Aluminum Distribution in ZSM-5 as Determined by X-Ray Photoelectron Spectroscopy

The distribution of aluminum in ZSM-5 is important in determining the selectivity of the catalyst, and is also relevant to the mechanism of crystallization (*1*). We now present X-ray photoelectron spectroscopy (XPS) measurements of the distribution of aluminum in ZSM-5 polycrystalline aggregates and show how this is altered by acid leaching. These results are supported by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

XPS measurements were made on a Vacuum Generators ESCALAB 5 at a working pressure of $\sim 10^{-9}$ Torr. Intensity ratios of Si/Al were calculated from the integral areas of the Al $2p$ and Si $2p$ peaks after a linear background subtraction was performed (no account was taken of loss peaks). The atom ratios were calculated from (*2*)

$$\frac{N_{Si}}{N_{Al}} = \frac{\sigma_{Al\,2p}}{\sigma_{Si\,2p}} \times \frac{I_{Si\,2p}}{I_{Al\,2p}} = 0.663 \frac{I_{Si\,2p}}{I_{Al\,2p}}, \quad (1)$$

where N_i = number of atoms contributing to the signal intensity I_i, and σ_i is the atomic cross section for the event (*3*).

Samples of ZSM-5 (*4*) were prepared by hydrothermal crystallization (2 days at 175°C) of a hydrogel formed from aluminum sulfate and sodium silicate solutions at a pH of 10–11 in the presence of tetrapropylammonium cations. The Si/Al ratio was varied between 10 and 100 while all other crystallization conditions remained constant. Na$^+$ leaching was performed by refluxing a 0.5 *M* NaNO$_3$ solution (100°C) for 2 hr over the "as prepared" ZSM-5, repeating the process once with fresh NaNO$_3$ solution. In a similar fashion the H$^+$ form was prepared from the Na$^+$ form by refluxing in 0.5 *M* HCl solution. In the leaching experiments

the ratio of liquid to solid was 150:1. The solid was removed from the solution by filtration, and then it was washed and dried. The zeolite morphology, determined by TEM and SEM, was consistent in each preparation and resulted in polycrystalline aggregates as shown in Fig. 1A. Aggregates were generally of the order of 5 μm while individual crystallites were in the range of 50–200 nm. Pelletizing the zeolite broke up the aggregates as shown in Fig. 1B. In this fashion the interior of the aggregates was exposed to analysis by XPS.

The effects of acid leaching the Na-ZSM-5 are shown in Fig. 2. Both the Na$^+$ and H$^+$ forms display a silicon-rich surface relative to the bulk analysis. Measurements of the Si/Al ratio by XPS and bulk chemical analysis on Na–mordenite, Na–A, and Na–Y showed no discrepancy between the two methods. Hence the silicon-rich surface of the Na-ZSM-5 is real and not a function of the experimental method. The possibility exists that the Si enrichment on the surface of the clusters is due to a thin skin of siliceous material coating the aggregates. Individual crystallites were, however, crystalline to within 10 Å of their edge as determined from interference fringes observed in TEM analysis. In fact calculations of the effects of a silica film on our measured XPS Si/Al ratios rule out the possibility of a film thicker than 2 Å. This is simply a consequence of the short mean free paths of electrons in aluminosilicates. Upon acid leaching, as seen in Fig. 2, the surface and bulk Si/Al are increased although a proportionately larger amount of aluminum is removed from the surface than from the bulk. SEM and TEM analysis of the Na$^+$ form showed no morphological
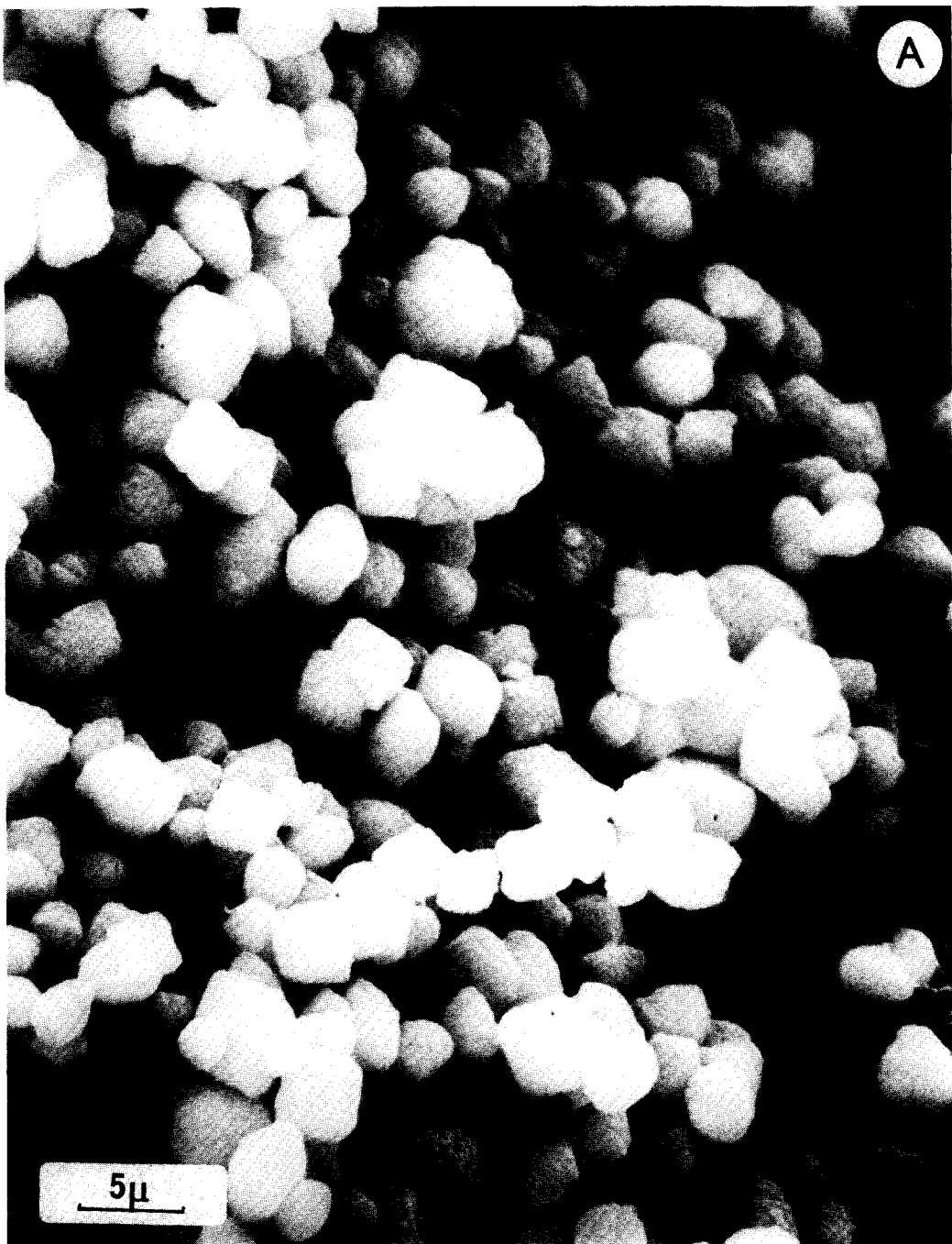
FIG. 1. (A) Polycrystalline aggregates composed of small crystallites of ~50–200 nm. (B) Pelletized sample showing the crushed and fragmented aggregates.

change after acid leaching. The loss of surface aluminum must therefore be from the zeolite framework, but the loss of bulk aluminum after acid leaching is most probably due to combined loss from amorphous material within the aggregates as well as from

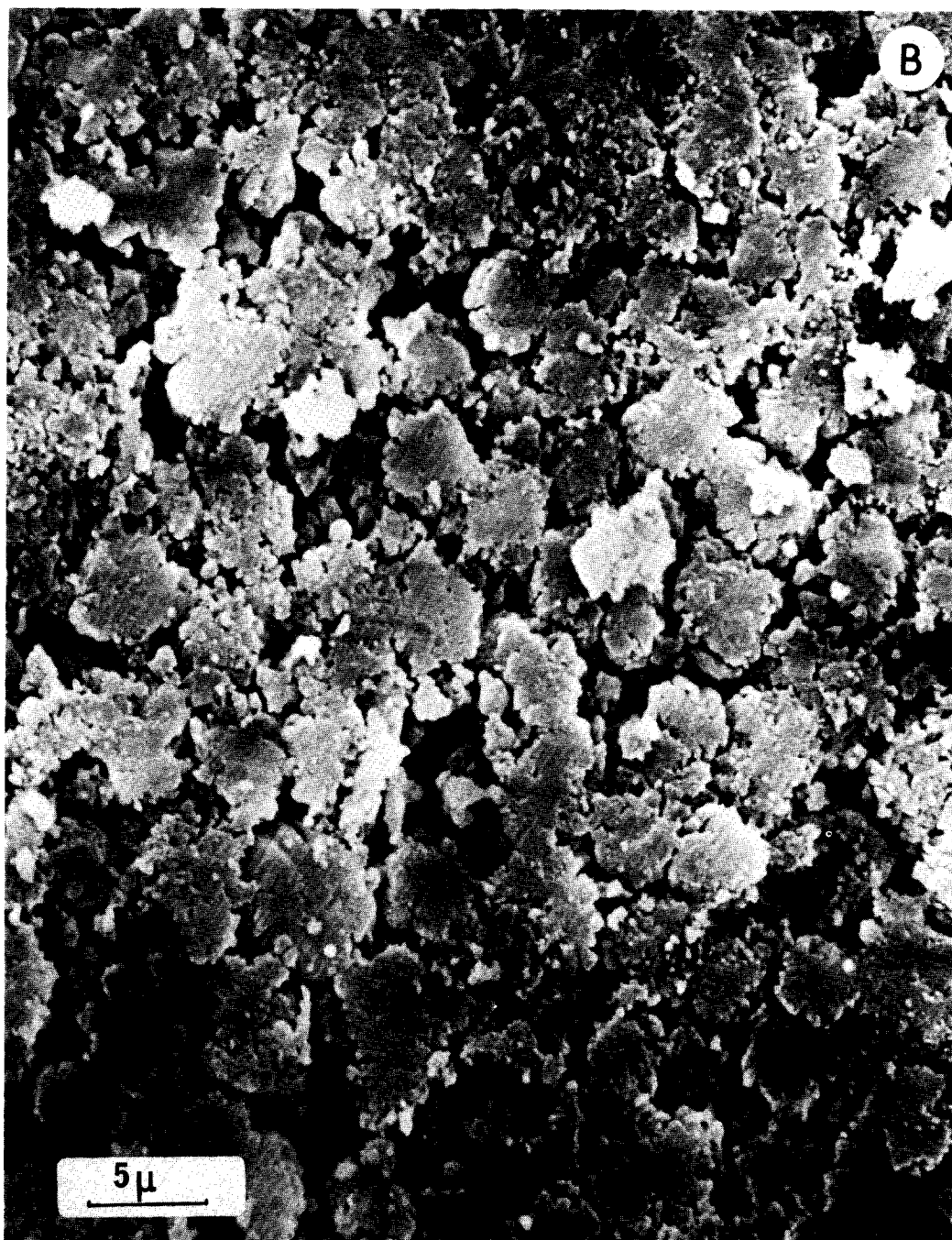FIG. 1—*Continued.*

the bulk zeolite framework.

The considerable decrease in the Si/Al ratio after pelletizing (Fig. 3) suggests that the interior of the aggregates contains an aluminum-rich material. (The decrease in the Si/Al ratio was not simply due to a
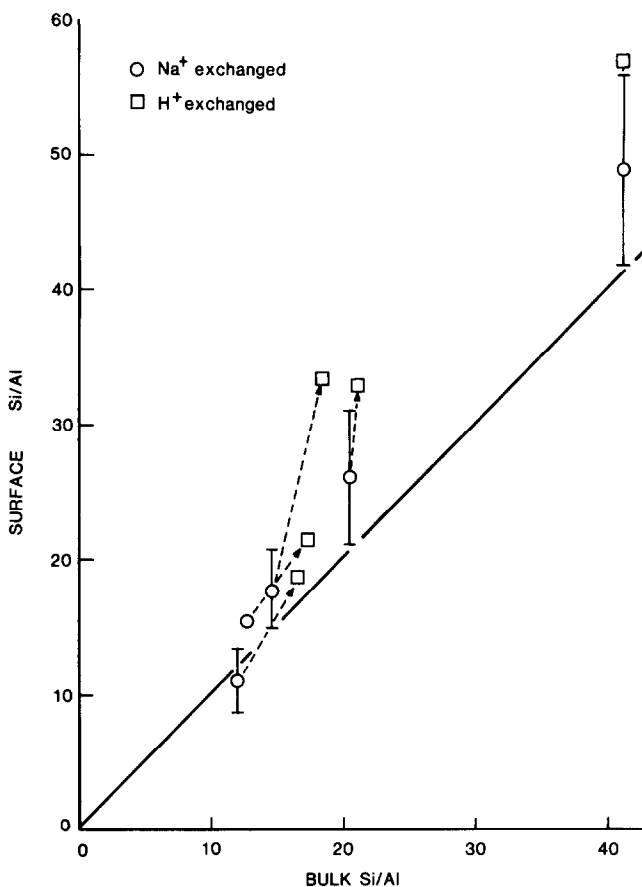
FIG. 2. Effects of acid leaching on the Na-ZSM-5 form. The arrows on dashed lines join the Na⁺ and acid-leached (H⁺) form of the same samples. Changes in bulk (Si/Al) represent a loss from the bulk as measured by bulk analysis and changes in surface (Si/Al) represent a loss from the surface as measured by XPS. All samples were prepared by dispersion with cyclohexane onto stainless-steel sample holders. The solid line represents equivalent surface and bulk analyses, i.e., surface (Si/Al) = bulk (Si/Al). (The error bars included on the Na form are representative also for the H⁺ form.)

change in surface roughness (5) upon pelletizing, since no difference was found between dispersed powder and pelletized Na–mordenite, Na–A, and Na–Y zeolites.) The nature of the material within the core of the polycrystalline aggregates is uncertain. X-Ray diffraction data disqualified the presence of other zeolitic material, yet bulk chemical analysis of the Na⁺-exchanged crystals in all cases showed the presence of an excess of aluminum (~25%) over the expected amount based on the sodium analysis. This suggests that some aluminum may

be present as nonzeolitic material probably as an amorphous phase.

From the above observations some rudimentary suggestions are made about the crystallization mechanism for the particular zeolite preparations used in this study. The crystal morphology, i.e., the presence of polycrystalline aggregates, suggests that crystallization may proceed via the initial segregation of the hydrogel phase into discrete amorphous particles exposed on all external surfaces to the solution phase.

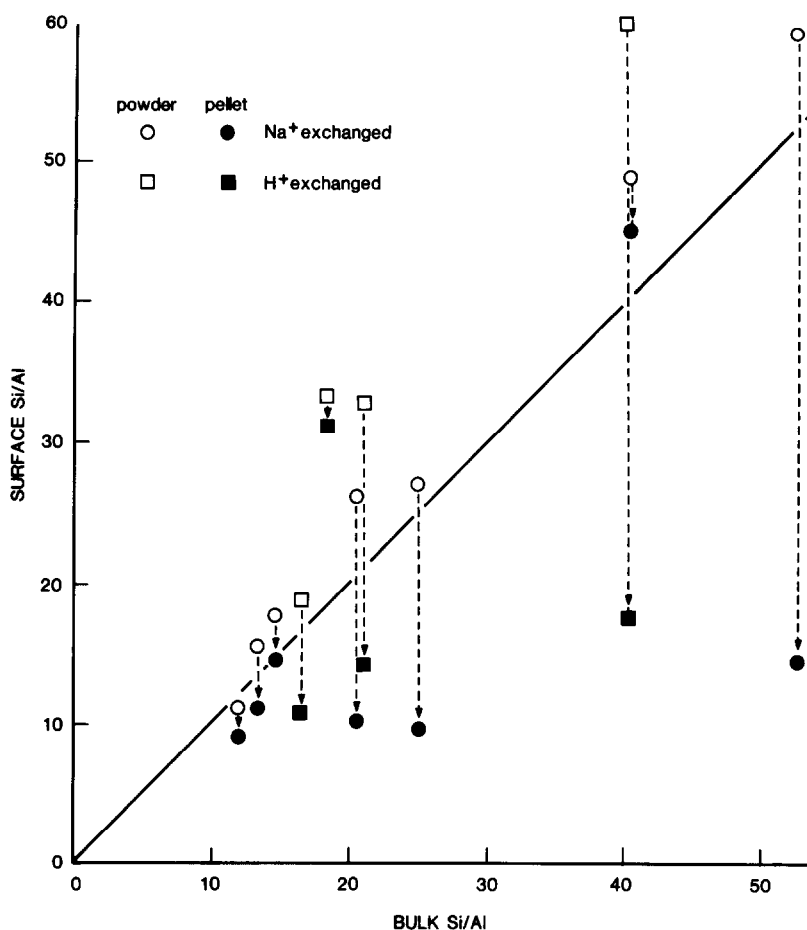We propose that nucleation occurs at the

FIG. 3. Effects of pelletizing: Solid symbols, pelletized; open symbols, dispersed with cyclohexane. The dispersed and pelletized samples (joined by dashed lines with arrows) have the same (bulk Si/Al) values. The solid line represents surface (Si/Al) = bulk (Si/Al). (The magnitude of the error bars is the same as in Fig. 2.)

surface of the amorphous gel particles and crystallization proceeds inwards. This would result in a high Si/Al ratio on the surface of the aggregates because under identical conditions we have found that silicalite crystallizes faster (2–3 times) than aluminum-rich ZSM-5 (Si/Al < 1000). This would also result in a higher concentration of aluminum in the interior of the aggregates due to the exclusion of aluminum at the early stages of crystallization. The presence of aluminum-rich material in the interior of the aggregates lends support to this hypothesis. However, as the location and

the chemical nature of the excess interior aluminum has not been definitely established our conclusions must be tentative.

In summary, we found an inhomogeneous distribution of aluminum in ZSM-5 polycrystalline aggregates, consisting of a siliceous outer surface and an aluminum-rich interior. The surface depletion of aluminum is in contrast with some recent surface studies (6–9) of ZSM-5, (see Table 1 for details). For example, Suib et al. (6) and Dwyer et al. (7) have found no variation between the Si/Al ratios of the surface and bulk. However, von Ballmoos and Meier

TABLE 1

Reference	Preparation	Particle size	Surface technique	Results
This study	Water glass, or sodium silicate 29% SiO$_2$, 9% Na$_2$O, TPABr, Al$_2$(SO$_4$)$_3$ 175°C 2 days	Small crystallites (50–200 nm) Aggregates 5 µm	XPS	Si-rich surface on aggregates. Occluded Al-rich material in interior
Suib et al. (6)	Ludox, TPABr, NaAlO$_2$ 175°C 8 days U.S. Pat. 3,702,886 Ex. 27	Large rods 8 × 20 µm Some cubes 25 µm	Auger	Homogeneous Al distribution
Dwyer et al. (7)	Water glass containing SiO$_2$ and Na$_2$O, TPABr, Al$_2$(SO$_4$)$_3$ 121°C 2 hr, 160°C 10 hr U.S. Pat. 3,926,782	Small crystallites 0.03 µm and agglomerates 0.1 → 0.3 µm	SIMS	Homogeneous Al distribution
von Ballmoos and Meier (8)	SiO$_2$, TPAOH, Al(NO$_3$)$_3$, NaOH 200°C for 5 days	60- to 200-µm crystals	Electron microprobe	Surface Al enrichment
Derouane et. al. (1, 9)	No information	5–8 µm 0.1–1.0 µm	XPS	Homogeneous Al distribution Surface Al enrichment

(8) have measured an enrichment of aluminum at the surface of ZSM-5, while Derouane et al. (9) have found similar surface and bulk Si/Al ratios for large crystals (5–8 µm) but an enrichment of surface aluminum for smaller crystals (<1 µm). As Derouane et al. suggest (9), this variety of results is due to the fact that ZSM-5 is not a unique material. Hence conclusions reached about the aluminum distribution of ZSM-5 prepared by one particular method may not necessarily be applicable to all ZSM-5 preparations. Our results, therefore, should be valid only for crystallizations designed to produce small crystals via a gel crystallization. On the other hand, it is probable that the effects of acid leaching, i.e., the removal of aluminum from the bulk and surface of ZSM-5, would be observed with most preparations of ZSM-5. Finally, for

surface techniques which do not have high spatial resolution (XPS, Auger, SIMS) a good test of the homogeneity of the sample is provided by comparing surface analyses of as prepared and pelletized samples, provided the pelletizing is effective in fracturing crystalline aggregates. This method may reveal non-ZSM-5 material occluded in the matrix of the original preparation.

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