Press: Birmingham, 1974; Vol IV.
9. Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175-3187.
10. Craven, B. M.; Mc Mullan, R. K.; Freeman, H. C.; Bell, J. D. *Acta Cryst.* **1977**, *B33*, 2585-2589.
11. Ranter, C. J.; Blaton, M. M.; Peeters, O. M. *Acta Cryst.* **1984**, *C40*, 1748-1750.
12. Larsen, I. K. *Acta Cryst.* **1984**, *C40*, 285-287.
13. Simon, K.; Kalman, A.; Schwartz, J. *Acta Cryst.* **1980**, *B36*, 2323-2328.
14. Kalman, A.; Van Meurs, F. A. *Cryst. Struct. Commun.* **1980**, *9*, 709-712.
15. Kratochvil, B.; Ondracek, J.; Hasek, J. *Acta Cryst.* **1988**, *C44*, 1579-1582.
16. Johnson, C. K. ORTEP Report ORNL-3794; Oak Ridge National Lab.; Tennesse, 1965.

Determination of Net Atomic Charges Using a Modified Partial Equalization of Orbital Electronegativity Method
V. Application to Silicon-Containing Organic Molecules and Zeolites

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The parameters for an empirical net atomic charge calculation method, Modified Partial Equalization of Orbital Electronegativity (MPEOE), were determined for the atoms in organosilicon compounds and zeolites. For the organosilicon family, the empirical parameters were determined by introducing both experimental and *ab initio* observables as constraints, these are the experimental and *ab initio* dipole moments, and the *ab initio* electrostatic potential of the organosilicon molecules. The Mulliken population was also introduced though it is not a quantum mechanical observable. For the parameter optimization of the atoms in the aluminosilicates, the dipole moments and the electrostatic potentials which calculated from the 6-31G** *ab initio* wave function were used as constraints. The empirically calculated atomic charges of the organosilicons could reproduce both the experimental and the *ab inito* dipole moments well. The empirical atomic charges of the aluminosilicates could reproduce the *ab initio* electrostatic potentials well also.

Introduction

Several empirical net atomic charge calculation methods have been developed for both saturated[1,2] and unsaturated molecules.[3-5] However, the parameters for each empirical method were developed mainly for typical organic molecules. The empirical methods are not suitable for the net atomic charge calculation of inorganic molecules, for example, zeolites. Since silicon shows similar chemical behavior with carbon, silicon is an important component of not only many inorganic compounds like zeolites but also organosilicon compounds.

Since *net atomic charge* is not a quantum mechanical *observable* in spite of the fact that it is one of the most important physical quantities in chemistry, many models have been proposed for calculating the net atomic charge. Two main roles of the magnitude of the net atomic charge are (i) to describe the deficiency or sufficiency of the electron population of the atom in a molecule and (ii) to reproduce the electrostatic potential around a given molecule.

The electrostatic interation energy is an important component in the description of the intermolecular interaction energy of polar molecules. Therefore there are lots of efforts to describe the electrostatic potential accurately. One of the most popular quantum mechanical approaches for point charge calculation is Mulliken population analysis method.[6] Though the charges are calculated from the electron density of a molecule, the Mulliken charge poorly describes the electrical moments and the electrostatic potential which are calculated from quantum mechanical wave functions.

Momany[7] and Cox and Williams[8] calculated the point charges located on every atomic centers in a molecule using the electrostatic potentials as constraints, namely Potential Derived (PD) method. In the method, it was assumed that the point charges which can reproduce the electrostatic potential well can be a good representation for the electrostatic interaction. The dipole moments of molecules which calculated with the PD point charges usually agreed well with the experimental dipole moments when a large basis set is used for the *ab initio* electrostatic potential calculation. Though the PD charge set is a good representation for the electrostatic potential, the point charges are not transferable between the molecules which have similar chemical environments.

For the calculation of the point charges of large molecules, for example, proteins and nucleic acids, several empirical methods were proposed on *electronegativity equalization* concept introduced by Sanderson (Electronegativity Equalization

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Method, EEM).[9] Gasteiger and Marsili proposed Partial Equalization of Orbital Electronegativity (PEOE) method,[10] and Mortier *et al.* proposed Full Equalization of Orbital Electronegativity (FEOE) method[11] based on the EEM concept. No *et al.*[12] modified the PEOE method (MPEOE). For the determination of parameters those empirical methods utilize the experimental electrical properties as constraints, for example, the dipole and quadrupole moments of gas phase molecules, and the ionization potential and electron affinity of atoms. The parameters for the atoms in molecular ion or in some groups of molecules can be hardly determined from experimental data because of the deficiency of the experimental data. Therefore, recently, the parameters were determined using the electrostatic potentials calculated from quantum mechanical wave functions as constraints.

Abraham and Grant[13] calculated the partial atomic charges of molecules containing silicon atom with concept of the electronegativity equalization. In addition, they modified the standard MM2 force field and program to include Si-O group and MM calculations were carried out for some organosilicon compounds.

The net atomic charges of the atoms in zeolites were obtained by several workers for the calcultion of the catalytic behavior and adsorption capability of zeolites. Cohen de Lara and Tan[14] calculated the electrostatic field inside of zeolite cavity with the assumption of purely ionic crystal in order to evaluate the binding energy of molecules adsorbed in the α-cage of zeolite A. Mortier[15a] explained the influence of Al contents and cation types on the catalytic properties of alluminosilicate using Sanderson's electronegativity model.[9]

No *et al.*[16] introduced the Sanderson's electronegativity equalization condition[9] and Huheey's electronegativity set[17] for the net atomic charge calculation of the zeolite A. Since all the methods mentioned above introduce the atomic properties for calculating the net atomic charges of the atoms in molecules, for example, ionization potential, electron affinity, and electronegativity of isolated atoms, the calculated charges are not physically realistic. The effective atomic properties, the atomic properties of the atoms in a molecules, are necessary for calculating the physically realistic point charges.

In this study, the MPEOE parameters for the atoms in the organosilicons and in the zeolites will be developed. Especially, several kinds of the empirical methods will be tested. For the parameter optimization, the gas phase electrical moments of some organosilicons and the *ab initio* electrostatic potentials of both organosilicons and the fragments of the zeolite will be introduced as constraints.

Methods

Empirical Charge Calculation Method (MPEOE)

In the MPEOE method,[12] the net atomic charge on atom A is obtained through iterative procedures that attain convergence when the transfer of the fractional charges between all the covalent bonding atomic pairs in a molecule approach to zero. The magnitude of the fractional charge transfer between the covalently bonded atoms A and B was described as[10]

$$dq^{\langle n\rangle}=\frac{\chi_B^{\langle n-1\rangle}-\chi_A^{\langle n-1\rangle}}{\chi_A^{+}}\ (f_{AB})^n \ \text{if}\ \chi_B^{\langle n-1\rangle}>\chi_A^{\langle n-1\rangle} \quad (1)$$

where χ_A and χ_B are the electronegativity of the atom A and B, respectively. f_{AB} is a damping factor which controls the degree of the fractional charge transfer through the covalent bond A-B. This parameter plays a role to attenuate the magnitude of the charge transfer as the iteration number n increases. In the original PEOE method,[10] only a single damping factor, 1/2, was used for every kind of covalent bonds.

The net atomic charge on the atom A at the nth iteration, $Q_A^{\langle n\rangle}$, is calculated as

$$Q_A^{\langle n\rangle}=Q_A^{\langle 0\rangle}+\sum_n\sum_B dq_{AB}^{\langle n\rangle} \quad (2)$$

where $Q_A^{\langle 0\rangle}$ represents the initial net atomic charge on atom A and usually assigns zero for the atoms in neutral molecules. $\sum_n$ and $\sum_B$ represent the summation over all the iterative steps and all the covalently bonded atoms B, respectively.

The electronegativity of an atom i at the nth iteration step is expressed as a linear function of the net atomic charge, $Q_i^{\langle n\rangle}$, as follows.

$$\chi_i^{\langle n\rangle}=a_i+b_iQ_i^{\langle n\rangle} \quad (3)$$

where a_i and b_i are the inherent electronegativity and the charge coefficient of atom i, respectively. χ_i^{+} corresponds to a_i+b_i independant of $\langle n\rangle$ because $Q_i^{\langle n\rangle}$ equals to $+1$.

Both the damping factors and the electronegativity parameters were determined in order that the following function F reaches minimum:

$$F=\sum_i\left|\left(\frac{\partial S}{\partial \alpha_i}\right)_{\alpha_{i\neq j}}\right| \quad (4)$$

where α_i represents the ith parameter (it may be one of the f's, a_i's and b_i's) to be determined, and S is a function which contains constraints. The form of the S will be discussed in the following section.

The molecular dipole moments are calculated approximately with the net atomic point charges. The dipole moment is thus given by

$$\vec{P}=\sum_i \vec{r}_iQ_i \quad (5)$$

where $\vec{r}_i$ is the vector from the center of mass of a molecule to ith atom.

Model Compounds for Organosilicons and the Parameter Optimization. The experimental dipole moment data of the organosilicon compounds are not enough to determine the empirical parameters. With the small number of constraints, the overfitting of the parameters are anticipated. To overcome this problem, the *ab initio* electrical moments and electrical potentials of some organosilicons were also introduced as constraints together with the experimental dipole moments for the parameter optimization. The MO calculations were carried out at RHF level with the 6-31G** basis set. All the geometries were optimized with the 6-31 G** basis set also. For the electrostatic potential calculation of each molecule, about one thousand points were generated between van der Waals surface and the 3 Å thickness region from the surface. Gaussian 90[18] program was used for the *ab initio* calculations.

In the parameter optimization, the experimental dipole

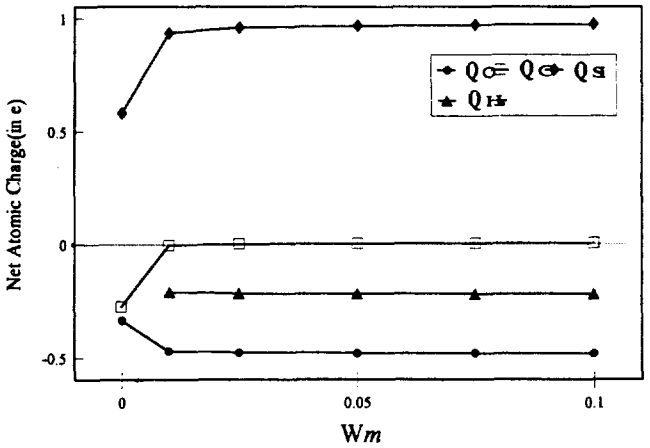

Figure 1. The net atomic charge of the atoms in CH_3OSiH_3 calculated with the MPCPD method are plotted against W_m.

moments, the magnitudes of Mulliken populations, and the electrostatic potentials were introduced as constraints. In the Dipole Derived (DD) MPEOE method, both the experimental and the *ab initio* dipole moments were introduced as constraints and the error, $S_{DD\text{-}MPEOE}$, was minimized to reach the minimum value of F described by equation (4).

$$S_{DD\text{-}MPEOE}=\sum_i[P_{i,cal}(\{f,a,b\})-P_{i,exp}]^2 \quad (6)$$

where $P_{i,cal}$ and $P_{i,exp}$ are the dipole moments calculated with the MPEOE charges and the experimental or the *ab initio* dipole moment of the *i*th molecule, respectively. $\{f,a,b\}$ represents the parameter set of MPEOE method.

Both the electrostatic potential and the Mulliken population obtained from the *ab initio* calculation were introduced as constraints in Mulliken Population Constrained Potential Derived (MPCPD) MPEOE method. The following function is minimized to reach the minimum value of F defined by equation (4).

$$S_{MPCPD\text{-}MPEOE}=[V_{cal}-W_sV_{ab}]^2+W_m[Q_{cal}-Q_{mul}]^2 \quad (7)$$

where W_s and W_m are the scale factors for the *ab initio* electrostatic potential and the weight factor for Mulliken population, respectively. Since the dipole moment and the electrostatic potential calculated with the *ab initio* method are usually overestimated compared with the experimental data. For the 6-31G** basis set, the calculated dipole moments must be scaled by 0.915[12] for the best agreement with experimental dipole moments. Though the Mulliken charges can not reproduce the electrostatic potential well, the magnitudes are transferable from one molecule to another. Therefore, in this work, the minimum W_m value which gave transferable point charges was taken. In Figure 1, net atomic charges obtained with the MPCPD method are plotted against W_m. Since the stable charges were obtained when W_m is 0.05 or larger, 0.05 was used for W_m throughout this work.

The classified atomic species which appear in the organosilicons are summarized in Table 1. Among the atomic species in Table 1, four of them are newly introduced and determined in this work and the parameters for the other atomic species are taken from our previous work.[12] The damping factors for the organosilicons are summarized in Table 2 and χ_H^+ in Table 3.

Table 1. The Atomic Species and their Electronegativity Parameters for Organosilicons

Atomic Species	Parameters		Values		Descriptions
	No *et al.*[12]		This Work		
	a	b	a	b	
$C^{ethylene}$	9.795	25.159			sp^2 Carbon in alkene
C_{sp^3}	7.967	4.862			sp^3 Carbon
$C_{sp^3\text{-}Si}$			7.767	12.429	sp^3 Carbon bonded to Si
H^{ar}	7.428	6.722			Hydrogen bonded to sp^2
H	7.711	31.958			Hydrogen bonded to sp^3
H_{Si}			9.097	3.727	Hydrogen bonded to Si
-O-	12.184	12.808			sp^3 Oxygen
$O_{sp^3\text{-}Si}$			12.810	11.067	sp^3 Oxygen bonded to Si
>N-	12.184	13.538			sp^3 Nitrogen
F	13.246	16.570			Florine
Cl	11.861	13.647			Chlorine
Si			4.042	7.703	Silicon

Table 2. The Damping Factors Introduced in this Study for Organosilicons

Damping factor	No *et al.*[12]	This work	Description
$f_{H\text{-}sp^3}$	0.482		H-sp^3 atoms
$f_{H\text{-}sp^2}$	0.569		H-sp^2 atoms
$f_{sp^3\text{-}sp^3}$	0.501		sp^3-sp^3 atoms
$f_{sp^3\text{-}sp^2}$	0.530		sp^3-sp^2 atoms
$f_{sp^2\text{-}sp^2}$	0.972		sp^2-sp^2 atoms
$f_{Si\text{-}H}$		0.501	Si-H atom
$f_{sp^3\text{-}Si}$		0.457	Si-sp^3 atoms

Table 3. Optimized Electronegativity Parameter χ_H^+ for Organosilicons

	Gasteiger *et al.*[10]	No *et al.*[12]	This work
$\chi^+_{Hsp^3}$	20.02	3.389	
χ^+_{HAr}	20.02	13.594	
χ^+_{HSi}			20.732

Model Compounds for Zeolites and the Parameter Optimization. Two model compounds which are the fragments of the zeolite framework were introduced for describing the electrostatic properties of zeolite. The model compounds are shown in Figure 2. The fragments of the A-type zeolite were taken and the broken covalent bonds were blocked with hydrogen atoms. The geometry of the model compounds were fully optimized with the STO-3G basis set with C_{2V} geometrical restriction. With the STO-3G optimized geometries, the electrostatic potentials were calculated with the 6-31G** basis set. The total charge of $AlSi_2O_6H_8$ model cluster was set to -1 and that of $Si_3O_6H_8$ model cluster was set to zero for the *ab initio* calculations.

For the sampling of the points for the electrostatic poten-

Model 1. $AlSi_2O_6H_8^-$ Model 2. $Si_3O_6H_8$

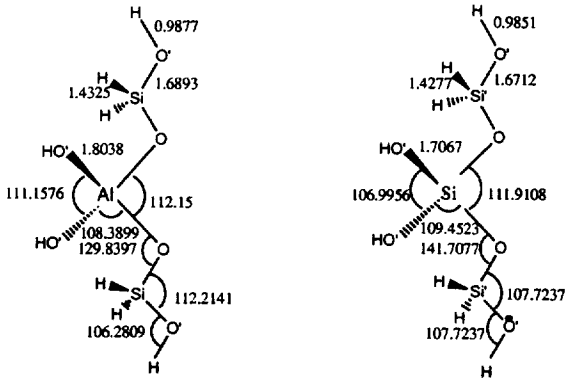

Figure 2. Molecular models for zeolite framework. (a) Model 1, $AlSi_2O_6H_8^-$, (b) Model 2, $Si_3O_6H_8$.

tial calculations, the same procedure was used with the case of the organosilicon compounds. The atomic species and the damping factors introduced for zeolite system are summarized in Table 4. Since there are no experimental electric moments of the zeolite fragments, both the PD-MPEOE and the MPCPD-MPEOE methods which are described by equation (7) were used. Since the PD-MPEOE method uses only the electrostatic potentials as constraints for the parameter optimization, W_m is set equal to zero in the equation (7).

Results and Discussion

Silicon-Containing Organic Molecules. In Table 1, the optimized MPEOE parameters for the organosilicons are summarized. The magnitude of the inherent electronegativity, *a*, of the carbon bonded to Si, (C_{sp3-Si}, 7.767), is similar to that of sp^3 carbon, (C_{sp3}, 7.967), in organic molecules. However, the charge coefficient, *b*, of C_{sp3-Si} is very large compared with that of C_{sp3}. The level of the electronegativity of the hydrogen which bonded to Si, *i.e. a* of H_{Si}, is higher than those of the H atoms bonded to sp^2 and sp^3 atoms in organic molecules, usually bonded to carbon atoms. The charge coefficient of the H_{Si} is very small, 3.727, compared with that of H and H^{ar} species, because the degree of the overlap of the diffused orbital of the Si with the hydrogen atomic orbitals is large. For this reason, the electron population of the hydrogen can be increased with small increment of the electronegativity of H. It means that the capacity of electron of the H_{Si} is larger than those of the H and the H^{ar} because the diffused orbital in the Si can stablize the electrons of the H_{Si} through the overlapping of the orbitals.

The inherent electronegativity of the Si is relatively small, 4.042, and the charge coefficient was obtained as 7.703 which is much smaller than those of the C_{sp3-Si} and the O_{sp3-Si}. For this reason, the silicon in the organosilicon can easily transfer electron with not much increasing of its electronegativity. f_{Si-H} and f_{sp3-Si} in Table 2 were newly optimized and the other damping factors were taken from our previous works.[12] Both damping factors were obtained around 0.5. The optimized value of χ^+_{HSi} in Table 3 is 20.732 which is very close to the ionization potential of neutral hydrogen atom, 20.02 eV. Gasteiger and Marsili[10] introduced 20.02 for the χ^+_H.

In Table 5, the dipole moments of organosilicons calculated with the DD-MPEOE and the MPCPD-MPEOE point charges, and obtained by Abraham and Grant.[13] Both dipole moments calculated with the DD-MPEOE point charges and by Abraham and Grant are reasonably well agreed with experiments. In Table 6, the dipole moments calculated from the 6-31G** wave functions, the Mulliken charges, the PD charges, the MPCPD charges, the PD-MPEOE charges, and with MPCPD-MPEOE charges are summarized. The dipole moments calculated with the Mulliken charges are poorly agreed with those calculated from the wave functions. Both the dipole moments calculated with PD and the MPCPD charges are agreed well with experimental dipole moments. Since the parameters of the PD-MPEOE method were determined by introducing both the experimental dipole moments and the *ab initio* electrostatic potentials as constraints, they

Table 4. Optimized Electronegativity Parameters and Damping Factors for Zeolite System

Atomic Species	Initial Charge	Electronegativity Parameters							
		PD-MPEOE				MPCPD-MPEOE			
		I		II		I		II	
	Q_0	a	b	a	b	a	b	a	b
H_O	0.0	4.940	10.117	4.558	32.329	4.882	10.101	4.556	32.328
H_T	0.0	11.030	5.160	14.021	3.850	10.731	5.141	14.026	3.850
O	0.0, $-0.5^{a,b}$ $(-0.25)^{a,c}$	14.673	10.836	18.529	11.818	14.335	10.854	18.532	11.817
Si	0.0	3.187	5.777	6.617	4.873	3.232	5.254	6.620	4.875
Al	1.0^b $(0.0)^c$	4.025	3.712	8.531	4.589	4.028	3.714	8.530	4.589

Damping factor	PD-MPEOE		MPCPD-MPEOE		Bond type
	I	II	I	II	
$f_{OXZEO-H}$	0.428	0.536	0.428	0.549	O-H
f_{T-O}	0.413	0.406	0.413	0.446	T^d-O
f_{T-H}	0.471	0.443	0.471	0.509	T^d-H

[a] O bonded to Al. [b] used for parameter set I. [c] used for parameter set II. [d] T=Si or Al

Table 5. The Calculated Dipole Moments (Debyes) for Organosilicon Molecules are Compared with Experimental Dipole Moments and with the Dipole Moment Obtained by Abraham and Grant

Molecules	Experimental	Wave function	Abraham *et al.*[13]	DD-MPEOE	MPCPD-MPEOE
		6-31G**			
$CH_3CH_2CH_2SiH_3$	0.811[a]			0.718	
$CH_3CH_2SiH_2CH_3$	0.758[b]			0.962	
$(CH_3)_2SiH_2$	0.750[c]		0.78	0.616	
$(SiH_3)_2CH_2$	0.819[d]		0.70	0.757	
$CH_2=CHCH_2SiH_3$	0.524[e]			0.474	
$CH_3SiH_2N(CH_3)_2$		0.730[j,k]			0.556
SiH_3SiH_2F	1.260[f]			1.341	
CH_3SiH_2F	1.700[g]		1.72	1.673	
$CH_3CH_2SiH_2F$	1.711[h]			1.657	
SiH_3OSiH_3	0.24[m]	0.0007[j,k]	0.177		0.0008
CH_3OSiH_3	1.15[l]	1.083[j,k]	1.068		0.995
$SiH_3CH_2OCH_3$	1.521[i]				1.607
$CH_3OSi(CH_3)_3$	1.18[n]	0.961[j,k]	1.287		1.186
$(CH_3SiH_2)_2O$		0.915[j,k]			0.898
$((CH_3)_2SiH)_2O$		0.792[j,k]			0.883
$Si(OCH_3)_4$		0.125[j,k]			0.0526

[a] Hayashi, M.; Nakagawa, J.; Aguni, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2468. [b] Hayashi, M.; Matsumura, C. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 732. [c] Pierce, L. *J. Chem. Phys.* **1961**, *34*, 498. [d] Shiki, Y.; Kuginuki, Y.; Hasegawa, A.; Hayashi, M. *J. Mol. Spec.* **1978**, *73*, 9. [e] Imachi, M.; Nakagawa, J.; Hayashi, M. *J. Mol. Str.* **1983**, *102*, 403. [f] Cox, A. P.; Varma, R. *J. Chem. Phys.* **1966**, *44*, 2619. [g] Shiki, Y.; Oyamada, M.; Hayashi, M. *J. Mol. Spec.* **1982**, *92*, 375. [h] Hayashi, M.; Imachi, M.; Oyamada, M. *J. Mol. Str.* **1981**, *74*, 97. [i] Shiki, Y.; Ibushi, N.; Oyamada, M.; Nakagawa, J.; Hayashi, M. *J. Mol. Spec.* **1981**, *87*, 357. [j] Hellwege, K. H.; Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structure Data of Free Polyatomic Molecule, Vol 7*; Londolt-Börnstein, Springer-Verlag, Berlin, Heidelberg, NewYork, 1976. [k] RHF/6-31G** Calculation. [l] LeCroix, C. D.; Cure, R. F.; McKinney, P. M.; Myers, R. J. *J. Mol. Spec.* **1974**, *53*, 250. [m] Varma, R.; McDiarmid, A. G.; Miller, J. G. *Inorg. Chem.* **1964**, *3*, 1754. [n] Matsumura, C. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 801.

Table 6. The Dipole Moments Calculated from Wave Function(6-31G**), and with Mulliken Population(6-31G**), PD, MPCPD, PD-MPEOE and MPCPD-MPEOE Charges

	Wave function	Mulliken	PD	MPCPD	PD-MPEOE	MPCPD-MPEOE
	6-31G**	6-31G**				
CH_3OSiH_3	1.0831	2.0041	1.0835	1.0873	0.9485	0.9949
SiH_3OSiH_3	0.0007	0.0017	0.0008	0.0013	0.0008	0.0008
$(CH_3SiH_2)_2O$	0.9145	0.0558	0.9145	0.9143	0.9078	0.8975
$CH_3SiH_2N(CH_3)_2$	0.7298	4.3872	0.7260	0.7692	0.5413	0.5558
$CH_3OSi(CH_3)_3$	0.9607	2.0991	0.9334	1.0054	1.0928	1.1862
$Si(OCH_3)_4$	0.1249	0.0986	0.1214	0.0947	0.0400	0.0526
$((CH_3)_2SiH)_2O$	0.7921	0.2276	0.7921	0.7921	0.9075	0.8830

are adjusted to reproduce both quantities. The dipole moment calculated with the MPCPD-MPEOE charges are a little more deviated from the dipole moments calculated with the 6-31G** wave functions compared with PD-MPEOE dipole moments. The dipole moments calculated with several point charge sets are plotted against the experimental values, in Figure 3. Except for the Mulliken charges, the calculated dipole moments agreed well with the experimental values.

In Figure 4, the magnitudes of the point charges of the silicon atoms located at similar chemical environments obtained with several methods are plotted. Since the fluctuation of the PD charge is so large even between the atoms locate at the similar chemical environments, the PD charges can not be transfered from one molecule to another. The large fluctuation seems to be physically unrealistic. In the case of the MPCPD-MPEOE charges, the magnitude of the charges tend to smoothed out.

The electrostatic potential surface of CH_3OSiH_3 calculated with PD charges (Figure 5-a), Mulliken charges (Figure 5-b), PD-MPEOE (Figure 5-c), and the charges obtained by

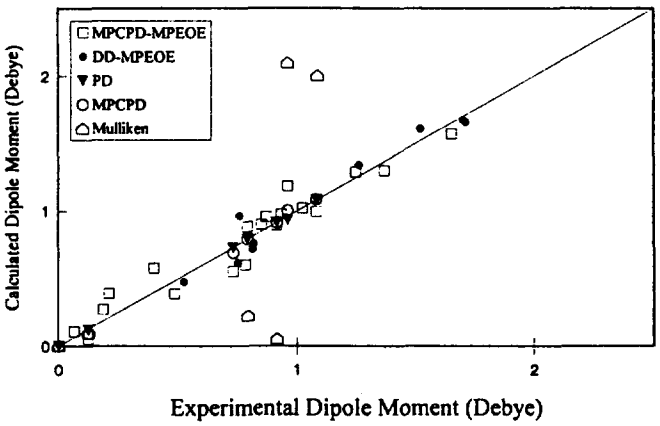

Figure 3. The calculated dipole moments of organosilicon are plotted against experimental values.

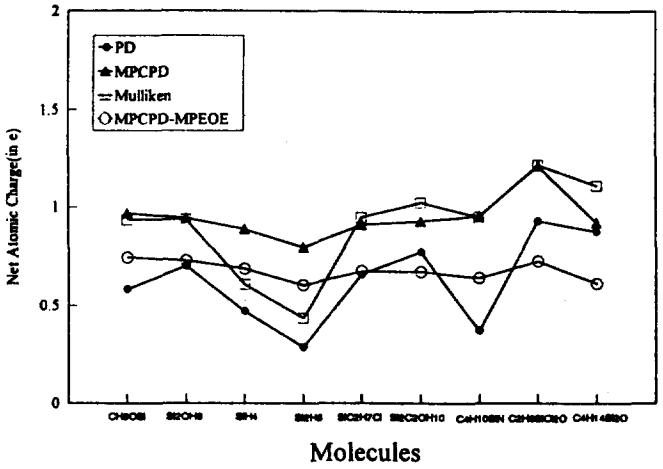

Figure 4. The net atomic charge on Si atom in each organosilicon molecule calculated with several methods are plotted.

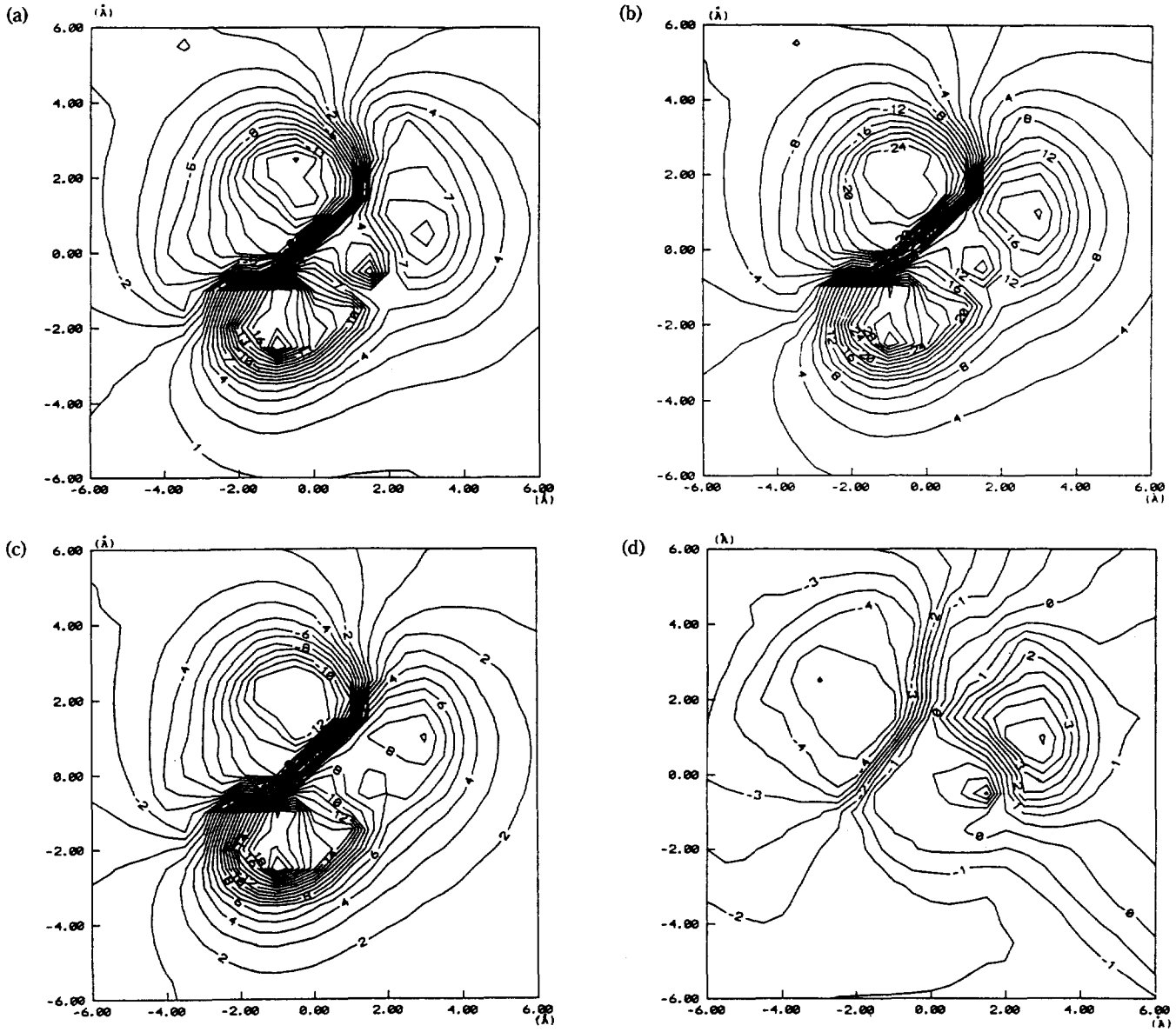

Figure 5. Electrostatic potential (unit=kcal/mol) surface of CH_3OSiH_3 calculated with (a) PD charges (b) Mulliken Population (c) PD-MPEOE charges (d) Abraham et al.'s charges.

Table 7. Net Atomic Charges of Some Organosilicons Calculated with the Mulliken Populations and from the PD, MPCPD, PD-MPEOE and MPCPD-MPEOE Methods

	Mulliken	PD	MPCPD	PD-MPEOE	MPCPD-MPEOE
CH_3OSiH_3					
O	−0.725	−0.334	−0.480	−0.401	−0.448
C	0.015	−0.276	0.002	0.087	0.092
H	0.100	0.130	0.056	0.024	0.025
Si	0.935	0.582	0.967	0.595	0.744
H(-Si)	−0.175	−0.120	−0.220	−0.118	−0.154
SiH_3OSiH_3					
O	−0.815	−0.499	−0.708	−0.449	−0.521
Si	0.938	0.702	0.945	0.584	0.728
H(-Si)	−0.177	−0.151	−0.197	−0.120	−0.156
SiH_4					
Si	0.608	0.470	0.889	0.549	0.688
H(-Si)	−0.152	−0.117	−0.222	−0.137	−0.172
SiH_3SiH_3					
Si	0.434	0.285	0.796	0.509	0.604
H(-Si)	−0.145	−0.095	−0.265	−0.170	−0.201
$(CH_3)_2SiHCl$					
Si	0.948	0.660	0.910	0.576	0.676
C	−0.584	−0.400	−0.340	−0.027	−0.035
H	0.132	0.101	0.064	−0.007	−0.012
Cl	−0.426	−0.334	−0.388	−0.323	−0.362
H(-Si)	−0.148	−0.134	−0.225	−0.138	−0.171
$(CH_3SiH_2)_2O$					
O	−0.824	−0.540	−0.728	−0.465	−0.535
Si	1.025	0.773	0.930	0.549	0.673
C(-Si)	−0.605	−0.373	−0.337	−0.028	−0.035
H	0.124	0.079	0.063	−0.006	−0.011
H(-Si)	−0.189	−0.184	−0.210	−0.136	−0.168
$CH_3SiH_2N(CH_3)_2$					
Si	0.952	0.371	0.956	0.527	0.642
N	−0.734	−0.338	−0.645	−0.315	−0.319
C	−0.093	−0.075	−0.183	−0.011	−0.021
H	0.104	0.059	0.108	0.025	0.024
C(-Si)	−0.589	−0.228	−0.481	−0.031	−0.037
H(-Si)	−0.189	−0.093	−0.219	−0.143	−0.1744
$((CH_3)SiCl)_2O$					
O	−0.800	0.616	−0.792	−0.449	−0.517
Si	1.219	0.932	1.214	0.623	0.726
Cl	−0.438	−0.346	−0.399	−0.331	−0.352
C	−0.613	−0.574	−0.619	−0.022	−0.031
H(NOR)	0.141	0.145	0.137	−0.004	−0.009
$CH_3OSi(CH_3)_3$					
O	−0.730	−0.360	−0.466	−0.424	−0.470
Si	1.195	0.938	1.229	0.474	0.568
C(-Si)	0.588	−0.623	−0.610	−0.038	−0.042
H	0.110	0.136	0.109	−0.002	−0.005
C	0.017	−0.337	−0.242	0.085	0.090
$Si(OCH_3)_4$					
Si	1.535	1.801	0.948	0.832	0.974
O(-Si)	−0.714	−0.598	−0.589	−0.370	−0.413
C	0.018	−0.264	−0.197	0.090	0.095
H	0.104	0.137	0.183	0.024	0.025
$((CH_3)_2SiH)_2O$					
O	−0.832	−0.554	−0.719	−0.480	−0.551
Si	1.113	0.877	0.923	0.508	0.613
H(-Si)	−0.199	−0.222	−0.228	−0.153	−0.180
C(-Si)	−0.600	−0.494	−0.342	−0.033	−0.0384
H	0.117	0.102	0.058	−0.008	−0.0134

Abraham and Grant[13] (Figure 5-d) are plotted. Since the PD electrostatic potential is almost the same with that calculated from wave function, it can be a reference for the test of the reliability of the point charges set. The Mulliken charges overestimate the electrostatic potential and the surfaces produced by MPCPD, PD-MPEOE, and MPCPD-MPEOE charge sets are quite similar to the PD surface. The shape of the surface calculated with the Abraham and Grant's charges is quite different from the PD surface and the electrostatic potentials are underestimated.

The point charges calculated with each method introduced in this work are summarized in Table 7. The magnitudes of the MPCPD charges are quite deviated from the Mulliken charges though the Mulliken populations were introduced as constraints. This means that, for the organosilicons, one can not find the point charge set which has similar quantities with Mulliken charges and can reproduce the *ab initio* electrostatic potentials well simultaneously. If the weight factor of the Mulliken charges, W_m, increased in equation (7), the MPCPD-MPEOE charges poorly describe the electrostatic potentials. Therefore, for the organosilicon compounds, the MPCPD-MPEOE method is not recommanded.

Zeolite. Two sets of the parameters (denoted as I and II) obtained for both the PD-MPEOE and the MPCPD-MPEOE methods are summarized in Table 4. Since the magnitudes of the point charges are very large (it means dq in equation (1) becomes large) it is necessary to introduce appropriate initial charge, $Q^{(0)}$ in equation (2).[12d] Since the location of the optimum point charges of the atoms in zeolite is quite far from the origin (all the point charges are zero) in the point charge space, it is hardly possible to reach the optimum point charge set with the iterative procedure of the PEOE method if the iteration starts at the origin. Therefore the initial charges were introduced to span the whole point charge space during the parameter optimization.

Several sets of the initial charges have tested. Among them two sets of the initial charges which give reasonable point charges were introduced in the calculations. In parameter set I, $Q^{(0)}$ of the oxygen is set to −0.5e if it is bonded to Al otherwise set to 0.0e and $Q^{(0)}$ of the Al is set to 1.0e. In parameter set II, $Q^{(0)}$ of the oxygen is set to −0.25e if it is bonded to Al. All the other initial charges are set to zero for both parameter sets. The charge coefficient of H_O of the parameter set II approaches to the similar value to that of sp^3 hydrogen, *i.e.*, about 32. The inherent electronegativities, a's, of the heavy atoms of the parameter set

Table 8. The Calculated Dipole Moments of Zeolite Model Compounds

	Wave function	Mulliken	PD	MPCPD	PD-MPEOE		MPCPD-MPEOE	
	6-31G**	6-31G**			I	II	I	II
$AlSi_2O_6H_8^-$	1.205	0.378	1.197	1.196	1.209	1.189	1.213	1.249
$NaAlSi_2O_6H_8$	8.733	5.712	8.728	8.727				
$Si_3O_6H_8$	0.665	0.911	0.662	0.662	0.628	0.644	0.680	0.662
$NaSi_3O_6H_8^+$	7.605	4.756	7.618	7.618				

Table 9. The Net Atomic Charges of the Atoms in Zeolite Models

	Mulliken	PD	MPCPD	PD-MPEOE		MPCPD-MPEOE	
				I	II	I	II
$AlSi_2O_6H_8^-$							
Al	1.150	1.246	1.109	1.214	0.793	1.145	0.827
O_1	−0.868	−0.849	−0.774	−0.753	−0.725	−0.737	−0.740
O_2	−0.776	−0.829	−0.804	−0.711	−0.622	−0.701	−0.638
Si	1.185	1.589	1.453	1.341	1.267	1.377	1.337
H	0.286	0.294	0.296	0.140	0.192	0.134	0.189
H(-Si)	−0.222	−0.397	−0.359	−0.336	−0.286	−0.346	−0.306
S[a]		0.0448	0.0583	0.0474	0.0513	0.0595	0.0690
$Si_3O_6H_8$							
Si	1.505	1.126	1.161	1.685	1.519	1.736	1.581
O_1	−0.803	−0.575	−0.593	−0.831	−0.749	−0.853	−0.773
O_2	−0.705	−0.663	−0.669	−0.701	−0.600	−0.705	−0.619
Si'	1.138	0.979	1.010	1.483	1.335	1.529	1.404
H	0.328	0.385	0.385	0.260	0.205	0.250	0.202
H(-Si)	−0.184	−0.206	−0.215	−0.306	−0.277	0.316	−0.293
S[a]		0.0001	0.0127	0.0112	0.0135	0.0333	0.0280

[a] calculated from equation (7)

II are 3-4 higher than those of the parameter set I. The damping factors are obtained between 0.4 and 0.55.

The dipole moments of the model compounds were calculated with several point charge sets and are summarized in Table 8. Both the MPCPD and the PD charges could well reproduce the dipole moments calculated from the wave function, whereas the Mulliken charges give poor dipole moments. In Table 9, the point charges of the two model compounds, $AlSi_2O_6H_8^-$ and $Si_3O_6H_8$, are summarized and the deviations of the electrostatic potential from that of the *ab initio*, which is described by the first term of equation (7), are also listed. The electronegativity of the Al is not so much higher than that of the Si in zeolite though the Al in zeolite is believed to be a negative charge center when the positive ion exists in the zeolite framework. The point charge difference between Al and Si in $AlSi_2O_6H_8^-$ was obtained in the range between 0.13e and 0.23e with the parameter set I and was obtained around 0.5e with the parameter set II. In the parameter set II, though the difference in the inherent electronegativity between Al and Si is only about 2, since both atoms have small charge coefficients, the large difference in the net atomic charges between the Al and the Si is expected. In the PEOE iterative procedure, the electronegativity of two covalently bonded atoms approach to similar value by varying in point charges. Since the Al atom has large positive point charge, it can not be a negative charge center alone. The negative charge is distributed among the AlO_4 unit and is stablized by the silicons bonded to this unit. The parameter set II seems to be physically more realistic from the view point of the negative charge localization on AlO_4 unit. Both the PD-MPEOE and the MPCPD-MPEOE could well reproduce the *ab initio* electrostatic potential when appropriate initial charges are used, whereas for the organosilicon compounds the MPCPD-MPEOE method poorly describe the *ab initio* electrostatic potential.

The empirical point charge calculation method can be used for the calculation of the point charges of zeolite frameworks, even for large model. The computing time depends linealy on the size of model.

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References

1. Chirlian, L. E.; Francl, M. M. *J. Comp. Chem.* **1987**, *8*, 894.
2. Hammarström, L.; Liljefors, T.; Gasteiger, J. *J. Comp. Chem.* **1988**, *9*, 424.

3. Singh, U. C.; Kollman, P. A. *J. Comp. Chem.* **1984**, *5*, 129.
4. Lavery, R.; Zakrzewska, K.; Pullman, A. *J. Comp. Chem.* **1984**, *5*, 363.
5. Houser, J. J.; Klopman, G. *J. Comp. Chem.* **1988**, *9*, 893.
6. (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. (b) *ibid*, **1955**, *23*, 1841.
7. Momany, F. A. *J. Phys. Chem.* **1978**, *82*, 592.
8. Cox, S. R.; Williams, D. E. *J. Comp. Chem.* **1981**, *2*, 304.
9. Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: New York, 1976; p 15.
10. Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219.
11. Mortier, W. J.; Genechten, K. W.; Gasteiger, J. *J. Am. Chem. Soc.* **1985**, *107*, 829.
12. (a) No, K. T.; Grant, J. A.; Scheraga, H. A. *J. Phys. Chem.* **1990**, *94*, 4732. (b) No, K. T.; Grant, J. A.; Jhon, M. S.; Scheraga, H. A. *J. Phys. Chem.* **1990**, *94*, 4740. (c) Park, J. M.; No, K. T.; Jhon, M. S.; Scheraga, H. A. *J. Comp. Chem.* **1993**, *14*, 1482. (d) Park, J. M.; Kwon, O. Y.; No. K. T.; Jhon, M. S.; Scheraga, H. A. *J. Comp. Chem.* **1995**, *16*, 1011.
13. (a) Abraham, R.; Grant, G. H. *J. Comp. Chem.* **1988**, *9*, 244. (b) *ibid*, **1988**, *9*, 709.
14. Cohen de Lara, E.; Tan T. N. *J. Phys. Chem.* **1976**, *80*, 1917.
15. Mortier, W. J. *J. Catal.* **1978**, *55*, 138. (b) No, K. T.; Grant, J. A.; Jhon, M. S.; Scheraga, H. A. *J. Phys. Chem.* **1990**, *94*, 4740.
16. (a) No, K. T.; Jhon, M. S. *J. Kor. Chem. Soc.* **1979**, *23*, 374. (b) No, K. T.; Chon, H.; Ree, T.; Jhon, M. S. *J. Phys. Chem.* **1981**, *85*, 2065. (c) No, K. T.; Kim, J. S.; Huh, Y. Y.; Kim, W. K.; Jhon, M. S. *J. Phys. Chem.* **1987**, *91*, 740. (d) No, K. T.; Huh, Y. Y.; Jhon, M. S. *J. Phys. Chem.* **1989**, *93*, 6413.
17. Huheey, E. *J. Phys. Chem.* **1965**, *69*, 3284.
18. Frisch, M. J.; Head-Gordon, M.; Foresman, J. B.; Trucks, G. W.; Raghavachari, K.; Schlegel, H. B.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian Inc., Pittsburgh, 1992.

Remarkable Structure Relaxation of Zeolite Windows in Rb_3- and K_3-A Crystal Structures of $M_3Na_{9-x}H_xSi_{12}Al_{12}O_{48}$, where M=Rb or K and x=1 or 0

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Four crystal structures of M_3-A ($M_3Na_{9-x}H_x$-A, M=Rb or K and x=1 or 0), Rb_3Na_8H-A (a=12.228(1) Å and R_1=0.046), Rb_3Na_9-A (a=12.258(3) Å and R_1=0.058), K_3Na_8H-A (a=12.257(3) Å and R_1=0.048) and K_3Na_9-A (a=12.257(3) Å and R_1=0.052), have been determined by single crystal x-ray diffraction technique in the cubic space group $Pm\bar{3}m$ at 21 ℃. In all structures, each unit cell contained three M^+ ions all located at one crystallographically distinct position on 8-rings. Rb^+ ions are 3.12 and 3.21 Å away respectively from O(1) and O(2) oxygens, about 0.40 Å away from the centers of the 8-rings, and K^+ ions are 2.87 and 2.81 Å apart from the corresponding oxygens. These distances are the shortest ones among those previously found for the corresoponding ones. Eight 6-rings per unit cell are occupied by eight Na^+ ions, each with a distance of 2.31 Å to three O(3) oxygens. The twelfth cation per unit cell is found as Na^+ opposite 4-ring in the large cavities of M_3Na_9-A and assumed to be H^+ for M_3Na_8H-A. With these noble non-framework cationic arrangements, larger M^+ ions preferably on all larger 8-rings and the compact Na^+ ions on all 6-rings, the bond angles in the 8-rings of M_3-A, 145.1 and 161.0 respectively for (Si,Al)-O(1)-(Si,Al) and (Si,Al)-O(2)-(Si,Al), turned out to be remarkably stable and smaller, by more than 12 to 17°, than the corresponding angles found in the crystal structures of zeolites A with high concentration of M^+ ions. It is to achieve these remarkably relaxed 8-rings, the main windows for the passage of gas molecules, with simultaneously maximized cavity volumes that M_3-A have been selected as one of the efficient zeolite A systems for gas encapsulation.

Introduction

Large quantities of gas molecules, having kinetic diameters somewhat larger than those of zeolite windows, can be encapsulated in the molecular-dimensioned cavities of zeolite by heating the zeolite and subsequent quenching to ambient temperature while the high pressure is maintained.[1~5] These encapsulated gas molecules in the zeolitic cavities can sustain high-pressure concentrations without leakage even at room temperature. The utilization of zeolites as such storage med-