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Limitations on the formation of oxygen-bridged divalent cations in FeZSM-5

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The probability of an $[\mathrm{FeOH}]^+$ ion charge compensating an Al-T-site finding another within a suitable distance, r, with which to form an Fe–O–Fe bridged species has been calculated. The result is a function of the iron loading (m) as well as r and the Si/Al ratio (n). The results suggest that with ratios commonly employed ($11 \leqslant \mathrm{Si/Al} \leqslant 25$) bridge formation is limited, yet may involve an important fraction of the iron. Bridge formation in zeolites having Si/Al ratios of 39 or greater will be extremely rare.

Keywords: catalytic sites for SCR, $[\mathrm{Fe{-}O{-}Fe}]^{2+}$ bridge formation, structure of FeZSM-5

1. Introduction

When NaZSM-5 is base-exchanged with a saturated solution of $\mathrm{FeC_2O_4}$ ($\sim 10^{-3}$ molar) under anaerobic conditions, the exchange capacity can be completely satisfied by $[\mathrm{FeOH}]^+$ and residual Na^+ ions [1]. Thus, the physical picture obtained following removal of the $\mathrm{H_2O}$ of hydration surrounding the Fe^{2+} is a random distribution of $[\mathrm{FeOH}]^+$ on the negatively charged Al-T-sites with the remaining sites populated by Na^+. At this point, one extra-lattice oxygen (ELO) has been introduced with each Fe^{2+}. The question that then arises is, what happens when the material is heated in vacuo?

Conventionally, it has been supposed that

$$2\mathrm{Fe(OH)}^+ \rightarrow \mathrm{H_2O} + [\mathrm{Fe{-}O{-}Fe}]^{2+} \tag{1}$$

This chemistry has been well established [2] for FeY where $\mathrm{Si/Al} \approx 2.5$ and the negatively charged centers are therefore reasonably close together. This simple condensation chemistry has been generally accepted for many years for a variety of divalent cations used in the faujasite system [3].

In the MFI zeolites, much higher Si/Al ratios are present; those commonly used for NO decomposition or for SCR catalysts usually fall in the range ($12 \leqslant \mathrm{Si/Al} \leqslant 25$). Thus, a number of workers have questioned whether bridging can occur according to eq. (1) because it has been supposed that the Al-T-sites would be too remote from each other for bridges to form, e.g., with $\mathrm{Si/Al} = 19$ only 5% of the T-sites contain Al. Consequently, it was proposed recently [4] that the chemistry of dehydration for CuZSM-5 should be described as

$$2\mathrm{Cu(OH)}^+ \rightarrow \mathrm{Cu}^+ + \mathrm{Cu}^{2+}\mathrm{O}^- + \mathrm{H_2O} \tag{2}$$

To date, there has been no reliable estimate of the fraction of sites which are suitably located so that the bridge species may form. This is attempted herein. It is recognized that the probability of a given $[\mathrm{Fe(OH)}]^+$ finding another such species within a reasonable distance will depend upon the Si/Al ratio, n, the loading, m, and the apex angle of the $\mathrm{Fe}{}^{\diagup\mathrm{O}\diagdown}\mathrm{Fe}$ bond. The latter will be fixed by the Fe to Fe distance and indirectly by the structural spacing between the aluminum-containing T-sites. With the CuZSM-5 system, EXAFS measurements have suggested that the mean Cu–Cu distance on the ionic lattice lies between 3.05 and 3.20 Å [5,6], requiring apex angles of 112° and 123°, respectively. The former is comfortably close to the tetrahedral angle ($109^\circ\ 28''$). Second nearest neighbors on a pentasil ring may be taken as the closest distance (4.2 Å) between Al-T-sites. If the $\mathrm{Fe(OH)}^+$ ions are sited directly above these centers (the distance between the two Fe remaining the same) the apex angle would be about 119° and this is admissible. All other cations would be further apart and require larger apex angles. The largest possible angle would be 180° and this allows us to estimate a maximum distance between Al-T-sites of 5 to 6.5 Å. Thus, bridging across the 5.2 Å channels becomes possible. Hence, we have made our calculations as a function of r and considered those T-site distances $4.2 < r < 6.5$ Å as suitable for bridge formation.

2. Method of calculation

The model used to obtain the structure containing the channels was four unit cells [7] put together in a square array. In the calculations the software required only the coordinates for a single unit cell to be used with periodic boundaries. The structural data of Olson et al. [7] define the positions of all the T-sites and allowed the distances between them to be calculated (including those on opposite sides of the 5.2–5.4 Å pores). For these high

Si/Al ratios, it was assumed that the T-sites containing Al were randomly distributed over the lattice after excluding nearest neighbors.

Molecular modeling was performed using computer software Chem 3D Pro version 3.2 obtained from CambridgeSoft Co. The crystal structure of ZSM-5, obtained from Olson et al. [7], provided the coordinates that define the positions of the T-sites by their coordinates (x_i, y_i, z_i). These data were fed into the computer. (Only coordinates for 16 T-sites were required; those for the remaining 80 in the unit cell were generated from these by the computer software.) The distance between any two T-sites may be calculated using the equation:

$$d_{1-2} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}. \quad (3)$$

It will be assumed that all the aluminum T-sites are populated with either [FeOH]$^+$ or Na$^+$ cations [1] randomly distributed over the Al-T-sites on the whole ZSM-5 lattice. Exclusion of nearest neighbors was accomplished manually by removing the few Al–O–Al sites. The fraction of aluminum T-sites (f_{Al}) is a function of the Si/Al ratio (n). This may be expressed by the dimensionless ratio:

$$f_{\mathrm{Al}} = 1/(n+1) = \text{fraction of all T-sites containing Al}. \quad (4)$$

The physical picture used in the calculation is based on the probability of finding a second [FeOH]$^+$ charge-compensated aluminum T-site within the volume of a sphere of radius r from the first [FeOH]$^+$ covered aluminum T-site at its center. Its coordinates thus will be (0, 0, 0) and the distance between any other T-site (x_1, y_1, z_1) to the center T-site is:

$$d = [x_1^2 + y_1^2 + z_1^2]^{1/2}. \quad (5)$$

3. Results

The total T-sites within a sphere of radius r, [$T(r)$], can be counted by the computer from the molecular model. The results of this calculation are shown in figure 1. The inset figure shows the data for the allowed range of sphere radii. Thus, the average number of Al-T-sites within the sphere will be given by

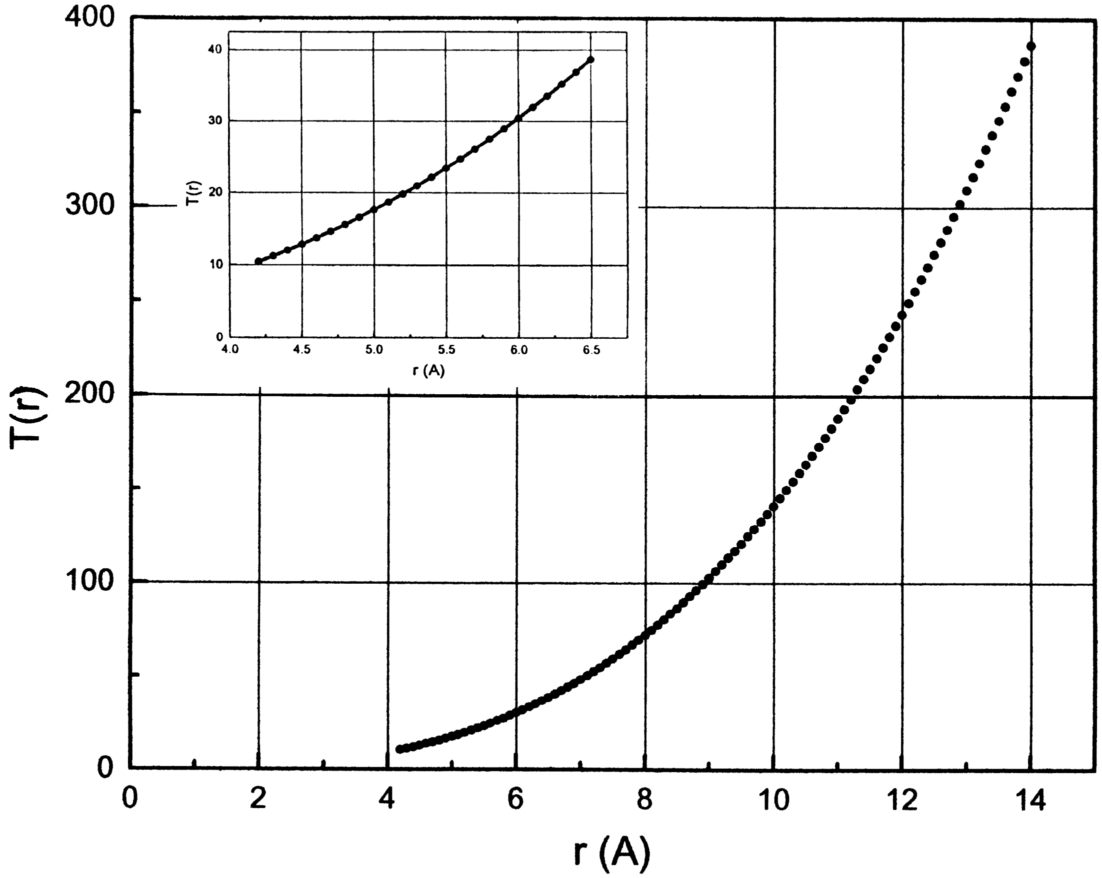

Figure 1. Calculated average number of T-sites, $T(r)$, within a sphere of radius r, in an infinite solid having the ZSM-5 structure. The inset shows the variation over the allowed range of r.

$$N_{Al} = T(r)f_{Al} = T(r)/(n+1)\,. \qquad (6)$$

The results of these calculations are shown on figure 2 for several Si/Al ratios. Since one of the aluminum T-sites has been chosen as the center of the sphere, the distance between that site and any other aluminum-containing site within this sphere is equal to or less than r.

The fraction of all the T-sites holding an $[Fe^{2+}(OH)^-]^+$ cation is a function of both the Si/Al ratio (n) and the $[Fe^{2+}(OH)^-]^+$ ion exchange level (m) as given by

$$\begin{aligned} f_{Fe} &= m/(n+1) \\ &= \text{fraction of all T-sites holding } [FeOH]^+\,. \qquad (7) \end{aligned}$$

Thus, N_{Fe} may be calculated by multiplying the results of eq. (6) by m. The results of these calculations are shown in figure 3 for different Si/Al ratios, n, and for different extents of exchange, m.

It has been shown previously [1] that over the pH range of interest ($4.5 < pH < 7.5$), the oxycation $[Fe^+(OH)^-]^+$ is virtually the only Fe species in an aqueous solution of concentration 10^{-3} molar and that $(Na + Fe)/Al \approx 1$. Hence the physical picture of the wet preparation is that all the Al-T-sites are charge-compensated by either Na^+ or $[Fe^{2+}(OH)^-]^+$. This assumption has been further supported by the experimental data contained in ref. [1] for Fe^{2+} and those for the Cu^{2+} exchange system [4]. The problem to be solved is how likely is it that a given $[Fe^{2+}(OH)^-]^+$ ion will find another such ion within a reasonable bridging distance for formation of an $[Fe–O–Fe]^{2+}$ species by condensation of the OH groups. For convenience and correctness the exchange level will be defined here as if only monovalent cations were present, viz., Na^+ and $[Fe(OH)]^+$. Hence at 100% exchange all Na^+ would have been removed and $m = 1$.

In figure 2 the calculated values of N_{Al} as a function of the radius of the sphere are shown for several values of n. These data extend from $r = 4.2$ Åto $r = 14$ Å. The former is the smallest allowed second nearest neighbor distance (found on a pentasil ring) while the latter is physically unrealistic; the Fe–O–Fe bridge cannot reach, by any stretch of the imagination, T-sites farther apart than about 6.0–6.5 Å. Data for this range are shown in the inset of figure 2. Spheres of $r < 5$ Å rarely contain more than one Al-T-site whereas the two lower Si/Al ratios shown can contain several when $r \to 6$ Å.

A calculation may be made of the density of T-sites within one unit cell, viz., there are 96 T-sites in the ortho-

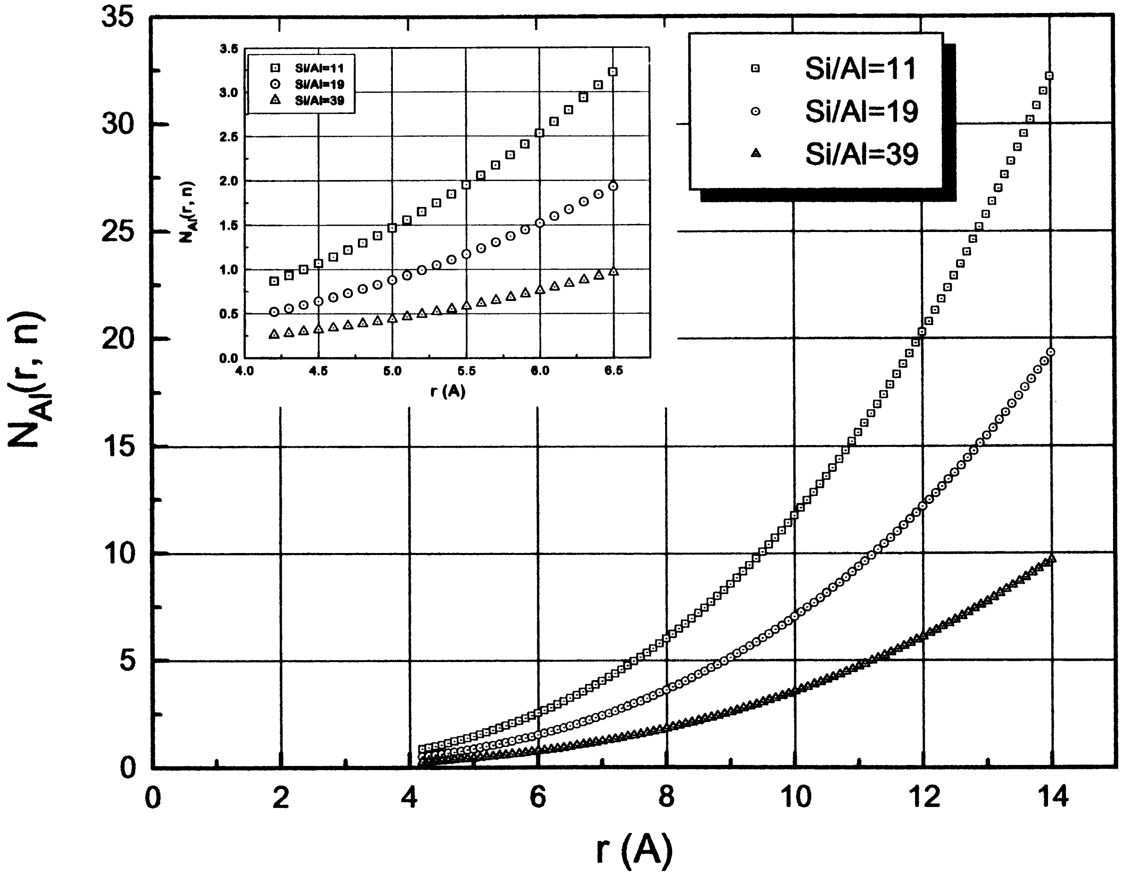

Figure 2. Calculated average number of Al-T-sites within a sphere of radius r, in an infinite solid having the ZSM-5 structure. The inset presents the data for the range of allowed values of r.

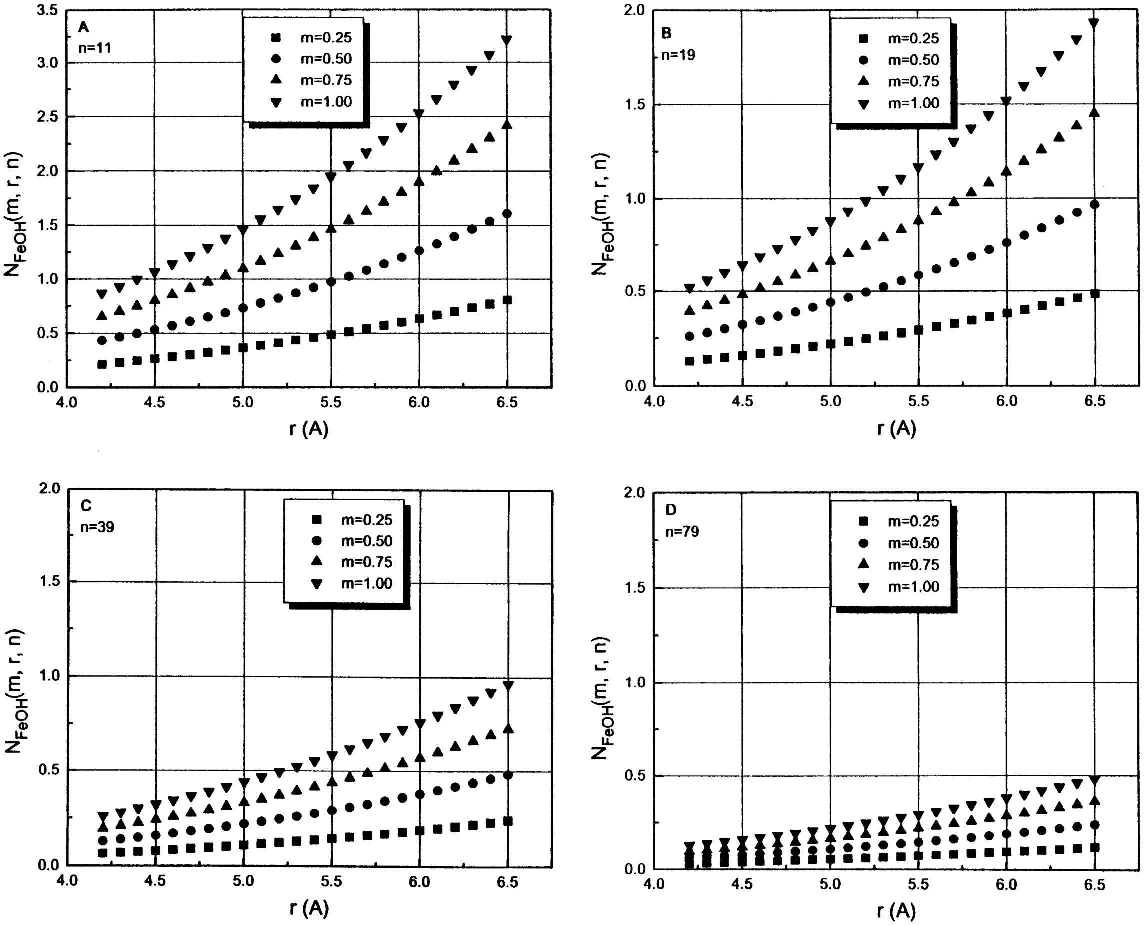

Figure 3. Calculated average number of Fe(OH)$^+$ sites within a sphere of radius r, in an infinite solid having the ZSM-5 structure for various loadings and (A) Si/Al = 11; (B) Si/Al = 19; (C) Si/Al = 39; and (D) Si/Al = 79.

rhombic cell having a volume of 5360 Å^3. Thus, there are 0.0179 T/Å^3. Using this figure, a sphere of 6.5 Å^3 would contain 20.6 T-sites. Reference to figure 1 shows that this value of $T(r)$ is only about half the 39 found by the computer calculation. The reason for this is quite clear. Not counted are the sites in the channels between adjacent unit cells. This suggests that bridging occurs mainly in these channels; this is not surprising when it is recognized that approximately 80% of all T-sites are adjacent to a channel. Interestingly, were the smaller value of $T(r)$ used, the possibility of bridge formation would be reduced accordingly

In figure 3 N_{FeOH} is plotted vs. r for several values of m for zeolites of different n. Since at least two Fe(OH)$^+$ must be contained within a sphere for formation of an [Fe–O–Fe]$^{2+}$ species, when $N_{\mathrm{FeOH}} < 1$, the probability of forming a bridge species may be taken as zero, and when the magnitude of this parameter reaches or exceeds 2.0, the probability of bridge formation approaches unity. The critical range is $1 < N_{\mathrm{FeOH}} < 2$. For this range we may write the probability, P, for bridge formation as

$$P = N_{\mathrm{FeOH}}(m, r, n) - 1.0\,. \qquad (8)$$

The results of these calculations are presented in figure 4. Interestingly, even at the highest loading ($m = 1$) only at the two lower Si/Al ratios ($n = 11$ and 19) is there much likelihood of formation of Fe–O–Fe bridged species. However, when $n = 11$ and $m = 1$, $P = 1.0$ while when $n = 19$ and $m = 0.75$, P drops to 0.45 (for $r = 6.5$ Å). Bridge formation with higher Si/Al ratios will be rare.

If the largest sphere permitted for [Fe–O–Fe]$^{2+}$ formation is 6.5 Å and since it contains all the smaller spheres, data for this value of r may be used for calculation of probabilities of bridge formation. These data are collected in table 1 for the three lowest Si/Al ratios ($n = 11, 19$ and 39). Since the data show almost no possibility of bridge formation exists with the $n = 39$, consideration of higher ratios was unnecessary. Thus, the conclusion reached from the data of table 1 and figure 3 is that bridge formation is highly unlikely when the Si/Al ratio is 40 or greater, provided the distribution of Al-T-sites is uniform. Otherwise, they represent lower limits.

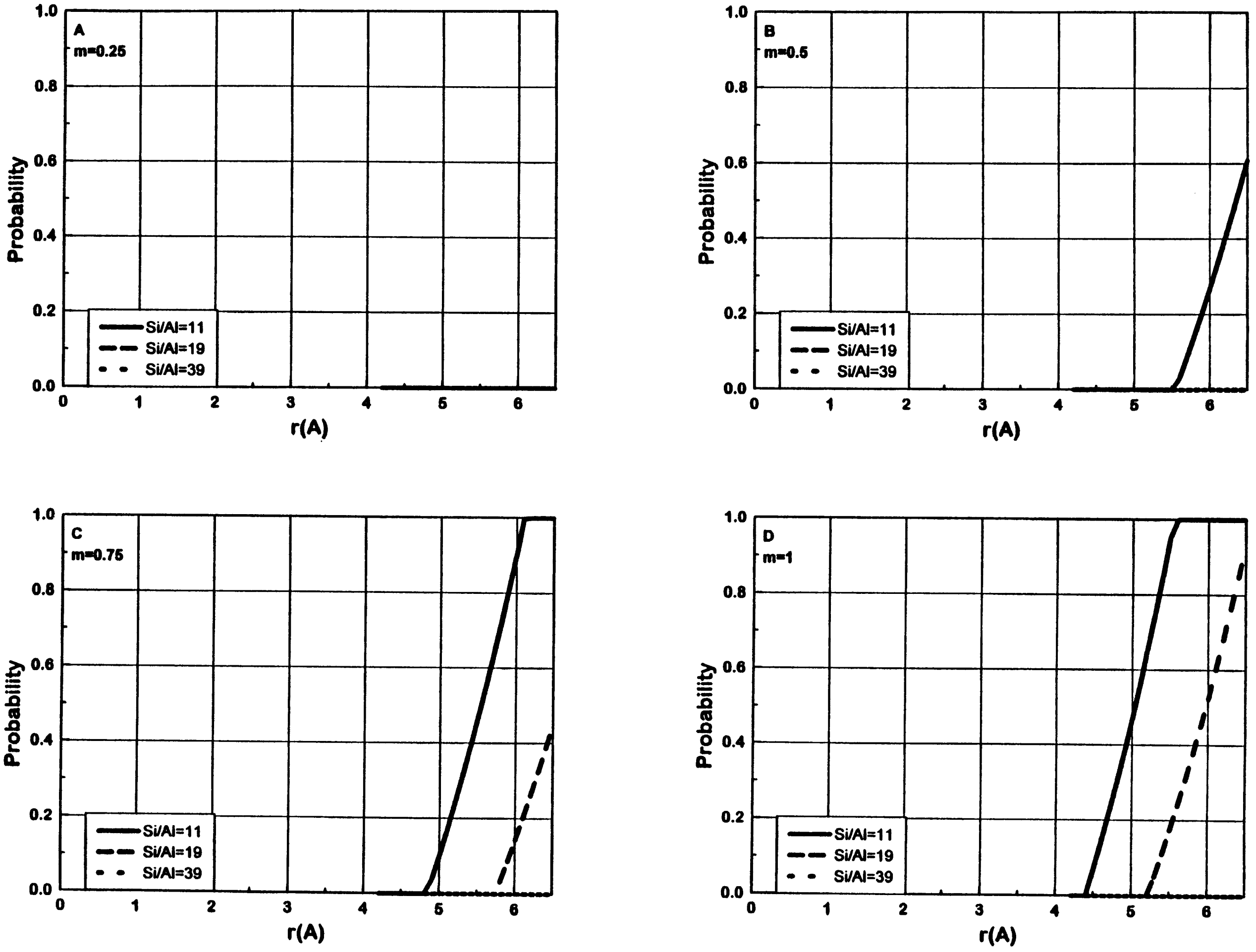

Figure 4. Probabilities of formation of bridged [Fe–O–Fe]$^{2+}$ ions as calculated by eq. (8) for various exchange levels and Si / Al ratios.

4. Discussion

This exercise has raised new questions concerning the chemistry that may occur within FeZSM-5 prepared by our method [1]. Figure 3 reveals that very few [Fe–O–Fe]$^{2+}$ bridges may be formed between second nearest neighbors ($r = 4.2$ Å). On the other hand, bridge formation becomes possible with overexchanged zeolites when $n = 11$ or 19, but not with higher silica–alumina ratios for sphere sizes of 6.5 Å. These findings may reflect the very dilute concentration of Al-T-sites, or perhaps may result from the constraining assumptions made. Our feeling is that if these results are not quantitatively correct, they are not far wrong either.

The FeZSM-5 acts as an oxygen carrier as the Fe^{2+} ions are stoichiometrically oxidized by O_2 to Fe^{3+} and then reduced back to Fe^{2+} by passing the oxygen on to another molecule, e.g., to NO to form NO_2. Since vir-

Table 1
Values obtained for a sphere of 6.5 Å for several Si / Al ratios, n, and extents of exchange, m, based on 1 Fe(OH)$^+$ = 1 Na$^+$. (These include the cross-channel bridges that may form between adjacent unit cells)

Extent of exchange	Number within a sphere of $r = 6.5$ Å						Probabilities of forming a (Fe–O–Fe)$^{2+}$		
	Al-T-sites			Fe(OH)$^+$					
	$n = 11$	$n = 19$	$n = 39$	$n = 11$	$n = 19$	$n = 39$	$n = 11$	$n = 19$	$n = 39$
$m = 0.25$	3.22	1.93	0.97	0.81	0.48	0.24	0	0	0
$m = 0.5$	3.22	1.93	0.97	1.61	0.97	0.49	0.61	0	0
$m = 0.75$	3.22	1.93	0.97	2.42	1.45	0.73	1	0.45	0
$m = 1$	3.22	1.93	0.97	3.22	1.93	0.97	1	0.93	0.05

tually all of the Fe centers appear to act in this way, and since we have no firm information about how this oxygen is held, it is not possible to attribute catalytic behavior to any particular kind of center. Indeed, one might assume that this oxygen is absorbed into the lattice with the Fe ions acting as a source or a sink for electrons. The present findings relate more directly to defining the nature and structure of the catalyst, as it is prepared and pretreated when the Fe is in its divalent state. More generally it should be considered a contribution to the understanding of zeolite chemistry.

The methodology used here for FeZSM-5 may be applied to other catalyst systems, e.g., CuZSM-5. Sarkany et al. [8] used TPR to analyze the Cu distribution in CuZSM-5-18-134. They reported 35% [Cu^{2+}–O^{2-}–Cu^{2+}]$^{2+}$, 25% CuO and 40% Cu^{2+}. Our calculation for this catalyst predicts that $\sim$ 40% of the bridged species should be present within a sphere of 6.5 Å. This suggests that our conclusions are reasonable. Interestingly, Beutel et al. [6] reported that [Cu–O–Cu]$^{2+}$ was formed in this ZSM-5 preparation only when the loading exceeds 40% ($m = 0.2$). This is in qualitative agreement with the predictions of figure 3B. Moreover, these workers and others have observed the segregation of an oxide phase on thermal treatments at high temperatures. Perhaps this results from [CuOH]$^+$ species [9] that cannot find a mate within an acceptable distance to form the bridged species by condensation. The chemistry might then be

$$\mathrm{Cu(OH)^+} \underset{\Delta}{\rightarrow} \mathrm{CuO} + \mathrm{H^+}$$

or

$$\mathrm{Fe(OH)^+} \underset{\Delta}{\rightarrow} \mathrm{FeO} + \mathrm{H^+} \qquad (9)$$

The H$^+$ can migrate and further react forming a Brønsted site, or perhaps react as follows:

$$\mathrm{H^+} + \mathrm{Cu(OH)^+} \underset{\Delta}{\rightarrow} \mathrm{H_2O} + \mathrm{Cu^{2+}}$$

or

$$\mathrm{H^+} + \mathrm{Fe(OH)^+} \underset{\Delta}{\rightarrow} \mathrm{H_2O} + \mathrm{Fe^{2+}} \qquad (10)$$

Admittedly, eqs. (9) and (10) are presently very speculative, but they will serve to illustrate that some as yet not understood chemistry is taking place. The unanswered questions become: if a portion of the base-exchange cations is removed as an oxide phase, how is the charge balance on the lattice maintained, are the remaining ions allowed to compensate two Al-T-sites, or does it lead to breakdown of the zeolite lattice, i.e., does dealumination occur?

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