Rational Design of Shape Selective Separation and Catalysis

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Zeolites are also known as "molecular sieves" as they can be used to separate molecules, based on their sizes and shapes. There is a large and growing list of zeolites and related nano-porous material with molecular size pores, with openings ranging from the 8-ring LTA with a 4.1 Å to the 20-ring CLO with 13.2 Å diameter. The shapes of the openings range from the circular LTA to the square RON, the highly elliptical CZP, and the clover leaf shaped CLO. The earliest method to screen for a zeolite that would separate two molecules is to assume that the molecules are rigid spheres, and the zeolite windows are rigid circles, and to compare their diameters. This method does not work very well since molecules are not spheres, but are fully three-dimensional figures. A normal decane can be approximated by a cylinder that presents different projections on the zeolite surface when it approaches, and must be rotated to align its major axis with the pore axis to enter. We define the molecular "footprint" as the projection that would present the least resistance to enter a given zeolite channel.

We present a method of computing the optimal translation and rotation and the footprint of each molecule, and characterizing it with a major and a minor diameter. This leads to a two-dimensional screening of molecule footprints against zeolite windows, which is far more accurate than the one-dimensional screening. However it is known that a molecule that is 10 to 20 % larger than the window can nevertheless enter, especially at high temperatures. The flexibility of molecules and windows must be taken into consideration. When a set of molecules approach a zeolite, the results is really described by a triage: some goes through without strain, some do not go in at all, and others require an activation energy and sufficiently high temperature to enter, at the cost of reduced equilibrium adsorption concentration and reduced diffusivity.

We next replace the hard sphere model of atomic radius with the Lennard-Jones potential between energy and radius, and replace the rigid bond lengths and angles with quadratic force fields. Then we compute the optimal degree of rotation and distortion of these multiple sets of parameters for both molecule and window, in order to arrive at a minimum energy of strain, E_s, that would be needed to squeeze a molecule into a window. We have compiled a database of 38 molecules and 220 zeolite channels, which is to say 8360 strain energies. The molecules include inorganic gases, paraffins, olefins, aromatics, sugars, sex hormones, fatty acids, and UF_6; the zeolites include all the structures in the 2001 edition of the "Atlas of Zeolite Framework Types".

This strain energy of a molecule would reduce the equilibrium adsorption concentration in comparison with an equivalent but unstrained molecule by the Boltzmann factor $\frac{c}{c_0} = \exp\left(-\frac{E_s}{RT}\right)$. Given two molecules with different strain energies, the degree of separation is given by $\gamma_{AB} = \exp(-\frac{E_A}{RT}) - \exp(-\frac{E_B}{RT})$. The best separation

is achieved when $E_A = 0$ and $E_B > 0$, so that molecule A can enter with ease at any temperature, but molecule B can enter only when temperature is sufficiently high, thus the best temperature of separation should be low. However if both strain energies are not zero, then neither can enter at absolute zero temperature and both can enter with ease at infinite temperature. The degree of separation achieves the maximum value at an intermediate temperature given by $T^* = \frac{1}{R} \frac{E_A - E_B}{\ln E_A - \ln E_B}$.

This set of theory and computations methods can be used to compile much larger databases of many more molecular footprints, major and minor diameters, as well as many more strain energies of molecule-window pairs. It can be used to screen for better separation methods for difficult problems, such as the separation of water from ethanol to produce motor fuel.