

Strong Molecular Traffic Control Effect in TNU-9 Zeolite Channel Topology

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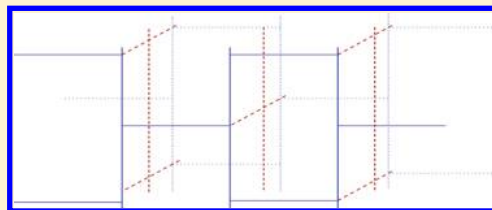
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ABSTRACT: Reactivity enhancement in a catalytic zeolite grain through molecular traffic control (MTC) rests on the basic notion that the reactant and product molecules prefer to diffuse along different channels inside the grain and therefore do not mutually hinder their transport in and out of the grain. We investigate the conditions of reactivity enhancement in the presence of MTC for a realistic channel topology that describes the pore structure of a TNU-9 zeolite. We compare the output current of an MTC system with a reference system, which does not show any channel selectivity. For a wide range of reaction rates and for different grain sizes, we find that there is a very significant enhancement of reactivity for the MTC system. This effect remains strong as the grain size increases. The mechanism behind reactivity enhancement is argued to be generic rather than being confined to the particular structure of TNU-9.



I. INTRODUCTION

Many important processes like isomerization or cracking of hydrocarbon molecules are known to take place inside the narrow pore system of a zeolite.^{1,2} Such pores are of molecular dimension, and quite often the guest molecules are not able to pass each other inside these pores. Therefore, molecular transport inside these pores takes place under single-file conditions. This has the effect that when a reaction occurs, the reactant and product molecules mutually block each other, which in turn results in a low output of product molecules from the catalytic grain. To overcome this problem, the concept of molecular traffic control (MTC) was introduced.^{3–6} The main idea of MTC is that inside the catalytic grain the reactant and product molecules diffuse through different channels, thereby avoiding mutual suppression of self-diffusion.

Molecular Dynamics simulations⁷ as well as experimental results^{8,9} provide evidence in favor of the concept of channel selectivity essential for MTC. For investigating whether MTC not only exists, but really enhances the output from a catalytic grain, one is faced with the double challenge of investigating a long-time stationary process not accessible by molecular dynamics methods and a nonequilibrium situation in which the stationary distribution does not have the form of a Gibbs state. Therefore, also traditional equilibrium Monte Carlo techniques cannot be applied. For this reason, a series of dynamical Monte Carlo simulation studies were carried out on stochastic model systems.^{5,6,10–15} In these studies, the catalytic grains were represented by bimodal channel

networks. In most of these studies, the traffic control of the molecules was implemented as follows: The catalytic grain is assumed to be surrounded by a gas phase from which the reactant molecules are added at a constant rate and the product molecules are constantly extracted to the gas phase. 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 to that from a reference system (REF), which is defined on the same channel topology but without channel selectivity; that is, both types of molecules can diffuse in both types of channels.

The network topologies studied so far are the NBK topology and the BrS topology (see Figures 1 and 2, respectively). An MTC effect for these topologies was found under certain conditions; that is, for an identical set of reaction parameters the MTC system yielded a larger output than did the reference system,^{5,6,10–15} the desired phenomenon that we refer to as reactivity enhancement through molecular traffic control, or MTC effect in short. In a two-dimensional NBK topology, it was found that if the number of channels is small, the MTC output is larger than REF.^{5,6,10–12}

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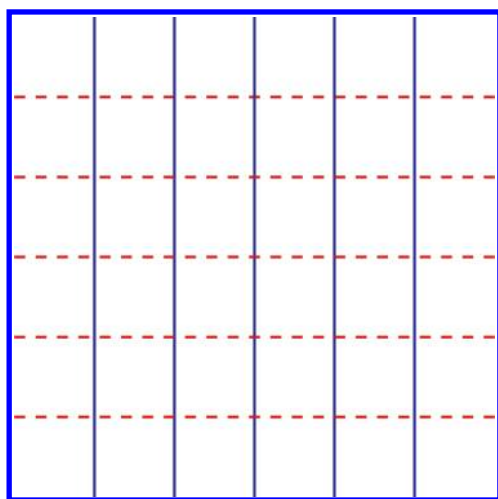


Figure 1. MTC system with NBK topology. The vertical channels (solid blue lines) carry reactant molecules, and the horizontal ones (dotted red lines) carry the product molecules; reaction takes place at the points of intersection.

To quantify the effectivity of the MTC system over REF, the efficiency ratio R was calculated, which was the ratio of output in MTC over REF. For a two-dimensional NBK network with $N \times N$ channels, R was shown to be proportional to $1/N$, which means that MTC output is larger than REF only for small N . Similar results were reported for a NBK model in three dimensions.¹³ Therefore, for an NBK topology, an MTC effect can be expected only for tiny nanometer-sized grains with few channels.

To study if an MTC effect can be observed for commercially relevant sizes of the catalytic grain, an alternative channel topology, known as BrS topology, was proposed in ref 14 (see Figure 2). The presence of MTC on this topology (in two dimensions) was examined using DMCS for 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.

Except in ref 13, all simulations were performed only in two dimensions. Moreover, even for the three-dimensional case of ref 13, these topologies are rather idealized. Therefore, from these studies, it is not possible to draw reliable conclusions about the existence of an MTC effect in real catalysts. With this in view, it is an important question to ask if any MTC effect can be found for a realistic three-dimensional channel topology. In this Article, we address this question for the first time. We investigate the conditions for reactivity enhancement through MTC inside a realistic channel topology that describes the structure of a TNU-9 zeolite.¹⁶ Our dynamical Monte Carlo simulation shows that this topology allows for strong enhancement of grain reactivity with MTC and this effect remains strong even for large grain size. Given the mechanism of MTC that is revealed by our study, MTC appears to be a generic phenomenon not confined to TNU-9.

II. PORE TOPOLOGY AND MODELING OF TNU-9

In ref 16, a detailed measurement of the pore topology of the synthetic zeolite TNU-9 is presented. A unit cell appears to have a $C2/m$ structure, with parameters $a = 28.2219 \text{ \AA}$, $b = 20.0123 \text{ \AA}$, $c = 19.4926 \text{ \AA}$, and $\beta = 92.33^\circ$. A schematic sketch of one unit cell is shown in Figure 3. We omit the structural connectivities of the Si-atoms, which make up the unit cell, and focus on the channel connectivities. The projection of TNU-9 along the b axis resembles

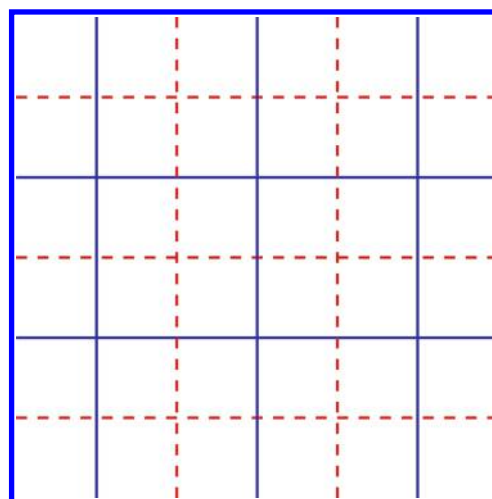


Figure 2. BrS channel topology with two types of channels placed in both directions. Color code is the same as in Figure 1.

that of ZSM-5, but the connectivity in the third direction is more complex. The resulting channel system, made up of 10 rings, has two types of channels, which differ in their diameter. The channels shown in blue (α -channels in the x - y plane of the figure) have been determined to have a diameter of 5.1 \AA , while the red β -channels, which connect planes of blue channels, are wider with a width of 5.7 \AA . At the connection points where blue and red channels meet, there is one β -channel and three α -channels. Only every other blue connection point (with three α -channels each) is also connected to a β -channel. Both α - and β -channel segments along the y -direction have the same length of $\sim 28 \text{ \AA}$, which we denote by Λ_1 . The experimental data also suggest that the β -channel segment along the z -direction and the α -channel segment along the x -direction have approximately the same length $\Lambda_2 \approx 20$.

Remarkably, for a complete crystal grain, this topology leads to short pathways from all intersection points to the surface. We model the channel network inside the grain with a three-dimensional $N \times N \times N$ array of unit-cells. To model MTC, we assume channel selectivity: The α -channels carry only reactant molecules, which are denoted by the symbol A. The product molecules, denoted as B, can diffuse only in the β -channels.

To simulate single-file diffusion inside the channels, each channel is modeled by a one-dimensional lattice with hard-core exclusion interaction between the molecules.^{10,17–19} An A (B) particle attempts to jump to the nearest neighbor site to the left or right with a rate w_A (w_B), provided the target site is empty. This diffusion of hard-core particles inside the channel is known as symmetric exclusion process (SEP).^{20,21} As chemical reaction, we consider a hypothetical isomerization reaction $A \rightarrow B$, which is catalyzed at the intersection points of α - and β -channels with rate c . This reaction constant is a parameter of our model.

Notice that a β -channel in the y -direction passes through the midpoint of a β -channel in the z -direction. To realize this in a lattice model, the number of lattice bonds present in a β -channel (i.e., $L_2 \propto \Lambda_2$) must be even. Similarly, by considering α channels in x - and y -directions, one can argue that $L_1 \propto \Lambda_2$ must also be even. To determine L_i , we argue that one lattice site should have a length similar to the empirical channel diameter. This is consistent with the hard-core exclusion requirement that one lattice site can host only one molecule. Hence, $L_i \approx \Lambda_i / (5 \text{ \AA})$. Hence, we obtain $L_1 = 6$ and $L_2 = 4$ as a good approximation to the

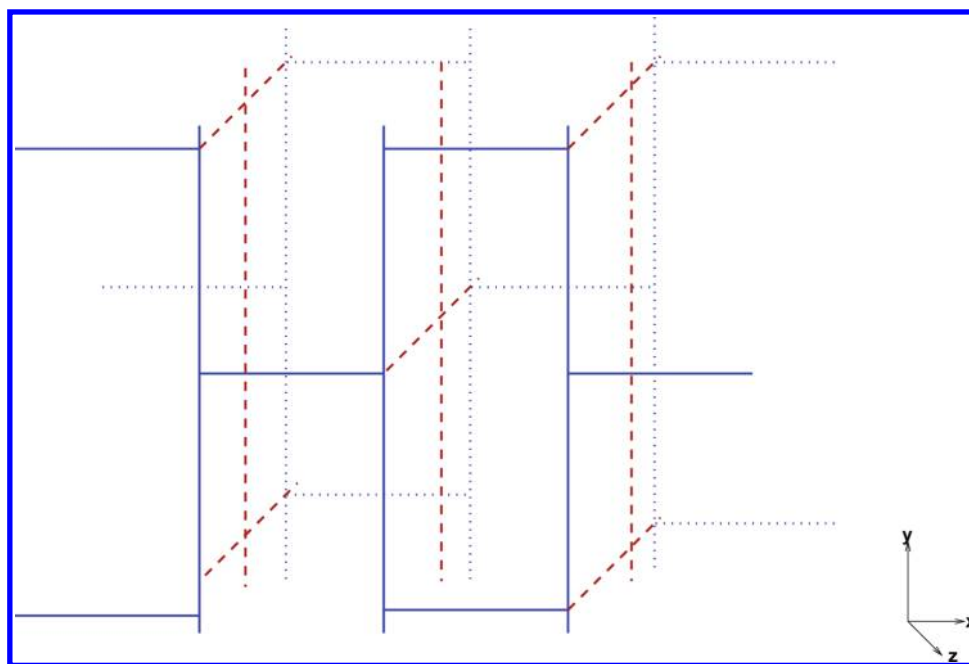


Figure 3. Channel topology inside a TNU-9 zeolite. α -Channels are shown in blue; β -channels are shown in red. Diagram obtained from Figure 2c in ref 16.

empirical data. We remark that both the exclusion principle of our model and the notion of single-file diffusion are consistent with the empirical pore diameter of 5 Å. For example, the diameter of an isobutene molecule (a commonly used reactant in isomerization processes) is ~ 5 Å. In what follows, we shall set the lattice constant to unity and consider only the dimensionless lattice lengths L_i .

The hopping rate w_A (w_B) is proportional to the self-diffusion coefficient for a single A (B) particle in an otherwise empty channel. The tracer diffusion coefficient in a channel of length L with particle density ρ has been calculated exactly and has the form:²⁰

$$D_s = w_s \frac{1 - \rho}{\rho} \frac{1}{L} \quad (1)$$

This means that the diffusion coefficient of any given particle inside a channel decays asymptotically as $1/L$, where L is the length of the channel segment between two intersection points.

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 α -channel. The injection process occurs with a rate $w_A \rho_A$, and the A particle can exit the grain with a rate $w_A(1 - \rho_A - \rho_B)$. We consider $\rho_A = \rho$ and $\rho_B = 0$, 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 β -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 β -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 β -channels, thereby obstructing the release of B particles

into the gas phase. Under such a circumstance, the effective exit rate of B should be $w_B(1 - \rho)$. In this Article, we consider both of these types of situations.

For the REF system, we choose the same model parameters and pore topology, but without channel selectivity. Both types of particles can diffuse in both types of channels. Therefore, A particles can enter both types of channels with rate ρw_A and leave with rate $w_A(1 - \rho)$, whereas B particles can exit with rate $w_B(1 - \rho)$. To compare the output of MTC system and REF, we follow standard procedure and measure the stationary outflow of the product molecules from the catalytic grain into the gas phase. 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, we compute the efficiency ratio, which is the ratio of the maximal output current of the two systems (defined below). The stationary current in the MTC system is proportional to the tracer diffusion coefficient (1), while in the REF system it is proportional to the self-diffusion coefficient.¹⁴ Hence, the mutual blockage of particles through single-file diffusion leads to the growth of the efficiency ratio with L . Note that actual time-scales in the measurement of the output current are immaterial as they get canceled in the definition of the efficiency ratio.

III. SIMULATION RESULTS

We compare the output current of MTC and REF systems 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. To estimate reaction rate or other reaction parameters, one can use transition state theory (for a review on transition state theory, see ref 22 and the references therein). However, in this study, we do not consider any specific reaction and are rather interested in the general conditions for

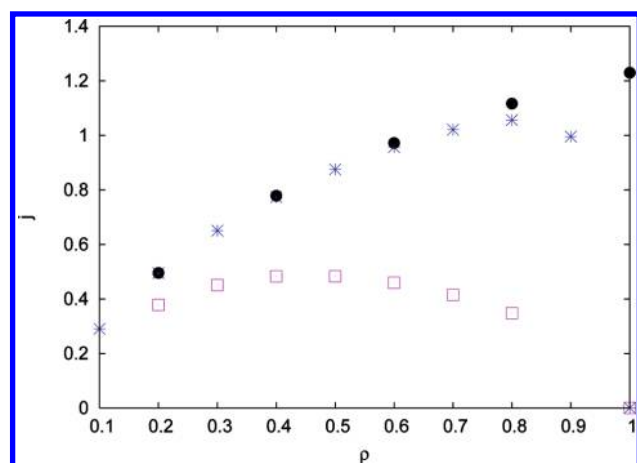


Figure 4. Output current j versus reservoir density ρ for MTC system with complete (●) and partial (*) channel selectivity and also for REF (□). We use a $6 \times 6 \times 6$ array of unit-cells, $w_A/w_B = 2$, and the reaction probability $c = 0.01$.

reactivity enhancement. Therefore, we work with a wide range of values for c .

Because we are interested in stationary properties inside a zeolite grain, the required time scales are way beyond what is accessible via molecular dynamics simulations. On the other hand, the stationary state is not an equilibrium state without Gibbs measure. We therefore measure the output currents through dynamical Monte Carlo simulations (DMCS) with random sequential update. During each update trial, one site is chosen at random, and its occupancy is updated following the steps of hopping, reaction, and exchange with the gas phase outlined above. The details of our algorithm will be described elsewhere.²³

A. Output Current. First, we consider the output current as a function of the reservoir density; see Figure 4. In the reference system, the current reaches a maximum j^* at an intermediate value ρ^* of ρ . For small ρ , the current j initially increases because more reactant molecules are fed into the grain. However, for large ρ , the reactant and product molecules block each other inside the grain, and also the channel exits get blocked by the reactant molecules in the gas phase. As a result, B particles cannot leave the grain, and the output current decreases. In the (somewhat artificial) limiting case $\rho = 1$, reactant molecules in the gas phase completely block the grain exits, and the current drops to zero.

On the other hand, we observe that in an MTC system with complete channel selectivity j increases monotonically as a function of ρ , and the highest value of j is reached at $\rho = 1$. This is due to the absence of any blocking of the grain exits even at high densities of reactants in the gas phase. More realistically, we consider partial channel selectivity. In this case, the reactant and product molecules show channel selectivity inside the grain, but the exits of the β -channels could get blocked by reactant molecules in the gas phase. The current then drops to zero at $\rho = 1$, but we observe a much higher maximum than in the REF system. Moreover, we find that for $\rho < \rho^*$, the currents are almost identical for partial and complete selectivity. Most importantly, in both cases, the currents are much higher than for the REF system with the same parameter values. In other words, in the presence of MTC, there is a strong enhancement of reactivity of the catalytic grain. Below, we investigate the various conditions of this reactivity enhancement as several system parameters are varied.

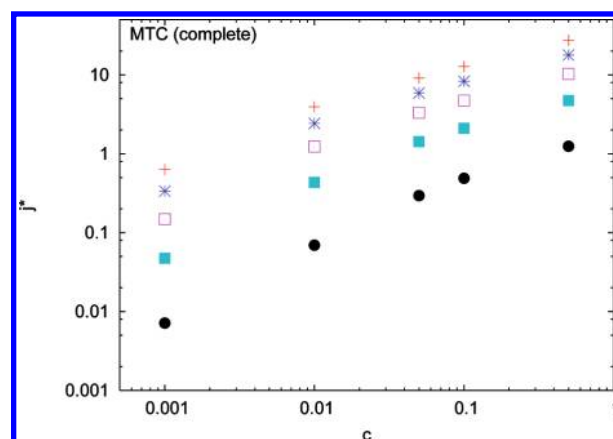


Figure 5. Maximal current as a function of reactivity for an MTC system with complete channel selectivity for different values of N . We have used $w_A/w_B = 2$ and $N = 2, 4, 6, 8, 10$ (moving upward).

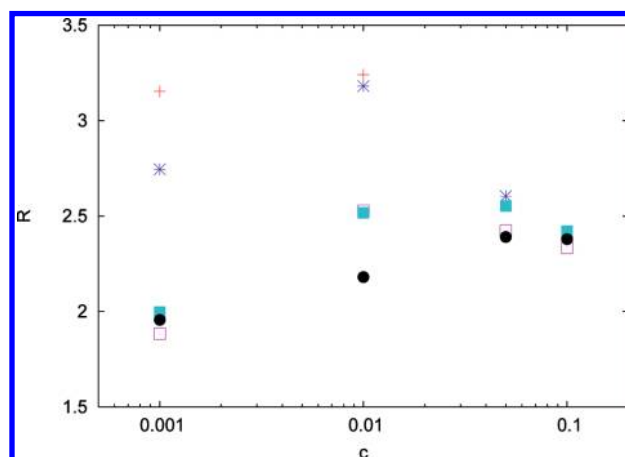


Figure 6. Efficiency ratio as a function of grain reactivity for $N = 2$ (●), $N = 4$ (■), $N = 6$ (□), $N = 8$ (*), and $N = 10$ (+). Data correspond to an MTC system with complete channel selectivity.

B. Efficiency Ratio. The reservoir density ρ can be tuned in an experiment by adjusting the pressure in the gas phase. In applications, it would be natural to choose $\rho = \rho^*$ where the reactivity of the catalytic grain is maximal. Therefore, we are particularly interested in studying the system in its maximal current state for a given reactivity and lattice parameters that are intrinsic material properties of the grain. To quantify the MTC effect, we compute the efficiency ratio defined as

$$R = \frac{j^*|_{\text{MTC}}}{j^*|_{\text{REF}}} \quad (2)$$

For $R > 1$, we have reactivity enhancement through MTC.

We consider first complete channel selectivity. For different values of the grain size N , we study j^* as a function of c . We find that the maximal current j^* for any fixed value of c increases with N , for the MTC system (Figure 5) and the reference system (data not shown). This behavior is in contrast to what was earlier observed for an NBK topology, where the REF output grows but the MTC output remains the same as N increases.¹² The fact that for the TNU-9 topology j^* for MTC grows with N indicates that

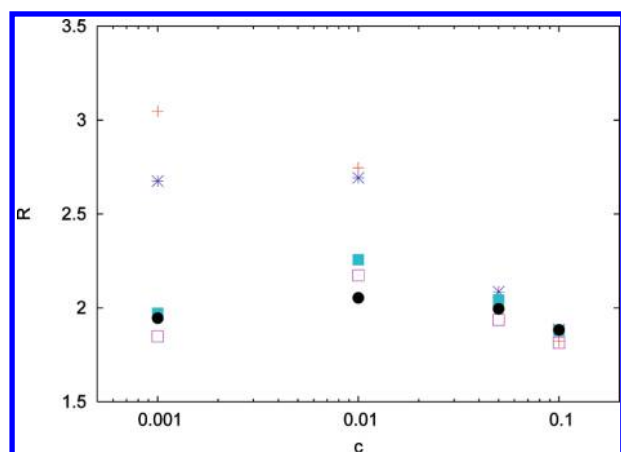


Figure 7. Efficiency ratio as a function of grain reactivity for $N = 2$ (●), $N = 4$ (■), $N = 6$ (□), $N = 8$ (*), and $N = 10$ (+) for partial channel selectivity.

it might be possible to find an MTC effect even for large N and therefore for realistic grain sizes in the micrometer range.

In Figure 6, we plot R as a function of c . Note that in the entire range of c considered, R is much larger than unity, which implies a strong MTC effect. Large values of R are obtained for large N , which indicates for a realistic grain size, strong reactivity enhancement is expected through MTC. We observe a reactivity enhancement of up to 220%.

For partial channel selectivity, the maximal current as a function of the reaction rate (data not shown) is quantitatively similar to the case of full selectivity, in agreement with the observations discussed above (see Figure 4). The reason is that the regime where the two systems differ is away from the technologically interesting maximal current point. To compute the strength of the MTC effect, we show the values of R across different values of c and N in Figure 7. We find a reactivity enhancement of up to 200%, which is slightly lower than the value for the complete channel selectivity case, but still implies a very strong MTC effect.

IV. CONCLUSION

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. Limited molecular transport in these micropores often poses a serious restriction in designing catalytic application of such materials. One way to circumvent this difficulty is to consider structures with hierarchical architecture of porosity where wide channels with mesoporous dimension facilitate physical transport and narrow channels with microporous dimension act as a nanoreactor.^{24,25} It has been demonstrated that such structures indeed show enhanced transport and improved catalytic conversion rate.^{24,26,27}

An alternative way of increasing catalytic efficiency of microporous zeolite grains is to consider molecular traffic control, where guest molecules show channel selectivity. In this Article, we have carried out a detailed study of the MTC effect for a realistic three-dimensional bimodal channel topology that represents the pore structure of a synthetic TNU-9 zeolite. We have performed dynamical Monte Carlo simulations on a reaction–diffusion system modeling an isomerization reaction inside a TNU-9 catalytic grain.

Generally, our 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. We have studied two cases, distinguished by surface effects on a catalytic grain resulting from adsorption from the gas phase. For a 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 observe a very strong reactivity enhancement through the MTC effect of about 200%. The effect is stronger for complete channel selectivity, when the surrounding gas phase does not affect the exit of product molecules into the gas phase. In this case, we find a reactivity enhancement up to 220%. We also find that a strong MTC effect is seen for a wide range of reaction rates of the catalytic process.

To our knowledge, this is the first evidence of the MTC effect in a channel topology that actually describes a real zeolite structure. At the same time, we argue that the effect is not confined to this particular channel topology, but is generic for all channel topologies that allow short diffusion pathways from the catalytic reaction centers to the surface of the catalytic grain. Even for large grain size, the MTC effect continues to be strong, which suggests the possibility of industrially relevant applications. Indeed, given modern methods of zeolite synthesis, it may be possible to design zeolite structures, which allow for the occurrence of the MTC effect. On the modeling side, more refined Monte Carlo models can be developed to obtain quantitative estimates for the strength of the MTC effect for a given channel topology and catalytic activity inside the channels.

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