku horizontal X-ray diffractometer with Ni-filtered monochromatic CuK α radiation. Surface area, pore volume, and pore-size distribution were determined using an automatically controlled nitrogen-adsorption apparatus (Sorptomatic 1800, Carlo Erba Strumentazione). Before measurements, samples were evacuated at 150°C overnight. Nitrogen adsorption was measured at liquid nitrogen temperature. The pore-size distribution was also measured by mercury porosimetry (Porosimeter 2000, Carlo Erba Strumentazione). Some delaminated clays were examined by transmission electron microscopy (Hitachi H-800) using a thin section technique. No laminar structure was observed in the electron micrographs of the prepared clays.

RESULTS AND DISCUSSION

Interactions between Na-montmorillonite and polyvinyl alcohol

After drying at 60°C, mixtures of Na-montmorillonite and polyvinyl alcohol were examined by XRD. The 001 XRD reflections of these three mixtures are shown in Figure 1. From the XRD patterns, the d(001) value of Na-montmorillonite in the mixture was found to be larger than that of the original Na-montmorillonite, indicating a larger interlayer distance for the Na-mont-

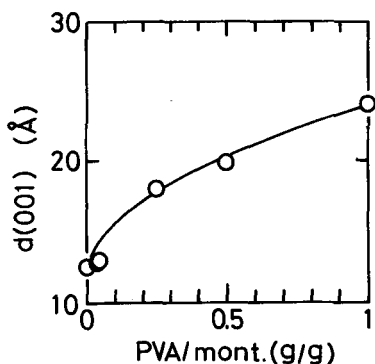


Figure 2. Effect of the amount of the added polyvinyl alcohol on the basal spacing, $d(001)$, of Na-montmorillonite.

morillonite product. It is well known that Na-montmorillonite swells in water, resulting in an expansion of the interlayer distance, and also that on dehydration of the swollen Na-montmorillonite, the interlayer distance decreases to the original value. Therefore, Figure 1 suggests that the Na-montmorillonite swelled even in the aqueous solution of polyvinyl alcohol and that after dehydration, the clay remained expanded due to the presence of the alcohol molecules in the interlayer space. Figure 2 shows the effect of the amount of the added polyvinyl alcohol on $d(001)$. The increase of $d(001)$ with increasing amount of the added alcohol indicates that the added molecules of polyvinyl alcohol penetrated the interlayer space of the Na-montmorillonite, resulting in an expansion of the interlayer distance. Calcination of the clay-alcohol mixture, however, resulted in a decrease in the interlayer distance to the original value prior to the mixing (*vide infra*) because the alcohol in the interlayer space had been lost by its combustion.

Exchange of exchangeable cations in Na-montmorillonite by Al^{3+} in the presence of polyvinyl alcohol

To pillar Na-montmorillonite with alumina, ion-exchange is a primary step for introducing the hydroxy-aluminum cations, the precursors of alumina pillars, into the interlayer space. Whether or not such an exchange reaction occurred in the presence of polyvinyl alcohol was therefore examined. Figure 3 shows the results of the exchange reaction, in which, instead of the COHA solution, $AlCl_3$ was used as an exchanging reagent. With increasing volume of the $AlCl_3$ solution added, the amount of Na^+ in the supernatant increased linearly and then remained constant at ~ 0.9 CEC, a value corresponding to the Na^+ content of the starting Na-montmorillonite. The amount of K^+ also increased linearly and then remained constant. The amount of Ca^{2+} was negligible in the small volume of the $AlCl_3$ solution (< 8 ml) and then steeply increased to a con-

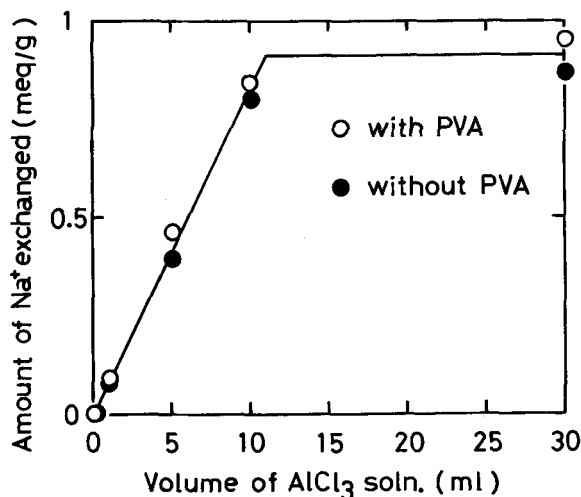


Figure 3. Ion exchange of Na^+ by Al^{3+} in the presence or absence of polyvinyl alcohol. Conditions: 1.0 g of Na-montmorillonite, 10 ml of polyvinyl alcohol solution (10 wt. %), $AlCl_3$ solution (0.12 N).

stant level. The total amount of these cations, including Na^+ , corresponded to the CEC of Na-montmorillonite. Thus, in excess $AlCl_3$, the exchangeable cations in the Na-montmorillonite were completely exchanged by Al^{3+} , even in the presence of polyvinyl alcohol.

The ion exchange was also examined in the absence of polyvinyl alcohol. As shown in Figure 3, similar results were obtained, indicating that complete exchange had occurred. Thus, the added polyvinyl alcohol did not appear to affect the cation-exchange reaction.

If the COHA solution was used under these same conditions, several types of exchangeable cations were found in the supernatant, the total amount of which corresponded precisely to the CEC of the Na-montmorillonite. The consistency of the total amount of the exchangeable cations with the CEC indicates that the exchange was complete even in the presence of polyvinyl alcohol and therefore that the added alcohol did not disturb the exchange reaction during the preparation of the alumina-pillared delaminated clay, as previously concluded.

Characterization of delaminated clay

In the absence of polyvinyl alcohol, Na-montmorillonite pillared using COHA gave distinct 001 XRD reflection, which suggests long-range ordering of a layer structure. Thus, the COHA used in the present study appears to be an efficient pillaring reagent.

Inasmuch as the procedure in which Na-montmorillonite was added to the polyvinyl alcohol solution followed by the addition of the COHA solution appears to have given the largest surface area and pore volume (*vide infra*), the clay thus prepared was characterized

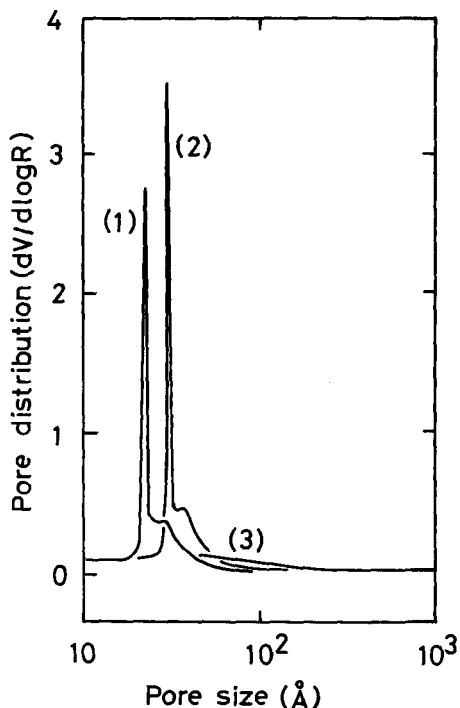


Figure 4. Pore-size distribution of delaminated clay. Curves 1 and 2 were determined on the basis of cylindrical capillary and parallel-plate pore models, respectively. Curve 3 was determined by mercury porosimetry on the basis of the cylindrical capillary model. Pore size corresponds to capillary radius for cylindrical capillary model and to pore-wall separation for parallel-plate model (see text).

in detail. As shown in Figure 4, the typical pore-size distribution determined by N_2 adsorption/desorption hysteresis was narrow and centered at about 25 Å. The peak width at half height of the distribution curve was <5 Å. From pore-size distribution data determined by mercury porosimetry, macropores (i.e., pore size > 100 Å) were absent in this product. Although pores can occur between particles of the clay (interparticle voids), the particle size of the starting Na-montmorillonite, seems to have been too large for the measured microporosity of the prepared clay. Microporosity due to interparticle voids may also have existed in the starting Na-montmorillonite, because, after preparation, the particle size appeared to be unchanged. Such microporosity was not found, however, and some other explanation (i.e., not interparticle voids) was probably responsible for the microporosity of the prepared clay.

The pore-size distribution in Figure 4 (curve 1) was determined on the basis of the cylindrical capillary model of Cranston and Inkley (1957); however, as discussed above, because the micropores of the pillared clay are due to interlayer space between parallel walls of silicate units, the parallel-plate pore model of Innes (1957) seems to be relevant to determine the pore-size

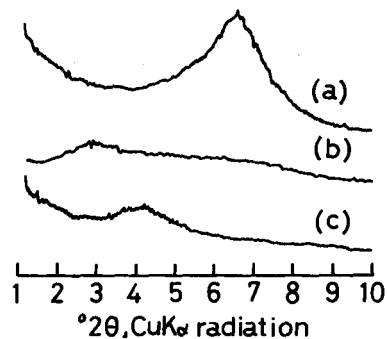


Figure 5. X-ray powder diffraction patterns of delaminated Na-montmorillonite: (a) mixture of Na-montmorillonite and polyvinyl alcohol after calcination at 400°C for 2 hr; (b) mixture of Na-montmorillonite, polyvinyl alcohol, and cationic oligomer of hydroxyaluminum (COHA) after drying at 60°C for 1 day; (c) mixture of Na-montmorillonite, polyvinyl alcohol, and COHA after calcination.

distribution. The pore-size distribution determined from this model is also shown in Figure 4 (curve 2), where pore size is represented as pore-wall separation. A narrow distribution centered at about 30 Å can be noted. Therefore, if the parallel-plate pore model is acceptable for the pore structure of the prepared clay, the basal spacing should have been near 40 Å, because the thickness of the silicate layer is about 10 Å.

The XRD pattern of the prepared clay is shown in Figure 5. In the absence of COHA, calcining the mixture of Na-montmorillonite and polyvinyl alcohol produced a clay having almost the same interlayer distance as the starting Na-montmorillonite, although the peak intensities were considerably smaller and the peak widths at half height were larger. After calcination, on the other hand, the mixture of Na-montmorillonite, polyvinyl alcohol, and COHA gave a weak XRD pattern having a basal spacing of about 21 Å. Inconsistent with our expectation from the pore-size measurements, however, the XRD measurements gave no reliable evidence for a ~40 Å basal spacing. For a swollen Na-montmorillonite having a basal spacing of about 40 Å, an XRD peak should have been present at $<2^\circ 2\theta$. The absence of such a low-angle spacing therefore suggests that as a result of delamination the pillared clay lost its long-range ordering. Electron micrographs of the prepared delaminated clay also gave no evidence of a laminar structure.

The lack of an XRD reflection, however, does not completely preclude the absence of short-range ordering. For a delaminated clay, Pinnavaia *et al.* (1984) proposed a model in which platelets having short-range ordering are arranged in a house-of-cards structure, the net result being a macroporous structure. Similar short-range ordering probably is present in the present delaminated clay, because the exchange reaction, being the requisite step for pillaring, was complete during the

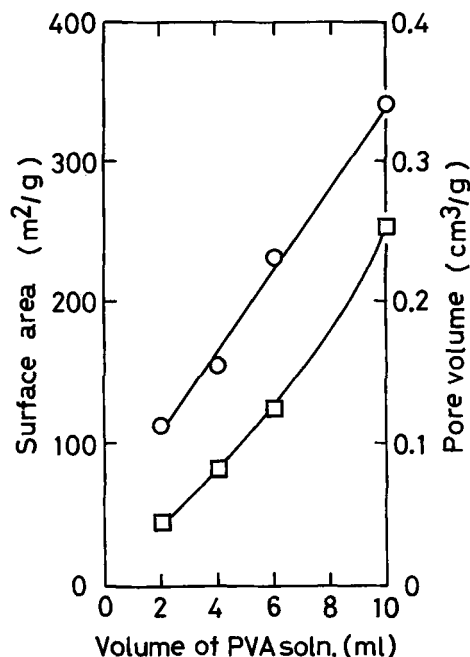


Figure 6. Effects of added polyvinyl alcohol on surface area (\square) and pore volume (\circ) of the delaminated clay. Conditions: 1.0 g of Na-montmorillonite, 2 ml of cationic oligomer hydroxyaluminum solution (10 wt. %). Amount of polyvinyl alcohol was altered by changing volume of 10 wt. % polyvinyl alcohol solution.

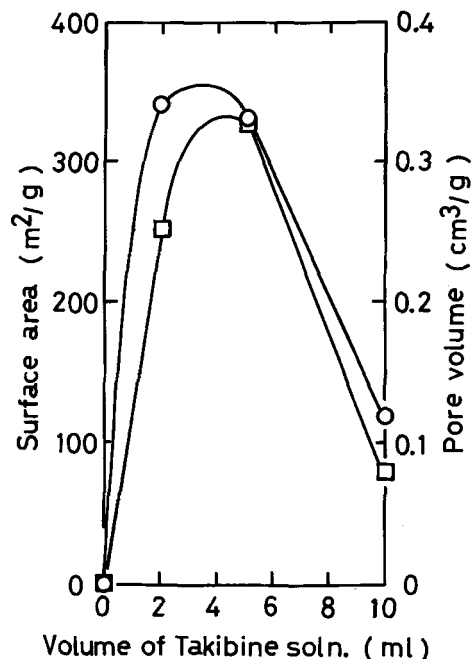


Figure 7. Effects of the amount of added cationic oligomer hydroxyaluminum (COHA) (Takibine solution) on surface area (\square) and pore volume (\circ) of the prepared delaminated clay. Conditions: 1.0 g of Na-montmorillonite, 10 ml of polyvinyl alcohol solution (10 wt. %). Amount of added COHA was altered by changing volume of a 10 wt. % solution.

preparation. The present delaminated clay has a microporous structure and a narrow pore-size distribution, which was lacking in the delaminated clay prepared by Pinnavaia *et al.* (1984). Instead, their delaminated clay had macroporosity, which is lacking in the present delaminated clay. This difference suggests that the house-of-cards structure is not important in the present delaminated clay. Unlike in hectorite, the starting material used by Pinnavaia *et al.* (1984), layers apparently aggregated in a face-to-face lamellar fashion, suggesting again that the house-of-cards structure is not an important element of the present delaminated clay. Despite the apparent lack of a house-of-cards structure, it is difficult to clarify how the observed delamination is compatible with the observed narrow micropore distribution. Polyvinyl alcohol may play a role, but further study is needed, to clarify this function.

Effects of the order of adding starting materials

In the present synthesis experiments, the order of adding the starting materials (Na-montmorillonite, polyvinyl alcohol, and COHA) significantly affected the properties of the delaminated clay. Typical results are summarized in Table 1. Both procedure I (order of adding: Na-montmorillonite, then COHA, then polyvinyl alcohol) and procedure II (COHA, then Na-

montmorillonite, then polyvinyl alcohol) resulted in no measurable surface area or pore volume, suggesting that the Na-montmorillonite was not pillared by alumina. Procedure III (polyvinyl alcohol, then COHA, then Na-montmorillonite) resulted in large surface areas and pore volumes. Procedure IV (polyvinyl alcohol, then Na-montmorillonite, then COHA), however, resulted in a delaminated clay having the largest surface area and largest pore volume.

Effect of the amount of added polyvinyl alcohol and COHA

The delaminated Na-montmorillonite prepared in the presence of the polyvinyl alcohol solution had a large surface area and a microporous structure. Figure 6 shows the effect of the amount of the alcohol on the surface area and pore volume of the delaminated clay product. Surface area and pore volume monotonically increase with increasing amount of added alcohol. These increases may have been due to the fact that almost all the added alcohol was able to penetrate the interlayer space of the Na-montmorillonite, resulting in an expansion of the interlayer distance, followed by a fixation of the expanded interlayer distance with alumina pillars. Figure 6 shows the results of changing the amount of the 10 wt. % alcohol solution. If the concentration of polyvinyl alcohol was changed, a similar

Table 1. Surface area and pore volume of clay prepared by altering the order of adding starting materials.

Proce- dure ¹	Order of adding ²			Surface area (m ² /g)	Pore volume (cm ³ /g)
	First	Second	Third		
I	Na-mont.	COHA	PVA	0	0
II	COHA	Na-mont.	PVA	0	0
III	PVA	COHA	Na-mont.	107	0.13
IV	PVA	Na-mont.	COHA	160	0.29

¹ Procedures III and IV produced a porous clay; procedures I and II produced smooth-faced clay blocks.

² Amounts of starting materials used: 1 g of Na-montmorillonite (Na-mont.); 10 ml of the 4 wt. % polyvinyl alcohol solution (PVA); 5 ml of 10 wt. % cationic oligomer of hydroxyaluminum (COHA) solution.

relation was observed, which suggests that the absolute amount of alcohol added was of primary importance in producing a delaminated clay having the largest surface area and largest pore volume.

Figure 7 shows the effect of the amount of added COHA on the surface area and pore volume of the delaminated clay. In contrast to the effect of polyvinyl alcohol, the surface area and pore volume increased to a maximum and then decreased with increasing amount of added COHA. The maximum surface area of the delaminated clay was 330 m²/g.

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