The Metric Sensitivity of Transient Adsorption-Diffusion Models for Hydrocarbon Transport in Microporous Materials was Investigated

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Abstract

The description of transient kinetic data in catalysis by, for example, acidic zeolites and zeotypes presents unique challenges due to the intricate nature of hydrocarbon transport in microporous materials. Surface barriers and hindered microporous diffusion, two processes that are known to affect gas transport in kinetic studies of zeolite-catalyzed reactions, are currently captured by very few models in the literature. During pulse-response experiments in the Temporal Analysis of Products (TAP) reactor, the aforementioned phenomena are reflected in our extended models in this paper. To help with the design of future experiments, systematic studies of models' parametric sensitivity are presented. The effects of realistic zeolites' thermodynamic adsorption properties on the shapes of the pulse-response are studied through numerical simulations. Microporous diffusion is shown to produce a distinctive bend in the mean residence time temperature dependence for some combination adsorption/diffusion parameters, which can be used as a model discrimination fingerprint.

Keywords: Microporous materials; Zeolites; Hydrocarbon transport; Transient kinetics

Introduction

One of the most challenging topics in Transient Kinetics and other natural and mathematical sciences is still the diffusion and reactions of hydrocarbons in zeolites and zeotypes. For gaining insight into and controlling the kinetics of catalytic reactions in numerous important industrial chemical processes, it is especially important to gain a deeper understanding of mass-transport in zeolite catalysts. Temporal Analysis of Products (TAP) and other transient kinetic techniques can provide information on intrinsic kinetic properties that can, in principle, be quantitatively compared to microscopic measurements on model materials and/or studies of ab initio. TAP experiments can be used to investigate pore diffusion concurrently with chemical reactions, which is in contrast to the majority of microscopic methods of diffusion characterization[1]. In addition, typical TAP Reactor Systems permit the rapid and reproducible evacuation of catalytic samples into the well-defined regime of Knudsen diffusion, where the impact of the flow pretreatment on the intrinsic kinetic and diffusion properties of the materials can be investigated. This allows catalytic samples to experience more realistic reaction conditions under ambient pressure flow of reactants. However, multi-scale transport phenomena, such as diffusion within crystallites or reactor-scale fluid transport, also have an effect on transient experiments. How well these transport phenomena are reflected in mathematical models used to estimate the intrinsic kinetic parameters from experimental measurements determines the kinetic resolution of transient data. After all, the measurement of kinetics is only as accurate as the standard transport process it is measured in. Therefore, systematic quantification of diffusion in zeolites has the potential to sharpen fundamental knowledge of reaction kinetics and ultimately contribute to the enhancement of industrial-scale zeolite-catalyzed processes [2].

The myriad of simultaneous processes present in zeolites present the primary obstacle to studying gas transport. Most common modes of diffusion (Knudsen, surface hopping, and single-file) and other major or minor case-specific interactions can coexist with diffusion mechanisms. The ratio of the guest molecules' sizes to those of the host channels, channel shape, crystal shape and size, and the strength and frequency of interactions between guests and either internal or external active sites have all been the focus of microscopic research. Phenomena that take place at the outer rim of zeolite crystallites also have an impact on diffusivity measurements in macroscopic transport studies of technologically relevant samples. A "surface barrier" is typically used to describe the hindrance that has been observed at the zeolite outer shell. Surface barriers' origins remain a mystery, and proposed explanations are highly case-specific. In addition, there is evidence that surface phenomena can both facilitate and hinder transport within the pore, particularly for molecules that have a strong interaction with a zeolite framework. In a large-scale industrial catalysis, zeolite-shaping additives, operating conditions, and time-on-stream also have an impact on gas transport [3].

Although multi-scale computational models and advanced model materials can theoretically account for some of the aforementioned transport complexities in zeolites, more robust and computationally tractable models are better suited for the routine regression of transient kinetic data for catalytic reactions. Without either under- or over-fitting the data, these models of "optimal complexity" must adequately and accurately represent the essential characteristics of transient responses at the appropriate time scales. Data regression can then accurately estimate the intrinsic parameters of diffusion, adsorption, and reactions.

Among a wide variety of materials, the Transient Analysis of Products (TAP) method is uniquely suited for gathering transient intrinsic kinetics data in zeolites. Low-pressure, millisecond-time resolution, and the possibility of reactor-scale gas transport by well-defined Knudsen diffusion characterize traditional TAP experiments.

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In addition, TAP measurements can be combined with steady-state and non-steady-state experiments under a variety of other conditions within the same device and for the same sample. This method can work with materials with a wide range of complexities, like perfectly defined zeolites, hierarchical materials, and porous pellets that are ready for use. Gas adsorption and diffusion, dehydration reactions, hydrocarbon conversion, cracking and reforming, MTH and MTO processes, and TAP applications in zeolite catalysis are just a few examples.

By incorporating terms that reflect surface barriers and the complex nature of microporous diffusion, we expand the range of transport models used for TAP data analysis with microporous diffusion. In order to map the sensitivity ranges of increasingly detailed models, numerical studies were used. Additionally, novel fingerprints in model behavior were discovered that can assist in data interpretation for upcoming experiments.

Methodology

Standard TAP model

It is shown how the TAP reactor, which is typically used to study reactions sparked by microporous materials, is set up. The reactor has three zones: two inert zones, one of which is usually filled with zeolite or another inert material like quartz, and one catalytic zone in the middle. The length of synergist zone can be acclimated to control how much impetus, subsequently the contact time with beat gas. Dissemination length of the passing particles can likewise be constrained by changing the length of zones and choosing materials of specific mass porosity. The assumption of negligible radial concentration gradients, radial and axial temperature gradients, and, most importantly, constant gas diffusivity within each zone is supported by appropriate reactor design. This is accomplished by employing a relatively small portion of particle sizes, typically sieved to 250 d 400 m. In practice, experiments are typically carried out in a thin-zone configuration of the reactor to ensure that the catalyst zone is in the isothermal reactor zone and that concentration non-uniformities are minimized. There are additional details about testing and proving these assumptions. The model in heterogeneous media is a straightforward one-dimensional diffusion equation for gases that do not interact with catalyst and do not experience microporous diffusion delay. The gas pulse in the reactor's inlet at time zero is assumed to be a Dirac delta function in the partial differential equation's initial conditions. According to the Neumann and Dirichlet boundary conditions, there is no gas concentration at the reactor's outlet and no influx at the reactor's inlet. The straightforward model and reactor assembly provide a solid foundation for estimating gases' Knudsen diffusivity.

Development of mathematical models

As a standard model, the two-parameter model of microporous diffusion in the TAP setting that was first proposed by Keipert was chosen. The gas transport inside the pore is constrained by a Henry-like steady of adsorption balance at the pore mouth KH and microporous diffusivity Dp. The transient one-dimensional 2nd Fick's law in this model describes the distribution of gas molecules along the micropores. The crystallite is assumed to have pores of equal size and distribution, creating a pseudo-homogeneous environment. A single microporous diffusivity, Dp, that is assumed to be isotropic and homogeneous throughout the zeolite crystal, describes potentially distinct modes of diffusion. The zeolite particle's intracrystalline diffusion is assumed to be symmetrical with respect to the crystal center. The diffusion equation can be solved in linear coordinates for crystals with 1D pore architecture, while a spherical coordinate system can be used for 3D pore systems. It is assumed that gas transport between crystals always follows bulk Knudsen diffusivity. All of the models developed here are based on the assumption that pores of equal size are distributed isotropically and uniformly throughout the crystallite, forming a pseudo-homogeneous diffusion domain. The models are at least valid for two broad categories of microporous materials that are frequently encountered in practice because of this assumption: 1D equal pores (for example TON, AFI) and 3D profoundly interconnected pores of equivalent measurement (for example MFI) or holes interconnected by windows (for example CHA, AEI). It may be necessary to develop models that are more intricate for other kinds of materials that have pore systems that are connected and have different sizes [4].

A dynamic, or non-equilibrated, adsorption at the pore mouth prior to pore diffusion is taken into account in an additional extension of the Keipert model, as shown by the two parameters adsorption constant ka and desorption constant kd. Non-equilibrated adsorption expressly represents the presence of a limited capacitance comparing to the inclusion of the adsorbate at the external surface of a zeolite, which is reflected by a committed spatially-confined variable θA [5]. This adsorbate capacitance at the external surface can all the while and powerfully (for example non-equilibrated at the time sizes of the investigation in question) trade with the mass as well as microporous areas. Importantly, cases in which strong adsorption at the outer surface may result in a measurable delay of the probe molecule with respect to the inert standard even without the pore entry are accurately represented by the model with a finite dynamic capacitance [6]. The absence of sufficient adsorption sites at the outer surface may also contribute to the restriction of diffusion into the pores. Model 1, on the other hand, fails to account for the minute transient effects of coverage shifts at the outer surface because it assumes instantaneous equilibrium between the bulk probe molecules and the boundary layer of the pseudo-homogeneous pore space. Disordered microporous materials like activated carbon, which are not taken into consideration in this work, are one example of a situation in which the concept of a unit cell thickness defined in boundary conditions may not apply in many situations that are of practical importance [7].

A sensitivity study of 3-, 5-, and 7-parametric models necessitates hundreds of thousands of simulations, which takes a significant amount of time, despite the fact that the available computational capacity allows for the numerical solution of the presented models on any office PC. In these terms, analytical solutions are much more appealing options. However, providing analytical solutions is a large undertaking unless some simplifications are made because of the heterogeneous non-linear nature of models. It is assumed that the reactor only contains one Zone—catalytic—to eliminate heterogeneity [8]. The assumption of "A" was made in order to linearize models; as a result, the term "1" could no longer be used in mathematical expression. We used inverse Laplace transformation to find solutions for a 1 Zone reactor using dimensionless models, following Colaris's approach. The resulting analytical expressions are comparable to those found in more realistic three-zone models and can be used more effectively for sensitivity studies. The final solutions to the dimensionless Laplace-transformed models are discussed in this section [9].

Results and Discussion

Parametric sensitivity is examined for enhanced models that

provide a more comprehensive representation of complex hydrocarbon transport. Insights into how additional parameters affect the sensitivity ranges to other parameters and the boundaries of parametric space where developed models can capture pulse-response curves were the goals of this study.

Before investigating the sensitivity ranges of more complex models, the Keipert model serves as a convenient starting point and a benchmark. The Keipert model only has two parameters, KH and Dp, so sensitivity can be seen on a 2D surface plot. The coefficient is used to represent Dp in dimensionless coordinates [10].

Keipert model can be seen to have three distinct regions: i) the high-intensity band, a constrained central region where the model is sensitive to parameter values; ii) the region above the sensitivity band where probe molecules cannot exit the reactor due to irreversible adsorption; iii) the region below the sensitivity band where adsorption is too weak to cause a pulse-response delay in comparison to the inert Standard Diffusion Curve (SDC). The sensitivity band itself can be divided into two arms with a distinct change in slope at ca. $\log(\alpha) = 0$. The model is sensitive to both the KH parameter and the left arm if $\log()$ is less than or equal to 0, while the right arm is only sensitive to KH [11]. The fact that the concentration gradient along the pore is established more quickly than the concentration gradient along the reactor bed when the value of $\log()$ is greater than zero indicates that the characteristic timescale of bulk diffusion is longer than that of microporous diffusion [12]. Keipert et al.'s findings are completely in line with this analysis and makes it abundantly clear that bulk diffusion in TAP experiments cannot be utilized as a sensitive measure of microporous transport unless the combination of transport and geometric parameters places it within the specified sensitivity band [13]. We note that Keipert et al.'s original analysis attempted to visually correlate our sensitivity metric with the first derivatives of log (MRT) and log(PT) aside from the general bounds on the sensitivity regions shown, did not reveal a straightforward correlation between the two sensitivity descriptor frameworks.

The sensitivity metric behaves differently in the extended model with dynamic (though not always non-equilibrated) adsorption at the pore mouth. For a fixed adsorption rate coefficient, results are presented in a familiar two-dimensional view, while the other two parameters are varied [14]. Despite its general similarity to the Keipert model, this model has a distinctly different sensitivity band structure, particularly in the left arm with 105. The presence of an additional (monolayer) adsorption capacity at the outer pore mouth required by the dynamic model is the cause of this variation in the sensitivity band structure in comparison to the Keipert model. For extremely sluggish microporous dissemination, the transaction of the limited adsorption/desorption rates into and out of this extra limit represents the variety of heartbeat reaction and blocks the model responsiveness towards microporous dispersion [15].

Conclusions

A wide range of processes that take place in microporous materials were taken into account in mathematical models of pulse-response TAP experiments. For the first time, models with surface barriers, decoupled intraporous adsorption, and diffusivity terms were created and studied. The parametric windows within which these models converge to the same behavior were identified by rigorous sensitivity analysis. In addition, novel fingerprints that can be used to identify parametric domains for regression of experimental data with distinct extrema in the temperature dependence of the mean residence time

were described. Validating these findings with experimental TAP data for well-defined zeolite materials that can exhibit target characteristics (such as slow microporous diffusion, energetic difference between surface and internal active sites, etc.) will be the primary focus of subsequent research. Utilizing more sophisticated mathematical methods of model interrogation, such as Sobolev's co-dispersion to quantify parameter correlations, will also be investigated as potential extensions of our analysis. Overall, we come to the conclusion that robust mathematical models are an essential component of any approach to transient kinetics and must be developed simultaneously with the creation of novel measurement methods and specialized catalytic materials. Materials descriptors previously unavailable from macroscopic measurements can now be accessed through appropriate high-fidelity models.

Acknowledgement

Conflict of Interest

None

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