# Number of isolated aluminum atoms in the framework of dealuminated acid zeolites

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Monte Carlo calculations restricted by Loewenstein rule predict correctly the variation of the intensities of the lines contributing to the $^{29}$Si MAS NMR spectra in dealuminated acid ZSM5, mordenites and Y zeolites covering a domain of ratios silicon/framework aluminum between 4 and 80. They are also used to calculate the numbers of isolated framework aluminum and the relationship with the Brønsted acidity is briefly discussed.

**Keywords:** zeolites; Monte Carlo calculation; isolated aluminum

## 1. Introduction

The use of zeolites as acid catalysts has triggered an unbelievable number of studies on the structural and surface modifications resulting from the activation of the acid zeolites by calcination and/or steaming. $^{29}$Si MAS NMR spectroscopy which at the early beginning [1,2] was mainly used by crystallographers for studying the ordering of the Si by Al substitution, became a tool of choice for understanding what was occurring when a catalytically inert solid, such as a Na faujasite, was converted into a very active acid catalyst. Indeed, if the Si/Al ratios are obtained from chemical analyses and $^{29}$Si MAS NMR, the number of dislodged nonframework aluminum (NFAl) is easy to calculate. The ratio Si/FAl (framework Al) is obtained by deconvoluting the $^{29}$Si spectra into five lines with intensity $^4Q(n\mathrm{Al})$ with $n = 0, 1, \ldots, 4$, numbers of next neighbors aluminum atom to silicon,

$$\mathrm{Si/Al} = \sum_{n=0}^{4} {}^4Q(n\mathrm{Al}) \Big/ \sum_{n=0}^{4} \frac{n}{4} {}^4Q(n\mathrm{Al}) \,. \tag{1}$$

By inverting eq. (1), the relative weight of the *links* between silicon and an Al neighbor is obtained. For instance,

$$\frac{n}{4} {}^4Q(1\mathrm{Al}) \Big/ \sum_{n=0}^{4} {}^4Q(n\mathrm{Al}) \tag{2}$$

represents the relative weights of all the links connecting Si to one Al. The number of isolated aluminum with no next nearer neighbor 0.n.n.n cannot be obtained unless model structures are considered, such as reported by Wachtler [3].

However, it has been shown that Monte Carlo calculations [4–6] are able to describe the evolution of the relative intensities of the $^{29}$Si $^4Q(n\mathrm{Al})$ contribution in a satisfactory manner, if the Loewenstein avoidance rule [7] is introduced in the calculation. For Si/Al < 4, the Dempsey rule stating that the number of Al–O–Si–O–Al clusters must be minimized has also been used successfully. From a Monte Carlo program (including the Loewenstein rule) the number of 0.n.n.n. Al is obtained easily.

The importance of gathering information on this number comes from earlier observations by Barthomeuf et al. [8,9] that strong Brønsted sites are linked to 0.n.n.n. Al. The aim of this letter is to show that for a set of 16 dealuminated acid zeolites, the three-dimensional Monte Carlo procedure applied to a diamond structure (with coordination number equal to four) can reasonably predict the experimental variation of $^4Q(n\mathrm{Al})$ component intensities with Si/FAl. This reasonable agreement is taken as proof that the simultaneous calculation of the fraction 0.n.n.n. Al/FAl with respect to Si/FAl is correct.

## 2. Experimental

The main characteristics of the zeolites analyzed here are given in table 1. References are made to their preparation procedures.

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Table 1
Chemical $Si/Al_{CA}$ ratio, $^{29}Si$ NMR Si/FAl ratio, FAl/Al, $FAl_1/FAl$ from Monte Carlo simulation for dealuminated acid ZSM5 (DHZ), various mordenites (DHM), DHY and ultrastable Y (USY) [a]

| Sample | | $Si/Al_{CA}$ | Si/FAl | $FAl/Al_t$ | $FAl_1/FAl$ |
|---|---|---|---|---|---|
| DHZ | 400 | 15.1 | 17.5 | 0.87 | 0.51 |
| | 500 | 15.1 | 17.8 | 0.85 | 0.5 |
| | 600 | 15.1 | 18.6 | 0.82 | 0.52 |
| | 700 | 15.1 | 37.1 | 0.42 | 0.72 |
| | 800 | 15.1 | 52.7 | 0.31 | 0.79 |
| | 900 | 15.1 | 76.3 | 0.21 | 0.85 |
| DHM | VG2 | 5.2 | 9.8 | 0.58 | 0.30 |
| | VG3 | 5.2 | 11 | 0.52 | 0.34 |
| | VG5 | 6.4 | 28 | 0.25 | 0.65 |
| | VG600 | 5.2 | 10 | 0.57 | 0.31 |
| | VG700 | 5.2 | 15.0 | 0.39 | 0.45 |
| USY | | 2.55 | 4.8 | 0.61 | 0.1 |
| DHY | 500 | 2.55 | 3.3 | 0.82 | 0.04 |
| | 600 | 2.55 | 4.6 | 0.64 | 0.09 |
| | 700 | 2.55 | 4.8 | 0.61 | 0.1 |
| | 800 | 2.55 | 4.9 | 0.61 | 0.1 |

[a] The preparations of the dealuminated sieves are described in refs. [10,11].

The Monte Carlo simulation, including the Loewenstein rule, was carried out on $10^6$ sites distributed on a three-dimensional diamond network. Periodicity conditions were imposed at the edges of the network in order to account for the border effect. In addition, the calculations were carried out on a network with linear dimensions twice as large ($8 \times 10^6$ sites); the results were practically the same. The ratios of 0.n.n.n. Al or $FAl_1$, to FAl are included in table 1.

## 3. Results

The experimental (open dots) and calculated variation of the relative $^4Q(0Al)$, $^4Q(1Al)$, $^4Q(2Al)$ and $^4Q(3Al)$ are shown in figs. 1a, 1b, 1c, and 1d, respectively, with respect to the NMR Si/Al ratio (or Si/FAl). Thus, the solid lines in fig. 1 are obtained directly from the Monte Carlo calculation. The agreement is excellent for $^4Q(0Al)$. The simulation apparently overestimates $^4Q(1Al)$ and underestimates $^4Q(2Al)$ but the discrepancies are of the order of magnitude obtained by others [1]. The deconvolution of the $^{29}Si$ MAS NMR spectra in its components is less accurate in dealuminated acid zeolites than in the parent materials because of the broadening of the linewidth. In brief, considering the wide span of Si/FAl shown in table 1, the results in fig. 1 suggest that the calculated $FAl_1$ contents shown in table 1 are reliable.

This assumption is supported by an elementary probability calculation. Consider fig. 2 and let us calculate what the probability is that the central Al atom has no nearest next neighbor,

$$\alpha_1 = \alpha(1-\alpha)^\beta, \tag{3}$$

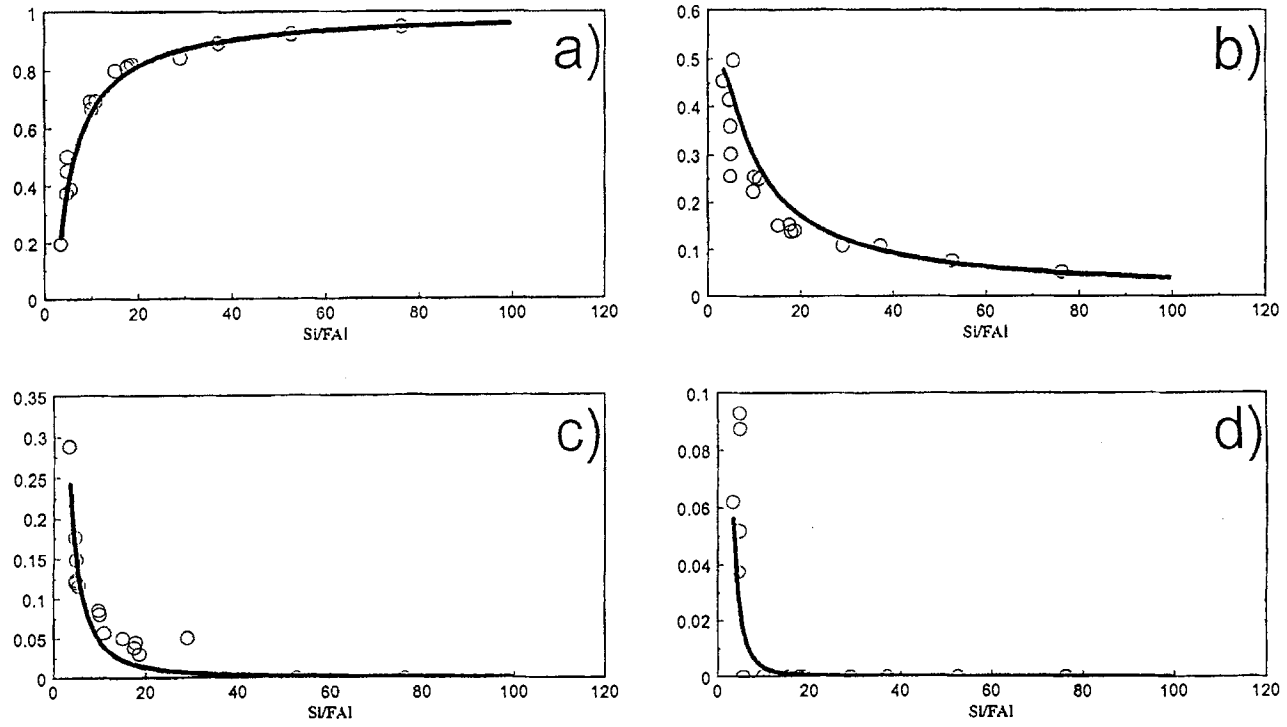


Fig. 1. Variation of the contributions of the $^4Q(n\text{Al})$ components to the $^{29}Si$ MAS NMR spectra calculated (solid line) by using the Monte Carlo technique and Loewenstein rule restriction, or experimental (open dots). The corresponding zeolites and their Si/FAl ratios are shown in table 1. (a) $^4Q(0Al)$; (b) $^4Q(1Al)$; (c) $^4Q(2Al)$ and (d): $^4Q(3Al)$.

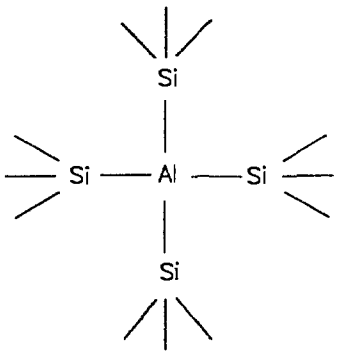


Fig. 2. Tridimensional structure model.

where $\alpha_1 = Al_1/(Si + Al)$ is a probability to find isolated $Al_1$ at a given site; while $\alpha = Al/(Si + Al)$ is a relative number of Al sites. $\beta$ is a number of sites in a second coordination sphere, 12 in our case. The solid line in fig. 3a was obtained from eq. (3) with a least-squares fit giving $\beta = 12.31$. This is slightly larger than the value ($\beta = 12$) which should follow from a simple statistical approach. The reason for this deviation is not clear; perhaps, it is due to the inclusion of the Loewenstein restriction rule in the calculations. The open dots in fig. 3 are the results of the Monte Carlo calculation. The datapoints correspond to the zeolites listed in table 1. Another way to present these data is to plot them as $Al_1$/Al vs. Si/Al (fig. 3b). This plot reflects the increase of the relative $Al_1$ content during dealumination.

The three sets of zeolites cover three domains of Si/Al (NMR) ratios and, as expected, the fractions of 0.n.n.n. Al are characteristic of each domain. In a recent paper Blumenfeld et al. [12], studying the topology of Brønsted sites by rotational echo double $^1H \rightarrow {}^{29}Si$ resonance (REDOR) suggested that bridging OH groups on Si–O–$Al_1$ linkages were acidic Brønsted sites whereas those on Si–O–$Al_n$ ($n > 1$) were not acidic. This observa-

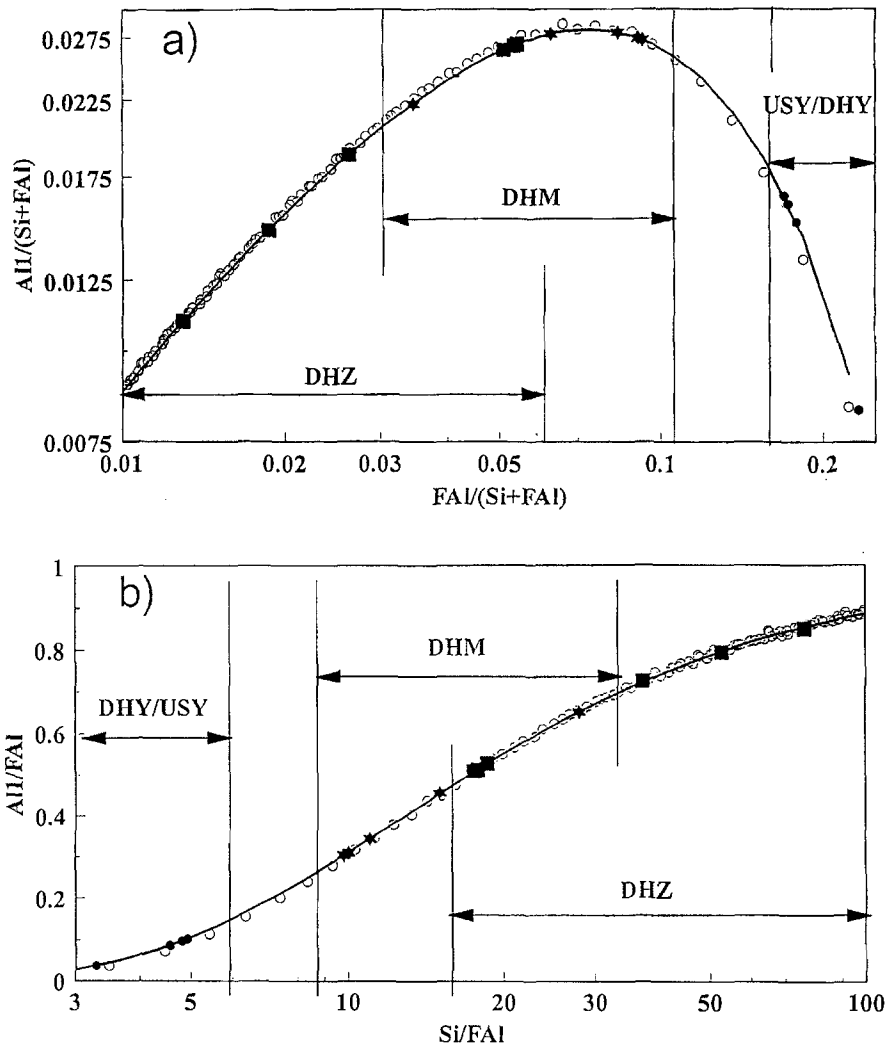


Fig. 3. (a) Variation of the fraction $Al_1$/number of sites with respect to the relative framework Al content. (b) Variation of the number of isolated Al, 0.n.n.n. Al = $Al_1$ with respect to Si/FAl ratio. The solid lines are obtained from eq. (3) with $\beta = 12.31$, the open dots are the Monte Carlo results. In both (a) and (b), the domains of application to the zeolites shown in table 1 are represented in putting on the curve the calculated values.

tion is in line with Barthomeuf's idea that the acid OH are linked to 0.n.n.n. Al.

## 4. Conclusions

The main purpose of this letter was to demonstrate that Monte Carlo calculations based on the random distribution of Al sites and Loewenstein rule provide a reliable way to estimate the numbers of isolated Al sites in dealuminated zeolites (Si/Al > 3), which could be a measure of the catalytic Brønsted activity. In order to obtain this value from the calibration curves (fig. 3) one has to only know the Si/Al ratio for a given sample. The latter can be easily obtained either by the standard method (eq. (1)) or using the Monte Carlo calibration curve for $Si^4Q(0Al)$ (fig. 1a). The approach can be easily extended to take into account the actual zeolite interconnectivity which would be different from that in the idealized diamond-line lattice.

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