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Site Availability and Competitive Siting of Divalent Metal Cations in ZSM-5

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Accommodation of divalent cations (M^{2+}) and dimer cations ($[MOM]^{2+}$) in zeolites requires the presence of two charge-exchange sites in close proximity to each other. Since each charge-exchange site is associated with a framework Al atom, this constraint requires that 2 Al atoms be located in next-nearest-neighbor T sites. The maximum number of divalent cations that can be accommodated by ZSM-5 as either $Z\text{-}M_2^+Z^-$ or $Z^-[MOM]^{2+}Z^-$ (where Z^- represents a cation-exchange site in the zeolite) has been calculated for a given value of Si/Al, and the results are reported as the maximum value of M/Al. Two cases for the distribution of framework Al atoms are considered: random placement in T sites and placement governed by equilibrium thermodynamics. For both M^{2+} and $[MOM]^{2+}$ the maximum value of M/Al is significantly less than 0.5 and 1.0, respectively, because of the required constraints on the Al–Al pairs, and decreases as the Si/Al ratio increases. For M^{2+} cations the distribution of specific cations (Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}) was determined using energies predicted from electronic structure calculations. M^{2+} cations are preferentially situated in rings containing either five or six T atoms. The manner in which the Al atoms are distributed among T sites affects the distribution of M^{2+} cations among different types of rings. © 2000 Academic Press

INTRODUCTION

ZSM-5 containing charge-exchanged, divalent cations are active catalysts for a number of reactions. Examples include Cu–ZSM-5 for NO decomposition (1, 2), Co–ZSM-5 for NO reduction by hydrocarbons (1, 2), Zn–ZSM-5 for dehydrocyclization of C_6 and C_7 alkanes to aromatics (3), Pd–ZSM-5 for methane combustion (4), and Pt–ZSM-5 for the production of acrylonitirile and acetonitirile from butane, isobutane, propane, or propene (5). Since the catalytic properties of the cations can depend on the location of the cation relative to the zeolite framework, there is an interest in understanding the manner in which metal cations are coordinated to the O atoms of the zeolite framework and the location of the charge-exchange sites within the channel system.

Divalent metal cations, M^{2+}, can be charge-exchanged into zeolites in several different ways. Where there are isolated charge-exchange sites (i.e., created by the presence of an Al atom in a T site such that their are no other Al atoms within 5.75 Å (6)) M^{2+} coordinates to 2 of the 4 O atoms connected to the framework Al atom and is further charge-compensated by an OH^- anion. Such a structure is designated $Z^-[M(OH)]^{2+}$. Divalent cations can also site at locations where there are two charge-exchange sites in proximity. Such circumstances are created when there are two Al atoms in a ring containing four, five, or six T atoms. This type of structure is represented by $Z^-M^{2+}Z^-$. Yet a third possibility exists when two metal cations form a dimer, e.g., $[MOM]^{2+}$. Charge compensation requires that the dimer is associated with two charge-exchange sites that are within a specified distance of each other. Structures containing a dimer cation can be described as $Z^-[MOM]^{2+}Z^-$. The three classes of sites are illustrated in Fig. 1.

While there are no constraints on the placement of M^{2+} as $Z^-[M(OH)]^+$, the maximum number of M^{2+} cations that can be held as $Z^-M^{2+}Z^-$ or $Z^-[MOM]^{2+}Z^-$ depends on the distribution of pairs of Al atoms in the framework and this, in turn, depends on the Si/Al ratio. Several efforts have been undertaken to predict the distribution of Al atoms in silicon-rich zeolites such as ZSM-5 (6–8). In the present study, we examine the distribution of Al under two assumptions. The first is that Al atoms are distributed randomly among the T sites in ZSM-5 and the second is that the Al is distributed in accordance with the Boltzmann probabilities associated with the binding energies of the metallic species to the zeolite (9). The number of potential pairs of charge-exchange sites that can accommodate M^{2+} or $[MOM]^{2+}$ cations is calculated and the results are represented as the maximum value of M/Al for a given Si/Al ratio. The distribution of M^{2+} cation among rings containing five and six T atoms is also determined for Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}.

COMPUTATIONAL METHODS

The methodology used to represent ZSM-5 and to count the number of sites that can accommodate M^{2+} and $[M–O–M]^{2+}$ cations is similar to that described previously (6). The zeolite is modeled with a periodic cell consisting of 2-unit cells based on the crystal structure of ZSM-5 (10)

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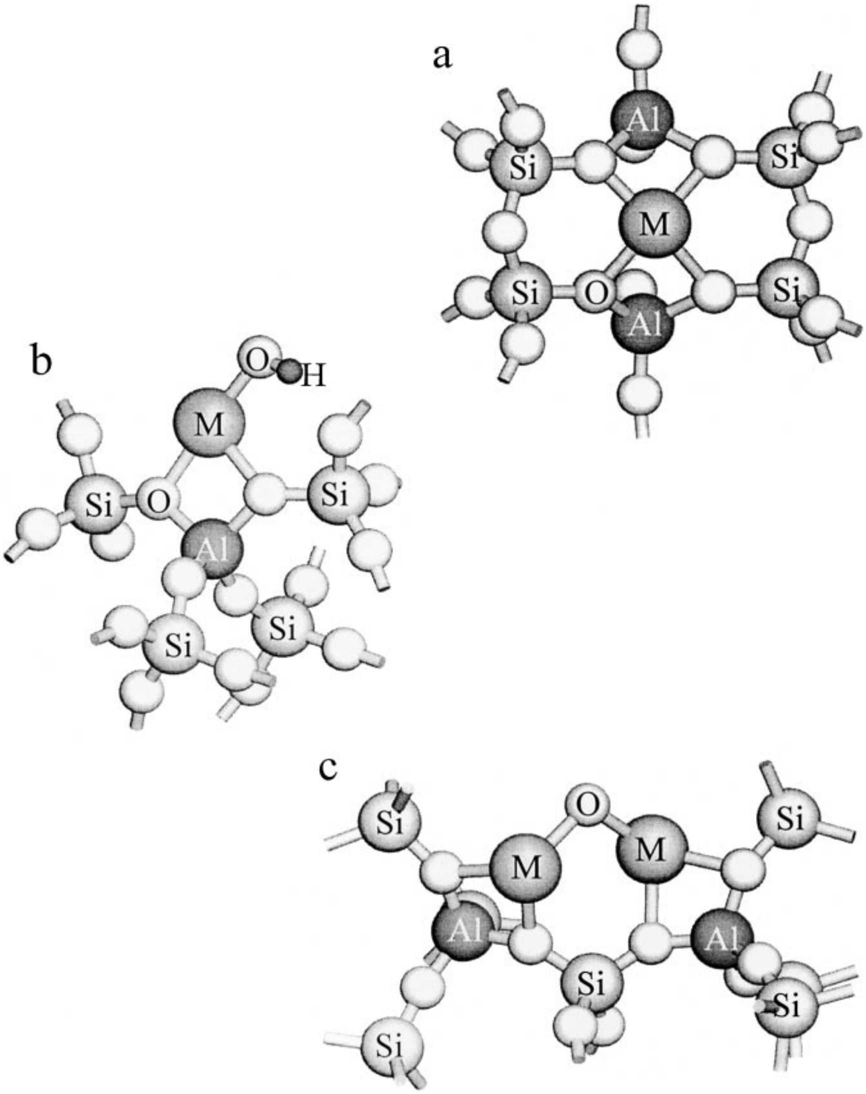

FIG. 1. Possible siting of divalent metal cations in ZSM-5: (a) $Z^-M^{2+}Z^-$; (b) $Z^-[M(OH)]^{2+}$; and (c) metal oxide complex, $Z^-[MOM]^{2+}Z^-$.

(see Fig. 2). Up to 18 Al atoms are placed within the periodic cell with the restriction that no two Al atoms can be placed at adjacent T sites (i.e., Löwenstein's rule). Each integer occupation of Al atoms (n) in the cell corresponds to a Si/Al ratio ($\mathrm{Si/Al} = (192 - n)/n$).

Two limiting cases were used for placement of Al atoms at T sites in the zeolite framework. In the first case, Al atoms were placed randomly with Löwenstein's rule as the only constraint. One million realizations of the Al distribution were sampled for each Al loading to determine the distribution of sites that could accommodate either an M^{2+} or an $[M–O–M]^{2+}$ cation. A realization is one particular arrangement of Al atoms for a given Si/Al ratio. In the second case, the energetic differences of placing Al in various T sites (9) were taken into consideration by using Boltzmann weights, together with Löwenstein's rule. For each Al loading, 10 million Metropolis Monte Carlo moves were attempted to reach an equilibrium distribution of Al atoms at 453 K (a typical ZSM-5 synthesis temperature). After equilibrium was achieved, one million more Metropolis Monte Carlo moves were attempted and each was considered a realization of the Al distribution. For each realization, the distribution of sites that can accommodate M^{2+} or $[M–O–M]^{2+}$ cations was determined.

Several requirements must be met to accommodate a $[M–O–M]^{2+}$ cation: a pair of framework Al atoms must be available within a specified distance of each other; the pair of Al atoms cannot be located on opposite sides of a zeolite wall; and each Al atom can be associated with only one $[M–O–M]^{2+}$ cation. A 192×192 matrix ($\mathbf{A}$) is defined to represent all possible T-site pairs in the periodic cell. Matrix element A_{ij} is assigned the value 1 if the i, j T sites composing a pair are within a given distance (d) and are not located on opposite sides of a zeolite wall. If these

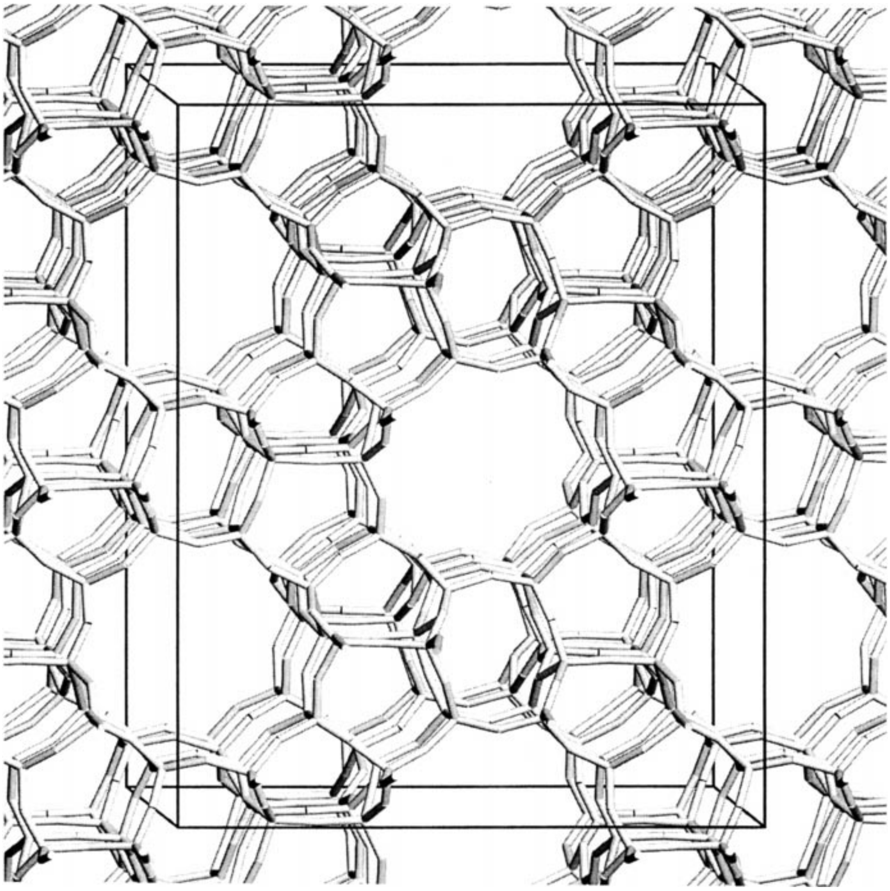

FIG. 2. Model of ZSM-5 containing 2-unit cells (192 T sites) with periodic boundary.

conditions do not hold, A_{ij} is assigned the value 0. For each realization, n Al atoms are placed at T sites randomly, with the restriction that they are not nearest neighbors to one another. These randomly selected Al T sites are associated with a vector **z**, such that the element z_i corresponds to the address of the ith Al T site. A matrix **B** is then constructed to represent the pairs of all selected Al sites for the bth realization. **B** is defined such that $B_{ij} = A_{z_i z_j}$. In each realization, many Al–Al pair configurations are possible. Due to the nature of the zeolite crystal structure, not all of these configurations are distinct from each other. The number of statistically distinct Al–Al pair configurations is given by $n!/(2^{n/2}(n/2)!) = 1 \times 3 \times 5 \cdots \times (n-1)$ (where n is always even). For each distinct Al–Al pair configuration, the number of Al–Al pairs is counted which satisfies the criteria that the Al–Al distance $\leq d$, the Al atoms in the pair are not separated by a zeolitic wall, and each Al atom is in only one pair. The number of allowed pairs (p) is given by

$$p = \sum_{l=1}^{n/2} B_{z_{2l-1}, z_{2l}} \qquad [1]$$

for each distinct Al–Al pair configuration. For each realization, the maximum number of allowed pairs is the maximum value of p determined from all unique Al–Al pairing configurations. This process is repeated for 10^6 realizations for a given Al occupation (n). The maximum number of allowed pairs is averaged over all realizations. The average number of maximum allowed pairs is related to the maximum M/Al ratio for the $[\mathrm{M–O–M}]^{2+}$ cation by the following formula: $\mathrm{M/Al} = (2 \times p)/n$. The M/Al ratio is determined for a range of Al contents (n), corresponding to Si/Al ratios between 11 and 95, and for a range of allowable Al–Al pair distances.

The distribution of divalent metal cations (M^{2+}) in ZSM-5 was based on calculations of the relative stability of placing M^{2+} cations in different sites (11). While an exhaustive examination of all sites was not undertaken, some general trends were determined. It was observed that the most stable sites for divalent metal cation coordination are 5- and 6-membered T-site rings with two Al T sites located within 5.75 Å. A second finding was that the Gibbs standard state free energy for the following process was negative for temperatures above 470 K for all of the metals and 5- and 6-membered rings considered,

$$\begin{aligned} &\mathrm{Z^-{}_{I5}M^{2+}(OH)^-} + \mathrm{Z^-H^+Z^-H^+} \\ &\quad \rightarrow \mathrm{Z^-{}_{I5}H^+} + \mathrm{Z^-M^{2+}Z^-} + \mathrm{H_2O_{(g)}}. \end{aligned}$$

Therefore, divalent metal cations will preferentially bind to rings containing two Al T sites. This does not preclude metal cation binding to sites with one Al T site if the zeolite has a high metal loading. Accordingly, we consider the placement of M^{2+} cations in four preferential locations: bent 5 T-site rings (5B), flat 5 T-site rings (5F), bent 6 T-site rings (6B), and flat 6 T-site rings (6F). The classification of rings as bent was based on visual inspection of each ring within the unit cell (an example of each is shown in Fig. 3). Rings with four T sites are not considered viable binding sites because they are statistically rare and extremely unfavorable energetically (7, 11). Therefore, the criterion for an available ring-binding site ($Z^-M^{2+}Z^-$) is 5- or 6-membered rings containing two Al T sites located within 5.75 Å of each other.

The technique for counting available ring sites that can accommodate M^{2+} cations is similar to that discussed for $[M–O–M]^{2+}$ cations. Each element of the matrix **A** represents a potential T-site pair and is assigned a value of 1 if it is an acceptable pair of sites and 0 if it is not. Acceptable pairs must be within 5.75 Å and share a 5- or 6-membered ring. Several scenarios were considered: M^{2+} cation placement in 5- or 6-membered rings, flat or bent, and M^{2+} cation placement in all 5- and 6-membered rings. The determination of the maximum number of acceptable Al–Al pairs and the averaging over 10^6 realizations is the same as that discussed previously for the $[M–O–M]^{2+}$ cations. The average value of the maximum number of Al–Al pairs is used to calculate the maximum value of M/Al by the following equation: $M/Al = p/n$. M/Al was determined for a range of Al contents (n) and for various types of rings or combination of all ring types.

To determine the distribution of metal cations among sites, one must account for the differences in binding energies of an M^{2+} cation binding to various sites. These are determined by considering processes such as

$$Z^-M^{2+}Z^-_{\text{(site 1)}} + Z^-H^+Z^-H^+_{\text{(site 2)}} \rightarrow Z^-H^+Z^-H^+_{\text{(site 1)}} + Z^-M^{2+}Z^-_{\text{(site 2)}}.$$

For this calculation all 5- and 6-membered rings containing two Al atoms within 5.75 Å of each other are considered acceptable sites for a divalent metal cation. For each divalent metal cation, the elements of a matrix **E** (192 × 192) representing possible Al–Al pairings, are assigned a nonzero value if they form an acceptable ring-binding site. Each

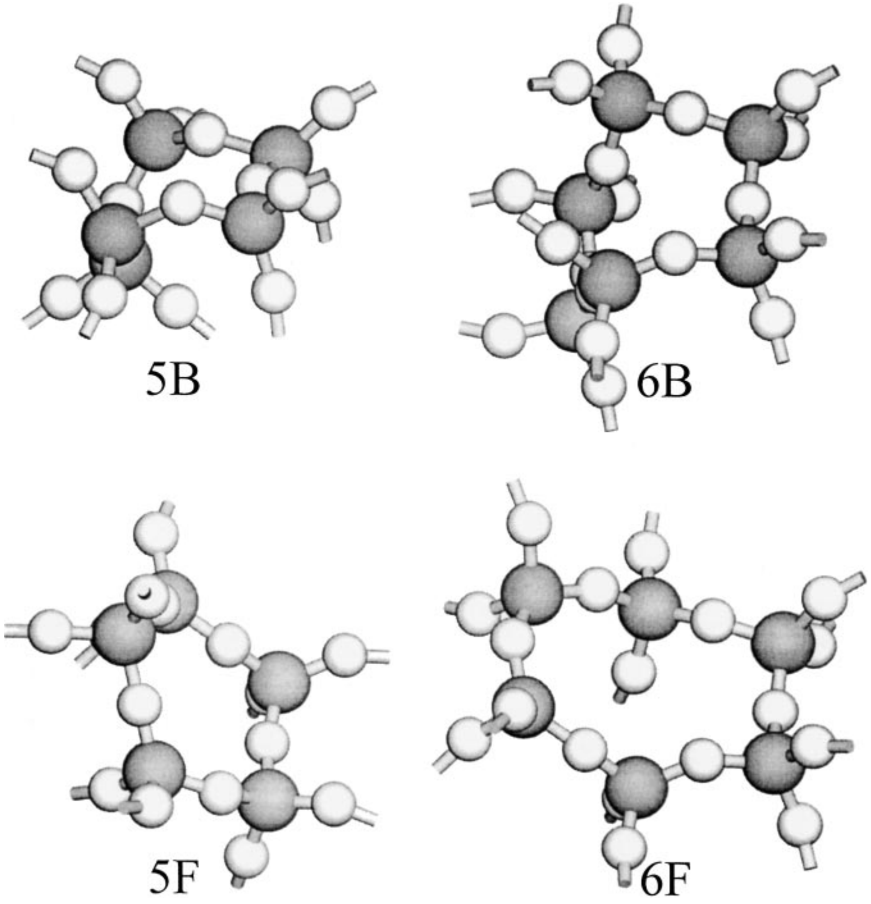

FIG. 3. Examples of each ring classification: bent 5 T (5B), flat 5 T (5F), bent 6 T (6B), and flat 6 T (6F).

matrix element, E_{ij}, is assigned the value of the relative energy of the metal cation located in that the particular type of ring (5B, 5F, 6B, or 6F) in which it is situated. For Al–Al pairs that share more than one ring, the matrix element is taken as a Boltzmann average of all available ring binding sites at $T = 773$ K

$$\left(\text{i.e., } \langle E_{ij}\rangle = \frac{\sum_k E_{ijk}\, e^{-E_{ijk}/kT}}{\sum_k e^{-E_{ijk}/kT}}\right),$$

where k is the number of shared ring types. For each Al realization (b), the fractional ring occupation by M^{2+} cations in each ring type, X_{ab} (where a = 5B, 5F, 6B, or 6F), is determined by a Boltzmann weighting over each configuration of Al–Al pairs (c), which contains the maximum number of acceptable pairs for the bth realization. The value of X_{ab} is then given by

$$X_{ab} = \sum_c X_{abc}\, e^{-E_c/kT} \Big/ \sum_c e^{-E_c/kT}, \qquad [2]$$

where E_c is the total energy associated with the placement of M^{2+} cations in the cth arrangement of Al pairs and X_{abc} is determined by dividing the number of sites of type (a) by the total number of ring sites for the bth realization and the cth arrangement. The value of E_c is given by

$$E_c = \sum_{l=1}^{n/2} E_{z_{2l-1},z_{2l}} \qquad [3]$$

where $E_{z_{2l-1},z_{2l}}$ represents the energy for an M^{2+} cation at a site for this configuration of Al–Al pairs. The fractional ring occupation is then averaged over 10^6 Al realizations.

$$X_a = \sum_{b=1}^{10^6} X_{a,b} \Big/ 10^6. \qquad [4]$$

This process is repeated for each of the seven divalent metal cations.

RESULTS

The maximum M/Al ratio for $[\text{M–O–M}]^{2+}$ cations is presented in Fig. 4 as a function of Si/Al. Curves are shown for several maximum allowable Al–Al distances for both random placement of Al atoms in the zeolite framework and for placement governed by thermodynamics. In both instances the M/Al ratio is noticeably less than 1.0 and decreases as the Si/Al ratio increases. For a given Si/Al ratio, the value of M/Al increases as the maximum allowable distance between Al atoms increases. We note that while the curves for random and thermodynamically governed placement of Al atoms are comparable for maximum Al–Al distances of 5.5 and 7.5 Å, the curves for the other three limits of Al–Al distance differ between the two cases. When the distribution of framework Al atoms is governed by thermodynamics, there is a tendency for Al atoms to site in an evenly distributed manner, at specific T sites. As a consequence, there is a greater probability of finding two Al

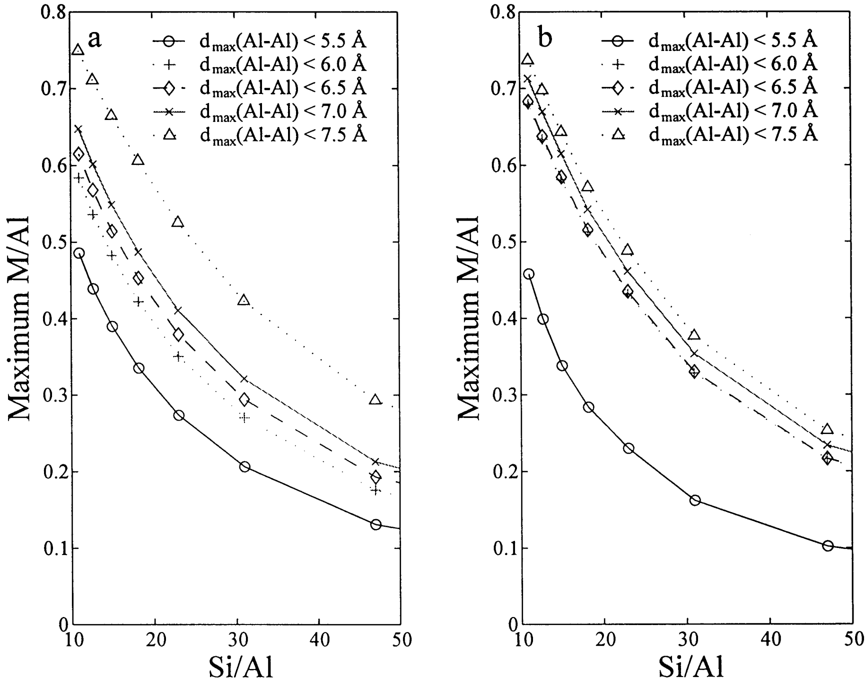

FIG. 4. Maximum M/Al ratio for $[\text{M–O–M}]^{2+}$ cations: (a) random placement of Al; and (b) equilibrium placement of Al (453 K).

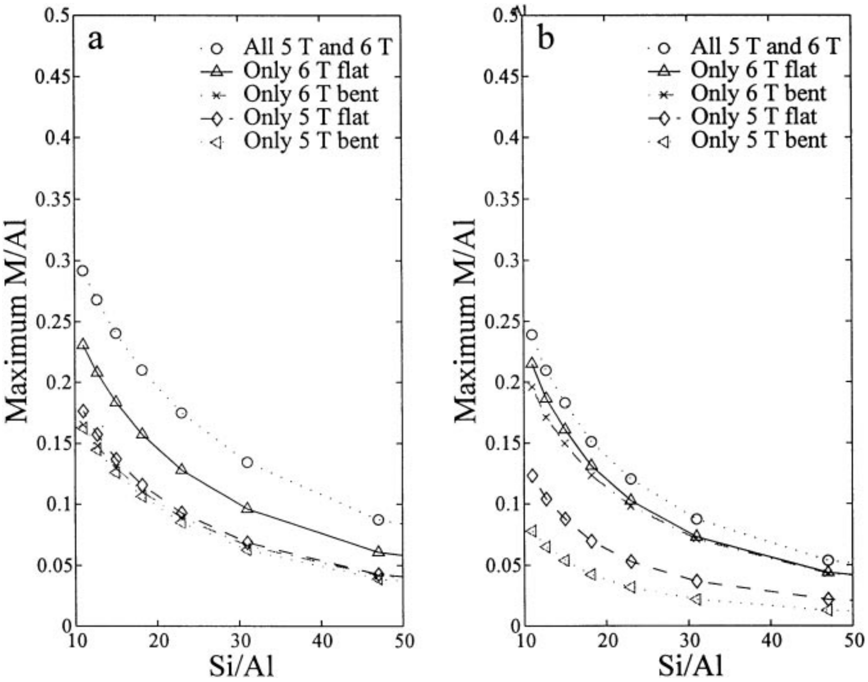

FIG. 5. Maximum M/Al ratio for M^{2+} cations in rings: (a) random placement of Al; and (b) equilibrium placement of Al (453 K).

atoms within the distances of these favored T sites, in this case 6.0 Å.

Figure 5 shows the maximum number of M^{2+} cations that can be accommodated in 5- and 6-membered rings containing two Al atoms separated by a distance of less than 5.75 Å. Again two cases are considered: one for random placement of framework Al atoms and the other for thermodynamically governed placement of Al atoms. If one considers all 5- and 6-membered rings, the maximum value of M/Al is slightly lower in the latter case. For both cases, the maximum value of M/Al decreases as the Si/Al ratio increases. Results assuming only one type of ring is available (5 T bent, 5 T flat, 6 T bend, or 6 T flat) are also presented. This number of available sites in bent 5 T and flat 5 T rings is significantly reduced when the distribution of Al is governed by thermodynamics rather than totally random placement of Al atoms. On the other hand, the number of sites in bent 6 T and flat 6 T rings remains the same or increases slightly if one places Al in accordance with thermodynamics. These changes are a result of a reduction in the number of Al atoms located in 5-membered rings. Table 1 shows the expected fractional occupations of Al in all T sites based on their relative energy and a Boltzmann distribution. Only four T sites (T1, T7, T8, and T9) have fractional occupations above 0.05. The number of available sites in 5-membered rings is reduced significantly because only 27% of 5 T rings have at least two of these highly occupied Al T sites in nonadjacent positions. By comparison, 58% of the 6-membered rings have at least two of these highly occupied Al T sites in nonadjacent positions.

As in the case of $[M–O–M]^{2+}$ cations, the maximum value of M/Al for placement of M^{2+} as $Z^-M^{2+}Z^-$ is significantly less than 0.5 and decreases with increasing Si/Al ratio. It is noted that M^{2+} cations can also be accommodated as $Z^-[M(OH)]^{2+}$ without any further constraint. What this means is that if $Z^-[M(OH)]^+$ and $Z^-M^{2+}Z^-$ are the only species present, then the maximum value of M/Al will be 1.0 for all values of Si/Al, but the fraction of all M^{2+} cations held as $Z^-M^{2+}Z^-$ will be governed by Fig. 5.

The distribution of M^{2+} cations among the four types of charge-exchange sites considered is shown in Fig. 6 for Si/Al ratios of 11 and 47 at 773 K. Results are presented for

TABLE 1

Equilibrium Distribution of Al among T Sites ($T = 453$ K)

T site	Relative energy (kcal/mol) [9]	Fractional occupation
T1	0.0	6.4×10^{-1}
T2	4.1	6.8×10^{-3}
T3	4.7	3.4×10^{-3}
T4	3.0	2.3×10^{-2}
T5	5.7	1.1×10^{-3}
T6	8.7	4.3×10^{-5}
T7	1.3	1.5×10^{-1}
T8	2.2	5.6×10^{-2}
T9	2.2	5.6×10^{-2}
T10	3.1	2.1×10^{-2}
T11	2.8	2.9×10^{-2}
T12	3.9	8.4×10^{-3}

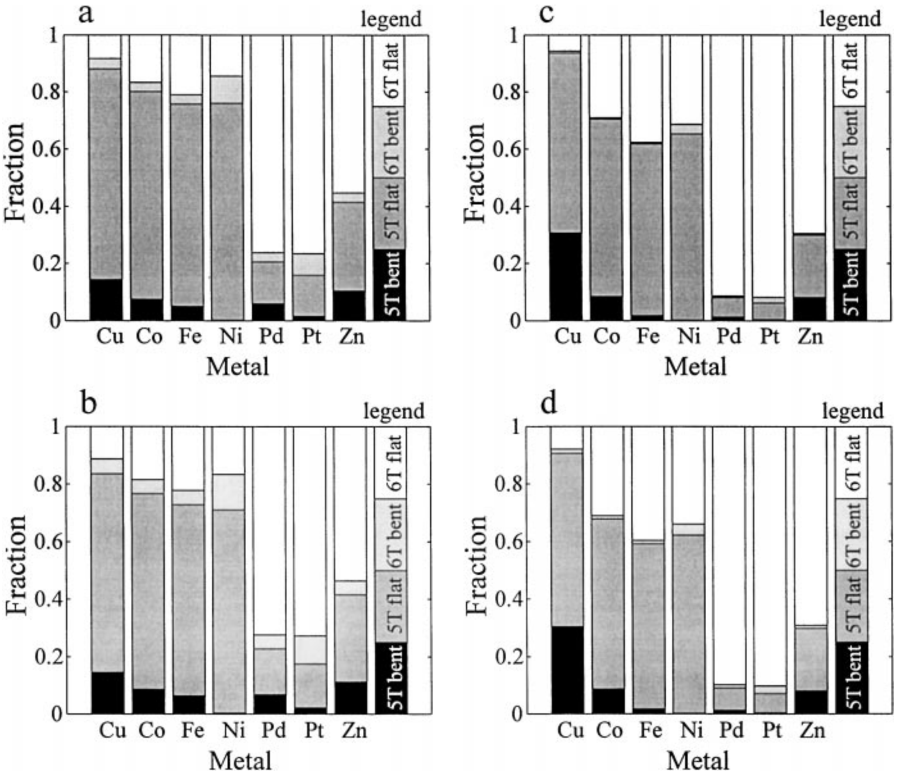

FIG. 6. Fractional distribution of metal cations in rings (773 K): (a) Si/Al = 11, random placement of Al; (b) Si/Al = 47, random placement of Al; (c) Si/Al = 11, equilibrium placement of Al (453 K); and (d) Si/Al = 47, equilibrium placement of Al (453 K).

both random and thermodynamically governed placement of framework Al atoms. Comparisons of Figs. 6a and 6b, and Figs. 6c and 6d show that the Si/Al ratio has little effect on the distribution of M^{2+} cations among the four sites. It is also observed that Co^{2+}, Cu^{2+}, Fe^{2+}, and Ni^{2+} prefer the flat 5-membered rings, whereas Pd^{2+}, Pt^{2+}, and Zn^{2+} prefer the flat 6-membered rings. The larger cations prefer the 6-membered rings because of size considerations. The flat rings are preferred over bent ones because they afford better overlap of the orbitals of the metal cation with those of the O atoms to which the cation is coordinated (11). Placement of Al atoms in the zeolite framework in accordance with thermodynamics, rather than randomly, causes significant shifts in the populations of each ring type. For metals that prefer flat 5-membered rings, there is a decrease in the population of flat 5-membered rings. For metals that prefer flat 6-membered rings, there is a notable increase in the population of the flat 6-membered rings. These trends can be explained by the decrease and increase in the fraction of flat 5- and 6-membered rings available, respectively, if the Al atoms are placed in accordance with thermodynamics.

CONCLUSIONS

Binding of M^{2+} and $[M–O–M]^{2+}$ cations requires a pair of charge-exchange sites that are in proximity to one another. The present work has shown that the maximum number of divalent cations, either M^{2+} or $[M–O–M]^{2+}$, that can be held per framework Al atom is considerably less that 0.5 and 1.0, respectively. This is because of the required constraints on Al–Al pairs. For $[M–O–M]^{2+}$, the two Al atoms composing the pair have to be within a certain distance (which depends on the metal considered), the Al atoms may not be separated by a zeolitic wall, and the Al atoms can belong to only one pair. For M^{2+}, there are the constraints that the two Al atoms share a 5- or 6-membered ring and be located at a distance less than 5.75 Å apart. The maximum value of M/Al for the accommodation of $[M–O–M]^{2+}$ and M^{2+} decreases as the Si/Al ratio of the zeolite increase.

Comparison of results determined for random Al placement versus Al placement governed by thermodynamics shows that the maximum value of M/Al is affected differently for $[M–O–M]^{2+}$ and M^{2+} cations. In the former case, for maximum allowed Al–Al separation distances $\geq$6 Å, the maximum M/Al ratio increases when Al placement at T sites is governed by thermodynamics, whereas when the maximum allowed Al–Al separation distance $\leq$5.5 Å the opposite effect is observed. For M^{2+} there is a slight decrease in the maximum value of M/Al when M^{2+} is placed in all types of rings (5B, 5F, 6B, and 6F) and placement of Al is governed by thermodynamics. The distribution of M^{2+}

among 5B, 5F, 6B, and 6F rings is dependent on the nature of the cation. Co^{2+}, Cu^{2+}, Fe^{2+}, and Ni^{2+} site preferentially in 5F rings, whereas Pd^{2+}, Pt^{2+}, and Zn^{2+} prefer 6F rings. Because there is a significant reduction in the number of available 5-membered ring sites when Al is placed according to thermodynamics, there is a corresponding shift in the distribution of M^{2+} among the types of rings (5B, 5F, 6B, and 6F).

The techniques reported here may be employed for other zeolites with minor modifications. The source code used for the present study is available at www.cchem.berkeley.edu/∼akcgrp/Al_dist.c.

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