CRYSTALLOCHEMICAL ASSESSMENT OF THE CHARGE BALANCE OF THE NaY ZEOLITE UNIT CELL BASED ON THE Si/Al RATIO

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Abstract. A computational assessment of the crystallochemical composition of hydrothermally synthesized FAU-type NaY zeolite is presented. Using previously obtained SEM-EDS results, the atomic Si/Al ratio was determined, the average numbers of Si and Al atoms per unit cell were calculated, and the theoretical amount of Na^+ cations required to compensate the negative framework charge was estimated. The applicability limits of the idealized model are also discussed.

Keywords: NaY zeolite; FAU; crystallochemical composition; Si/Al; unit cell; electroneutrality; sodium cations.

INTRODUCTION. FAU-type zeolites are crystalline aluminosilicates with a three-dimensional pore and channel system. Their framework consists of SiO_4 and AlO_4 tetrahedra connected through shared oxygen atoms. Incorporation of aluminum into tetrahedral positions in place of silicon produces a negative framework charge that must be balanced by extra-framework cations. In the sodium form of zeolite Y, Na^+ is

one of the principal charge-compensating ions. Determining the Si/Al ratio is therefore important not only for characterizing composition but also for estimating the cation balance [1, 2].

Unlike morphological and textural characteristics, the crystallochemical charge balance is directly related to the number of framework Al atoms. Nevertheless, the experimentally determined elemental composition and an idealized chemical formula are not equivalent: the former depends on the analytical method and sample condition, whereas the latter follows from structural and stoichiometric assumptions. This distinction is particularly important when energy-dispersive X-ray spectroscopy data are used.

The aim of this study was to calculate the atomic Si/Al ratio of hydrothermally synthesized NaY zeolite from previously acquired SEM-EDS data, estimate the idealized composition of the FAU unit cell, and determine the theoretical sodium cation content on an anhydrous mass basis.

MATERIALS AND CALCULATION METHODS. Previously obtained SEM-EDS results for a NaY sample were used. The original report gave silicon and aluminum mass fractions of 24.14 and 11.01%, respectively. For comparison, the sodium mass fraction of 8.66% and the atomic fractions listed in the same report were also considered. No new experimental measurements were performed as part of the present computational analysis.

The atomic Si/Al ratio was calculated as the ratio of the amounts of the respective elements derived from their mass fractions: $Si/Al)=(w_{Si}/M_{Si})/(w_{Al}/M_{Al})$, where w is the elemental mass fraction and M is its molar mass. Values of M_{Si}=28.085 g/mol and M_{Al}=26.982 g/mol were used. The unit-cell calculation assumed 192 tetrahedral positions in the FAU structure, such that $N_{Al}+N_{Si}=192$ [1, 2].

For the idealized model, the relationships $N_{Al}=192/(1+Si/Al)$ and $N_{Si}=192-N_{Al}$ were used. Assuming that each tetrahedral Al atom generates one negative charge and

that compensation occurs exclusively through monovalent Na^+ ions, $N_{Na}=N_{Al}$ was adopted. This model does not establish the actual distribution of sodium among crystallographic sites.

The molar mass of the hypothetical anhydrous unit cell was obtained by summing the contributions from Na, Al, Si, and O. The theoretical sodium content, expressed in mmol/g, was calculated from the number of Na^+ ions per formula unit and the molar mass of the idealized cell. Because the model is anhydrous, this value should not be directly equated with analytical results for a hydrated material.

RESULTS AND DISCUSSION. Recalculation of the reported mass fractions yielded Si/Al=(24.14/28.085)/(11.01/26.982)=2.106, or approximately 2.10. The atomic fractions provided in the EDS report yielded a similar result, 16.19/7.69=2.105. Agreement between these two representations of the same dataset demonstrates the arithmetic consistency of the conversion but cannot be regarded as an independent validation of EDS accuracy.

At Si/Al=2.10, the number of aluminum centers in the idealized cell is $N_{Al}=192/3.10=61.94$, while the number of silicon atoms is $N_{Si}=130.06$. Assuming complete charge compensation by monovalent sodium cations, their calculated number is also 61.94. Accordingly, the conditional average crystallochemical formula is $Na_{61,94}Al_{61,94}Si_{130,06}O_{384}$.

The fractional subscripts in this formula do not imply fractional numbers of atoms in an individual real unit cell. Rather, they represent an average composition calculated from the experimentally estimated Si/Al ratio. Each individual unit cell contains integer numbers of atoms, and their distribution among tetrahedral sites cannot be determined from the Si/Al ratio alone.

The molar mass of the idealized anhydrous unit cell is approximately 12,891.5 g/mol. The corresponding theoretical sodium cation content is (61.94/12,891.5)×1000=4.80 mmol/g. This value is the calculated charge-

compensation equivalent of the aluminosilicate framework, not the experimentally measured ion-exchange capacity of the sample.

The calculated value does not establish that all Na^+ cations are equally accessible to adsorbate molecules. The distribution of extra-framework cations among FAU sites depends on the material composition and state; identifying their locations requires dedicated structural investigations [3]. Thus, the value of 4.80 mmol/g represents the stoichiometric limit of the selected model, rather than a measured concentration of accessible active sites.

Interpretation must also account for the fact that SEM-EDS characterizes the elemental composition of a local analyzed region. The available dataset does not directly establish how aluminum is distributed between framework and possible extra-framework environments, the degree of hydration, or the completeness of cationic charge compensation. The formula is therefore used as a theoretical basis for subsequent verification, not as a proven structural description of the particular sample.

A distinctive feature of the calculation is its stepwise progression from measured mass fractions to a dimensionless atomic ratio, then to the number of framework atoms in an idealized unit cell, and finally to the theoretical content of compensating cations. Each stage requires a separate assumption. The first assumes that EDS results can be used to estimate Si/Al; the second assumes that the aluminum considered belongs to the FAU framework; and the third assumes that all negative charges are compensated exclusively by Na^+. Without independent verification, these conditions must be treated as model assumptions.

The practical value of this approach lies in providing an order-of-magnitude estimate of theoretical cation content and identifying requirements for subsequent experiments. In particular, comparison with actual ion-exchange capacity will require an independent measurement, while assessing hydration effects will require

quantitative determination of water in the sample. The calculated result can therefore guide further experimental design without substituting for such experiments.

CONCLUSIONS. Reanalysis of previously obtained SEM-EDS data for hydrothermally synthesized NaY yielded an atomic Si/Al ratio of approximately 2.10. For an idealized FAU unit cell containing 192 tetrahedral positions, average values of N_{Al}=61.94 and N_{Si}=130.06 were obtained, corresponding to 61.94 theoretical charge-compensating Na^+ cations. The sodium content calculated for the idealized anhydrous structure is 4.80 mmol/g. This value should be interpreted as a stoichiometric estimate of charge balance rather than as the experimental ion-exchange capacity or a measure of actual cation accessibility.

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