interpret the mechanism of forming $PbTiO_3$ by hydrolysis of alkoxide, the hydrolysate which had been calcinated for 3 h at 400 °C was treated with 1:1 acetic acid; after filtration dilute H_2SO_4 was added into the filtrate, and a large amount of white precipitate was observed. The precipitate was confirmed to be $PbSO_4$ by XRD analysis, indicating that the sample contains free PbO in large amount. Meanwhile, the sample calcinated at 600 °C exhibited only slight turbidity at the same condition, probably due to a small amount of excess PbO, and the sample calcinated at 800 °C showed no precipitate at all. These results indicate that although a complex alkoxide of lead and titanium was formed in the reaction,[7,8] it may be converted to hydrolysates of Pb and Ti alkoxides individually during hydrolysis and then to a mixture of their respective hydrous oxides with a high degree of homogeneous mixing. The formation of hydrous oxides seems to be an inevitable intermediate step in the conversion process from hydrolysate of alkoxide to perovskite phase of $PbTiO_3$ by calcination.

Molecular Recognition in Microporous Organo-Minerals. Shape-Specific Interactions of Carbon Dioxide in Functionalized Organo-Montmorillonite Microcavities

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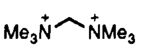
The study of the microporosity of organo-smectites was pioneered in the 1950s by Barrer.[1] In a series of papers,[1] which he recently reviewed,[2] Barrer, with his co-workers, showed that when the natural interlamellar inorganic cations of montmorillonite and hectorite are replaced by small alkylammonium organic cations, permanent microporosity is created, and sorption of gases and of organic molecules is very favored.

Polymeric,[3] ceramic,[4] or composite[5] membranes have been developed for gas-separation purposes, including the separation of gaseous mixtures of CO_2 and CH_4. Ion-exchange modified zeolites were used for chromatographic gas separation.[6]

The incorporation of organic cations into smectites can result in a microporous material with a network of cavities whose height and volume are controlled by the size and the shape of the organic cation. Moreover, functionalities, such as ester groups, can be attached to the organic cation, so that one can easily synthesize a material with tortuous channels whose walls combine hexagonal arrays of silicate oxygens and organic functions. Given the almost infinite availability of potential organic intercalates, a large flexibility is offered in the design of these materials, which could be tailored for specific recognition and separation purposes.

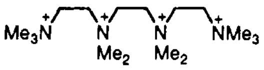
The gas chromatographic properties of such organo-smectites are reported in this paper, with a focus on their ability in separating carbon dioxide–methane mixtures. The shape of the microcavities is the most important parameter controlling the gas interactions with the microcavities walls.

The clay material was a source clay, SWy-1, obtained from the Clay Source Repository, University of Missouri. The <0.2-μm fraction was obtained according to standard gravitation procedures.[7] It was checked by particle size analysis (Sedigraph 5100) that more than 90% of the sample was <0.2 μm esd. The homoionic Na^+ montmorillonite (Na-M) was prepared, purified by dialysis, and freeze-dried. Ten different quaternarized and esterified amino acid derivatives were prepared[8] and incorporated into the interlamellar spaces of Na-M, at full cationic exchange capacity (cec; 87 ± 5 mequiv/100 g of Na-M). The percentage of incorporation was controlled by determination both of the quantity of sodium released (sodium selective electrode) and of the quantity of organic cation absorbed (colorimetric methods). In all the cases, the amine function of the amino acid was trimethylated. Both amine functions were trimethylated in the cases of Orn and Lys.[9] Tetramethylammonium and some quaternarized polyammonium cations (**1**–**3**)[10] were also incorporated at full loading of the clay (100% of the cec). The organo-clay was dried under vacuum at 60 °C overnight. Particles of size 60–120 mesh were selected as packing material for chromatographic columns (3 ft × 1/8 in. o.d.). Prior to use, the packed column was conditioned under He flow at 90 °C for 8 h. It was checked that the results could be reproduced with columns aged more than 2 months and reconditioned prior to use:



1 (MMDA)

2 (MEDA)



3 (MTETA)

The interlamellar distances (i.d. = d_{001} – 9.6 Å)[11] of the organo-clays were systematically measured and found to be in the range 4.0–5.0 Å, showing that the trimethylammonium group (height measured on space-filling models, 5.0 Å) determines the interlamellar distance, with the side chains of the organic derivatives lying parallel to the clay surfaces.

Figure 1 shows typical chromatograms. While no separation was observed for Na-M (i.d. = 2.8 Å), CO_2/CH_4 separation factors of 12 and 20 were obtained for ORN-Me-M and MTETA-M, respectively. The retention times and the separation factors (ratios of retention times of CO_2 and CH_4 relative to air)[12] were highly dependent upon the

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(1) (a) Barrer, R. M.; MacLeod, D. M. *Trans. Faraday Soc.* **1955**, *51*, 1290–1300. (b) Barrer, R. M.; Reay, J. S. S. *Trans. Faraday Soc.* **1957**, *53*, 1253–1261. (c) Barrer, R. M.; Hampton, G. *Trans. Faraday Soc.* **1957**, *53*, 1462–1475.

(2) (a) Barrer, R. M. *Pure Appl. Chem.* **1989**, *61*, 1903–1912. (b) Barrer, R. M. *Clays Clay Mineral.* **1989**, *37*, 385–395.

(3) Koros, W. J.; Paul, D. R. In *Synthetic Membranes*; Chenoweth, M. B., Ed.; MMI Press Symposium Series; Hardwood Academic: New York, 1986; Vol 5, pp 155–189.

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(8) Latieule, S. Thèse de Maîtrise, Université d'Ottawa, 1991.

(9) Abbreviations are used for the quaternized and esterified amino acids: for example, ALA-Me is the trimethylated quaternary ammonium derivative of the alanine methyl ester, 1-(methoxycarbonyl)ethyl trimethylammonium. The same type of notation applies to the other amino-acid derivatives.

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(11) van Olphen, H. *An Introduction to Clay Colloid Chemistry*, 2nd ed.; Wiley Interscience: New York, 1977.

(12) Miller, J. M. *Chromatography: Concepts and Contrasts*; Wiley: New York, 1988; p 21.

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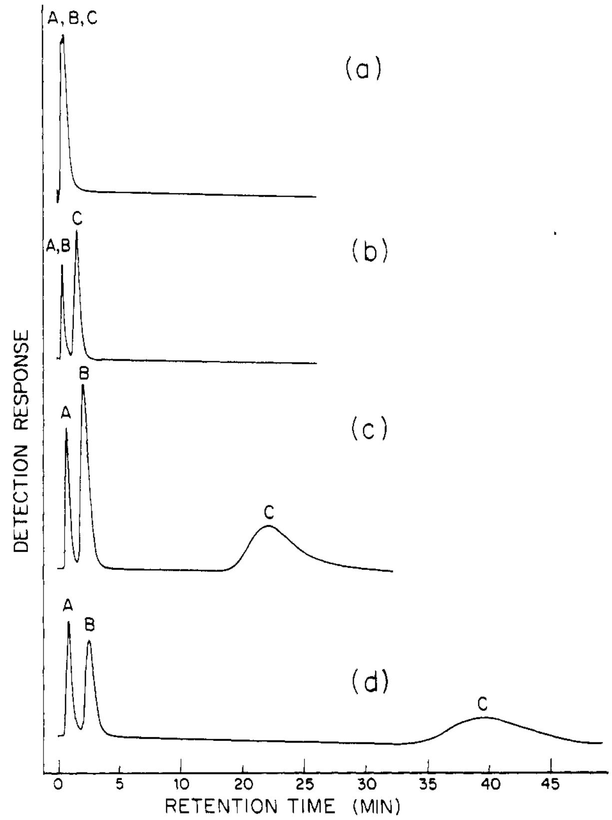

Figure 1. Chromatograms of methane/carbon dioxide mixtures using montmorillonite-based packing material (60–120 mesh). Instrument: Gow-Mac 550P, with thermal conductivity detector. Column: 3 ft × $^1/_8$ in. o.d. Carrier gas: He at 25 mL/min. Column temperature: 30 °C. (a) Na montmorillonite; (b) GLYEt montmorillonite; (c) ORNMe montmorillonite; (d) MTETA montmorillonite. Peak identification: A = air; B = methane; C = carbon dioxide.

nature of the organic intercalate: for example, no measurable separation could be observed in the case of ALA-Pent-M, the pentyl ester of the alanine derivative, while a separation similar to the case b of Figure 1 was observed for ALA-Me-M, the methyl derivative. This is highly suggestive of a separation mechanism based on the amount of microporosity in the organo-clay material. The CO_2 retention times were correlated with a parameter dependent upon the shape of the organic cation and, consequently, upon the shape of the organo-clay microcavities. From the knowledge of the total surface area of SWy-1 (740 m^2/g)[13] and of its cationic exchange capacity (0.87 mequiv/g), the density of charge on the surface (0.71 e/nm^2, corresponding to 1 charge/140 $Å^2$)[13] could be determined. The subtraction from 140 $Å^2$ of twice the value of the cross-sectional area of the organic cation (obtained by projection of space-filling models) afforded the free surface area per charge of the organo-clay.[14] Figure 2 shows the relationship between the retention times of CH_4 and CO_2 on the column and the aluminosilicate surface area not covered by organic cations, in potential direct contact with gas molecules (free surface area). Contrary to the case of methane, a strong dependence of the CO_2 retention times upon the value of the free surface area can be observed. This suggests that the cylindrical CO_2 molecule (dimensions 3.3 Å by 5.3 Å), constrained in a space of reduced dimensionality (galleries height 4–5 Å), is strongly interacting with the aluminosilicate surface, in strong contrast with the spherical, nonpolar, CH_4 molecule (diameter 3.8 Å). An alternate interpretation for the long retention times of carbon dioxide could be a chemical interaction with residual water molecules on the clay surface. This interpretation can be ruled out since very short retention times of CO_2 were observed when the samples were not, or imperfectly, dried, plausibly because of the decrease of microporosity. However, at this stage, we cannot distinguish between physisorbed or chemisorbed CO_2. Carbonate could be transiently formed by binding of the carbon atom to the framework oxygens or hydroxyl groups, as was shown, for example, for ion-exchanged zeolites[15] or for mica surfaces.[16]

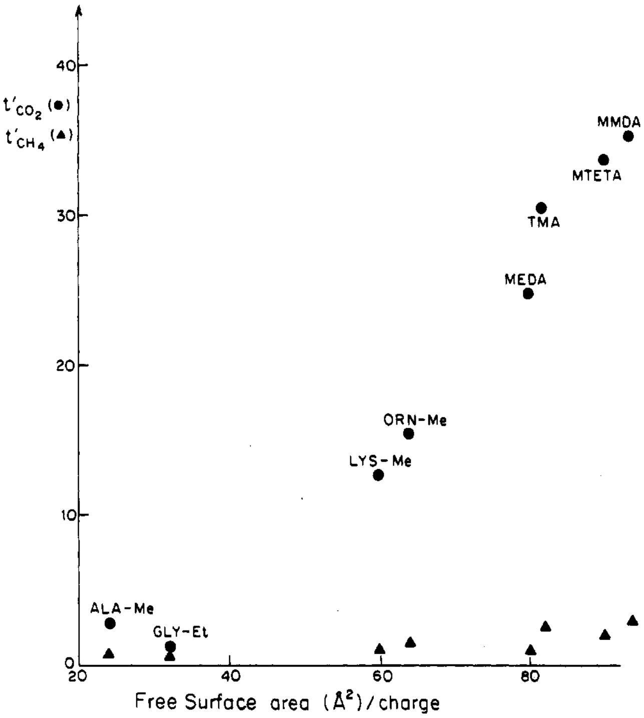

Figure 2. Relative retention time of methane (▲) and of carbon dioxide (●) on a series of organo-montmorillonites, as a function of the free surface area per charge of the organo-montmorillonite. TMA = tetramethylammonium; ORN-Me, LYS-Me, ALA-Me, and GLY-Et are the methyl or ethyl esters of methyl-quaternarized ornithine, lysine, alanine, and glycine, respectively.

The separation methane/carbon dioxide is principally controlled by interactions with the clay surface and not by interactions with the polar substituents of the alkylammonium chain. The shape of the microcavities plays a major role in reducing the dimensionality of the chromatographic pathways: an optimum separation is observed when the height of the galleries is slightly larger than the kinetic diameters of the gases. As further evidence supporting this conclusion, one should consider the results obtained for tetraphenylphosphonium montmorillonite (TPP-M). The interlamellar distance was 9.2 Å, a value in good agreement with an orientation of TPP^+ such that its C_3 axis be perpendicular to the clay layers. Even if the calculated free surface area (75 $Å^2$) was comparable to the one obtained for **2**-M, which gave one of the largest CO_2 retention times of this study, TPP-M did not permit the separation of CH_4/CO_2 mixtures, presumably because the height of the galleries network was much larger than the

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[13] Villemure, G. *Clays Clay Mineral.* **1990**, *38*, 622–630.

[14] This statement is valid only for the case of organic monocations. More generally, the free surface area per charge of this organo-clay (FSA, in $Å^2$) is given by FSA = $(n \times 140 - 2 \times \mathrm{CSA})/n$, where CSA is the cross-sectional area of the organic cation and n is its charge.

[15] Förster, H.; Schumann, M. *J. Chem. Soc., Faraday Trans. 1*, **1989**, *85*, 1149–1158.

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kinetic diameter of the two gases. A similar result was obtained with an alumina-pillared montmorillonite[17] characterized by an interlamellar distance of 7.4 Å.

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Soft Chemical Synthesis of New Compounds with the Hexagonal Molybdenum Oxide Structure

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Introduction

Many transition-metal oxides are of great interest for catalytic and electrochemical applications, and metastable structures often demonstrate new or enhanced properties compared to their thermodynamically stable forms. These materials can often be prepared at low temperatures by electrochemical intercalation, inorganic ion exchange, or organic precursor methods. In this paper we report the synthesis in aqueous acid of $A'_{0.13}V_{0.13}Mo_{0.87}O_3{\cdot}nH_2O$ (A′ = H, Na) from the compounds $AVMoO_6$ (A = Li, Na) which have the layered brannerite structure (Figure 1a). The framework of the new structure is isotypic with the hypothetical hexagonal "tunnel" structure of MoO_3[2,4] shown in Figure 1b. Although previous syntheses have been used to stabilize this structure by incorporating large cations or hydrated Na^+ into the tunnels,[3,4] there have been no reports of the successful preparation of the structure containing empty tunnels. In the current work, we have found that the alkali-metal brannerites undergo a novel "leaching" reaction, which for A = Li leads to the formation of $H_{0.13}V_{0.13}Mo_{0.87}O_3{\cdot}nH_2O$. Subsequent dehydration of this compound permits the preparation of a "microporous" form of hexagonal MoO_3, $V_{0.13}Mo_{0.87}O_{2.935}$, in which the one-dimensional tunnels are empty.

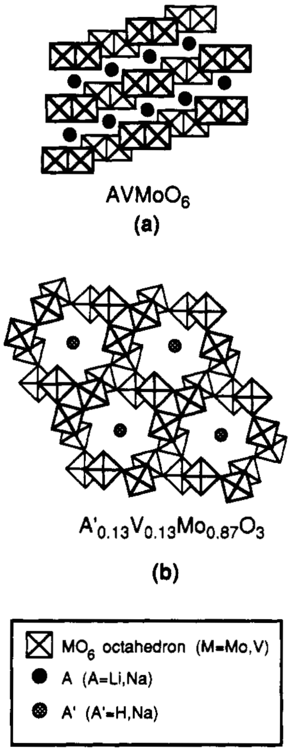

Figure 1. Structures of (a) brannerite and (b) hexagonal molybdenum oxide.

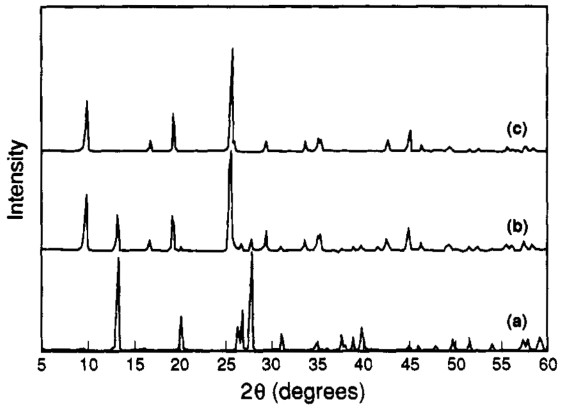

Figure 2. Powder X-ray diffraction patterns of $NaVMoO_6$ (a) before, (b) after one treatment, and (c) after two treatments in 0.25 M HCl.

Experimental Section

The new materials have been prepared by a novel soft chemical route involving the acid treatment and dehydration of alkali-metal brannerites. Lithium and sodium brannerites were prepared by solid-state reaction of AVO_3 (A = Li, Na) and MoO_3 as reported by Galy et al.[5] The Na brannerite was stirred in 0.25 M HCl for 12 h at 60°C, and the solid was recovered by vacuum filtration. The process was repeated to ensure complete conversion of the brannerite to the tunnel structure. $LiVMoO_6$ was immersed in 0.25 M HCl for 36 h with stirring at 60 °C. The solution was then

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(1) Current address: Du Pont Experimental Station, Wilmington, DE 19880-0262.

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