JOURNAL OF CATALYSIS 83, 480–486 (1983)

On the Crystallography of Twinned ZSM-5 Type Zeolites

The potential use of ZSM-5 type zeolites as one-step catalysts for obtention of high octane gasolines and aromatic organic molecules from low alcohols and oxygenated compounds (*1, 2*), raised increasing interest in that type of zeolitic materials.

Structural studies based on X-ray diffraction (*3*) indicated that the framework of ZSM-5 contained a configuration of linked tetrahedra consisting of 5-membered rings; the three-dimensional framework is formed by two intersecting channel systems with apertures formed by 10-membered rings of tetrahedra. Those channel systems were found to run parallel to [100] and [010], respectively, the first of them being sinusoidal while the other was found rather straight along [010]. The "free" channel cross sections have been reported (*3, 4*) to be 0.54 ± 0.02 nm for the nearly circular zigzag channels and 0.57 to 0.58 × 0.51 to 0.52 nm for the elliptical cross-sectioned straight channels parallel to [010]; so, ZSM-5 is intermediate between the narrow- and wide-pore zeolites such as Faujasites.

Although the parameters given above are widely accepted, there is no crystallographic aspects reported, proper of ZSM-5, which could make it recognizable from conventional microscopy observations. Thomas *et al.* have published several times the high resolution image of ZSM-5 (*8–10*), but no details about the ED patterns and crystal habits dependence on the preparation mode were given so far. So, the aim of this note was to report the main crystallographic features of ZSM-5 zeolites as characterized by conventional electron microscopy, but also the direct images of the characteristic straight channel system are presented. For the first case electron diffraction of selected areas was applied, while high resolution electron microscopy (HREM) was applied for the second purpose.

The preparation of ZSM-5 used in this study was carried out accordingly to methods reported elsewhere (*5*). Essentially, the H-ZSM-5 form was obtained after calcination at 550°C and through the exchange and use of amminated bases such as TPA-OH. After identification by XRD the samples were mounted on copper grids as usual for EM studies. So, upon evacuation overnight the zeolites were observed in a JEOL-100 CX instrument fitted with a top-entry pole piece. A typical low-magnification picture of ZSM-5 is shown in Fig. 1, where three morphologies, Z-1 to Z-3, are clearly distinguishable. The twinned, Z-1 type plates were found very much common with typical mayor dimensions comparable to those of Z-2 type plates, of about 1 μm in length, and parallel to the c axis.

For electron diffraction purposes, single crystals of both Z-1 and Z-2 type plates were taken, as shown in Figs. 1b and c. So, Fig. 2a contains the electron diffraction pattern of a single Z-1 type plate (Fig. 1b) showing a diamond-like symmetry which indicates the high degree of crystallinity typical of those twinned crystals. Figure 2b contains the explanation of such a pattern and a full indexation which is consistent with orthorhombic symmetry with [010] zone axis. The mean unit cell parameters $\bar{a}$ and $\bar{c}$ were found from this series of ED patterns through the use of gold standards and were found to be equal to 20.02 ± 0.04 and 13.46 ± 0.04 Å, respectively. The corresponding values reported elsewhere (*3, 4*) were $\bar{a}$ = 20.067 and $\bar{c}$ = 13.39 Å; so, a good agreement is obtained within the experimental error. However, a scanning of

0021-9517/83 $3.00
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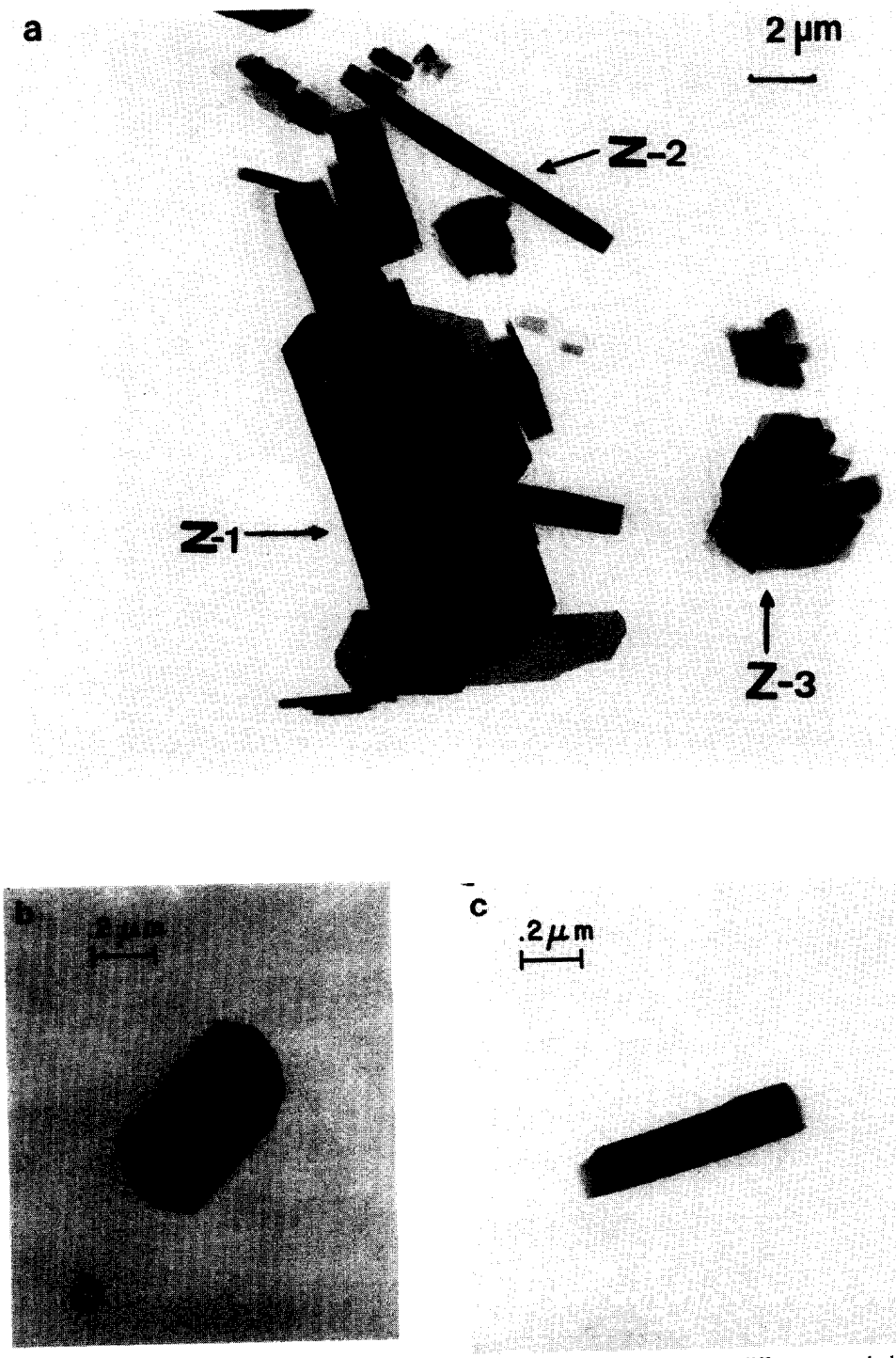
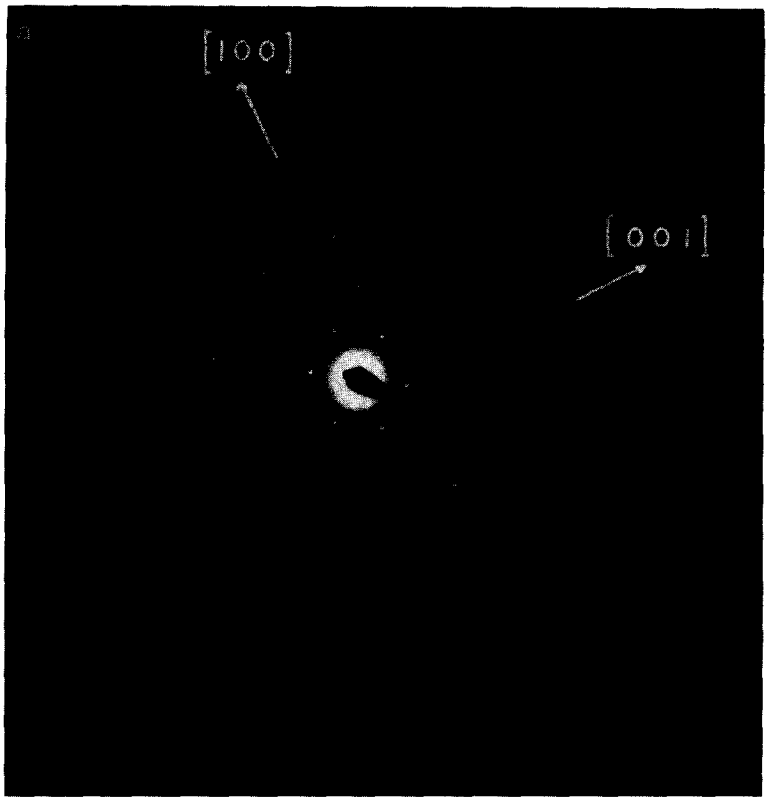


FIG. 1. (a) Typical low magnified image of a typical region of ZSM-5. Three different morphologies are apparent: Z-1, Z-2, and Z-3. (b) Typical single crystal of Z-1 type. (c) Typical single crystal of Z-2 type.



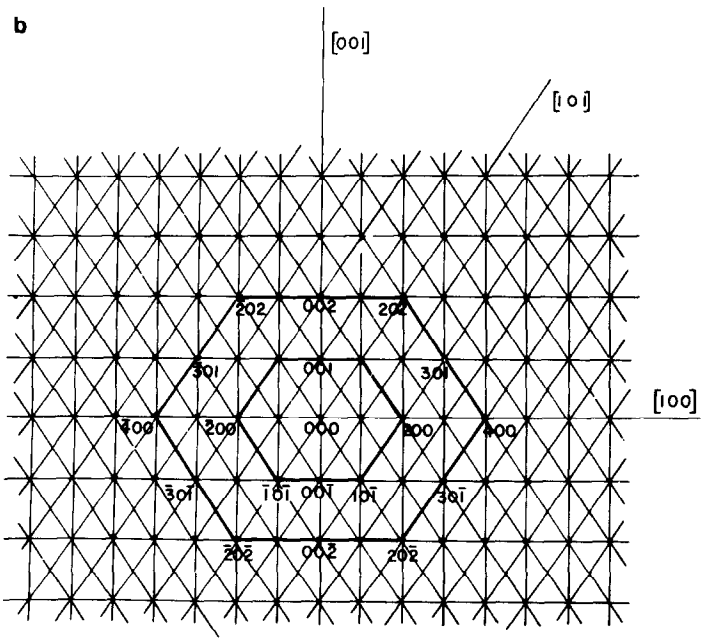


FIG. 2. (a) Selected area diffraction pattern of the Z-1 type plate shown in Fig. 1b. (b) Indexed diffraction pattern corresponding to Fig. 2a zone axis is [010].

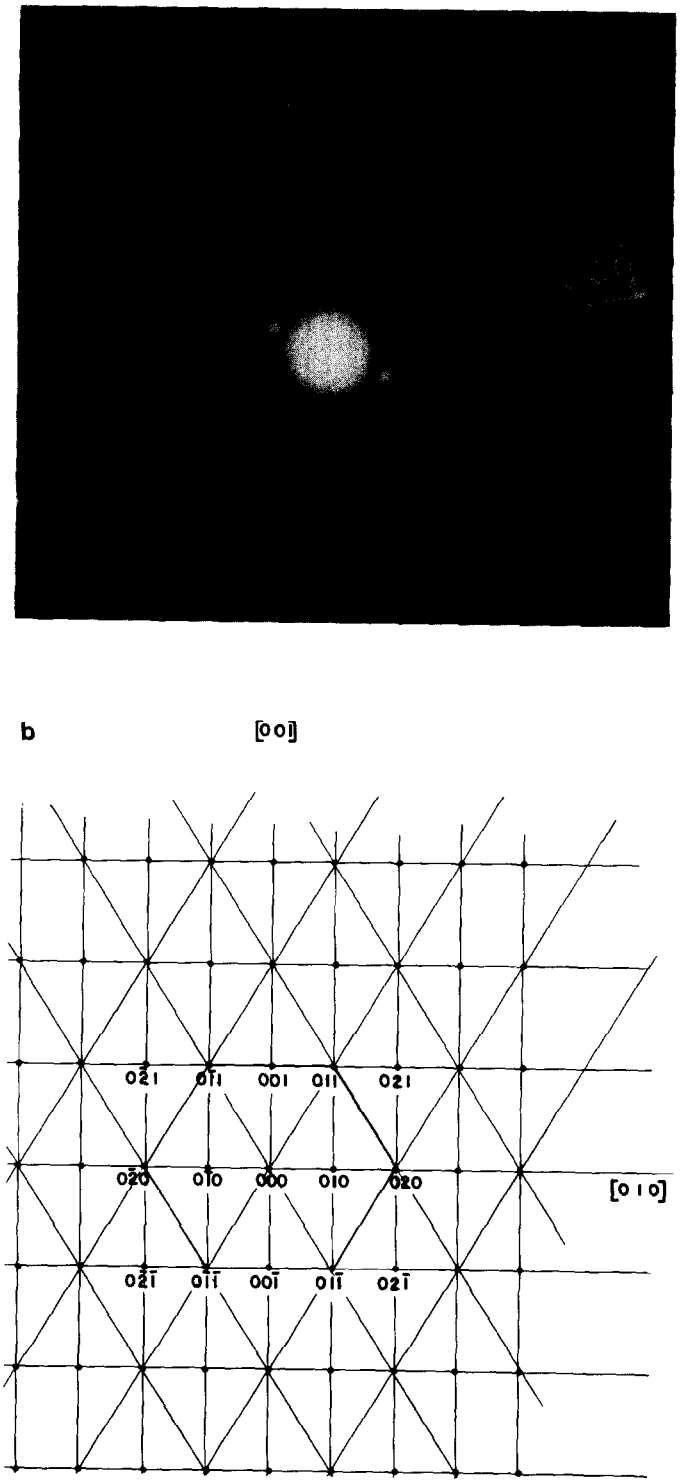


FIG. 3. (a) Selected area diffraction pattern of the Z-2 type plate shown in Fig. 1c. (b) Indexation of the EDP shown in Fig. 3a, consistent with orthorhombic symmetry with [100] zone axis.

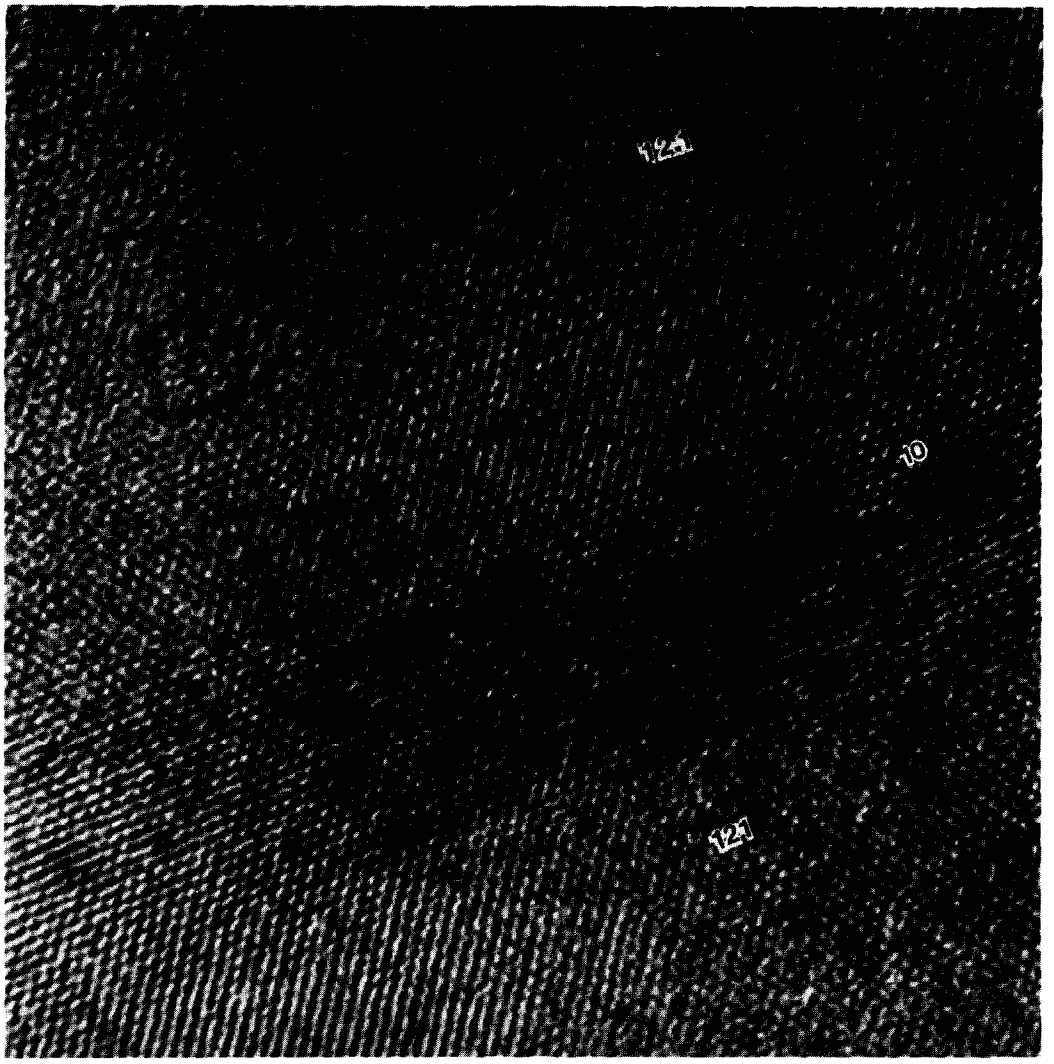


FIG. 4. (a,c) Lattice resolution image of ZSM-5 crystallite in [010] orientation. The straight system of channels is directly observed from this picture. (b) Dimensions of interchannel distances (in Ångstroms) measured on the $a-c$ plane.

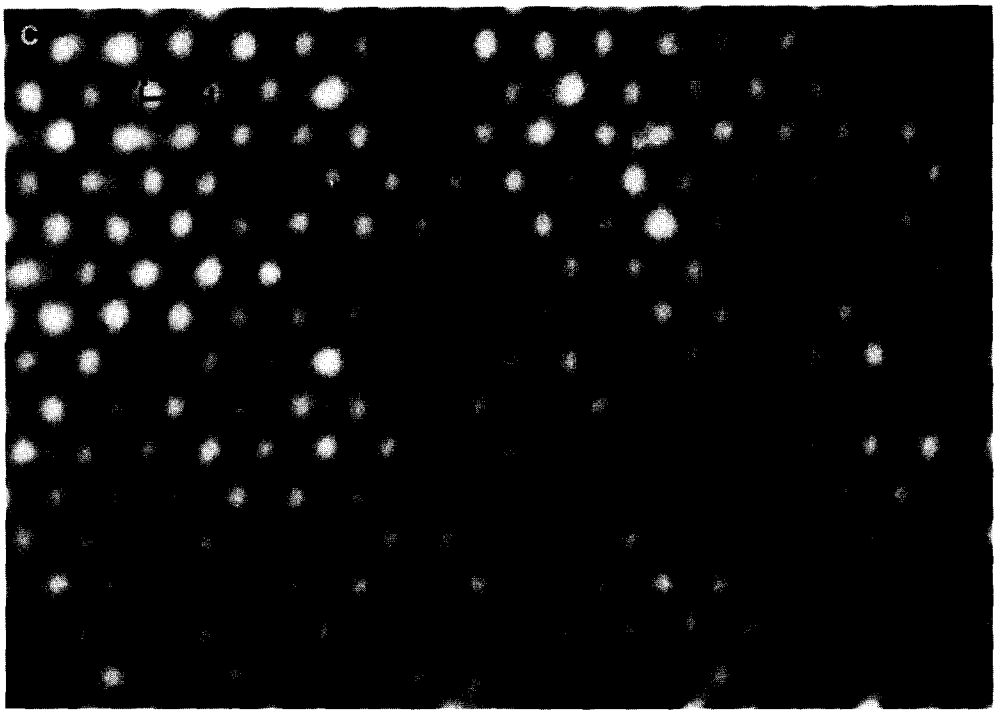


FIG. 4—*Continued.*

the samples showed that slight variations of the *c*/*a* ratios existed from one crystallite to another, perhaps following a local variation in aluminum concentration as reported recently (*6*). Further work is being pursued in this direction.

The Z-2 type plates shown in Figs. 1a and c gave rise to a second set of ED patterns, as shown in Figs. 3a and b. The full indexation of such patterns demonstrates that the whole pattern belongs to orthorhombic symmetry with a [100] zone axis. That is, the Z-2 type plates are edge-on views of Z-1 type plates. From this pattern a determination of the magnitude of *b* axis is possible, giving $b = 19.6 \pm .04$ Å against $b = 19.93$ reported previously from XRD measurements (*3*, *4*).

The last type of morphology, called Z-3 in this paper, is a polycrystalline aggregate formed by stacking of Z-2 type plates along the [010] direction. Sometimes those aggregates appear formed onto the main face of Z-1 plates, giving rise to rings in the ED patterns which contain the two orientations described here.

On the other hand, a high resolution, high magnified crystallographic zone of ZSM-5 is shown in Figs. 4. The first and second-order reflections, of the unit cell seen along [010], were used to resolve the lattice planes and cavities. The black and white, nearly circular dots observed at the crossing of lattice planes correspond to the straight channel system seen along *b* axis, as pointed out above. It is observed that black or white sets at the plane crossing are positioned equivalently and both sets present a honeycomb-like pattern corresponding to the straight-channel [010] zone. The apertures of these elliptical channels have 0.56×0.54 nm as major and minor axis, respectively, which are very close to the reported values (*3*, *4*). A schematic drawing is added to the bottom of the micrograph in Figs. 4 to illustrate better the

situation with respect to the three-dimensional framework of ZSM-5 under same orientation.

CONCLUSION

High resolution electron microscopy together with selected area diffraction studies have a great value to characterize the entire crystallography of zeolitic materials as the one presented in this article. It was found that the ZSM-5 has a high degree of crystallinity as well as a uniform distribution of pores, but there are local irregularities, both crystalline and compositional, which can be further studied by transmission electron microscopy at a nearly atomic scale.

ACKNOWLEDGMENTS

We acknowledge the PNCB-CONACYT program for support and Mr. G. Arciniega for technical help.

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Received January 25, 1983