Statistical analysis of Al distributions and metal ion pairing probabilities in zeolites

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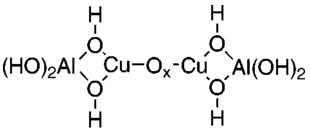
The distributions of Al tetrahedral sites are studied as a function of Si : Al ratio (from 11 to 95) in three zeolites: ZSM-5, ferrierite, and mordenite. Al configurations obeying Loewenstein's rule are generated by a Monte Carlo procedure and analyzed in terms of accessibility to specific channels. The distribution of pairs of Al sites accessible to the same channel segregates into distinct nearest-neighbor and ring-bridging types. Such pairs provide favorable binding environments for extraframework MO_xM^{2+} cations in the metal-ion-exchanged forms of the zeolites. In all three zeolites, the probability of a given Al site having at least one suitable partner for pairing within 8.5 Å is close to unity for typical Si : Al ratios. The probability at shorter distances is more sensitive to the zeolite structure, reflecting the larger number of highly puckered five- and six-membered rings in ZSM-5. This sensitivity, and its implications for CuO_xCu^{2+} formation in the three Cu-exchanged forms, may explain why Cu-ZSM-5 is the most active of the three for catalytically decomposing NO.

Keywords: zeolites, Al pairs, Cu oxocations, ZSM-5, mordenite, ferrierite, Monte Carlo sampling, NO decomposition

1. Background

Metal-ion-exchanged ZSM-5 catalysts have among the highest known activities for the catalytic decomposition and selective catalytic reduction (SCR) of NO_x [1]. Despite considerable experimental [2–7] and theoretical [8–10] effort, fundamental questions remain concerning the nature of the metal ion active sites, including their oxidation states, coordination environments, and states of aggregation. ZSM-5 zeolites are high in silica, typically having Si : Al ratios greater than 15 : 1. Most exchanged metal ions are believed to be atomically dispersed, and these isolated ions are often presumed to dominate the NO_x catalytic chemistry. However, recent evidence indicates that divalent oxocations (MO_xM^{2+}, $x = 1,\ 2$) may also be important intermediaries. For instance, the high activity of Fe-ZSM-5 in NO_x SCR has been attributed to the existence of $FeOFe^{2+}$ or $(HO)FeOFe(OH)^{2+}$ oxocations [11–13]. Density functional theory (DFT) calculations [14,15], empirical models [16–18], and indirect experimental results [19–27] support a role for CuO_xCu^{2+} oxocations in NO decomposition catalysis in Cu-ZSM-5, and Cu oxocations have also been invoked to explain the "autoreduction" of Cu^{2+}-exchanged ZSM-5 [23,24,28].

The ability of zeolites to host metal ions arises from charge balance. While a completely siliceous zeolite would be charge neutral, isoelectronic substitution of Al for Si in some SiO_4 tetrahedral (T) sites introduces negative charges into the lattice that are compensated by extra-lattice cations. Monovalent cations, such as Cu^+, are well known to coordinate to lattice O adjacent to individual Al substitution sites [3,9,29–32]. In the same way, the MO_xM^{2+} oxocations are expected to be charge compensated by a pair of nearby Al T sites [14,15,31]. In previous work, DFT calculations were used to investigate the stability of divalent Cu oxocations in model zeolite supports consisting of two unlinked Al T sites terminated with H atoms (**1**) [14].



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The oxocations were found to be strongly bound over a range of Cu–O_x–Cu separations and T-site orientations, with the Cu–Al separations nearly constant and the Cu–O_x–Cu moiety stretching or bending as necessary to accommodate the T-site locations. Calculations using larger zeolite models consisting of five- or six-membered rings containing a pair of Al T sites confirm these results [15].

A prerequisite for forming Cu oxocations is thus the existence of pairs of suitably located Al T sites accessible within the same zeolite channel. Approximate analytic models have been developed to estimate the probability of next-nearest-neighbor Al T sites (–Al–O–Si–O–Al–) that ignore the long-range zeolite structure [33,34]. Because of the complicated topology of zeolite lattices and the requirement of satisfying Loewenstein's rule, which forbids nearest-neighbor Al T sites (–Al–O–Al–) [35], more general treatments of Al separation statistics have relied on Monte Carlo simulations and have been restricted to the

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ZSM-5 crystal structure [11,36]. Feng and Hall attempted to determine the probability of $FeOFe^{2+}$ pair formation in ZSM-5 as a function of Si : Al ratio and Fe loading [11], but their approach had serious deficiencies that render the results suspect [36]. More recently, Rice et al. [36] used a Monte Carlo approach to examine the distribution of Al T sites in ZSM-5 and used the results to estimate the number of binding sites suitable for divalent oxocations for several Si : Al ratios.

In this work, we use Monte Carlo simulations to determine the distribution of Al–Al pairs suitable for MO_xM^{2+} oxocation binding in ZSM-5, ferrierite, and mordenite, including all channels and intersections in which oxocations might reside. These three zeolites are of particular interest because they are structurally similar, sharing the same secondary building unit, the same typical ranges of Si : Al ratio, and similarly sized channels [37,38], but the Cu-exchanged forms of the latter two are much less active for NO decomposition than is ZSM-5 [39–42]. We find the distribution of Al–Al pairs to segregate into distinct structural types as a function of Al–Al separation. While the distributions among the three zeolites are superficially similar, closer inspection reveals distinct differences, particularly at short separations, which may contribute to their differing catalytic activities.

2. Approach and models

Previous studies [43,44] support the assumption that the Al substitution can be treated as essentially random within the restrictions of Loewenstein's rule. Thus, we use a Monte Carlo approach to generate random samples of Al substitution in a zeolite supercell (following Loewenstein's rule) and count Al-substituted T-site pairs that satisfy certain pairing rules. These rules guarantee that an oxocation could bridge the two Al T sites: i.e., that the two are within a particular distance and that the intervening lattice does not block the bridging. We do not count situations in which the two T sites are close but reside in parallel channels or in intersecting channels, either of which would preclude formation of a bridging oxocation. We do include Al T-site pairs that are both close together and accessible from the same channel, thus allowing bridging along the channel, across the channel, or some combination of the two. To exclude interchannel bridging, we assign each T-site membership in particular channels and only count pairs between two sites that are both members of the same channel. To properly treat the channel intersections, each T site is allowed to have membership in multiple channels simultaneously. These rules are illustrated for ZSM-5 in figure 1.

The success of this channel-membership approach rests on the specific channel definitions. The ZSM-5 lattice includes four-, five-, and six-membered rings that combine to form the ten-membered straight and sinusoidal channels (table 1). The straight channels can be characterized as all T sites within 4.75 Å of a line running down the center of the channel, and these sites can be readily selected by looking at the (010) face of the ZSM-5 supercell (figure 2). Earlier Monte Carlo simulations only included these straight channels [36]; here we also include the sinusoidal channel T sites, which can be identified in a similar manner by looking at the (100) face and manually excluding 12 extra-channel T_8 sites to prevent unrealistic "around the corner" pairing (figure 2).

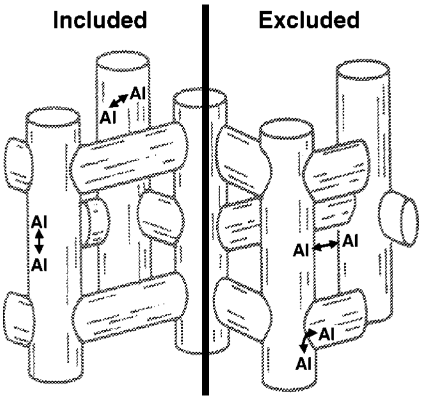

Figure 1. Bridging types in the ZSM-5 channels.

Table 1
Types of channels, number of T sites per unit cell, and average number of Al atoms per unit cell for given Si : Al ratios in ZSM-5, ferrierite, and mordenite.

	ZSM-5	Ferrierite	Mordenite
		Channels type	
	10-straight 10-sinusoidal	10-straight 8-straight 6-straight	12-straight 8-straight
		T sites/unit cell	
	96	36	48
Si : Al		Average Al/unit cell	
11	8.00	3.00	4.00
15	6.00	2.26	3.00
23	4.00	1.52	2.00
47	2.00	0.74	1.00
95	1.00	0.37	0.52

Ferrierite contains straight channels only. Ten- and six-membered rings form parallel channels running in the [001] direction. Eight-membered rings form channels that run in the [010] direction, perpendicular to the other two, and intersect the six-membered ring channels. Because only a single layer of T sites separates the eight-membered ring channels, some T sites border three channels concurrently. We define T-site membership in the eight- and ten-membered ring channels as above for ZSM-5. By this definition, the eight-membered ring channels also include all T-site pairs separated by less than 13 Å in six-membered ring channels; because in this work we are only interested in pairing separations less than 10 Å, it was not necessary to explicitly define six-membered ring channels.

Mordenite has two parallel straight channels, one bounded by circular twelve-membered rings and the other by elliptical eight-membered rings. Both are defined sim-

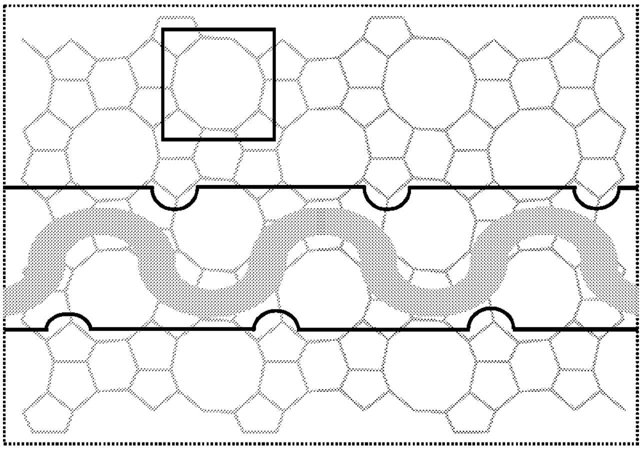

Figure 2. (010) projection of the ZSM-5 supercell, showing an end-on view of a straight channel and side view of a sinusoidal channel (shaded). The square (top) surrounds the T sites included in the straight channel definition and the irregular box (bottom) surrounds T sites assigned to the sinusoidal channel. O atoms are omitted for clarity.

ilarly to the straight channels in ZSM-5. The two channels are interconnected by cavities defined by two eight-membered rings and two four-membered rings. We incorporated the additional ten possible bridging combinations introduced by these cavities by defining specific pairing allowances based on T-site symmetry and explicit distances.

For each zeolite, a periodic supercell consisting of $3 \times 3 \times 3$ unit cells was constructed. A connectivity table was generated for each, which included the symmetry type, coordinates, the four nearest-neighbor T sites, and the channel membership information for each T site. These large supercells ensure that the periodicity in any direction is greater than twice the maximum Al–Al separations considered, preventing artificial interactions between the periodic images. The large cells also implicitly incorporate an averaging over local variations in Si : Al ratio. In their study of Al substitution in ZSM-5, Rice et al. [36] simulated a single unit cell and used a Poisson distribution to explicitly average over local variations in Si : Al ratio in a single unit cell; such averaging was found to have little effect on the Al statistics.

Because of the complicated lattice and pairing rules, the distribution of Al T-site pairs is non-analytic, and a stochastic Monte Carlo method is required to sample the distribution. A high quality random number generator [45,46] was used to create sample distributions of Al substitution in the zeolite lattice. By mapping the random numbers to an integer representation of the T sites, Al was substituted for Si. If a selected site was already marked as an Al, or if any of the four nearest-neighbor T sites contained an Al (Loewenstein's rule), the selection was rejected and another candidate site was chosen. This procedure was repeated until the specified amount of Al had been substituted into the sample. The Si : Al ratio was varied over a range from 11 to 95; because of their differing unit cell sizes, a given Si : Al ratio implies a different number of Al atoms per supercell for each zeolite (table 1).

We generated 10^4 samples for each zeolite and Si : Al ratio. The resulting expectation values and associated statistics were converged to less than a 0.1% change and verified by generating an additional 4×10^4 samples for ZSM-5 with no change in the averaged results. Each pair of Al-substituted T sites satisfying the pairing rules and within a distance of 10 Å was logged, including the T-site symmetry types, the Al–Al separation, and the channel membership types. From this data we determined the total number of Al pairs and the distribution of pairs by ring, channel, and T-site type.

The number of Al T-site pairs thus identified is an upper limit to the maximum loading of $\mathrm{MO}_x\mathrm{M}^{2+}$oxocations for a given Si : Al ratio. For instance, three unique pair configurations can be constructed from three Al-substituted T sites in close proximity (i.e., between sites A and B, B and C, and A and C), but only one of these configurations can be occupied with a $\mathrm{MO}_x\mathrm{M}^{2+}$ cation at a time. This overcounting of total oxocation coordination sites is difficult to correct for. In a dynamical, chemically reacting system in which these oxocations are continuously generated and consumed, however, the more important question to answer is the number of Al-substituted T sites that have the possibility of participating in oxocation bonding, i.e., the number that are not isolated by the pairing rules from all other Al-substituted sites. Thus, from the simulations we calculate the number of "accessible" partner Al sites that a particular Al-substituted site has within a given distance, averaged over all Al-substituted sites.

3. Results

Before using Monte Carlo sampling to look at samples with varying Si : Al ratios, we first examine the distributions of potential T-site pairs imposed by the ZSM-5, ferrierite, and mordenite lattice structures. Consistent with our assumption that any realistic Al distribution obeys Loewenstein's rule, we restrict our attention to distances beyond the first T-site neighbor (>4.2 Å). Figure 3 contains histograms of the number of accessible T-site partners binned by distance and averaged over all T sites. Between 4.2 and 10 Å the allowed T-site pairs can be segregated into four distinct groups corresponding to different nearest neighbor (NN) and ring types. The relative abundances of each type reflect the differing lattice structures of the three zeolites.

The first class, contained entirely between 4.2 and 5.8 Å, includes all second-NN Al T sites within rings of any size. The distribution with respect to distance varies somewhat, and all three zeolites have roughly the same number of accessible partners of this type. Those at shorter distances generally correspond to second NN in five- and six-rings, while those at greater separations correspond to larger rings typical of channel walls.

The second class includes third-NN Al in six-membered rings. The mordenite lattice contains two symmetry-equivalent six-membered rings per unit cell. Two T sites of the

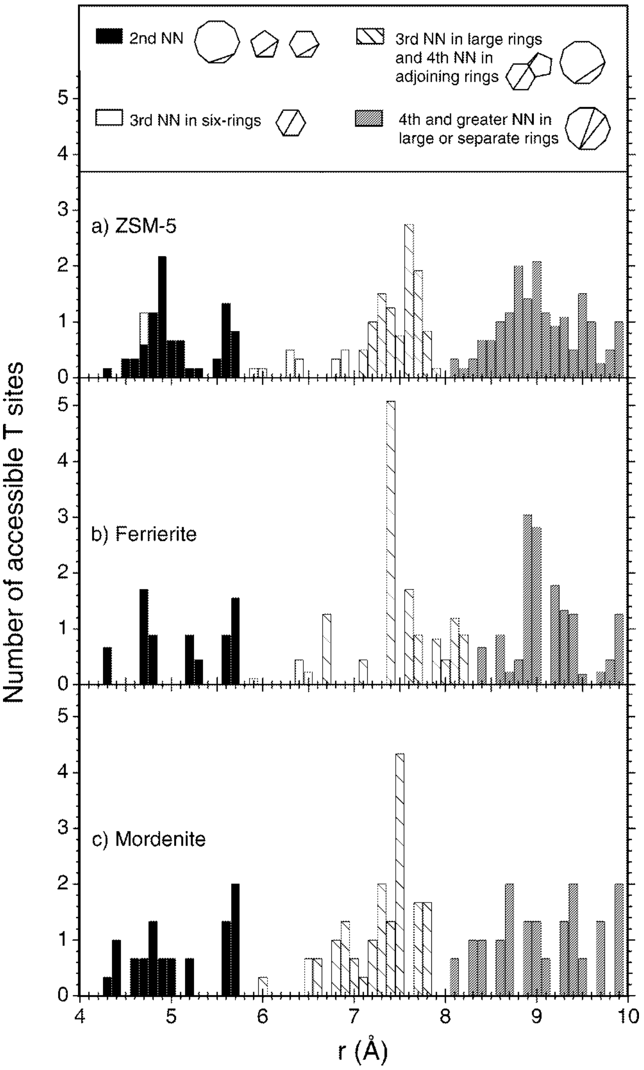

Figure 3. Number of accessible T-site partners averaged over all T sites, in ZSM-5 (a), ferrierite (b), and mordenite (c). The shadings approximately represent the partitioning into different nearest-neighbor (NN) classes.

ring are bridged by an additional framework T site that puckers the ring and pushes apart the remaining T sites (**2**).

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Al pairs between the unbridged T sites produce the single histogram peak at about 6.5 Å (figure 3(c)).

The ferrierite lattice includes two types of symmetry-distinct six-membered rings per unit cell. One is similar to **2** and also contributes Al pairs with separation of about 6.5 Å. The other six-membered ring is unbridged and flat: it forms one of the ferrierite straight channels, and Al pairs across this ring are separated by approximately 5.9 Å (figure 3(b)). The ZSM-5 lattice has thirteen symmetry-distinct six-membered rings [36]. Most of the resultant Al pair sites are in the same 5.9–6.5 Å range as in mordenite and ferrierite (figure 3(a)) and reside in similar types of rings. Visual inspection of these Al pair sites indicates that, in many cases, other geometric effects make the Al sites poorly situated to support bridging MO_xM^{2+} oxocations. A distinguishing feature of ZSM-5 is the existence of a significant fraction of Al pairs within six-membered rings separated by only 4.7 Å, a distance more typical of nearest neighbors. These pairs occur in fused six-membered rings unique to the ZSM-5 lattice (**3**).

3

Two of the T sites are simultaneously members of three different six-membered rings, and, because of this bridging, Al atoms in these two third-NN sites are unusually close together. DFT calculations have shown Cu oxocations to bind comfortably within this type of Al pair site [15].

The third class includes third-NN Al pairs in rings with more than six members, and fourth-NN Al pairs bridging neighboring five- and six-membered rings. Many of these pairs are good candidates for MO_xM^{2+} binding. Mordenite has eight-membered rings and ferrierite eight- and ten-membered rings which form parallel straight channels. Third-NN Al within these rings contribute many pairs between 5.8 and 8.2 Å. ZSM-5, which has ten-membered but no eight-membered rings, has pairs skewed to the higher end of this range (7.1–7.9 Å). Inter-ring bridging also contributes substantially in this range, reflecting the large number of neighboring five- and six-membered rings in ZSM-5.

Finally, the fourth class, which starts at roughly 8 Å, includes many different Al pair types, including those crossing ten-membered rings and between different rings along channel walls.

The actual numbers of Al pairs – and thus of potential MO_xM^{2+} binding sites – is a function of the Si : Al ratio in a particular sample. We first consider the expected number of such partners within a radius r of an Al-substituted site, $E(r)$. If the probability of a particular T site being occupied by an Al atom within a mostly siliceous lattice was uniform, then $E(r)$ would simply be the integral of the distribution in figure 3 multiplied by the fractional Al occupation. Loewenstein's rule introduces correlations into the Al distribution, and $E(r)$ must be determined stochastically.

Figure 4(a) shows $E(r)$ for ZSM-5 at five different Si : Al ratios. $E(r)$ is found to increase monotonically with r and to be inversely related to the Si : Al ratio. For a uniform density of Al atoms, $E(r)$ would scale with the volume of a sphere of radius r. The lattice causes $E(r)$ to be jagged; the sharp rises around 5 Å and just below 8 Å reflect the peaks in the T-site pair histogram (figure 3). At a moderately high Si : Al ratio of 23 and cutoff distance of 8.5 Å, roughly corresponding to the maximum separation bridgeable by a $Cu–O_x–Cu^{2+}$ oxocation, we calculate E to

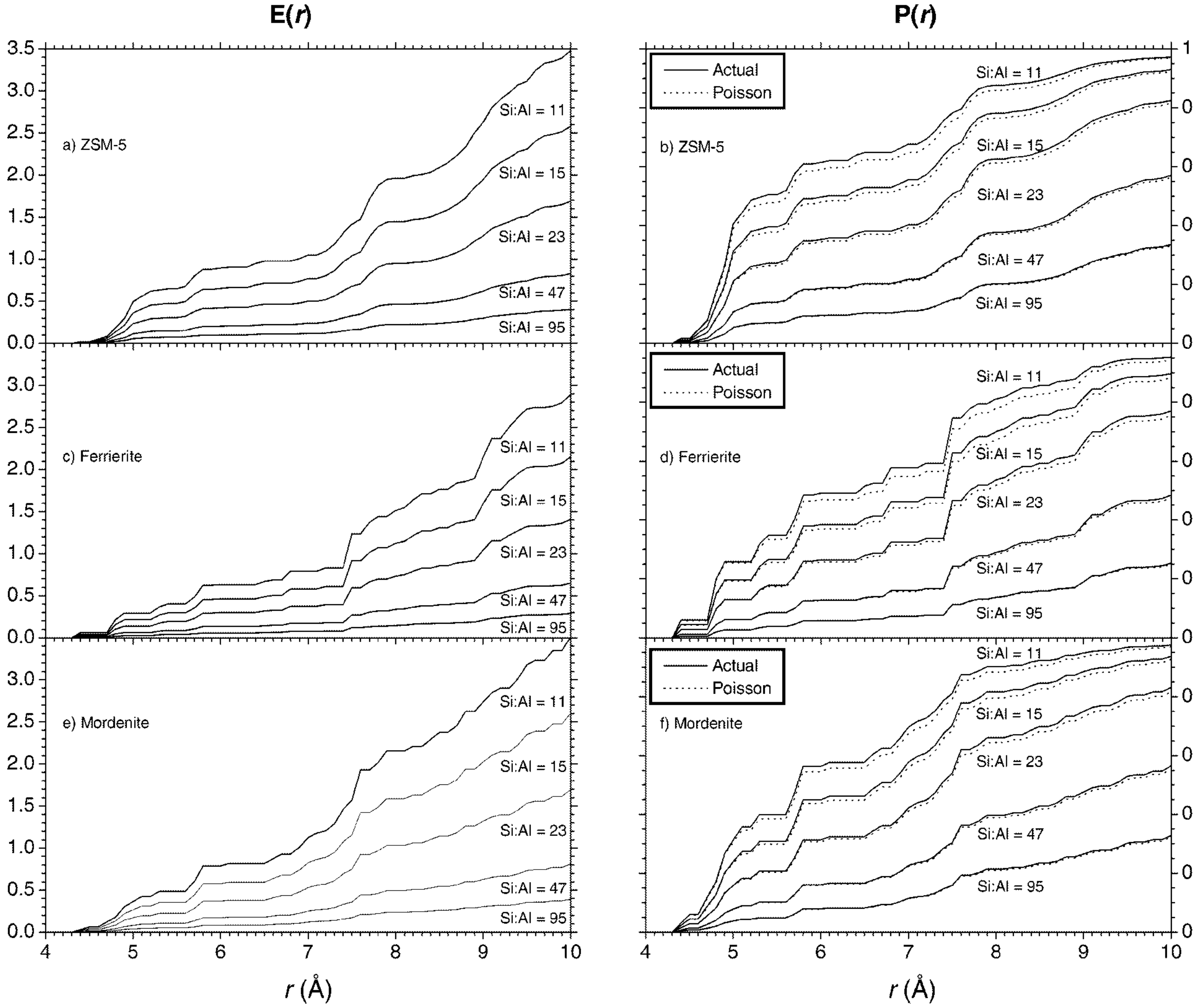

Figure 4. Expected number of accessible Al, and probability of at least one accessible Al within r of an Al-substituted T site in ZSM-5, ferrierite, and mordenite with various Si : Al ratios. Both actual and estimated probabilities from a Poisson distribution are shown.

be unity: i.e., every Al-substituted site is expected statistically to have one Al-substituted neighbor within 8.5 Å.

Rice et al. have calculated $E(r)$ in the limiting cases in which all pairs are counted irrespective of their channel membership and in which only pairs within the straight channels are counted. In general, the results bracket those found here in which pairs in both straight and sinusoidal channels are considered. For instance, at $r = 10$ Å and Si : Al $= 11$, they report $E = 6.3$ and $E < 2.0$ without channel restrictions and considering only straight channels, respectively, compared to $E = 3.5$ found here. We see that inclusion of all channel types does quantitatively influence the final results.

The number of accessible Al T sites around a given Al T site might be expected to follow a Poisson distribution [47]. In fact, previous analyses [36] have assumed this to be the case. If this distribution is followed, then the probability P of finding x accessible Al T sites within r of a given T site is given by

$$P\big(x; E(r)\big) = \frac{E(r)^x \mathrm{e}^{-E(r)}}{x!}, \qquad (1)$$

and the probability of finding at least one accessible Al T site is given by

$$\begin{aligned} P\big(x > 0; E(r)\big) &= 1 - P\big(x = 0; E(r)\big) \\ &= 1 - \mathrm{e}^{-E(r)}. \end{aligned} \qquad (2)$$

To examine this approximation, we compare the results with exact evaluation from the Monte Carlo simulations. The actual probability was obtained by counting the number of isolated Al T sites in each configuration and subtracting the value from one.

Figure 4(b) shows both the actual and estimated (Poisson) probabilities for ZSM-5. The estimated probability is the result of applying equation (2) to the values in figure 4(a). At high Si : Al ratios the agreement is good, and at lower Si : Al ratios the Poisson approximation slightly under-predicts the probability of finding at least one accessible Al neighbor. The Al correlations omitted from the Poisson approximation cause the Al atoms to be more evenly dispersed than a purely random (uniform; without Loewenstein's rule) distribution, especially at lower Si : Al ratios, and thus increase the chances of finding at least

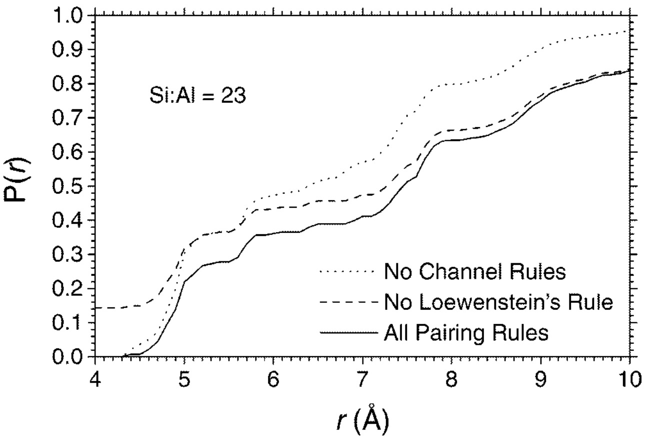

Figure 5. Effect of pairing rules on the probability of at least one accessible Al within a radius r of an Al-substituted T site in ZSM-5 with Si : Al = 23.

Table 2
Distribution of pairs (%) by T-site type in ZSM-5 with Si : Al = 23.

T-site type	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}	T_{11}	T_{12}
T_1	0.4											
T_2	1.2	0.4										
T_3	1.7	0.8	0.4									
T_4	1.3	1.3	0.4	0.2								
T_5	1.2	1.3	1.7	0.4	0.4							
T_6	2.1	1.3	1.3	1.3	1.2	0.4						
T_7	2.5	2.5	2.5	0.4	2.1	2.9	–					
T_8	1.2	0.8	1.3	–	1.6	1.3	0.4	0.2				
T_9	2.5	2.1	2.1	1.7	2.1	0.8	2.9	0.4	–			
T_{10}	0.4	1.3	1.7	1.6	1.7	1.7	0.8	–	1.3	–		
T_{11}	2.1	2.9	2.1	0.8	2.1	2.5	0.4	1.3	2.1	0.4	0.2	
T_{12}	2.1	1.3	0.8	0.8	2.1	2.1	2.1	1.2	2.1	1.7	1.3	–

Table 3
Distribution of pairs (%) by T-site type in ferrierite with Si : Al = 23.

T-site type[a]	T_1	T_2	T_3	T_4
T_1 (1)	1.4			
T_2 (2)	5.4	6.9		
T_3 (2)	–	9.8	3.7	
T_4 (4)	9.6	24.5	18.1	20.8

[a] The number of T sites of given symmetry type/unit cell are given in parentheses.

one partner Al atom. The discrepancies are small, and the Poisson approximation for the distribution of the number of neighboring Al atoms is quite reasonable.

As one would expect, the actual probability of finding one or more accessible Al atoms for a given Al atom in ZSM-5 increases with r and decreases with higher Si : Al ratio. At Si : Al = 23 and $r = 8.5$ Å, P is 0.65, i.e., the probability of a given Al T site of having one or more "pairable" neighbors is nearly two-thirds. Applying the Poisson approximation and considering only T sites within straight channels, Rice et al. [36] obtained a somewhat lower value of P of 0.38 when Si : Al = 24, and $r = 8.5$ Å. The neglect of sinusoidal channels is the largest contributor to the underestimation of P.

The expected number of pairs and the pair probability distributions for ferrierite (figure 4 (c) and (d)) and mordenite (figure 4 (e) and (f)) are largely similar to those in ZSM-5. E and P are systematically lower in ferrierite than in the other two, reflecting fewer opportunities to form bridge species under similar conditions. For small r, mordenite also has lower values of E and P than ZSM-5. For example, at $r = 5$ Å and Si : Al = 23, $P = 0.16$ and 0.21 for mordenite and ZSM-5, respectively. Above $r = 7$ Å, the probability of forming pairs within mordenite is comparable to that in ZSM-5.

We can also evaluate the effect of the pairing rules on the probability functions. The channel rules and Loewenstein's rule were each turned off independently and ZSM-5 samples were evaluated with a Si : Al ratio of 23 (figure 5). Not surprisingly, the removal of restrictions on pairing increases the probability of pairing for all values of r. The largest effect of Loewenstein's rule is seen at short distances, particularly below 4.2 Å, where any Al pairs would necessarily be nearest neighbors. Turning off Loewenstein's rule increases the probability of pairs from zero to 0.14 at these distances. At larger values of r the effect of Loewenstein's rule diminishes to nearly zero. The channel rules play a negligible role at short r, but become important around 5 Å, roughly the thickness of the walls between parallel channels in ZSM-5. Neglect of the channel rules increases the pairing probability by upwards of 30–40%: clearly the channel rules are essential in quantifying metal oxocation pair probabilities.

The distribution of pairs by channel type for the three zeolites with Si : Al = 23 are dependent on how the channels are defined, but they can still provide a qualitative picture of the likely pair locations. In ZSM-5, only 14% of the possible pairs reside in the intersections of the channels. The other 86% are distributed roughly evenly between the straight (39%) and sinusoidal (47%) channels. In mordenite the pairing occurs predominantly in the twelve-ring (44%) or eight-ring (21%) straight channels. Because the larger and smaller straight channels share a wall, some pairs can be members of both parallel channels yet not require bridging through the wall. Only 6% have this both-sides-of-the-wall characteristic. The remaining 29% are located in the eight-membered ring cavities connecting the larger and smaller straight channels. In contrast to both ZSM-5 and mordenite, the pairs in ferrierite are located mostly in the channel intersections (68%). A minor 3% belong only to the larger straight channels, while 29% are localized in the smaller straight channels.

The pairs with $r < 10.0$ Å are fairly evenly distributed by T-site type in ZSM-5, with 72 different combinations represented (table 2). Only a few combinations do not lead to acceptable pairs. These include T_4–T_8 and T_8–T_{10}, because T_8 sites are only accessible from straight channels while T_4 and T_{10} only belong to sinusoidal channels, and T_7–T_7, T_9–T_9, T_{10}–T_{10}, and T_{12}–T_{12} that are all nearest neighbors with periodic images too distant for pairing. Pairs in ferrierite (table 3) are dominated by T_4, which is

Table 4
Distribution of pairs (%) by T-site type in mordenite with Si : Al = 23.[a]

T-site type	T_1	T_2	T_3	T_4
T_1 (2)	10.3			
T_2 (2)	16.2	7.3		
T_3 (1)	12.9	17.7	3.2	
T_4 (1)	22.4	8.2	–	1.6

[a] The number of T sites of given symmetry type/unit cell are given in parentheses.

involved in 73% of the observed combinations. In mordenite (table 4), no pairs form between T_3 and T_4, and 80% of the pairs occur in only five of the ten possible combinations. These combinations all include T_1 or T_2, which are twice as common as T_3 and T_4.

4. Discussion

These simulation results demonstrate that, at moderate Si : Al ratios, the probability of an Al-substituted T site having an accessible Al neighbor within 10 Å in the same channel is quite high. These Al T-site pairs represent potential binding sites for divalent metal oxocations. As noted earlier, DFT calculations have been used to examine the stability of zeolite-supported Cu–O$_x$–Cu^{2+} ($x = 1, 2$) oxocations (**1**) as a function of Cu separation and T-site relative orientation [14,15]. Using model zeolite supports based on two unlinked T sites, a rich variety of Cu oxocation isomers were identified. In all cases the Cu atoms were found to prefer to be doubly coordinated to lattice oxygen, to sit 2.5 Å from the T-site Al, and to be symmetrically bridged by the extra-lattice oxygen. These oxocations were most stable over Cu–Cu separations of 2.5–3.5 Å, consistent with the Cu–Cu distances observed in extended X-ray absorption fine structure (EXAFS) measurements of highly exchanged Cu-ZSM-5 [19–22,48] and Cu-mordenite [49]. Assuming the T-site Al atoms and oxocation Cu atoms to be collinear, then the range of maximum Al separations that could support a Cu oxocation is 7.5–8.5 Å. As shown in figure 3, all three zeolites considered here have a large number of potential Al pair sites within this range of separations.

Further DFT calculations indicate an even greater insensitivity to the Al atom separation than these simple arguments suggest. The strong preference for two-fold, symmetric coordination of Cu ions to lattice oxygen constrains the Cu ions to lie along the lines bisecting the edges of AlO_4 tetrahedra. Both unlinked T-site and more sophisticated zeolite models show the Cu oxocations to be fairly insensitive to this additional constraint: the Cu oxocations readily pucker to accommodate significant deviations of the two Al–Cu vectors from collinearity. Calculations using five- and six-membered rings extracted from the ZSM-5 lattice and substituted with two Al show that, by such puckering, Cu oxocations can accommodate Al separations as small as 4.3 Å [14,15], at the lower end of second-nearest-neighbor range.

From figure 4, at a moderate Si : Al ratio of 23 the probabilities of an Al-substituted T site having an accessible Al neighbor between 4.3 and 8.5 Å away are 0.65, 0.59, and 0.70 for ZSM-5, ferrierite, and mordenite, respectively. The probabilities are inversely related to the Si : Al ratios, approaching 0.90 at a Si : Al ratio of 11. Because these statistics say nothing about the clustering of Al-substituted T sites, for instance, the occurrence of Al triples that can support only one oxocation, it is impossible to use them to quantify the maximum possible number of Cu oxocation pairs at a particular Si : Al ratio. We can conclude, however, that based on the distance and channel membership criteria, binding sites suitable for supporting Cu oxocations are quite common in all three zeolites.

The number of possible oxocations is also a function of the metal ion loading. Cu-ZSM-5, for instance, shows the onset of catalytic activity for NO decomposition at a Cu loading of only 20% [23]. Assuming the exchanged Cu to be uniformly distributed among available Al T sites, then at a Si : Al ratio of 23, the probability of a particular Cu ion having a pairable neighbor Cu ion is 20% of 0.65 or 0.13. Because of the large Cu oxocation binding energy, the actual fraction of “paired” Cu could be much higher. The activity of Cu-ZSM-5 for NO decomposition depends sigmoidally on both the Si : Al ratio and the Cu loading [25–27, 50–53], which has been interpreted as evidence for the participation of Cu oxocations in the decomposition reaction.

While the three zeolites have qualitatively the same Al pair statistics when summed to large separations, they do have distinguishing short-range features and channel structures that affect oxocation structure and siting. Unique to ZSM-5 are third-nearest-neighbor Al pairs with separations (approximately 4.7 Å) more typical of second-nearest neighbors, as previously noted [36]. In part because of these close third-nearest-neighbor pairs, and in part because the five- and six-membered rings of ZSM-5 tend to be more puckered, at a given Si : Al ratio ZSM-5 has a higher probability of short distance ($r < 5.5$ Å) Al pairs than either ferrierite or mordenite (figure 4). The Cu oxocations supported by these close Al pairs also tend to be highly puckered [15] and are likely more reactive than less strained oxocations. In addition, the open ZSM-5 channel structure favors Al pairs that lie along one side of a channel wall rather than across a channel. A metal oxocation associated with same side Al T sites will be readily accessible to small molecules diffusing through the channel. In contrast, most Al pair sites in ferrierite or mordenite lie across ten- or twelve-membered-ring channels or within smaller six- or eight-membered-ring channels, and oxocations bridging these sites will block the channel to diffusing gases [54]. Thus, Cu oxocations in ZSM-5 will tend to be both more reactive and more accessible than oxocations in ferrierite or mordenite. These differences may account for the higher catalytic activity of Cu-exchanged ZSM-5 for NO decomposition.

As noted above, both the Al pair separation and the relative orientations of the Al–Cu vectors – which are fixed by the lattice oxygen – affect the structure and potential stability of bound oxocations. The Al pairing rules employed here do not account for these orientational effects, and thus their impact on the probability of oxocation formation cannot be explicitly determined. Visual inspection of the ZSM-5, mordenite, and ferrierite lattices shows that the puckered rings in ZSM-5 contain vectors that point both towards each other and into open channel space. The associated Al T-site pairs in ZSM-5 are particularly well suited to support Cu oxocations, especially in the Al separation ranges of 4.2–5.5 and 7.0–8.0 Å. Sayle et al. compared Cu oxocation formation in model ZSM-5 and mordenite samples at a single Si : Al ratio and Cu-exchange level, using empirical potential models that explicitly include lattice oxygen [18,55], and similarly found the ZSM-5 lattice more favorable to oxocation formation. Thus, these orientational considerations also support a greater role for Cu oxocations in Cu-exchanged ZSM-5 than in mordenite or ferrierite.

5. Conclusions

For typical ranges of Si : Al ratios, Al pairs accessible within the same channel are found to be quite common in zeolites ZSM-5, mordenite, and ferrierite. Integrated over Al separations up to 8.5 Å, the probability of an Al-substituted T site having an accessible Al neighbor is both large and comparable for all three. At shorter separations (<5.5 Å) more significant differences become apparent between ZSM-5 and the other two, reflecting in particular the large number of highly puckered rings in the former. The Al pairs provide coordination sites for divalent metal oxocations MO_xM^{2+}; based on the Al distribution statistics and previous DFT calculations, Cu oxocations in particular are predicted to be common in the Cu-exchanged forms of these zeolites. The prevalence of short-range Al pairs in five- and six-membered rings and the relative openness of the ZSM-5 channels even in the presence of Cu oxocations both may contribute to the higher NO decomposition catalytic activity of Cu-exchanged ZSM-5 over mordenite and ferrierite.

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