



## REFERENCES

- Ackley, M.W., Giese, R.F., and Yang, R.T. (1992). Clinoptilolite: untapped potential for kinetic gas separations. Zeolites, 12, 780-788.
- Ackley, M.W., and Yang, R.T. (1991a). Adsorption characteristics of high-exchange clinoptilolite. Industrial Engineering Chemical Research 30, 2523-530.
- Ackley, M.W., and Yang, R.T. (1991b). Diffusion in ion-exchange clinoptilolites. AIChE Journal, 37(11), 1645-1656.
- Arcoya, A., Gonzalez, J.A., Llabre, G., Seoane, X.L., and Travieso, N. (1996). Role of the counterions on the molecular sieve properties of a clinoptilolite. Microporous Materials, 7, 1-13.
- Armbruster, T. (1993). Dehydration mechanism of clinoptilolite and heulandite: single-crystal x-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K. American Mineralogist, 78, 260-264.
- Ballmoos, R.V., Higgins, J.B., and Treacy, M.M.J. (1992). Characterization of the clinoptilolite-rich tuffs of bigadic: variation of the ion-exchange capacity with pretreatments and zeolite content. Proceeding from the Ninth International Zeolite Conference, 2, 223-231.
- Bernal, M.P., and Lopez-Real, J.M. (1993). Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. Bioresource Technology, 43, 27-33.
- Chao, C.C. (1990). U.S. Patent 4964889.
- Chao, C.C., and Rastelli, H. (1990). U.S. Patent 4935580.
- Chao, C.C., and Rastelli, H. (1991). U.S. Patent 5019667.
- Chon, H., and Seo, G. (1976). Adsorption and catalytic characteristics of acid-treated clinoptilolite zeolite. Journal of the Korea Chemical Society, 20(6), 469-478.

- Hernandez, M.A., Corona, L., and Rojas, F. (2000a). Adsorption characteristics of natural erionite, clinoptilolite and mordenite zeolites from Mexico. Adsorption, 6, 33-45.
- Hernandez, M.A., Rojas, E., and Lara, V.H. (2000b). Nitrogen-Sorption Characterization of the Microporous structure of clinoptilolite-type zeolites. Journal of Porous Materials, 7, 443-454.
- Kesraoul-Oukl, S., Cheeseman, C., and Perry, R. (1993). Effects of conditioning and clinoptilolite prior to lead and cadmium removal. Environmental Science and Technology, 27(6), 1108-1116.
- Kiovsy, J.R., and Koradia, P.B. (1977). U.S. Patent 4059543.
- Lee, H.C., Woo, H.C., Ryoo, R., Lee, K.H., and Lee, J.S. (2000). Skeletal isomerization of n-butenes to isobutene over acid-treated natural clinoptilolite zeolites. Applied Catalysis A: General, 196, 135-142.
- Newalkar, B.L., Jasra, R.V., Kamath, V., Bhat, S.G.T. (1998). Sorption of water in aluminophosphate molecular sieve  $AlPO_4-5$ . Microporous and Mesoporous Materials, 20, 129-137.
- Ouki, S.K., and Kavannagh, M. (1999). Treatment of metals-contaminated wastewaters by use of natural zeolites. Wat. Sci. Tech., 39(10-11), 115-122.
- Pozas, C., Kolodziejcki, W., and Roque-Malherbe, R. (1996). Modification of clinoptilolite by leaching with orthophosphoric acid. Microporous Materials, 5, 325-331.
- Predeseu, L., Tezel, F.H., and Stelmack, P. (1995). Adsorption of nitrogen and methane on natural clinoptilolite. Zeolites, 507-512.
- Perason, A., and Grant, M.H. (1992). Encyclopedia of Chemical Technology. New York: Wiley.
- Ruthven, D.M. (1984). Principles of Adsorption and Adsorption Process. New York: Wiley.

- Sirkecioglu, A., Altav, Y., and Erdem-Senatalar, A. (1995). Adsorption of H<sub>2</sub>S and SO<sub>2</sub> on Bigadic Clinoptilolite. Separation Science and Technology, 30(13), 2747-2762.
- Triebe, R.W., and Tezel, F.H. (1995a). Adsorption of nitrogen, carbon monoxide, carbon dioxide and nitric oxide on molecular sieves. Gas Separation Purification, 9(4), 223-230.
- Triebe, R.W., and Tezel, F.H. (1995b). Adsorption of nitrogen and carbon monoxide on clinoptilolite: determination and prediction of pure and binary isotherms. The Canadian Journal of Chemical Engineering, 73, 717-724.
- Tsitsishvili, G.V., Kirov, G.N., and Filizova, L.D. (1992). Natural Zeolite. New York: Ellis Horwood.

## APPENDIX A

**The composition of the clinoptilolite modified by ion-exchange with 1 M of chloride salt at 80°C for 30 hours and at 80°C for 5 hours.**

**Table A.1** Composition of clinoptilolite modified by ion exchange with two different conditions.

<b>Adsorbent</b>	<b>Si (%wt)</b>	<b>Al (%wt)</b>	<b>Na (%wt)</b>	<b>K (%wt)</b>	<b>Mg (%wt)</b>	<b>Ca (%wt)</b>	<b>Si/Al</b>
Na-clino-30	67.87	13.11	12.57	5.02	0.87	0.56	5.18
Na-clino	65.85	12.74	12.74	5.56	1.67	1.44	5.17
K-clino-30	64.11	11.95	1.78	20.17	1.33	0.68	5.36
K-clino	64.47	12.13	2.08	19.48	1.08	0.75	5.31
Mg-clino-30	69.39	15.53	2.91	6.49	2.22	3.47	4.47
Mg-clino	70.61	13.39	2.07	7.60	1.98	4.35	5.27
Ca-clino-30	69.03	12.04	6.03	6.06	1.69	5.23	5.73
Ca-clino	69.91	12.89	3.54	6.44	1.55	5.84	5.42

## APPENDIX B

The pore size of the pretreated clinoptilolite and clinoptilolite modified by the thermal treatment, acid treatment, ion exchange, and acid treatment prior to ion exchange resulted from BET surface area measurement.

**Table B.1** The comparison of the pore size of the pretreated clinoptilolite and modified clinoptilolite.

<b>Modification technique</b>	<b>Adsorbent</b>	<b>Pore size (nm)</b>
	Pretreated clino	12.90
Thermal treatment	Clino (300)	15.03
	Clino (400)	14.72
	Clino (500)	17.65
Acid treatment	H-clino (0.1)	4.69
	H-clino (1)	3.76
	H-clino (3)	3.52
Ion exchange	Na-clino	11.37
	K-clino	13.39
	Mg-clino	11.35
	Ca-clino	13.83
Acid treatment prior to ion exchange	Acid-Na-clino	3.61
	Acid-K-clino	3.64
	Acid-Mg-clino	3.50
	Acid-Ca-clino	3.66

## APPENDIX C

The d-spacings of the pretreated clinoptilolite and clinoptilolite modified by thermal treatment, acid treatment, ion exchange, and acid treatment prior to ion exchange resulted from x-ray diffraction.

**Table C.1** The comparison of the four most intense d-spacings from literature, the pretreated clinoptilolite and modified clinoptilolite.

Adsorbent	The four most intense d-spacings (°A)			
Literature	8.9200	3.9640	3.8970	2.9740
Pretreated clino	8.9996	3.9727	3.9140	2.9742
Clino (300)	8.9996	3.9727	3.9174	2.9742
Clino (400)	8.9632	3.9622	3.8937	2.9684
Clino (500)	9.1862	3.9868	3.9242	2.9723
H-clino (0.1)	8.9996	3.9798	3.9106	2.9723
H-clino (1)	8.9632	3.9868	3.9072	2.9703
H-clino (3)	8.9813	3.9798	3.9072	2.9703
Na-clino	8.9996	3.9798	3.9106	2.9723
K-clino	8.9632	3.9868	3.9072	2.9703
Mg-clino	8.9813	3.9798	3.9072	2.9703
Ca-clino	8.9996	3.9692	3.9140	2.9723
Acid-Na-clino	8.9996	3.9868	3.9140	2.9723
Acid-K-clino	8.9813	3.9762	3.9106	2.9761
Acid-Mg-clino	8.9996	3.9868	3.9174	2.9742
Acid-Ca-clino	8.9813	3.9762	3.9004	2.9588

**An estimate of the dimension of the crystallites calculated by the Scherrer equation.**

Crystallites can be obtained through the three most intense d-spacings of x-ray diffraction peaks, measured at one-half of the height.

**The Scherrer equation.**

$$d = 0.89\lambda / \beta \cos\theta \quad (C-1)$$

where

d = crystallite size

$\lambda$  = wave length (1.5406 $\text{\AA}$  for CuK radiation)

$\beta$  = peak width at the half height

$\theta$  = diffraction angle

## APPENDIX D

The reference for FTIR analysis.

**Table D.1** Zeolite infrared assignments.

Vibration type	Wavenumber (cm <sup>-1</sup> )
<i>Internal tetrahedra:</i>	
Asymmetric stretching Si(Al)-O	1250-950
Symmetric stretching Si(Al)-O	720-650
Bending O-Si(Al)-O	420-500
<i>External linkages:</i>	
Double ring vibrations	650-500
Pore opening modes	300-420
Symmetric stretching Si(Al)-O	750-820
Asymmetric stretching Si(Al)-O	1050-1150



## APPENDIX E

Scanning electron micrographs of the pretreated clinoptilolite.

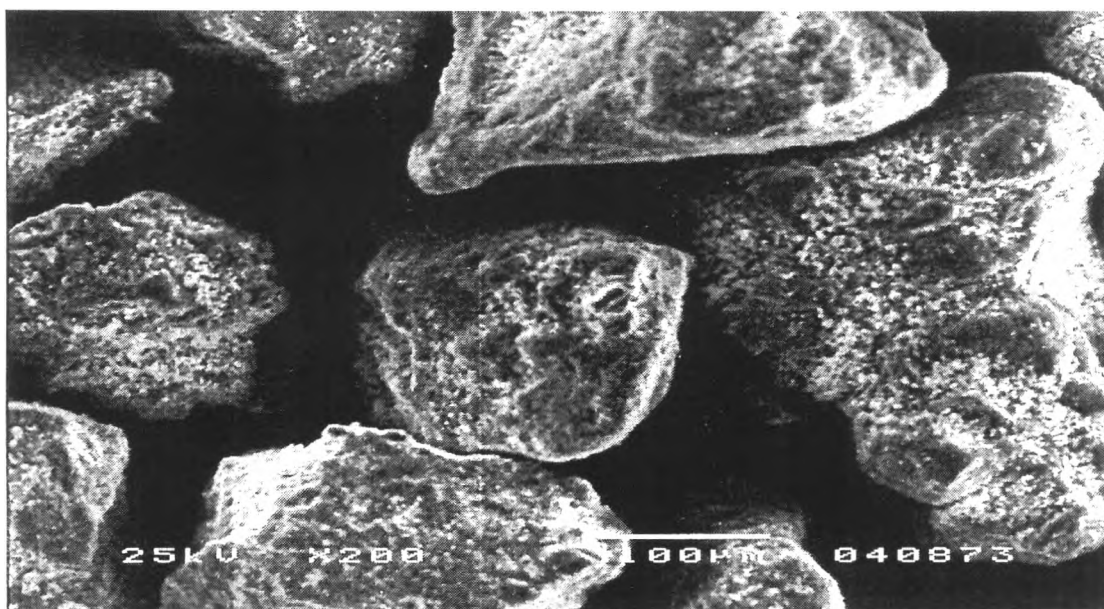


Figure E.1 Scanning electron micrograph of the pretreated clinoptilolite at 200 X Magnification.

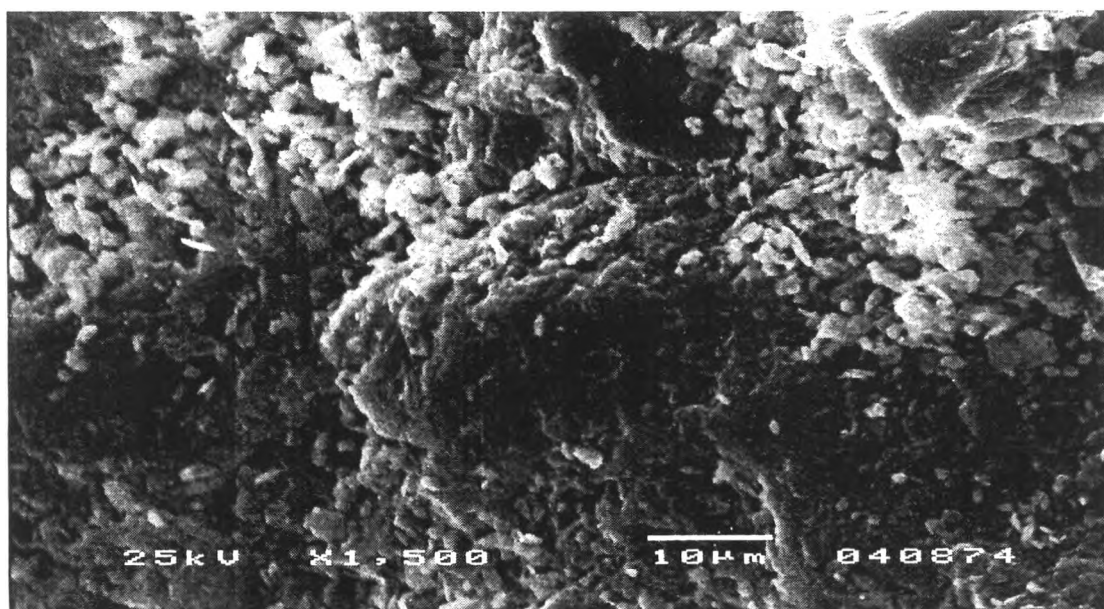


Figure E.2 Scanning electron micrograph of the pretreated clinoptilolite at 1500 X Magnification.

## APPENDIX F

### The adsorption capacity of the clinoptilolite column.

The mass balance for the whole column:

$$\frac{\rho V C_0}{M} \int_0^t \left(1 - \frac{C}{C_0}\right) dt = \int_0^q dq \quad (\text{E-1})$$

where

$C_0$  = initial concentration (%vol)

$C$  = concentration at any time (%vol)

$M$  = mass of the dry zeolite in the column (g)

$q$  = adsorbate concentration (%vol/g zeolite)

$t$  = adsorption time (minute)

$V$  = volumetric flow rate (ml/min)

$\rho$  = gas density (g/cm<sup>3</sup>)

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