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Development and Application of Tools for Modeling Mass Transport and Catalytic
Reaction in Nanostructured Membranes

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ABSTRACT

Development and Application of Tools for Modeling Mass Transport and Catalytic Reaction in Nanostructured Membranes

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Modeling and simulation at different scales were used to study mass transport, residence times and selective oxidation in nanostructured membranes. First, analytical equations of the possible mass transport mechanisms inside the pores were used to determine that diffusion dominates over convection under the conditions of interest for selective oxidation: 700 K and pressure near atmospheric. Molecular dynamics simulations showed that surface diffusion is not present at these conditions. Knudsen diffusion was then identified as the dominant mechanism. Simulations based on its principles were performed using an ensemble of particles in a boundary driven simulation cell. Cylindrical pores with uniform diameter and with multiple sections of different diameters were studied. The average number of hits between a particle and the pore wall were obtained, as well as the dependence of the residence times on the dimensions of the pores, or of the pore sections, and the ratio of their cross-sectional areas in the case of pores with multiple sections. Both sweep-gas and pass-through modes of operation were examined. Analytical expressions were developed to relate the transmission probability in pores of multiple sections to the transmission probabilities of the constituent sections.

The catalytic reactions in the nanostructured membranes were studied using the oxidative dehydrogenation of ethane as a representative system. A continuum-level model and reactive Knudsen dynamics simulations were employed to investigate different operational modes, including the pass-through and the sweep-gas modes. It was found that, by adjusting the pore dimensions, the pass-through mode is capable of achieving high conversions even for slow reactions. This is not possible in the sweep-gas mode, making it attractive only for faster reactions. Pores partially covered in catalyst were also studied in the pass-through mode. It was found that the location of the catalyst affects how effectively it is used, but it does not improve the selectivity for a given conversion over the value obtained for a pore fully covered in catalyst.

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1 Introduction

Oxidation processes in which hydrocarbons are dehydrogenated or oxygenated to form alcohols, aldehydes, or acids and their anhydrides are a fundamental piece of the modern chemical industry. A large proportion of materials and commodities in daily use undergo a selective catalytic oxidation process as a critical step in their production cycle. More than half the products obtained using catalytic processes are obtained by selective catalytic oxidation, ranging from the synthesis of small amounts of pharmaceuticals and fine chemicals to large scale production of practically all monomers used in manufacturing artificial fibers and plastics (Oyama and Hightower, 1993; Horvath, 2003).

The demand for innovation in the field of selective oxidation in terms of raw materials, ecological issues and process simplification has stimulated research toward the development of new synthetic routes starting from alkane feedstocks. Alkanes are characterized by the absence of reactive sites, such as hydrogen atoms that can be easily abstracted and double bonds; furthermore, they are largely less reactive than most of the possible reaction products. These issues have driven the search for catalysts and new reactor technologies that can control the reactivity and maximize the selectivity. Currently, the syntheses of maleic anhydride from butane and of cyclohexanol from cyclohexane are the only large scale industrial applications of alkane selective oxidation by heterogeneous gas-solid catalytic processes (Centi et al., 2001).

The earliest observations of the role of catalysis in oxidation reactions date back to the beginning of the eighteenth century. The first conscious use of catalysis in an industrial process is considered to be the lead chamber process for the oxidation of SO_2 to SO_3 introduced in the mid-eighteenth century. From that point on, many changes and advances in catalyst and reactor design, as well as discoveries of new catalytic materials, have allowed an improvement in process economics, a reduction in process complexity and a decrease in waste formation (Horvath, 2003).

A simplified network of selective oxidation is presented in figure 1-1, where k_1 is the rate coefficient for formation of the selective oxidation product, and k_2 and k_3 are the rate coefficients for formation of total oxidation products. All the reactions are exothermic and thermodynamically favored. This means that if the reactant(s) and hydrocarbon products are allowed to remain in contact with the catalyst for sufficient time, total oxidation products will be obtained. Therefore, thermodynamic equilibrium must be avoided by kinetically isolating the reaction products before the thermodynamically stable total oxidation products can be formed (Hodnett, 2000).

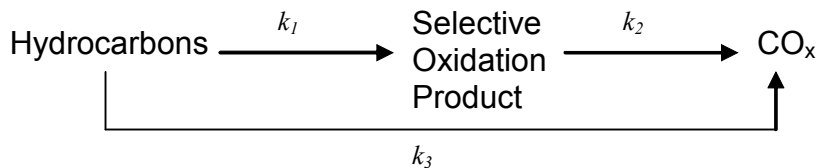


Figure 1-1: Reaction network in selective oxidation.

The desire to avoid thermodynamic equilibrium to increase product selectivity and decrease undesirable by-products provides an opportunity to improve processes for oxidation catalysis. These improvements could be achieved by either catalyst development or engineering of the process or both. Other efforts might be focused on minimizing energy consumption, utilizing and controlling exothermicities, and reducing process steps with multifunctional catalysts (Centi et al., 2001). As a consequence of the massive volume of chemicals produced yearly using selective oxidation, even modest improvements could have a big impact on the overall economics.

Partial oxidation processes are difficult to characterize. The standard paradigm in catalysis research of beginning with microreactor studies, then scaling to a pilot plant and finally to the full-scale process is argued to be ineffective with partial oxidation (Schmidt et al., 1994). First, oxidation reactions are frequently so fast that kinetics usually cannot be obtained meaningfully because the reactions become mass transfer limited. The second problem is that they are highly exothermic, which almost inevitably leads to nonisothermal catalysts. The third problem is safety; reactions can become autothermal and destroy the catalyst, reactor and laboratory, so dilution and downsizing are used, but they change the process in unacceptable ways (Schmidt et al., 1994). These considerations stress the need for experiment and theoretical modeling to be employed together in studying selective catalytic oxidation. Theoretical modeling can be a powerful tool in guiding experiments.

Recently, nanostructured membranes have been fabricated at Argonne National Laboratory by employing a combination of anodic aluminum oxidation (AAO) to

electrochemically produce the membranes and atomic layer deposition (ALD) to alter the pore diameter and wall composition (Xiao et al., 2002a; 2002b). These membranes have pore diameters between 20 and 200 nm that can be narrowed to values as small as 5 nm using ALD. The pore diameter can be altered along the full length of the pore or, by controlling the exposure time of the ALD reactants, only on a portion of it (Elam et al., 2003). The combination of AAO/ALD offers the possibility to produce a wide range of pore sizes of interest in oxidation catalysis. It also allows designing the pore to control the residence times of reactants and products inside the pores and their contact with the catalyst on the pore walls.

In order to take advantage of the possibilities offered by AAO/ALD, it is essential to understand the mass transport inside the pores. In this work we develop and apply models and simulations for the mass transport and catalytic reactions in the membranes at different scales. The theoretical models developed here complement the experimental efforts by providing valuable insight into the process. This helps in the identification and understanding of the governing processes and mechanisms occurring in the catalytic oxidation inside the membranes. The models and simulations are also useful to identify possible new directions of interest to investigate.

In the next chapter, a short background on catalytic oxidation, nanostructured membranes and on relevant simulation techniques is provided. Then, in chapter 3 the mass transport inside the membranes is studied using a combination of continuum modeling, molecular simulations and Knudsen dynamics simulations. The results include the relevant mass transport mechanisms in the pore, as well as details about

the residence times and contact with the wall of the particles diffusing through the pore. Chapter 4 employs Knudsen dynamics simulations to look at cylindrical pores with sections of different diameters that can be synthesized using the combination of AAO/ALD. The results relate the contact between the particles and the wall to the case of uniform diameter pores. Models combining mass transport and oxidation reactions inside the pore are presented in chapter 5. Here the oxidative dehydrogenation of ethane is studied using continuum modeling and reactive Knudsen dynamics simulations. The effect of the pore dimension and of the catalyst location on the conversion, selectivity and yield of ethylene are explored. Finally, chapter 6 summarizes the results obtained and presents recommendations for future related studies.

2 Background

2.1 Catalytic oxidation

Catalytic oxidation of hydrocarbon molecules proceeds as a multistep process of consecutive abstractions of hydrogen atoms and addition of oxygen atoms. If conditions exist for the abstraction of a hydrogen atom to be followed by the abstraction of a second hydrogen atom and desorption of water, a new bond between two carbon molecules may be formed. Such reactions are known as oxidative dehydrogenation. When the abstraction of hydrogen is followed by addition of an oxygen atom, oxidation takes place and an oxygenated hydrocarbon derivative is formed. The catalysts usually employed for selective oxidation are pure metals (e.g., Ag, Pd, Pt, Ni) or metal oxides (e.g., Fe_2O_3 , Cr_2O_3 , V_2O_5) either supported or unsupported (Masel, 1996).

Heterogeneous oxidation catalysis is generally described by one of the following basic kinetic laws: Mars and van Krevelen, Eley-Rideal, Langmuir-Hinselwood and power law (Hodnett, 2000). The first three of these are described in more detail below.

The Mars-van Krevelen mechanism, the most widely applied in heterogeneous oxidation catalysis, proposes that the reaction proceeds in two independent steps. First, the hydrocarbon extracts lattice oxygen from the surface layer of the catalyst, generating a reduced catalyst, and second, the lattice oxygen is replenished by gas phase oxygen in a reoxidation process. The rate equation is derived from the assumption of a steady state of the oxidation and reduction reactions. The oxidation rate is taken to be proportional to the pressure of the hydrocarbon and to the surface

coverage of oxygen atoms participating in the reaction. The rate of reoxidation is assumed to be proportional to a power n of the oxygen partial pressure and to the fraction of catalyst surface not covered by the active oxygen. The mechanism may be visualized as follows (Hodnett, 2000):



where β is the stoichiometric requirement in lattice oxygen, O_L represents a lattice oxygen anion, P is the product and S is a vacancy on the surface. The rate equation can be expressed as:

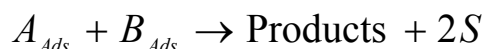
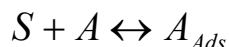
$$\frac{1}{r} = \frac{1}{k_{red} p_{HC}} + \frac{\beta}{k_{ox} p_{O_2}^n} \quad (2-3)$$

where r is the overall rate of oxidation, k_{red} is the rate constant of the oxidation of hydrocarbon, p_{HC} is the partial pressure of the hydrocarbon, k_{ox} is the rate constant of the reoxidation of the surface, p_{O_2} is the partial pressure of oxygen and n is the exponent on the oxygen pressure in the reoxidation rate.

The Eley-Rideal mechanism pictures a simple reaction between an adsorbed species and a second species reacting without adsorbing. This means that the gas phase reactant does not reside on the surface for longer than 10^{-13} s, which is the time required to define a physisorbed state (Hodnett, 2000). The mechanism derives from

the Langmuir adsorption isotherm, so it is constrained to describing energetically and chemically uniform adsorption and reaction sites (Hodnett, 2000).

The Langmuir-Hinshelwood mechanism can be written for the reaction between two species A and B as follows (Masel, 1996):



It assumes that the last step is much slower than the rest, so each adsorbed species is in thermodynamic equilibrium with the corresponding gas phase species following the appropriate adsorption isotherm. A different expression of the rate will be obtained if adsorption can be on a single type of surface site or if each adsorbing species can adsorb on its own type of site. The kinetic expression predicts reaction orders in both reactants varying from one to zero as the partial pressures increase (Hodnett, 2000).

The achievement of selectivity in oxidation of hydrocarbons depends on many factors that must be controlled. Thermodynamics favor the formation of carbon dioxide and water; therefore, all partial oxidation products are derived by kinetic control. The hydrocarbon-oxygen mixture can usually react along many different pathways, and thus the catalyst must accelerate those steps that lead to the desired products. The C-H bonds of the initial reactant are usually stronger than those in the intermediate products, which makes the intermediates prone to rapid further oxidation. All oxidation processes

are exothermic, and the temperature must be controlled to avoid overoxidation and hot spots (Horvath, 2003).

Structured reactors, i.e., those where the catalyst is not shaped in the usual way, such as monolith and membrane reactors, can be used to carry out the oxidation process with very low residence time and in adiabatic autothermal conditions. In these structured reactors the heat developed in the exothermic oxidation reactions heats the catalyst surface to high temperatures, where the processes are usually under mass transfer control. At these conditions, the distribution of products is mainly dictated by the hydrocarbon to oxygen ratio, the residence time and the temperature at the catalyst surface (Centi et al., 2001).

2.2 Nanostructured membranes

The nanostructured membranes used as the support to carry out the selective oxidation reactions are constructed by collaborators at Argonne National Laboratory in sequential steps. First, anodic aluminum oxide membranes are synthesized (Xiao et al., 2002a; 2002b). Then the diameter of the pores and their wall composition can be altered using atomic layer deposition (Elam et al., 2002).

Anodic aluminum oxide membranes are produced electrochemically with precisely controlled pore geometries and highly aligned, uniform diameter cylindrical pores with nanometer dimensions ranging from 20 to 200 nm (Xiao et al., 2002a; 2002b). Thus, the AAO membranes generally provide larger pores than conventional

mesoporous materials. Images of the membranes are presented in figure 2-1 and demonstrate clearly the regularity and uniformity of the pores.

The membranes have a thickness between 0.5 and 200 μm , with the most common being 40 μm , and they have a pore density greater than 10^9 cm^{-2} . Previous work using AAO membranes as active catalysts or supports is scarce. Our collaborators are currently pioneering their use in catalysis.

The AAO membranes can be treated using atomic layer deposition. This is a technique for depositing films with atomic layer control. ALD uses a pair of sequential surface reactions and is able to coat high aspect ratio structures such as deep trenches or porous materials. The process typically results in nearly atomically smooth films (Elam et al., 2002). The coating may be done employing different materials, such as aluminum oxide (Al_2O_3), titanium dioxide (TiO_2) and silicon oxide (SiO_2). It is also possible to modulate the surface composition along the length of the pores. The diameter of the pores can be precisely controlled and narrowed to values as small as 5 nm.

2.3 Molecular simulation

The objective of molecular simulation is to model the behavior of matter on the molecular scale using statistical mechanics as the theoretical framework. The microscopic state of a system can be specified as a function of the positions, velocities and forces associated with an ensemble of particles. Molecular simulation provides a way to validate and analyze theoretical models (Tester and Modell, 1994), and it allows

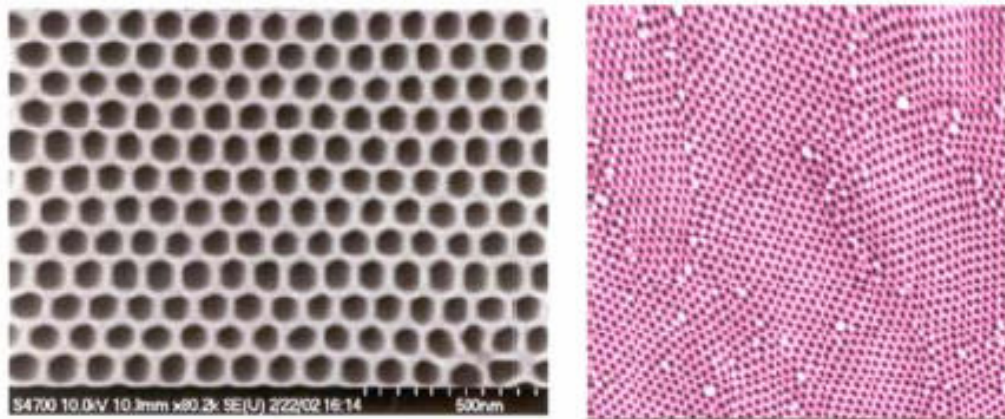


Figure 2-1: Images of anodic aluminum oxide membranes. Left: Field emission secondary electron microscopy (FESEM) and right: atomic force microscopy (AFM, $5 \times 5 \mu\text{m}^2$). Taken from Xiao et al (2002a).

one to observe processes in molecular detail. A detailed treatment of the subject is presented in Leach (2001), Reed and Gubbins (1973), Allen and Tildesley (1987) and Frenkel and Smit (1996). The following paragraphs present a short explanation of the two main molecular simulation techniques, molecular dynamics and Monte Carlo.

Molecular dynamics is a deterministic technique where successive configurations of the system are generated by integrating Newton's law of motion in discrete time intervals for each particle. The result is a trajectory that specifies how the positions and velocities of the particles in the system vary with time. The integration method employed is usually the Verlet algorithm or the Gear predictor-corrector (Allen and Tildesley, 1987). Since Newton's equations of motion are solved, both thermodynamic and transport properties can be obtained from the simulation. By default the method works in the microcanonical ensemble (constant NVE), but algorithms have been proposed to work in the canonical (NVT), isothermic-isobaric (NPT) and other ensembles (Nose, 1984; Hoover, 1985; Sadus, 1999).

The central idea of Monte Carlo is to use a stochastic method to generate a sequence of configurations of a system by making successive random changes in the positions and orientations of the species present, as well as performing insertions and deletions when appropriated (Tester and Modell, 1994; Leach, 2001). The thermodynamic properties of the system are then obtained from the averages of the values of those properties over the different configurations. In this method, the Boltzmann factor is used to allow more probable configurations to be visited more often than the less probable configurations (Haile, 1992). Since there is no time scale

associated with this simulation technique, the orders in which the configurations are generated have no physical meaning. This is why, as opposed to molecular dynamics, traditional Monte Carlo can only be used to obtain thermodynamic (static) properties and not transport (dynamic) properties (Tester and Modell, 1994). Variations of the method such as kinetic or dynamical Monte Carlo, which is explained below in section 2.4, associate the evolution of the system with a real time scale, thus allowing one to obtain dynamic properties.

Diffusivities are usually calculated using one of the following four simulation techniques: equilibrium molecular dynamics (EMD), transient molecular dynamics (TMD) (Maginn et al., 1993; Arya et al., 2001), external field nonequilibrium molecular dynamics (EF-NEMD) (Arya et al., 2001) and dual control volume grand canonical molecular dynamics (DCV-GCMD) (Heffelfinger and van Swol, 1994; MacElroy, 1994; Arya et al., 2001; MacElroy and Suh, 2001). EMD is the standard molecular dynamics simulation of a system in thermodynamic equilibrium. In TMD, an actual concentration gradient is set up within a simulation cell, and the system is then allowed to relax using MD. This method presents some practical issues, including difficulties in setting up an initial concentration profile and uncertainty about whether or not the simulation is occurring in the linear response regime (Arya et al., 2001), so it will not be discussed further. In EF-NEMD, an external field that mimics the influence of a chemical potential gradient is introduced into the Hamiltonian to generate a flux. DCV-GCMD involves the construction of high and low concentration reservoirs on opposite sides of a transport zone, which creates a flow of molecules (Arya et al., 2001), and maintenance of them

using Monte Carlo moves. Even with all these powerful techniques in hand, an unequivocal description of transport in porous materials has not emerged, partly because the proposed macroscopic transport models have arbitrary fitting parameters (Bhatia and Nicholson, 2003a).

Travis and Gubbins stated (2000) that the diffusivity calculated using EF-NEMD contains only the viscous component, while DCV-GCMD yields the combined effects of diffusive and viscous flow. This is not, however, universally accepted. It has also been proposed (Cracknell et al., 1995) that diffusivities calculated from EMD simulations only account for the diffusive component since there is no bulk flow involved in this method. More recently, it has been found that all three techniques yield the same transport coefficient in micropores (Arya et al., 2001) and also in mesopores, even in the presence of viscous transport (Bhatia and Nicholson, 2003a, 2003b).

2.4 Kinetic Monte Carlo

The traditional approach to describe chemical reacting systems assumes that the number of molecules can be approximated as a continuously varying quantity that changes deterministically over time (Gibson and Bruck, 2000). Based on this, an ordinary differential equation can be written to describe the changes in concentration of each species as a function of the rate of the reactions in which it is involved. The complete system development can then be calculated by solving the resulting set of coupled differential equations.

A stochastic formulation is the other fundamental approach to analyzing chemical reacting systems. It is event-based and describes the system using the master equation, a single differential-difference equation for a grand probability function in which time and all the species populations appear as independent variables. Gillespie (1976) proposed two different, but equivalent, Monte Carlo methods to calculate the stochastic time evolution of a spatially homogeneous chemical system.

The first method, called the Direct Method, probabilistically decides which reaction occurs next and when it occurs. The second method, called the First Reaction Method, generates a tentative time for each reaction and chooses the reaction with the smallest tentative time as the one that occurs next. Recently, new methods (Gibson and Bruck, 2000; Gillespie, 2001) that are more computationally efficient have been proposed.

The kinetic Monte Carlo principles have been extended to other applications besides homogeneous systems, including the study of reactions on surfaces (Dooling and Broadbelt, 2001) and the combined study of reaction and diffusion in zeolites (Tsikoyiannis and Wei, 1991; Keil et al., 2000). In kinetic Monte Carlo simulations of diffusion in zeolites, the pore space through which molecules diffuse is simplified to a lattice, consisting of a grid of coarse-grained adsorption sites. Molecules occupy a certain fraction of the sites and are assumed to hop between neighboring sites. Their movement is therefore described by the set of master equations for each site. A number of molecular trajectories that is sufficiently large to gather meaningful statistics

are followed, and quantities of interest are collected after the system has reached steady state (Keil et al., 2000). The transient behavior can also be studied.

2.5 Multiscale modeling

The concept of a multiscale framework consists of modeling different scales of the system using diverse modeling approaches and tools (Raimondeau and Vlachos, 2002). Multiscale modeling can also be termed a hybrid approach. The approaches incorporated into a multiscale model can range from simulations at the atomic scale up to the macroscopic continuum scale (Broadbelt and Snurr, 2000).

There are two main categories of multiscale models: serial and parallel. The serial approach encompasses problems where information gathered at a given scale is passed on to other levels, thus resulting in a flow of information (Raimondeau and Vlachos, 2002). This approach is typically used when the system is not parameterized, and the information passed is in the form of parameters required for the models at the different scales. The techniques typically applied at the lower levels are various quantum mechanical and statistical mechanical methods.

The second category encompasses problems where strong coupling between scales exists; therefore, a single level of description does not capture the behavior. In the parallel approach, the flow of information is simultaneously bi-directional, and solvers of the different techniques used in parallel communicate “on-the-fly”.

3 Multiscale modeling of transport and residence times in nanostructured membranes

3.1 Introduction

Mesoporous materials find widespread application in catalysis (Trong On et al., 2001; Coronas and Santamaria, 2004). Typically these materials are used in powder or pellet form, for example in a packed bed reactor. Robust mesoporous membrane reactors could find interesting applications and might have some advantages over pellets. For example, membrane reactors can enhance the selectivity and yield in networks of series and parallel reactions (Tota et al., 2004). This chapter focuses on new, ultra-uniform, inorganic, nanostructured membranes, fabricated by a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD) (Pellin et al., 2005). The combination of these two techniques provides a flexible synthesis route to control the membrane pore diameter and the structure and composition of the pore walls (Pellin et al., 2005). AAO allows the electrochemical production of membranes with uniform cylindrical pores having diameters that range from 20 to 200 nm and lengths between 0.5 and 200 μm (Xiao et al., 2002a; 2002b). The pore diameter and wall composition can later be tailored by placing layers of oxides (e.g., Al_2O_3 , SiO_2 , TiO_2) or other materials using ALD (Elam and George, 2003; Elam et al., 2003). Experimental results employing AAO/ALD membranes fabricated with different diameters show improved selectivity towards the desired products in the oxidative dehydrogenation of

cyclohexane compared to a conventional alumina powder catalyst at the same conversion (Pellin et al., 2005).

In the oxidation of hydrocarbons, both desired and undesired reactions are exothermic and thermodynamically favored, meaning that if the reactants and products are allowed to remain in contact with the catalyst for sufficient time, total oxidation products will be obtained. Therefore, to obtain the desired partial oxidation products, thermodynamic equilibrium must be avoided by kinetically isolating the reaction products before the thermodynamically stable total oxidation products can be formed (Hodnett, 2000). It is suspected that the short residence times that can be achieved with the nanostructured membranes synthesized by AAO and ALD play an important role in the improved selectivity results reported recently (Pellin et al., 2005). This synthesis route offers many possibilities to adjust and control the contact between reagents and catalytic sites on the walls by selecting the pore diameter, length, and composition. ALD should allow the possibility of creating asymmetric pores, for example with narrow entrances to control access and wide interiors to decrease mass transfer resistance. The wall composition could be designed to range from hydrophobic to hydrophilic, and it may be possible to place catalytic sites or zones with precision along the length of the channels (Pellin et al., 2005).

To fully take advantage of the possibilities offered by AAO/ALD, it is necessary to understand the mass transport inside the pores so that optimal pores for a particular application can be designed. Modeling and simulation have proven useful in previous studies of transport in porous materials, with various simulation techniques being

commonly used including equilibrium molecular dynamics (EMD), nonequilibrium molecular dynamics (NEMD) and dual control grand canonical molecular dynamics (DCV-GCMD) (Keil et al., 2000). These techniques have been successfully applied to a variety of systems, including many studies in zeolites (Theodorou et al., 1996; Keil et al., 2000). In a recent investigation of single-walled carbon nanotubes (Bhatia et al., 2005), for example, pores up to 8.1 nm in diameter were studied, and the authors combined molecular dynamics simulations with a theoretical approach to evaluate the viscous contribution to the transport coefficient (Bhatia and Nicholson, 2003b).

The present chapter will address pores of up to 150 nm in diameter, making it necessary to use various modeling and simulation techniques to cover the range of relevant time and length scales. The following sections will cover each of the modeling approaches separately, presenting in turn the technique, its implementation and the results obtained. First, a review is presented of the mass transport mechanisms of importance in pores between 10 and 150 nm. We then use analytical equations to assess the relative contributions of convection and diffusion. Following this, molecular dynamics simulations, performed to address the contribution of surface diffusion, are discussed. The results obtained up to that point will lead into the following section, where we present modeling and simulations based on Knudsen diffusion in order to study residence time and number and position of hits on the pore wall for a particle traveling through it.

3.2 Mass transport mechanisms in nanopores

Different mass transport mechanisms are possible inside pores, including convection, molecular diffusion, Knudsen diffusion and surface diffusion (Cussler, 1997). These possible mechanisms are illustrated in figure 3-1 and discussed in the following paragraphs.

Knudsen diffusion occurs when the mean free path of the molecules becomes greater than the pore diameter, so that collisions between a molecule and the pore wall occur more frequently than intermolecular collisions. Thus this type of diffusion occurs in small pores or at low pressures. In Knudsen diffusion the collisions with the walls are assumed to be diffusive. That is, the speed and direction of the molecule leaving the surface bear no relation to the incoming values. The Knudsen diffusivity, D_K , in cylindrical pores can be calculated from kinetic theory (Knudsen, 1909):

$$D_K = \frac{2}{3} r \sqrt{\frac{8RT}{\pi M}} \quad (3-1)$$

where r is the radius of a cylindrical pore, R is the universal gas constant, T is the absolute temperature and M is the molecular weight of the diffusing molecule.

When the pore diameter is large relative to the mean free path, collisions among molecules will occur far more frequently than collisions between a molecule and the pore wall. Under these conditions, the influence of the wall is minor, and diffusion occurs by essentially the same mechanism as in the bulk fluid and is called molecular diffusion. The molecular diffusivity in a binary mixture, D_M , can be calculated by the

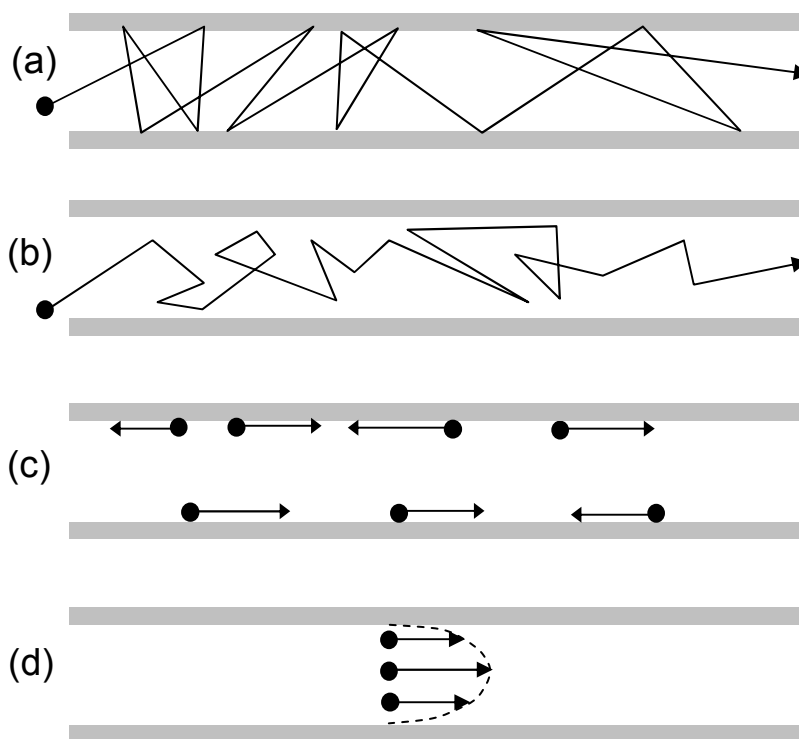


Figure 3-1: Mass transport mechanisms in nanopores. (a) Knudsen diffusion, (b) molecular diffusion, (c) surface diffusion, (d) convective flow.

Chapman-Enskog equation, which can be expressed as follows (Chapman and Cowling, 1970; Kärger and Ruthven, 1992):

$$D_M = \frac{3}{8\sqrt{2}\sigma_{AB}^2} \left(\frac{kT}{p} \right) \left(\frac{kT}{m^* \pi} \right)^{0.5} \quad (3-2)$$

where σ_{AB} is the mean molecular diameter ($\sigma_{AB} = (\sigma_A + \sigma_B)/2$), k is Boltzmann's constant, m^* is related to the molecular masses ($1/m^* = 1/m_A + 1/m_B$) and p is the pressure.

Molecular diffusion occurs when the collisions of molecules with the pore wall are unimportant compared to molecular collisions. Knudsen diffusion occurs under the opposite conditions. There will exist a transition region where both types of collisions are important. Pollard and Present (1948) showed that the overall diffusivity, D_{K+M} , can then be approximated as the addition of the reciprocals of these two diffusivities:

$$\frac{1}{D_{K+M}} = \frac{1}{D_K} + \frac{1}{D_M} \quad (3-3)$$

This form emphasizes that resistance to the motion of molecules is serial and is caused by collisions with other gaseous molecules and by collisions with the wall (Satterfield, 1970).

In some cases, there may be a high concentration of molecules adsorbed on the wall, and they may exhibit mobility, although the mobility is substantially less than in the vapor phase. Transport by movement of molecules over a surface is known as surface diffusion. The fluxes through the gas phase and the adsorbed phase are to a first approximation independent, and thus, they are additive. The overall diffusivity will be

given by the sum of the pore and surface contributions, duly weighted to take into account the difference in molecular densities between the adsorbed and vapor phase (Kärger and Ruthven, 1992). Surface diffusion is an activated process and its diffusivity, $D_{surface}$, can be described by an equation of the Arrhenius form (Satterfield, 1970):

$$D_{surface} = D_{surface,\infty} \exp(-E_s / RT) \quad (3-4)$$

where $D_{surface,\infty}$ is the surface diffusion coefficient at infinite temperature and E_s is the activation energy of the process.

If there is a difference in total pressure between the ends of the pore, and under no slip conditions, there will be a bulk flow in accordance with Poiseuille's equation. This convection contribution could be represented alternatively by an equivalent Fickian diffusivity (Kärger and Ruthven, 1992):

$$D_{Poiseuille} = \frac{pr^2}{8\eta} \quad (3-5)$$

where p is the average pressure and η is the viscosity, which can be computed from kinetic theory. Since any such forced flow operates in parallel with the diffusive flux, it is reasonable to assume that this contribution is additive. Poiseuille flow becomes more important as the pressure and the pore diameter increase (Kärger and Ruthven, 1992).

The resultant diffusivity for a given component, incorporating the contributions from all the possible mass transfer mechanisms, D_{total} , can be expressed as follows:

$$D_{total} = \frac{1}{\frac{1}{D_K} + \frac{1}{D_M}} + D_{Poiseuille} + KD_{Surface} \quad (3-6)$$

where K is the dimensionless adsorption equilibrium constant expressed in terms of pore volume (moles adsorbed per unit pore volume/moles per unit volume in gas phase). Equation (3-6) stresses that these mass transport mechanisms could be present for any system. Their relative values will determine which of them dominates or if their contributions are comparable creating a transition region.

In the next section these equations are applied to the dimensions and conditions of typical AAO/ALD systems used in selective catalytic oxidation to determine the importance of the contributions of the different mass transport mechanisms.

3.3 Convection vs. diffusion

In this section the contributions of convection, Knudsen and molecular diffusion to the global mass transport coefficient are compared to determine the dominant mechanism. A main objective is to identify if the system is dominated by convection or by diffusion, as this will define the behavior of the system and how the membrane should be operated. Due to the difficulty in predicting surface diffusion coefficients analytically, the role of this mechanism will be addressed in the next section through molecular dynamics simulations. We expect that surface diffusion will be relatively unimportant under the conditions for selective catalytic oxidation (SCO), which is typically carried out at elevated temperatures (600-1200 K). The system examined was typical for SCO and consisted of trace ethane in a nitrogen carrier stream with a total average pressure

ranging from 1 to 2 atm and a temperature of 700 K. Using the equations presented in the previous section, the contribution of Poiseuille flow to the total mass transport coefficient is presented in figure 3-2 as a function of the average pressure and pore diameter for ethane in a nitrogen carrier gas system. It shows that the major contribution to mass transport comes from the diffusive mechanisms and not from convection, especially for pores under 50 nm in diameter, where over 90 % of the transport is due to diffusion. The relative contributions from Knudsen and molecular diffusion can be compared by calculating the Knudsen number, defined as the ratio between the mean free path and the pore diameter (Roy et al., 2003). We find that the Knudsen mechanism dominates in the entire region, although the contribution from molecular diffusion becomes more important for the bigger pores and at the higher pressures.

Figure 3-2 provides a good general idea about the dominant mass transport mechanism in the pores as the pore size and pressure are varied. However, it assumed no contribution from surface diffusion. Molecular dynamics simulations in the next section confirm that this assumption is valid at these conditions. The simulations may also help identify any other deviations from the mechanisms considered here that may be present in the system and could provide additional detail about the contact of reagents and catalytic sites on the pore walls.

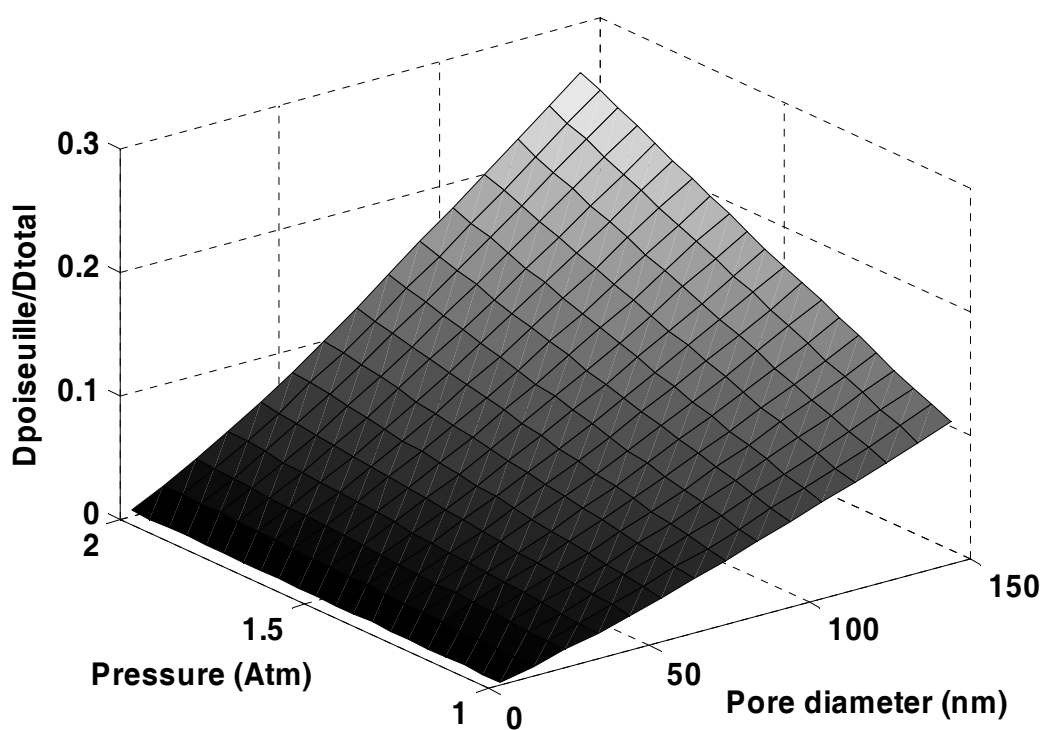


Figure 3-2: Convection contribution to the mass transport coefficient for ethane in a nitrogen carrier gas stream at 700 K as a function of pore diameter and average pressure.

3.4 Molecular dynamics simulations

Diffusivities can be calculated through molecular dynamics simulations by looking at a system in equilibrium (Theodorou et al., 1996), letting a system with a concentration gradient relax (Maginn et al., 1993; Arya et al., 2001), applying an external field to simulate a chemical potential gradient (Maginn et al., 1993; Arya et al., 2001; Chempath et al., 2004) or by constructing high and low concentration reservoirs on opposite sides of a transport zone (Heffelfinger and van Swol, 1994; MacElroy, 1994; Arya et al., 2001; MacElroy and Suh, 2001). In this work a modified version of the Music code (Gupta et al., 2003) was employed to perform equilibrium molecular dynamics to obtain the self-diffusivity of species inside the pores. At the low loadings of interest, it should be expected that the self-diffusivity and Fickian diffusivities are equal (Theodorou et al., 1996).

In order to perform molecular dynamics simulations in the pores, it is necessary to appropriately represent the alumina walls. A straightforward approach would be to fully reproduce the configuration of the walls with atomic detail. However, due to the size of the pores this would involve an impractical number of atoms and an unnecessarily expensive calculation. A simplification usually introduced is to recognize that the oxygen atoms are responsible for most of the interaction between the walls and the diffusing molecules, as was done by Fernandes and Gavalas (1999) for a silica pore and by Blas et al. (1998) for an alumina pore. This assumption is also extremely common in the zeolite literature.

Including only the oxygen atoms greatly accelerates the calculations, but the number of wall atoms is still too large to achieve an efficient simulation for such large-diameter pores. Thus, further simplifications need to be introduced. Everett and Powl (1976) derived the following analytical expression to represent the Lennard-Jones interaction between a molecule and two parallel semi-infinite slabs, usually called the slit-pore potential:

$$V(d_c) = \frac{2}{3} \pi n \varepsilon_{sg} \sigma_{sg}^3 \left[\frac{2}{15} \left(\left(\frac{\sigma_{sg}}{R_p + d_c} \right)^9 + \left(\frac{\sigma_{sg}}{R_p - d_c} \right)^9 \right) - \left(\left(\frac{\sigma_{sg}}{R_p + d_c} \right)^3 + \left(\frac{\sigma_{sg}}{R_p - d_c} \right)^3 \right) \right] \quad (3-7)$$

where n is the volumetric number density of atoms in the solid, R_p is half the distance between the two parallel slabs, d_c is the distance between the particle and the midpoint between the two slabs, and σ_{sg} and ε_{sg} are the Lennard-Jones parameters for the solid-gas interactions. For larger cylindrical pores, this analytical expression can be employed with R_p as the pore radius to obtain values that are very close to that of the true cylindrical potential (Fernandes and Gavalas, 1999).

Equation (3-7) integrates the potential over a smooth and regular surface, and thus the potential is not a function of the axial coordinate z , but only of the distance to the wall. As a consequence, no force is obtained in the axial direction from the particle-wall interactions when it is employed alone, and the reversals in the axial velocity that are necessary to represent Knudsen diffusion are not captured. Fernandes and Gavalas (1999) recognized this problem and introduced “scattering centers”, i.e., clusters of particles placed on the surface of the analytical potential whose number and

size determine the frequency of the velocity reversals. These centers are an additive contribution to the smooth slit-pore potential and create reversals in the axial velocity.

Here we synthesized these ideas to develop a similar approach that resulted in a realistic representation of the alumina pores. An explicit layer of the surface oxygen atoms of the wall was added to the analytical potential. These atoms were added by randomly placing them without overlapping in a shell 2 Å thick with the desired internal diameter of the pore until the reported (Cascarini de Torre et al., 1995) density of oxygen ions in alumina, 0.052 ions/Å³, was achieved. Ethane was treated as a sphere, and the Lennard-Jones parameters used for the ethane-alumina interaction were $\varepsilon/k = 95$ K and $\sigma = 3.403$ Å as adjusted by Blas et al. (1998) for the adsorption of ethane in alumina pores. The Lennard-Jones parameters for ethane-ethane interactions were $\varepsilon/k = 104.15$ K and $\sigma = 3.775$ Å (Blas et al., 1998). A cut off radius of 13 Å was applied for all the potentials. The interaction between the wall and an ethane molecule was compared when using a full representation of the wall and when the simplified representation (slit-pore potential plus layer of explicit atoms) was employed. Excellent agreement between the potentials exerted by the two models was observed for pores greater than 10 nm in diameter, corroborating that the slit-pore approximation is valid in large cylindrical pores and that the proposed simplified model reproduces the potential of the wall-molecule interaction very well.

Using the simplified model, molecular dynamics simulations were performed for ethane inside alumina nanopores of diameters between 10 and 150 nm at a pressure of 0.25 atm and temperatures of 700 K, 450 K and 300 K. The conditions of the

simulations reflect a pressure that exceeds the expected typical partial pressure of the reactant and a typical elevated temperature (700 K) used to carry out SCO. Lower temperatures were also included for comparison.

In the simulations, periodic boundary conditions were applied in all directions and a simulation cell containing the complete cross section of one pore was employed. The length of the simulation cell ranged from a minimum of 27 Å for the larger pore diameters to 400 Å for the smallest diameter studied. (The cell was made longer to have enough particles in the smaller diameter pores.) The initial configurations for the MD simulations were obtained from grand canonical Monte Carlo simulations performed at the desired temperature and pressure. The number of ethane molecules obtained ranged from 20 to 290. The MD simulations were equilibrated during 300 ps and run for 3000 ps using a time step of 0.005 ps under canonical (constant density and temperature) conditions. Constant temperature was obtained by employing the Gauss thermostating method (Anderson, 1980). Finally, the mean square displacement was computed and Einstein's formula was used to calculate the self-diffusivity.

The self-diffusivities obtained from the MD simulations are presented in figure 3-3 along with the results from the analytical equations, which only include contributions from Knudsen and molecular diffusion. At 700 K the agreement between the theoretical and simulation values is excellent; this concordance indicates that surface diffusion is not present in the system under these conditions. However, as the temperature is lowered, the simulation results deviate from the theoretical results, the deviation being more accentuated for the lowest temperature studied. To explore the origin of this

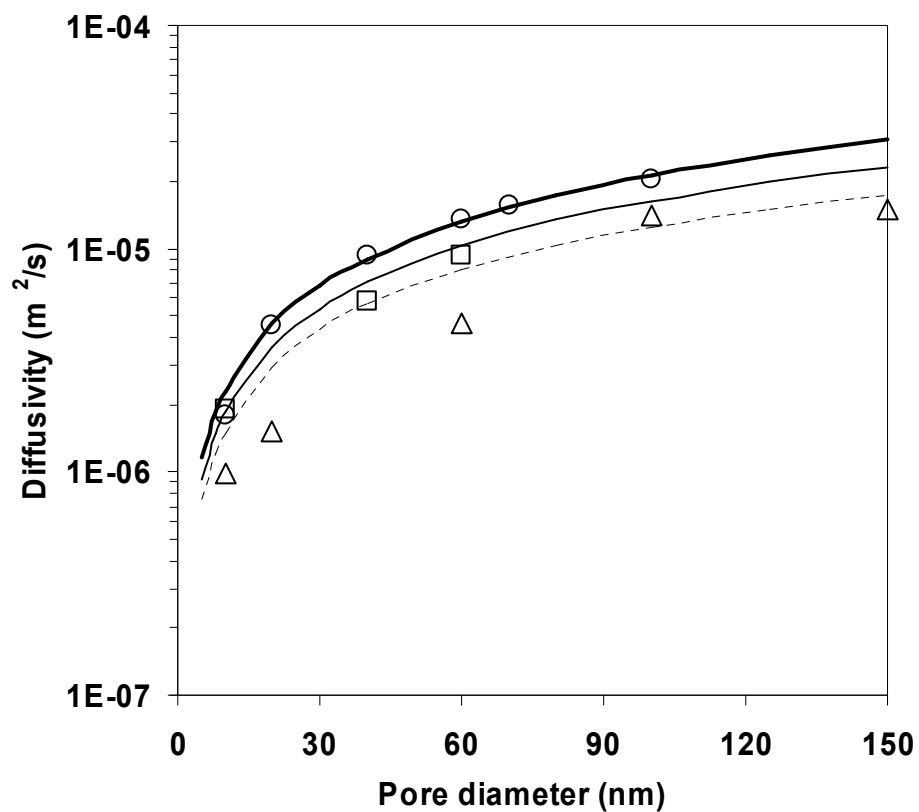


Figure 3-3: Self-diffusivity of ethane in alumina pores at 0.25 atm. Lines are analytical results not including surface diffusion calculated at 700 K (—), 450 K (—) and 300 K (---). Points are molecular dynamics simulation results at 700 K ($\circ$), 450 K ($\square$) and 300 K (Δ).

deviation, the radial density profiles were calculated in the simulations and the normalized densities as a function of distance to the wall for pores of 60 nm in diameter are presented in figure 3-4. At 700 K the radial profile inside the pore is flat, presenting no evidence of adsorption on the pore walls, and therefore, of surface diffusion. For the lower temperatures a significant fraction of the particles is preferentially adsorbed on the wall, indicating that surface diffusion is present in the system and it influences the overall diffusivity.

These results lead to the conclusion that at elevated temperatures, where selective catalytic oxidation is carried out, surface diffusion is not present in the pores studied; its influence is only noticeable at much lower temperatures. Furthermore, under the range of pore sizes and conditions of interest, Knudsen diffusion is the dominating mass transport mechanism. Based on this, in the following section we develop a simulation method to study Knudsen diffusion in these pores.

3.5 Knudsen dynamics simulations

Knudsen diffusion is based upon two concepts: first, that a particle diffusing through the pore does not encounter other particles and collides only with the wall; and second, that these collisions are diffusive. Therefore, a simulation of a pure Knudsen regime does not require the calculation of interactions between the gas particles or between the pore wall and the gas particles; consequently the simulations are less computationally intensive and will allow accessing longer time and length scales than molecular dynamics. Simulations following this idea have been performed for pores of different

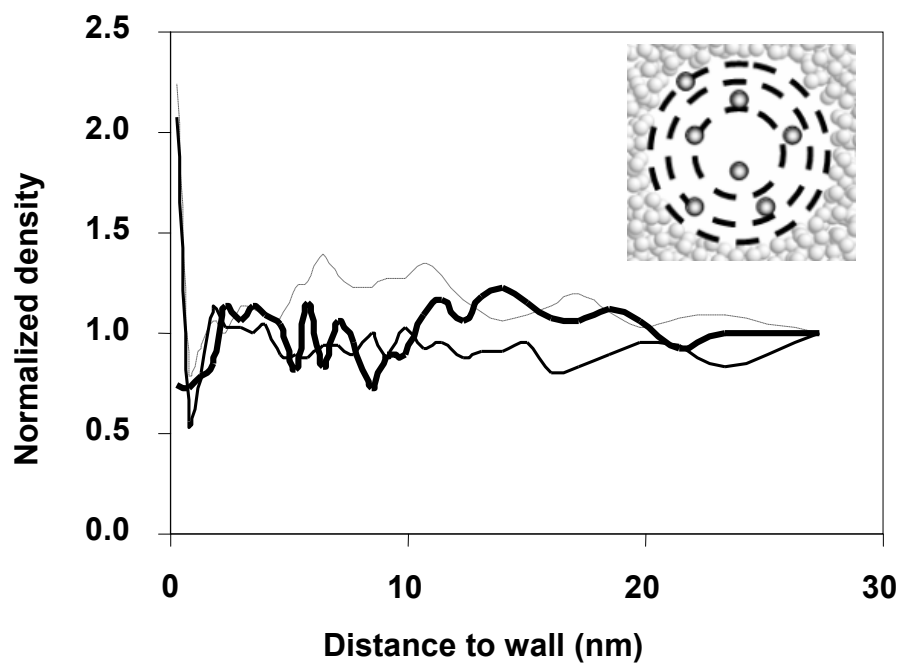


Figure 3-4: Radial density profile for ethane in alumina pores of 60 nm in diameter obtained from molecular dynamics simulations at 0.25 atm and 700 K (**—**), 450 K (**—**) and 300 K (**⋯**). Molecules in inset are not drawn to scale. Densities are normalized by dividing by the density at the center of the pore.

shapes (Davis, 1960; Evans et al., 1980; Nakano et al., 1985; 1987) and roughness (Malek and Coppens, 2001, 2002, 2003). In all of these works the particle trajectories were considered one at a time, taking advantage of the lack of interaction among particles. Here we perform the simulation for an ensemble of particles to avoid the use of an equilibration length (Malek and Coppens, 2001, 2002, 2003), which could introduce an error in the results (Russ et al., 2005), and also to allow the expansion of the model to study a multicomponent mixture with catalyzed reactions in the future.

It should be noted that the assumption of pure diffusive collisions between the particles and the wall might not be valid for all systems. Recent simulation studies of diffusion in carbon nanotubes have found transport diffusivities that are orders of magnitude faster than those observed in other nanoporous materials (Skoulidas et al., 2002; Chen and Sholl, 2006). These high transport rates are a consequence of the reflection from the carbon nanotube being nearly specular (Chen and Sholl, 2004; Bhatia et al., 2005). In general, the nature of the collisions with the wall can be described as partly diffusive and partly specular, the relative contribution of each depending on the physical roughness of the wall and the attractiveness of the wall to the fluid (Arya et al., 2003a, 2003b). In our case, the MD simulations were performed without any assumption regarding the nature of the collisions with the walls; the good agreement of their results with Knudsen diffusion indicates that in our system the collisions can be described as purely diffusive.

The simulation cell is set up to resemble the experimental conditions where a pressure drop exists across the pores. Following the scheme of the Dual Control

Volume Grand Canonical Molecular Dynamics (DCV-GCMD) technique (Heffelfinger and van Swol, 1994; MacElroy, 1994; Arya et al., 2001), high and low pressure reservoirs are maintained on the extremes of the pore as shown in figure 3-5. Since the particles do not interact with each other, the simulation is conducted by comparing the times to collide with the wall of all the particles in the system and determining the shortest time (Δt) to the next collision. Then all trajectories are advanced by Δt . The particle that collides with the wall is now assigned a new direction defined by random polar and azimuthal angles corresponding to a cosine distribution (Greenwood, 2002). If a particle reaches one of the extremes of the simulation cell, it is deleted. All particles maintain the average speed, $\bar{v}$, calculated from kinetic theory:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad (3-8)$$

After this procedure is repeated for a number of collisions, the simulation must be stopped to replenish the reservoirs. Since the particles are treated like hard spheres, no interactions need to be calculated, and insertions or deletions are performed in each reservoir until the specified pressure is achieved. The insertions are done in random positions anywhere in the reservoir as long as there is no overlap with other particles. The newly inserted particles are each assigned a random travel direction. It has been shown (Arya et al., 2001) that DCV-GCMD requires the addition of the streaming velocity calculated in the transport region of the simulation cell to the particles that are inserted in the reservoirs. To incorporate this in our simulations, the streaming velocity

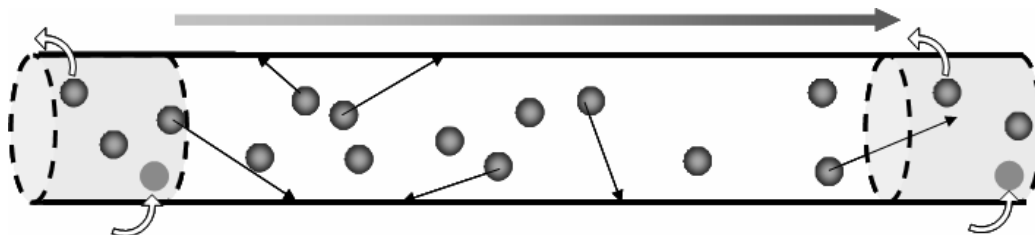


Figure 3-5: Boundary driven Knudsen simulation cell. A flow is created between the high pressure reservoir (left) and the low pressure reservoir (right). Insertions and deletions maintain the pressure in the reservoirs.

calculated in the transport region is used as the net average velocity in the reservoirs when these are replenished, thus eliminating any discontinuity at the borders between the different regions. To minimize the time required to attain equilibrium, the simulations are started by filling the transport section with a linear concentration profile between the reservoirs. The flux is then measured and monitored at seven planes distributed throughout the transport section. The simulation is considered to achieve steady state when the fluxes in all the planes converge to the same value. The pores simulated had diameters between 10 and 70 nm and lengths from 0.05 to 5 μm . The length of the reservoirs ranged from equal to the length of the transport zone (short pores) to 10 % of it (long pores). The simulated times varied from 500 to 5000 ns, with the reservoirs being replenished every 0.001 to 0.01 ns. Intervals of 0.01 to 0.1 ns were used to calculate the streaming velocity. The number of trajectories in each simulation was between 10^4 and 10^6 .

From the simulations the diffusivity is calculated from Fick's law using the flux measured at the different planes and the concentration gradient. The values obtained at different pore diameters are presented in figure 3-6. As expected they agree with those predicted by equation (3-1), verifying that the simulations are performed correctly.

The Fickian diffusivity is given by the net flux in the pore; it does not, however, provide information about the residence time of the particles or about the location and number of collisions between the particles and the wall. To look at these quantities we need to study the individual trajectories of the particles. Given that the collisions are diffusive, a fraction of the particles entering the pore will exit through the same end

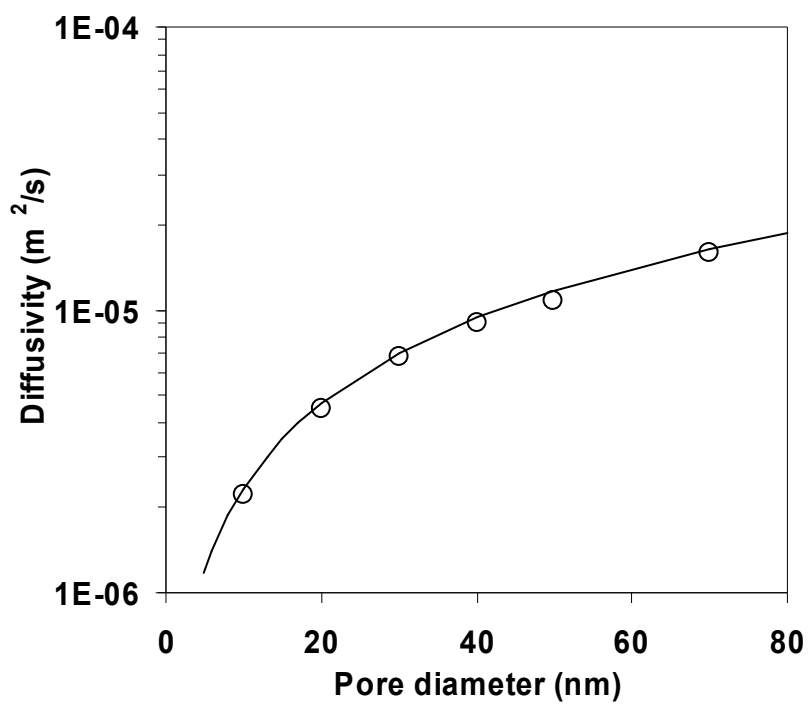


Figure 3-6: Ethane diffusivity from the boundary driven Knudsen simulations ($\circ$) and theoretical values (equation (3-1)) (—) at 700 K.

where they entered, while the rest will travel through the whole length of the pore and leave it at the opposite end. The ratio of the trajectories that reach the opposite end of the pore to the number of trajectories that enter the pore is called the transmission probability. Figure 3-7 shows good agreement between the values of this variable obtained from the simulation and those calculated from Clausing (1932). The values of the transmission probability indicate that the particles enter the pore multiple times before reaching the opposite end of the pore, especially for larger values of the aspect ratio of pore length to pore diameter (L/d). For this reason, results for the residence times and number of hits are presented below for the two distinct trajectories: those that reach the opposite end and those that return to the initial end. In addition, it is interesting to consider a particle that is allowed to reenter the starting end as many times as needed in order to leave the membrane at the opposite end.

Given the potential to place catalytic sites in particular locations along the pore length by ALD and other techniques, it is of interest to determine the distribution of molecule-wall hits as a function of the distance to the entrance. This could help in choosing the sections of the pore where the catalyst should be located to optimize the contact between catalyst and reactants. This information also contributes to the identification of the differences achieved when operating the reactor in a sweep-gas mode versus operating in a pass-through mode, where particles are removed only on the downstream side of the membrane, as depicted in figure 3-8. The distributions of the average number of hits along a pore are shown in figure 3-9 for a pore of aspect ratio (L/d) equal to 10. Pores of other aspect ratios have similar distributions, although

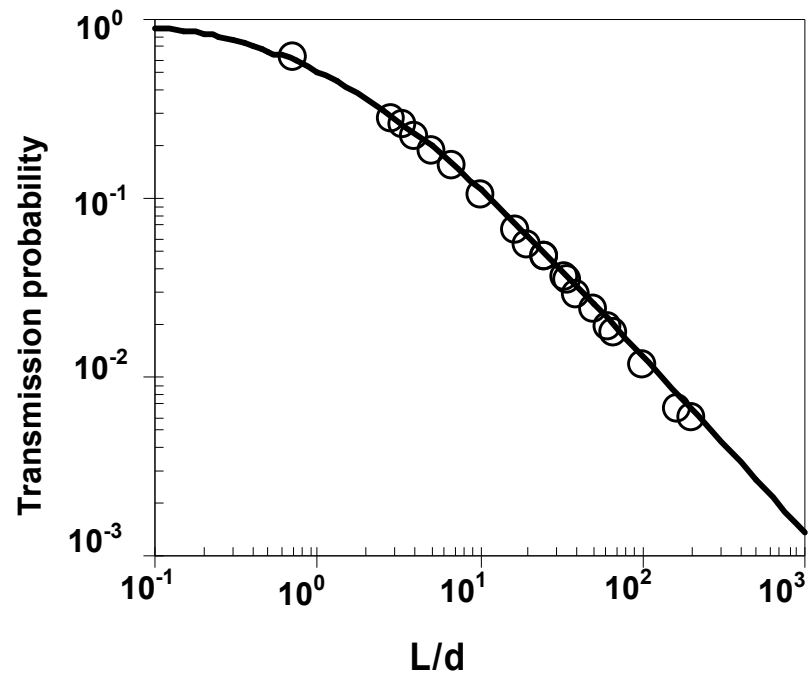


Figure 3-7: Transmission probability obtained from Knudsen simulations ($\circ$) and from equation 44 in the work of Clausing (1932) (—) for pores of different aspect ratios.

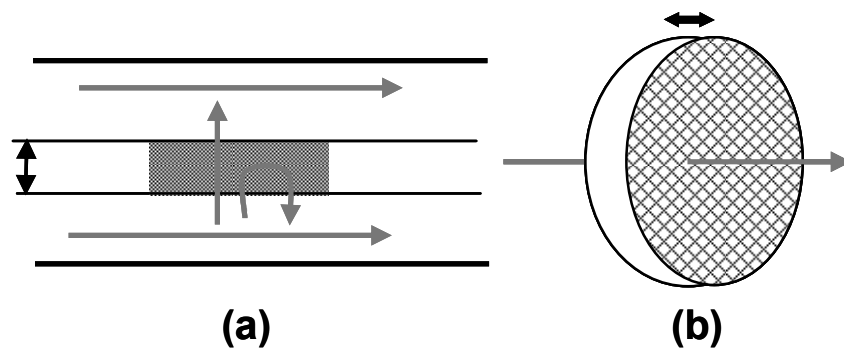


Figure 3-8: Possible operational modes for the membranes. (a) Sweep-gas
(b) Pass-through.

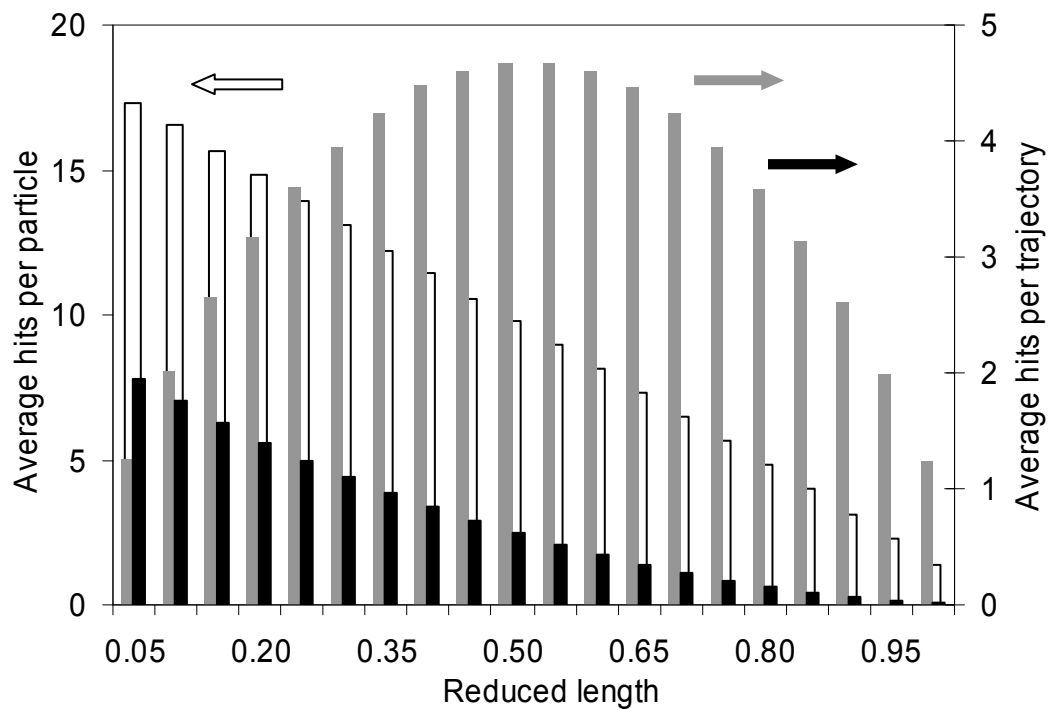


Figure 3-9: Average number of hits on the wall per section of a $L/d=10$ pore for individual trajectories that reach the opposite end of the pore (grey), for those that return to the starting end of the pore (black) and the total average number of hits for particles recovered on the downstream end of the membrane (open bars).

the smaller the aspect ratio is, the more uniform the number of hits is along the pore length (the slopes of the distributions are smaller). When the reactor is operated in a sweep-gas mode, the relevant distributions of hits are for trajectories that return to the starting end of the pore, where they are removed by the retentate sweep gas, and for trajectories that reach the opposite end, where they are removed by the permeate sweep gas. The shapes of the two distributions are very different. When the particles return to the starting end of the pore, the majority of the hits are located near the entry point, decreasing sharply with the distance traveled inside the pore. For individual trajectories that reach the opposite end of the pore, the distribution of average hits is symmetric, with the maximum located in the center of the pore. The total average number of hits per trajectory is also important to consider for catalytic purposes. In figure 3-10 this quantity is shown as a function of the aspect ratio for both types of individual trajectories. It is observed that it scales with $(L/d)^{1.79}$ for the trajectories that reach the opposite end and with $(L/d)^{0.91}$ for those trajectories returning to the initial end.

If the reactor is operated in a pass-through mode, particles are removed only when they reach the opposite end of the pore. Then, the relevant distribution of hits will account not only for the final trajectory that reached the opposite end of the pore but also for all prior trajectories that returned to the initial end of the membrane before the particle was able to reach the downstream side. The total number of hits will then be related to the transmission probability of the membrane. Figure 3-9 shows that the distribution of hits in this case has its maximum at the entrance of the pore and

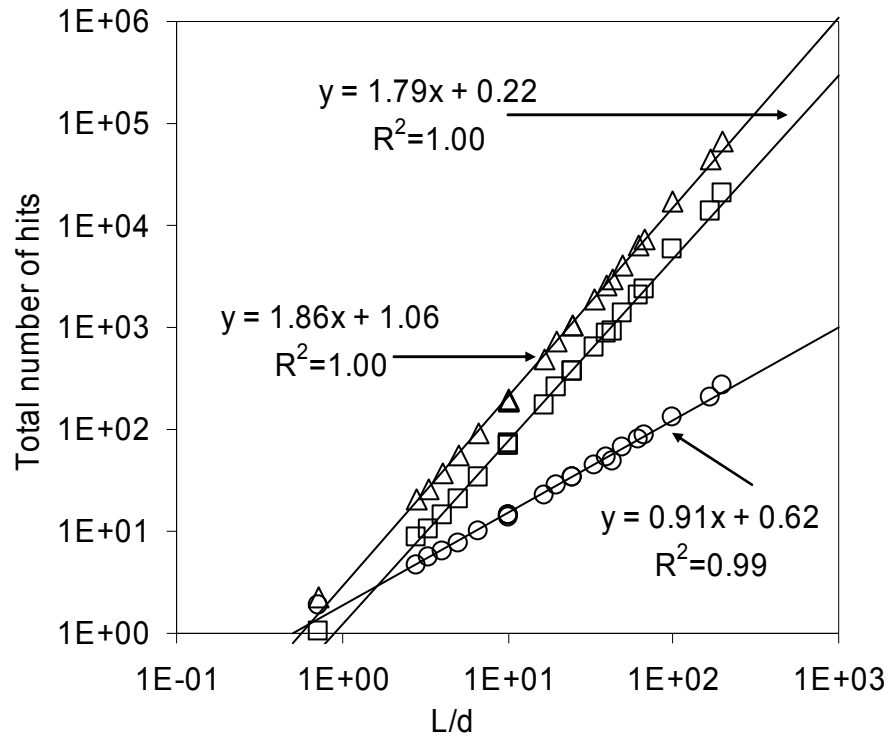


Figure 3-10: Average total number of hits on the wall as a function of L/d for individual trajectories that reach the opposite end of the pore ($\square$), individual trajectories that return to the starting end of the pore ($\circ$) and the average total number of hits for a particle recovered on the downstream end of the membrane (Δ).

decreases linearly with the distance traveled. It can be appreciated that the total number of hits is considerably higher than for the previously mentioned distributions. This is also observed in figure 3-10, along with its scaling with $(L/d)^{1.86}$.

The residence time of particles inside the pore should be proportional to the number of hits and the average distance traveled between them and inversely proportional to the velocity of the particles. To investigate this relationship, figure 3-11 shows the average residence time of individual trajectories plotted against the product of the average number of hits and the diameter of the pore, divided by the average velocity of the particles. A good fit is obtained with a slope value close to one, indicating that the average distance traveled between hits is close to the diameter of the pore. It is worth mentioning that the residence time of particles in the pores follows a distribution of values. In the case of the individual trajectories that reach the opposite end, it resembles a normal distribution but with a tail expanded to longer times, as illustrated by figure 3-12 (a). For individual trajectories that return to the starting end of the pore, the distribution has a peak at very short times and then a tail at longer times as shown in figure 3-12 (b). The existence of this wide distribution of residence times and number of hits should be kept in mind when designing catalytic membrane reactors based on AAO/ALD materials.

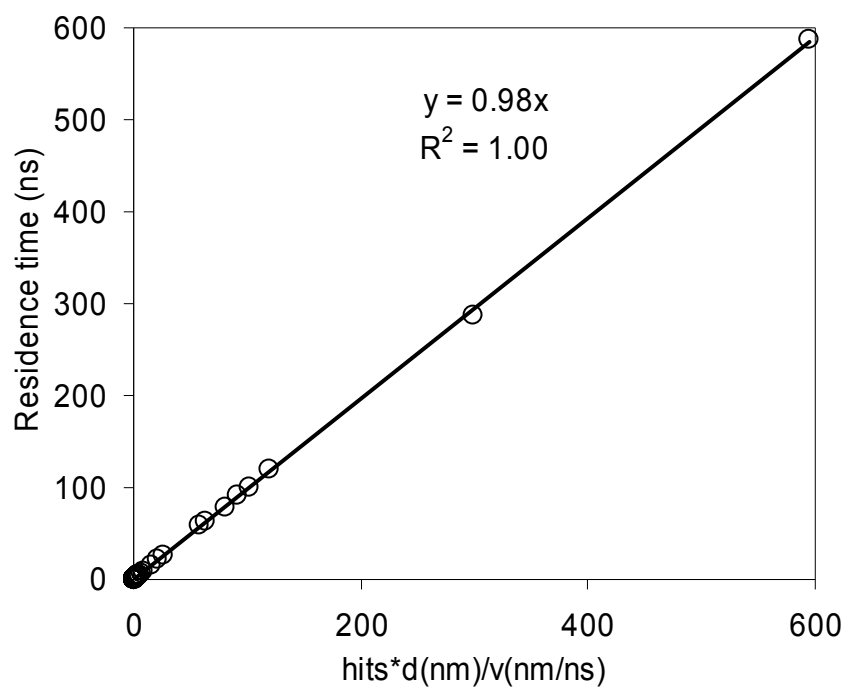


Figure 3-11: Residence time as a function of the number of hits, diameter of the pore and average speed for all individual trajectories.

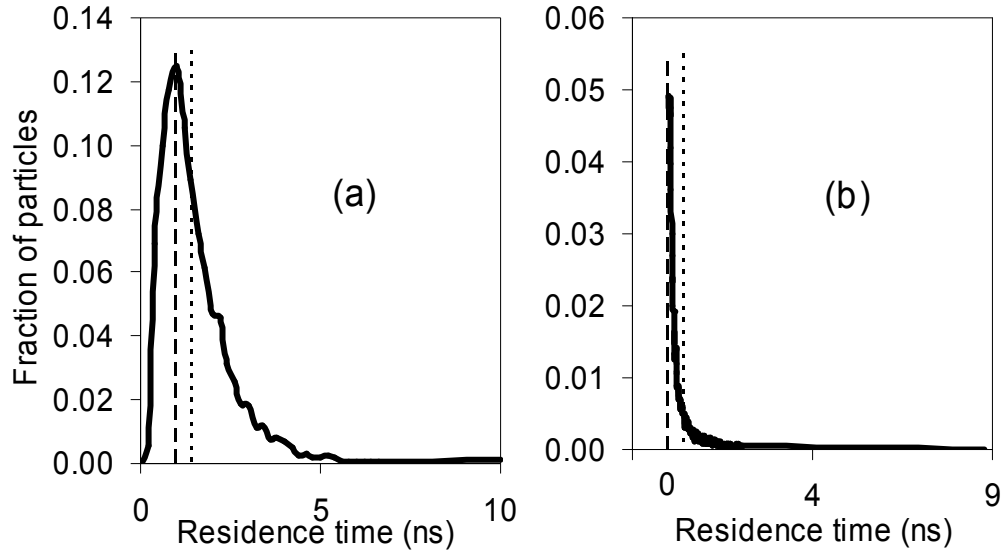


Figure 3-12: Residence time distribution (—), average residence time (···) and most probable residence time (---) in a pore of $L=0.20\ \mu\text{m}$ and $d=30\text{nm}$ for (a) individual trajectories that reach the opposite end of the pore and (b) individual trajectories that return to the starting end of the pore.

3.6 Conclusions

The combination of AAO and ALD for membrane fabrication offers the possibility to control the geometry of membrane reactors to regulate the residence time of particles inside the pores. In this chapter AAO/ALD membranes were modeled employing a multiscale approach: analytical equations were used to determine the role of convection, molecular dynamics simulations were carried out to determine the contribution of surface diffusion and Knudsen dynamics simulations were executed to quantify the contact between the particles traveling through the pore and the pore walls. It was found that Knudsen diffusion is the dominant mass transport mechanism under the conditions of interest, i.e. high temperature and low pressure. In this regime, it was determined that if the membrane is operated in a sweep-gas mode, particles traveling through the pore that reach the opposite end are more likely to hit the wall in the center of the pore, while the particles that return to the initial end of the pore will likely hit the wall near the entrance more frequently. If the membrane is operated in pass-through mode, then all particles will hit the wall near the entrance more frequently. The average number of hits per particle is higher in pass-through mode than in sweep-gas mode. The residence time was related to the number of hits and the velocity of the particles, revealing that the average distance traveled between hits is approximately the pore diameter. In general, the number of hits and the residence times grow with the aspect ratio (L/d) of the pore. These trends can be employed as guidelines for the placement of the catalyst within the pores to optimize the contact between the catalyst and diffusing molecules.

4 Transmission probabilities and particle-wall contact for Knudsen diffusion in pores of variable diameter

4.1 Introduction

Exceedingly uniform cylindrical pores can be fabricated using a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD), allowing precise control of the pore diameter, length and wall composition (Pellin et al., 2005; Xiong et al., 2005). Membranes fabricated with AAO can have thicknesses ranging from 0.5 to 200 μm and pore diameters between 20 and 200 nm (Xiao et al., 2002a; 2002b). ALD allows the placement of layers of Al_2O_3 , SiO_2 , TiO_2 or other oxides (Elam and George, 2003; Elam et al., 2003), effectively decreasing the diameter of the pores and changing the wall composition. This can be done along the full length of the pore or, by controlling the exposure time of the ALD reactants, only on a portion of it (Elam et al., 2003). The range of dimensions and wall compositions that can be achieved makes these membranes attractive for catalytic applications, as they offer the possibility to control not only the catalyst, but also the contact time of reactants and products with the catalyst. As an example, AAO/ALD membranes have been employed in the oxidative dehydrogenation of cyclohexane, and the results show an improved selectivity towards cyclohexene compared to similar conversions employing the same catalyst as a powder (Pellin et al., 2005; Stair et al., 2006).

In order to interpret the experimental results and to be able to design a pore that will maximize the desired product in a given reacting system, it is vital to understand the mass transport and the contact with the walls for particles traveling through the pores. In the previous chapter, we studied the contributions of the different mass transport mechanisms in cylindrical pores with diameters ranging from 10 to 150 nm under conditions relevant for the selective oxidation of ethane, namely atmospheric pressure and a temperature of 700 K. We found that Knudsen diffusion strongly dominates mass transport over convection, molecular diffusion and surface diffusion. Under Knudsen diffusion, the mean free path of the molecules is greater than the pore diameter, so the particles collide more frequently with the wall than with other molecules; these collisions are assumed to be diffusive. We used Knudsen dynamics simulations to obtain the distribution and total number of hits between the particles and the pore walls for different operational modes of the membrane (Albo et al., 2006).

In this chapter we use Knudsen dynamics simulations to study the changes in the transmission probability and the number of hits due to introducing a change in diameter, as might be done by applying ALD partially to the pore. The transmission probability is defined as the ratio of the number of trajectories that reach the opposite end of the pore to the number of trajectories that enter the pore. The objective is to identify trends that will help in the design of the pore geometry to alter the conversion and selectivity and maximize a desired product in a catalytic membrane reactor. In the next section, the simulations are briefly described. Then we present results for the effect of the angle of the transition between two diameters. Next, the effect of the diameters and aspect ratio

(pore length/pore diameter) of each individual section is studied in pores with two different diameters, and lastly we discuss pores with more than two sections.

4.2 Knudsen dynamics simulations

The simulations are based on the main assumptions of Knudsen diffusion: first, that there are no interactions or collisions between particles and second, that particles collide diffusively with the pore walls. Simulations following this idea have been performed for pores of different shapes (Davis, 1960; Evans et al., 1980; Nakano et al., 1985; 1987) and roughness (Malek and Coppens, 2001, 2002, 2003). In our simulations, the trajectories of an ensemble of particles inside one pore are followed. A step of the simulation consists of comparing the times to collide with the wall of all the particles in the system, determining the shortest time (Δt) to the next collision, and then advancing all trajectories by Δt . Following this, the particle that collides with the wall is assigned a new direction defined by polar and azimuthal angles drawn from a cosine distribution (Greenwood, 2002). All particles maintain the average speed calculated from kinetic theory. At the extremes of the pores, two reservoirs at constant pressures are maintained; this is done to produce a pressure drop across the pore. The pressures in the reservoirs are maintained constant by frequently stopping the simulation to perform insertions and deletions of particles in each reservoir until the specified pressure is achieved. The simulations are started by filling the transport section of the pore with a linear pressure (concentration) profile between the reservoirs. The flow of particles is monitored at seven planes distributed throughout the pore. The simulation is

considered to achieve steady state when the flows at all planes converge to the same value. A more detailed description of the simulation method can be found in our previous work (Albo et al., 2006).

The pores studied here include cylindrical sections with different diameters. Accordingly, the reservoirs at the extremes of the pore will have the diameters of the sections next to them. The transition between two cylindrical sections of uniform diameter is represented by a conic section characterized by an angle (α) with the horizontal, as represented in figure 4-1. In the next section we study the effect of this angle on the profile of hits on the pore wall and on the transmission probability. All the simulations are performed for ethane at a temperature of 700 K and pressures of 0.40 and 0.05 atm in the high and low pressure reservoirs, respectively. The pores simulated have section diameters between 10 and 50 nm and total lengths equal to 1 μm . The length of the reservoirs in all simulations was equal to 0.10 μm . The production time in the simulations was 1000 ns, with the reservoirs being replenished every 0.01 ns. The number of trajectories in each simulation was between 10^5 and 10^6 .

4.3 Transition angle

ALD is an outstanding technique to coat the inside of pores by using a pair of sequential self-limiting chemical reactions to deposit a thin film of the desired material. It has been shown that the depth of infiltration of the coating is proportional to the exposure time to the ALD reactants (Elam et al., 2003). Therefore, by controlling the exposure time it is possible to coat only a section of the pore, introducing a change of

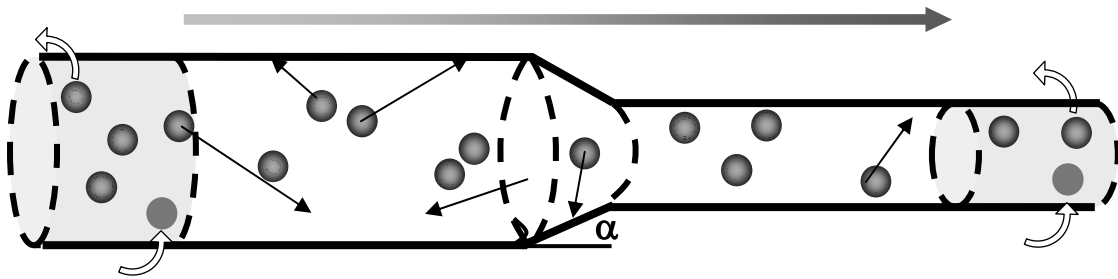


Figure 4-1: Simulation setup for a pore with two sections of different diameters. The angle α characterizes the transition region between the two different sections.

the diameter at a certain length. This does not appear to happen as a step change, but more gradually (Elam et al., 2003), such that an angle characterizes the transition as shown in figure 4-1. Here we will study the effect of this angle on the quantities of interest: the transmission probability and the number and positions of hits on the wall of the pore.

Knudsen dynamics simulations were performed for different transition angles ranging from 2 to 88°. This was done for two diameter reductions: from 50 to 30 nm and from 50 to 10 nm, and for two diameter augmentations: from 30 to 50 nm and from 10 to 50 nm. In all cases the total length of the pore was 1 μm and the two sections of different diameters were of equal length. The lengths of the transition section are determined for each simulation by the diameter change and the transition angle. Table 4-1 presents the resulting lengths of the transition section and of the sections of uniform diameters for different angle values for the two sets of diameters simulated. The transmission probabilities obtained in the simulations were normalized by the value at $\alpha=45^\circ$ and are presented in figure 4-2. From this figure it is clear that the transmission probability is independent of the angle of transition except when the transition is done extremely smoothly (with an angle close to 0°). Smooth transitions present a long conic section, as illustrated in table 4-1: when an angle of 2° is used to transition between 50 and 10 nm in diameter the conic section has a length of 0.573 μm , more than half the length of the simulated pore, compared to just 0.020 μm when the angle is 45°. This longer conic section has two effects; first it avoids a sudden change in diameter that

Table 4-1: Lengths of the transition and uniform diameter sections for different angles in pores with 1 μm total length and transitions in diameter between 50 and 30 nm and between 50 and 10 nm.

Angle	<i>Diameters = 50 and 30 nm</i>		<i>Diameters = 50 and 10 nm</i>	
	Transition section (μm)	Uniform diameter sections (μm)	Transition section (μm)	Uniform diameter sections (μm)
2°	0.286	0.357	0.573	0.214
10°	0.057	0.472	0.113	0.443
30°	0.017	0.491	0.035	0.483
45°	0.010	0.495	0.020	0.490
60°	0.006	0.497	0.012	0.494
88°	0.000	0.500	0.001	0.500

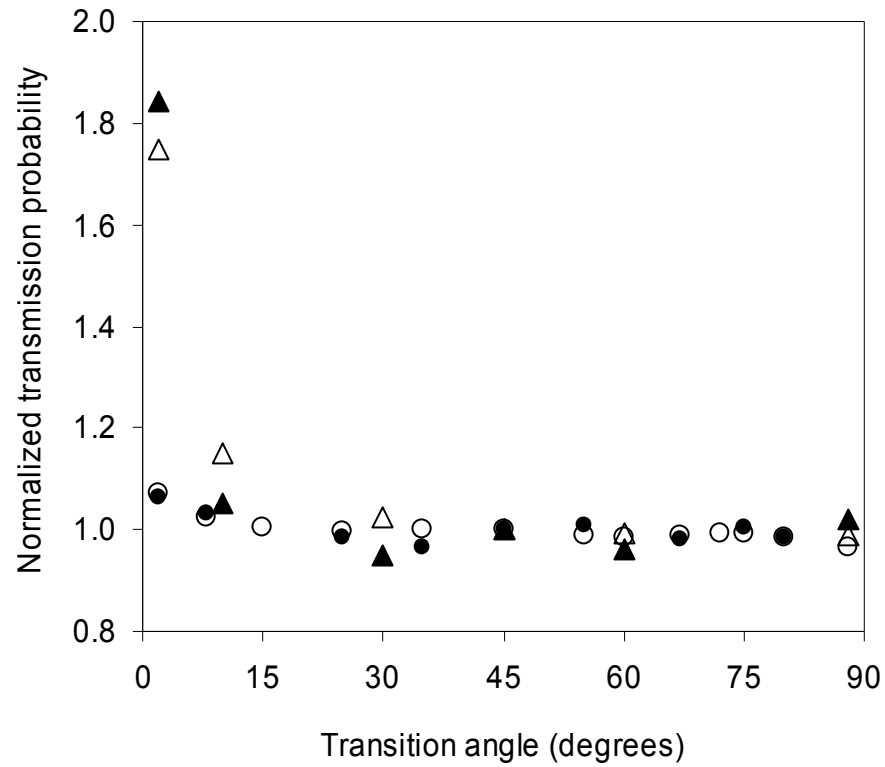


Figure 4-2: Normalized transmission probability as a function of the transition angle for pores with a change in diameter from 50 to 30 nm (○), from 30 to 50 nm (●) from 50 to 10 nm (△) and from 10 to 50 nm (▲). Values are normalized by the value at $\alpha=45^\circ$.

would create a bottleneck for particles, and second, it reduces the length of the uniform diameter sections, effectively increasing their, and the total, transmission probabilities.

The number of hits and their distribution along the pore are presented in figure 4-3 for pores with a diameter change from 50 to 30 nm and a total length of 1 μm for $\alpha=45^\circ$. For other changes in diameter the results are analogous. The pore was divided in 20 segments of equal length and the number of hits on each of the segments was recorded. In evaluating these results it is important to consider that the membrane reactor might be operated in two different modes: the sweep-gas mode and the pass-through mode.

In the sweep-gas mode, a sweep gas flows perpendicular to the pores of the membrane on the retentate and permeate ends of the pores. Reactant molecules from the retentate side may diffuse into the membrane. The relevant distributions of hits are those for trajectories that return to the starting end of the pore, where they are removed by the retentate sweep gas, and for trajectories that reach the opposite end, where they are removed by the permeate sweep gas. It can be observed in figure 4-3 that those trajectories returning to the starting end of the pore (black bars) concentrate most of their hits over the length of the first section, having an almost constant number of hits on each segment. These trajectories present only a small number of hits after the diameter changes at 0.5 μm . For individual trajectories that reach the opposite end (grey bars), the distribution of hits resembles the combination of two symmetric distributions. (For pores of uniform diameter the distribution of hits in such trajectories is symmetric with its maximum at the center of the pore (Albo et al., 2006).) The shapes of the distributions

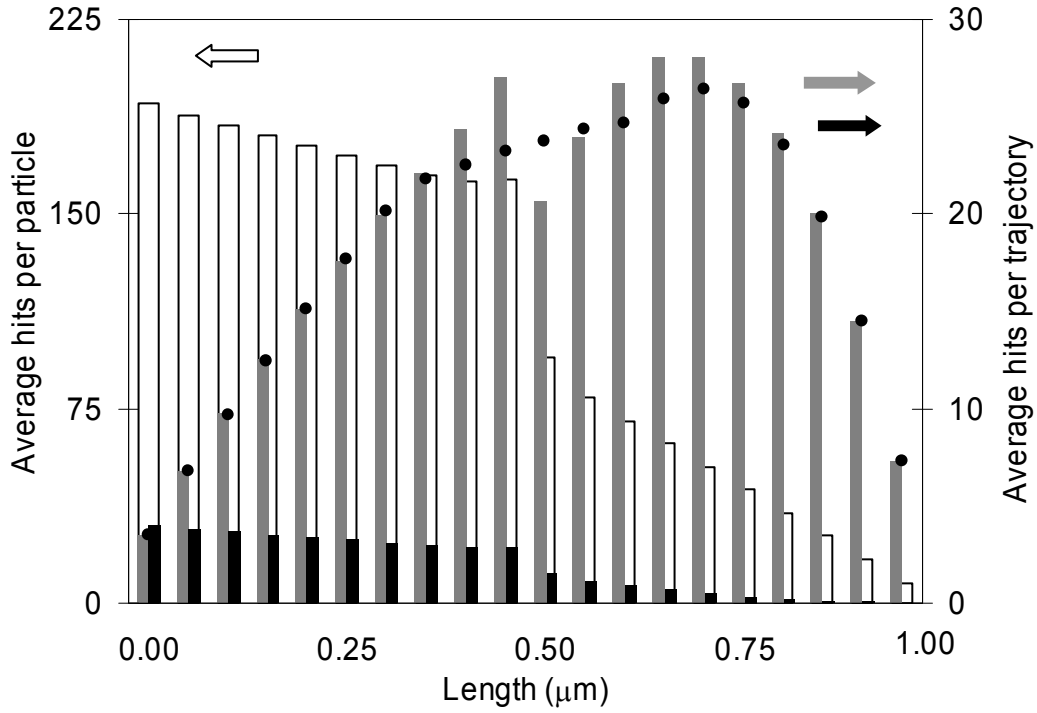


Figure 4-3: Average number of hits on the wall per segment for a pore of $L=1\ \mu\text{m}$ ($L_1 = L_2$) and a change in diameter from 50 to 30 nm. For individual trajectories that reach the opposite end of the pore when $\alpha=45^\circ$ (grey bars) and when $\alpha=2^\circ$ (•), for those that return to the starting end of the pore when $\alpha=45^\circ$ (black bars) and for the total average number of hits for particles recovered on the downstream end of the membrane when $\alpha=45^\circ$ (white bars).

are very similar for most transition angles, the only exception being for very small values of the transition angle. As an example, the distribution of hits for $\alpha=2^\circ$ is presented for individual trajectories that reach the opposite end (black circles). It can be observed that the change in the number of hits with the position in the pore is more gradual than for $\alpha=45^\circ$.

In the pass-through mode, all gas in the upstream reservoir is forced through the membrane, and particles are removed only when they reach the opposite end of the pores (Stair et al., 2006). The relevant distribution of hits accounts not only for the final trajectory that reached the opposite end of the pore, but also for all prior trajectories that returned to the initial end of the membrane before the particle was able to reach the downstream side. In figure 4-3 it can be observed that the number of hits (white bars) decreases linearly along the length of the pore, having a change of slope and a strong reduction where the pore diameter changes.

The distributions of hits for the different operational modes show that the number of hits can be concentrated in different regions. In the next section this will be investigated by exploring the effect of the dimensions of the individual sections of the pore on the transmission probability, number of hits and locations of the hits in two-section pores. The results obtained regarding the transition angle suggest that an angle of 45° can be used as a representative value for a wide range of transition angles, disagreeing only with very small transition angles. Furthermore, Monte Carlo simulations of ALD coverage (Elam et al., 2003) reveal that the transition from one region to another is gradual but not exaggeratedly smooth.

4.4 Pores with two sections

The profiles of hits in pores of uniform diameter were studied in chapter 3. In this chapter we will consider pores composed of two sections with different diameters. Knudsen dynamics simulations were performed for pores with a first section diameter $d_1=50$ nm and $d_2=30$ nm in the second section. The total length of the pore was maintained constant at 1 μm and the transition angle was also kept constant at 45° . The lengths of the sections were varied, effectively changing the aspect ratio (pore length / pore diameter) of both sections.

Figure 4-4 illustrates the distribution of the average hits per area for a pore with a total length equal to 1 μm and the midpoint of the transition at 0.4 μm . The distributions are similar to those presented in figure 4-3. However, by plotting the number of hits per area instead of the number of hits, a more gradual and continuous transition is obtained between the two sections of different diameters, which will simplify the comparison between results of multiple pores. The absolute number of hits can still be obtained from this data by using the area of the pore. The profiles of the average number of hits per area obtained from the simulations for pores with different section lengths are presented in figure 4-5. For clarity, lines are used instead of bars, but they still represent the profile of hits obtained by dividing the pore into 20 segments of equal length. In figure 4-5 (a) it can be observed that pores with uniform diameters (50 and 30 nm) have different slopes for their profiles. The results for the pores with two sections are bounded by the uniform diameter cases. The profiles start by following the slope of

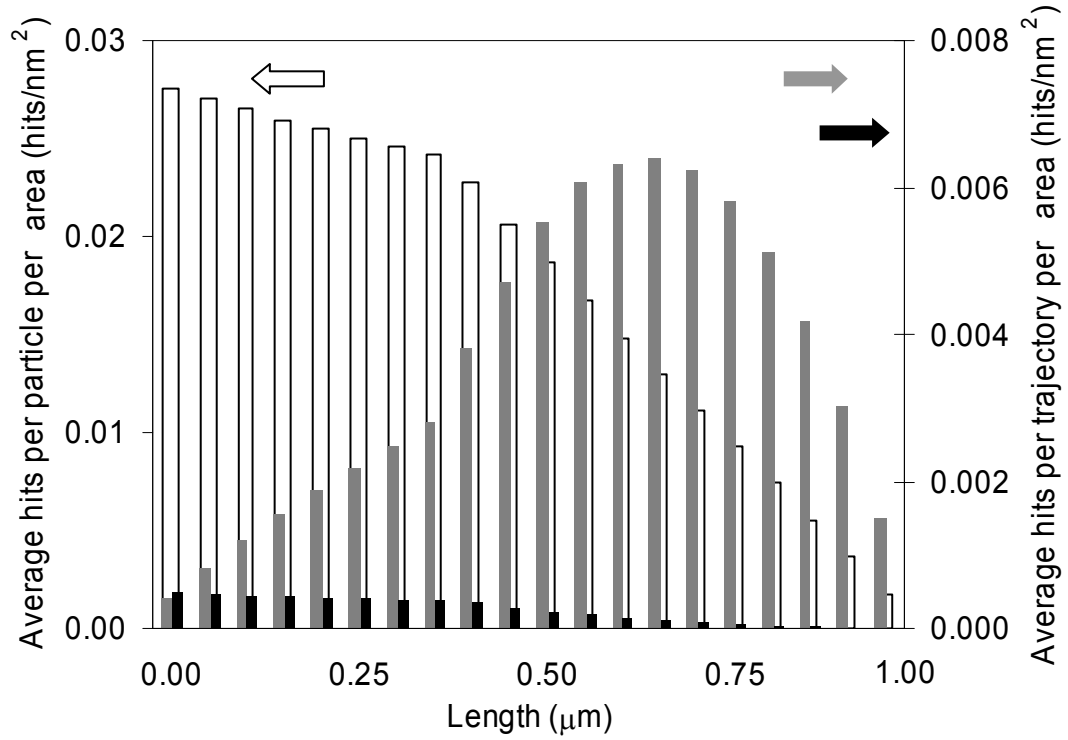


Figure 4-4: Average number of hits per area per segment for a pore of $L_1=0.4 \mu\text{m}$, $d_1=50 \text{ nm}$ and $L_2=0.6 \mu\text{m}$, $d_2=30 \text{ nm}$ for individual trajectories that reach the opposite end of the pore (grey), for those that return to the starting end of the pore (black) and for particles recovered on the downstream end of the membrane (white).

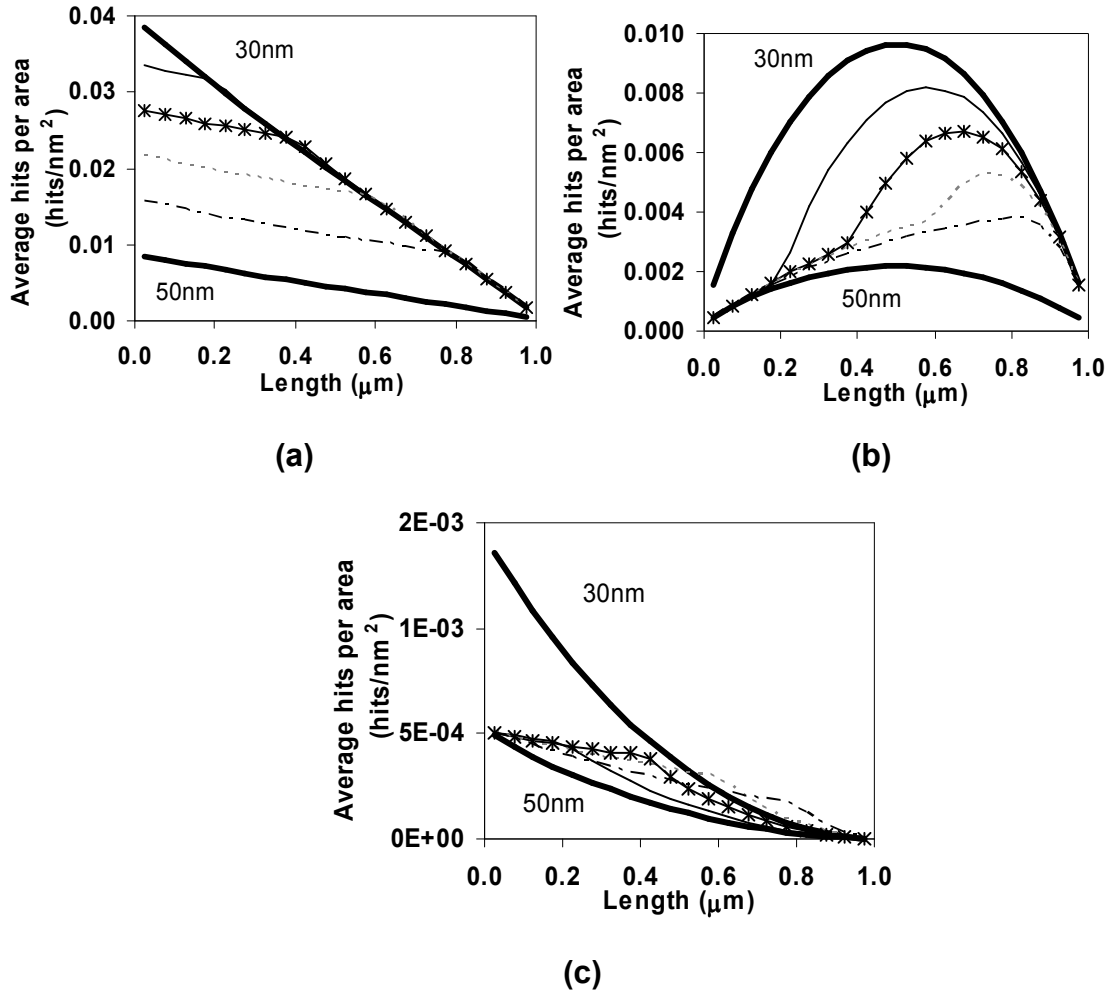


Figure 4-5: Average number of hits per area per segment for pores with $d_1=50$ nm, $d_2=30$ nm, total length = 1 μm and $L_I=0.2$ μm (—), $L_I=0.4$ μm (—*), $L_I=0.6$ μm (···) and $L_I=0.8$ μm (---) for a) particles recovered on the downstream end of the membrane b) individual trajectories that reach the opposite end of the pore and c) individual trajectories that return to the starting end of the pore. The profiles for pores with uniform diameters of 50 and 30 nm are also shown.

the 50 nm uniform diameter case, and at the length where the diameter changes to 30 nm they join the profile of the 30 nm uniform diameter pore. So, it is possible to predict the number of hits and their locations in a pore with two sections of different diameters if the profiles for the cases of uniform diameters are known. It is also feasible to tune the number of hits and to concentrate them in different sections of the pore. Notice how, for multiple segments of the pore, the number of hits per area decreases as the length of the first section is increased. This could be related to how effectively the catalyst would be used if placed on each of these segments and how that could change by varying the dimensions. Figure 4-5 (b) and (c) present the number of hits per area for individual trajectories that reach the opposite end and for those trajectories that return to the starting end of the pore, respectively. As in figure 4-5 (a), it is possible to observe a change in the behavior at the point where the diameter of the pore changes. In figure 4-5 (b), all the distributions start by following the profile of the 50 nm uniform case and end by following the profile of the 30 nm uniform case, merging the shapes of the two profiles at the different transition points. The behavior in figure 4-5 (c) differs subtly from that observed in figure 4-5 (a) and (b) in that the profiles of the pores with two sections are not always bounded by the profiles of the uniform cases, yet the behavior in pores with multiple sections can still be related to that of the uniform cases. All the distributions of hits in figure 4-5 (c) start at the point where the 50 nm uniform pore distribution starts, then follow a linear profile until the transition point, where they continue to follow the shape of the distribution for the 30 nm uniform case. In both cases, i.e., trajectories that reach the opposite end and those that return to the starting

end of the pore, it is still possible to tune the number of hits and their location in the pore.

The transmission probability can also be obtained from the simulations. Figure 4-6 presents the values of the forward transmission probability (entering through section 1 and exiting the pore through section 2) obtained for pores with $d_1=50$ nm and $d_2=30$ nm for different lengths of the sections and also for pores with $d_1=30$ nm and $d_2=50$ nm. For pores with $d_1=50$ nm and $d_2=30$ nm the transmission probability grows with increasing length of the first section, while for pores with $d_1=30$ nm and $d_2=50$ nm the transmission probability decreases with increasing length of the first section. The transmission probability in both series of pores approaches the value corresponding to a pore of uniform diameter d_1 and $L=1$ μm as L_1 is increased. From these results it is apparent that the transmission probability in pores of multiple sections is related to the transmission probabilities of the sections comprising the pore and to their arrangement. In the remainder of this section we show the development of analytical expressions to quantify this relation.

The transmission probability of a cylindrical pore, or pore section, of uniform diameter is a function of its aspect ratio, and it can be calculated analytically from equation 44 in the work of Clausing (1932), which we showed in chapter 3 to be in agreement with our Knudsen dynamics simulations of uniform pores. In pores with two sections, the transmission probability of the first section (ft_1) determines the fraction of particles entering the pore that will reach the junction between the two sections. The particles reaching the junction could then follow different routes before exiting through

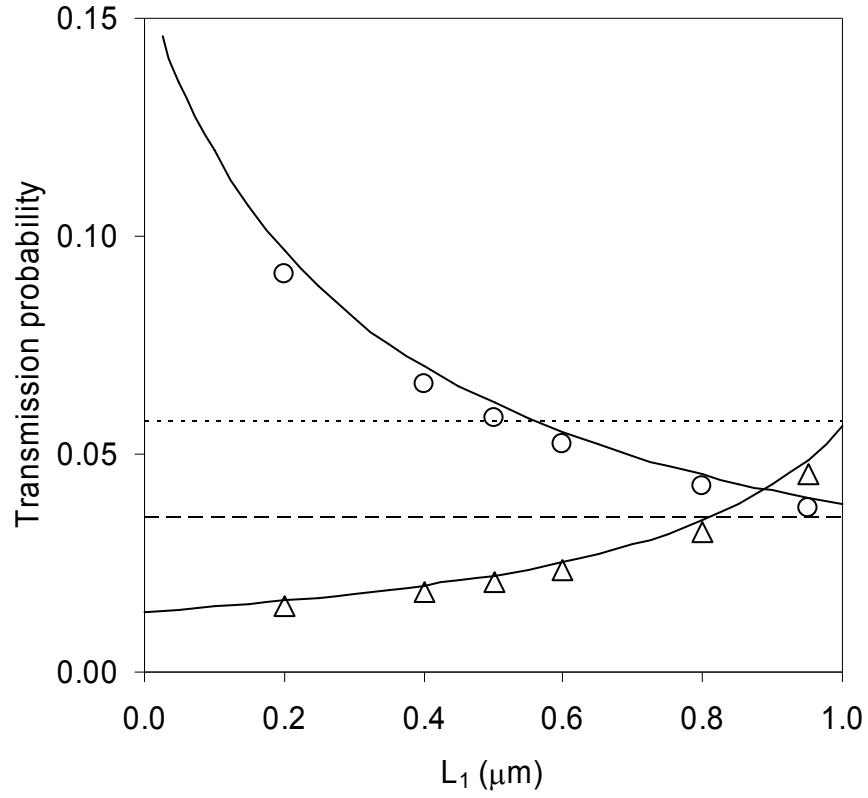


Figure 4-6: Transmission probability for pores with two sections and 1 μm total length as a function of the length of section 1: simulations for pores with diameters $d_1=50$ nm and $d_2=30$ nm (Δ), simulations for pores with diameters $d_1=30$ nm and $d_2=50$ nm ($\circ$), and calculated using equations (4-4) and (4-7) (—). The values for pores of uniform diameter 50 nm ($\cdots$) and 30 nm (---) are also shown.

one of the ends of the pore. For a pore with $d_2 > d_1$, we identify four possible routes to follow: 1) some particles will bounce back, reenter the first section and exit the pore through the starting end; 2) a fraction ft_2 of the particles at the junction will exit the pore through the opposite end; 3 and 4) some will follow routes 3a or 4a, as shown in figure 4-7, that will return them again to the junction where they will face the same options.

The probabilities of staying inside the pore by following routes 3a and 4a are:

$$p_{3a} = (1 - ft_{2F}) \left(1 - \frac{A_1}{A_2} \right) \quad (4-1)$$

$$p_{4a} = (1 - ft_{2F}) \frac{A_1}{A_2} (1 - ft_{1B}) \quad (4-2)$$

where A_1 and A_2 are the cross-sectional areas of sections 1 and 2, respectively. The subscripts F and B refer to “forward” and “backward” transmission probabilities. (In sections of uniform diameter $ft_F = ft_B$.) A particle could follow routes 3a and/or 4a several times before exiting the pore. The forward transmission probability for the two-section pore, given by the fraction of the particles that enter through section 1 and exit through section 2, can then be expressed as an infinite summation of terms:

$$ft_F = ft_{1F} \left(\sum_{i=0}^{\infty} \left[(1 - ft_{2F}) \left(1 - \frac{A_1}{A_2} \right) + (1 - ft_{2F}) \frac{A_1}{A_2} (1 - ft_{1B}) \right]^i \right) ft_{2F} \quad (4-3)$$

In this expression, the first term ft_{1F} accounts for the particles that reached the junction of the sections, the i term in the summation represents the fraction of particles that

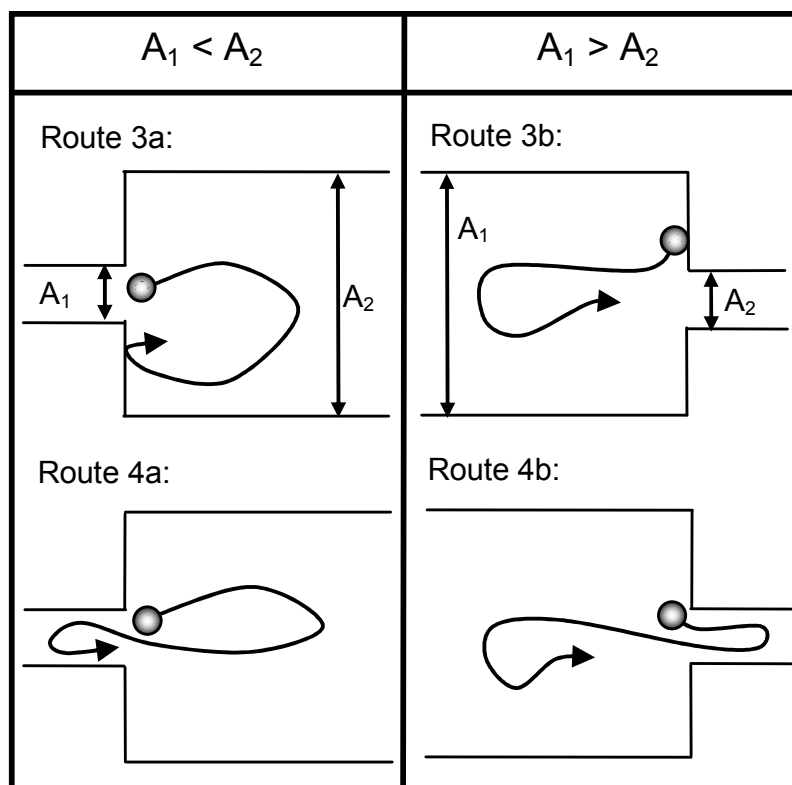


Figure 4-7: Routes followed by particles in two-section pores that start and end at the junction of the sections.

remain in the pore by returning to the junction after following i times routes 3a and/or 4a, and ft_{2F} accounts for the fraction of those particles that will leave the pore through section 2. Rearranging expression (4-3):

$$ft_F = ft_{1F} ft_{2F} \sum_{i=0}^{\infty} \left[(1 - ft_{2F}) \left(1 - \frac{A_1}{A_2} ft_{1B} \right) \right]^i \quad \text{when } A_1 < A_2 \quad (4-4)$$

A similar approach can be applied to pores with $d_1 > d_2$. In this case, the routes proposed to be followed by the particles are: 1) stay in the first section and exit the pore through the starting end; 2) a fraction $ft_2 * A_2/A_1$ of the particles at the junction will exit the pore through the opposite end; 3 and 4) follow routes 3b or 4b, as shown in figure 4-7, that will return them to the junction where they will face the same options. The probabilities of following routes 3b and 4b are:

$$p_{3b} = \left(1 - \frac{A_2}{A_1} \right) (1 - ft_{1B}) \quad (4-5)$$

$$p_{4b} = \frac{A_2}{A_1} (1 - ft_{2F}) (1 - ft_{1B}) \quad (4-6)$$

The transmission probability for the pore can then be expressed as:

$$ft_F = ft_{1F} ft_{2F} \frac{A_2}{A_1} \sum_{i=0}^{\infty} \left[(1 - ft_{1B}) \left(1 - \frac{A_2}{A_1} ft_{2F} \right) \right]^i \quad \text{when } A_1 > A_2 \quad (4-7)$$

Equations (4-4) and (4-7) are similar; the main difference is given by how the ratio of the areas influences the trajectories of the particles. These equations can be used to calculate the transmission probability knowing just the transmission probability of the sections and the ratio of their areas at their junction. Consequently, the expressions are applicable to pores of any geometry, not just cylindrical. In figure 4-6 the predictions

from equations (4-4) and (4-7) show excellent agreement with the results of the simulations. By comparing equations (4-4) and (4-7) and by looking at the results of the simulations in figure 4-6, it is evident that in pores with a change in diameter, the overall forward and backward transmission probabilities are different. This is not the case for pores of uniform diameter.

4.5 Transmission probability in pores of more than two sections

Pores with more than two sections of different diameters are also of interest, as they could offer further options to control the transmission probability and the number of hits with the wall.

Here we investigate the transmission probability for pores with three sections to illustrate how the methodology and results obtained for two-section pores can be expanded. Simulations were performed for five pores presenting a variety of shapes and diameter changes; the diameters and lengths of the sections are presented in table 4-2.

Analytical predictions for the transmission probabilities can also be obtained by expanding the application of equations (4-4) and (4-7). These expressions can be applied to two sections of the pore to obtain their combined transmission probability. These two adjacent sections can then be treated effectively as one section and be represented by their combined transmission probability. The equations can be reapplied as many times as needed, depending on the total number of sections, to obtain the total transmission probability of the pore. Figure 4-8 presents the

transmission probability obtained from simulations and from the application of equations (4-4) and (4-7) for the pores described in table 4-2. Excellent agreement is observed between both quantities in all five cases. It is interesting to compare the transmission probabilities for pores 4 and 5, as these two pores are composed of three sections of equal length and alternating diameters, starting with 40 nm (pore 4) or with 20 nm (pore 5). The results show that although the transmission probabilities of the independent sections are higher for pore 4 (which has two sections of $d=40$ nm, each having a higher transmission probability than sections with $d=20$ nm) the total transmission probability is lower than for pore 5. It is also worth noting that pores labeled 1 to 3 present different transmission probabilities even though they are composed using the same three sections (same pore diameter and length), the only difference being the order in which they are arranged. The results for these two sets of pores highlight that for pores of multiple sections both the transmission probability of the independent sections and the order in which these sections are arranged strongly influence the overall transmission probability.

4.6 Conclusions

Employing AAO and ALD to synthesize membranes allows fine control of the pore dimensions, and by adjusting the exposure time of the ALD reactants it is possible to construct pores with multiple sections of different diameters. The potential to control the residence time and the contact with the walls makes these membranes attractive for

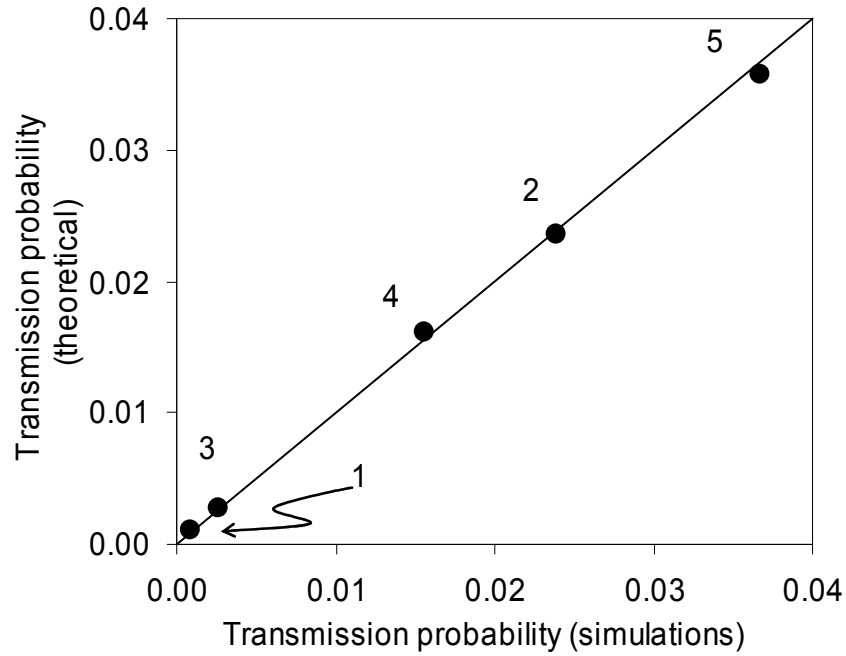


Figure 4-8: Theoretical and simulated transmission probabilities for pores of three sections. The numbers correspond to the pore configurations detailed in table 4-2. The line represents the line of parity ($x=y$).

Table 4-2: Diameters and lengths of the sections in simulated pores of three sections.

The transition angle is 45° in all cases.

Pore	$d_1(\text{nm})$	$L_1(\mu\text{m})$	$d_2(\text{nm})$	$L_2(\mu\text{m})$	$d_3(\text{nm})$	$L_3(\mu\text{m})$
1	50	0.20	30	0.30	10	0.50
2	10	0.50	50	0.20	30	0.30
3	30	0.30	10	0.50	50	0.20
4	40	0.30	20	0.30	40	0.30
5	20	0.30	40	0.30	20	0.30

catalytic applications. Under the conditions of interest for selective oxidation, atmospheric pressure and elevated temperature, Knudsen diffusion dominates mass transport inside the pores. Knudsen dynamics simulations performed in two-section pores showed that the angle of transition between the different diameters has little effect on the transmission probability and the distribution of hits on the wall, except when the transition angle is very small and the transition is extremely smooth. The distributions of hits inside pores of multiple sections for trajectories relevant in sweep-gas and pass-through operational modes present different profiles, and each of them can be related to the distributions in pores of uniform diameters. The number and location of the hits can be changed by altering the dimensions of the sections; this can be used to decide the best geometry and location of the catalyst to achieve better conversion and selectivity in a reacting system. The transmission probability in pores of multiple sections can be related to the transmission probabilities of the sections constituting the pore and to the ratio of the cross-sectional areas between sections. For this purpose, analytical expressions were derived and applied to pores of two and three sections. Their predictions agree well with the simulation results.

5 Designing nanostructured membranes for oxidative dehydrogenation of alkanes: A multiscale modeling approach

5.1 Introduction

The oxidative dehydrogenation (ODH) of alkanes is an attractive path to produce alkenes. The advantages of ODH include that it proceeds exothermically, it is carried out at lower temperatures than dehydrogenation, and side reactions such as the cracking of alkanes and coke formation that cause deactivation are reduced. Its main disadvantage is the difficulty in controlling the consecutive reactions to carbon oxides (Grabowski, 2006). Recently, new ultra-uniform, inorganic, nanostructured membranes have been used to carry out ODH of cyclohexane (Pellin et al., 2005; Stair et al., 2006). The results obtained in these studies show a higher conversion per gram of catalyst and an improved selectivity towards the desired products when compared to a conventional alumina powder catalyst at the same conversion. These membranes are built using a combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD). The electrochemical conditions in AAO can be adjusted to produce membranes with uniform cylindrical pores with diameters ranging from 20 to 400 nm and lengths between 0.5 and 250 μm (Stair et al., 2006). The pore diameter and wall composition can later be tailored using ALD by placing layers of oxides (e.g., Al_2O_3 , SiO_2 , TiO_2) along the full or partial length of the pore (Elam and George, 2003; Elam et al., 2003).

The ability to control the pore diameter and length of the membrane results in the possibility of controlling the residence times of particles inside the pores. We have previously studied the mass transport in these nanostructured membranes, as well as the contact between the particles traveling through them and the pore walls (Albo et al., 2006, 2007). We found that in pores of up to 50 nm in diameter at the conditions of interest for selective oxidation, 700 K and atmospheric pressure, Knudsen diffusion strongly dominates mass transport inside the pores. Under these conditions, the transmission probability and number of hits between the particle and pores can be related to the aspect ratio of the pore length to the pore diameter (L/d).

ALD can be used not only to tailor the pore diameter, but also to place the catalyst inside the pore. The exposure time to the ALD reactants can be controlled to achieve full or partial catalyst coverage along the length of the pore (Elam et al., 2003). Thus, the location of the catalyst becomes an additional parameter, together with the pore dimensions and operational mode, that could be altered to improve the yield of the desired product. The literature contains many studies that have focused on the effects of creating a non-uniform distribution of a catalytic material inside porous supports. For example, Varma, Morbidelli and coworkers studied a variety of systems under different conditions and recommended the optimal distribution of the catalyst for each case (Morbidelli et al., 2001). However, most of these studies were concentrated on placing the catalyst inside pellets and only a small number of cases dealt with the optimal distribution of the catalyst in reactive membranes. In addition, the series of investigations did not focus on the Knudsen diffusion regime or consider operational

modes different from the sweep-gas mode in membrane reactors. Thus, it is still germane to investigate the possibilities offered by the combination of AAO and ALD.

In this work, a combination of continuum-level modeling and Knudsen dynamics simulations was used to explore the effect of the pore dimensions, catalyst location and operational mode on a network of series-parallel reactions representing a selective oxidation system in AAO/ALD membranes. Two operational modes were studied for pores with uniform catalyst coverage: pass-through and sweep-gas. In the sweep-gas mode, a sweep gas flows perpendicular to the pores of the membrane on the retentate and permeate ends of the pores. Reactant molecules from the retentate side may diffuse into the membrane and are swept away when they exit the membrane through either end. In the pass-through mode, all gas in the upstream reservoir is forced through the membrane, and particles are removed only when they reach the downstream end of the pores.

With the results for the case of uniform catalyst coverage established, different configurations for the catalyst coverage were explored for the pass-through mode, ranging from uniform coverage to an extreme of only a few catalytically active sites located inside each pore. The overall objective was to identify trends that help rationalize improvements in conversion and selectivity that are observed experimentally in the membranes, and also to identify interesting configurations for future experimental efforts.

In the next section, the kinetics and the reaction network used in the models and simulations are introduced. Then, the continuum model and the Knudsen dynamics

simulations are presented. Next, the results for pores with full catalyst coverage are discussed, the different operational modes are compared, and sensitivity analysis of the rate constants is described. Finally, results for pores with different degrees of partial coverage of catalyst are presented.

5.2 Kinetics and reaction network

The ODH of alkanes has been the subject of a large number of studies. Grabowski (2006) recently reviewed the proposed mechanisms and kinetic models for the ODH of ethane, propane and butane. Although some aspects of the mechanism and of the kinetic model depend on the specific choice of alkane and catalyst, ODH is generally described using a parallel-series reaction network, depicted in figure 5-1 for ethane. This network includes the formation of the alkene and water and the subsequent oxidation of the alkene to carbon oxides, as well as the direct formation of carbon oxides from the alkane. The majority of the CO_x is formed from the alkene and only a small amount comes from the direct oxidation of alkane (Grabowski, 2006).

The most frequently used mechanism to describe ODH reactions of light alkanes is Mars-van Krevelen (Grabowski, 2006), which assumes that the oxygen for the reaction comes from the lattice of the catalyst and the reduced catalyst is then reoxidized by gas-phase oxygen. In all the models reviewed by Grabowski, the reaction order with respect to hydrocarbon (both alkane and alkene) was equal to one, and the reaction order with respect to gas-phase oxygen was less than or equal to 0.5.

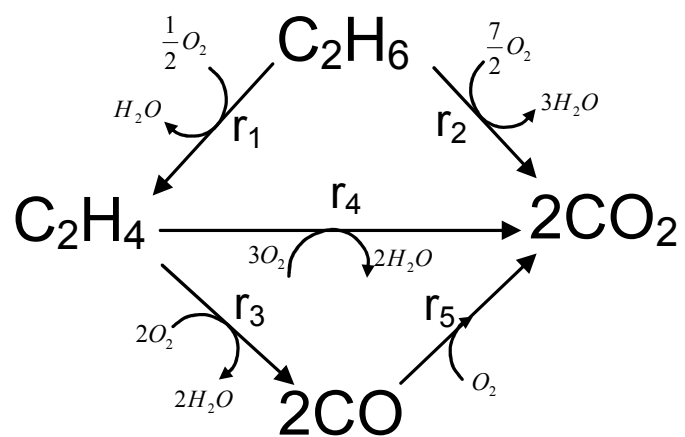


Figure 5-1: Reaction network for the ODH of ethane. Adapted from Tota et al. (2004).

In the present work, we selected ODH of ethane as presented in figure 5-1 at a temperature of 700 K as a representative system. The rate constants and reaction orders were chosen to match the general features of an ODH system. Thus, the observed trends should be extensible to other systems. All the reactions were considered to be first order with respect to alkane, alkene or carbon monoxide and zero order with respect to oxygen. The relationships between the rate constants were $k_2/k_1 = 0.1$; $k_3/k_1 = 0.5$; $k_4/k_1 = 1$; $k_5/k_1 = 0.5$. These reflect that most of the CO_x is formed from the alkene, and also that the alkene is more reactive than the alkane at the temperature selected (Grabowski, 2006). The range of values of k_1 studied was between 10^{-5} and $10^1 \text{ m}^3_{\text{pore_volume}} / (\text{m}^2_{\text{pore_area}} \cdot \text{s})$.

5.3 Model and simulation details

5.3.1 Continuum model

In the classical approach to reaction-diffusion systems, the mass balance is combined with the expression for the diffusive flux and with the reaction rates (Rawlings and Ekerdt, 2002). If the system is isothermal and the ideal-gas law can be used to substitute partial pressures for the concentrations, the resulting expression for component j is:

$$\frac{dp_j}{dt} = \frac{-D_j}{L^2} \frac{d^2 p_j}{dz^2} - RT \sum_{i=1}^{N_{\text{reactions}}} \nu_{j,i} k'_i \prod_m^{N_{\text{components}}} \left(\frac{p_m}{RT} \right)^{\alpha_{m,i}} \quad (5-1)$$

where p_j is the partial pressure of component j , t is the time, z is the non-dimensional axial position, L is the length of the pore, R is the gas constant, T is the absolute

temperature, $v_{j,i}$ is the stoichiometric coefficient of component j in reaction i , k_i' is the rate constant for reaction i in units of inverse time ($k_i' = k_i \cdot \text{pore area/pore volume}$), $\alpha_{m,i}$ is the reaction order of component m in reaction i , and D_j is the diffusivity of component j . In our case the diffusivity is the Knudsen diffusivity, which in cylindrical pores is equal to (Knudsen, 1909):

$$D_{K,j} = \frac{d}{3} \sqrt{\frac{8RT}{\pi m_j}} \quad (5-2)$$

where d is the diameter of the pore and m_j is the molecular weight of the diffusing molecule. When solving equation (5-1) it is common to introduce the Thiele modulus, a non-dimensional parameter, which for a reactant j involved only in first order reactions can be written as:

$$\phi_j = L \sqrt{\frac{\sum_{i, v_{j,i} \neq 0} k_i'}{D_j}} \quad (5-3)$$

This can be interpreted as the ratio between the reaction and diffusion rates and will be the only parameter affecting the non-dimensional concentration profile inside the pore. If ϕ is large, then the system has a fast rate of reaction in comparison with diffusion, and diffusion is rate limiting. If ϕ is low, then the opposite is true, and the system is kinetically controlled.

To model the ODH of ethane, a system of differential equations, each of the form of equation (5-1) with one equation for each species shown in figure 5-1, and also for oxygen and water (not shown), was solved. It was necessary to establish the boundary

conditions to solve the model. These depend on the operational mode employed. Figure 5-2 presents a general scheme for the operation of the membrane. The pass-through and the sweep-gas modes studied here are two limiting cases of the generalized operation. In the pass-through mode, the flow rate of stream 2 is equal to zero; therefore, all of the feed must pass through the membrane. Since Knudsen diffusion dominates the mass transport in the system, this means that the particles will have to re-enter the pores in the membrane several times, as defined by the transmission probability, before they are able to reach the downstream end. The boundary conditions for this case are:

$$\begin{aligned}
 \text{Reactants: } & \begin{cases} t < 0 & p_j = 0 & 0 \leq z \leq 1 \\ t \geq 0 & p_j|_{z=0} = p_j^o & p_j|_{z=1} = 0 \end{cases} \\
 \text{Products: } & \begin{cases} t < 0 & p_j = 0 & 0 \leq z \leq 1 \\ t \geq 0 & \left. \frac{dp_j}{dz} \right|_{z=0} = 0 & p_j|_{z=1} = 0 \end{cases}
 \end{aligned} \tag{5-4}$$

where p_j^o is the known pressure of the reactants on the upstream side of the membrane.

In the other limiting case, the sweep-gas mode, particles only have one chance to enter the membrane before they are swept away. Therefore, the fraction of the feed recovered downstream will be directly determined by the transmission probability of the

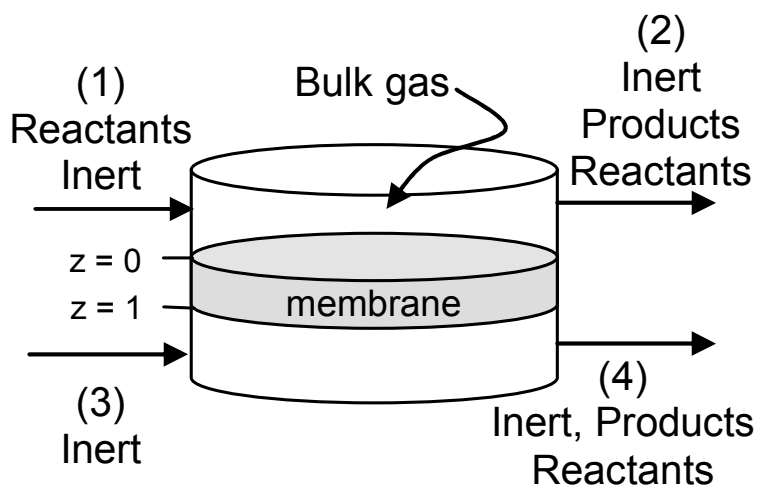


Figure 5-2: Generalized schematic for the setup of the membrane reactor. The flow rates of streams 1 and 2, together with the volume at the entrance of the membrane, determine the fraction of the feed that must travel through the membrane. The pass-through mode is a limiting case in which F_2 is zero. The sweep-gas mode is a second limiting case in which the ratio of F_2 to F_1 is dictated by the transmission probability.

membrane. The boundary conditions in this case are:

$$\begin{aligned} \text{Reactants: } & \begin{cases} t < 0 & p_j = 0 & 0 \leq z \leq 1 \\ t \geq 0 & p_j|_{z=0} = p_j^o & p_j|_{z=1} = 0 \end{cases} \\ \text{Products: } & \begin{cases} t < 0 & p_j = 0 & 0 \leq z \leq 1 \\ t \geq 0 & p_j|_{z=0} = 0 & p_j|_{z=1} = 0 \end{cases} \end{aligned} \quad (5-5)$$

Operating in either of these modes, or in an intermediate mode, where only a fraction of the feed is forced through the membrane, will potentially result in different conversion, selectivities and yields.

5.3.2 Knudsen dynamics simulations

At the conditions of interest, Knudsen diffusion dominates mass transport inside pores of less than 50 nm in diameter (Albo et al., 2006). Performing Knudsen dynamics simulations specifically for this regime will provide a greater level of detail and understanding than the continuum model. The movement of the particles in the simulations is based on the two main assumptions of Knudsen diffusion: first, that there are no interactions or collisions between particles and second, that particles collide diffusively with the pore walls. In our simulations, the trajectories of an ensemble of particles inside the pore are followed simultaneously. In the previous chapters, we have used Knudsen dynamics simulations without reaction to study the transmission probability and the number and distribution of hits between the particles and the wall in cylindrical pores of uniform diameter (Albo et al., 2006) and in cylindrical pores of

variable diameter (Albo et al., 2007). In this chapter, we add the possibility that particles that hit the wall will react. Other researchers have performed simulations for Knudsen diffusion but considering one particle at a time for pores of different shapes (Davis, 1960; Evans et al., 1980; Nakano et al., 1985; 1987), roughness (Malek and Coppens, 2001, 2002, 2003) and with diffusion-limited reactions (Coppens and Malek, 2003).

A step of the reactive simulation consists of comparing the times to reach the wall of all the particles in the system, determining the shortest time and then advancing all trajectories by it. The particle that reaches the wall will either bounce diffusively or react. The reactions are considered to occur following a Mars-van Krevelen mechanism where the hydrocarbons react with the lattice oxygen. The oxidation of the reduced catalyst has not been included in the model, as an excess of oxygen inside the pore is assumed. The transformation of the reactant into the product(s) is considered to occur instantaneously, after which the product leaves the wall. The probability of reaction, c , of the particle that reaches the wall can be related to the reaction rate constant used in continuum models (Coppens and Malek, 2003):

$$c = \frac{\text{Formation of products}}{\text{Incidence of reactants}} = \frac{k \left(\frac{p_j}{RT} \right)}{\frac{p_j}{\sqrt{2\pi mRT}}} = \frac{4k}{u} \quad (5-6)$$

where k is the reaction rate constant in $\text{m}^3_{\text{pore_volume}} / (\text{m}^2_{\text{pore_area}} \cdot \text{s})$ and u is the average molecular speed of the reactant. In the simulations, when a particle reaches the wall, a random number is generated and compared with the reaction probability to decide if the reaction occurs. If no reaction occurs, the particle colliding with the wall is assigned a

new direction defined by polar and azimuthal angles drawn from a cosine distribution (Greenwood, 2002). If a reaction occurs, then the product molecule(s) receives a new direction drawn from the cosine distribution. All particles maintain the average speed of their species, calculated from kinetic theory.

At the extremes of the pores, two reservoirs are maintained according to the specified boundary conditions. For a pass-through simulation, at the upstream side the pressure of the reactant is maintained constant. The molecules of the products that reach this reservoir are not deleted. Instead they are allowed to re-enter the pore until they travel to the downstream end. At the downstream side all particles exiting the pore are deleted. For the sweep-gas case, at the upstream side the pressure of the reactant is maintained constant, and the molecules of the products that reach this reservoir are deleted. At the downstream side, all particles exiting the pore are deleted. The conditions in the reservoirs are maintained by frequently stopping the simulation to perform the necessary insertions and deletions of particles in each reservoir until the specified pressures are achieved.

The simulations are started by filling the transport section of the pore with a linear pressure (concentration) profile of the reactant between the reservoirs. The simulation is considered to achieve steady state when the fluxes at the ends of the pore are steady. These fluxes are used to calculate the conversion and selectivities. All the simulations are performed at 700 K maintaining an ethane pressure equal to 0.40 atm in the high pressure reservoir and 0 atm in the low pressure reservoir. The pores simulated have diameters between 10 and 50 nm and total lengths equal to 1 μm . The

length of the reservoirs in all simulations was equal to 0.30 μm . The production time in the simulations was 10000 ns, with the reservoirs being replenished every 0.01 ns.

5.4 Results

5.4.1 Uniform catalyst coverage

Pores with uniform catalyst coverage on the walls were studied to determine the effect of the rate constant (k_1) and of the pore aspect ratio (L/d) on the ethane conversion and on the selectivity to ethylene. The influence of the pore length and rate constant is observed directly in equation (5-1), while the pore diameter will affect the Knudsen diffusivity as shown in equation (5-2). The reaction network and the relation of the other rate constants to k_1 as presented in the section on the kinetics and reaction network were used. Both the pass-through and the sweep-gas configurations were considered, and results from both the continuum model and the Knudsen dynamics simulation were obtained.

Figure 5-3 presents the continuum model results for the ethane conversion, the selectivity to ethylene and the yield of ethylene as a function of the Thiele modulus of ethane $\phi = (L^2(k'_1 + k'_2)/D_{\text{ethane}})^{0.5}$ for pores operated in the pass-through mode. Conversion is calculated using the flow rate of ethane into the membrane on the upstream side and its flow out on the downstream side. Selectivity is defined here as the ratio of the moles of ethylene leaving the pore to the moles of ethane that reacted, and the yield is defined as the number of moles of ethylene obtained per mole of ethane in the feed. It can be observed that conversion grows and selectivity decreases sharply

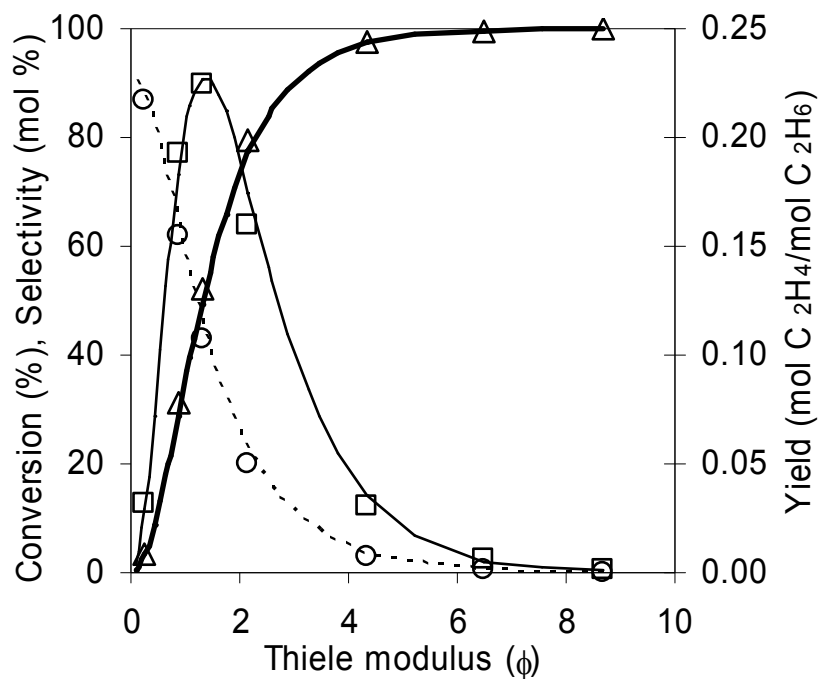


Figure 5-3: Ethane conversion and selectivity and yield to ethylene in pass-through mode for pores with uniform catalyst coverage as a function of the Thiele modulus of ethane. Lines correspond to the continuum model result for conversion (—), selectivity (---) and yield (—). Symbols correspond to Knudsen dynamics simulation values for conversion (Δ), selectivity ($\circ$) and yield ($\square$).

with the Thiele modulus up to a value close to 4, where nearly 100 % conversion and 0 % selectivity are reached. Since the objective is to maximize the production of the intermediate product ethylene, it is useful to look at its yield, which reaches a maximum near $\phi=1.5$. The pore dimensions to achieve this Thiele modulus, and as a consequence, to maximize the desired product, will depend on the actual value of k_1 . The optimum Thiele modulus found is specific for the reaction network and kinetics employed, but the solution method can be applied to other cases in a straightforward manner.

To investigate the effect of different kinetics, a simple sensitivity analysis of conversion and selectivity as a function of the relationships of the rate constants to k_1 was performed. Table 5-1 presents the four additional sets of rate constants employed in the sensitivity analysis. Two features are important to note: first, the value of k_5 was not altered, as it does not affect either the conversion or the selectivity, and second, k_3 and k_4 are grouped together since their combined effect is the relevant one. The resulting selectivities and conversions are presented in figure 5-4, where it can be observed that conversion maintains the same dependence on the Thiele modulus for all sets of parameters. On the other hand, the dependence of the selectivity on the Thiele modulus does depend on the rate constants. Higher values of k_2/k_1 (sets 1 and 4), which controls the selectivity of the ethane reactions, translate into lower maximum selectivities (achieved at very low conversions). For all sets of parameters, the selectivity decreases as the Thiele modulus increases until it reaches a value of zero. This decrease is faster with higher values of k_3+k_4 , as this value represents a faster

Table 5-1: Sets of parameters used in the sensitivity analysis (reactions labeled according to figure 5-1).

Rates	Base set	set 1	set 2	set 3	set 4
k_2/k_1	0.10	0.50	0.10	0.10	0.50
$(k_3+k_4)/k_1$	1.50	1.50	0.50	2.50	2.50
k_5/k_1	0.50	0.50	0.50	0.50	0.50

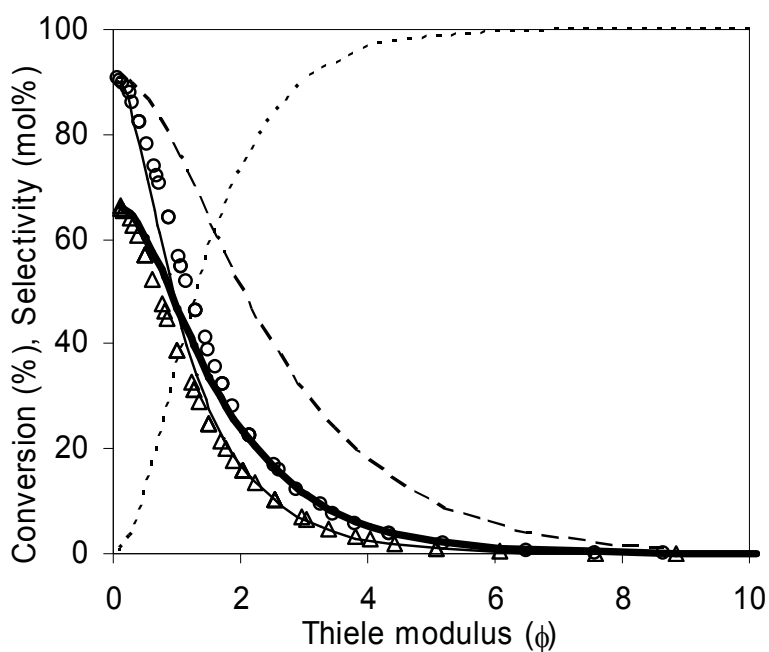


Figure 5-4: Sensitivity analysis: Conversion of ethane for all sets of parameters (···) and selectivity to ethylene for base set (○), set 1 (—), set 2 (---), set 3 (—) and set 4 (Δ) as a function of the Thiele modulus of ethane. All results were obtained from the continuum model.

consumption of the desired product. In general, different absolute values of the rate constants will not affect how the conversion depends on the Thiele modulus and the trends in the selectivity will be qualitatively similar.

In the other limiting operational mode, the sweep-gas mode, conversion is calculated using the difference between the number of particles entering and leaving the pore on both ends of the pore per unit of time and area, similar to the calculation done by Coppens and Malek (2003). Pores with the same Thiele modulus yield the same non-dimensional profile of concentration with axial position; however, the conversion in the pores depends on k_I . For a given k_I , the conversion increases sharply with the Thiele modulus up to a value close to 4, where it reaches its maximum, as shown in figure 5-5. The selectivity gives the opposite trend, decreasing up to $\phi=4$, where it stabilizes at around 40 %. The value of the maximum conversion increases with k_I , so if the reactions are slow, conversion for this operational mode will be too low for any practical application, but the sweep-gas mode could be viable for faster reactions. This is more clearly observed in figure 5-6, which presents the yield of ethylene in the sweep-gas mode for different values of k_I together with the yield in the pass-through mode. The yield in the sweep-gas mode at any given ϕ increases with k_I , as a consequence of the higher conversion achieved. At a constant k_I , for larger ϕ the yield is constant, indicating that the reactions are taking place mostly at the entrance of the pore. For the reaction network and kinetics studied, the pass-through mode allows the maximum yield to be achieved, and the sweep-gas mode becomes attractive only for very fast reactions.

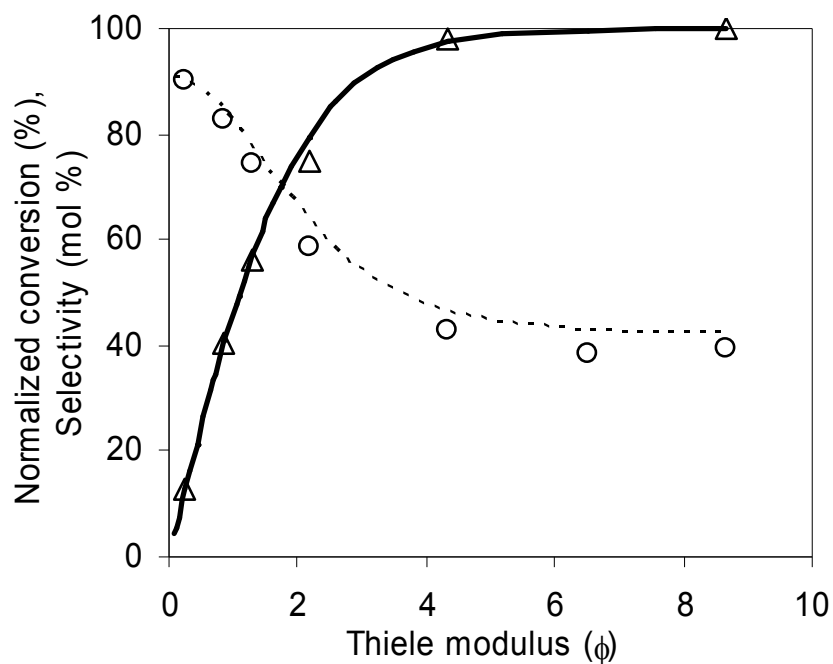


Figure 5-5: Ethane conversion normalized by the maximum conversion achievable for a given value of k_l and selectivity to ethylene in sweep-gas mode for pores with uniform catalyst coverage. Lines correspond to the continuum model result for conversion (—) and selectivity (---). Symbols correspond to Knudsen dynamics simulation values for conversion (Δ) and selectivity ($\circ$).

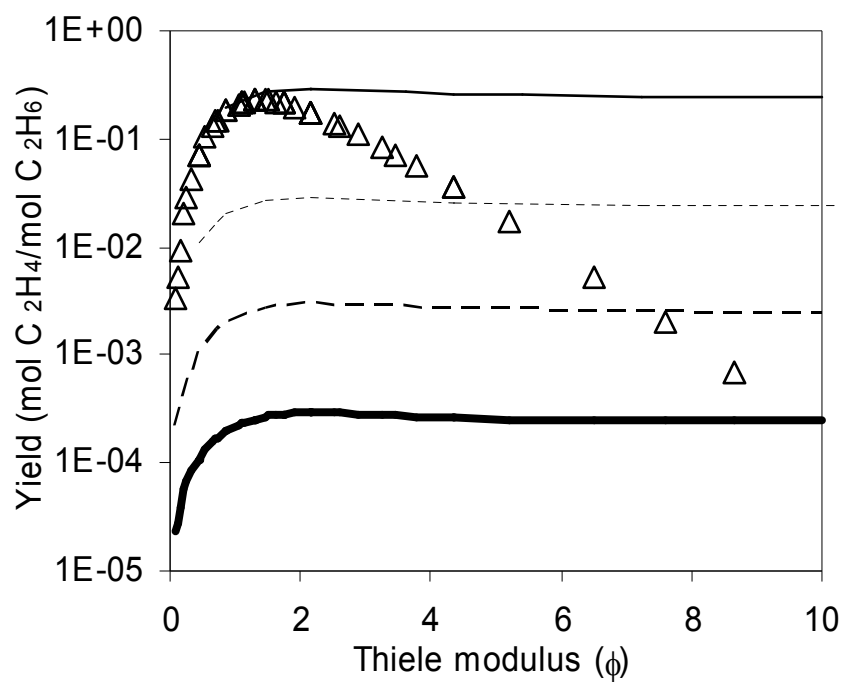


Figure 5-6: Ethane yield to ethylene as a function of the Thiele modulus of ethane in the sweep-gas mode for $k_l=10^{-5} \text{ m}^3/(\text{m}^2\cdot\text{s})$ (—), $10^{-3} \text{ m}^3/(\text{m}^2\cdot\text{s})$ (---), $10^{-1} \text{ m}^3/(\text{m}^2\cdot\text{s})$ (···), $10^1 \text{ m}^3/(\text{m}^2\cdot\text{s})$ (—). The yield in the pass-through mode (Δ) is shown for comparison. All results were obtained from the continuum model.

Knudsen dynamics simulations were also performed in pores with uniform catalyst coverage. The results are in good agreement with those from the continuum model, as can be observed in figures 5-3 and 5-5. From these simulations, it is also possible to obtain the positions where the reaction events take place for each species. As an example, the profiles for the reaction events in pass-through and sweep-gas modes in pores of $\phi = 2.16$ are presented in figure 5-7 (a) and (b). In both cases, the locations of the reaction events follow the concentration profiles (not shown). In the sweep-gas mode, the products react more towards the center of the pore length, while ethane concentrates most of its reaction events near the entrance of the pore. In the pass-through mode, all species follow a similar trend with the maximum number of reaction events at the entrance of the pore. These profiles will depend on the Thiele modulus. As its value increases, the number of reaction events will concentrate more towards the entrance of the pore for both operational modes.

The pass-through and sweep-gas modes are the limiting cases in the setup presented in figure 5-2. It is possible to regulate the flow rates of streams 1 and 2 to achieve intermediate operational cases. In these, part of the feed is required to go through the membrane and part of it will be removed after it has entered the pores several times but has not reached the opposite end. Depending on the specific reaction network and kinetics under study, these intermediate operational modes could also offer alternatives to maximize the yield of the desired product.

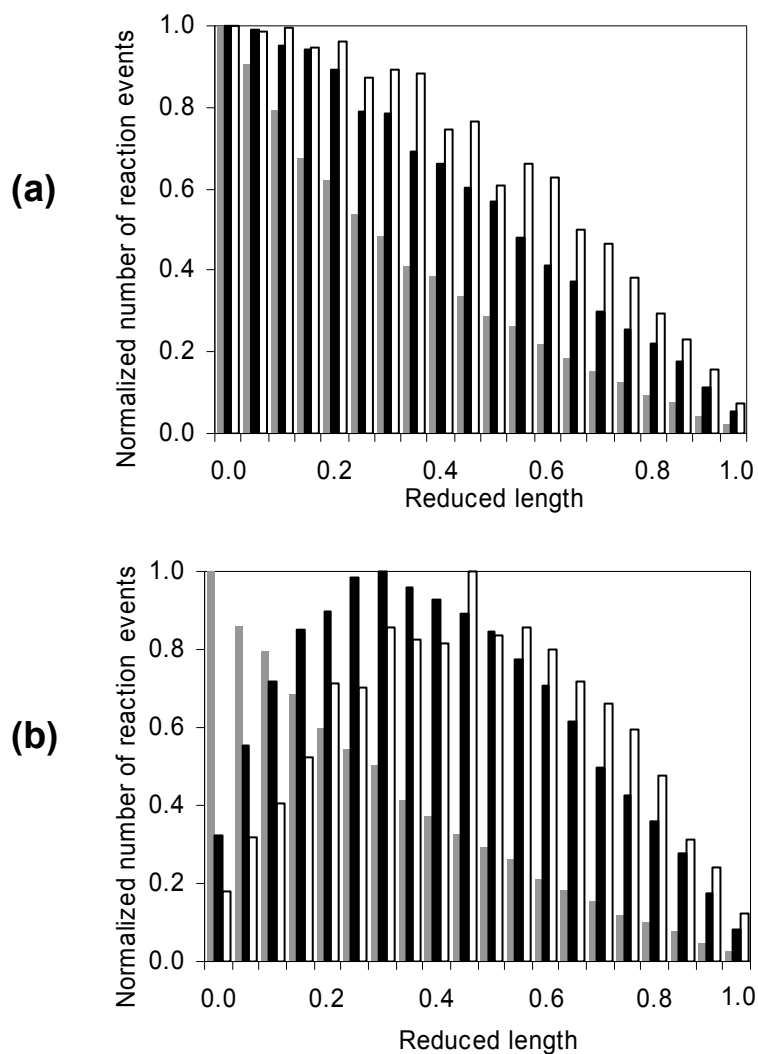


Figure 5-7: Normalized number of reaction events for ethane (grey), ethylene (black) and CO (white) in a pore of $\phi=2.16$ under (a) pass-through and (b) sweep-gas mode as a function of reduced pore length. The pore is divided in 20 sections of equal length and the reaction events are normalized by the maximum number for all sections.

5.4.2 Partial catalyst coverage

ALD can be employed to achieve partial catalyst coverage along the length of the pore (Elam et al., 2003). This option is explored here in pores operating in the pass-through mode. Previous studies related to finding the optimal distribution of the catalyst in pores have been performed under the constraint of distributing a fixed total amount of active material inside porous supports. The general results for pellets point to a Dirac delta function to position the active material at a specific radial position in the pellet (Morbidelli et al., 1982; Gavriilidis et al., 1993). In membranes operating in the sweep-gas mode, for reaction rates that increase with the reactant concentration, it was found that the optimal catalyst distribution corresponds to a Dirac delta function located at the upstream end of the membrane (Morbidelli et al., 2001). The profile of reaction events shown in figure 5-7(b) qualitatively agrees with this result, as it shows the reaction events of ethane peaking towards the upstream end of the pore and those of ethylene peaking towards the center of the pore.

Here we assume that the catalyst placed using ALD will maintain a constant activity per area. Therefore, covering the pore partially will employ less active material than fully covering it. The conversion and selectivity were evaluated for the partial placement of the catalyst in different sections of the pore in the pass-through mode.

Pores with catalyst covering only one third of their area were studied. The catalyst was placed at the entrance, center or end of the pore, as well as in 17 rings of equal area spaced at regular intervals inside the pore. Schematics of these different coverages are presented in figure 5-8 (a) to (d). The pores were solved using the continuum model, which was discretized in space and time. Since the reactions are all first order, a linear system of equations was obtained and solved until the steady state was reached. The resulting conversion and selectivity for each type of coverage as a function of the Thiele modulus are presented in figure 5-9 (a). It is noticeable that at a given value of the Thiele modulus, the lowest conversion invariably corresponds to the case where the catalyst is positioned at the end of the pore, followed by the pores having the catalyst at its center and spaced using several rings, then the pore with the catalyst at its entrance, and lastly the highest conversion is for the pore fully covered by catalyst. These results can be qualitatively explained by examining figure 5-7 (a), where the number of ethane reaction events decreases as the distance from the pore entrance increases. Therefore, a catalyst placed at the entrance of the pore will be in contact more frequently with ethane molecules, allowing for a higher conversion than the catalyst located at the center, which is in turn higher than that for catalyst at the end. The catalyst spaced throughout the pore averages the different sections and presents an intermediate conversion value close to that of the catalyst located at the center of the pore.

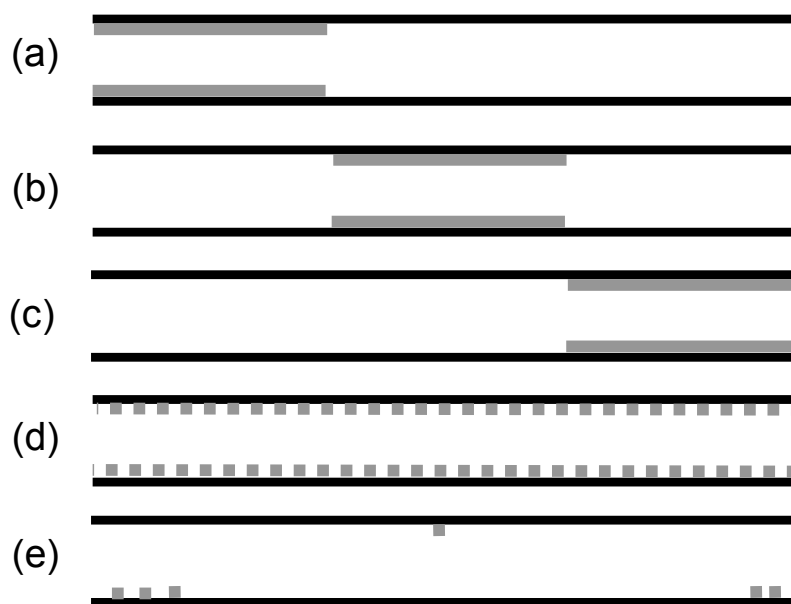


Figure 5-8: Pores with partial catalyst coverage: (a) 1/3 of the area at the entrance of the pore; (b) 1/3 of the area at the center of the pore; (c) 1/3 of the area at the end of the pore; (d) 1/3 of the area using 17 rings uniformly spaced throughout the pore; (e) patches of catalyst at the entrance, center and/or end of the pore.

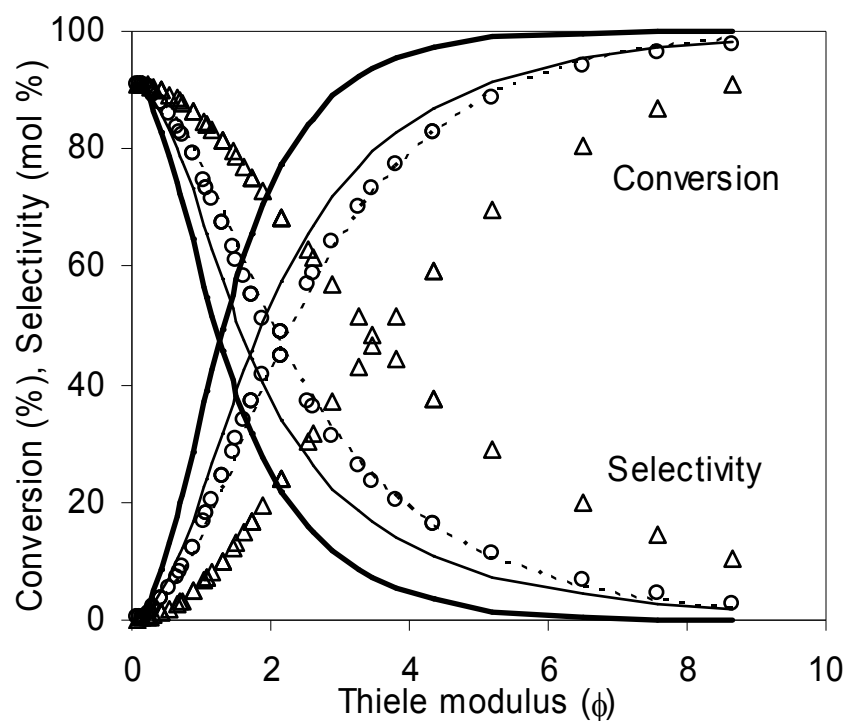


Figure 5-9 (a): Conversion of ethane and selectivity to ethylene in pores with catalyst coverage on 1/3 of the area as a function of the Thiele modulus and (b) as a function of the Thiele modulus multiplied by the fraction of the pore that is covered by catalyst. Results are shown for the catalyst located at the entrance of the pore (—); center of the pore (○); end of the pore (△); and 17 rings uniformly spaced throughout the pore (⋯).

Pores fully covered (—) are presented for comparison.

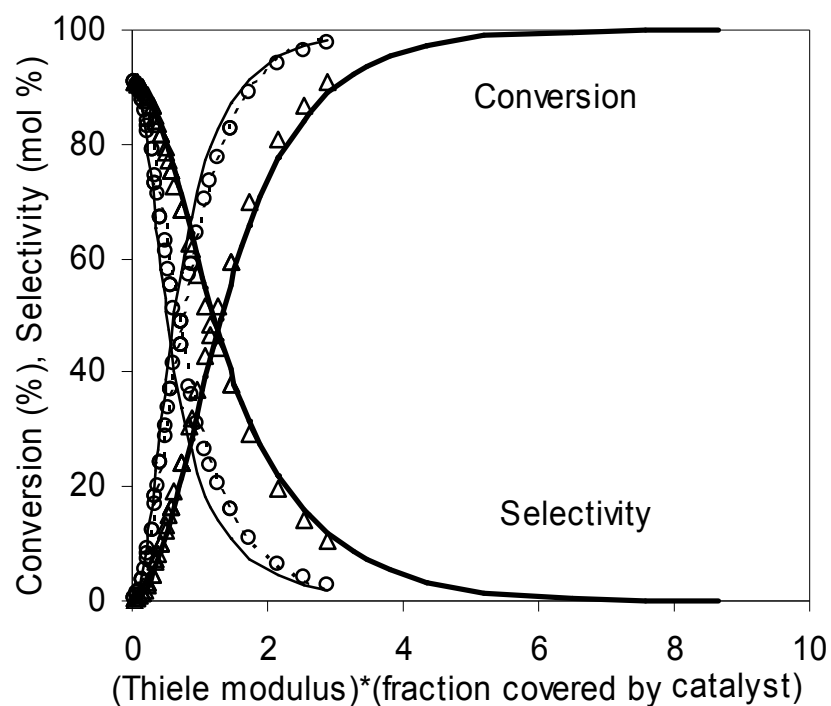


Figure 5-9 (b): Conversion of ethane and selectivity to ethylene in pores with catalyst coverage on 1/3 of the area as a function of the Thiele modulus multiplied by the fraction of the pore that is covered by catalyst. Results are shown for the catalyst located at the entrance of the pore (—); center of the pore (○); end of the pore (Δ); and 17 rings uniformly spaced throughout the pore (⋯). Pores fully covered (—) are presented for comparison.

The fully covered pore still gives a higher conversion than any of the other cases. However, this is misleading since it also contains a higher amount of catalytic material. A fairer comparison, which also accounts for the amount of catalyst in each pore, is presented in figure 5-9 (b). From this figure, it can be extracted that a higher conversion per amount of catalyst is achieved by its placement at the entrance of the pore, followed closely by locating it at the center or spaced throughout the pore. The lowest conversion per amount of catalyst is obtained for the catalyst location at the end of the pore and for the case of full coverage. This result is a consequence of particles having to re-enter the pore many times before they reach the downstream end. Therefore, they spend more time in the areas closer to the entrance and less time in the areas closer to the downstream end of the pore.

The effect on the selectivity of placing the catalyst only partially on the surface of the pore is more clearly observed in a plot of selectivity versus conversion, as shown in figure 5-10. In this figure, it is not possible to discern any significant differences due to the choice of catalyst location, with the exception of a slightly lower selectivity for a given conversion when the catalyst is located at the entrance of the pore. The inability to alter the selectivity for a given conversion by choosing the location of the catalyst in the pore can be related to the similar shapes of the distributions of the reaction events of ethane and ethylene, as presented in figure 5-7 (a).

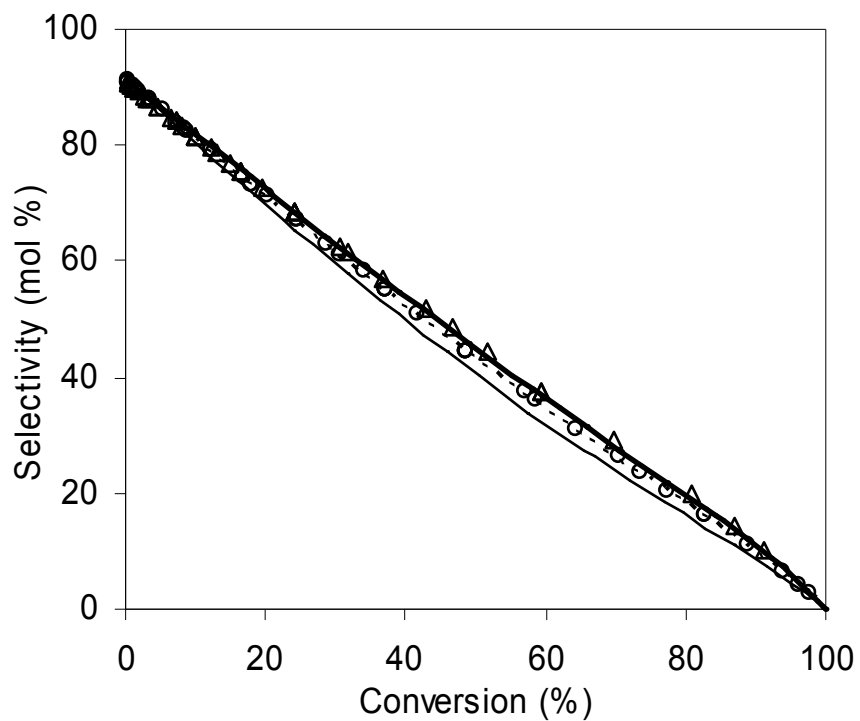


Figure 5-10: Selectivity of ethylene as a function of conversion of ethane in pores with catalyst coverage on 1/3 of the area for the catalyst located at the entrance of the pore (—); center of the pore (○); end of the pore (Δ); and using a number of rings uniformly spaced throughout the pore (···). Pores fully covered (—) are presented for comparison.

5.4.3 Isolated catalyst particles

The notion of designing a reaction pore by placing the catalyst only in specific sections, in an attempt to maximize its use and to improve the selectivity and conversion, can be extended to include the idea of placing just small patches of catalyst or small catalyst particles inside each pore, as presented schematically in figure 5-8 (e). However, even in the case of very fast reactions on the catalyst, it is not clear if just a few active catalyst particles will be enough to achieve relevant conversions for practical applications. To explore this idea, Knudsen dynamics simulations were employed, since the continuum model breaks down due to its inability to handle the scales involved.

The Knudsen dynamics simulations were performed in a pore of $d=10$ nm and $L=1$ μm . The active particles were considered to have an area equal to 1 nm^2 , with rate constants between 0.87 and $8.7\text{ m}^3/(\text{m}^2\cdot\text{s})$, giving a probability of reaction of ethane between 0.05 and 0.5 for each hit on the active particles. Several simulations were performed with between 1 and 10 catalyst particles inside the pore. The simulations can be grouped into four categories according to the location of the catalyst: entrance, center, end and spaced throughout the pore. Figure 5-11 presents the selectivities and conversions that were obtained.

From these results, it is clear that good conversion values can be achieved by having very active particles that cover only a small fraction of the surface of the pore. However, as observed for the cases of partial coverage of the pore in figure 5-10, there

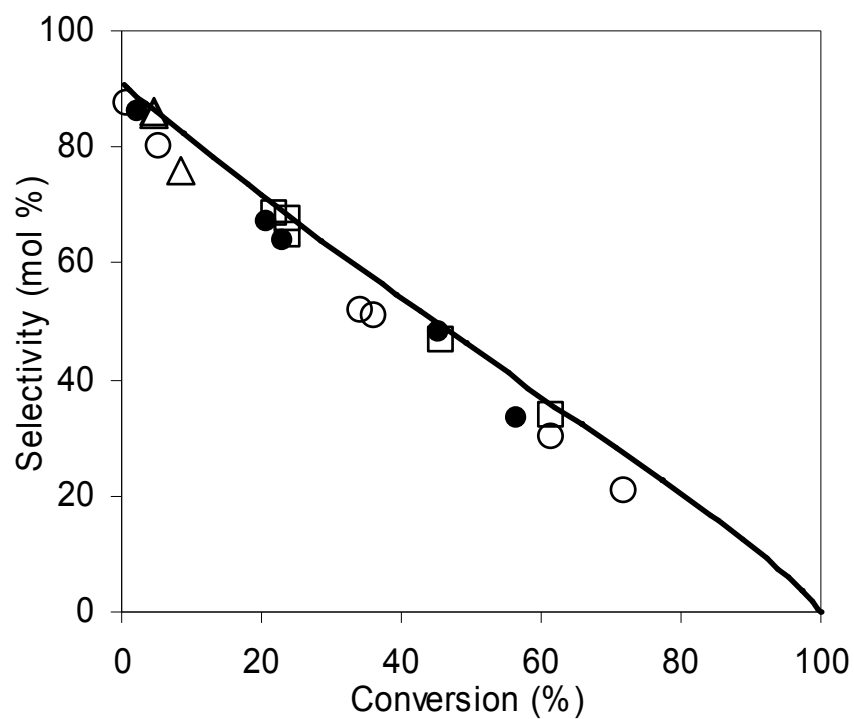


Figure 5-11: Selectivity as a function of conversion in pores with patches of catalyst located at the entrance of the pore (○); center of the pore (●); end of the pore (△); and equally spaced throughout the pore (□). Pores fully covered in catalyst (—) are presented for comparison.

is no selectivity improvement for a given conversion over the case of full catalyst coverage, and in fact slightly lower selectivities are achieved.

5.5 Conclusions

The combination of AAO and ALD to synthesize membranes allows fine control of the pore dimensions and the possibility to cover the pore walls fully or partially with the catalyst. Using the ODH of ethane as a representative system, we employed a continuum-level model and Knudsen dynamics simulations to investigate different operational modes, including the pass-through and the sweep-gas modes. In the pass-through mode, since particles are forced to travel through the pore it is possible to achieve any desired value of conversion by varying the aspect ratio (L/d) of the pore, even for slow reactions, as evidenced by the dependence of the conversion only on the Thiele modulus. In this mode there will be a Thiele modulus that maximizes the yield of the desired product for a given reaction network and kinetics. In the sweep-gas mode, the velocity of the reaction limits the conversion that can be achieved; there is a point where larger aspect ratios (L/d) will not further increase the conversion. Therefore, this operational mode will not be attractive for slow reactions.

The continuum model and Knudsen dynamics simulations were employed to study pores partially covered with catalyst, ranging from large bands to just one active particle of catalyst inside the pore. In general, it was found that the location of the catalyst affects how well it is used, i.e. how frequently reacting particles find the catalyst,

but it does not improve the selectivity for a given conversion over the value obtained for a pore fully covered in catalyst.

Operation of these membrane reactors when Knudsen diffusion dominates maximizes the contact of the reactants and the products with the catalyst on the walls, which will be very favorable if the catalyst inherently produces the desired conversion/selectivity, but it offers little control if that is not the case. Increasing the pore size, to add some contribution of molecular diffusion and convection, could be an interesting option to obtain some selectivity benefits out of placing the catalyst at specific locations, while still allowing reactants to contact the wall frequently.

6 Conclusions and recommendations

In this chapter the most important conclusions from this work are highlighted, and at the end, recommendations for future research are included.

6.1 Mass transport in nanostructured membranes

Mass transport in AAO/ALD membranes was modeled employing a multiscale approach that included analytical equations, molecular dynamics simulations and Knudsen dynamics simulations. It was found that Knudsen diffusion is the dominant mass transport mechanism under the conditions of interest, i.e. high temperature and low pressure. In this regime, the number of hits and the residence times were related to the aspect ratio (L/d) of the pore. The number and distribution of hits were obtained for the sweep-gas and pass-through operational modes. The two modes differ in the average number of hits per particle and also in the location of the hits. The observed trends can be employed as guidelines for the placement of catalyst within the pores to optimize the contact between the catalyst and diffusing molecules.

6.2 Transmission probabilities and particle-wall contact in pores of variable diameter

Pores with sections of different diameters were studied under conditions where Knudsen diffusion controls. Knudsen dynamics simulations showed that the angle of transition between the diameters of the sections has little effect on the transmission

probability and the distribution of hits on the wall, except when the transition angle is very small. The distributions of hits inside pores of multiple sections for the sweep-gas and pass-through operational modes can be related to the distributions in pores of uniform diameters. The number and location of hits can be tuned by altering the dimensions of the sections, which can be an advantage for catalysis applications. Analytical expressions were derived to relate the transmission probability in pores of multiple sections with the transmission probabilities of the sections constituting the pore and with the ratio of the cross-sectional areas between sections.

6.3 Pore design for oxidative dehydrogenation

The ODH of ethane was studied using a continuum-level model and Knudsen dynamics simulations. It was found that in the pass-through mode high conversions could be achieved for any reacting system by tuning the aspect ratio of the pore, while the sweep-gas mode is practical only for faster reactions. Pores partially covered with catalyst were studied; it was found that the location of the catalyst affects how well it is used, i.e. how frequently reacting particles find the catalyst, but it does not improve the selectivity for a given conversion over the value obtained for a pore fully covered in catalyst. Operating the membranes under Knudsen diffusion maximizes the contact of the reactants and the products with the catalyst on the walls, which will be favorable if the catalyst inherently produces the desired conversion/selectivity, but it offers little control if that is not the case.

6.4 Recommendations and future research

Knudsen dynamics simulations were performed here under the assumption that collisions between the particles and the wall are purely diffusive. This was shown to be the case for our system by the MD simulations reported in chapter 3. However, a number of other systems have collisions that are partly diffusive and partly specular (Arya et al., 2003a, 2003b). Systems with specular collision present diffusivities much higher than systems with diffusive collisions (Chen and Sholl, 2004; Bhatia et al., 2005). It would be interesting to perform simulations to relate the residence time, transmission probabilities and the number and distribution of hits in the membranes to the degree of specularity of the collisions.

The transmission probability and number of hits were studied in pores with sections of different diameters. It was found that the number and location of hits could be tuned by altering the dimensions of the sections. Performing reactive Knudsen dynamics simulation in these pores would help determine if it is possible to obtain better yields for the desired product in a reacting system like ODH of ethane than in pores of uniform diameters.

Reactive Knudsen dynamics simulations were performed here for a Mars-van Krevelen mechanism with the reduction of the catalyst only implicitly included in the model, as an excess of the oxidant inside the pore was assumed. It is possible to expand the simulations to track the state of the catalyst, i.e. reduced or oxidized. This would allow performing simulations for different concentrations of the oxidant. It would

also be possible to modify the simulations to represent other common mechanisms in oxidation reactions.

The ODH of ethane was chosen in chapter 5 as a representative system to study. It would be interesting to look at other systems commonly studied, including the ODH of propane and of cyclohexane. It would also be valuable to develop more detailed kinetic models for the catalyst in the membranes and to determine accurate values of the rate constants.

Lastly, for the pore sizes and conditions studied here Knudsen diffusion was the dominating mass transport mechanism. It would be interesting to increase the pore size studied in order to add some convection contribution. This could help obtain some selectivity benefits out of placing the catalyst at specific locations, as opposed to the results obtained in chapter 5 for pure Knudsen diffusion.

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