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A simulated annealing study of Si,Al distribution in the omega framework [1]

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Abstract

The Si,Al framework distribution of zeolite omega is studied by three different models, in which the model 3 provides numerical results manifesting the fact that site T_B, one of the two crystallographically unequivalent tetrahedral sites, is preferentially occupied by Al atoms in parent zeolite omega. The dependence of the partitioning ratio of Al atoms in the two crystallographically unequivalent tetrahedral sites, on the Si/Al is predicted correctly. The agreement between the calculated Si building units, {$Si_k(nAl)$; k = A or B, $n = 0–4$}, and that obtained from ^{29}Si MAS NMR is excellent. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Si,Al framework; Zeolite omega; Tetrahedral sites

1. Introduction

By historical reasons, a large amount of studies on the faujasites have been accumulated, most of them have thrown light on the research field of zeolites. However, some problems of zeolites are not covered by those studies because of, for instance, their different structural natures from the faujasite. Zeolite omega is in fact isostructural with the natural zeolite mazzite (hexagonal, space group $P6_{3/mmc}$ with $a = b = 18.392$ and $c = 7.646$ Å [1]). Two crystallographically unequivalent tetrahedral sites are present: one in the four-membered rings (24 l tetrahedral sites by Wyckoff notation, referred as T_A) and the other in the six-membered rings (12 j, T_B). It was found early by Fyfe et al. that the ^{29}Si chemical shift dispersion due to structurally distinct SiO_4 tetrahedral was comparable in magnitude to the first coordination sphere effects. The ^{29}Si MAS NMR spectra of zeolite omega were more complex than zeolites A, X and Y since the crystallographically unequivalent tetrahedral sites gave rise to multiple resonances [2].

Soon after, Jarman et al. [3] interpreted the ^{29}Si NMR spectrum of synthetic mazzite (parent omega) with the assignments of ^{29}Si chemical shifts of Si building units $Si_k(nAl)$; k = A or B, $n = 0–4$} listed in Table 1 and based on the assumption that the partitioning of Al atoms between the two crystallographically unequivalent sites was equal to the site density (N_A/N_B

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Table 1
Comparison of the assignments of chemical shifts for the various $Si_A(nAl)$ and $Si_B(nAl)$ building units in ^{29}Si MAS NMR spectra of zeolite omega by previous references

	$Si_A(0Al)$	$Si_A(1Al)$	$Si_A(2Al)$	$Si_A(3Al)$	$Si_A(4Al)$	References
Chemical shift (ppm)	−103.4	−98.8	−93.7	−89.1		[3]
	−103.4	−98.6	−93.1			[5]
	−105.7	−100.2	−94.8			[6,7,9]
	−104.9	−100.3				[8]
	$Si_B(0Al)$	$Si_B(1Al)$	$Si_B(2Al)$	$Si_B(3Al)$	$Si_B(4Al)$	References
Chemical shift (ppm)	−112.0	−107.0	−98.8	−93.7	−89.1	[3]
	−113.1	−107.1	−103.4			[5]
	−113.1	−107.7	102.3			[6,7,9]
	−112.5					[8]

$= 2$). This assumption indicated that in parent omega, crystallographically unequivalent sites were identical to the aluminum occupation. The same view was held by Raazt et al. [4].

Based on the ^{27}Al NMR observations, Fyfe et al. [5] and Klinowski and Anderson [6] came to the opposite conclusion that the Si,Al distribution were not random in nature in the framework of zeolite omega. In the ^{27}Al MAS NMR spectra of parent zeolite omega there are two distinct Lorentzian signals. After a careful discussion, Klinowski and Anderson assigned the 61.5 and 54.5 ppm signals to aluminum atoms located in sites T_A and T_B, respectively. The spectra intensity ratio $I_A(Al)/I_B(Al) = 1.41$ for the parent zeolite omega with Si/Al ratio of 4.24 was much less than the site density ($N_A/N_B = 2$), and thus they concluded that the less numerous T_B sites were favored by aluminum. By using the ratio of 1.41 experimentally obtained, which indicated in fact the partitioning ratio $N_A(Al)/N_B(Al) = r$ of the Al atoms between the two crystallographically unequivalent sites, Klinowski and Anderson [6] made a further discussion and excluded the possibility of the random distribution of Si and Al within each site group as well.

The ^{29}Si MAS NMR spectra of zeolite omega are composites of two types overlapping signals. The chemical shifts for the various $Si_A(nAl)$ and $Si_B(nAl)$ can be calculated by using the relationship developed by Ramdas and Klinowski [7]. The resultants are also listed in Table 1 (the resultants of Anderson [8] are also listed), and in comparing with the previous assignments by Jarman et al. [3] and Fyfe et al. [5], some explicit discrepancies between them can be seen. The distinction of the assignments would undoubtedly exert significant influence on the results of the deconvolution of ^{29}Si MAS NMR spectra.

Si,Al distribution in samples of zeolite omega synthesized under various experimental conditions was studied by Massiani et al. [9]. For a quantitative interpretation of the data, the deconvolution of ^{29}Si MAS NMR spectra were followed the scheme proposed by Ramdas and Klinowski [7]. The partition ratio r's were calculated from ^{27}Al MAS NMR spectra. Five samples with a series of Si/Al ratios from 3.0 to 5.5 manifested their aluminum partitioning ratios between the two crystallographically unequivalent sites, r's, from 0.92 to 1.27. Though the study demonstrated the synthesis condition dependence of the Si–Al distribution within the framework of zeolite omega, a main fact that aluminum occupying site T_B preferentially was reconfirmed [9].

The fact that the partitioning ratio r varies regularly with Si/Al of the sample indicates that the inherent crystallographic unequivalence should not be the unique reason determining the aluminum partitioning. In dilute Al concentration limit, all the Al atoms are isolated from

each other in the sample. Therefore, for those zeolite omega samples with low Al concentration, in which there are only two structurally distinct situations of Al atom location, the partitioning ratio keeping constant is expected. In case the Al concentration becomes denser, the close environments of Al sites are complicated. Besides the structural distinctions, the classifications of Al site have to extend to the presence of the other Al atoms in its second coordination shell. In general, the populations of class Al site are component (Si/Al) dependent. The aluminum partitioning between the two crystallographically unequivalent sites is a statistical result affected by multi-factors.

In the present work, a numerical study attempts to interpret the main fact that the less numerous T_B sites are favored by aluminum in parent zeolite omega, to provide a correct component dependence of the aluminum partitioning between the two crystallographically unequivalent sites and to match the simulated spectra decently with the ^{29}Si MAS NMR observations of the zeolite omega sample.

The Monte Carlo method is adequate to study problems of substitutional disorder in solids such as the Si–Al distribution in the framework of zeolites [10]. In the present work, the 'simulated annealing' procedure (suggested by Kirpatrick et al. [11]) is employed, in which there exist a deep connection between the statistical mechanics and the combinatorial optimization.

2. Simulated annealing

Simulated annealing is a procedure of standard Monte Carlo finite temperature techniques. During the procedure achieving the global optimum, Metropolis algorithm is employed which provides the way of getting unstuck from local optimums and bring about a deep connection between the statistical mechanics and the combinatorial optimization. In the study of the Si–Al distribution in the framework of zeolites, the following conditions are defined.

(1) $2^3 = 8$ unit cells composed of 288 tetrahedral sites with cyclic boundary conditions are considered as a representation portion of the framework of zeolite omega, by which the statistical behaviors of the system are simulated.

(2) The numbers of Al atoms, N, is determined according to the given Si/Al ratio of the being simulated samples. Any one microscopic configuration of the system is well defined by corresponding occupations of all the N Al atoms and $(288 - N)$ Si atoms in the representation portion. A starting configuration is created by using a random number generator in which Si and Al atoms are randomly positioned in the 288 T sites.

(3) In the combinatorial optimization problem, there is an objective function depending on the freedoms of the system and making the quantitative measure of the 'goodness' of the system or scaling the degree of the optimization. In the present study, the energy of the system is defined as the objective function. The energy value depends on the configuration of the system. The expression of the energy is the key point of the present study. The simulated annealing procedure is aimed at seeking those optimized configurations which possess of the lowest energies.

(4) The system being studied is assumed in thermal contact with a heat bath of temperature T. A configuration of the system with energy $E^{\text{tot.}}$ is weighted by factor $\exp(-E^{\text{tot.}}/K_B T)$.

(5) The randomly generated starting configuration of the system is optimized by iterative reconfigurations. In each step, by randomly searching, an Al–Si nearest-neighbors (nn) pair in the original configuration is found, and then as a disturbance, an interchange of their locations is attempted. According to Metropolis algorithm, if the energy of the new disturbed configuration, E', is lower than the energy of the original one, E, the interchange is accepted and the new configuration is used as the starting one for the next step; if $E' - E = \Delta E > 0$, the new configuration is accepted with the probability of $P(\Delta E) = \exp(-\Delta E/K_B T)$. If the new

configuration is rejected, the original one is kept for the next attempt.

It is obvious that as $T = 0$, the probability for a new configuration with larger energy, $\Delta E > 0$, to be accepted is zero. Though the zero temperature Monte Carlo method provides for rapid rate of progress because of the unidirectional optimization ('improvement-only' rule), it often gets stuck in local optimums and leads to metastable states which are of no interest here. According to Metropolis algorithm, the standard Monte Carlo finite temperature techniques, the acceptance of energy unfavorable disturbances maintains non-zero probabilities which is the way of getting unstuck from local optimums. Though the optimization gets somewhat tortuous, the system will not get caught in a metastable state and the objective achieving the global optimum is ensured.

(6) In order to equilibrate the system at the temperature of zeolite omega formation, T_F, a 'simulated annealing' procedure is carried out. The temperature starts at T_s ($\sim 5.5T_F$), and then steps down to T_F. In each step, T is reduced by a factor of 0.95, i.e., $T(n) = 0.95^n T_s$, till $T(n) = T_F$. At each $T(n)$, enough reconfigurations are attempted (either the number of attempts exceeds 10^5 or the cumulative number of accepted interchanges exceeds 10^4) for the equilibrium of the system.

(7) After the 'simulated annealing' procedure, the configuration of the system has been optimized, by which we begin to built up the canonical ensemble sample space of the system with 10^5 reconfiguration attempts. According to Metropolis algorithm, the accumulative sample set either gets a new configuration or adds in again an original one for each of the attempts. The sample set consists of 10^5 configurations at last and possesses with the canonical ensemble characters since the energies of the configurations are of Boltzmann distribution.

(8) The number of $N_A(\mathrm{Al})$, $N_B(\mathrm{Al})$ and $\mathrm{Si}_k(n\mathrm{Al})$'s can be counted for each configurations, respectively. The aluminum partitioning ratio, $N_A(\mathrm{Al})/N_B(\mathrm{Al})$, and the relative populations of the Si building units, $\{\mathrm{Si}_k(n\mathrm{Al})$; k = A or B, $n = 0$–$4\}$, are obtained by taking an average from the sample space. Those numerical results can then be compared with experimental data to assess the rationality of the model considerations.

3. Model considerations

In our present study, a basic simplification is adopted, in which the oxygens and compensating cation (for instance Na^+ and Ca^{2+}) are ignored. The energy concerned with Si,Al distribution regards only the Al–Al interaction.

3.1. Model 1

The energy of the system is expressed as

$$E = \frac{1}{2} J_{nn} \sum_{i,i'} \delta_{i,Al} \delta_{i',Al} \quad (1)$$

where the summation involves only the nearest neighbor pairs, (i,i′), and the Kronecker delta insures that only Al–Al pairs are counted. The interaction of Al–Al nn pair is characterized by parameter J_{nn}. In model 1, the value of J_{nn} is the only adjustable trial number. It was found that as setting value of J_{nn} up to $10K_BT_F$, the Al–Al nn pair is eliminated from optimized configurations.

Since there are not any considerations relating to the nature of the crystallographic unequivalence in model 1, the Al atoms share equally in T_A and T_B sites is expected, and a consequential numerical result of the aluminum partitioning ratio is close to the site population ratio, 2, and departs explicitly from experimental data [9].

The calculated relative populations of $\mathrm{Si}_k(n\mathrm{Al})$ for sample of $\mathrm{Si}/\mathrm{Al} = 4.24$ from model 1 also depart from that deduced from the corresponding ^{29}Si MAS NMR observations [6] (see Table 2).

Table 2
Comparison between Si building units {$Si_k(nAl)$; k = A or B, $n = 0–4$} quoted from NMR observations and binomial distribution model of Ref. [6] and calculated by the present study

$Si_k(nAl)$ k	n	^{29}Si MAS NMR observation	Binomial distribution	Model-1	Model-3
A	0	15.82	25.1	23.21	17.54
	1	44.58	28.7	27.41	43.18
	2	8.28	12.3	12.86	8.14
	3	0.0	2.3	2.93	0.32
	4	0.0	0.1	0.25	0.0
B	0	9.87	9.1	11.67	9.30
	1	9.72	13.2	13.6	10.63
	2	11.82	7.2	6.46	9.37
	3	0.0	1.7	1.46	1.45
	4	0.0	0.2	0.14	0.07
		$r = 1.41$	$r = 1.41$	$r = 2.064$	$r = 1.385$

3.2. Model 2

The expression of energy is

$$E = \left(J_{nn} \sum_{i,i'} \delta_{i,Al}\delta_{i',Al} + \sum_{j,j'} J_{nnn}(j,j')\,\delta_{j,Al}\delta_{j',Al} \right)/2 \qquad (2)$$

The first term is the same as that of model 1 and by keeping the value $J_{nn} = 10K_BT_F$ the Loewenstein's rule has come true. The augmented second term sums up all the contributions from Al–Al next nearest neighbor pairs. Based on the point charge model, the value of parameter $J_{nnn}(j,j')$ are assumed to be inversely proportional to the distance between j and j′ sites, namely

$$J_{nnn}(j,j') = \frac{1}{r_{j,j'}} J_{nnn} \qquad (3)$$

Since those $r_{j,j'}$ are determined structurally (see Table 3), J_{nnn} is the second adjustable trial number in model 2. It was found that when the value of J_{nnn} varies from 0.0 to $18.0K_BT_F$ Å, the calculated aluminum partitioning ratio $N_A(Al)/N_B(Al)$ varies correspondingly from 1.95 to 2.16 and, therefore, fails to predict the fact that T_B sites are favored by aluminum.

3.3. Model 3

In model 2, the energy consideration has extended to Al–Al nnn pairs and various in kind of Al–Al nnn interactions have already got in touch with the crystallographic unequivalence. Nevertheless, model 2 fails in describing the distribution of Si and Al in the framework of zeolite omega due to holding the point charge model which reduces the complicacy of the nnn pair interaction to the simple geometrical distance differences only.

In model 3, the consideration of Al–Al nnn-interaction goes further into the types of both sites of the interactive Al–Al nnn-pairs and their intermediate Si site. Nine different nnn-triplets are classified as Al_A–Si_A–Al_A, Al_A–Si_A–Al_B, Al_A–Si_B–Al_B, and Al_x–Si_B–Al_x (x = A or B; see Table 3). Though the energy expression employed by model 3 is the same as its counterpart in model 2 formally, the $J_{nnn}(j,j')$'s in Eq. (3) are modified as

$$J_{nnn}(j,j') = \frac{1}{r_{j,j'}} J_{jkj'} \qquad (j,j',k = A \text{ or } B) \qquad (4)$$

the four adjustable trial number, J_{AAA}, J_{AAB}, J_{ABB} and J_{ABA} or J_{BBB} are determined by trial and error to match all the numerical results with the corresponding experimental data.

Table 3
Nine possible next-nearest-neighbor triplets of Al–Si–Al in the framework of zeolite omega

Al location site T_j	Intermediate Si site T_k	Al location site $T_{j'}$	Distance between Al–Al pair (Å)
A	A	A	4.357
A	A	A	4.803
A	A	A	5.846
A	A and B	B	4.403
A	A	B	4.614
A	A	B	5.749
A	B	B	5.612
A	B	A	4.523
B	B	B	5.524

Table 4
The component (Si/Al) dependences of aluminum partitioning ratio between the two crystallographically unequivalent sites in the framework of zeolite omega determined from ^{27}Al MAS NMR spectra [9] and calculated by the present study

Si/Al[a]	$r = N_A(Al)/N_B(Al)$		
	r[b]	Model 1	Model 3
3.0	0.92	1.98	0.931
3.3	1.14	2.04	1.046
3.4	1.25	2.03	1.181
4.4	1.00	2.04	1.262
5.5	1.27	2.09	1.495

[a] From ^{29}Si MAS NMR spectra, Ref. [9].
[b] From ^{27}Al MAS NMR spectra, Ref. [9].

We find that the following setting values of

$$J_{AAA} = 3.79,\ J_{AAB} = 10.46,\ J_{ABB} = 0.44 \text{ and}$$
$$J_{ABA} = J_{BBB} = -4.79K_BT_F \text{ Å} \quad (5)$$

bring the simulation to satisfactory results.

The calculated aluminum partitioning ratios, r, are much less than the site density, 2, and show explicitly the preferential location of the Al atoms in the T_B sites. The calculated r's coincide with experimental data of ^{27}Al MAS NMR [9] and show the reasonable tendency of the component (Si/Al) dependence (see Table 4).

The relative populations of Si building units, $Si_k(n\text{Al})$, are also calculated from model 3 with the same set of parameter values of Eq. (5). In order to compare the results with the ^{29}Si MAS NMR data of Klinowski and Anderson [6], the last input parameter, Si/Al, is chosen as 4.24. Both the calculated aluminum partitioning ratios and the relative populations of $Si_A(n\text{Al})$ and $Si_B(n\text{Al})$ (normalized to 100%) are in excellent agreement with experimental results [6] (see Table 2).

4. Results and discussion

The experimental data are basic to the numerical study. All the parameters employed in the simulation are determined by trial and error to match the calculated results with the corresponding experimental data. In the present study, the data provided by Ref. [6] are chosen because of the following reasons: (1) The assignments of the chemical shift for various $Si_A(n\text{Al})$ and $Si_B(n\text{Al})$ by Ramdas and Klinowski [7] is generally acknowledged up to date. (2) In fact, as we know so far, Ref. [6] offered a complete set of the most detailed analytic results for both the ^{29}Si and ^{27}Al MAS NMR experiments of the parent zeolite omega (Si/Al = 4.24).

The Si and Al distributions are not random in nature in the framework of parent zeolite omegas. It has been proved true by ^{27}Al MAS NMR observations that the less numerous T_B sites are favored by aluminum. The present study, maybe for the first time, gains a series of numerical results to illustrate the preferential location of Al atoms in the T_B sites and the correct component (Si/Al) dependence of aluminum partitioning between T_A and T_B sites.

It is a rigorous test of the present model considerations to match the calculated relative populations of various Si building units with the ^{29}Si MAS NMR observations. In comparing with model 1 (and binomial distribution model [6] as well), in which the random distribution of Al atoms is subject to the constraint of Loewenstein's rule only, the model 3 achieves improvements in the decreased population of $Si_A(0\text{Al})$ (17%, instead of 23%), the increased population of $Si_A(1\text{Al})$ (43%, instead of 27%), and the approximately equal populations of $Si_B(0\text{Al})$, $Si_B(1\text{Al})$, $Si_B(2\text{Al})$ ($\sim 10\% \pm 0.7\%$). Therefore, the calculated relative populations of $Si_k(n\text{Al})$ by model 3 coincide satisfactorily with the corresponding ^{29}Si MAS NMR data of Klinowski and Anderson [6] (see Table 2).

In the present study, the J_{nn}, and J_{nnn}'s are called interaction parameters and are introduced into the equivalent and phenomenological description of the energy of an interacting many-body system. Though the reasonableness of the model await to be proved by more experimental facts, the success of the present phenomenological theory provides leads for further studies.

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