

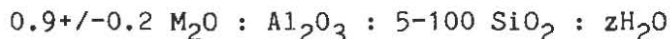
Shape-Selective Catalysis with ZSM-5 Zeolites

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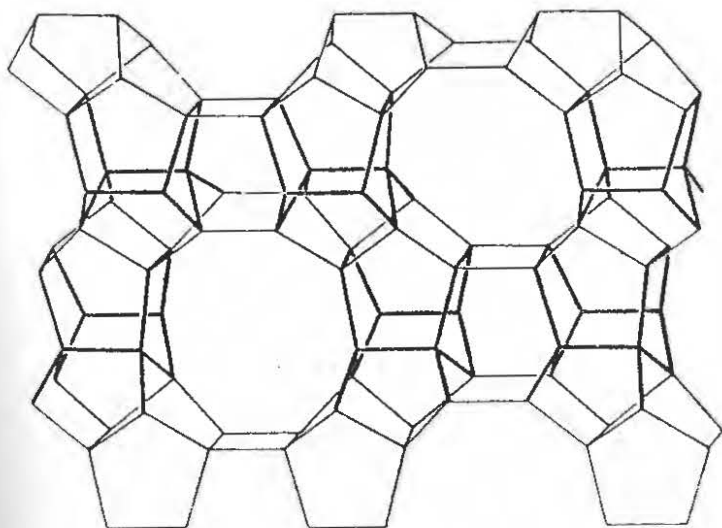
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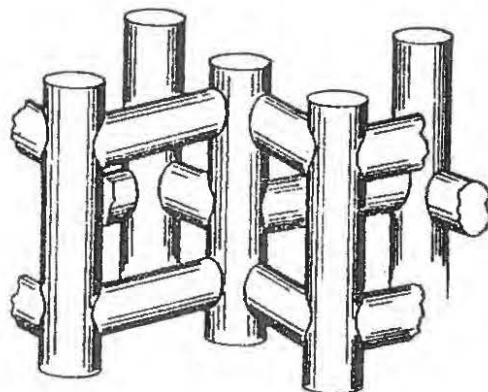
Most shape selective catalysts in use today are molecular sieve zeolites. Structurally these are framework aluminosilicates which are based on infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked by sharing all the oxygens [2]. Of all the synthetic zeolites available ZSM-5 stands out as a shape-selective catalyst. In its preferred form ZSM-5 has a formula in terms of mole ratios of oxides of:



where M is Na^+ , K^+ , R_4N^+ , etc. Crystals are generally made from a solution of the oxides along with water and a template such as tetraalkylammonium hydroxide. The crystals can then be modified by standard cation exchange methods [3]. ZSM-5 is made of successive pentasil layers which results in a unique channel network (see figures below). The channel network consists of elliptical straight channels ($5.1 \times 5.5 \text{ \AA}$) orthogonal to circular zig-zag channels ($5.4 \times 5.6 \text{ \AA}$). It is this channel network which accounts for the shape-selective properties of ZSM-5 [3,4].



The Pentasil Layer



Channel Network

Shape-selective chemical reactions in zeolites can be thought to occur in three distinct ways [1]. The first, known as "reactant selectivity", occurs when only a fraction of the reactant molecules are small enough to diffuse through the catalyst pores. Secondly, "product selectivity" occurs when some of the products formed within the pores are too bulky to diffuse out as observed products. Finally, there is "restricted transition state selectivity" where neither reactant nor potential product molecules are necessarily prevented from diffusing. Instead, certain reactions are prevented because the corresponding transition state would require more space than available in the zeolite cavity.

The shape selective potential of ZSM-5 is often utilized in the alkylation of toluene and in the Mobil methanol-to-gasoline process. The industrial alkylation of toluene (necessary since para-xylene is a valuable starting material in the synthesis of many polymer precursors) is normally an expensive process due to the high cost involved in separating the desired para-isomer, formed in its equilibrium amount of only 24%, from its close boiling ortho and meta isomers. However with modified ZSM-5 zeolites the amount of para isomer in the reaction mixture can be raised to as high as 96% due to its preferred diffusion through small catalysis pores [5].

In the methanol-to-gasoline process, cheap and easily available methanol is converted to high octane (RON 90-95) gasoline and water over ZSM-5. The hydrocarbons obtained span a relatively narrow range of molecular weights, terminating at C₁₀. The very high percentage of iso-compounds and aromatics produced accounts for the high octane number. The shape selectivity observed in this case is responsible for the sharp cut-off in molecular weights [6].

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