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Al Next Nearest Neighbor, Ring Occupation, and Proximity Statistics in ZSM-5

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The distribution of framework Al in ZSM-5 was simulated for various Si/Al ratios and the results used to determine the fraction of Al atoms in next nearest neighbors (NNN) T sites. All the 4-, 5-, and 6-membered rings were identified in the unit cell and the fraction of these rings with 0, 1, 2, and 3 Al was calculated. Lastly, the radial distribution function of Al–Al pairs, the number of Al's expected within a sphere of radius, *r*, centered around an Al (E), and the probability of finding at least one Al within a sphere of radius, *r*, centered around an Al (P) were calculated for different Si/Al ratios. Based on these results, the probability of locating NNN pairs of Al atoms situated at a distance suitable for the stabilization of M^{2+} and $[M–O–M]^{2+}$ cations were carried out and then used to determine maximum values for M^{2+}/Al and $[M–O–M]^{2+}$/Al. The value of M^{2+}/Al is 0.12 for Si/Al = 12 and 0.07 for Si/Al = 24, and the value of $[M–O–M]^{2+}$ is 0.30 for Si/Al = 12 and 0.19 for Si/Al = 24. The values of M^{2+}/Al obtained theoretically are in reasonable agreement with those observed experimentally for Pd–ZSM-5. A significant finding of our simulation is that Löwenstein's rule is the dominant factor governing short-range correlations of framework Al atoms, and hence the distribution of NNN pairs of Al atoms. As a consequence, analytical theories that include consideration of Löwenstein's rule provide rather accurate estimates of the probability of finding Al NNN pairs.

INTRODUCTION

The distribution of Al in a silicon rich zeolite such as ZSM-5 can affect the structure and properties of catalytically active centers (e.g., H^+, M^+, $[M(OH)]^+$, M^{2+}, $[M–O–M]^{2+}$). Quantum chemical calculations have shown that the proton affinity of a Brønsted acid proton can be affected significantly by cations associated with the oxygen atoms bonded to an Al atom situated at a next-nearest neighbor (NNN) T site (1). Stabilization of divalent metal cations, M^{2+}, metal–oxygen–metal clusters of the type $[M–O–M]^{2+}$ (see Fig. 1) also require the presence of two proximate charge-exchange sites (2, 3). Such sites might be created by having two Al atoms in NNN T sites or in next-next-nearest neighbor (NNNN) T sites.

Only two previous attempts have been made to calculate the distribution of Al in silicon-rich zeolites. Sonnemans *et al.* (4) present an analytical expression for calculating the number of NNN T sites for a given Si/Al ratio. Their model recognizes that each T site is connected to four others and takes into account Löwenstein's rule, but it does not fully account for the longer range connectivity of the zeolite. Feng and Hall (5) have carried out Monte Carlo simulations of the distribution of Al atoms in ZSM-5. These results were then used to determine the number of Al atoms within a sphere of radius *r*, calculated as the product of the fraction of all T sites occupied by Al times the number of T sites within a radius *r*. The authors assume that two Al atoms will be in NNN T sites if $0.42\ \text{nm} < r < 0.65\ \text{nm}$ and the number of Al atoms within the sphere is greater than 2.

In the present study, Monte Carlo simulations of the distribution of Al in ZSM-5 are used to determine the fraction of Al atoms having Al atoms in NNN T sites, the fraction of 4-, 5-, or 6-membered rings containing *n* Al atoms, the radial distribution function of Al pairs, the number of Al atoms expected near a given Al atom as a function of radial distance, and the probability of finding at least one other Al near a given Al atom as a function of radial distance. Each of these properties is calculated as a function of the average Si/Al ratio. Variations in the local Si/Al ratio are accounted for using a Poisson distribution. As a clarification, we note that we use the term Monte Carlo to mean a stochastic method, not Metropolis Monte Carlo with Boltzmann sampling.

COMPUTATIONAL METHODS

We model ZSM-5 using one or two unit cells of 96 T sites with periodic boundary conditions as shown in Fig. 2. The geometry of the unit cell is that of Olson *et al.* (6). The first step in our calculation is the creation of a table which specifies the connectivity of the unit cell. This table is used to establish the identity of the nearest four T sites connected

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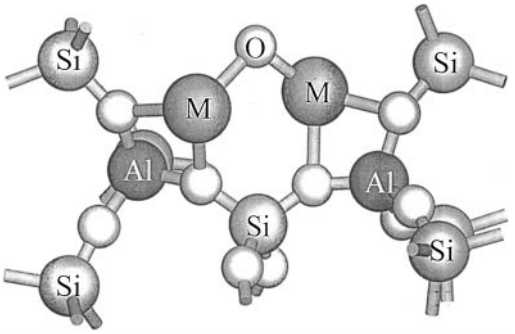

FIG. 1. Metal–oxygen–metal $[M–O–M]^{2+}$ complex interacting with 2 Al T sites.

to a given T site. All 4-, 5-, and 6-membered rings in the unit cell are then identified by stepping to the neighboring sites four, five, and six times, respectively; if the last site is the same as the first and the steps do not backtrack, this sequence of T sites is considered a ring.

A random T site is selected and that site is then considered occupied by Al. Another T site is then selected. If this second T site is occupied by Al or is next to an occupied T site this selection is rejected, as stipulated by Löwenstein's rule. This process is repeated until the desired occupation of the unit cell is achieved. Occupations up to 25 Al atoms per unit cell are considered. Above 25 Al atoms per unit cell, the probability of a cell with such a high occupation is very low (for a Si/Al ratio of 12, only 7×10^{-7} of the unit cells will have an occupation of 25). For each Al occupation, properties are determined by averaging over different Al atoms. Further averaging is done using 10^6 representations of the distribution of Al atoms.

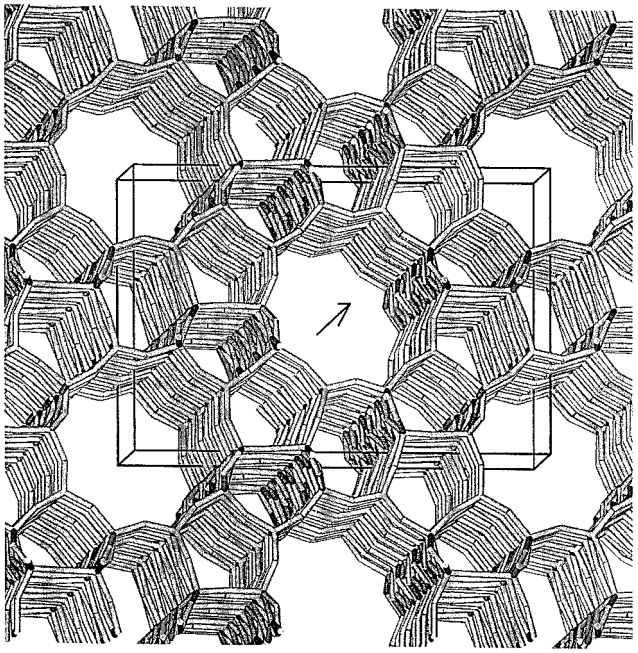

FIG. 2. Unit cell of ZSM-5 with periodic boundaries (arrow denotes straight channel).

The following properties are determined: the fraction of Al with next nearest neighbors; the fraction of rings containing 0, 1, 2, or 3 Al's; the Al pair radial distribution function (rdf); and the expectation (E) and probability (P) of finding an Al T site within a given radius of another.

To account for the nonuniform distribution of Al in the zeolite, we average over the variation in local Si/Al ratio using a Poisson distribution:

$$\mathrm{P}(x;\lambda) = \frac{e^{-\lambda}\cdot\lambda^{x}}{x!}. \qquad [1]$$

In Eq. [1] x is the number of Al atoms occupying T sites in our model (one or two unit cells) and λ is the average number of Al T sites expected. The expectation of the Poisson distribution (λ) is $N/(\mathrm{Si/Al}+1)$ where N is the number of available T sites in our model. Averaging over the Poisson distribution is done in the following way. We define F_x to be the average fraction or expectation of a property of the Al distribution determined from the Monte Carlo sampling procedure described above. Then the values of F_x are averaged with the Poisson distribution yielding S. If the property of the Al distribution is not based on a conditional probability, such as the fraction of rings with two Al atoms, S is defined as

$$S(\lambda) = \sum_{x=0}^{\infty} \mathrm{P}(x;\lambda)\cdot F_x. \qquad [2]$$

If the property of the Al distribution is based on a conditional probability, such as the Al–Al pair rdf, S is defined as

$$S(\lambda') = \sum_{x=0}^{\infty} \mathrm{P}(x;\lambda')\cdot F_{x+1}. \qquad [3]$$

The index on F is now $x+1$ to account for the one Al required by our conditional probability and λ' is now $(N-5)/(\mathrm{Si/Al}+1)$ to account for Lowenstein's rule.

Given E averaged by the methods described above, the probability (P) of finding at least one additional Al within a given radius is determined by calculating the probability of zero Al atoms being located within that radius. Assuming a Poisson distribution, the probability of no other Al atoms within a given radius and Si/Al ratio is

$$\mathrm{P}(x=0;\mathrm{E}) = \frac{e^{-\mathrm{E}}\cdot\mathrm{E}^{0}}{0!} = e^{-\mathrm{E}}, \qquad [4]$$

where E is the average number of nearby Al atoms located within a radius r of a given Al and at a given Si/Al ratio. The

probability of at least one Al atom located within a radius r is therefore

$$P(x \geq 1; E) = 1 - e^{-E}. \quad [5]$$

RESULTS

The fraction of Al atoms having Al atoms in NNN T sites is presented in Fig. 3 as a function of Si/Al ratio. This fraction is 0.64 for Si/Al = 12, the upper limit for ZSM-5, and decreases monotonically as the Si/Al ratio increases. Included in Fig. 3 is the fraction of next nearest neighbors not using the Poisson averaging (i.e., uniform Al distribution). It is clear that Poisson averaging has relatively little effect on the predicted fraction of next nearest neighbors. This is simply a reflection of the fact that for properties like the fraction of NNN which are influenced by correlation on scales shorter than 0.6 nm, the effect of long-range correlation such as variations of Si/Al ratio on the scale of the unit cell are not significant. On these short scales the correlation induced by Löwenstein's rule are dominant. Also shown in Fig. 3 are the calculations of Sonnemans *et al.* (4). The analytical expression developed by these authors is in close agreement with the result obtained from our Monte Carlo simulations, particularly in the region of high Si/Al ratio. At low Si/Al ratios, the analytical expression underpredicts the results of Monte Carlo simulation. It appears that the analytical theory does not account for the short-ranged correlations as well for low Si/Al ratios. The likely reason is that the model used by Sonnemans *et al.* disallows the occupation by Al at nearest neighbor (NN) T sites around a given Al atom but not for all surrounding Al T sites, since their model does not account for the long-range connectivity of ZSM-5. This becomes a more significant omission as the number of Al atoms per unit cell increases.

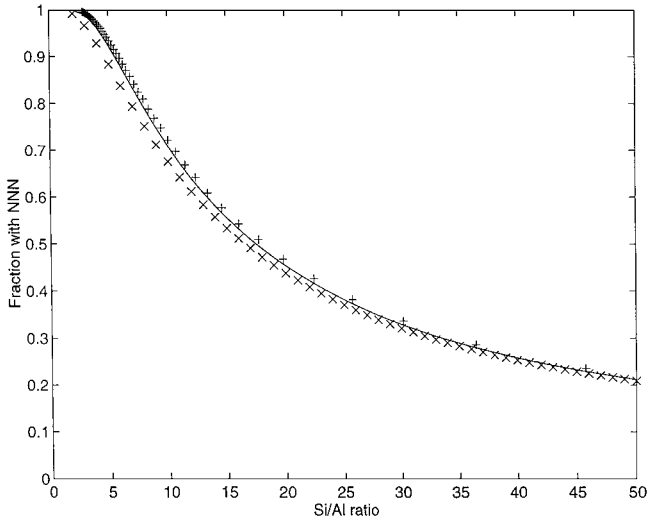

FIG. 3. Fraction of Al atoms with next nearest neighbors versus Si/Al ratio: stochastic distribution without averaging over a Poisson distribution in Si/Al ratio (+); stochastic distribution with averaging over a Poisson distribution in Si/Al ratio (———); a uniform distribution and the analytical expression of Sonnemans *et al.* (4) (×).

TABLE 1

Rings of the ZSM-5 Unit Cell

T_{site} rings						Location in unit cell	Rings per unit cell
4-membered rings							
T_9	T_9	T_{10}	T_{10}			Sinusoidal	4
5-membered rings							
T_1	T_2	T_6	T_3	T_4		Wall	8
T_1	T_2	T_6	T_9	T_{10}		Sinusoidal	8
T_1	T_2	T_8	T_7	T_4		Straight	8
T_1	T_4	T_5	T_{11}	T_{10}		Wall	8
T_1	T_4	T_7	T_{11}	T_5		Straight	8
T_2	T_3	T_4	T_5	T_6		Sinusoidal	8
T_2	T_3	T_6	T_9	T_8		Straight	8
T_2	T_6	T_3	T_{12}	T_8		Wall	8
T_3	T_4	T_7	T_8	T_{12}		Sinusoidal	8
T_3	T_6	T_5	T_{11}	T_{12}		Straight	8
T_8	T_9	T_{10}	T_{11}	T_{12}		Wall	8
6-membered rings							
T_1	T_2	T_8	T_7	T_{11}	T_5	Straight	8
T_1	T_2	T_8	T_{12}	T_3	T_4	Wall	8
T_1	T_4	T_3	T_6	T_9	T_{10}	Wall	8
T_1	T_4	T_5	T_1	T_4	T_5	Sinusoidal/Wall	4
T_1	T_5	T_4	T_7	T_{11}	T_{10}	Sinusoidal	8
T_2	T_6	T_3	T_4	T_7	T_8	Wall	8
T_2	T_6	T_5	T_{11}	T_{12}	T_8	Straight/Wall	8
T_7	T_7	T_8	T_9	T_9	T_8	Sinusoidal	4
T_7	T_7	T_8	T_{12}	T_{12}	T_8	Wall	4
T_7	T_7	T_{11}	T_{10}	T_{10}	T_{11}	Sinusoidal	4
T_7	T_7	T_{11}	T_{12}	T_{12}	T_{11}	Straight	4
T_8	T_9	T_9	T_8	T_{12}	T_{12}	Straight/Sinusoidal	4
T_{10}	T_{10}	T_{11}	T_{12}	T_{12}	T_{11}	Straight/Sinusoidal	4

All of the 4-, 5-, and 6-membered rings were identified in the ZSM-5 unit cell. As noted in Table 1, there are 4 4-membered rings, 88 5-membered rings, and 76 6-membered rings per unit cell. Because of the 8-fold symmetry within the unit cell, many of the rings we consider are identical (e.g., there are 4 4-membered rings in each unit cell but each consists of the same T sites, T_9-T_9-T_{10}-T_{10}). All of the 4-membered rings are located on the surface of the sinusoidal channels. The 5- and 6-membered rings are located on the surface of the straight and sinusoidal channels or within the wall of ZSM-5.

Figure 4 illustrates the average occupation of each type of ring by 0, 1, or 2 Al atoms. The fraction of 6-membered rings with 3 Al atoms is too small to be seen in this figure. Since no significant difference is observed in the statistics for individual rings of a given class, the occupations are averaged for all rings within each of the ring classes. One should expect the occupation of rings by two Al's to increase with ring size. For a 4-membered ring containing one Al

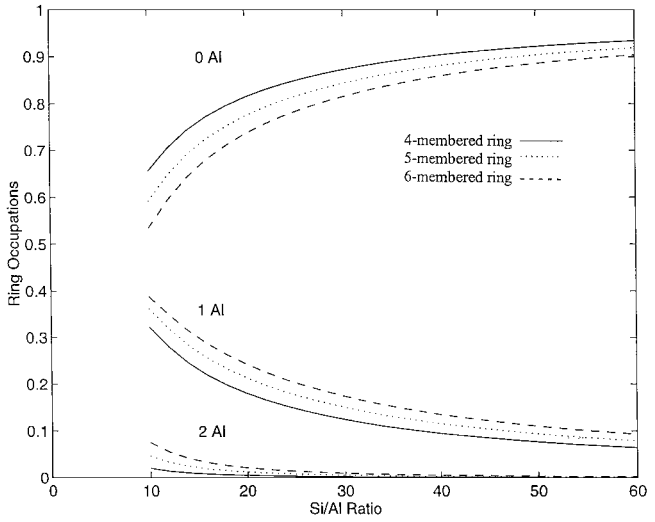

FIG. 4. Ring occupation for 0, 1, and 2 Al's versus Si/Al ratio.

atom there is only one position available for a second Al atom, whereas for 5- and 6-membered rings, there are two and three sites available for a second Al atom, respectively. The increase in occupation of rings by two Al atoms with increasing ring size is clearly seen in Fig. 4.

The fraction of rings containing more than one Al decreases as the Si/Al ratio increases. For the Si/Al range often used experimentally, 12 to 24, the fractions are small. At a Si/Al ratio of 12, the fraction of rings with two Al atoms is 0.014, 0.033, and 0.054 for 4-, 5-, and 6-membered rings, respectively, and at a Si/Al ratio of 24, the fraction of rings with two Al atoms are 0.004, 0.009, and 0.015, respectively. The fraction of 6-membered rings with three Al's per ring is only 0.001 even at a Si/Al ratio of 12.

It is also of interest to determine the fraction of Al atoms which are in a ring containing two Al atoms. This characteristic can be determined following the procedure used by Sonnemans *et al.* (4). First we considered the connectivity of each T site to its NN, NNN, and NNNN shells. Each of these surrounding T sites is checked to ascertain that they share a ring with the center Al T site. Averaging over all 12 T sites yields 10.333 NNN sites and 3.333 NNNN sites sharing a ring with the center Al T site. Therefore, the fraction of Al atoms sharing a 5- or 6-membered ring with another Al atom is 0.66 and 0.43 for a Si/Al ratio of 12 and 24, respectively.

The radial distribution function of Al–Al pairs is shown in Fig. 5. For $r < 0.42$ nm there are no Al neighbors since any such neighbor would be a nearest neighbor and such neighbors are forbidden by Löwenstein's rule. Next-nearest neighbors are found between 0.42 and 0.58 nm and next-next-nearest neighbors are found between 0.47 and 0.78 nm. The jagged nature of the rdf is due to the crystalline structure of ZSM-5. The magnitude of the peaks in the rdf decrease as the Si/Al increases but the shape of the rdf remains the same. The contributions of the rdf from NNN and NNNN are given in Fig. 5b for Si/Al = 12.

Figure 6 shows the expected number of Al atoms (E) and the probability of finding a second Al atom (P) within a sphere of radius r around a given Al atom. Two cases are shown. The first is for Al atoms irrespective of where they are located and the second is for Al atoms restricted to the straight channels. In both cases it is observed that for a given value of r, E and P decrease as the Si/Al ratio increases. There is a significant reduction in E from the case with no restrictions (Fig. 6a) to the restriction of both Al atoms being in the straight channel (Fig. 6b). The values of E reported in Fig. 6a are consistent with what would be expected on the basis of a rough calculation of the product of the density of Al atoms, ρ, times the volume of a sphere defined by the radius r (excluding the nearest neighbor range less than 0.42 nm). For example, taking $\rho = 1.38$ Al/nm^3 (at Si/Al = 12) and a spherical shell defined by the radius $r = 1.0$ nm one obtains E = 5.1. This value is close to the value of E = 5.8 obtained from our calculations for $r = 1.0$ nm and Si/Al = 12. Again the short-range correlations induced by Löwenstein's rule dominate; therefore there is good statistical agreement over long ranges.

The values of E presented in Fig. 6 can also be compared with those reported by Feng and Hall (5). These authors report a value of E = 11.8 for Si/Al = 11 and $r = 1.0$ nm. For identical conditions our calculations yield a value of E = 6.3, assuming a uniform density sphere. This near two-fold discrepancy in the values of E can be ascribed to the significantly different approach used by Feng and Hall, as compared to ours. In Feng and Hall's study, E is determined by taking the product of the fraction of all T sites occupied

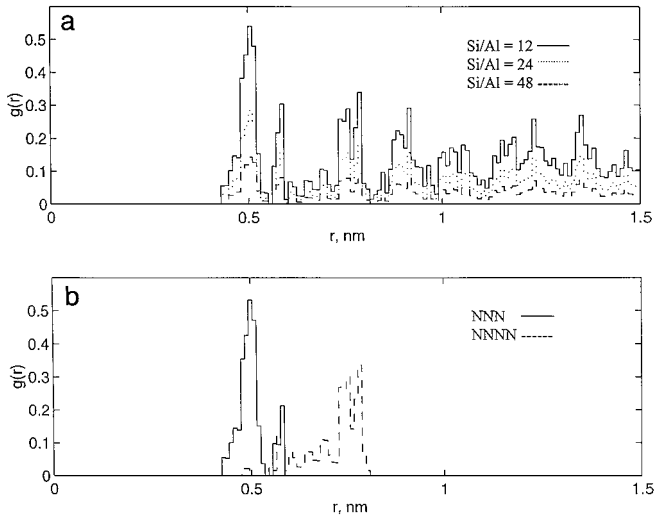

FIG. 5. Al–Al radial distribution function: (a) based on a stochastic distribution of Al atoms for Si/Al ratios of 12, 24, and 48 and (b) the NNN and NNNN contributions to the rdf for a Si/Al ratio of 12.

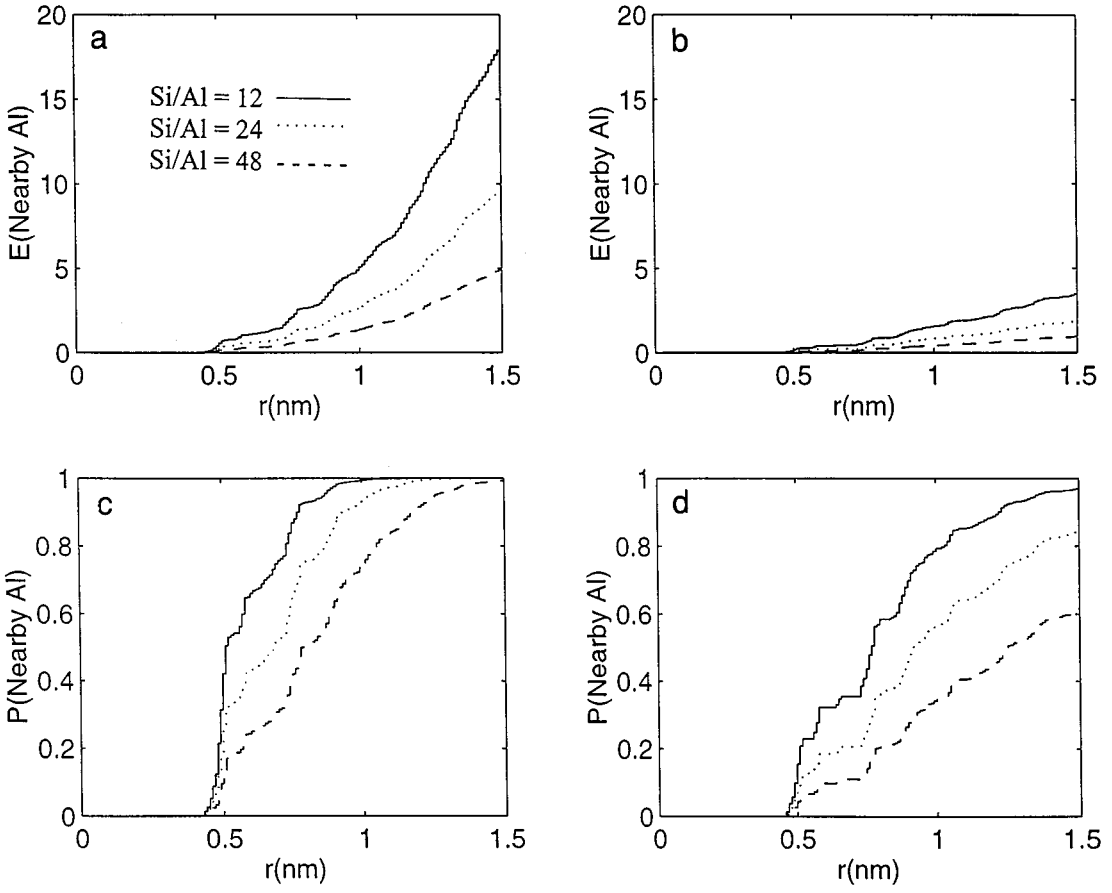

FIG. 6. Expectation of nearby Al within a given radial distance from a given Al (a) without restrictions and (b) restricted to the straight channel and probabilities of at least one nearby Al with a given radial distance (c) without restrictions and (d) restricted to the straight channel. Calculations are shown for Si/Al ratios of 12, 24, and 48.

by Al atoms times the number of T sites within a sphere of radius $r = 1.0$ nm. This approach does not restrict the center of the sampling sphere to T sites occupied only by Al atoms and, hence, over counts the number of Al atoms in a sphere surrounding one Al atom. It also ignores the dominant short-range correlations.

The fraction of Al atoms located in pairs of charge-exchange sites where M^{2+} or $[M–O–M]^{2+}$ cations can be stabilized and the maximum expected values of M^{2+}/Al and $[M–O–M]^{2+}$/Al are determined in the following manner. If it is assumed that there are no preferential pairs of sites for either type of cation, then it is only necessary to determine the probability of an Al atom lying within an acceptable range. Based on the bond lengths and angles we have observed in our quantum chemical calculations on Pd [2], we estimate the radial separation between Al atoms to be 0.55 and 0.85 nm for M^{2+} and $[M–O–M]^{2+}$ cations, respectively. For the stabilization of M^{2+} cations, Fig. 6 shows that for $r = 0.55$ nm $P = 0.54$ when Si/Al = 12 and $P = 0.34$ when Si/Al = 24. Since this calculation includes Al–Al pairs occurring within the walls of the zeolite, a better estimate of P is to look only at those pairs occurring at the surface of the straight channels. A similar result is expected for the sinusoidal channels but is more difficult to calculate. For these accessible sites, the values of P decrease to $P = 0.23$ for Si/Al = 12 and $P = 0.13$ for Si/Al = 24 and $r = 0.55$ nm. The corresponding estimates of M^{2+}/Al are then 0.12 for Si/Al = 12 and 0.07 for Si/Al = 24. Consistent with these estimates, recent experiments show that for ZSM-5 with Si/Al = 18 the maximum loading of Pd^{2+} for highly selective NO reduction by CH_4 is approximately Pd^{2+}/Al = 0.05 (7).

For the stabilization of the $[M–O–M]^{2+}$ cations, Fig. 6 shows that for $r = 0.85$ nm, $P = 0.59$ when Si/Al = 12 and $P = 0.38$ when Si/Al = 24 along a straight channel. The present results concerning the stabilization of $[M–O–M]^{2+}$ cations differ considerably from those reported by Feng and Hall (5). These authors report that for $[Fe–O–Fe]^{2+}$ the maximum value of P is 1.0 for Si/Al = 11 and 0.93 for Si/Al = 19. The difference between our calculations and those of Feng and Hall lies in the method used to calculate P. Our calculation is based on Eq. [5], whereas Feng and Hall determine the maximum value of P as $P = E - 1$,

a relationship that does not have a theoretical basis. Using the values of P reported here, we estimate that the maximum value of $[M–O–M]^{2+}/Al$ is 0.30 for Si/Al = 12 and 0.19 for Si/Al = 24.

CONCLUSIONS

The statistics of Al distribution in ZSM-5 have been determined using a stochastic method and compared with those based an approximate analytical treatment. Many properties of catalytic importance in zeolites (e.g., the number of NNN) are influenced by short-range structural features. Our simulation shows that the dominant correlations that influence such properties are well represented by Löwenstein's rule. Thus, analytical models that incorporate this rule are adequate for determining many properties of relevance to catalysis. This result is quite general and not restricted to a particular type of framework. We demonstrate our findings using ZSM-5 as an example.

The fraction of Al atoms having Al atoms in NNN T sites is found to vary from 0.64 for Si/Al = 12 to 0.22 for Si/Al = 48. Since only the nearby pairs of Al T sites located on the walls of the straight and sinusoidal channels are capable of stabilizing M^{2+} and $[M–O–M]^{2+}$ cations, the fraction of such pairs of sites has been estimated and from this maximum values for M^{2+}/Al and $[M–O–M]^{2+}/Al$. The corresponding values are 0.12 and 0.30 for Si/Al = 12 and 0.07 and 0.19 for Si/Al = 24. The theoretically determined values of M^{2+}/Al are consistent with experiment observation for Pd–ZSM-5.

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