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Concerning the Aluminum Distribution Gradient in ZSM-5 Zeolites

A recent paper in this journal (*1*) examines the surface and bulk compositions of various zeolites, including zeolite ZSM-5. It concludes that the surface (Si/Al) ratio for the zeolites which were investigated (A,X,Y, and ZSM-5) is close to that of the bulk, in contrast to previous XPS studies. It could be inferred from this report that the aluminum distribution in zeolite ZSM-5 is homogeneous. We have performed a detailed investigation of the synthesis of ZSM-5-type materials, using various synthesis routes and with an in-depth characterization of several isolated intermediate phases (*2*). It is our deduction that aluminum can be distributed inhomogeneously in ZSM-5 crystals, the distribution being affected by such factors as the source of silica, the duration of the autoclave treatment, and the concentration of aluminum in the reactant mixture. For example, large (greater than 5 μm) single (or twinned) ZSM-5 crystals have been found to consist of a silica-rich core (Si/Al = 95 or more) surrounded by an outer shell containing more aluminum (Si/Al = 15), while smaller crystallites (0.1–0.5 μm) of lower average aluminum content (Si/Al = 35–40) can be homogeneous or can terminate with a siliceous rim. These conclusions were arrived at from chemical analyses of intermediate phases with a varying degree of crystallinity (*2*). Recently, von Ballmoos and Meier (*3*) proved by electron microprobe analysis the existence of aluminum distribution gradients in large ZSM-5 crystallites.

It was then well appreciated by us that ZSM-5 zeolite is not a unique material, not only because it can be synthesized over a broad range of Si/Al ratios (*4*) and can contain other pentasil-like structure domains (*5*), but also because the aluminum distribution in the crystallites (in particular, homogeneous vs inhomogeneous) can vary depending on the synthesis conditions which are used. Our views have since been substantiated by measuring the surface and the bulk compositions of several ZSM-5-type materials, using XPS (intensity ratio of the Si_{2p} and Al_{2p} peaks, corrected by the Scofield cross sections (*6*)) and proton-induced γ-ray emission (*2*), respectively. The corresponding analytical depths are about 1 and 10^4 nm. Typical data are reported in Table 1.

Example A shows that XPS can indeed be used to measure the surface composition without too much distortion from screening effects (*7*). Cases B and C are examples of surface enrichment in aluminum for as-synthesized materials. Chemical modifications which aim to increase the aluminum content (example C, $AlCl_3$) or to decrease it (example D) are clearly quantified and most of the effect seems to occur, in these particular cases, in the outer shell of the crystallites.

It is obvious that increasing attention should be paid to the actual distribution of aluminum in ZSM-5-type materials. We suggest that it should not be considered a priori as homogeneous. As the presence of aluminum is intimately related to the existence of acidic (active) sites, it is obvious that this observation is of particular importance when it is considered that the external surface of these materials is not shape selective, that some catalytic reactions may occur essentially in the outer shell of such structures because of diffusion restrictions, and that inhomogeneities in the aluminum (active) site distribution will affect the "effective contact time per site" of the reactants.

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TABLE 1

Surface vs Bulk Composition of ZSM-5 Zeolites

Zeolite and chemical treatment	$\left(\frac{Al}{Al + Si}\right)_{av}$ [a]	$\left(\frac{Al}{Al + Si}\right)_{surf}$ [b]
A. Large particles (5–8 μm)		
(Na,H)-ZSM-5, after calcination at 773 K	0.066	0.065
B. Small particles (0.1–0.5 μm)		
(Na,H)-ZSM-5, after calcination at 773 K	0.034	0.039
C. Small particles (0.5–1.0 μm)		
(Na,H)-ZSM-5, after calcination at 773 K	0.009	0.018
Treated by $AlCl_3$, calcined at 773 K	0.020	0.156
D. Large particles (2-4 μm), (Na,H)-ZSM-5		
Calcined at 773 K, acidified by HCl 0.5 *N*	0.049	0.051
Calcined at 1173 K, acidified by HCl 0.5 N	0.047	0.041

[a] Average atomic ratio from proton-induced γ-ray emission.
[b] Average atomic ratio from XPS measurements.

Although the validity of the data and conclusions of Suib *et al.* (*1*) should not be questioned, we believe that they should not be generalized as far as ZSM-5 and other pentasil materials are concerned, in view of the observations of von Ballmoos and Meier (*3*) and our present data.

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