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Rational design of shape selective separation and catalysis—I: Concepts and analysis

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Abstract

A molecule can enter a zeolite channel when it fits the size and shape of the opening. Zeolites have been used commercially for their ability to admit selectively molecule A but not molecule B. The search and design of zeolites for separation has been based on finding a channel with a diameter that is larger than molecule A, but smaller than molecule B. This method is not sufficiently accurate when the molecule is not a sphere or the channel is not a circle. We present here first a more accurate screening method based on comparing both the major and minor diameters of the molecule projection, called the “footprint”, with the diameters of the channel. Then we present an even better method that is based on the activation energy required to strain and distort a molecule to fit a given channel, thus leading to a lowering of its Boltzmann concentration in this channel. This paper compiles the activation energies encountered among thirty-eight (38) molecules and two hundred and seventeen (217) zeolite channels into a database, and shows how one can use this database to identify the most promising zeolites for the separation of a set of molecules of interest. Such a screening method would help to identify a zeolite that has much lower activation energy for molecule A than for molecule B. The appropriate temperature range for separation would be centered around the optimal temperature T^*, where the degree of selectivity is at a maximum. The separation of the three pentane molecules was selected as an illustration.

Keywords: Catalysis; Molecular sieves; Selectivity; Separations; Supramolecular chemistry; Zeolites

1. Introduction

Zeolites have been extensively used in industry as molecular sieves. Selective separation is based on the sizes and shapes of the molecules in comparison with the windows and channels of zeolites (Chen et al., 1996; Kresge and Dhingra, 2004). An example of this shape selectivity is the separation of para-xylene, used in polyester production, from its ortho- and meta-isomers by the 10-ring ZSM-5. Other zeolites are used in selective catalysis, such as in catalytic dewaxing where the normal but not the branched paraffins are removed from lubricating oils by the 10-ring SAPO-11. The biggest potential for selective separation with zeolites is in sets of molecules that are very closely related in physical properties (e.g., boiling points), making other separation processes (e.g., distillation) not practical. Such adsorptive separation can be achieved by three mechanisms: steric separation is achieved when only small and properly shaped molecules can diffuse into the adsorbent, but larger molecules are totally excluded; kinetic separation is achieved when different molecules have different diffusivities and speeds of adsorption; and equilibrium separation is achieved when the equilibrium adsorption concentrations of different molecules are reduced due to their shapes (Yang, 2003).

At this time, only circular and near-circular channels are used for most of the current zeolite-based industrial separation methods. There exist many opportunities for shape selective separation schemes waiting to be exploited, especially involving non-circular channels and windows. There are also excellent opportunities to design new zeolites or modify existing ones to make them more selective. There is a variety of available modification methods that include ion exchange with suitable ions, such as K^+, and Ca^{2+}, and deposition of coke and other substances to modify the size of the free channels.

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The interaction of a guest molecule with a host zeolite is in the realm of supramolecular chemistry (also called host–guest chemistry) and is of critical importance in a range of phenomena besides separations. For example, the binding of substrates to enzymes, as well as that of drugs to receptors, are all influenced by their steric relations which are often compared to the "lock-and-key" analogy. Lehn (1993) described the binding of metallic ions with crown ethers as an example of molecular recognition. There are many other types of hosts or receptors including cryptands, spherands, cavitands, calixarenes, cyclophanes, cryptophanes and so forth (Pedersen, 1988). The ability to recognize selectively some molecules but not others leads to selective binding and adsorption, which can be used to promote selectively some reactions and to act as a carrier for escorting chosen molecules and ions across cell membranes.

Despite the vast variety of potential applications, there is no systematic study in the current literature to quantify molecular sizes and shapes and to compile them into a database for the design of separation schemes. There is also no systematic study to quantify zeolite channel sizes and shapes, suitable for selective molecular passages. Thus, there are no accurate and systematic methods to suggest which zeolite would be the most promising candidate to separate a given set of molecules, or how one can modify a given zeolite to improve its selectivity. The simple method of comparing the diameters of molecules with the diameters of zeolite windows, as given by Breck (1974), cannot do justice to the rich variety of shapes of molecules and zeolites.

This paper is written as the first of a series to provide novel quantitative methods and a compilation of their results in databases for the rational design of shape selective separation schemes. It includes a systematic method to quantify the sizes and shapes of molecules, as well as a novel approach to quantify the strain energy encountered when a guest molecule attempts to pass through a host portal. The results are subsequently used to identify candidate portals that exhibit promising molecular sieving action when applied to a given set of molecules of interest.

2. Characterization of molecule projections and footprints

For spherical molecules going through circular windows, such as the noble gases approaching a Linde Type A (LTA) window, the molecular shape and rotational orientation are not important for penetration into a channel since every possible rotation results in the same projection. Fig. 1 depicts the Lennard-Jones length of a number of molecules, which is often used as an order-of-magnitude estimation of the size of the molecule (Reid et al., 1987). It is also the starting point for several attempts to compare these lengths with nominal zeolite window diameters so as to identify zeolite windows that are suitable for separating a set of molecules. For instance, zeolite 3A has a diameter that is between that of H_2 and O_2, thus it would be a good candidate for their separation. Since most molecules are not spherical, and most windows are not circular, we need more accurate methods to characterize molecules.

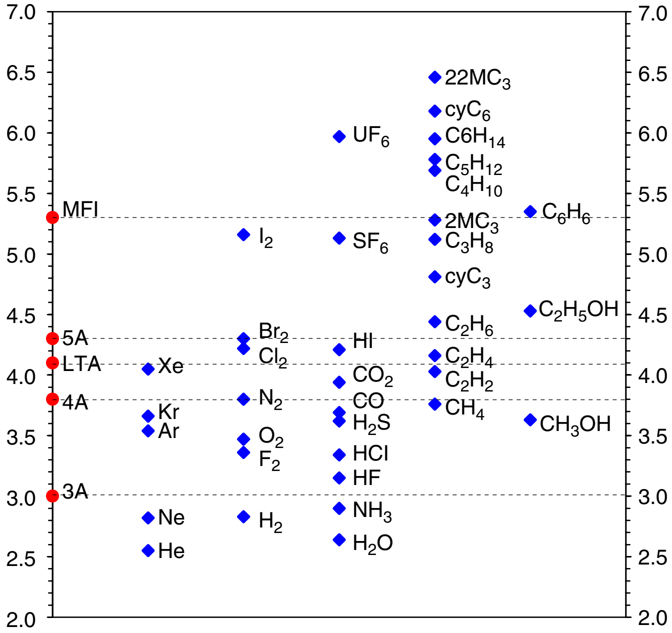

Fig. 1. Lennard-Jones lengths (in Å) and one-parameter screening.

We start from a simple model of a molecule as atoms connected by bonds, obtained by a quantum mechanics or a molecular mechanics calculation. In the hard sphere model, each atom is represented by a sphere with the van der Waals radius, and the bond lengths and angles are considered fixed—equivalent to an inflexible molecule at absolute zero temperature.

When an elongated molecule such as n-decane approaches a channel, various rotational orientations of the molecule give rise to different projections on the horizontal plane. From this ensemble of projections, the ones that are most favorable for penetration are usually the smallest, which we would call the "footprints". Fig. 2 depicts three projections of the n-decane molecule, one of which can be considered its footprint. If the molecule is an ellipsoid with three different axes, then the molecule should be oriented so that the longest axis is perpendicular to the plane, and the footprint is the ellipse formed by the two smaller axes. If the molecule is a rectangular parallelepiped, then the footprint is the rectangle formed by the two smaller axes. This suggests the following useful quantitative measures of the size of a footprint involving no more than two parameters:

(a) The footprint is the projection that can be enclosed by the smallest possible circle, characterized by its radius ρ_0.
(b) The footprint is the projection that can be enclosed by the ellipse with the smallest possible area. This footprint is characterized by its major and minor radii, which are denoted, respectively, with ρ_1 and ρ_2. Its eccentricity is defined as $e = \sqrt{1 - \rho_2/\rho_1}$.
(c) The footprint is the projection that can be enclosed by the rectangle with the smallest possible area. This footprint is characterized by its major and minor lengths, which are denoted, respectively, with α_1 and α_2. The aspect ratio is defined as $\mathrm{AR} = \alpha_2/\alpha_1$.