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INTERCALATION OF SUGAR ALCOHOLS INTO THE INTERLAYER OF MONTMORILLONITE BY WET AND DRY PROCESSES

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ABSTRACT

Organic and inorganic complexes are formed by the intercalation of ethylene glycol and glycerol into the interlayer of montmorillonite. Glycerol and ethylene glycol have the molecular formula $C_2H_6O_2$ and $C_3H_8O_3$, respectively, and the general formula is $C_nH_{2(n+1)}O_n$. This formula represents a sugar alcohol group: erythritol for n = 4, xylitol for n = 5, sorbitol for n = 6, and so on. Complexes were produced by a wet process, in which erythritol, xylitol and sorbitol solutions, and montmorillonite, were mixed to a paste; and by a dry process, in which montmorillonite and erythritol, xylitol and sorbitol, in the solid state, were mixed by automatic agate mortar. X-ray diffraction, FT-IR and X-ray photoelectron spectroscopy analyses of the resulting complexes showed that erythritol, xylitol and sorbitol were intercalated into the interlayer of montmorillonite in both wet and dry processes. The resulting complexes also showed an increase in the basal spacing with increasing n (or molecular weight or carbon chains). The difference between the wet and dry processes lies in the *d*-spacing in each montmorillonite-sugar alcohol system. The *d*-spacing of the complexes formed by the wet intercalation process were about 0.4 nm larger than those formed by the dry intercalation process. This is the length of the longest part of the water molecule. In the wet process, the sugar alcohols were intercalated with water molecules, and the montmorillonite swelled, while it expanded in the dry process.

Key words: erythritol, xylitol, sorbitol, swelling, expansion, X-ray photoelectron spectroscopy

INTRODUCTION

MacEvan (1944) and Bradray (1945) showed by X-ray diffraction analysis that montmorillonite expands due to the intercalation of glycerol molecules (MacEvan, 1944) and glycol molecules (Bradray, 1945) into the interlayer of montmorillonite. Subsequently, the molecular structure of ethylene glycol and glycerol in the interlayer was reviewed (Brindley, 1966; MacEvan and Wilson, 1980). Today, the intercalation of ethylene glycol and glycerol into the interlayer of montmorillonite is commonly used to identify swelling clay minerals. Both ethylene glycol and glycerol belong to a sugar alcohol group. A sugar alcohol is a type of sugar produced by the reduction of the carbonyl group of an aldose or ketose. Polyhydroxyalkanes produced by the reduction of an aldose are called alditols, and occur naturally in plants. The general formula is $C_nH_{2(n+1)}O_n$ where n is 3, 4, 5, 6, 7, 8, 9, or 10, representing tritol, tetritol, pentitol, hexitol, heptitol, octitol, nonitol and decitol, respectively. Ethylene glycol is a dihydric

alcohol. In this study, we attempted to intercalate sugar alcohols (n = 4 to 6) into the interlayer of montmorillonite, with increasing molecular weight for the first time and to elucidate the difference of the intercalation mechanism in the wet or dry processes.

This paper is dedicated to Prof. Ryuji Kitagawa, who passed away on August 9, 2009, and who gave us many suggestions on the properties of clay minerals and the operation of the Clay Science Society of Japan (CSSJ).

MATERIALS AND METHODS

In the experiment on the intercalation of sugar alcohols into the interlayer of montmorillonite, Reference Clay JCSS-3101 Montmorillonite (Tsukinuno, Yamagata Prefecture, Japan) was used for clay mineral as the host compound. Data on the chemical properties of this montmorillonite are provided in a study by Miyawaki *et al.* (2010). For sugar alcohols as the guest molecules, ethylene glycol (dihydric alcohol: $C_2H_6O_2$), glycerol (trihydric alcohol: $C_3H_8O_3$), erythritol (tetrahydric alcohol: $C_4H_{10}O_4$), xylitol (pentahydric alcohol: $C_5H_{12}O_5$), and sorbitol (hexahydric alcohol: $C_6H_{14}O_6$) were used. Reagents

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available from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) were used for ethylene glycol and glycerol. Those available from Nikken-Chemicals, Ltd. (Tokyo, Japan) were used for erythritol, xylitol, and sorbitol.

At room temperature, ethylene glycol and glycerol are liquids, and erythritol, xylitol and sorbitol are solids. Because of this, saturated erythritol, xylitol and sorbitol solutions were used in the experiment on the intercalation of liquid sugar alcohols into the interlayer of montmorillonite at room temperature.

In the experiment using the wet process, 1 ml each of the saturated sugar alcohol solutions and 0.3 g of montmorillonite were mixed for 5 minutes to form a paste using an agate mortar. A preferred-oriented sample was produced by placing the paste between two sheets of slide glass and sliding the glass by hand; the sample was immediately analyzed by X-ray diffraction. In the measurement of montmorillonite alone, a paste of water and montmorillonite was produced at the same mixing ratio as above. A preferred-oriented sample was dried and analyzed.

In the experiment using the dry process, 1 g each of glycerol, erythritol and xylitol and 5 g of montmorillonite were mixed for 20 minutes using an automatic agate mortar, and filled in an aluminum holder for analysis. An X-ray diffractometer RAD-X System (Rigaku Corporation, Tokyo, Japan) was used for X-ray diffraction analysis. The analysis was performed using a scan speed of $2°$ min^{-1}, a scan step of $0.02°$, $1°$ DS-SS slits, a 0.3 mm RS slit, and a 0.80 mm RS slit for monochromator.

Infrared absorption spectra measurements were performed to check for the presence of O-H and C-H, using a FT-IR System (HORIBA, Ltd., Kyoto, Japan) with diamond ATR and FT-720 with DuraScope[TM]. The diamond ATR method can measure the spectra of liquids. Infrared spectra measurements were performed on the starting materials, 5 different sugar alcohols, paste samples, and the samples of the complexes produced by the dry process. X-ray photoelectron spectroscopy was performed on the starting materials, and the samples

produced by the dry process, to study the change in the state of electrons due to the intercalation of a sugar alcohol into the montmorillonite. X-ray photoelectron spectra were collected on a VG-Scienta ESCA-300 with monochromatized $AlK\alpha$ (1486.6eV) X-ray source. The take-off measured with respect to the sample surface is $90°$. The high vacuum chamber had a pressure of 5×10^{-7} Pa. Narrow region XPS spectra were acquired with an analyzer pass energy of 75 eV, X-ray power of 1 kW, a step energy of 0.02 eV, a time per step of 0.5 sec, a slit of 0.3 mm, a number of sweeps of 3, and a flood gun of 3 eV.

RESULTS AND DISCUSSION

Erythritol, xylitol and sorbitol are solid and have high crystallinity (Fig. 1). The basal reflection of preferred-oriented montmorillonite in the starting material was 1.235 nm, and the nth order diffraction peak, a $d00\ell$ reflection, was clearly observed. In all of the complexes, the peak of $d00\ell$ shifted toward lower angles due to the reaction of the montmorillonite with ethylene glycol, glycerol, erythritol, xylitol, and sorbitol in the liquid state (Fig. 2). As is well known, in montmorillonite complexes with ethylene glycol and glycerol, the peak shifts, due to intercalation, to 1.663 and 1.741 nm for complexes with ethylene glycol and glycerol, respectively. In montmorillonite complexes with saturated erythritol, xylitol, and sorbitol solutions, the peak of $d001$ shifts to 1.762, 1.769 and 1.782 nm, respectively, due to the reaction with the solutions. However, in the reaction between montmorillonite and the saturated erythritol solution, the intensity of $d001$ of the formed complex is low, and the erythritol recrystallizes quickly. As a result, the diffraction peaks of erythritol overlap with some of the peaks of $d00\ell$ of the montmorillonite-erythritol complex. The peak positions in each montmorillonite-sugar alcohol complex were compared with the molar mass of the sugar alcohol. The comparison shows that the interlayer spacing increases with increasing CH_2O, or carbon chains (Fig. 3).

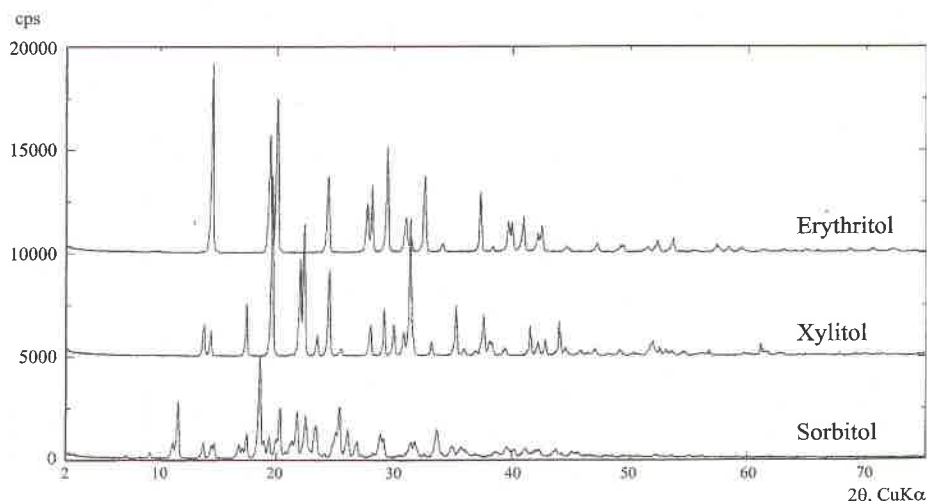The original sugar alcohols present in the crystal state have

Fig. 1.   X-ray diffraction patterns of the sugar alcohols in the solid state.
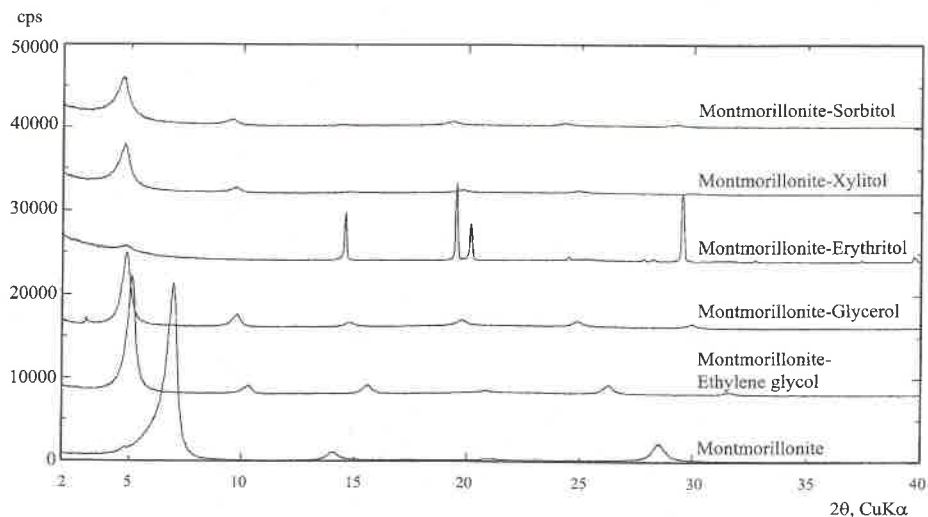
Fig. 2.   X-ray diffraction patterns of the preferred-oriented montmorillonite and montmorillonite-sugar alcohol complex pastes.
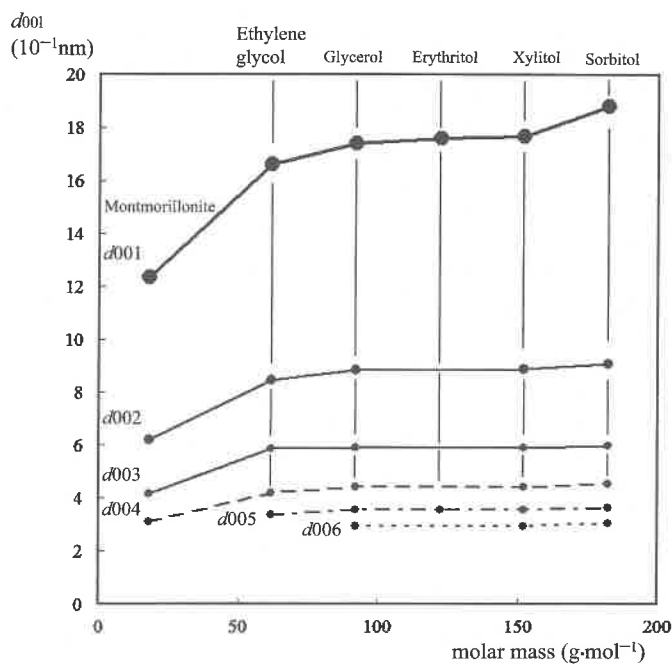

Fig. 3.   Changes in the basal spacing, $d00\ell$, of the montmorillonite and montmorillonite-sugar alcohol complex pastes.
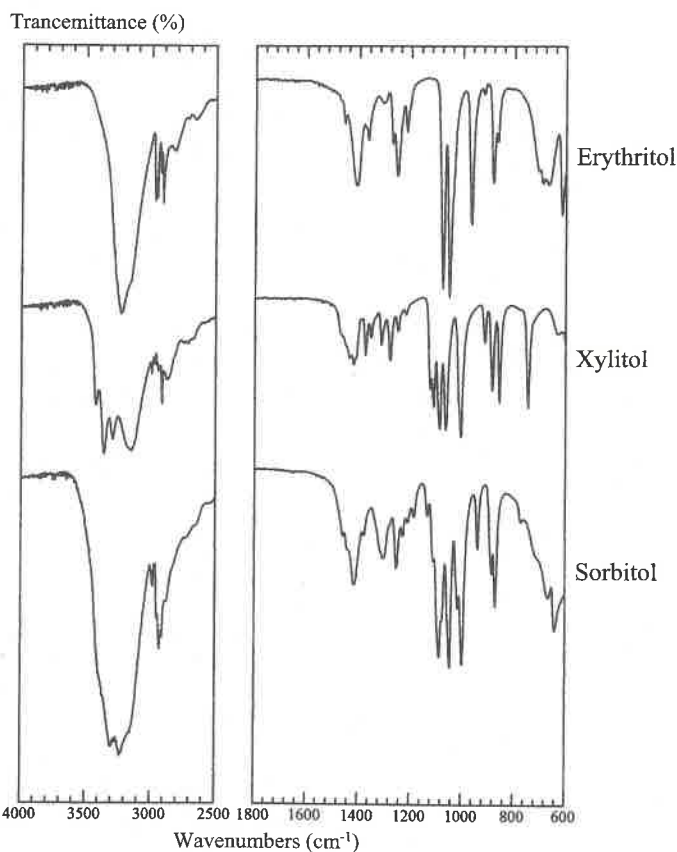

Fig. 4.   IR spectra of the sugar alcohols in the solid state as the guest molecules.

different infrared spectra (Fig. 4). The saturated erythritol, xylitol and sorbitol solutions have similar spectra in the high-wavenumber region where the spectra of O-H and C-H appear (Fig. 5). In montmorillonite-water and montmorillonite-sugar alcohol complex pastes, there is no significant difference in the spectra of the montmorillonite-ethylene glycol complex and the montmorillonite-glycerol complex (Fig. 6). However, the montmorillonite-xylitol complex has more peaks than the montmorillonite-erythritol and -sorbitol complexes. In the starting materials of the sugar alcohols in the solid state, the fact that (as shown in Fig. 4) starting xylitol has more spec-

trum peaks, indicates the presence of xylitol molecules, which was not observed in the X-ray diffraction analysis as shown Fig. 2.

The X-ray diffraction analysis confirmed that montmorillonite-sugar alcohol complexes are formed by mixing

Trancemittance (%)

Trancemittance (%)

Ethylene glycol

Glycerol

Erythritol

Xylitol

Sorbitol

Montmorillonite

Montmorillonite-
Ethylene glycol

Montmorillonite-
Glycerol

Montmorillonite-
Erythritol

Montmorillonite-
Xylitol

Montmorillonite-
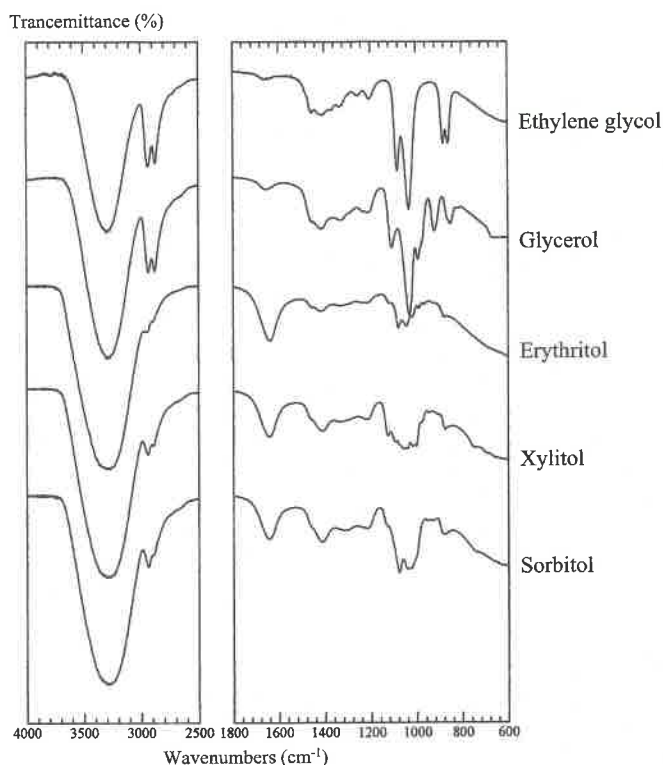Sorbitol

Wavenumbers (cm⁻¹)

Wavenumbers (cm⁻¹)

FIG. 5. IR spectra of the sugar alcohols in the liquid state as the guest molecules.
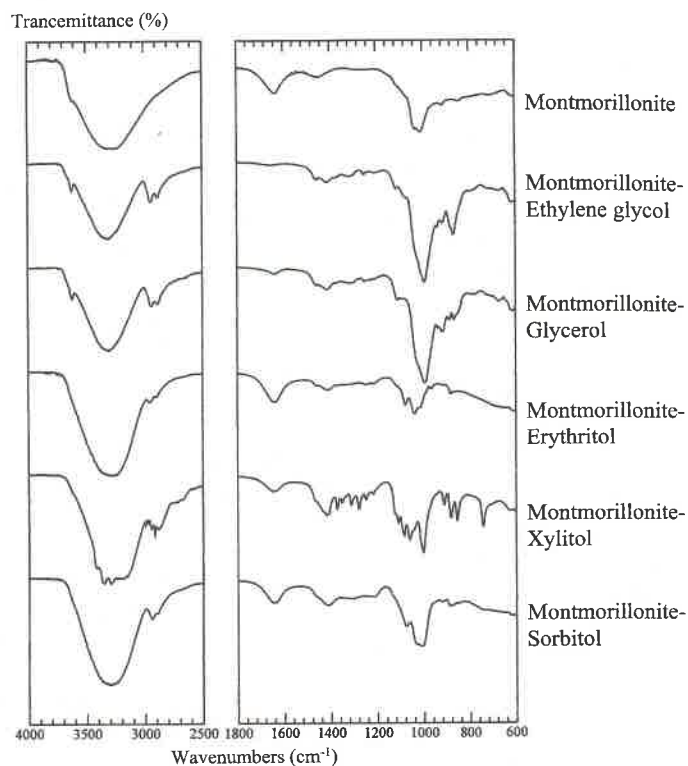
FIG. 6. IR spectra of the montmorillonite and montmorillonite-sugar alcohol complex pastes.

cps

Montmorillonite-Sorbitol

Montmorillonite-Xylitol

Montmorillonite-Erythritol
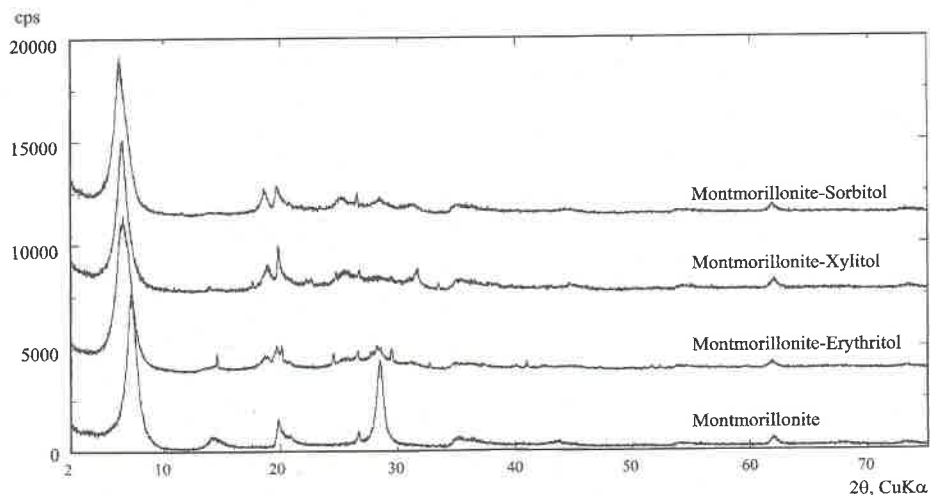
Montmorillonite

2θ, CuKα

FIG. 7. X-ray diffraction patterns of powdered montmorillonite-sugar alcohol complexes synthesized in the dry process.

montmorillonite and sugar alcohols in the dry process as well (Fig. 7). The samples were not preferred-oriented, and therefore the peak intensity of basal reflections is low except for d001. Peaks of a small amount of remaining sugar alcohols are observed. The d001 of the montmorillonite-erythritol, -xylitol and -sorbitol complexes shifts to 1.360, 1.373 and 1.436 nm, respectively. The peak positions in each montmorillonite-

sugar alcohol complex were compared with the molar mass of the sugar alcohol. The comparison shows that the interlayer spacing increases with increasing CH_2O, as in the measurement of the complex pastes in the wet process (Fig. 8).

A comparison of the infrared spectra of the three complexes produced by the dry process, and the montmorillonite as the starting material, shows no significant difference in the low-
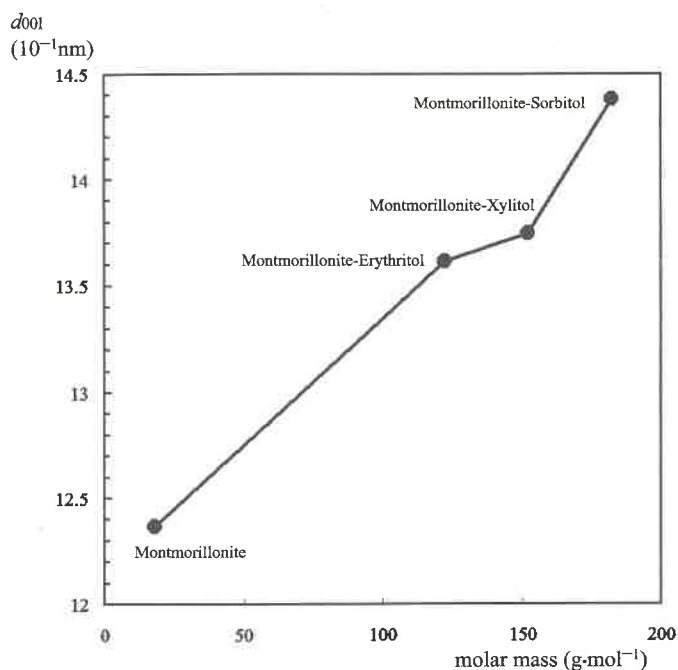
FIG. 8. Change in the basal spacing, *d*001, of the powdered montmorillonite-sugar alcohol complexes synthesized in the dry process.
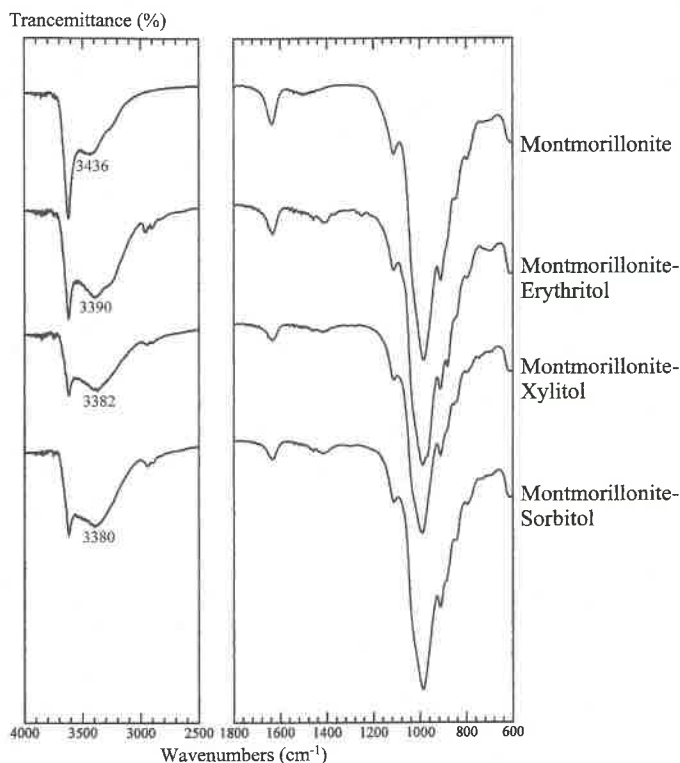

FIG. 9. IR spectra of the powdered montmorillonite-sugar alcohol complexes synthesized in the dry process (the numbers in the figure are O-H stretching frequencies, ν).

wavenumber region and the presence of the spectrum of C-H in the high-wavenumber region in the complexes (Fig. 9). It is notable that the percent transmittance of the spectrum of 3620 cm^{-1} of OH decreases when the interlayer contained water molecules in the complexes than in the montmorillonite.

A calculation was performed using the relationship between O-H stretching frequency (cm^{-1}) and d (O$\cdots$O) Å proposed by Libowitzky (1999):

$$\nu = 3592 - 304 \cdot 10^9 \cdot \exp(-d/0.1321),$$

where ν is the O-H stretching frequency and d is (O$\cdots$O) Å. The calculation shows that (O$\cdots$O) Å is 2.83 Å for the montmorillonite as the starting material, and 2.79, 2.79 and 2.78 Å for the montmorillonite-erythritol, -xylitol, and -sorbitol complexes, respectively; and the O$\cdots$O distance decreases with increasing CH$_2$O content in the sugar alcohol.

In the X-ray photoelectron spectroscopy, the spectrum of solid sugar alcohols has an asymmetrical C*1*s peak, and a tail slightly on the low-energy side. Therefore, this part was determined to be C-C, and deconvolution was accomplished using curve-fitting software attached to the XPS operating system. The peak on the low-energy side observed in the calculation was set to 284.5 eV as the reference value (Fig. 10). In the montmorillonite-sugar alcohol complexes, the peaks are clearly separated at C*1*s. The presence of peaks on the high-energy side indicates a change to a new combined state of C and O resulting from the formation of a complex. It also shows the chemical shift of O*1*s from the binding energy of the original sugar alcohol to the lower energy side. The full width at half maximum increased when the sugar alcohol formed a complex in the montmorillonite crystal. There is no significant difference in the binding energy for Si*2p* and Al*2p*

of the montmorillonite and the complex. No chemical shift indicates the intercalation of sugar alcohol molecules into the interlayer by the dry process.

The difference in the interlayer spacing due to intercalation was obtained for the wet and dry processes by X-ray diffraction analysis. The spacing is 0.402, 0.396 and 0.446 nm for the montmorillonite-erythritol, -xylitol and -sorbitol complexes, respectively, and is larger for the wet process than for the dry process. The size of a water molecule is 0.38 nm at the longest. The interlayer with the sugar alcohols intercalated by the wet process may contain at least one water molecule per unit in the c-axis direction.

CONCLUSION

The glycerol and ethylene glycol molecules intercalate into the interlayer of the montmorillonite. When the montmorillonite is mixed with erythritol, xylitol or sorbitol, which are sugar alcohols that have more carbon chains than glycerol and ethylene glycol, sugar alcohol molecules intercalate into the interlayer in both wet and dry processes. In the process of the formation of montmorillonite-sugar alcohol complexes, the montmorillonite swelled in the wet process, due to the involvement of water molecules in the intercalation of sugar alcohols into the interlayer of the montmorillonite, while it expanded in the dry process.
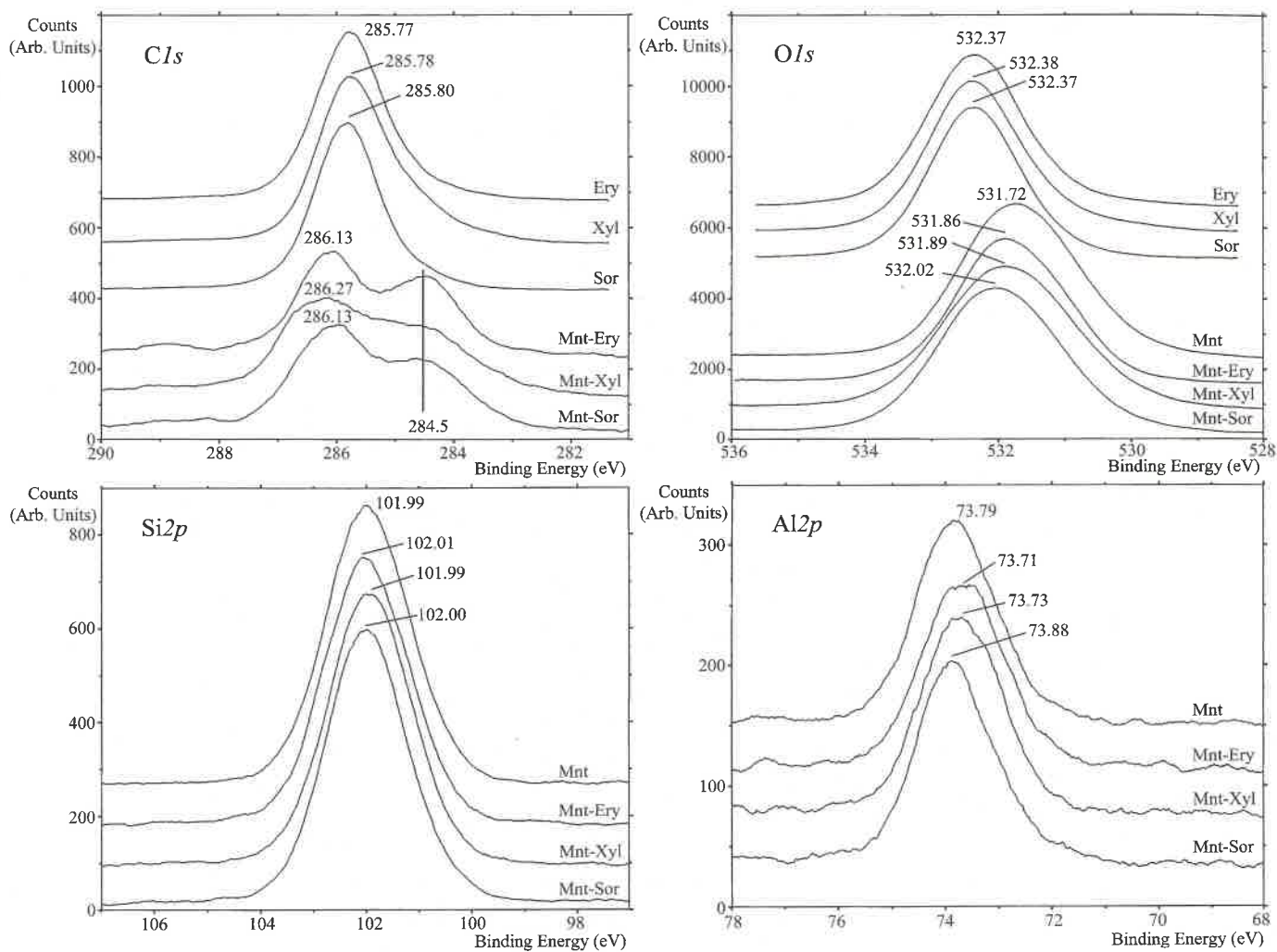
FIG. 10.   XPS narrow spectra of montmorillonite-powdered sugar alcohol complexes synthesized in the dry process.

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