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PRIORITY COMMUNICATION

Reactivity Enhancement by Molecular Traffic Control

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For two decades, the concept of reactivity enhancement by "molecular traffic control" has been controversially discussed. According to this concept, effective reactivity in zeolite catalysis may be enhanced if reactant and product molecules do not interfere with each other on their diffusion paths. As a major deficiency of this concept, so far no clear criteria for the occurrence of this effect are known. Considering a network of channels with single-file confinement and selective adsorption affinity to either the reactant or the product molecules, a model is introduced in which the possibility of reactivity enhancement may be rigorously demonstrated.

INTRODUCTION

Many processes in nature are based on the mutual exclusion of host–guest complexes. The existence of specific cation channels in cell membranes is one of the celebrated examples of this phenomenon (1–3) and a *conditio sine qua non* for the functional operation of cells in living organisms. Recent molecular dynamic simulations of diffusion in zeolites (4, 5) have revealed a similar type of mutually excluding preferential accommodation of guest molecules in parts of the host structure. These studies have in particular been carried out for zeolites of structure type MFI which are known to consist of two mutually intersecting channel systems. The simulations provided clear evidence that—similarly as with the cation channels in biological membranes—the accommodation probability of the two channel types may vastly differ for different guest molecules.

Shortly after the successful synthesis of MFI type zeolites, Derouane and Gabelica (6) proposed the concept of molecular traffic control (MTC). It is based on the assumption that two molecular species (i.e., the reactant and product molecule of a chemical reaction) are accommodated by two channel types with different probability. One expects, therefore, that the "traffic" of the reactant molecules to the catalytically active sites and the "traffic" of the product molecules from these sites to the surrounding atmosphere is facilitated in comparison with the case that the two types of channels accommodate the two types of molecules with identical probability. Up to now, this concept has been controversial (7–10). Even from a theoretical point of view it is not obvious whether molecular confinement to certain pathways may at all be able to lead to enhanced overall reactivities. A decision of this question must be based on quantifiable model considerations. We are going to demonstrate that a network of mutually intersecting single-file systems (11–13) is well suited to serve as such a model system.

Single-file systems are one-dimensional entities of particles which—like the pearls on a string—are unable to change their order. As a consequence of this mutual confinement, their intrinsic transport properties significantly deviate from normal diffusion. As a most characteristic feature, the mean square displacement of the particles in an infinitely extended single-file system increases with the root of the observation time, rather than with the observation time itself (11–13). Originally introduced as a model for explaining the transport properties in the ion channels of biological membranes (1, 2, 14, 15), single-file behavior has been found to occur in a large variety of systems, including zeolites of one-dimensional channel structure (16–18).

METHOD

The network of intersecting channels of single-file character is assumed to be in contact with an outer atmosphere containing a particular molecular species ("A-type" molecules) in vast abundance. Within the network, the channel intersections give rise to a unidirectional molecular reaction $A \rightarrow B$ with the site reaction rate k_{R}. Molecular traffic control is simulated by assuming that one set of channels (the α channels) is only able to host A molecules, while the channels perpendicular to them (β channels) only accommodate the B molecules (MTC system). The rates of hopping from site to site within the channels and the rates of desorption from the marginal sites are identical. The gain in reactivity in this system must be revealed in comparison

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with a reference (REF) system, where the sites of both channels are equally accessible to both types of molecules and the reactivity is the same as in the MTC system.

RESULTS AND DISCUSSION

As an example, Figs. 1a–1f show the distribution of the reactant (A) and product (B) molecules in a system under molecular traffic control (a–c) and within the reference system (d–f). It consists of 2×5 single-file channels with 15 sites between the channel intersections. The representations show the mean values of molecular distributions attained in 10^6 independent simulation runs. Starting from an arbitrarily chosen initial distribution, molecules were selected at random to attempt jumps to a particular one of the adjacent sites. The attempts are only successful if they are directed to vacant sites. A-type molecules on sites formed by the channel intersections are converted to B-type molecules with the probability $k_R = 0.01$ of a jump attempt. A- and B-type molecules were assumed to desorb from marginal

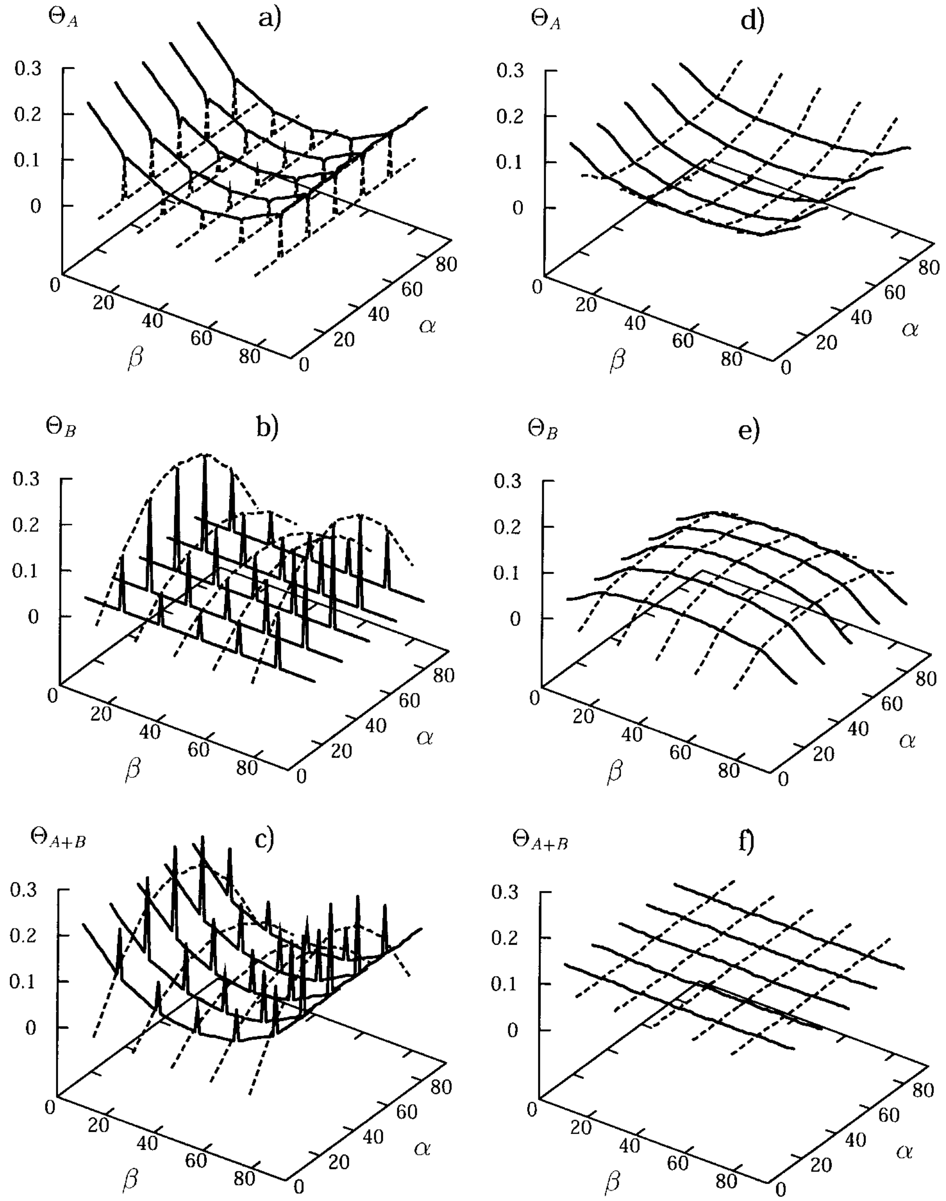

FIG. 1. Concentration profiles of the reactant (A) and product (B) molecules in a network of single-file systems during unidirectional reaction $A \to B$ represented in relative occupancies Θ. The left column of presentation (a–c) represents the situation when A-type molecules are only accommodated by α channels and B-type molecules by β channels (condition of molecular traffic control, MTC). The right column (d–f) describes the analogous situation in the reference system (REF), where both types of molecules are accommodated by both channel types.

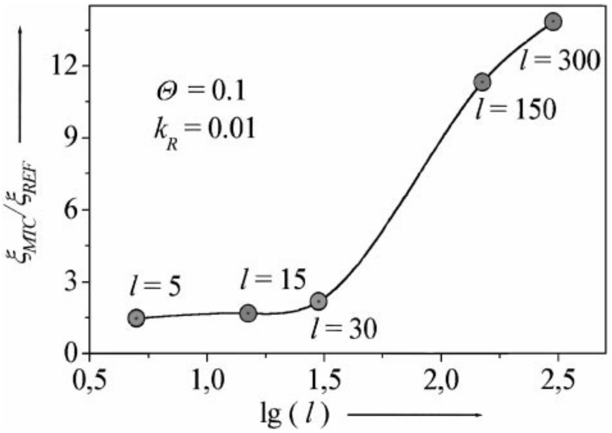

FIG. 2. Ratio $\xi_{\mathrm{MTC}}/\xi_{\mathrm{REF}}$ of the occupation numbers of reactant molecules on the reactive sites (i.e., in the channel intersections) under molecular traffic control (MTC) and in the reference system (REF) as a function of the numbers of sites between the intersections for a medium overall site occupancy $\Theta = \Theta_{\mathrm{A+B}} = 0.1$ and a reaction probability in the channel intersections of $k_{\mathrm{R}} = 0.01$ of the probability of a jump attempt.

sites at the rate of the jump attempts. In order to maintain the initially chosen mean occupancy of $\Theta_{\mathrm{A}} + \Theta_{\mathrm{B}} = 0.1$ over the whole simulation run, any desorption event is immediately followed by occupying a randomly chosen vacant marginal site by an A-type molecule. Each simulation run has been carried out until the rate of particle conversion is observed to be constant, indicating the establishment of stationary conditions.

As required for transport-dependent processes, in both the MTC and REF systems the concentration of the reactant molecules decreases toward the network center (Figs. 1a and 1d), while the concentration of the product molecules decreases toward the margins (Figs. 1b and 1e). As a remarkable feature, in contrast to the behavior of the REF system (Fig. 1f), molecular traffic control (Fig. 1c) leads to a pronounced deviation from a constant occupancy over the network. The number of B-type molecules generated per unit time is proportional to the number of A-type molecules occupying the sites in the channel intersections. Hence, as the key quantity for reactivity enhancement by molecular traffic control, one may consider the ratio of these numbers in the MTC and REF systems. The representation of this ratio as a function of the number of sites between the channel intersection in Fig. 2 indicates a most impressive reactivity enhancement by molecular traffic control.

The reactivity enhancement may be rationalized as an immediate consequence of the differences in the total concentration profiles. While as a consequence of the constancy of the concentration in the reference system (Fig. 1f) molecular exchange of the product molecules is dramatically slowed down by the single-file confinement of the molecules between adjacent channel intersections, the overall concentration gradient in the MTC system (Fig. 1c) directs the reactant molecules into and the product molecules out of the system. It is well known that the mean time of molecular passage through single-file systems increases with the third power of the file length (19, 20). The dramatic increase in reactivity enhancement with increasing site numbers between the channel intersections is an immediate consequence of this relation.

It has been demonstrated that reactivity enhancement by molecular traffic control has a well-defined and -definable microdynamic basis. The experimental realization and verification of this phenomenon is doubtless one of the most attractive issues of research in zeolite science and technology.

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