**Strong Reactivity Enhancement through Molecular Traffic Control in Zeolites**

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**Dedicated to Prof. Dr. Jörg Kärger on the occasion of his 70th birthday**

In the past, the investigation of catalytic reactivity enhancement through molecular traffic control (MTC) by means of dynamical Monte Carlo simulations of catalysis was initiated in simple, idealized zeolite channel networks. These results are reviewed here and, emphasizing more recent work, the conditions of reactivity enhancement through MTC are examined for a realistic channel topology based on the pore structure of the zeolite TNU-9. For a wide range of reaction rates a very strong MTC effect can be found that increases with grain size. This effect is argued to be a generic feature of a certain class of zeolite pore topologies.

**Keywords:** Catalysis, Molecular traffic control, Reaction diffusion model, Zeolites

## 1 Introduction

Zeolites are microporous crystalline solids with a wide variety of industrial applications. In chemical and petrochemical industries, zeolites are often used as catalysts for processes like isomerization or cracking of hydrocarbon molecules [1, 2]. The zeolite pores inside which catalysis takes place are of molecular dimension and quite often the guest molecules are not able to pass each other. The molecular transport inside these pores, therefore, occurs in a single-file mode. When a reaction occurs, the reactant and product molecules mutually block each other and this results in a low output of product molecules from the catalytic grain. To avoid this adverse side-effect of single-file diffusion, the concept of reaction enhancement by molecular traffic control (MTC) was suggested by Kärger and collaborators [3, 4]. The main idea of MTC, originally proposed in [5, 6], is that inside the catalytic grain the reactant and product molecules diffuse through different channels, thereby avoiding the mutual suppression of self-diffusion. The existence of MTC has remained controversial for a long time.

Indirect evidence in favor of MTC was reported in [7] where a mixture of two different species of molecules adsorbed inside a zeolite channel was studied using molecular dynamics simulations. The sorbate molecules were assumed to interact with each other and with the zeolite channel via a Lennard-Jones potential. It was found in the simulation that two different species show preferential adsorption at two different portions of the zeolite, thereby tentatively supporting the concept of channel selectivity underlying the idea of MTC. However, in a zeolite with two different types of channels, a mere segregation of species is not a sufficient condition to observe MTC. More insight was obtained by investigating the diffusion of SF₆ and xenon inside a Boggsite zeolite with pores of two different sizes using molecular dynamics simulation [8]. SF₆ (large molecule) is known to preferentially get adsorbed in the wide pores and xenon (small molecule) in the narrow pores [9]. The self-diffusivities of the two different species were measured in both the channels. Comparing the value of these diffusivities, it was shown that the large (small) molecules prefer to diffuse along wide (narrow) channels [8]. Thus for this model system in equilibrium, it was shown that it is possible to observe MTC for diffusion of molecules of different sizes. Of course, the situation in a real catalytic grain is far more complex. The presence of chemical potential gradients, irreversible chemical reactions etc. drive the system strongly out of equilibrium. However, in [8] it was argued that the underlying causes for this intriguing diffusive behavior persist even in non-equilibrium situations.

A series of numerical studies were carried out on stochastic model systems to investigate whether MTC not only ex-
ists, but really enhances the output from a catalytic grain, [3, 4, 10–15]. In these studies the catalytic grains were represented by bimodal channel networks and various reaction-diffusion dynamics were considered. In most of these studies the traffic control of the molecules was implemented as follows: In one type of channels (denoted as α-channels) only the reactant molecules can diffuse and in the other type (β-channels) only the product molecules can diffuse. The catalytic sites are located at the intersections of these two types of channels, where the reactant transforms into the product at a certain rate. The output current of product from this system was compared with that from a reference system which is defined on the same channel topology but without channel selectivity, i.e., both types of molecules can diffuse in both types of channels.

The catalytic grain is surrounded by a gas phase to which the reactant molecules are added at a constant rate and the product molecules are constantly extracted from the gas phase. Such a boundary condition gives rise to local concentration gradient of reactant and product molecules inside the channels of the catalytic grain, thereby driving the system into a strongly non-equilibrium steady state. For such a stationary process far from thermal equilibrium, there is no Gibbs measure and equilibrium Monte Carlo techniques cannot be applied to measure the stationary state properties. For this reason dynamical Monte Carlo simulations were used to measure the output current of product molecules from the catalytic grain.

The first network topologies to be studied were the NBK topology and the BrS topology (see Figs. 1 and 2). An MTC effect for these topologies was found under certain conditions. For an identical set of reaction parameters the MTC system yielded a larger output than the reference system [3, 4, 10–15]. This is the desired phenomenon which we refer to as reactivity enhancement through molecular traffic control, i.e., MTC effect.

Except in [13] all simulations of these topologies were performed only in two dimensions. Moreover, even for the three-dimensional case of [13] these topologies are rather idealized. Therefore, it is not possible to draw definite conclusions about the existence of an MTC effect in real catalysts from these studies. Therefore, it is an important question if any MTC effect can be found for a realistic three-dimensional channel topology. This issue was addressed for the first time by us in [16] for a more realistic channel topology that describes the structure of a TNU-9 zeolite [17]. The dynamical Monte Carlo simulation (DMCS) showed that this topology allows for strong enhancement of grain reactivity with MTC and this effect remains strong even for large grain size. To put these results into perspective some of the relevant earlier results are reviewed in the following section. In Section 3 a detailed description the model is provided, followed by a discussion of simulation results in Section 4. Some new simulation data not yet reported elsewhere are presented. In the final section 5 some conclusions are drawn and future perspectives for the investigation of MTC are outlined.

## 2 Earlier Studies on Molecular Traffic Control and Single-File Diffusion inside Zeolites

Investigation of the MTC effect for various channel topologies often include modeling the transport of molecules inside zeolite channels by a symmetric exclusion process (see Section 3). In other words, the motion of molecules inside the channels is modeled by single-file diffusion of hard-core particles [18–22]. This approach might appear to be rather simple-minded, but turned out to be justified through careful theoretical analysis [21, 22] of an interesting experiment involving diffusion of binary mixture of hydrocarbon molecules inside narrow zeolite pores [23]. Detailed measurements of the temperature-dependent desorption profile for various zeolites demonstrated that inside quasi one-dimensional channels small and light propane molecules are not able to diffuse past large and heavy toluene molecules because of the single-file restriction [23]. In other words, the small molecules are trapped inside the zeolite channel by the large molecules. As a result, the effective desorption temperature of the small, weakly adsorbed hydrocarbon molecules is significantly raised in presence of the heavy, strongly adsorbed species [23]. In [21, 22] the diffusion of a hydrocarbon mixture inside a narrow zeolite channel was modeled by a two-species symmetric exclusion process. The diffusivities of the molecules were assumed to have an Arrhenius dependence on temperature and it was indeed possible to obtain quantitative agreement with the experimental desorption profile within this simple model [22].

Starting with the work of Kärger and coworkers [3, 4, 10] the conditions of reactivity enhancement of the catalyst using MTC were investigated by a series of dynamical Monte Carlo simulations carried out on stochastic model systems involving networks of channels with NBK topology. This is a two-dimensional network of perpendicular sets of intersecting channels where the vertical channels carry reactant molecules (α-channels) and the horizontal ones carry product molecules (β-channels) as shown in Fig. 1. The catalytic sites where the reaction takes place are located at the intersections. In [3, 4, 10–12] the existence of an MTC effect in this topology was established by comparing the output current, i.e., the current of product molecules, with a reference system (REF).

The MTC output was found to be larger than REF if the number of channels is small and the channel segments between the intersections are long. An efficiency ratio $R$ was introduced and calculated (see Eq. (2) for the definition of $R$) to quantify the efficiency of the MTC system over REF. For a NBK network with $N \times N$ channels, $R$ was shown to be proportional to $1/N$, meaning that the MTC output is larger than REF only for small $N$. This behavior can be explained by analytical calculations for the limit of large reaction rate. It turned out that as the boundary density of the reactant molecules was increased, the output current of product molecules increased initially. However, gradually the intersections sites get saturated as in the case of two dimensions [11]
and the output current undergoes non-analytic changes as a function of boundary density. For moderate values of the reaction rate, the stationary density profile of the reactant inside the channels is observed to decrease exponentially as a function of the distance from the boundary. The localization length is inversely proportional to local reaction rate. As a result, for a grain with a diameter larger than the localization length, the effective reactivity does not scale with the surface area of the grain, but only with its diameter. This implies that for NBK topology an MTC effect can be expected only for tiny nanometer-sized grains with a few channels.

Concerning the dependence of the MTC effect on the length $L$ of the channel segment between two successive intersections, it was found that the MTC current scales as $1/L^2$, as expected for an ordinary diffusive system. However, because of the single-file diffusion present in REF, the output current for REF scales as $1/L^3$ (see Eq. (1)). This means that $R$ scales with $L$ and, therefore, an MTC system is more efficient than REF for large $L$. On the other hand, the absolute value of the output current in an MTC system becomes small as $L$ increases, even though the relative value of the current in MTC system becomes larger than in REF. A low value of the absolute output is not useful for the purpose of industrial application and, therefore, the observed MTC effect seems to be of little technical use.

In order to further probe this negative finding the NBK model was extended to three dimensions in [13]. Using dynamical Monte Carlo simulation and analytical calculations, the phenomena reviewed above for the two-dimensional case were shown to persist. In other words, no MTC effect can be found for the industrially relevant grains with this or similar pore topologies. The fundamental problem is that even close to the surface of the grain molecules have long pathways before they can leave the grain.

To overcome this problem, an alternative channel topology was introduced in [14]. This consists of a two-dimensional network of bimodal channels, where both types of channels are alternately placed in horizontal as well as vertical directions (Fig. 2). The catalytic sites are located at the intersections of black and gray channels. This is referred to as BrS topology. The crucial feature is that it is always possible to find short pathways to the boundary starting from any region close to the surface inside the grain. In this case the efficiency ratio $R$ scales only with the channel length $L$, but not inversely with the number of channels. The presence of MTC in this topology (in two dimensions) was examined using DMCS both for the isomerization and cracking reaction [14, 15]. It was indeed found that as the grain size (i.e., the number of channels) increases, the MTC effect becomes stronger. This finding indicates that it may be possible to observe the MTC effect in grains of realistic size.

Most of the studies of MTC effect are carried out for isomerization reactions. A related issue is the universality of the MTC effect with regard to different types of catalytic reactions. In [15] the cracking reaction $A \rightarrow 2B$ was studied inside a two-dimensional BrS topology (see Fig. 2) for a wide range of reaction rate and diffusivities. In that work, the MTC system shows a size selectivity: depending on the size of the molecules, their diffusion pathways are determined. Also, the dynamics is a combination of both exclusion and non-exclusion dynamics (see [15] for details). The results found for that model are qualitatively similar to those for an isomerization process. Therefore, the main conclusion to be drawn from these works is the general possibility of a com-
mercially relevant MTC effect. However, from the study of these two-dimensional systems with an idealized pore topology not known to exist in real zeolites, it is not possible to estimate the expected strength of the MTC effect in a realistic three-dimensional topology. Therefore, it is essential to model realistic pore topologies that at least in principle allow for MTC to occur.

3 Basic Features of TNU-9 and of the Model

In [17] the authors report a detailed measurement of the pore topology of the synthetic zeolite TNU-9 (see Fig. 3 for a schematic sketch of the channel connectivity). Remarkably, this topology satisfies the criterion of short pathways to the surface which, according to [14], is required for an MTC effect in large grains. Therefore, this pore topology has been chosen as the basis of our investigation. First the salient features of the approach are presented. The details are described in the next section.

The channel network inside the grain is modeled with a three-dimensional $N \times N \times N$ array of unit cells and an isomerization reaction $A \rightarrow B$ is considered as described in detail below. To compare the output of the MTC system and REF, the outflow of the product molecules from the catalytic grain into the gas phase is measured. The stationary output current is defined as the average number of $B$-particles coming out of the catalytic grain in stationary state per unit time. This quantity is a measure of the reactivity of the grain. As a measure of merit of the MTC system over REF, the efficiency ratio is computed, which is the ratio of the maximal output current of the two systems (defined below). Note that actual time scales in the measurement of output current are immaterial as they get cancelled in the definition of the efficiency ratio.

In the model MTC system of TNU-9, the particles show channel selectivity: the $a$-channels carry only reactant molecules, which are denoted by the symbol $A$. The product molecules, denoted as $B$, can diffuse only in the $b$-channels. For the REF system no such channel selectivity is present, both types of particles can diffuse in both types of channels. At the intersection between the $a$- and $b$-channels the catalytic sites are located where the irreversible isomerization reaction $A \rightarrow B$ takes place with rate $c$. In order to keep the model numerically tractable, the interaction between the molecules inside the channels is described by hard-core exclusion. Each channel is modeled by a one-dimensional lattice and the molecules are assumed to undergo diffusion on that lattice. An $A/B$-particle attempts to jump to the nearest neighbor site to the left or right with a rate $w_a$ or $w_b$, respectively, provided the destination site is empty. This single-file diffusion of hard-core particles inside the channel is known as symmetric exclusion process (SEP) [24–29]. Note that $w_a$ and $w_b$, respectively, is the self-diffusion coefficient for a single $A/B$-particle in an otherwise empty channel. For a finite density $r$ of the same species of particles, the tracer diffusion coefficient has been calculated exactly and has the form [26]

$$D_r = w_a / L \cdot (1-r)/r \quad (1)$$

This means that the diffusion coefficient of any given particle inside a channel decays asymptotically as $1/L$, where $L$ is the dimensionless length of the channel segment between two intersection points. This is the result of the mutual blockage of particles through single-file diffusion that leads to the growth of the efficiency ratio with $L$.

The catalytic grain can exchange particles with the surrounding gas phase through the boundary sites. For an MTC system, an $A$-particle can enter or leave the grain through the boundary site of an $a$-channel. The injection process occurs with a rate $w_a r_A$ and the $A$-particle can exit the grain with a rate $w_A (1-r_A-r_B)$. We consider $r_A = r$ and $r_B = 0$, in accordance with the assumption that there are no $B$-particles in the gas phase. Such a boundary condition means that no $B$-particle can enter the grain from the gas phase. $B$-particles are created inside the grain as a result of the isomerization reaction and they diffuse along the $b$-channels to finally come out of the grain through the boundary site. A complete channel selectivity implies that $A$-particles do not block the exit of the $b$-channel and, hence, a $B$-particle leaves the grain with a rate $w_B$. On the other hand, in a real system it is possible that $A$-particles in the gas phase can hover around the exit of the $b$-channels, thereby obstructing the release of $B$-particles into the gas phase. In this case, the effective exit rate of $B$ should be $w_B (1-r)$. In this paper, both types of situations are considered and the efficiency of MTC over REF is examined for both cases. Note that for the REF system there is no channel selectivity and, therefore, $A$-particles can enter both types of channels with rate $w_A$ and leave with rate $w_A (1-r)$, whereas $B$-particles can exit with rate $w_B (1-r)$.

4 Dynamical Monte Carlo Simulation Results

Here it is described in detail how the model sketched above is simulated and simulation results are presented. As discussed in the previous section, the main quantity of interest is the average number of $B$-particles leaving the grain per unit time in steady state. This output current of MTC and REF systems is compared for a range of values of the grain size $N$ and the reaction rate $c$. Note that the reaction rate depends on detailed microscopic properties of the grain and the reactant molecules. However, in this study, we do not consider any specific reaction. Instead, we are interested in the general conditions for reactivity enhancement. That is why we do not focus on a reasonable estimate for $c$, but work with a wide range of values for $c$. 
4.1 Modeling of the TNU-9 Topology

There are additional lattice parameters in the TNU-9 topology that need to be fixed at this stage. As shown in Fig. 3, the \( \alpha \)-channels are present along the direction of \( x \)-axis and \( \gamma \)-axis and \( \beta \)-channels are present along \( y \)-axis and \( z \)-axis. The question is how to choose the length of the channel segments between two successive intersections. A closer examination of the channel diagram obtained from the experiment (see Fig. 3) reveals that both \( \alpha \)- and \( \beta \)-channel segments along \( y \)-direction have the same length \( L_1 \). Experiments also suggest that the \( \beta \)-channel segment along \( z \)-direction and \( \alpha \)-channel segment along \( x \)-direction have approximately the same length \( (L_2) \) and the ratio \( L_1/L_2 = \sqrt{2} \) [17]. In terms of our lattice model, \( L_1 \) and \( L_2 \) denote the number of lattice bonds in the respective segments and both these numbers must be even. Note that in Fig. 3 a \( \beta \)-channel in \( y \)-direction passes through exactly the midpoint of a \( \beta \)-channel in \( z \)-direction. To realize this in a lattice model, the number of lattice bonds present in \( \beta \)- \( (i.e., L_2) \) must be even. Similarly, by considering \( \alpha \)-channels in \( x \)- and \( y \)-direction, one can argue that \( L_1 \) must also be even. The smallest possible choice for which all these conditions are met is \( L_1 = 6 \) and \( L_2 = 4 \). In comparison to the channel lengths considered in earlier theoretical studies, these channels are rather long and so we do not consider any variation of \( L_1 \) and \( L_2 \) to even larger values. Note: The diameter of an isobutene molecule is \( \approx 5 \) Å and the experimentally measured channel lengths for TNU-9 crystal are \( \approx 28 \) Å and \( 20 \) Å. From the ratio of the channel length to the molecular size we derive our choice of \( L_1 \) and \( L_2 \).

![Figure 3. Schematic picture of the three-dimensional channel topology of a TNU-9 zeolite, based on Fig. 2c in [17], with \( \alpha \)-channels in the plane of the picture and \( \beta \)-channels in the plane perpendicular to the picture.](image)

4.2 Monte Carlo Algorithm

In this subsection the dynamical Monte Carlo update scheme is described. Each Monte Carlo time step consists of \( N_u \) update trials, where \( N_u \) is the total number of sites present in the catalytic grain. During each update trial one site is chosen at random and its occupancy is updated following the steps outlined below. We have considered the processes of diffusion inside a channel and reaction at the catalytic junctions. All these processes are assumed to have rates less than 1, allowing to directly interpreting these rates as probabilities. To perform an elementary move with rate \( w \), a random number \( \xi \) is chosen from a uniform distribution between 0 and 1. The move is performed successfully if \( \xi \leq w \). If \( \xi \) is larger than \( w \), the move is not performed. This makes sure that the probability with which the process occurs is \( w \).

Several options are possible for a site chosen uniformly at random during one update trial:

1) If the site lies inside an \( \alpha \)- or \( \beta \)-channel, respectively, it can be either empty or occupied by an \( A \)-particle or \( B \)-particle, respectively. If the site is occupied, the particle on it hops to one of the two neighboring sites at random with probability \( w_A \) (\( w_B \)) if the destination site is empty. Otherwise the hopping attempt is rejected. So the effective hopping probability to one particular neighboring site is \( w_A/2 \) (\( w_B/2 \)).

2) If the site is located at the junction between two \( \alpha \)-channels in \( x \)- and \( y \)-directions, it has three neighboring sites, one along \( \alpha \)- and two along \( \beta \)-. If the chosen site is occupied by an \( A \)-particle, the particle can hop towards any of these three neighbors with equal probability (provided they are empty) and with probability \( w_A \). In this case, the effective hopping probability to one particular destination site is \( w_A \).

3) If the site is located at the junction between two \( \beta \)-channels in \( y \)- and \( z \)-directions and if it is occupied by a \( B \)-particle, the particle can hop towards any of the four possible neighboring sites at random with probability \( w_B \). Again, hopping probability to one particular neighboring site is \( w_B/4 \).

4) If the site is at a junction between \( \alpha \)- and \( \beta \)-channel and contains an \( A \)-particle, an isomerization reaction replacing the \( A \)-particle by a \( B \)-particle occurs with probability \( c \). If the reaction does not occur, the \( A \)-particle can diffuse along the \( \alpha \)-channel in \( y \)- or \( x \)-direction following the procedure discussed in scenario (2). If the catalytic site is occupied by a \( B \)-particle, the particle attempts to diffuse along the \( \beta \)-channel in \( z \)-direction, as described in scenario (1).

5) If the chosen site lies at the boundary, the particle on it can hop towards all possible available directions with equal probability. If the particle hops towards one of its neighboring sites in the lattice, diffusion takes place as described in scenario (1). If the particle chooses to hop towards the direction of the reservoir, it is taken out of the lattice with a certain probability and the site is left empty. An \( A \)-particle leaves the lattice with a probability
$w_A(1-r)$. For a B-particle, the extraction probability is $w_B$ for an MTC system with complete channel selectivity and $w_B(1-r)$ for an MTC system with partial channel selectivity. If the chosen site is at the boundary of an $a$-channel and empty, an A-particle is injected onto the site with probability $rw_A$.

For a REF system, no channel selectivity is present and an A- or B-particle does not distinguish between an $a$- or a $b$-channel, as explained in the previous section. For such a system, the above update scheme is accordingly modified. The starting point is an initially empty lattice with only the boundary sites of $a$-channels occupied by A-particles with probability $rw_A$. The system is evolved for a time long enough to bring it into the steady state. In this steady state ensemble, the average number of B-particles coming out of the grain per unit time is measured. In all simulations $w_A/w_B = 2$ is used.

4.3 DMCS Results

In this section, the simulation results of [16] are discussed for a system with reactivity enhancement through MTC. Additionally, some new simulation data for the maximal current as a function of reactivity in the MTC case with partial channel selectivity and in the reference topology are presented. These data support the conclusion of [16]. As mentioned before, two different types of channel selectivities for the MTC case are considered, complete channel selectivity and partial channel selectivity. The results for these two cases are discussed below.

4.3.1 MTC System with Partial Channel Selectivity

As explained earlier, in this case the reactant and product molecules show channel selectivity inside the grain but the exits of the $b$-channels could get blocked by reactant molecules in the gas phase. Fig. 4 in [16] shows the plot of the output current $j$ as a function of the reservoir density for a fixed value $c = 0.01$ of the reaction probability. When $r$ is small, the $j$ values are essentially the same as those for complete channel selectivity. However, as $r$ increases, MTC with partial channel selectivity yields a lower output than in the case of complete channel selectivity. This is because as $r$ grows, the exit rate of the product molecules decreases and finally for $r = 1$, when no particle can come out, the exit rate becomes zero. Hence, after an initial increase in $j$ with $r$, the effect of the boundary blockage is noticeable for larger values of $r$ and finally at $r = 1$ the current becomes zero, unlike the case for complete selectivity where the current is highest at this density value. Note however that the maximal current is still significantly larger than in REF. In other words, even for this case of partial channel selectivity, where $j$ cannot grow all the way with $r$, one can still find a strong MTC effect.

Studying the system in its maximal current state for a given reactivity and lattice parameters, which are intrinsic material properties of the grain, is of particular interest. The reservoir density $r$, on the other hand, can be easily tuned in an experiment. The density for which the output current reaches a maximum is denoted as $c^*$ and the corresponding current as $j^*$. For different values of the grain size $N$, $j^*$ is plotted as a function of $c$ for the MTC system (Fig. 4) and for the REF system (Fig. 5).

![Figure 4.](image)

**Figure 4.** Maximal current $j^*$ as a function of reactivity $c$ for an MTC system with partial channel selectivity for different values of $N = 2, 4, 6, 8, 10$ (moving upwards).

![Figure 5.](image)

**Figure 5.** Maximal current $j^*$ as a function of reactivity $c$ for the REF system with partial channel selectivity for different values of $N = 2, 4, 6, 8, 10$ (moving upwards).

As one might expect, $j^*$ increases with the reactivity $c$. More significantly, $j^*$ increases also with $N$, which is the key feature of the TNU-9 topology as by extrapolation this observation suggest that reactivity enhancement through MTC even occurs in commercially relevant grain sizes. To quantify the extent of reactivity enhancement through MTC, the efficiency ratio $R$ is considered:

$$R = j_{MTC}^*/j_{REF}^*$$  \(2\)

This quantity depends on the reactivity $c$ in a non-monotonic fashion, but in the entire range of $c$ considered, $R$ is much larger than 1 (see Fig. 7 in [16]). A reactivity enhancement
of up to approximately 200% was observed, which implies a very strong MTC effect.

4.3.2 MTC System with Complete Channel Selectivity

For an MTC system with complete channel selectivity, the output current \( j \) (steady state current of \( B \)-particles) as a function of the reservoir density \( r \) increases monotonically and the highest value of \( j \) is reached at \( r = 1 \) (see Fig. 4 in [16]). This behavior can be explained as follows: As the reactant density \( r \) in the surrounding gas phase increases, a large inflow of the reactant molecules into the grain develops. This results in a large number of isomerization reactions and, hence, a large number of product molecules. In presence of complete channel selectivity, these product molecules diffuse in the \( \beta \)-channels and leave through the \( \beta \)-exits with a constant rate \( w_b \). As a result, maximal current is obtained at the largest reservoir density \( r = 1 \).

However, for REF, the maximal current is reached at an intermediate value of \( r \). In this case, \( j \) initially increases with \( r \) because of the abundance of reactant (and consequently, product) molecules, as explained in the previous paragraph. But with increasing \( r \), the reactant and product molecules offer mutual blockage to each other inside the grain. Also, the channel exits get blocked by the reactant molecules in the gas phase. As a result, \( B \)-particles cannot exit the grain easily and after an initial increase the output current decreases and finally vanishes as \( r \) approaches 1.

The most important point to note is that also for complete channel selectivity the maximal current in the MTC system is much larger than that in REF. In other words, in the presence of MTC a strong enhancement of reactivity of the catalytic grain occurs. Second, both for the MTC system and REF the maximal current \( j^* \) for any fixed value of \( c \) increases with \( N \). This behavior is in contrast to what was observed earlier for the NBK topology, where the REF output grows with \( N \), but the MTC output remains the same as \( N \) increases [12]. Such behavior explains the absence of the MTC effect in the NBK topology for large \( N \). However, for a TNU-9 topology, an increase in \( N \) causes an increase in the number of catalytic sites and also in the number of available \( \beta \)-exits, thereby increasing the MTC output.

In the entire range of \( c \) considered, the efficiency ratio \( R \) is much larger than 1, which implies a strong MTC effect (see Fig. 6 of [16]). Large values of \( R \) of more than 3 are obtained for large \( N \), indicating that strong reactivity enhancement is expected through MTC for realistic grain sizes. The reactivity enhancement of up to 220% in the TNU-9 topology is much stronger than the maximum of 65% reported in BrS topology [14] and slightly stronger than for partial channel selectivity (see above).

5 Conclusions

In view of the wide application of zeolites as catalysts in the chemical industry, it is important to understand the reaction-diffusion mechanisms of molecules inside the narrow zeolite pores. In order to circumvent the mutual blockage of the reactant and product molecules during their single-file diffusion in the zeolite channels, we allow for MTC through a bimodal channel topology. Earlier studies employing dynamical Monte Carlo simulation on the NBK topology (Fig. 1) have revealed that an MTC effect can be found only when the grain size is unrealistically small [13]. In [14] the existence of an MTC effect for a catalytic grain of larger size was reported for an alternative channel topology in two dimensions, denoted BrS topology (Fig. 2). Scaling arguments suggest that for pore topologies of this type, where all molecules in the surface region of the grain have short pathways to the surface of the grain, the MTC effect persists in three dimensions and for industrially relevant grain sizes.

Dynamical Monte Carlo simulations on a reaction-diffusion system modeling an isomerization reaction were performed for a detailed study of the MTC effect in a realistic three-dimensional channel topology that represents the pore structure of a TNU-9 zeolite. Complete and partial channel selectivity was studied and the output current was compared to a reference system without channel selectivity. The results show that the presence of channel selectivity greatly enhances the reactivity of the catalytic grain in a wide range of the reaction rate and grain size. The effect is stronger for complete channel selectivity, when the surrounding gas phase does not affect the \( \beta \)-exits. In this case a reactivity enhancement up to 220% is found. The optimal MTC effect is somewhat less strong (about 200%) but still very substantial for partial channel selectivity, when a high density of reactant molecules in the gas phase can effectively obstruct the outflow of product molecules from the grain (a more realistic case).

We have focused on the general conditions for reactivity enhancement rather than considering one particular reaction. A strong MTC effects is seen for a wide range of model parameters. In particular, the MTC effect grows with grain size. It is concluded that a significant MTC effect in industrially relevant grain sizes and for pore topologies that can be synthetized may be expected. This suggests future research in several directions. On the engineering side, it would be desirable to develop synthetic zeolites beyond TNU-9 that are catalytically active and have a pore topology allowing for an MTC effect. From a modeling perspective there are two tasks to be solved in parallel. The first is to determine Monte Carlo model parameters for specific processes in specific zeolites, using theoretical approaches such as transition state theory [30] and molecular dynamics simulations. The second is to use these data as input parameters for more refined dynamical Monte Carlo models in order to obtain quantitative estimates for the strength of the MTC effect.
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