

Early Transition Metal Silicates: New Microporous Materials

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A major scientific and technological achievement since 1949 has been the discovery and development of synthetic zeolites as molecular sieve adsorbents and catalysts. A zeolite is a crystalline aluminosilicate with a framework based on an extensive three-dimensional network of oxygen ions. Situated within the tetrahedral sites formed by the oxygen can be either a Si^{4+} or an Al^{3+} ion. The AlO_2^- tetrahedra in the structure determine the framework charge. This charge is balanced by cations that occupy nonframework positions.¹ The synthesis of silicalite, a polymorph of SiO_2 , in 1978 demonstrated the ability to create molecular sieves without framework charge. Unlike the aluminosilicate zeolites which are hydrophilic, silicalite is hydrophobic and organophilic, and selectively adsorbs organic molecules in the presence of water.² Incorporation of early transition metals into silicalite frameworks produce new microporous materials that combine the shape selectivity provided by the framework with the reactivity of early transition metals.

In 1983, the synthesis of a silicalite containing titanium (TS-1)³ initiated a new approach to catalyzing the heterogeneous, selective oxidations of organic molecules by H_2O_2 .^{4,5} The isomorphous substitution of titanium for silicon gives a solid that retains the MFI structure, in which TiO_4 tetrahedra are connected to SiO_4 tetrahedra by corner sharing. The pore system contains 10-membered rings.⁶ The MFI framework (Figure 1a) is also adopted by ZSM-5, an aluminosilicate, and on silicalite itself, and exhibits a characteristic XRD powder pattern (Figure 1b).

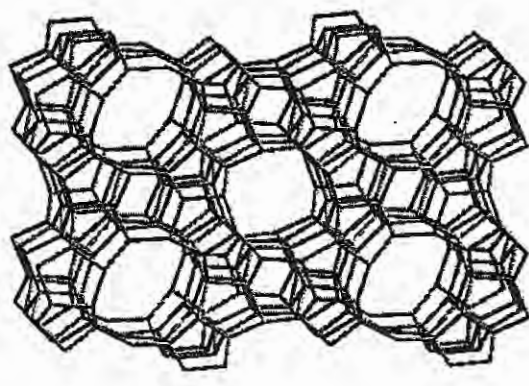


Figure 1a. MFI projection along [010]

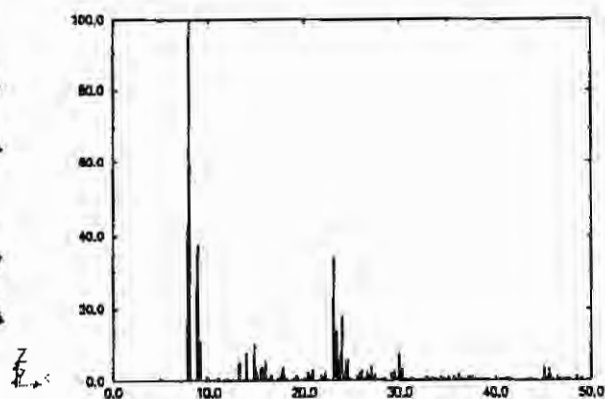


Figure 1b. MFI XRD pattern

In 1989, a family of microporous titanosilicates (generally denoted ETS) was discovered in which the metal atoms (Ti^{4+}) are octahedrally coordinated.⁷ Using a combination of high-resolution electron microscopy (HREM), powder X-ray diffraction (XRD), X-ray absorption spectroscopy (EXAFS), solid-state NMR (MAS), molecular modeling, and chemical analysis, the structure of a prominent member of this family, ETS-10, has been elucidated.^{8,9,10} The structure of ETS-10 may be described in terms of an intergrowth of two end member polymorphs, termed A and B, both of which consist of a three-dimensional 12-membered ring structure. Because Ti is only part of the small 7-member ring channels (Figure 2), water molecules in the wider 12-member ring channels do not bond to the framework as strongly as in conventional aluminosilicate zeolites, so that much lower drying temperatures are possible for

ETS-10. On the other hand, because of the long-range electronic interactions induced by the negative charges, bonding between water in the 12-member ring channels and the framework is not as weak as in silica where there are no charge centers. These properties make ETS-10 economically competitive to replace CFCs for manufacturing air conditioning systems.

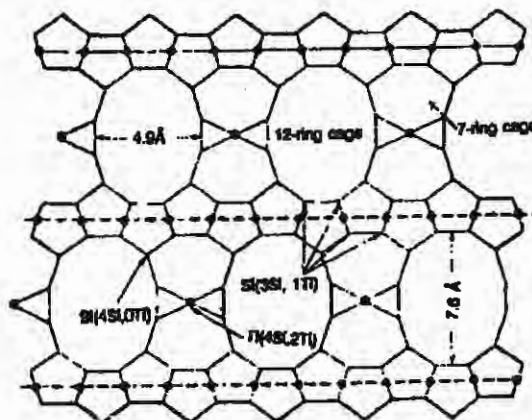


Figure 2. Schematic of ETS-10 showing Si and Ti connectivity

The isomorphous substitution of Si^{4+} by Zr^{4+} or V^{4+} in the silicalite-2 (ZSM-11, MEL) framework has also been reported and the resulting solids are active oxidation catalysts.^{11,12} The MEL framework (Figure 3a) exhibits a characteristic XRD powder pattern (Figure 3b). In the case of vanadium, EPR spectra of the as-synthesized and reduced samples indicate that vanadium (in the tetravalent state) is in an atomically dispersed state, but not in T_d symmetry positions. Only V^{5+} ions were present on calcination, and the V^{4+} to V^{5+} transition was found to be reversible.¹³

The incorporation of two transition metals into the MEL framework has also been carried out in the hopes of preparing useful and interesting catalysts with shape selective features. One such microporous material is VTS-2, a vanadotitanium silicate.¹⁴

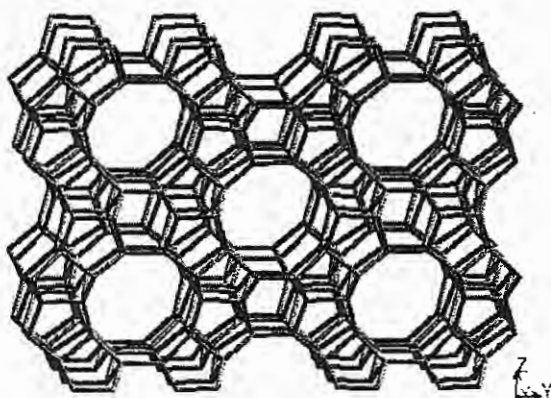


Figure 3a. MEL projection along [100]

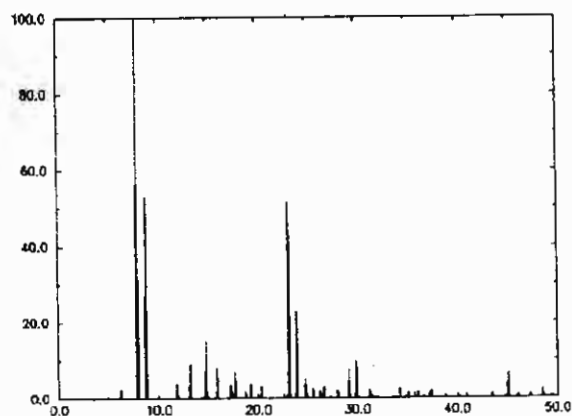


Figure 3b. MEL XRD pattern

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