Materials Research, Vol. 5, No. 4, 475-479, 2002. © 2002

N_2 and CO_2 Adsorption by TMA- and HDP-Montmorillonites

C. Volzone, J. O. Rinaldi, J. Ortiga*

Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC)-CONICET
C.C. 49, Cno. Centenario y 506, (1897) M. B. Gonnet, Prov. Buenos Aires, Argentina

Received: February 1, 2002; Revised: July 2, 2002

N_2 and CO_2 gases adsorption by tetramethylammonium(TMA)-montmorillonites and hexadecylpyridinium(HDP)-montmorillonites was carried out using volumetric equipment at 25 °C and 0.1 MPa. The addition of organic compounds to montmorillonites was 1 and 4 times the cation exchange capacity (CEC) of the montmorillonites and the contact times between the TMA (or HDP) and the montmorillonites were 4 and 24 h. The adsorptions of CO_2 by TMA-montmorillonites (0.383-0.477 mmol/g) were higher than those by HDP-montmorillonites (0.027-0.060 mmol/g). N_2 gas retentions by organo-montmorillonites were small: in the range of 0.038-0.065 mmol/g TMA-montmorillonites and around 0.010 mmol/g HDP-montmorillonites. The interlamellar spacing of the organo-montmorillonites, the structure of the intercalated organic molecule, and the type of montmorillonites influenced the gas adsorption values.

Keywords: *gas adsorption, CO_2, N_2, TMA, HDP, organo-montmorillonite*

1. Introduction

Gas adsorption by carbon and zeolites has been reported for gas separation in different papers. The montmorillonite clays are recognized as good adsorbents due to their ability to exchange interlayer cations for charged organic or metal cations in solution. The montmorillonite can be converted into organo-montmorillonite and it could be effective for adsorption organic compounds[1-9]. Yang and Baksh[10] and Yang and Cheng[11] started studies of gas adsorption by pillared clays. Recently, the studies about gas retention by inorganic modified clays (pillared clays, modified aluminum pillared clays, acid clays, amorphyzed kaolinitic) have indicated that these materials have potential for gas separation[12-18]; nevertheless, up to now there is only scarce information about retention of gases by organo-clays. The montmorillonites are clay minerals 2:1 layer phyllosilicates: two Si tetrahedral sheets are separated by one Al octahedral sheet (T-O-T). The isomorphic substitutions in the sheets, mainly in octahedral ones for montmorillonites, originate deficits of positive electric charges. These charges are balanced by exchangeable cations in interlayer positions (Fig. 1). The organo-montmorillonites can be obtained by intercalating organic species within the interlayer sites of the montmorillonites. Cheto- and Wyoming-montmorillonites are the main types of montmorillonite; the Cheto-type has higher Mg content than the Wyoming-type in octahedral sheet.

The aim of this paper is to analyze the adsorption of N_2 and CO_2 gases at 25 °C and 0.1 MPa by TMA- and HDP-montmorillonite clays. The organo-montmorillonites were obtained by tetramethylammonium (TMA) or hexadecylpyridinium (HDP) cation intercalation into two different type-montmorillonites. One n-alkylammonium and one n-alkylpyridinium were chosen as organic cations, as example of different molecule structure, because different results can be obtained on gas retention by organo-smectites.

2. Materials and Methods

The montmorillonites used in this study were SAz-1, Ca montmorillonite (Cheto type), Apache County, Arizona, U.S.A. and Swa-1, Na montmorillonite (Wyoming type), Wyoming, U.S.A. The samples were named M1 and M2, respectively.

Tetramethylammonium (TMA) and hexadecylpyridinium (HDP) cations were used to prepare organo-montmorillonites as it has been informed in a previous paper[9]. Aqueous solution of TMA chloride or HDP chloride salts were added to montmorillonite suspensions and allowed to stand for 4 and 24 hours. The solids were washed to re-

---

*e-mail: volzcris@netverk.com.ar

move the excess of salts and stored at room temperature. The amounts of organic cations added to the montmorillonites were 1 and 4 times the Cation Exchange Capacity (CEC) of the montmorillonites. The organo-montmorillonites were named M1 or M2, followed in brackets by two numbers: the first was the amount of organic cation in CEC time added, 1 or 4; and the second ones was the contact time, 1 or 24 hours. The CEC of the M1 and the M2 montmorillonites were 110 and 97 meq/100 g, respectively; the half-unit cell compositions calculated in a previous paper[19] are shown in Table 1. The higher CEC of M1 is due to higher isomorphous substitution in the structure in which the Al^{3+} was replaced by Mg^{2+} in the octahedral sheet.

X-ray diffraction (XRD) patterns were obtained by scanning at 1 °(2θ)/min between 3-70 °(2θ) using a Philips 3020 Goniometer with PW 3710 Controller using Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 20 mA and Ni filter.

Equilibrium adsorption was measured using standard volumetric apparatus. Samples were degassed at 100 °C for 12 hours prior to measurement. N_2 and CO_2 were the gases tested for their adsorption behavior. Adsorption was measured at 25 °C and 0.1 MPa.

3. Results and Discussion

The distance between the top of the Si tetrahedral silica sheet (T) and the top of the Si tetrahedral sheet in the next layer (Fig. 1) is the d(001) spacing or basal spacing of the montmorillonite. The initial d(001) spacings of M1 and M2 montmorillonites were 13.00 Å and 14.90 Å, Ca^{2+} and Na^{+} being the principal cations in interlayer position, respectively, Table 1, Fig. 2a and 2b shows the XRD of the M1 and M2 montmorillonites before and after TMA treatments. The intercalation of TMA cations in montmorillonites changed the d(001) spacings to the range of 13.71 to 14.87 Å. According to Lagaly *et al.*[20] the alkylammonium cation, such as TMA, is arranged in monolayer form. Lee *et al.*[21] found the d(001) spacing value of 13.80 Å in montmorillonite treated with similar amount of added TMA (3-5 times CEC). In general, an increase of the basal spacing was observed in montmorillonites treated with higher additions of such organic substance. The final XRD of the TMA-montmorillonites was modified after different additions of TMA (1-4 times of CEC) and contact time (4-24 h), where the TMA-M1 and TMA-M2 patterns showed peaks corresponding to TMA species (Figs. 2a and 2b).

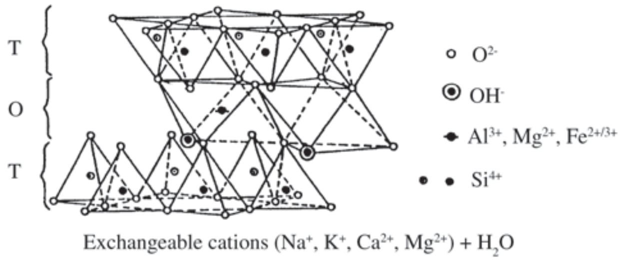

Figure 1. Montmorillonite structure. T: tetrahedral sheet; O: octahedral sheet.

The intercalation of montmorillonites with HDP cations resulted in an increase in basal spacing from 13.00-14.90 Å of the original montmorillonites, M1 and M2, respectively, to the range of 18.15-26.75 Å, as it was showed in Figs. 3a and 3b. HDP produces larger basal spacing due to its arrangement in the interlayer[22]. Lagaly *et al.*[20] mentioned that n-alkylpyridinium cations (as HDP) occur as a bilayer. High contact time and several additions of HDP originated an important modification in XRD patterns (Figs. 3a and 3b), where new peaks as HDP species appeared.

The higher d(001) spacing of organo-M1 samples than that of organo-M2 samples could be attributed to the more retention organic substance in interlayer position due to the greater CEC of the M1 in relation to that of the M2 original montmorillonites, Table 1.

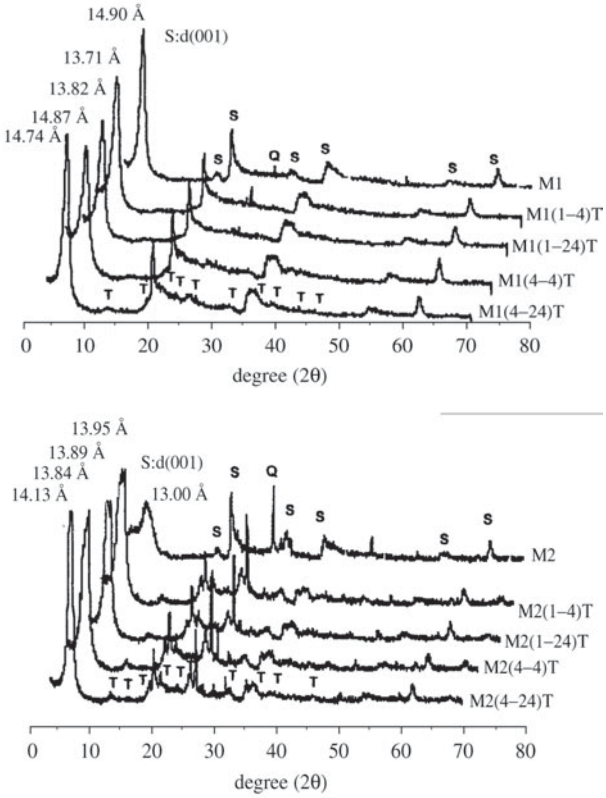

Figure 2. X-ray diffraction: a) TMA-M1 serie; b) TMA-M2 serie. T: tetramethylammonium specie; S: smectite; Q: quartz.

Table 1. Half unit-cell composition and cation exchange capacity (CEC) of montmorillonites[19] .

	Tetrahedral sheet		Octahedral sheet			Interlayer cations				CEC meq/100g
Sample	Si_{IV}^{4+}	Al_{IV}^{3+}	Al_{VI}^{3+}	Fe^{3+}	Mg^{2+}	K^+	Na^+	Ca^{2+}	Mg^{2+}	
M1	3.94	0.06	1.36	0.06	0.60	-	0.02	0.24	0.05	110
M2	3.91	0.09	1.61	0.13	0.26	0.01	0.23	0.06	-	97

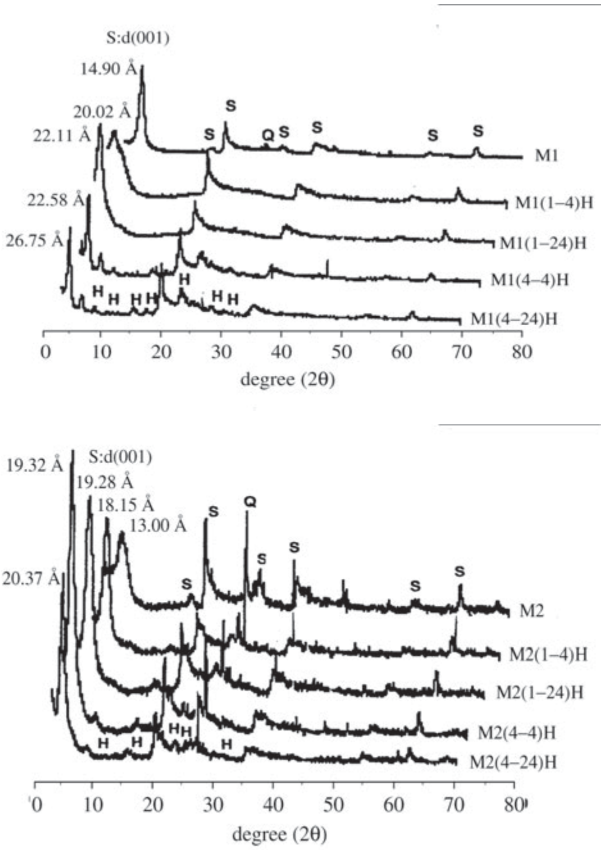

Figure 3. X-ray diffraction: a) HDP-M1 serie; b) HDP-M2 serie. H: hexadecilpyridinium specie; S: smectite; Q: quartz.

Table 2 shows the adsorption of gases by original montmorillonites and after TMA or HDP cation intercalations. The N_2 retentions by organo-montmorillonites were lower than the CO_2 ones. The reason could be attributed to the fact that compared to N_2, the CO_2 possesses a larger quadruple moment (-1.5×10^{-26} and -4.3×10^{-26} $Erg^{1/2}.cm^{5/2}$, respectively). Previous studies conduced that the amount of gas retention varies either as function of physicochemical properties of the adsorbates, as it was observed by Yang and Baksh[10] or as function of physicochemical characteristics of the adsorbents (clays, modified clays, zeolites)[10-18]. Different types of binding interaction may occur between the gas molecule and the interlayer of the organo-montmorillonite, depending on the structural composition of montmorillonite. The montmorillonites treated with TMA retained larger amounts of gases than the original montmorillonite; however, after treatment with HDP the adsorption values were smaller. This could be due to the smaller size of TMA that do not form a continuous organic phase on the clay surface and in the interlayer, leaving a free siloxane mineral surface[23].

The retention values of CO_2 by TMA-M2 samples (0.423-0.477 mmol/g) were higher than those by TMA-M1 samples (0.383-0.445 mmol/g). The N_2 gas retentions by TMA-M2 samples (0.055-0.065 mmol/g) were also higher than those by TMA-M1 samples (0.038-0.055 mmol/g). This behavior could be explained by the fact that the montmorillonite with higher CEC (M1), Table 3, retained more TMA in interlayer position, leaving less free space available for gas adsorption. Lee *et al.*[21] mentioned that the closer packing of TMA ions in the high-charge smectite (similar to our M1) resulted apparently in a decrease in the free surface area of the clay mineral.

The original montmorillonite with similar d(001) spacing than that of the TMA montmorillonite showed smaller gas adsorption (Table 2). The original montmorillonites, M1 and M2, have mainly Ca^{2+} and Na^+ ions in interlayer position, respectively, (Table 1) and these strongly hydrated cations may inhibit the sorption of gases.

Compared with the original montmorillonites an important reduction in retention gas was observed in montmorillonites intercalated with HDP, where 0.009-0.015 mmol of N_2 per gram of sample and 0.027-0.060 mmol of CO_2 per gram of HDP-montmorillonites were measured (Table 2).

The Fig. 4 shows the influence of the interlayer spacing values of organo-montmorillonites *vs.* adsorption gases. Higher retention occurred when the d(001) spacing of organo-montmorillonite was smaller than around 14.5 Å. The higher gas retention by TMA-M2 in comparison with TMA-M1 also could be attributed to different d(001) spacings originated by TMA. Higher d(001) spacings values originated low retention (Fig. 4). The HDP-M1 and HDP-M2 samples showed different high d(001) spacings, which showed low gas retention values, Fig. 4. Probably,

Table 2. Gas adsorption of samples at 25 °C and 0.1 MPa.

Sample	N_2, mmol/g			CO_2, mmol/g		
	Original	TMA	HDP	Original	TMA	HDP
M1	0.017			0.210		
M1(1-4)		0.055	0.010		0.439	0.038
M1(1-24)		0.044	0.015		0.445	0.049
M1(4-4)		0.038	0.009		0.383	0.038
M1(4-24)		0.049	0.009		0.423	0.060
M2	0.011			0.125		
M2(1-4)		0.065	0.010		0.445	0.033
M2(1-24)		0.060	0.010		0.423	0.027
M2(4-4)		0.060	0.010		0.461	0.043
M2(4-24)		0.055	0.010		0.477	0.054

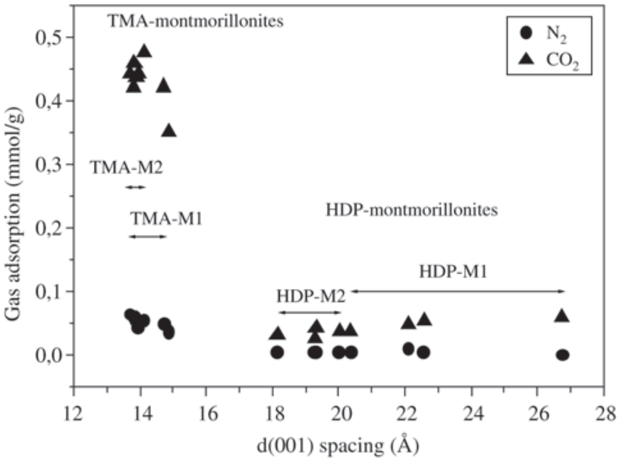

Figure 4. Gas adsorption *vs.* d(001) spacing of the organo-montmorillonites.

the large HDP molecule in interlayer position originated less free space available for sorption capacity.

The CO_2 gas retentions by the TMA-montmorillonites (0.383-0.477 mmol/g) were higher than those by Al-, Zr-, Cr- and Ti-pillared clays (0.210, 0.185, 0.100 and 0.141-mmol/g); the modified Al-PILCs (0.300 mmol/g)[14]; the amorphous kaolinite derivatives (0.226-0.294 mmol/g)[15-16] and the acidified smectites (0.357 mmol/g)[17]; however, they were smaller than those by acid modified kaolinite (0.602 mmol/g)[18] under the same experimental adsorption conditions as it was reported in previous papers. However, it is important to take into account that the modified clays were prepared under different experimental conditions.

The relative high gas retention by TMA-montmorillonites may be explained by the combined effect of the interaction between gas and TMA and the adsorption on the montmorillonite surface.

4. Conclusions

The N_2 and CO_2 gas adsorptions by two Cheto and Wyoming types montmorillonites increased after treatment with tetramethylammonium (TMA). Nevertheless, an important reduction in adsorption values after intercalation of hexadecylpyridinium (HDP) cation was observed.

The retention of N_2 gas by TMA-montmorillonites was small (0.038-0.065 mmol/g) whereas the values corresponding to CO_2 retention were high (0.383-0.477 mmol/g).

The interlayer spacing of the organo-montmorillonite, the structure of organic substance intercalated into the montmorillonite and the type of montmorillonite strongly influenced the N_2 and CO_2 gas retention values.

Acknowledgement

The authors wish to thank Dr. Francisco Rodríguez Reinoso of Departamento de Química Inorgánica, Universidad de Alicante, Spain and Dr. Carlos Costa of Laboratorio de Engenharia de Processos Ambiente e Energia de la Universidade de Porto, Portugal, for the design of the gas adsorption equipment.

References

1. Lagaly, G. Characterization of clays by organic compounds, *Clay Miner*., v. 16, p. 1-21, 1981.
2. Lagaly, G. Clay-organic interactions, *Phil. Trans. R. Soc. Lond*. A 311, p. 315-332, 1984.
3. Mortland, M.M.; Shaobai, S.; Boyd, S.A. Clay-organic complexes as adsorbents for phenol and chlorophenols, *Clays and Clay Minerals*, v. 34, p. 581-586, 1986.
4. Valenzuela-Díaz, F.R.; Abreu, L.D.V. de; Souza-Santos, P. Preparação e propriedades reológicas de argilas esmectíticas organofílicas, *Anais do 37º Congresso Brasileiro de Cerâmica*, Curitiba, PR, v. 2, p. 988-995, 1993.
5. Valenzuela-Díaz, F.R.; Abreu, L.D.V. de; Souza-Santos, P. Obtenção de argilas esmectíticas organofílicas partindo-se de argilas de Vitória da Conquista, BA, *Anais do 38° Congresso Brasileiro de Cerâmica*, Blumenau, SC, v. 1, p. 354-359, 1994.
6. Valenzuela-Díaz, F.R.; Amaral, M.S.O. de; Souza-Santos, P. Obtenção de argilas esmectíticas organofílicas a partir de suspensões de bentonita sódica comercial, *Anais do 39° Congresso Brasileiro de Cerâmica*, Águas de Lindoia, SP, v. 1, p. 231-236, 1995.
7. Volzone, C.; Rinaldi, J.O.; Ortiga, O. Adsorption of N_2 and CO_2 gas by tetramethylammonium-montmorillonites,

Anais do 43º Congresso Brasileiro de Cerâmica e 4º Congresso de Cerâmica do Mercossul, Florianópolis, Santa Catarina, p. 32401, June/1999.

8. Volzone, C.; Rinaldi, J.O.; Ortiga, J. Utilización de organobentonitas para la retención de tolueno en agua, *Actas VI Jornadas Argentinas de Tratamiento de Minerales*, Salta, 18-20 de October. p. 255-259, 2000.
9. Volzone, C.; Rinaldi, J.O.; Ortiga, J. Swelling of TMA (tetramethylammonium)- and HDP (hexadecylpyridinium)-Montmorillonites in Water and Toluene Media: Influence of the Type Montmorillonites, *Materials Research*, v. 3, n. 4, p. 115-118, 2000.
10. Yang, R.T.; Baksh, M.S.A. Pillared clays as a new class of sorbentc for gas separation, *AIChE Journal*, v. 37, p. 679-686, 1991.
11. Yang, R.T.; Cheng, L.S. *in Äccess in Nanoporous Materials*, Ed. T.J.Pinnavaia and M.F.Thorpe, Plenum Press, N.Y., p. 73-92 , 1995.
12. Volzone, C.; Ortiga, J. Adsorciones de gases en bentonitas modificadas, *9º Congreso Argentino de Cerámica, Vidrios y Refractarios y 3º Del Mercosur*, Olavarría, Prov. Buenos Aires, Argentina. p. 19-23, 1998.
13. Volzone, C.; Ortiga, J. O_2, CH_4 and CO_2 gas adsorption by acid di- and tri-octahedral smectites, *Proceedings of International Workshop of Activated Clays*, 6-8 de diciembre, La Plata, Argentina, p. 45-54, 1998
14. Volzone, C.; Garrido, L.B.; Ortiga, J.; Pereira, E. in "Desarrollo de adsorbentes para la separación de gases", Programa Iberoamericano de Ciencia y Tecnología (CYTED) Subprograma V. Catálisis y Adsorbentes. Proyecto V.3., edited by F.Rodríguez-Reinoso and P. Andreu. (CYTED-España, 1998) p. 97-113, 1998.
15. Volzone, C.; Thompson, J.G.; Melnitchenko, A.; Ortiga, J.; Palothorpe, R.S. Selective gas adsorption by amorphous clay mineral derivatives". *Clays and Clay Minerals*, v. 47, n. 5, p. 647-657, 1999.
16. Melnitchenko, A.; Thompson, J.G.; Volzone, C.; Ortiga, J. Selective gas adsorption by metal exchanged amorphous kaolinite derivatives", *Applied Clay Science,* v. 17, n. 1-2, p. 35-53, 2000.
17. Volzone, C.; Ortiga, J. Retention gas O_2, CH_4 and CO_2 by acid smectites with and without thermal treatment, *Journal of Materials Science*, v. 35, p. 5291-5294, 2000.
18. Volzone, C.; Ortiga, J. Retention of gases by acidified kaolin", *17th Biennial Conference of the Australian Clays Minerals Society Inc.- 2nd Symposium on Activated Clays*, 9-14 April, Adelaide, South Australia, p. 45-46, 2000.
19. Volzone, C.; Cesio, A.M. Structural modifications of OH-Cr-smectites after thermal treatment up to 1000 °C, *Mater. Chem. Phys.*, v. 48, p. 216-219, 1997.
20. Lagaly, G.; Beneke, K.; Weiss, A. Magadiite and H-magadiite: I. Sodium magadiite and some of its derivatives, *Am. Mineral.*, v. 60, p. 642-649, 1975.
21. Lee, J-F.; Mortland, M.M.; Chiou, C.T.; Kile, D.E.; Boyd, S. Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities, *Clays and Clay Miner.*, v. 38, p. 113-120, 1990.
22. Kim, C.S.; Yates, D.M.; Heaney, P.J. The layered sodium silicate magadiite: an analog to smectite for benzene sorption from water, *Clay Miner.*, v. 45, p. 881-885, 1997.
23. Sheng, G.; Boyd, S.A. Polarity effect on dichlorobenzene sorption by hexadecyltrimethylammonium-exchanged clays, *Clays and Clay Minerals*, v. 46, p. 43-50, 1998.