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CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN
FRESH AND AGED CATALYST EXTRUDATES

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CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN FRESH AND AGED CATALYST EXTRUDATES

Executive Summary

The overall objective of this project was to investigate the diffusion of coal and petroleum asphaltenes in the pores of a supported catalyst. Experimental measurements together with mathematical modeling was conducted to determine how the diffusion rate of asphaltenes, as well as some model compounds, depended on molecule sizes and shapes. The process of diffusion in the pores of a porous medium may occur by several mechanisms. Hindered diffusion occurs when the sizes of the diffusion molecules are comparable to those of the porous pores through which they are diffusing. Hindered diffusion phenomena have been widely observed in catalytic hydrotreatment of asphaltenes, heavy oils, coal derived liquids, etc. Pore diffusion limitations can be greater in spent catalysts due to the deposition of coke and metals in the pores.

In this work, a general mathematical model was developed for the hindered diffusion-adsorption of solute in a solvent onto porous materials, e. g. catalysts, from a surrounding bath. This diffusion model incorporated the nonuniformities of pore structures in the porous media. A numerical method called the Method of Lines was used to solve the nonlinear partial differential equations resulting from the mathematical model. The accuracy of the numerical solution was verified by both a mass balance in the diffusion system and satisfactory agreement with known solutions in several special

cases.

Several tests were made to rule out the presence of external mass transfer in the diffusion experiments, so that the results were dependent on the intraparticle diffusivity. Theoretical analysis showed that if external mass transfer were present, a plot of t^* (dimensionless time) vs. t (real time) would not be a straight line through the origin, as required by the intraparticle diffusion process. If the plot of t^* vs. t is forced to be straight in the presence of mass transfer influence, the slope would not be -2, and the data points would lie below the straight line at lower t values and then tend upward above the line at higher t values. These plots allowed us to check for the presence of external mass transfer. Using this methodology, in the uptake experiments of this work, the external mass transfer effect was found to be negligible by using experiments with different particle sizes, by calculating the particle surface concentration, and by performing experiments with varying stirring speeds.

Both bimodal and unimodal catalysts were used in the diffusion experiments. The unimodal catalyst had a very narrow pore size distribution, while the bimodal catalyst had two basic pore sizes. Both catalysts were well characterized by methods such as BET surface area and mercury porosimetry. In experiments with fresh and spent catalysts, the pore volumes, porosities, surface areas and adsorption capacities for both spent unimodal and bimodal direct coal liquefaction catalysts were much less than those for the fresh catalysts. The equilibrium adsorption isotherms of quinoline in cyclohexane with fresh, spent and regenerated unimodal and bimodal catalysts were all nonlinear, and were well represented by the Freundlich isotherms. The loss in active sites during the coal

liquefaction process, as indicated by reduced adsorption of the basic N compound quinoline, was much greater than would be estimated from the loss in BET surface area. Carbonaceous deposits, rather than metals, were the dominant factor causing a decrease in the effective diffusivity for the spent catalysts, and this decrease was much greater than would be estimated from the decrease in average pore diameter calculated based on surface area and pore volume of the spent catalysts. Regeneration by controlled oxidation of spent unimodal and bimodal catalysts significantly restored the effective diffusivities, although not completely to the levels for the fresh catalysts, with the regeneration extent for the bimodal catalyst exceeding that of the unimodal catalyst.

A diffusion model based on uniform particle properties satisfactorily fit the experimental data with fresh catalysts, with the effective diffusivity for the bimodal catalyst being greater than that for the unimodal catalyst. The uniform particle model was not valid for spent catalyst extrudates as was evident from unrealistically high tortuosity factors. Experiments with crushed spent particles indicated a nonuniform coke deposit in both spent unimodal and bimodal catalyst extrudates. A diffusion model incorporating a nonuniform deposit distribution gave a satisfactory fit of the observed data for the spent catalyst extrudates, including reasonable tortuosity factors, and indicated that nonuniformity of pore deposits should be considered when modeling intrapore diffusion in spent catalyst extrudates.

A mathematical model, termed the shrinking pore model, was developed and applied to the diffusion controlled adsorptive uptake of a solute from a finite bath into a porous medium. The model extends previous generally used models by incorporating the

enhanced restrictive effect of an adsorbed solute layer of finite thickness on the pore walls. This layer tends to further restrict the solute uptake rate by decreasing the effective local pore size and porosity and increasing hindrance effects. Comparison of model simulations with experimental data showed that although both the shrinking and the uniform pore models fitted the experimental uptake data of quinoline well, the shrinking pore model was required to obtain a satisfactory representation of adsorptive uptake for a larger polystyrene solute.

The diffusion of both coal and petroleum asphaltenes was studied in the project. Both the coal and petroleum asphaltenes used in this study had very broad molecular weight distributions, with the molecular weights of the coal asphaltenes (50-2000) being much smaller than those of the petroleum asphaltenes (300-30000 for P-AAK and 200-20000 for P-AAG). Examination of prior literature data showed that SEC elution data, based on polystyrene calibration standards, could be used to develop a correlation for estimating the molecular weights of asphaltene fractions. The coal asphaltene fractions had estimated effective diffusivities which spanned 1 order of magnitude, whereas these spans were more than 3 orders for the two petroleum asphaltenes. The uptake rates for individual asphaltene fractions with different molecular weights were different, depending on their diffusion rates and adsorption constants. Even though the properties of the asphaltenes used were quite different, the values of model parameters for the fractions of the three asphaltenes had the same trend; with increasing molecular weight of the fraction, the adsorption constant increased and the effective diffusivity decreased monotonically. Thus the behavior of coal and petroleum asphaltenes were quite similar providing that appropriate allowance was made for the differences in molecular weights,

size, and diffusivities. The experimental diffusion controlled uptake data for the three asphaltenes was represented fairly well in most molecular weight regions by the same mathematical model using appropriate parameter values, although some departures were observed in the high molecular weight region. While only three asphaltenes were tested in the current study, it might be speculated that the uptake of additional asphaltenes as a function of molecular weight could be estimated using the present model. Comparison of uptake results using different solvents showed that the adsorption constants with toluene as a solvent are much larger than those with THF solvent. This could be attributed to the fact that toluene is not as good a solvent for asphaltenes as is the THF, which is capable of hydrogen bonding interactions. These solvent and asphaltene interactions could give rise to aggregation, i. e. self-assemblies, of asphaltenes which would be different in the different solvents. The effect of concentration was examined at two different concentration levels of asphaltenes, viz., 0.5 and 0.05 mg/cm³. The results showed that the adsorption constants were different at the two concentration levels, suggesting a nonlinear adsorption isotherm, possibly due to differing asphaltene aggregation effects at the two concentration levels. The effect of temperature on the diffusion coefficient was represented by the Stokes Einstein equation. The effect of temperature on the adsorptive uptake of coal asphaltene was complex, with the adsorptivity at 35 °C exceeding that at 25 °C in the lower (<10³) molecular weight region. In general the effects of temperature, concentration and solvent type on the asphaltene adsorption/diffusion behavior were rather complex, possibly due to the formation of differing asphaltene aggregates at the various conditions.

Project Summary

The objective of this research was to determine the relationship between the size and shape of coal and petroleum macromolecules and their diffusion rates, i.e., effective diffusivities, in catalyst pore structures. That is, we wanted to determine how the effective intrapore diffusivities depend on molecule configuration and pore geometry. The basic approach in the project was to perform adsorptive uptake experiments of certain model compounds, as well as coal and petroleum asphaltenes into a porous catalyst particles from a surrounding bath. Then, from a mathematical model developed for the uptake process, we obtained the appropriate diffusion coefficients and adsorptivities from fitting the experimental data to the decrease in bath solute concentration. The various parameters including diffusion coefficients and adsorptivities were found to depend in a complex manner on factors such as solvent type, asphaltene concentration, and temperature. In the overall project, the work was comprised of several tasks as listed below.

- Task 1. Relationship Between Effective Intrapore Diffusion Coefficients, Molecular Size and Pore Geometry.
- Task 2. Effects of Solvent Composition, Solute Concentration and Temperature on the Molecular Configuration and Diffusion Rate of Coal and Petroleum Asphaltenes in Catalyst Pores.
- Task 3. Assessment of Diffusional Limitations in Aged Catalysts.

Catalysts with both bimodal and narrow unimodal pore size distributions were used in the experiments. We found that the diffusion coefficients of the asphaltenes and the model compounds, quinoline, and polystyrene, could be modeled fairly well as rigid spheres and that the diffusivity could be represented by the Renkin equation, which has been developed for diffusion of spherical solutes in cylindrical pores. This equation, while approximate, seemed to work quite well for both planar molecules such as quinoline, or asphaltenes, and coil shaped molecules such as the polystyrene. Thus the effects of molecule size and pore geometry were modeled quite well by the hindered diffusion theory based on the ratio of molecule (sphere) to pore diameter.

The effects of solvent composition, solute concentration, and temperature level on the diffusional uptake process were studied using coal and petroleum asphaltene uptake experiments together with a simplified mathematical model. The studies revealed that these experimental factors influenced the adsorptive uptake process in a rather complex manner, possibly suggesting the presence of asphaltene aggregation, which might occur to differing degrees under the various conditions studied. The differences observed in the uptake experiments could be suggestive of the fact that the molecular configuration of the asphaltenes might be different as a result of the differences in solvent type, asphaltene concentration, and temperature. The effect of solvent composition on asphaltene diffusion was studied by using two different solvents, THF and toluene. Using a simple diffusion model the adsorption constants with the aromatic toluene solvent were found to be much greater than the case with the THF solvent. This increase in adsorptivity could be due to the fact that toluene is not as "good" a solvent for the asphaltenes as the THF solvent,

with the result that larger asphaltene aggregates are adsorbed onto the catalyst surface, or that the THF is a better competitor for surface adsorption sites than the toluene. The THF solvent is capable of hydrogen bonding interactions where the toluene is not. The effects of temperature on the diffusion of asphaltenes were studied at three temperatures. The effect of temperature on the diffusivity was modeled by the Stokes Einstein equation, and the effect of temperature on the adsorptivity was determined from a fit of the experimental uptake data. The temperature behavior was complex, possibly as a result of self aggregation of the asphaltene molecules. Some overlapping of the GPC curves as a function of molecular weight also suggested the presence of aggregation or self assemblies of molecules. This aggregation effect was primarily limited to higher molecular weights, $> 10^4$. Uptake experiments conducted at two different concentration levels showed that the adsorption behavior of the asphaltenes was nonlinear in nature. It was speculated that this might be due to the presence of differing degrees of asphaltene aggregation, i. e. differences in molecular configuration, at the different concentration levels.

Diffusivity measurements were conducted with both aged and fresh catalysts. Rather than producing our own catalysts in the laboratory, as had been originally planned, we were able to procure sufficient quantities of both aged and fresh catalysts of both bimodal and unimodal types from the Wilsonville Coal Liquefaction R&D Facility. This use of actual coal liquefaction catalysts from a uniform source allowed us to spend more time on the diffusional aspects of the project, rather than production of the various catalysts themselves. From the data obtained the effect of catalyst structural changes as

caused by coke and metals deposits on the intraparticle diffusivity was evaluated. The diffusivity of the spent catalysts were greatly reduced from the values in the fresh catalysts. Regeneration by controlled oxidation restored the diffusivity partly, but not completely. Thus in a practical coal liquefaction process, regeneration can extend, but not indefinitely prolong, the catalyst life. At some point the catalysts must be disposed of, or sent to a metals reclamation facility to reclaim the metals from the supports.

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4. Pore Diffusivities in Deactivated Coal Liquefaction Catalysts, *Applied Catalysis*, 141, 153-174(1996).
5. Hindered Diffusion of Asphaltenes in a Hydrotreating Catalysts, *ACS Preprints, Div. Fuel Chem.*, 41(3), 1013-1019(1996).
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7. Diffusion-Controlled Uptakes of Asphaltenes in a Hydrotreating NiMo/Al₂O₃ Catalyst, submitted to *Chemical Engineering Communication*, 1996.
8. Hindered Diffusion of Asphaltenes in Porous Catalyst Particles, Presented at the ACS 212th National Meeting, Orlando, Florida, August 25-29, 1996.
9. Deposit Induced Changes in Pore Geometry and Diffusivities of Deactivated Unimodal and Bimodal Catalysts, Presented at the AIChE Annual Meeting, San Francisco, Ca, Nov. 13-18, 1994.

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I. INTRODUCTION

Chemical reactions in heterogeneous catalysis can be significantly influenced by intrapore diffusion phenomena involved in the transport of reactant molecules in and out of the catalyst pores, resulting in the dependencies of both catalyst activity, selectivity and stability on the intrapore diffusional limitations. Evidence for the intrapore diffusional influences has been widely observed as in the cases of heavy oil upgrading and coal liquefaction processes, in which it is necessary to catalytically upgrade the primary products and to effectively reduce the molecular weight prior to downstream processing to obtain higher value products. In these processes, the catalysts are generally made of metal sulfides supported on porous supports, e.g., Al_2O_3 , with complex and tortuous pore structures, while the reactants are usually composed of macromolecules, e.g. asphaltenes, being mixtures of macromolecules with different molecular weights, shapes and sizes. In an attempt to minimize the limitations due to diffusional processes, various catalyst pellet shapes, e.g. trilobed vs. cylindrical, and various pore size modifications, e.g. bimodal vs. unimodal, have been utilized. However, the intrapore diffusion mechanisms of complex macromolecules, e.g. asphaltenes, are often not fully understood.

Hindered, restricted or configurational diffusion occurs when the sizes of the diffusion molecules are comparable to the pore sizes of the catalysts, as the cases in hydrotreatment of heavy oils and asphaltenes. In hindered diffusion regimes, the diffusion rates or the effective diffusivities of the macromolecules

within the pores are dramatically reduced from those within the free solution. It is generally recognized that hindered diffusion in the pores of the catalysts is caused by two factors, steric partition effects and viscous drag influence. Steric effects account for the fact that the diffusing molecules can enter a pore only if they do not strike the wall of the pore. Viscous drag influence deals with the fact that the molecules experience an increased frictional drag (hydrodynamic resistance) due to the confinement of the fluid by the pore wall, over and above the drag that would be experienced by the molecules diffusing in an unconfined solvent. When the diffusing molecules adsorb on the pore walls, as is the case in most heterogeneous catalytic processes, a solute adsorption layer would further enhance the steric and hydrodynamic effects and additionally hinder the diffusion process due to the confinement of the pores.

During catalyst usage, the pore geometry of the catalyst could be changed due to the deposition of carbonaceous and/or metals, resulting in a reduction in the pore sizes. These changes in pore geometry in spent catalysts further enhance the hindered diffusional limitations and reduce the effective diffusivity. Moreover, it is not necessary for the deposits to be evenly distributed throughout the catalyst pellets, as happens in most catalyst deactivation processes. This uneven deposit distribution in the pores results in the nonuniform pore sizes throughout the catalyst pellets. Therefore, hindered diffusion behavior in spent catalysts could be different from that in fresh ones.

The objective of this work was to investigate, in a non-reactive environment, the relationship between molecule size and pore size as it pertains to the diffusion rates of macromolecules, e.g. asphaltenes, in porous catalyst pellets with complex and tortuous pore structures. In other words, we wished to better understand the hindered diffusion of asphaltenes as it applies to catalytic

hydroprocessing, with the long range goal of aiding in the design and improvement of catalysts and operation conditions for the processing of macromolecular feedstocks. We also wished to learn how the adsorption of the diffusing molecules, as it appears in most heterogeneous catalysis, affects the hindered diffusion process. Another objective of this work was to elucidate the changes in pore structure and thus the hindered diffusion mechanisms in spent catalysts with nonuniform depositions.

To achieve the objectives, adsorptive diffusion experiments were performed in a diffusion bath using both fresh, spent and regenerated porous catalysts. The diffusion rates of various molecular species, including both model compounds and coal/petroleum asphaltenes, into the porous catalyst pellets were measured. To describe the adsorption-diffusion behavior of the molecules in the pores of both fresh, spent and regenerated catalysts, a general mathematical model was developed. The hindered diffusion parameters of the various molecules and catalysts were obtained by fitting the mathematical model with the experimental data.

II. LITERATURE REVIEW

Introduction

Diffusion of molecules in a solvent through the pores of porous materials has been widely utilized in both scientific research and many technological applications, e.g., separation, chromatography, heterogeneous catalysis, etc. In a pore diffusion process, several diffusion mechanisms may be observed, e.g., ordinary, surface, Knudsen and hindered diffusions. Hindered, restricted or configurational diffusion occurs when the sizes of the diffusing molecules are comparable to the sizes of the pores through which they are diffusing, such as the cases in the separation of macromolecules with membranes and the catalytic hydrotreatment of asphaltenes and other heavy ends with hydrotreating catalysts. It is generally recognized that hindered diffusion is caused by steric partition influences and/or hydrodynamic viscous drag effects. Hindered diffusion phenomena have been observed in various porous materials, e.g., membranes with relatively well defined uniform pores, alumina and silica with fairly tortuous nonuniform pores, zeolites with rather smaller interconnected pores and cages.

In this literature review, we will first discuss several basic diffusion mechanisms in the pores of porous materials. Then we will devote our attention to the hindered diffusion phenomena through different porous materials. Finally, we will focus on the pore diffusion of asphaltenes and other macromolecules.

Classification of Diffusion in Porous Materials

Diffusion in the pores of a porous medium may occur by one or more of the following several mechanisms, ordinary diffusion, Knudsen diffusion, surface diffusion, shape-changeable diffusion, and/or hindered diffusion. Ordinary diffusion is the molecular diffusion in free solution. Knudsen diffusion occurs when the diffusing molecules collide with the pore wall much more frequently than with each other. Surface diffusion is the diffusion of adsorbed molecules in the pores of porous materials. In some cases, when molecules diffuse into the pores of a porous medium, they will change their shape or configuration from that in free solution, which is known as shape-changeable diffusion. When the sizes of diffusing molecules are comparable to the sizes of the pores in which they diffuse, hindered diffusion occurs due to steric partition and/or viscous drag effects.

Ordinary Diffusion

In many situations of technological and scientific interest, the dimensions of the solute molecule are at least several times greater than those of the solvent. In such cases the resistance to Brownian motion of the solute may be equal to the hydrodynamic drag on a particle of equivalent size and shape, and the diffusion in these cases is called ordinary, bulk, molecular, or intrapore-volume diffusion. Generally, ordinary diffusion is the predominate mode of diffusion into porous materials.

According to ordinary diffusion, the flux of a solute in a porous material is reduced from its value in the bulk solution by simple geometric factors. Thus if the flux of solute "A" in the bulk solution is given by Fick's law

$$N_{A\infty} = -D_{\infty} \nabla C \quad (2.1)$$

then the corresponding ordinary molar flux for the diffusion in the pores of the porous material is given by

$$N_{Ap} = -D_{ep} \nabla C \quad (2.2)$$

where D_{ep} is the effective diffusivity and can be expressed as (Satterfield, 1970)

$$D_{ep} = \frac{\epsilon}{L'S'} D_{\infty} = \frac{\epsilon}{\tau} D_{\infty} \quad (2.3)$$

In this equation, ϵ is the porosity and reduces the flux simply because the fraction $(1-\epsilon)$ of the total area is occupied by the solid and is thus not available for diffusion. S' is a shape factor and L' a length or angle factor, both being greater than unity, accounting for the pore nonuniformities and irregularities. Theoretical models of pores with constrictions to estimate the value of S' have been proposed by Petersen (1958), Currie (1960), and Michaels (1959). Petersen represented the pores as a series of hyperbolas of revolution with constrictions at the vertices of the hyperbolas, and Currie assumed the pores being tubes of sinusoidal form, while Michaels proposed the pores as a repetition of two cylindrical capillaries of different diameters and lengths joined in series. L' is always predicted to increase with decreasing porosity (Satterfield, 1970). For most real porous systems it is impossible to separate L' and S' , so they are multiplied together and represented by τ , called tortuosity, a single factor to allow for both varying diffusion direction and varying pore cross section. The tortuosity τ is an empirical attempt to account for several factors including the fact that the actual diffusion path length is lengthened through the porous media by the circuitous route of the pores, as well as the fact that the pores contain constrictions and are of nonuniform diameter.

In the above equations, D_{∞} is the molecular or bulk diffusivity. For hydrodynamic spherical solutes diffusing in free solution, the molecular diffusivity can be expressed by the Stokes-Einstein equation (Einstein, 1956)

$$D_{\infty} = \frac{kT}{6\pi\eta r_m} \quad (2.4)$$

The hydrodynamic basis for the above equation, and its limitations were summarized in a review by Russel (1981). For nonspherical solutes of known D_{∞} the value of r_m in above equation is termed the Stokes-Einstein radius, the radius of a sphere of equal diffusivity. Some other correlations for the molecular diffusivity have also been suggested, one of which is the widely used Wilke-Chang equation (Reid et al., 1987) which is equivalent to the Stokes-Einstein equation if the solute radius exceeds two or three times that of the solvent.

Knudsen Diffusion

If the density of the diffusion solution is low, or if the pores are quite small, or both, the molecules collide with the pore wall much more frequently than with each other. This is known as Knudsen diffusion. Evidently, the molecules hitting the wall are momentarily adsorbed and then given off in random directions (diffusely reflected). For Knudsen diffusion through straight cylindrical pores in a porous solid, the effective Knudsen diffusivity can be estimated by (Kärger and Ruthven, 1992)

$$D_K = 9700r_p \sqrt{\frac{T}{M}} \quad (2.5)$$

It is generally recognized that Knudsen diffusion occurs only in gas systems, not in liquids.

Surface Diffusion

When a diffusing molecule diffuses in a pore, it can adsorb on the pore wall, and this adsorbed molecule is not necessarily stationary and may diffuse to other adsorption active sites, or diffuse to return to the liquid phase. Such a diffusion flux of the adsorbed molecules is referred as surface diffusion. The surface diffusion can be modeled as an additional flux with a surface diffusivity D_s (Froment and Bischoff, p155, 1990)

$$N_{As} = -\rho_p D_s \frac{\partial q}{\partial r} \quad (2.6)$$

The contribution due to the surface diffusion to the total diffusional flux can be substantial (Schneider and Smith, 1968; Reed and Butt, 1971), sometimes exceeding that due to the pore-volume diffusion (Komiyama and Smith, 1974; Furusawa and Smith, 1974), particularly on the surface of more active adsorption sites in a porous material.

Shape-Changeable Diffusion

Generally, only a molecule with smaller size than the pore size can diffuse in the pores of a porous material. On the other hand, some large molecules can

still diffuse into a pore whose size is smaller than the molecule size, during which the molecules will change their shapes or configuration to fit the pore. The diffusion phenomena in this case is termed as shape or configuration changeable diffusion. As shown by Moore and Katzer (1972), molecule having a critical diameter of 9.2 Å can still freely counterdiffuse in cyclohexane through the pore structure of Y zeolite having free pore diameter of 7.4 Å. During this diffusion, the shape, or the kinetic diameter of the molecule, could change to fit the size of the pore. This occurred because the three dimensional array of large cages or cavities with a maximum diameter of about 12 Å allowed molecules to pass one another, and partially because the unsaturated attractive forces of the adsorption active sites in the cages enhanced the diffusion process.

For the diffusion of long-chain polymers, Gennes and coworkers (Gennes, 1979; Brochard and Gennes, 1977) proposed a scaling theory which deals with the fact that a flexible polymer chain is trapped in a cylindrical pore as an elongated cigar with elementary units of the same size as the pore diameter. Several other investigators also noted the behavior of larger flexible polymer chains diffusing into smaller porous medium at either high concentration or large flow rate or both (Satterfield et al., 1978; Long and Anderson, 1984; Chauveteau et al., 1984; Guillot et al., 1985).

Hindered Diffusion

When the size of the diffusing molecule is appreciable compared to the pore size of the porous material in which it diffuses, the mass transfer flux can be greatly reduced. The diffusion in this case is called hindered, restricted, or configurational diffusion. It is generally recognized that hindered diffusion is

caused by two factors, steric hindrance and viscous drag effects. The steric hindrance or partition effect was first proposed by Ferry(1936) in regard to diffusion in membranes. It was based on the assumption that the diffusing molecules could enter a pore only if they did not strike the wall of the pore, which means that a steric exclusion, or concentration reduction of macromolecules from a portion of volume exists near the wall of the pore, as depicted in Figure 2.1.

On the other hand, viscous drag effect accounts for the fact that the molecule experiences an increased frictional drag (hydrodynamic resistance) due to the confinement of the fluid by the pore walls, over and above the drag that would be experienced were the molecule diffusing in an unconfined solvent (Deen, 1987; Pappenheimer et al., 1951; Faxen, 1923).

Hindered Diffusion Phenomena in Porous Materials

There is considerable evidence that hindered diffusion phenomena do exist in porous materials, particularly when the diameters of the diffusion molecules are comparable to the pore sizes of the porous materials. Hindered diffusion phenomena can be explained in part by the fact that the constrained space of a pore causes the molecular diffusivity to exceed its value for an unbounded solution. In addition, because the driving forces are usually expressed in terms of concentrations in the adjacent bulk solutions, the magnitudes of the corresponding transport coefficients are affected by factors that influence the equilibrium partitioning of solutes between pores and bulk solution, including steric exclusion. Steric restrictions and long-range intermolecular forces also affect the radial distribution of solutes within a pore, which in turn influence the hydrodynamic

Figure 2.1 Available volume in a single pore.

interactions between the solutes and the pore wall.

Hindered diffusion has been observed in different mediums with different pore structures, e.g., membrane, alumina, silica, zeolite, activated carbon, etc.. In this literature review, we will mainly concern ourselves with the hindered diffusion in membranes, alumina, silica and metal supported porous catalysts, even though hindered diffusion has also been observed in zeolites (Moore and Katzer, 1972; Haynes, 1988; Kärger and Ruthven, 1992), activated carbons (Furusawa and Smith, 1974) and other porous materials.

Hindered Diffusion in Membranes

Membranes have been widely used in separation and other applications in both industrialization and scientific research due to their special pore geometries. It is generally recognized that the pore structure in membranes can be described as uniform and well-defined cylindrical pore geometry (Deen et al., 1981; Bohrer et al., 1984; Guillot, 1987; Bohrer et al., 1987; Kathawalla and Anderson, 1988; Kathawalla et al., 1989; Cannell and Rondelez, 1980; Malone and Anderson, 1978). Thus, it is obvious that hindered diffusion studies with membranes of simple structures are easier and more explicit than those with porous materials of complex pore geometries such as alumina catalysts.

Hindered diffusion was first observed in membranes more than half a century ago. It has been shown (Weech and Michal, 1928) that the diffusion rates of organic molecules through membranes in very small pores decreased as a function of molecular sizes far more rapidly than could be accounted for on the basis of the molecular diffusion. From that time on, hindered diffusion studies in porous pores have been continued by numbers of investigators, and the hindrance

effects on diffusion rate were usually correlated with the ratio of molecule size to pore size. A comprehensive theoretical analysis of hindered diffusion was conducted by Anderson and Quinn (1974), and many applications of theories of hindered transport through membranes were reviewed by Solomon (1968) and Deen (1987).

Most hindered diffusion studies considered two hindrance factors, steric or partition factor K_p and hydrodynamic drag factor K_r . One of the earliest influential studies was that of Ferry (1936), who derived hindrance factor for convective transport from steric considerations. It was based on the assumption that the diffusing molecules could enter a pore only if they do not strike the pore walls. For spherical particles entering circular openings, the steric factor K_p can be expressed as the ratio of the effective diffusion area to the total cross section, viz.

$$K_p = \frac{A_e}{A_t} = (1-\lambda)^2 \quad (2.7)$$

where λ is the ratio of molecule size to the pore size,

$$\lambda = \frac{d_m}{d_p} \quad (2.8)$$

Several other expressions for the steric factor have also been suggested. To name a few, Casassa (1967) obtained the following analytical expression for a neutral, random-coiling macromolecule,

$$K_p = 4 \sum_{i=1}^{\infty} \frac{1}{\beta_i^2} \exp\left(-\frac{4}{\beta_i^2} \frac{\langle s^2 \rangle}{d_p^2}\right) \quad (2.9)$$

where β_i are the roots of zero order Bessel function $J_0(\beta)=0$, $\langle s^2 \rangle$ is the mean-square radius of gyration, being a function of molecular weight and solvent. In

scaling theory, the steric partition factor K_p was related to the confinement free energy F_N by (Bohrer et al., 1987)

$$K_p \propto \exp\left(-\frac{F_N}{kT}\right) \quad (2.10)$$

The effect of hydrodynamic viscous drag on the solute transport rate is determined by calculating the local Stokes friction coefficient as a function of position and taking the spatial average. For larger values of λ ($\lambda < 0.5$), Pappenheimer et al. (1951) assumed that the local Stokes coefficient is equal to the centerline value and is calculated by the following equation, first derived by Faxen (1923) for a rigid sphere in a cylindrical tube,

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (2.11)$$

Another expression for the viscous drag effect was described by the Ladenburg equation accounted for the viscous drag between sedimenting particles and the walls of cylinder in Stokes law (Solomon, 1968)

$$K_r = \frac{1}{1 + 2.4\lambda} \quad (2.12)$$

Davidson and Deen(1988, 1988a) obtained the enhanced drag for hindered diffusion of flexible macromolecules as

$$K_r = 1 - 2.848\lambda + 3.269\lambda^2 - 1.361\lambda^3 \quad (2.13)$$

For small values of λ ($\lambda < 0.1$) of hard spherical molecules interacting with the pore wall by a "hard sphere" potential, the equation of Brenner and Gaydos(1977) is accurate, where

$$K_r = \frac{1 + \frac{9}{8}\lambda \ln \lambda - 1.539\lambda}{(1-\lambda)^2} \quad (2.14)$$

The ratio of effective to bulk diffusivity, which is usually expressed as a function of the ratio of some molecule size to pore size, indicates quantitatively the hindered effect on diffusion rate, generally defined by the production of steric and viscous drag factors

$$\frac{D_e}{D_\infty} = F(\lambda) = K_p K_r \quad (2.15)$$

Pappenheimer (1953) used Ferry's steric factor and Ladenburg's viscous drag factor to describe the restriction to diffusion and proposed the following equation

$$\frac{D_e}{D_\infty} = \frac{(1-\lambda)^2}{1+2.4\lambda} \quad (2.16)$$

Renkin(1954) combined the Ferry's steric factor and the Pappenheimer's viscous drag effect, giving the hindered diffusivity as the so-called Renkin equation

$$\frac{D_e}{D_\infty} = (1-\lambda)^2(1-2.104\lambda+2.089\lambda^3-0.948\lambda^5) \quad (2.17)$$

The validity of the Renkin equation has been verified by most hindered diffusion studies with membranes (Cannell and Rondelez, 1980; Beck and Schultz, 1970; 1972; Kathawalla and Anderson, 1988; Kathawalla et al., 1989). On the other hand, some other investigators stated that their results were not in good agreement with the Renkin equation. To name a few, Bohrer et al. (1987) found that the reduction in D_e for the star branched polymers was much larger than for the linear polymers of same hydrodynamic radii. The magnitude of the decrease did not agree with a theoretical model of hindered diffusion from Renkin

equation, however, the data were in qualitative agreement with size exclusion chromatography of branched polymer molecules. Davidson and Deen (1988; 1988a) showed that the effective diffusivities of ficoll (crosslinked structure) were in excellent agreement with those predicted by a hydrodynamic theory of Renkin equation for a solid spherical solute, while the D_e 's for linear poly(ethylene oxide) were between those predicted for a solid sphere and for a flexible linear polymer (Casassa's equation (2.9)). In contrast, linear poly(vinylpyrrolidone) and nearly linear dextran diffused more rapidly than predicted by either theory.

There have been other hindered diffusion models developed. For hard spherical molecules interacting with the pore wall by a "hard sphere" potential, Brenner and Gaydos (1977) used the following equation when the ratio of molecule to pore radius λ is less than 0.1,

$$\frac{D_e}{D_\infty} = 1 + \frac{9}{8}\lambda \ln \lambda - 1.539\lambda \quad (2.18)$$

When λ approaches 1, Mavrovouniotis and Brenner (1986) showed that

$$\frac{D_e}{D_\infty} = 0.984(1-\lambda)^{9/2} \quad (2.19)$$

Beck and Schultz (1970; 1972) used the following empirical equation to correlate their membrane diffusion data

$$\frac{D_e}{D_\infty} = (1-\lambda)^z \quad (2.20)$$

where z is a constant and equal to 4 as $\lambda < 0.2$. Uzelac and Cussler (1970) suggested a modified Stokes-Einstein equation as

$$D_e = \frac{kT}{6\pi\eta r_m K_r} \quad (2.21)$$

and found substantial agreement for experimental data involving the diffusion of polystyrene latex through membranes. Conlon and Craven (1972) studied the diffusion of polystyrenes with membranes and proposed the following equation

$$\frac{D_e}{D_\infty} = \exp\left(-\frac{\delta G^*}{RT}\lambda\right) \quad (2.22)$$

where R is the gas constant, δG^* is the sum of the free energy of interaction between the particles and pores and that between the particles and solvent. The best fit of their data gave the value of δG^* to be $2RT$.

Finally, the scaling theory is of importance when studying the diffusion of flexible polymers. By modeling a flexible polymer chain trapped in a cylindrical pore as an elongated cigar with elementary units of the same size as the pore diameter, Gennes and co-workers made the scaling prediction (Gennes, 1979; Brochard and Gennes, 1977)

$$\frac{D_e}{D_\infty} \sim \lambda^{-2/3} \quad (2.23)$$

which is equivalent to $D_e \sim M^{-1}$ for good solvent ($D_e \sim D_\infty \lambda^{-2/3} \sim M^{-1}$).

Based on the above literature it can be seen that hindered diffusion occurred in the diffusion of macromolecules through membranes, and the hindered diffusion rate could be related somehow to the ratio of the molecule size to the pore size. However, neither of the above hindered diffusion models is universally applicable for different diffusion systems.

Hindered Diffusion in Alumina, Silica and Porous Catalysts

Porous alumina and silica have been widely used as catalyst supports in heterogeneous catalysis. Several studies on hindered diffusion have been conducted with alumina, silica and metal supported porous catalysts. Most of the investigators tried to correlate their diffusion data with the theoretical models developed for membranes. Some studies showed that their data could be well represented by the Renkin equation (Chantong and Massoth, 1983; Limbach and Wei, 1990; Tsai et al., 1991; Rhee and Guin, 1994), while others observed the agreement of their results with the Beck and Schultz's power law of different z values ranging from 3.5 to 5.2 (Chantong and Massoth, 1983; Spry and Sawyer, 1975; Cheng et al., 1990; Tsai et al., 1991; Lee et al., 1991; 1991a). Guo et al. (1990) used the Davidson and Deen equation (equation 2.13) and showed satisfactory agreement of the theoretical prediction with their polystyrene diffusion data in silica.

On the other hand, due to the different pore structures between membranes and porous alumina and silica, some different results have been observed, and different hindered diffusion concepts were proposed. Satterfield et al. (1973) studied hindered diffusion of binary systems of paraffins and hydrocarbons and of aqueous solutions of sugars in homogeneous silica-alumina catalyst beads of 3.2 nm pore diameter with λ ranging from 0.1 to 0.5. They combined the solute adsorption on the pore wall into the pore concentration term and defined the partition factor K_p to be the ratio of concentration inside the pore (including both fluid concentration and surface adsorption) to that outside the pore, in which the value of K_p could be much larger than unity, depending on the solute adsorption strength. It was found that this K_p factor was approximately

unity for solutions of saturated hydrocarbons and aqueous solutions of salts and sugars, even when the solute molecules had critical diameters one-half the diameters of the pores. These results were in contrast to the theoretical hindered diffusion predictions and implied the absence of a geometric exclusion effect. Using their definition for the partition factor, they obtained the following effective diffusivity expression

$$D_e = \frac{K_r}{\tau} D_\infty \quad (2.24)$$

which contains neither porosity factor ϵ nor partition factor K_p . For nonadsorbing solute, they showed that the logarithm of the ratio of effective to bulk diffusivities decreased linearly with increasing ratio of solute critical diameter to pore diameter, viz.

$$\frac{D_e}{D_\infty} = \exp(-0.85 - 4.6\lambda) \quad (2.25)$$

By introducing a tortuosity of 2.3 obtained by extrapolating D_e/D_∞ as λ approaches zero, the above equation was written as

$$K_r = \frac{D_e \tau}{D_\infty} = \exp(-4.6\lambda) \quad (2.26)$$

Prasher and Ma (1977), who studied the hindered diffusion of hydrocarbons in microporous alumina pellets, used a different definition for the effective diffusivity

$$D_e = \frac{D_\infty}{K_p \tau} f(r_m, r_p) \quad (2.27)$$

where the factor K_p included both partition and surface adsorption coefficient, and $f(r_m, r_p)$ was some function of the solute radius r_m and pore radius r_p . They

suggested the following empirical equation (Prasher and Ma, 1977; Prasher et al., 1978)

$$\frac{D_e K_p \tau}{D_\infty} = \exp(b\lambda^3 + a) \quad (2.28)$$

where a and b are constants obtained from the best fit of the experimental data.

Chantong and Massoth(1983) studied the hindered diffusion of polyaromatic compounds through alumina of different pore sizes with $\lambda < 0.4$, and proposed the following equation

$$\frac{K_p K_r}{\tau} = \frac{D_e}{D_\infty \epsilon} = \exp(-4.5\lambda - 0.23) \quad (2.29)$$

From the extrapolation of $K_p K_r$ as λ approaches zero they obtained the value of tortuosity as 1.3, and rearranged the above equation as

$$K_p K_r = \frac{D_e \tau}{D_\infty \epsilon} = 1.03 \exp(-4.5\lambda) \quad (2.30)$$

The effect of temperature was investigated by Seo and Massoth(1985) who obtained the following relationship,

$$K_p K_r = \exp\left(-\lambda \exp\left(\frac{1.30}{T} - 2.62\right)\right) \quad (2.31)$$

where T is the absolute temperature.

Some other results conflicting with hindered diffusion theory have also been observed in the diffusion of polystyrenes with porous glasses (Colton et al., 1975; Giddings et al., 1977; Kline and Grüneberg, 1981), which showed significantly lower and essentially constant effective diffusivities. For example, Colton et al. (1975) studied the diffusion of polystyrenes of molecular weight from 600 to 670000 in leached borosilicate glass cubes of 2.5 to 47.6 nm pore sizes and

found that the ratio of effective to bulk diffusivities was constant for different polystyrene sizes. They suggested that the random coiling polystyrenes behaved like free-draining macromolecules, and for restricted diffusion the effective size scale of the polymer was comparable to that of the monomer unit. On the other hand, Bishop et al. (1989) stated that the significantly lower and essentially constant effective diffusivities with different molecule sizes could be due to a large boundary layer resistance.

In an attempt to minimize diffusional limitations, catalysts with bimodal pore size distribution have been utilized. Lee et al. (1991a) proposed a random-pore model for hindered diffusion in bidispersed pores, in which it was assumed that diffusion was hindered only in micropores, rather than in macropores. A qualitative criterion for micropore-diffusion control, being relatively small macroporosity and/or high catalyst pellet density, was proposed. They suggested that increasing the size of micropores could be more effective than incorporating macropores alone to reduce intraparticle diffusion resistance for hydrotreating catalysts. On the other hand, Rhee and Guin (1993, 1994) used the following equation to estimate the effective diffusivity of a bimodal catalyst in their studies of a coal liquefaction process,

$$D_e = \frac{D_\infty}{\tau} (\epsilon_1 F(\lambda_1) + \epsilon_2 F(\lambda_2)) \quad (2.32)$$

where the subscripts 1 and 2 represented the properties of macro- and micropores respectively.

For used catalysts, the pore geometry may be changed due to metallic and/or carbonaceous deposition by blocking or choking the pores and decreasing the pore diameter. Thus, intrapore diffusion can also be affected by catalyst deactivation. It has been observed that as coke content (Muegge and Massoth,

1991) or catalyst age (Guin et al., 1986; Zhang et al., 1995) increased, the effective diffusivity decreased. Guin et al. (1986) studied intrapore diffusion in the catalysts used for hydrotreatment of coal derived liquid and observed substantial reductions, of up to 2 orders of magnitudes, in effective diffusivity. The tortuosity factor was found significantly increased by the pore blockage resulting in longer diffusion path lengths as well as changes in pore constrictivity (ratio of maximum to minimum cross section). Johnson et al. (1986) studied the changes in effective diffusivity on resid deactivated HDS catalysts and found that the deactivation process lowered the D_e values by a factor of over 500 resulted from a wedge-type deposit of both the coke and metals. Prasher et al. (1978) showed that the hindered diffusion in alumina based catalysts was enhanced during the hydrocracking of residuum process. They explained the reduction in effective diffusivity by the increase in pore constrictivity and decrease in pore connectivity due to the coke and metal deposits. Haynes and Leung (1983) proposed a "parallel mechanism" of deposits in cylindrical pore geometry and suggested a relationship for the ratio of effective diffusivity with and without the effect of deposit

$$\frac{D_e}{D_{e0}} = \frac{(1-\lambda)^4}{(1-\lambda_0)^4} \left(\frac{\lambda_0}{\lambda} \right)^2 \quad (2.33)$$

where λ and λ_0 were the ratios of solute size to pore size with and without the deposit effects respectively. For bimodal catalyst, Leung and Haynes (1984) showed experimentally that the deposit was mainly in the micropore region, rather than in macropores. By considering the hindered diffusion in micropores with uniform deposition they developed the following equation

$$\frac{D_e}{D_\infty} = \epsilon_1^2 + (1 - \epsilon_1)^2 \epsilon_2^2 \lambda_0^4 \left(\frac{1}{\lambda} - 1\right)^4 + \frac{4\epsilon_1(1 - \epsilon_1)\epsilon_2^2 \lambda_0^4 \left(\frac{1}{\lambda} - 1\right)^4}{1 + \epsilon_2^2 \lambda_0^4 \left(\frac{1}{\lambda} - 1\right)^4} \quad (2.34)$$

where ϵ_1 and ϵ_2 were the initial (free of deposit) macro- and microporosities respectively. As $\lambda=1$ the micropores are effectively plugged and only the macropores contribute to intraparticle mass transfer, reducing the above equation to

$$\frac{D_e}{D_\infty} = \epsilon_1^2 + (1 - \epsilon_1)^2 \epsilon_2^2 (1 - \lambda_0)^4 + \frac{4\epsilon_1(1 - \epsilon_1)\epsilon_2^2 (1 - \lambda_0)^4}{1 + \epsilon_2^2 (1 - \lambda_0)^4} \quad (2.35)$$

It is worth pointing out here that in hindered diffusion studies, the dimensions of the diffusing molecule and porous pore are important factors. Due to the nonspherical configurations of the diffusing molecules and the nonuniformities and irregularities of pore structures, several methods have been used to estimate the sizes of pores and nonspherical molecules, as shown in Tables 2.1 and 2.2. Usually the pore size of alumina was measured by mercury porosimetry, while the pore size of membrane was estimated by fluid flow rate measurement based on the Poiseuille equation. As for the determination of nonspherical solute molecule sizes, several different methods have been employed, e.g., the critical diameter, the Stokes-Einstein diameter, the radius of gyration and the molar volume diameter. Limbach and Wei (1990) used different length scales in the two hindrance factors, in which the molecule size was best described by a mean projected molecule radius for partitioning and a Stokes-Einstein radius for hydrodynamic drag.

From above literature review, it can be seen that several hindered diffusion models have been suggested for both alumina and membranes in terms of the

Table 2.1 Estimation methods for pore size

porous materials	estimation methods	references
Membranes	flow rate ^(a)	Davidson and Deen, 1988; Beck and Schultz, 1972; Bohrer et al., 1984; Cannell and Rondelez, 1980; Bohrer et al., 1987;
	TEM ^(b)	Malone and Anderson, 1978.
alumina, silica	Hg porosimetry	Cheng et al., 1990; Guo et al., 1990; Tsai et al., 1991; Colton et al., 1975; Satterfield et al., 1978; Lee et al., 1991a; Chantong and Massoth, 1983.
	$4V_p/S$	Satterfield et al., 1973.

(a) Based on the Poiseuille equation

$$d_p = (128 \eta L Q / n \pi A_u \Delta P)^{1/4}$$

where A_u , L , and n are the exposed area, the length of the pores, and the pore number density of the membrane respectively, Q , ΔP are the flow rate and pressure drop across the membrane respectively, and η is the fluid viscosity.

(b) Transition Electron Microscopy.

Table 2.2 Estimation methods for nonspherical molecule size

molecular size	molecules	references
critical diameter ^(a)	paraffins	Satterfield et al., 1973; Rhee and Guin, 1994.
	polyaromatics	Tsai et al., 1991; Lee et al., 1991; 1991a; Chantong and Massoth, 1983.
	polymers	Davidson and Deen, 1988; Bohrer et al., 1984; Cannell and Rondelez, 1980.
	porphyrins salts	Kathawalla et al., 1989. Satterfield et al., 1973.
hydrodynamic diameter ^(b)	polystyrenes	Guo et al., 1990.
radius of gyration ^(c)	polystyrenes	Colton et al. 1975; Rhee and Guin, 1994; Satterfield et al., 1978.
molar-volume diameter ^(d)	hydrocarbons	Prasher and Ma, 1977; Prasher et al., 1978.

(a) The critical molecule diameter was the diameter of smallest cylinder through which the molecule can pass without distortion, usually calculated from the bond lengths, bond angles and Van der Waals radii.

(b) The hydrodynamic diameter was calculated by the Stokes-Einstein equation.

(c) The radius of gyration was defined as the square root of the mean square distance away from the center of gravity of a random coiling polymer.

(d) The molal-volume diameter was derived from molal-volume at the normal boiling point by assuming the molecule to be spherical.

hindrance factor $F(\lambda) = K_p K_r$. As shown by Massoth and coworkers (Chantong and Massoth, 1983; Tsai et al., 1991), these different empirical or semiempirical expressions are basically the same. Furthermore, hindered diffusion behavior in alumina is different from that in membranes. First, unlike the straight and uniform pores in membranes, the pores in alumina are rather tortuous and irregular. Second, studies have shown that during the diffusion in the pores of porous alumina, both surface adsorption and pore diffusion may occur simultaneously in the pores (Satterfield et al, 1973; Chantong and Massoth, 1983), whereas only pore diffusion takes place in the pores for membrane systems. Additionally, during the catalyst usage the pore size of the catalyst is reduced or even plugged due to the deposition of carbonaceous and/or metals (Guin et al., 1986; Haynes and Leung, 1984; Johnson et al., 1986; Prasher et al., 1978), which further enhances the diffusional limitation. Finally, since alumina, silica and supported porous catalysts are usually made as powders or extrudates of some shapes, direct measurements of effective diffusivities were usually performed in a finite diffusion cell containing a particle holding basket with either solute uptake or desorption (Guin et al., 1986; Prasher and Ma, 1977; Satterfield et al., 1973; Rhee and Guin, 1994; Chantong and Massoth, 1983; Tsai et al., 1991), whereas hindered diffusion studies with membranes were normally conducted in a diaphragm diffusion cell (Malone and Anderson, 1978; Conlon and Craven, 1972; Bohrer et al., 1987; Kathawalla and Anderson, 1988; Guillot et al., 1985; Cannell and Rondelez, 1980; Beck and Schultz, 1972; Davidson and Deen, 1988).

Asphaltene Diffusion

Characterization of Asphaltenes

Asphaltene is a generic term describing a complex mixture of macromolecules which are soluble in aromatic hydrocarbons, such as benzene or toluene, but insoluble in certain paraffins, such as pentane or hexane. Thus, the characteristics of one asphaltene may be somewhat different from that of another, depending on the origin from which it is derived and the procedure through which it is obtained. The term "asphaltene" originally was used to denote a heavier petroleum sub-fraction, but now has been extended to depict similar fractions of materials derived from coal, oil shale or other sources. Asphaltenes are thus described by an operational solubility classification, rather than a detailed set of chemical criteria.

Many studies have been conducted to characterize petroleum and coal-derived asphaltenes. Pfeiffer and Saal (1940) first assumed that the asphaltenes were solvated in the oil by the molecules in the non-asphaltenic fraction to form 'micelles', being a macromolecular structure. That is, the micelles are composed of both asphaltenic and non-asphaltenic molecules. Yen (1976) proposed a coal asphaltene cluster model, a hypothetical cross-sectional view of which is presented in Figure 2.2. According to this model, asphaltene particles consist of condensed aromatic rings coupled by π - π bonds (bond strength: *ca.* 10-15 kcal/mol) existing between condensed aromatic rings and by hydrogen bonds (bond strength: *ca.* 5 kcal/mol) occurring between acidic and basic functionalities. Thus the various subunits could be considered to be held together by weak hydrogen bonding and Van der Waals forces. Steedman (1985) has provided a relatively comprehensive

Figure 2.2 Hypothetical cross-sectional view of coal asphaltenes proposed by Yen (1976).

review of asphaltenes derived from coal, and Bunger and Li (1981) collected some of the useful studies on the chemistry of asphaltenes.

Recently, Sane et al. (1992) and Jennings (1990) showed that the asphaltene particles were the results of association of smaller subunits, themselves made of condensed aromatic sheets. Baltus and coworkers attempted to model the asphaltene structure as multisubunits (Baltus and Anderson 1983; 1984; Baltus, 1989; Nortz et al., 1990). More recently, Galstsev et al. (1995) studied asphaltene association in crude oil (Russia Harjaga) using electron-nuclear double resonance (ENDOR) spectroscopy and found that most of the asphaltene molecules were associated with each other in the range from room temperature up to 90 °C, with the core of the associate being a stack of condensed aromatic sheets of characteristic radius of around 10 Å. The outer coordination sphere of a micelle with the asphaltene associate as a core was assumed to be sufficiently labile to allow the low-molecular-weight solvents used to reach the core, irrespective to their polarity. Storm and Sheu (1995) showed that the asphaltenic molecules (derived from the vacuum residue of Ratawi crude oil) were not macromolecules, instead, around 100 asphaltenic molecules with molecular weights of around 1000, spontaneously self-associated to form micelle-like particles. Sheu et al. (1992) confirmed experimentally the existence of a critical concentration, above which self-association of petroleum asphaltene subunits occurred, a phenomenon similar to that occurring in surfactant systems.

The sizes of asphaltenes at different conditions were also investigated. By using SAXS (Small Angle X-ray Scattering), Kim and Long (1979) indicated that the asphaltenes from Jobo atmospheric resid had a radius of gyration of about 25 Å and exhibited the same size in all the solvents used, with the size being independent of concentration. While the Tia Juana asphaltenes showed smaller

particle size with better solvents, and the size of lower molecular weight bituminous coal asphaltenes appeared to be below the resolution of their SAXS employed, ca. 10 Å. Xu et al. (1995) studied Athabasca asphaltenes in toluene using SAXS and found that in most cases, the asphaltene sizes were concentration independent. Only small proportion of the particles appeared to form larger aggregates due to interparticle correlation, with the size being decreased with increasing concentration of the dispersion. The majority of the polydispersed spheres was found to have a main distribution peak at an average radius of 33 Å, with the size distribution being slightly skewed to the higher-value side which was also observed by Storm et al. (1993). On the other hand, Jennings (1990) found that the apparent size of petroleum asphaltenes was dependent on factors such as solvent composition, asphaltene concentration, and temperature.

The properties of coal and petroleum asphaltenes were compared by several investigators (Bockrath and Schweighardt, 1981; Gorbaty and Ouchi, 1981). The results of one such study, conducted by Bockrath and Schweighardt (1981), are provided in Table 2.3. As shown in this table, a major difference between coal and petroleum asphaltenes is the average molecular weight, with coal asphaltenes having a considerably lower number average molecular weight and being more highly functionalized. Other major differences are as follows; The aromaticity of coal-derived asphaltene ($f_a=0.6-0.7$) is higher than that of petroleum-derived asphaltene ($f_a=0.4-0.5$); the aromatic ring systems within petroleum-derived asphaltenes are much more condensed ($H_{ar}/C_{ar}=0.3-0.5$) than those of coal derived asphaltenes ($H_{ar}/C_{ar}=0.5-0.7$); the substituents of the petroleum-derived asphaltenes are longer ($n=4-6$) than those of coal derived asphaltenes ($n=1-2$); and the aromatic system of petroleum-derived asphaltenes is

Table 2.3 Comparisons of Properties Between Petroleum
and Coal-Derived Asphaltenes (Bockrath and Schweighardt, 1981)

Property	Coal Asphaltenes	Petroleum Asphaltenes
Number-average MW	400-800	2000-20,000
Weight percent carbon	84-89	80-86
Weight percent hydrogen	5.8-7.3	7.7-9.3
Weight percent oxygen	2-6	1-2.7
Weight percent nitrogen	1-3	0.3-0.5
Weight percent sulfur	0.1	3-9.3
Percent ash by low or high temperature	<0.1	<2
Aromaticity, by NMR	0.6-0.7	0.4-0.55
H/C	0.94	1.12
Forms of oxygen	OH, -O-	OH, -C=O, -O-
Forms of nitrogen
Metals	iron 100-300 ppm titanium 20-50 ppm	vanadium 100-400 ppm nickel 50-150 ppm

extensively substituted (50%-70%), whereas coal-derived asphaltenes are more sparingly substituted (30%-50%).

Hindered Diffusion of Asphaltenes

Due to the comparability of the sizes of reactant molecules to those of catalyst pores, intrapore diffusion has been widely observed in the hydrotreatments of heavy crudes, resids, coal derived liquids, and other macromolecular feeds. Ho and Weller (1979) indicated that the conversion of West Virginia coal and the yield of asphaltenes in the presence of Co-Mo/Al₂O₃ increased as pore diameter increased from 100 to 500 Å. Eigenson et al. (1977) found increases in the catalytic activity of MoO₃/Al₂O₃ when pore size was increased from 70 to 150 Å. Song et al. (1991) showed that the conversions of asphaltenes derived from Akabira coal and Athabasca oil sand bitumen increased with increasing catalyst pore diameters up to 290 Å and then remained constant or decreased up to 730 Å. Recently, Ying et al. (1995) found that a large-pore catalyst (252 Å average pore diameter) was more active than a commercial catalyst (99 Å average pore diameter) for hydrodemetalization, equally active for hydrodesulfurization, and less active for hydrodenitrogenation. Similar pore size effects have been observed with catalysts for coal liquefaction (Sooter and Crynes 1975; Yen et al. 1976; Kang, 1983). Curtis et al. (1983) and Gollakato et al. (1984) stated increased yields of pentane soluble oils for catalytic coal liquefaction as the sizes of the catalyst particles decreased. Spry and Sawyer (1975) showed that effectiveness factors could be quite low for reaction of coal and petroleum asphaltenes. Furthermore, the effect of internal diffusion was much more significant for aged catalysts, as indicated by other investigators (Tsai, 1985;

Zhang et al. 1995). All these results indicated the presence of intrapore diffusional resistances in the catalyst pores during macromolecular hydrotreating processes.

The recognition of pore diffusion limitations such as noted above in coal conversion has led to the development of catalyst supports with macro-micro, i.e. bimodal, pore structures in an attempt to minimize these effects (Guin et al., 1989). In this attempt, the macropores could provide the access of reaction molecules to the catalyst active sites, while the micropores could provide sufficient surface area for the catalytic reaction. This effect resulted in an optimal catalyst pore size, where the increased surface area gained with smaller pores was balanced by decreased Brownian mobility of the reactants within the pores. Inoguchi (1977) observed that an optimum in catalyst activity for residua desulfurization occurred with pore radius around 100 Å, while the optimal rate for vanadium removal occurred with 130 Å pores. Attempts have been made to develop mathematical models, incorporating a competition between hindered diffusion and larger surface area as pore radius becomes smaller, to arrive at predictions for optimal catalyst pore size (Jaffe 1981; Ruckenstein and Tsai 1981). All these results showed that a better understanding of the hindered diffusion mechanism of asphaltenes in porous catalyst is of importance in the hydrotreating processes.

Direct measurements of asphaltene intrapore diffusion in porous catalysts are recent and very few in number. Shimura et al. (1982) were the first who conducted the asphaltene diffusion in porous catalysts using uptake experiments. Mieville et al. (1989) measured the diffusion of petroleum asphaltenes in toluene through porous catalysts by uptake experiments. They treated the asphaltenes as a monodispersed material and used a UV detector at 510 nm wavelength to monitor

the concentration change in the solution. A linear adsorption isotherm was found for the Jobo asphaltene/toluene/alumina system. In their study of several asphaltenes, Hondo asphaltenes were found to have the highest diffusivity which was attributed to their smaller average aromatic clusters and thus smaller particle sizes.

More recently, by using kinetic reaction data, Li et al. (1995) investigated hindered diffusion of Kuwait residual oils in CoMo/Al₂O₃ catalysts at hydrotreating conditions. They indicated two hindered diffusion regimes for both HDM and HDS reactions, with the relationship between D_e/D_∞ and λ being expressed by the Beck-Schultz's power law with different z values. For $\lambda < 0.3$, z values were 3.5 and 3.8 for HDS and HDM respectively. While at higher λ , e.g., $0.5 < \lambda < 0.9$, z values decreased to 0.5 and 1.0 respectively, indicating a smaller hindered effect, which was explained by the interactions of molecule-pore and molecule-molecule.

Several other studies on asphaltene diffusion were conducted with membranes. Baltus and co-workers (Baltus and Anderson 1983; 1984) studied the relationship between the diffusivities of petroleum asphaltenes and pore sizes using track-etched mica membranes with varying pore radius of 80-2200 Å. The asphaltenes were divided into five regions and analyzed in term of size fractions (or molecular weights) defined by their elution characteristics from SEC (size exclusion chromatography). The results showed very strong pore size (in the range 70-500 Å pore radius) effects on diffusivities of asphaltene fractions when the equivalent polystyrene molecular weights were larger than 3000, and there was a broad variation (by a factor of up to 10) of diffusivities among the different asphaltene fractions. Using the exponential equation $D_e/D_\infty = \exp(-4.6\lambda) = \exp(-4.6r_m/r_p)$, they obtained the bulk diffusivity D_∞ and molecule size r_m of each

asphaltene fraction by extrapolating the experimental values of $\ln(D_e)$ vs. $1/r_p$ as $1/r_p$ approached zero, with the intercept being $\ln(D_\infty)$ and slope related to r_m . On the other hand, the hydrodynamic radius of asphaltene fraction was also calculated from the Stokes-Einstein equation with D_∞ being obtained from the above method. The molecule radii of each asphaltene fractions from above two methods were in excellent agreement and verified the hindered diffusion theory. The effective diffusivity of each fraction was found to relate to the ratio of molecule size to pore size by the Renkin equation. These studies have been continued by Kyriakou et al. (1988) and Nortz et al. (1990) with various fractionated samples from heavy oils by using polycarbonate membranes and Taylor-dispersion-type experiments.

Sane et al. (1988) used a concentration average effective diffusivity to describe the hindered diffusion of petroleum asphaltenes in membranes and found that the effective diffusivity of asphaltenes was a function of diffusion time. Recently, Sane et al. (1992) introduced the dynamic concepts of asphaltene diffusion, according to which the properties such as the effective diffusivity of the asphaltenes were not considered to be time-independent constants during the diffusion process. Through the dependence of transport properties on temperature and concentration, they found that the activation energies for asphaltene diffusion were from 6 to 13 Kcal/mol, which were similar to typical values of 14 to 20 for association energies of individual asphaltene sheets as reported by Dickie and Yen (1967), rather than the usually observed activation energies of the order of 1 Kcal/mol for diffusion. These results, along with other experimental data, were explained by the dynamic behavior of asphaltenes during membrane diffusion.

In the studies of asphaltene diffusion, some investigators attempted to correlate the behavior of asphaltenes with polystyrenes, the latter being widely

used as calibration standards in SEC analysis. Shimura et al. (1982) stated that the mass transfer characteristics of polystyrenes could provide a good model for petroleum asphaltenes, however, Baltus and Anderson (1983) showed that molecular diffusivities for polystyrenes were about a factor of two larger than those for asphaltene fractions with same SEC elution volumes. It is commonly assumed that SEC elution volume is correlated with Stokes-Einstein radius (or some other measure of "hydrodynamic radius"), while the microscopic structure of asphaltenes resembles a stacked-sheet geometry (Yen, 1976), which is quite different from the random coil configuration of polystyrene.

Conclusions

Diffusion in the pores of a porous medium may occur by several mechanisms. Hindered diffusion occurs when the sizes of the diffusion molecules are comparable to those of the porous pores through which they are diffusing. Hindered diffusion phenomena have been widely observed in variety of applications, e.g., membrane separation and catalytic hydrotreatment of asphaltenes, heavy oils, coal derived liquids, etc. Hindered diffusion limitations could be further enhanced in the spent catalysts due to the deposition of coke and metals in the pores.

In previous studies, most investigators related hindered diffusion rate to the ratio of the molecule size to the pore size. Although several hindered diffusion models have been suggested, none of the models is universally applicable for different diffusion systems, particularly in the presence of asphaltenes, being mixtures of highly dispersed components differing greatly in molecular weights or sizes. In order to better understand hindered diffusion behavior and aid in the design of catalysts and catalytic reactors as well as the selection of operation conditions, further studies on hindered diffusion are needed.

III HINDERED DIFFUSION MODEL DEVELOPMENT AND NUMERICAL SOLUTION

Introduction

In order to describe hindered diffusion of solute molecules in the pores of porous catalysts, a mathematical model is needed. The diffusion parameters in the model can be determined by fitting the mathematical model to the experimentally observed diffusion data. Generally, in studies of this type, catalyst properties are considered to be uniform throughout the catalyst particles. However, in the model developed here, it is assumed that the values of porosity and pore size in the catalyst particles may be functions of radial position. This assumption, motivated by experimental results to be discussed in the following chapters, results in an effective diffusivity which is also a function of radial position inside the catalyst particle. Thus, the model presented here is somewhat more general than previously used models which assumed constant average values for catalyst properties and a resulting constant effective diffusivity (Guin et al., 1986; Chantong and Massoth, 1983; Zhang et al., 1995; Stiegel et al., 1982; Stephens and Stohl, 1984; Johnson et al., 1986; Prasher et al., 1978; Butt et al., 1975).

In this chapter, the hindered diffusion model was first developed. A numerical method was employed to solve the model equations. The accuracy of the numerical solution was verified by both material balance in the system and known solutions in several special cases.

Hindered Diffusion Model Development

The diffusion model developed here is based on the mass transport of solute molecules in a solvent through the catalyst particles in a finite diffusion bath. The porous catalyst particles prefilled with solvent are immersed in the finite well-stirred bath containing solute and solvent. Solute molecules diffuse into the porous particles where they are adsorbed onto the solid catalyst surface. As a result of this diffusion-adsorption process, the concentration of solute in the surrounding bath is depleted.

The model developed in this study also assumes negligible solute transport by surface diffusion, spherical catalyst particle geometry, negligible external fluid solid mass transfer resistance, and local adsorption equilibrium inside the particle pores. While most of these assumptions are generally valid in system of this type, they are nevertheless examined in a series of preliminary experiments. The error involved in modeling the cylindrical extrudates as equivalent spheres is only around 5%, providing an appropriate length scale (radius of equivalent sphere) based on the ratio of particle volume to external surface area is used (Ma and Evans, 1968). The model also incorporates hindrance effects present when the catalyst pore size approaches the size of the diffusing solute molecule.

Based on the above assumptions, the following mathematical model can be derived. The mass balance for the solute in the porous particles is:

$$\frac{\partial(K_p e C)}{\partial t} + \frac{\partial(\rho_p q)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 D_e \frac{\partial C}{\partial r}) \quad (3.1)$$

with initial and boundary conditions:

$$C|_{\substack{t=0 \\ r=R}} = 0 \quad (3.2)$$

$$\frac{\partial C}{\partial r}|_{r=0} = 0, \quad C|_{r=R} = C_b(t) \quad (3.3)$$

A material balance for the solute in the bath yields:

$$\frac{d(V_b C_b)}{dt} = -4\pi R^2 k' (D_e \frac{\partial C}{\partial r})|_{r=R} \quad (3.4)$$

with the initial condition:

$$C_b|_{t=0} = C_{bi} \quad (3.5)$$

In above equations, D_e is the effective pore diffusivity expressed by

$$D_e = \frac{\epsilon K_p K_r}{\tau} D_\infty \quad (3.6)$$

in which K_p and K_r factors are hindered diffusion parameters due to steric and hydrodynamic factors, respectively. These two hindrance factors will be estimated by Ferry's steric equation (Ferry, 1936) and Pappenheimer's viscous drag expression (Pappenheimer et al., 1951), respectively, derived for spherical solutes diffusing in cylindrical pores

$$K_p = (1 - \lambda)^2 \quad (2.7)$$

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (2.11)$$

Other mathematical expressions have been developed for these factors as shown in the preceding chapter, however, they gave essentially the same numerical values as equations (2.7) and (2.11). A unique aspect of the model developed here

is that these hindrance factors are evaluated locally as a function of radial position inside the catalyst particles. However, the tortuosity factor τ in equation (3.6) is considered as a constant average value independent of radial position, although values of τ in some cases, e. g. spent catalysts, will generally differ from the value τ_0 for the fresh catalyst.

In the pore diffusion equation (3.1), q is the adsorption term, being usually expressed by several equilibrium adsorption isotherms, viz.,

$$\text{linear isotherm: } q = KC \quad (3.7)$$

$$\text{Freundlich isotherm: } q = mC^{\frac{1}{n}} \quad (3.8)$$

$$\text{Langmuir isotherm: } q = \frac{q_m K_L C}{1 + K_L C} \quad (3.9)$$

Figure 3-1 shows the behavior of these isotherms with some special values of isotherm constants.

By defining the following dimensionless variables, the above equations can be put into dimensionless forms, where the "0" subscript denotes properties of the fresh catalyst used as a reference state.

$$\xi = \frac{r}{R}, \quad t^* = \frac{D_{e0}}{K_{p0}\epsilon_0 R^2} \frac{\tau_0}{\tau} t, \quad \theta = \frac{C}{C_{bi}}, \quad \theta_b = \frac{C_b}{C_{bi}}, \quad \theta_q = \frac{q}{q_i} \quad (3.10)$$

$$g = \frac{K_p \epsilon}{K_{p0} \epsilon_0}, \quad h = \frac{K_p K_r \epsilon}{K_{p0} K_{r0} \epsilon_0} \quad (3.11)$$

$$E = \frac{\rho_p q_i}{K_{p0} \epsilon_0 C_{bi}}, \quad F = \frac{V_b \rho_p}{W K_{p0} \epsilon_0} \quad (3.12)$$

Figure 3.1 Comparison of different equilibrium adsorption isotherms

where, constant E indicates the ratio of equilibrium adsorption capacity to fresh catalyst pore fluid accumulation capacity, evaluated at initial diffusion conditions. F is the ratio of surrounding bath volume to the available fresh catalyst pore volume. Functions g and h embody the radial dependence of catalyst properties, and reflect the *local* degree of pore clogging. Two factors will be considered which affect the local values of g and h and thus the hindered diffusion rate, namely, the nonuniform coke/metal deposits in the pores of the particles due to catalyst deactivation, and the solute adsorption layer on the pore wall during the adsorption-diffusion process. The nonuniform deposits and the solute adsorption layer result in the nonuniform pore size through the particle radii and thus nonuniform value of λ . Therefore, the hindrance factors K_p and K_r , the porosity ϵ , and thus functions g and h , are dependent on the radial position. More detailed discussion on the dependence of radial position for functions g and h will be given in the following chapters.

Use of these variables gives the dimensionless diffusion model as

$$\frac{\partial(g\theta)}{\partial t^*} + E \frac{\partial(\theta_a)}{\partial t^*} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi}) \quad (3.13)$$

$$\theta|_{t^*=0} = 0 \quad \xi < 1 \quad (3.14)$$

$$\left(\frac{\partial \theta}{\partial \xi} \right) |_{\xi=0} = 0, \quad \theta|_{\xi=1} = \theta_b(t^*) \quad (3.15)$$

$$\frac{d\theta_b}{dt^*} = -\frac{3}{F} \left(h \frac{\partial \theta}{\partial \xi} \right) |_{\xi=1} \quad (3.16)$$

$$(\theta_b)|_{t^*=0} = 1 \quad (3.17)$$

in which the dimensionless adsorption θ_q for different isotherms can be expressed as

$$\text{linear isotherm: } \theta_q = \theta \quad (3.18)$$

$$\text{Freundlich isotherm: } \theta_q = \theta^{\frac{1}{n}} \quad (3.19)$$

$$\text{Langmuir isotherm: } \theta_q = \frac{(1+G)\theta}{1+G\theta} \quad (3.20)$$

where

$$G = K_L C_{bi} \quad (3.21)$$

It can be seen that for linear adsorption isotherm, θ_q is equal to θ , whereas for nonlinear isotherms, an additional parameter appears in the expression, i. e., n and G for Freundlich and Langmuir isotherms respectively.

Numerical Method

To simulate the experimental uptake data with the mathematical diffusion model, the above partial differential equations (PDEs) should be solved. Due to the complexity of these equations, usually an analytical solution can not be obtained. Thus we use the following numerical method to solve these PDEs.

We first rearrange the pore diffusion equation (3.13). The left hand of this equation can be rewritten as

$$\frac{\partial}{\partial t^*}(g\theta) + E \frac{\partial \theta_q}{\partial t^*} = g \frac{\partial \theta}{\partial t^*} + \theta \frac{\partial g}{\partial \theta_q} \frac{\partial \theta_q}{\partial \theta} \frac{\partial \theta}{\partial t^*} + E \frac{\partial \theta_q}{\partial \theta} \frac{\partial \theta}{\partial t^*} \quad (3.22)$$

then equation (3.13) can be rearranged as

$$(g + (E + \theta \frac{\partial g}{\partial \theta_q}) \frac{\partial \theta}{\partial \theta}) \frac{\partial \theta}{\partial t^*} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi}) \quad (3.23)$$

therefore

$$\frac{\partial \theta}{\partial t^*} = \frac{\frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi})}{g + (E + \theta \frac{\partial g}{\partial \theta_q}) \frac{\partial \theta}{\partial \theta}} \quad (3.24)$$

We use the Method of Lines (MOL) and a time integrator to solve the PDEs by setting up a grid system of N lines in ξ direction with equal grid line distance $\Delta \xi$, as shown in Figure 3.2, where

$$\Delta \xi = \frac{1}{N-1} \quad (3.25)$$

$$\xi_i = (i-1)\Delta \xi \quad (3.26)$$

in which, $i=1, 2, 3, \dots, N$.

At point i , the numerator of the right hand side in equation (3.24) can be expressed as

$$(\frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi}))_i = \frac{2}{\xi_i} h_i (\frac{\partial \theta}{\partial \xi})_i + (\frac{\partial h}{\partial \xi})_i (\frac{\partial \theta}{\partial \xi})_i + h_i (\frac{\partial^2 \theta}{\partial \xi^2})_i \quad (3.27)$$

Using central difference at point i for the derivatives in above equation, we have

$$(\frac{\partial \theta}{\partial \xi})_i = \frac{\theta_{i+1} - \theta_{i-1}}{2\Delta \xi} \quad (3.28)$$

$$(\frac{\partial h}{\partial \xi})_i = \frac{h_{i+1} - h_{i-1}}{2\Delta \xi} \quad (3.29)$$

Figure 3.2 Grid lines in a catalyst particle for numerical method.

$$\left(\frac{\partial^2 \theta}{\partial \xi^2}\right)_i = \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta \xi)^2} \quad (3.30)$$

hence, at point i , where $i=2, 3, \dots, N-1$,

$$\left(\frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi})\right)_i = h_i \frac{\theta_{i+1} - \theta_{i-1}}{(i-1)(\Delta \xi)^2} + \frac{(h_{i+1} - h_{i-1})(\theta_{i+1} - \theta_{i-1})}{4(\Delta \xi)^2} + h_i \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta \xi)^2} \quad (3.31)$$

At $i=1$, or $\xi=0$, according to the symmetry property at particle center,

$$\left(\frac{\partial h}{\partial \xi}\right)_{i=1} = \left(\frac{\partial \theta}{\partial \xi}\right)_{i=1} = 0 \quad (3.32)$$

We use L'Hopital's rule for the first term in the right hand side of equation(3.27)

$$\frac{2}{\xi_1} h_1 \left(\frac{\partial \theta}{\partial \xi}\right)_1 = 2h_1 \frac{\left(\frac{\partial}{\partial \xi} \left(\frac{\partial \theta}{\partial \xi}\right)\right)_1}{\left(\frac{\partial \xi}{\partial \xi}\right)_1} = 2h_1 \left(\frac{\partial^2 \theta}{\partial \xi^2}\right)_1 \quad (3.33)$$

thus at point $i=1$ or the particle center, equation (3.27) becomes

$$\left(\frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi})\right)_1 = 3h_1 \left(\frac{\partial^2 \theta}{\partial \xi^2}\right)_1 = 3h_1 \frac{\theta_2 - 2\theta_1 + \theta_0}{(\Delta \xi)^2} \quad (3.34)$$

where $(\theta)_0$ is a fictional point. Because of the symmetry at the particle center,

$$\theta_0 = \theta_2 \quad (3.35)$$

therefore, at $i=1$

$$\left(\frac{1}{\xi^2} \frac{\partial}{\partial \xi} (h \xi^2 \frac{\partial \theta}{\partial \xi})\right)_{i=1} = 6h_1 \frac{\theta_2 - \theta_1}{(\Delta \xi)^2} \quad (3.36)$$

At $i=N$ or $\xi=1$, using the boundary condition at the surface of catalyst particle we get

$$\left(\frac{\partial \theta}{\partial t^*}\right)_{i=N} = \frac{d\theta_b}{dt^*} = -\frac{3}{F} \left(h \frac{\partial \theta}{\partial \xi}\right)_{i=N} \quad (3.37)$$

We use a five point formula (Burden and Faries, 1989, p150) to evaluate the derivative in the right hand side of the above equation and obtain

$$\left(\frac{\partial \theta}{\partial t^*}\right)_N = \frac{h_N}{4F\Delta\xi} (-25\theta_N + 48\theta_{N-1} - 36\theta_{N-2} + 16\theta_{N-3} - 3\theta_{N-4}) \quad (3.38)$$

Now there are N equations for $i=1, 2, 3, \dots, N$. They are:

for $i=1$:

$$\left(\frac{\partial \theta}{\partial t^*}\right)_1 = \frac{6h_1 \frac{\theta_2 - \theta_1}{(\Delta\xi)^2}}{(g + (E + \theta \frac{\partial g}{\partial \theta_q}) \frac{\partial \theta_q}{\partial \theta})_1} \quad (3.39)$$

for $i=2, 3, \dots, N-1$:

$$\left(\frac{\partial \theta}{\partial t^*}\right)_i = \frac{h_i \frac{\theta_{i+1} - \theta_{i-1}}{(i-1)(\Delta\xi)^2} + \frac{(h_{i+1} - h_{i-1})(\theta_{i+1} - \theta_{i-1})}{4(\Delta\xi)^2} + h_i \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{(\Delta\xi)^2}}{(g + (E + \theta \frac{\partial g}{\partial \theta_q}) \frac{\partial \theta_q}{\partial \theta})_i} \quad (3.40)$$

for $i=N$:

$$\left(\frac{\partial \theta}{\partial t^*}\right)_N = \frac{h_N}{4F\Delta\xi} (-25\theta_N + 48\theta_{N-1} - 36\theta_{N-2} + 16\theta_{N-3} - 3\theta_{N-4}) \quad (3.41)$$

The initial conditions are:

at $i=1, 2, 3, \dots, N-1$

$$\theta_i|_{t^*=0} = 0 \quad (3.42)$$

at $i=N$

$$\theta_i|_{t^*=0} = 1 \quad (3.43)$$

Thus, given values of constants E and F and the expression for the adsorption isotherm θ_q , as well as the dependence of g and h on the radial position, we can solve these ODEs by using the IVP RK subprogram in the IMSL math package (IMSL, 1991), with the computer program shown in Yang (1996).

In practice, the numerical solution is expressed as either the dimensionless bath concentration or the fractional uptake as a function of dimensionless time. The fractional uptake is defined as the ratio of the total amount of diffusion solute entering the particles at any time to that at equilibrium,

$$\frac{Q_t}{Q_e} = \frac{C_{bi} - C_b}{C_{bi} - C_{b\infty}} = \frac{1 - \theta_b}{1 - \theta_{b\infty}} \quad (3.44)$$

where $\theta_{b\infty}$ is the dimensionless bath concentration at infinite time, which can be calculated from the mass balance between the particles and the bath solution at equilibrium, viz.,

$$V_b(C_{bi} - C_{b\infty}) = k' \int_0^R (\rho_p q_{\infty} + K_p \epsilon C_{\infty}) 4\pi r^2 dr \quad (3.45)$$

with dimensionless form of

$$F(1 - \theta_{b\infty}) = E\theta_{q\infty} + 3\theta_{\infty} \int_0^1 g\xi^2 d\xi \quad (3.46)$$

where

$$C_{b\infty} = C_{\infty}, \quad \theta_{b\infty} = \theta_{\infty} \quad (3.47)$$

Verification of the Numerical Solution

Mass Balance in Diffusion System

The numerical method discussed above can be verified by the mass balance of the diffusing solute in the diffusion system at each time step. According to mass balance, the amount of solute in the bath solution at initial conditions should be equal to the total amount of solute entering the particles and that remaining in the diffusion bath at any time, viz.,

$$VC_{bi} = VC_b + k' \int_0^R (\rho_p q + K_p \epsilon C) 4\pi r^2 dr \quad (3.48)$$

with dimensionless form of

$$1 = \theta_b + \frac{3}{F} \int_0^1 (E\theta_q + g\theta) \xi^2 d\xi \quad (3.49)$$

We use a Composite Trapezoidal rule (Burden and Faries, 1989, p177) with N-1 subintervals for the integration in above equation, as shown in the following equation and the computer program in Yang (1996),

$$\int_0^1 (E\theta_q + g\theta) \xi^2 d\xi = \frac{\Delta \xi}{2} ((E\theta_q + g\theta)_N + 2 \sum_{i=2}^{N-1} (E\theta_q + g\theta)_i) (\Delta \xi)^2 (i-1)^2 \quad (3.50)$$

The computation results showed that equation (3.49) was quite satisfied, with an error of less than 10^{-4} , depending on the model parameters used.

Comparison with Known Solutions

To verify the accuracy of above numerical method, the numerical solution of the mathematical diffusion model was compared to several known analytical and numerical solutions with different adsorption isotherms.

(1). Zero Adsorption

For zero adsorption, Crank (1975, p86) showed that the diffusion equations with constant bath concentration could be solved analytically, with the fractional uptake being expressed by

$$\frac{Q_t}{Q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 t^*) \quad (3.51)$$

In this case, if we give a zero value of E and a large value of F in our model, the diffusion equations can be solved numerically, with the following simplifications

$$g=h=1, \quad t^* = \frac{D_{e0}}{K_{p0} \epsilon_0 R^2} t, \quad \theta_q = 0, \quad \frac{\partial g}{\partial \theta_q} = 0, \quad E=0, \quad F \gg 1 \quad (3.52)$$

As shown in Figure 3.3, the numerical solution and the analytical solution agree quite well.

(2). Linear Adsorption Isotherm

If the amount of adsorption in pores is linearly dependent on the pore concentration, as shown in equation (3.7), the diffusion model can be solved analytically (Bird et al., 1960, p357), and the solution for dimensionless bath concentration is

Figure 3.3 Comparison of the numerical solution of this work with Crank's analytical solution (1975) for zero adsorption

$$\theta_b = \frac{B}{1+B} + \sum_{k=1}^{\infty} \frac{6B \exp(-b_k^2 t_l^*)}{B^2 b_k^2 + 9(1+B)} \quad (3.53)$$

where, the b_k 's are the non-zero roots of

$$\tan(b_k) = \frac{3b_k}{3+Bb_k^2} \quad (3.54)$$

and

$$t_l^* = \frac{t}{R^2} \frac{De}{K_p \epsilon + \rho_p K} \quad (3.55)$$

$$B = \frac{V_b}{\frac{4}{3} k' \pi R^3} \frac{1}{K_p \epsilon + \rho_p K} = \frac{V_b \rho_p}{W} \frac{1}{K_p \epsilon + \rho_p K} \quad (3.56)$$

On the other hand, for linear isotherm in the numerical solution, the mathematical model can be simplified, where

$$g=h=1, \quad t^* = \frac{D_{e0}}{K_{p0} \epsilon_0 R^2} t, \quad \theta_q = \theta, \quad \frac{\partial g}{\partial \theta_q} = 0 \quad (3.57)$$

The relationships between dimensionless parameters in the numerical method and those in the analytical solution are

$$B = \frac{F}{1+E} \quad (3.58)$$

$$t_l^* = \frac{t^*}{1+E} \quad (3.59)$$

Figure 3.4 compares the results of the numerical solution and the analytical solution with linear adsorption, indicating a satisfactory agreement of these two solutions.

(3). Langmuir Adsorption Isotherm

For diffusion with Langmuir adsorption isotherm and negligible pore fluid accumulation, the diffusion equations were solved numerically by Hashimoto et al. (1975), in which the dimensionless concentration was defined as

$$t_H^* = \frac{C_{bi}}{\rho_p q_i} \frac{D_e}{R^2} t \quad (3.60)$$

which relates to our definition by

$$t^* = \frac{t_H^*}{E} \quad (3.61)$$

Figure 3.5 shows several data points from Hashimoto's numerical solution. For comparison, we chose a larger value of E in our numerical solution, in which case the pore accumulation could be neglected, and the results are also shown in Figure 3.5. From this figure it can be seen that the results from both numerical solutions are about the same.

(4). Freundlich Adsorption Isotherm

For Freundlich adsorption isotherm, if the pore fluid accumulation is negligible and the bath concentration is constant, Gray and Do (1992) showed that the diffusion model had a good approximate analytical solution up to 50% fractional uptake, with the solution being expressed as

Figure 3.4 Comparison of the numerical solution with analytical solution for linear adsorption isotherm

Figure 3.5 Comparison of the numerical solution from this work with that from Hashimoto et al. (1975) for Langmuir adsorption isotherm.

$$\frac{Q_t}{Q_e} = 6\sqrt{\frac{np}{2(p+1)}}t_G^* - \frac{4(1+np)}{p+2}t_G^* \quad (3.62)$$

where n is the Freundlich constant and

$$p = \frac{4-n+\sqrt{n^2+4n+12}}{2(3n-1)} \quad (3.63)$$

$$t_G^* = \frac{t^*}{E} \quad (3.64)$$

For comparison of the analytical solution with the numerical solution of this work, Figure 3.6 shows the results obtained from these two methods. When the fractional uptake is less than 50%, these two solutions agree very well.

For Freundlich adsorption isotherm with negligible pore fluid accumulation, Hashimoto et al. (1975) also solved the diffusion equation numerically. Figure 3.7 compares the numerical solution from this work and that from Hashimoto et al. (1975), indicating a good agreement between these two numerical solutions.

Conclusions

A general mathematical model was developed for the hindered diffusion-adsorption of solute in a solvent through porous materials in a bath. This diffusion model incorporated the nonuniformities of pore structures in the porous mediums. A numerical method called the Method of Lines was used to solve the nonlinear partial differential equations. The accuracy of the numerical solution was verified by both the mass balance in the diffusion system and satisfactory agreement with known solutions in several special cases.

Figure 3.6 Comparison of numerical solution with analytical solution (Gray and Do, 1992) for Freundlich adsorption isotherm.

Figure 3.7 Comparison of numerical solution from this work with that from Hashimoto et al. (1975) for Freundlich adsorption isotherm.

IV INFLUENCE OF EXTERNAL MASS TRANSFER ON DIFFUSION EXPERIMENTS

Introduction

As discussed in the preceding chapter, one of the basic assumptions in the development of mathematical diffusion model is that in the finite diffusion bath, the external mass transfer around particles is negligible. Generally, the elimination of the external mass transfer in a diffusion bath can be achieved by one or more of several improvements, e.g., increasing the stirring speed and particle size. Otherwise, if the external mass transfer resistance exists, it should be included as an additional term in the mathematical diffusion model.

To insure that the external mass transfer effect is negligible and to verify the diffusion experimental apparatus, several theoretical and experimental studies were performed.

Experimental

Chemicals and Catalysts

Quinoline (99+%, Aldrich Chemical Company) and HPLC grade cyclohexane (99.9+%, Fisher Scientific) were used as solute and solvent, respectively, in diffusion studies. Both were pretreated with 4A molecular sieves.

prior to use to remove impurities and water. Cylindrical NiMo/Al₂O₃ catalyst extrudates, Shell 324 developed by Shell Catalyst Company, were used in this study. The catalyst extrudates were crushed or broken and sieved in order to obtain particles of different radii. Four different particle sizes were used, 0.018, 0.039, 0.055 and 0.080 cm in radius respectively. The effective radii of the catalyst particles were taken as the geometric mean of adjacent screen openings. The catalyst samples were heated at 400 °C for 12 hours to remove moisture and organic impurities, and kept in a sealed bottle until used.

Diffusional Uptake Experiments

Diffusional uptake experiments were performed in either magnetically or mechanically stirred diffusion cell containing a screen wire basket for holding catalyst particles at 303 K. Figures 4.1 and 4.2 show schematic diagrams of the finite bath diffusion experiments with magnetic and mechanical stirring, respectively. Catalyst samples were presaturated with cyclohexane before diffusion runs, during which the uptake of quinoline was monitored periodically by UV spectrophotometry at 274 nm wavelength.

Results and Discussion

Theoretical Analysis of External Mass Transfer Effect

For a finite bath diffusion system, if there is a significant external mass transfer resistance, the flux from bulk solution to the particle is

Figure 4.1 Schematic diagram of diffusion cell with magnetic stirring.

Figure 4.2 Schematic diagram of diffusion cell with mechanical stirring.

$$N_A = -D_e \frac{\partial C}{\partial r} \Big|_{r=R} = k_c(C_b - C_s) \quad (4.1)$$

where C_s is the surface particle concentration, and k_c is the mass transfer coefficient. Suppose a non-adsorption process holds, then the fractional uptake will have the following form (Crank, 1975, p92)

$$\frac{Q_t}{Q_e} = 1 - \sum_{n=1}^{\infty} \frac{6Sh^2 \exp(-\beta_n^2 t^*)}{\beta_n^2 (\beta_n^2 + Sh(Sh-1))} \quad (4.2)$$

where, β_n 's are the roots of

$$\beta_n \cot(\beta_n) + Sh - 1 = 0 \quad (4.3)$$

and Sh is called the Sherwood number defined as,

$$Sh = \frac{Rk_c}{D_e} \quad (4.4)$$

In above equation, the mass transfer coefficient k_c around a particle can be estimated by the following empirical equation (Bird et al., 1960, p647)

$$Nu = 2 + 0.60(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{3}} \quad (4.5)$$

where

$$Nu = \frac{2k_c R}{D_e}, \text{ Nusselt number} \quad (4.6)$$

$$Re = \frac{2\rho u_{\infty} R}{\eta}, \text{ Reynolds number} \quad (4.7)$$

$$Sc = \frac{\eta}{\rho D_{\infty}}, \text{ Schmidt number} \quad (4.8)$$

thus

$$k_c = \frac{D_{\infty}}{2R} [2 + 0.60 (2 \frac{\rho u_{\infty} R}{\eta})^{\frac{1}{2}} (\frac{\eta}{\rho D_{\infty}})^{\frac{1}{3}}] \quad (4.9)$$

For a particular solvent/solute/catalyst diffusion system in a well-stirred diffusion bath, the value of the Reynolds number is usually large. In this case, according to above equation, the mass transfer coefficient k_c at constant stirring speed is approximately inversely proportional to the square root of the particle size, or

$$k_c \propto 1/\sqrt{R} \quad (4.10)$$

Suppose a series of experiments with different size particles at same conditions were performed, the differences in the values of the Sherwood number Sh are caused only by different particle sizes, with the Sh values being proportional to the square root of the particle size if one combines equations (4.4) and (4.10), viz.,

$$Sh \propto \sqrt{R} \quad (4.11)$$

On the other hand, if there is no external mass transfer influence, or in equation (4.2) the value of Sherwood number Sh approaches infinity, the solution can be simplified as,

$$\frac{Q_t}{Q_e} = 1 - \sum_{n=1}^{\infty} \frac{6}{\beta_n^2} \exp(-\beta_n^2 t^*) \quad (4.12)$$

Now, suppose a series of experiments with "infinite" Sh values were performed in which Q_t/Q_e 's were determined at different times, t . The values of dimensionless time t^* corresponding to these experimental Q_t/Q_e values can be found from equation (4.12). From the definition of t^*

$$t^* = \frac{D_e}{K_p \epsilon R^2} t \quad (4.13)$$

we see that a plot of t^* vs. t will be linear through the origin. The question to be answered now is that if an experiment were performed in which there was significant mass transfer control, e.g., $Sh=0.1$, would a plot of t^* calculated from equation (4.12) vs. t still be linear? To answer this question, we took several hypothetical Q_t/Q_e values and computed the corresponding t^* values from equation (4.2) with $Sh=0.1$, and then calculated arbitrarily the diffusion time t from equation (4.13). This gave us a set of hypothetical "experimental" ($Q_t/Q_e, t$) data with mass transfer control present. We then used the values of t^* calculated from equation (4.12) with each Q_t/Q_e to plot vs. t . The result is shown in Figure 4.3, where it is observed that the data do not fit a straight line through the origin.

Figures 4.4 to 4.7 show similar analyses for various degrees of mass transfer control (various Sh values). As Sh value becomes larger, the degree of mass transfer control decreases and the data more closely fit a straight line through the origin. If the nonlinear plots of t^* vs. t in Figures 4.3 to 4.7 are forced to be straight lines through the origin, several hypothetical "slopes" can be obtained, as shown in the figures. These hypothetical "slopes" from the straight lines should be

Figure 4.3 Plot of t^* vs. t for $Sh=0.1$.

Figure 4.4 Plot of t^* vs. t for $Sh=0.5$.

Figure 4.5 Plot of t^* vs. t for $Sh=2.0$.

Figure 4.6 Plot of t^* vs. t for $Sh=5.0$.

Figure 4.7 Plot of t^* vs. t for $Sh=100$.

proportional to R^{-2} in the absence of mass transfer, in which the R values corresponding to the Sh values could be obtained arbitrarily from equation (4.11). Then a log-log plot of the slopes from Figures 4.3 to 4.7 vs. the corresponding R 's can be made as shown in Figure 4.8. It is observed that the slope of this curve is not equal to -2 as it should be in the absence of mass transfer. However, as the particle size (thus the Sherwood number) increases, or the degree of the external mass transfer control decreases, the slope does approach -2.

Interestingly, as shown in Figures 4.3-4.7, when the values of Sh are less than 5, or the external mass transfer is significant, the data points are below the straight lines at lower t values and then tend upward above the lines at higher t values.

From the above analysis it can be concluded that if mass transfer is influencing the Q_t/Q_e data, a plot of t^* (from equation (4.12)) vs. t will not be linear, and the presence of external mass transfer will be thereby detected. Conversely, if such a plot is a straight line through origin, the external mass transfer effects are absent. Similarly, if mass transfer is present and experiments are performed with several particle sizes, a plot such as in Figure 4.8 will not have a -2 slope. Conversely, if such a plot does have a -2 slope, we can conclude that external mass transfer effects are absent.

Actual Experiments with Different Particle Sizes

To verify the experimental apparatus and validity of model assumptions, quinoline uptake experiments were performed using several catalyst particle sizes obtained by crushing a fresh Shell 324 NiMo/Al₂O₃ unimodal catalyst. Particle radii were 0.08, 0.055, 0.039 and 0.018 cm, as estimated from the geometric mean

Figure 4.8 Plot of $\ln(t^*/t)$ vs. $\ln(R)$.

of adjacent sieve openings. Adsorptive uptake results from these experiments are shown in Figure 4.9 as dimensionless bath concentration C_b/C_{bi} vs. time, in which the effect of various particle sizes on the quinoline uptake rates is reflected in the uptake curves.

According to the above theoretical discussion, the slope of a $\ln\ln$ plot of t^*/t vs. R should be -2 providing the external mass transfer is absent. When the data for the four particle sizes are plotted as shown in Figure 4.10, a least square slope of - 1.97 is obtained. This value, being very close to -2, supports the assumptions made in the model development and indicates that the adsorption-diffusion process is controlled by intrapore diffusion at a rate inversely proportional to R^2 in accordance with theory and model assumptions.

Figure 4.11 plots dimensionless time t^* vs. t/R^2 for different catalyst particle sizes. According to equation (4.13), a plot of dimensionless time t^* vs. t/R^2 should be linear with the slope proportional to the effective diffusivity D_e . As discussed above, had the external mass transfer been a controlling mechanism in the diffusion process, the data points in Figure 4.11 would have been below the straight line at lower t/R^2 values and then would have tended upward above the line at higher t/R^2 values. Thus Figure 4.11 supports the assumption involving the neglect of external mass transfer as a controlling mechanism.

For a diffusion controlled process without external mass transfer effects, the effective pore diffusivity should be the same regardless of differences in catalyst particle sizes. The effective diffusivity determined from the slope of Figure 4.11 using experimental data for all particle sizes is $(3.0 \pm 0.2) \times 10^{-6} \text{ cm}^2/\text{s}$. These results indicate the model satisfactorily fits experimental data with different particle sizes, and serves to verify assumptions made earlier in the model development. In particular, the effective diffusivity is independent of the particle

Figure 4.9 Uptake rates of quinoline in cyclohexane with Shell 324 catalyst of different particle sizes

Figure 4.10 Relationship between t^*/t and catalyst particle sizes.

Figure 4.11 Plot of t^* vs. t/R^2 for quinoline uptake data in Figure 4.9 for four catalyst particle sizes.

size in keeping with model assumptions, and the overall adsorption-diffusion uptake process is controlled by intrapore diffusion.

Estimates of Particle Surface Concentration from Experiments

During a finite bath diffusion experiment, if the external surface concentration around a porous particle is approximately the same as the bath bulk concentration at any diffusion time, the particle external mass transfer can be neglected. To verify the elimination of the external mass transfer effects in our experiments, the particle external surface concentration and bath bulk concentration were compared for the adsorptive uptake experiments with varying particle sizes.

Suppose the molecules are diffusing from the bulk solution in a bath to the particle surface through a boundary layer. The mass transfer flux from the diffusion bath to the boundary layer is

$$N_{A\infty} = -V_b \frac{dC_b}{dt} \frac{1}{4\pi R^2 k} = -\frac{R}{3} \frac{V_b \rho_p}{W} \frac{d\theta_b}{dt} C_{bi} \quad (4.14)$$

The external mass transfer flux from the bulk bath to the particle surface can be expressed as

$$N_{Ae} = k_c (C_b - C_s) \quad (4.15)$$

According to material balance, at steady state the mass transfer from the bath to the boundary layer should be equal to the external mass transfer from the boundary layer to the particle surface, viz.,

$$N_{A\infty} = N_{Ae} \quad (4.16)$$

or

$$-\frac{R}{3} \frac{V_b \rho_p}{W} \frac{d\theta_b}{dt} C_{b0} = k_c (C_b - C_s) \quad (4.17)$$

thereby

$$\theta_b - \theta_s = -\frac{R}{3k_c} \frac{V_b \rho_p}{W} \frac{d\theta_b}{dt} \quad (4.18)$$

In above equation, given the parameter values of a diffusion system, as shown in Table 4.1, the mass transfer coefficient can be estimated from equation (4.9). The derivative of θ_b with respect to t can be approximated by

$$\frac{d\theta_b}{dt} \approx \frac{\Delta\theta_b}{\Delta t} \quad (4.19)$$

Thus, the difference between dimensionless bath and surface concentration, $\theta_b - \theta_s$, along with the relative difference $(\theta_b - \theta_s)/\theta_b$, can be estimated according to equation (4.18).

Table 4.2 gives the calculated values of the mass transfer coefficients and the estimated values of $(\theta_b - \theta_s)$ and $(\theta_b - \theta_s)/\theta_b$ at different particle sizes. From this table it can be seen that the difference between θ_b and θ_s as well as the relative difference $(\theta_b - \theta_s)/\theta_b$ are relatively small, particularly at longer diffusion time. These results indicate that the resistance for the external mass transfer in our diffusion experiments can be neglected.

Also listed in Table 4.2 are the values for the Sherwood number. As shown by Nerethieks (1976), for adsorptive pore diffusion in a finite bath, the influence of the external mass transfer resistance was negligible if Sh was greater than 25.

Table 4.1 Parameter Values for quinoline/cyclohexane/catalyst system

cyclohexane solvent density ρ , g/cc	0.7
cyclohexane solvent viscosity, g/cm-s	0.0065
diffusivity of quinoline in cyclohexane D_{∞} cm ² /s	1.16×10^{-5}
fluid linear velocity around catalyst particle, u_{∞} cm/s	$168^{(a)}$
diffusion bath volume, cc	195
catalyst particle density, g/cc	1.4
catalyst weight, g	0.2

(a). Calculated from $u_{\infty} = 2\pi\omega r_B/60$, where r_B and ω are the basket radius and the rotational speed respectively.

Table 4.2 Estimated Surface Concentration and Sherwood Number

	t min	θ_b	$-d\theta_b/dt$ $\times 10^5, 1/s$	θ_s	$\theta_b - \theta_s$	$(\theta_b - \theta_s) / \theta_b$ %
R=0.08 cm	30	.923	4.28	.852	.071	7.7
kc=0.022	60	.863	3.33	.808	.055	6.4
Sh=583	120	.790	2.03	.756	.034	4.3
	180	.747	1.19	.727	.020	2.7
	310	.684	0.81	.670	.013	2.0
	540	.610	0.54	.601	.009	1.5
	720	.568	0.39	.562	.006	1.1
	1380	.479	0.23	.475	.004	0.8
R=0.055 cm	30	.810	10.60	.710	.100	12.3
kc=0.026	60	.740	3.89	.703	.037	5.0
Sh=484	120	.655	2.36	.633	.022	3.4
	240	.550	1.46	.536	.014	2.5
	458	.490	0.46	.486	.004	0.9
	693	.433	0.39	.429	.004	0.8
	1320	.370	0.17	.368	.002	0.4
R=0.039 cm	30	.763	13.17	.689	.074	9.7
kc=0.031	60	.681	4.56	.655	.026	3.8
Sh=408	120	.570	3.08	.553	.017	3.1
	180	.530	1.11	.524	.006	1.2
	300	.465	0.90	.460	.005	1.1
	601	.380	0.47	.377	.003	0.7
R=0.018 cm	10	.741	43.17	.665	.076	10.3
kc=0.046	30	.620	10.08	.602	.018	2.9
Sh=279	60	.481	7.72	.467	.014	2.8
	90	.420	3.39	.414	.006	1.4
	120	.382	2.11	.378	.004	1.0

Crank's results (1975) showed that for a non-adsorption system, if Sh was greater than 30, the mass transfer effect could be neglected. As shown in Table 4.2, the values of Sherwood number in our experiments are all greater than 250. Thus, it can again be concluded from these calculations that the external mass transfer effects in our diffusion runs are negligible.

Stirring Speed Experiments

Stirring speed experiments were carried out in a mechanically stirred diffusion cell to verify the effect of external mass transfer. As we know, the external mass transfer can be minimized by using higher stirring speed. To locate the minimum stirring speed at which the external mass transfer is negligible, several diffusion runs with different stirring speeds, varying from 60 rpm to 1000 rpm, have been performed for the uptake of quinoline in cyclohexane from Shell 324 catalyst with particle radius of 0.08 cm. Figure 4.12 shows the dimensionless bath concentration vs. time at different stirring speeds. From this figure it can be seen that at stirring speed greater than 800 rpm, the external mass transfer resistance appears to be negligible.

Figures 4.13 and 4.14 also plot t^* vs. t at two stirring speeds, 60 and 800 rpm respectively. As shown in Figure 4.13, the plot of t^* vs. t is not a straight line at the stirring speed of 60 rpm, indicating the presence of external mass transfer as discussed in the first section of this chapter. On the other hand, if the stirring speed is increased to 800 rpm, the plot of t^* vs. t is a straight line through origin, as shown in Figure 4.14. Based on the theoretical analysis discussed before, we can conclude that the external mass transfer effect is negligible at stirring speeds of 800 rpm or higher. Thus we choose a stirring speed of 800 rpm for the adsorptive uptake experiments.

Figure 4.12 Effect of stirring speed on quinoline uptake rates.

Figure 4.13 t^* vs. t at 60 rpm stirring speed for quinoline uptake experiment.

Figure 4.14 t^* vs. t at 800 rpm stirring speed for quinoline uptake experiment.

adsorptive uptake experiments.

Comparison of Results in Mechanically and Magnetically Stirred Diffusion Cells

In the diffusion uptake experiments, both the magnetically and the mechanically stirred diffusion cells were used, as shown in Figures 4.1 and 4.2, respectively. Figure 4.15 compares the quinoline uptakes from Shell 324 catalyst with particle radius of 0.08 cm in both diffusion cells at stirring speeds of 800 rpm. It is observed that the uptake rates in both diffusion cells agree quite well, with an error of less than 10%, providing a further indirect evidence that the external mass transfer is negligible in both diffusion cells.

Conclusions

From the above results and discussion the following conclusions can be obtained.

- (1). Theoretical analysis showed that if external mass transfer is present, a plot of t^* vs. t will not be a straight line through origin. If the plot of t^* vs. t is forced to be straight in the presence of mass transfer influence, the slope will not be -2, and the data points will be below the straight line at lower t values and then tend upward above the line at higher t values.
- (2). In the uptake experiments of this work, the external mass transfer effect is negligible as verified by several methods, e.g., the experiments with different particle sizes, the calculation of particle surface concentration and the experiments of varying stirring speeds.

Figure 4.15 Quinoline uptake rates in both mechanically and magnetically stirred diffusion cells.

V CHANGES IN PORE GEOMETRY AND DIFFUSIVITIES IN DEACTIVATED COAL LIQUEFACTION CATALYSTS

Introduction

Catalyst deactivation is a wide ranging problem in direct coal liquefaction. Deactivation is caused by several phenomena among which are physical changes in the catalyst pore structure due to the deposition of carbonaceous and metallic deposits (Leung and Haynes, 1984; Guin et al., 1986; Zhang et al., 1995; Stiegel et al., 1982; Stephens and Stohl, 1984; Johnson and Massoth, 1986; Prasher et al., 1978). These deposits can lead to greatly decreased pore diffusion coefficients and associated reductions in overall catalytic activity (Guin et al., 1986; Zhang et al., 1995; Stiegel et al., 1982; Stephens and Stohl, 1984; Johnson and Massoth, 1986; Prasher et al., 1978; Butt et al., 1975; Dadyburjor and Raje, 1994). The prediction of intraparticle diffusivities in actual used catalysts is important for an estimation of catalyst effectiveness factors and resulting global reaction rates.

This work investigates the nature and extent of changes in catalyst pore structure due to coke and metals deposition along with the associated effects on pore diffusion rates. Two catalysts, one unimodal and one bimodal, from a 4 ton/day direct coal liquefaction process were studied. Comparisons were made of fresh, spent and regenerated catalysts. A mathematical model was formulated and compared with experimental diffusion data.

Experimental

Chemicals and Catalysts

Quinoline (99+%, Aldrich Chemical Company) and HPLC grade cyclohexane (99.9+%, Fisher Scientific) were used as solute and solvent, respectively, in diffusion studies. Both were pretreated with 4A molecular sieves prior to use to remove impurities and water.

Two NiMo/Al₂O₃ catalysts were used in this study. Criterion 324 catalyst, denoted as catalyst A, is a unimodal catalyst developed by Criterion Catalyst Company (formerly Shell). EXP-AO-60 catalyst, denoted as catalyst B, is a bimodal catalyst designed by Amoco. Both catalysts were utilized for direct coal liquefaction in an ebullated bed hydrotreater at the Wilsonville Coal Liquefaction Research and Development Facility, Wilsonville, Alabama. Properties of the fresh catalysts are given in Table 5.1. Additional fresh catalyst properties are given later for comparison with spent and regenerated catalysts. Fresh catalysts were calcined at 673 K for 12 hours prior to use in diffusion experiments to remove moisture and adsorbed impurities.

The spent catalyst samples were obtained from Run 261 performed at the Wilsonville Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama. Run 261 liquefied Illinois No. 6 Coal from the Burning Star Mine #2 at a feed rate of about 4 tons/day. The process was operated in the Close-Coupled Integrated Two Stage Liquefaction (CC-ITSL) mode with the primary purpose of the run being to achieve high distillate yields at high coal throughput rates and to test a new attrition resistant bimodal catalyst (catalyst B). The CC-ITSL mode of operation refers to the use of two sequential ebullated bed

Table 5.1 Properties of Fresh Catalysts

Catalysts	A (Criterion 324)	B (EXP-AO-60)
support	unimodal Al_2O_3	bimodal Al_2O_3
shape	cylindrical	cylindrical
D, mm	1.6	1.6
L/D	2.3	3.6
metals, wt%		
Ni	3.7	2.5
Mo	13.2	10.7

catalytic reactors directly coupled without any pressure let-down or deashing between reactors (Nalitham et al., 1987). The spent catalyst samples were withdrawn from the first reactor and thus were exposed to raw coal, ash, and preasphaltenes/cresol insolubles(recycle solvent) in the reactor. Both catalysts were operated at about 2650 psia H_2 pressure at a coal feed rate of 60 lbm mf coal/hr-ft³-cat with a 2/1 solvent/coal ratio. Catalyst B was operated at 694 K, and was withdrawn at a catalyst age of 1375 lbm mf coal/lbm-cat. Catalyst A was operated at a slightly higher temperature of 705 K and was withdrawn at an age of 884 lbm mf coal/lbm-cat. A detailed log of operations is contained in the pertinent technical report (Wilsonville, 1991). The spent catalysts were Soxhlet extracted with THF for 9 days to remove residual liquids and were vacuum dried at 383 K for 24 hours. The remaining deposits, both carbonaceous and metallic, are lumped together as "coke" for the purposes of this work.

Regenerated catalysts were prepared in the laboratory using air as the coke burnoff gas. The regeneration temperature program was: 4 hours-503 K, 4 hours-573 K, 14 hours-673 K, and 30 hours-773 K, during which the ratio of air flow to catalyst volume was 1000 sccm/cc-cat. The fresh, spent and regenerated catalyst samples were stored in sealed bottles under nitrogen atmosphere in a desiccator until used.

Apparatus and Procedures

Catalyst pore volume, particle density and porosity were measured by pycnometry. Catalyst surface area was determined by the single point BET method using N_2 . Pore size distribution was determined by Hg porosimetry to 60,000 psia.

Equilibrium adsorption experiments were performed to measure solute (quinoline) uptakes of catalysts at different concentrations. Solutions of 25 cc of quinoline in cyclohexane at various concentrations were placed in bottles containing $-45\text{ }\mu\text{m}$ (-325 mesh) weighed catalyst particles. The bottles were placed in an environmental shaker at 303 K for 10 to 14 days until equilibrium was attained. Quinoline concentration was determined by UV spectrophotometry at 274 nm.

Effective pore diffusivities were determined using the uptake of solute (quinoline) from a finite bath surrounding the catalyst pellets. This basic technique has been used by a number of investigators (Guin et al., 1986; Stephens and Stohl, 1984; Johnson and Massoth, 1986; Prasher et al., 1978). In some experiments, catalyst extrudates were crushed or broken in order to obtain particles of different radii. For these particles, effective radii were taken as the geometric mean of adjacent screen openings. For the whole cylindrical pellets, effective spherical radii were calculated as 3 times the ratio of pellet volume to external surface area (Ma and Evans, 1968). Diffusion experiments were performed in a magnetically stirred glass diffusion cell containing a screen wire basket for holding catalyst particles at 303 K, as discussed in the preceding section. Catalyst samples were presaturated with cyclohexane before diffusion runs, during which the uptake of quinoline was monitored periodically by UV spectrophotometry at 274 nm. In general terms, the solute uptake rate depends on the intrapore diffusivity and the equilibrium adsorption isotherm.

Nonuniform Particle Model

When a catalyst has been used in a catalytic process, the pore structure in the catalyst could be changed due to coke and metals deposition. The deposits are not necessarily distributed evenly in the pores through out the catalyst particle radius, as the cases happened in most catalytic processes. In these cases, the diffusion parameters inside the pores could be nonuniform, and a resulting nonuniform particle model is required to describe the hindered diffusion in the spent catalysts.

As discussed in the model development chapter, the diffusion model presented here is somewhat more general than previously used models in that it allows for a nonuniform catalyst pore structure in which the local porosity and pore diameter can be functions of radial position inside the catalyst particle. This radial dependence of catalyst properties appears in the local hindrance functions g and h , which reflect the local degree of diffusive hindrance, as shown in the following equations,

$$g = \frac{K_p \epsilon}{K_{p0} \epsilon_0} \quad (5.1)$$

$$h = \frac{K_p K_r \epsilon}{K_{p0} K_{r0} \epsilon_0} \quad (5.2)$$

where the subscript "0" represents properties of fresh catalysts used as a reference state. In above equations, the local steric and drag factors K_p and K_r can be estimated by the following equations

$$K_p = (1 - \lambda)^2 \quad (2.7)$$

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (2.11)$$

and the ratio of porosity ϵ at local position to that at the reference state ϵ_0 is

$$\frac{\epsilon}{\epsilon_0} = \frac{\lambda_0^2}{\lambda^2} \quad (5.3)$$

Therefore the local expressions of functions g and h will be

$$g = \frac{(1-\lambda)^2 \lambda_0^2}{(1-\lambda_0)^2 \lambda^2} \quad (5.4)$$

$$h = \frac{1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5}{1 - 2.104\lambda_0 + 2.089\lambda_0^3 - 0.948\lambda_0^5} \frac{(1-\lambda)^2 \lambda_0^2}{(1-\lambda_0)^2 \lambda^2} \quad (5.5)$$

Accordingly, the uneven deposits result in a nonuniform pore size distribution thus nonuniform parameters along the particle radius. The diffusion model in this case is termed as *nonuniform particle model*, in which case, the pore diffusivity is a local value expressed as

$$D_e = \frac{K_p K_r \epsilon}{\tau} D_\infty = h \frac{\tau_0}{\tau} D_{e0} \quad (5.6)$$

The local diffusivity D_e can be significantly reduced from the fresh catalyst value D_{e0} by the local value of h which reflects the hindrance effects due to local reduction in pore diameter caused by coke/metal deposition, as will be shown later.

On the other hand, if the pores in a used catalyst are assumed to be uniform, or the deposits are uniformly distributed through the catalyst particle, then the effective diffusivity D_e and the functions g and h are constant

independent of particle radial position, with values of g and h less than 1. Meanwhile, for a fresh catalyst, functions g and h are constant, however with values of $g=h=1$. The mathematical diffusion model in this case is called the *uniform particle model*.

Results and Discussion

Physical Characterization of the Catalysts

Table 5.2 gives measured physical properties for fresh, spent and regenerated catalysts. Figures 5.1 and 5.2 show mercury injection pore size distributions for these catalyst samples. As shown in Figure 5.1, the major difference in fresh catalysts A and B is the presence of macropores and micropores in B, giving rise to a bimodal pore size distribution as compared to unimodal A. The presence of macroporosity in fresh bimodal catalyst B is apparent, as reflected in its lower particle density and higher pore volume, as well as the fact that B has about double the pore volume of A. On the other hand, the presence of smaller micropores in catalyst B as compared to catalyst A is reflected in its higher surface area, as shown in Table 5.2. The lower density of a bimodal catalyst such as catalyst B is usually reflected in a lower crush strength, while the greater pore volume and surface area are expected to give rise to higher activity and deposit capacity. Apparent from Figure 5.2 is the fact that the regenerated catalysts have the same pore size distribution as the fresh catalysts, except for the region of micropores in catalyst B which appears to be unrecovered in the regenerated catalyst. Figure 5.2 also shows the dramatic loss of pore volume due to coke deposition in the spent catalysts.

Table 5.2 Measured Properties of Fresh, Spent and Regenerated Catalysts

Catalysts	ρ_p , g/cc	$V_p^{(a)}$, cc/g	ϵ , cc/cc	$S^{(b)}$, m ² /g	$d_p^{(c)}$, Å
Catalyst A					
fresh	1.40	0.47	0.66	150	125
spent	1.96	0.14	0.27	76	74
regenerated	1.41	0.43	0.61	134	128
Catalyst B					
fresh	1.00	0.76	0.76	221	138
spent	1.33	0.30	0.40	147	82
regenerated	1.08	0.67	0.72	175	153

(a) Water pycnometry

(b) N₂ BET method(c) Average pore diameter calculated from $d_p = 4V_p/S$

Figure 5.1 Differential pore size distribution obtained by mercury injection for fresh catalysts A and B.

Figure 5.2 Cumulative pore size distribution obtained by mercury injection for fresh, spent and regenerated catalysts A and B

From Table 5.2 it can be seen that due to deposits in the catalyst pores during the coal liquefaction process, the particle densities increased by 40% and 33% for catalysts A and B, respectively, and the associated pore volumes decreased by 70% and 61%, respectively. Upon regeneration by controlled oxidation, the surface area for catalyst A recovered nearly to that of fresh catalyst (90%), but the percent restoration for catalyst B, 79%, was not as large. This is probably associated with the loss of micropores in catalyst B, as shown in Figure 5.2. On the other hand, for both catalysts, the volumetric properties of particle density, pore volume and porosity were restored nearly to those of fresh catalysts. The high percent recovery of volumetric properties such as particle density and pore volume shown in Table 5.2 indicates that deposits in these direct coal liquefaction catalysts are primarily carbonaceous, rather than metallic. As measured by weight loss of the spent catalysts upon regeneration, organic deposits in both catalysts A and B were more than 20 wt% of the spent samples. This observation is in contrast to the situation typically observed in deactivated petroleum resid catalysts, where deposits contain a high percentage of metals, primarily V and Ni. For example, Johnson et al. (1986) found the deposits of V and Ni metal sulfides in resid deactivated $\text{CoMo/Al}_2\text{O}_3$ HDS catalysts to be greater than 20 wt% of the spent catalyst, whereas organic deposits were less than 15 wt%.

One should also note from Table 5.2 that the average pore diameters D_p for both spent catalysts A and B were decreased by 41%. It will be seen later that these percentage decreases are not commensurate with the much greater decreases observed in the effective diffusivities. The estimated *average* pore sizes for the regenerated catalysts were slightly larger than those for fresh catalysts, as shown in Table 5.2. This is probably a result of the averaging process, especially

for the bimodal catalyst in which the pore size is an average of the micropores and macropores, considering the fact that a major loss of pore volume of the bimodal catalyst was in the micropore region, as shown in Figure 5.2.

Equilibrium Adsorption Isotherms

The equilibrium adsorption of solute on the catalyst surface, q_e , was obtained from the following mass balance equation,

$$q_{\infty} = \frac{V_b}{W}(C_{bi} - C_{b\infty}) + \frac{(1-K_p)eC_{b\infty}}{\rho_p} \quad (5.7)$$

The second term on the right side of equation (5.7) accounts for the solute in the catalyst pore fluid with the exclusion factor K_p estimated from equation (2.7). This term was generally less than 1% of the right hand side due to the strong adsorption of the basic N molecule quinoline on the catalyst surface. In this work, the equilibrium adsorption data were fitted by the Freundlich adsorption isotherms according to equation (3.8). Figure 5.3 shows the isotherms for the adsorption of quinoline from cyclohexane with fresh, spent and regenerated catalysts, and Table 5.3 gives the corresponding Freundlich isotherm parameters m and n for these catalysts. The Freundlich equation yields a satisfactory fit of the equilibrium data. As shown in Figure 5.3, presumably due to deposits on the spent catalysts, the adsorption capacities of these samples were less than 20% of those for the fresh catalysts. The regeneration procedures only partially restored the adsorption capacities. Figure 5.4 shows the same adsorption data on a per unit surface area basis for the fresh, spent and regenerated catalysts. It is observed that the loss in adsorption capacity is significantly greater than would be expected based on the corresponding loss in total BET surface area. Considering the basic

Figure 5.3 Adsorption per unit mass of catalyst for quinoline in cyclohexane with fresh, spent and regenerated catalysts A and B.

Table 5.3 Freundlich Isotherm Parameters for Quinoline in Cyclohexane
with Fresh, Spent and Regenerated Catalysts

Catalysts	m	n
catalyst A		
fresh	52.4	7.03
spent	13.6	3.16
regenerated	35.1	6.03
catalyst B		
fresh	59.4	7.25
spent	22.1	3.90
regenerated	47.9	4.89

Figure 5.4 Adsorption per unit of surface area for quinoline in cyclohexane with fresh, spent and regenerated catalysts A and B.

nature of the quinoline adsorbate, these results indicate a preferential loss of catalyst active sites, primarily of an acidic nature, greater than would be estimated from the decrease in total BET surface area.

Effective Diffusivities from Uniform Particle Model

To obtain the effective diffusivity, diffusion experiments with fresh, spent (both extrudates and crushed particles) and regenerated catalysts were performed. Figures 5.5 and 5.6 show two sets of typical data for uptakes of quinoline in the surrounding bath as a function of time, together with the curves fitted from the model solutions for fresh, spent and regenerated catalysts. Two time scales were required due to the extremely slow uptakes with the spent extrudates. The model solution used in this section assumes constant (uniform) values for catalyst particle properties and hence has a constant effective diffusivity D_e which is found from the least square fit of the data. From Figures 5.5 and 5.6 it can be seen that the uniform particle diffusion model with constant D_e fits most of the uptake data fairly well, although some departure can be seen, particularly in the data for the spent catalyst extrudates. Table 5.4 shows the diffusion parameters resulting from the fits of experimental uptake data in Figures 5.5 and 5.6 with the uniform particle diffusion model. The tortuosity value for each catalyst was calculated from equation (5.6) using the values of D_e together with D_∞ and estimated K_p , K_r factors. The molecular diffusivity D_∞ for quinoline in cyclohexane was estimated from the Wilke-Chang equation as $1.16 \times 10^{-5} \text{ cm}^2/\text{s}$. The critical diameter of quinoline was calculated as $6.9 \text{ \AA}$, based on bond lengths, bond angles and atomic radii of the molecular structure. Detailed estimation of these parameters are shown in Yang (1996). Restrictive diffusion factors K_p and

Figure 5.5 Fit of diffusion data with uniform particle model for the uptake of quinoline in cyclohexane with fresh, spent (both extrudates and crushed particles) and regenerated catalyst A.

Figure 5.6 Fit of diffusion data with uniform particle model for the uptake of quinoline in cyclohexane with fresh, spent (both extrudates and crushed particles) and regenerated catalyst B.

Table 5.4 Fitted Effective Diffusivities and Model Parameters with the Uniform Particle Model for Fresh, Spent and Regenerated Catalysts

Catalysts	R cm	λ	K_p	K_r	$D_e * 10^6$ cm ² /s	D_e/D_{e0} %	$\tau^{(c)}$
Catalyst A							
fresh	0.08 ^(a)	0.055	0.89	0.88	3.0	100	2.0
spent(extrudates)	0.10 ^(b)	0.094	0.82	0.80	0.0019	0.06	1080
spent(crushed)	0.016 ^(a)	0.094	0.82	0.80	0.20	6.8	10.5
regenerated	0.10 ^(b)	0.054	0.90	0.89	0.48	16.0	11.5
Catalyst B							
fresh	0.08 ^(a)	0.050	0.90	0.90	6.3	100	1.1
spent(extrudates)	0.11 ^(b)	0.075	0.84	0.83	0.028	0.44	116
spent(crushed)	0.016 ^(a)	0.075	0.84	0.83	0.75	12.0	4.3
regenerated	0.11 ^(b)	0.045	0.91	0.91	2.2	34.9	3.1

(a) Estimated from geometric mean of upper and lower sieve openings

(b) Calculated from $R=3V/S_{ext}$

(c) Determined from equation (5.6)

K_r were estimated by equations (2.7) and (2.11), respectively, based on the critical diameter of quinoline and the average pore diameter for each catalyst in Table 5.2. These calculations gave values of λ ranging from 0.045 to 0.094, and corresponding values of K_p and K_r from 0.82 to 0.91 and 0.80 to 0.91 for catalyst A and B, respectively. Thus hindrance effects for quinoline as based on the uniform properties model with an *average* pore diameter are not extremely large, although the product $K_p K_r$ in equation (5.6) does lower the effective diffusivity by a factor of almost 50%.

Table 5.4 shows that the effective diffusivity for fresh bimodal catalyst B is higher than that for fresh unimodal catalyst A, a fact which could significantly affect the catalyst activity for macromolecular (eg., asphaltene and preasphaltene) reactions, such as occur in direct coal liquefaction. In addition, the calculated tortuosity for fresh catalyst B is smaller than that for fresh catalyst A. These results may be attributed to the more accessible bimodal pore size distribution for fresh catalyst B as compared to unimodal catalyst A. Thus, based on consideration of only fresh catalyst diffusivities, the bimodal catalyst would appear to offer possible advantages in a coal liquefaction process.

Effective diffusivities for both A and B spent catalyst extrudates were extremely low as suggested by the extended time scale required in Figures 5.5 and 5.6. As shown in Table 5.4, the actual diffusivity values were less than 1% of those for the fresh catalysts. Based on this observation it would seem that in the coal liquefaction process, a primary advantage evidenced by the fresh bimodal catalyst would not be fully maintained, although its diffusivity does remain an order of magnitude higher than that of the unimodal catalyst. As shown in Table 5.4, calculated tortuosity factors were of reasonable magnitudes for the fresh and regenerated catalysts; however, for spent catalysts A and B, calculated apparent

tortuosities were 1080 and 116, respectively. These extremely high values are a direct consequence of the very low D_e values for the spent catalyst extrudates. Tortuosity values can be seen via models to result from pore constrictions and increased diffusional path length as compared to uniform pores (Petersen, 1958; Michaels, 1959), and while coke deposits may lead to some increase in tortuosity, values of this magnitude, i.e. 1080 and 116, are not physically realistic, as normally observed tortuosity values are in the range from 1 to 10 (Satterfield, 1980; Froment and Bischoff, 1990), and typically average around 3 to 4 (Sharma et al., 1991). The extremely high tortuosity values for the spent catalysts indicate that the uniform particle model does not satisfactorily model diffusion in the spent catalyst extrudates. Viewed in another way, the extremely low values of effective diffusivities for the spent catalyst extrudates are much lower than would be predicted by a uniform particle model using physically reasonable values of tortuosity. Based on these results, it was hypothesized that the very low spent catalyst diffusivities might be due to a nonuniform coke deposition in the spent catalysts, whereby the diffusivity at certain points in the catalyst particle, namely near the outer surface, was reduced to a much lower value than that calculated from equation (5.6) by using the constant K_p , K_r and ϵ factors based on the *average* pore diameter as measured in Table 5.4. Thus it was postulated that a radially nonuniform coke deposition profile might account for the extremely low diffusivities and correspondingly high apparent tortuosities for the spent extrudates.

To experimentally test for the presence of a nonuniform coke deposit, the spent catalyst extrudates were crushed to produce particles with radii of 0.016 cm, and additional uptake experiments were performed. The results with the crushed particles also are shown in Table 5.4 and Figures 5.5 and 5.6. As shown by the

preliminary experiments discussed earlier in chapter 4 with fresh catalysts of varying particle sizes, when the properties of the catalyst particles are uniform, the values of effective diffusivity and tortuosity are independent of particle size. From Table 5.4 it can be seen that in the case of the spent catalysts, the calculated effective diffusivities for the crushed particles are much greater than for the extrudates. In addition, the data from the crushed particles yields more reasonable (lower) tortuosity factors as compared to the extrudates. These observations confirm the existence of nonuniform coke deposits in the spent extrudates. Higher diffusivities observed with crushed particles indicate that the interior of the extrudates is not as clogged by deposits as the outer region of the extrudates. The percentage increase in diffusivities obtained by crushing the extrudates is greater for catalyst A than for catalyst B, suggesting a more severely clogged outer pore region for the unimodal catalyst, possibly due to the lack of macroporous access channels as are present in bimodal catalyst B.

Diffusion experiments were also performed with regenerated catalysts A and B. The model fitted effective diffusivities thus obtained are also shown in Table 5.4. The regeneration process significantly restores the effective diffusivities, by about two orders of magnitude, for both unimodal and bimodal catalysts, although not completely to the original levels for fresh catalysts. The percent effective diffusivity restoration for bimodal catalyst B (35%) is, however, greater than for unimodal catalyst A (16%). Thus even though the overall volumetric parameters were recovered by regeneration, the pore diffusivities were not completely recovered, possibly due to a small amount of metallic deposits near the outer particle surface, which is not evident in measurement of overall volumetric properties. The significant restoration of diffusivities in our experiments following oxidative regeneration can be contrasted with the results of

Zhang et al. (1995) who found very little restoration of diffusivities following regenerative oxidation alone. In this latter case, their results were found to be due partly to a mineral shell surrounding the catalyst particles which could not be removed by oxidation, but which could be removed by additional acid treatment. Following oxidation and acid treatment their diffusivities were completely restored. In our case, the extremely low values of spent catalyst diffusivities seem to be caused primarily by carbonaceous deposits in that they are significantly restored by oxidative regeneration alone. Furthermore, in contrast to the work of Zhang et al. (1995), SEM micrographs of our spent and regenerated catalyst extrudates did not show any external shell surrounding the pellet exterior. However, examination of the spent catalysts by EDS (Energy Dispersive X-Ray Spectroscopy) did show a small amount of metallic deposits, particularly Ti, Fe, Ca, near the outer surface of the particles.

A Nonuniform Particle Model for Spent Catalyst Extrudates

As noted in the preceding section, the extremely low values of effective diffusivity for the spent extrudates, (or correspondingly high values of tortuosity), together with the higher diffusivities and more reasonable values for the tortuosities of the crushed particles indicated a nonuniform distribution of deposits in the extrudates. In the case of a nonuniform deposit distribution, the porosity, pore size, and other physical properties in the spent catalysts would be functions of radial position in the catalyst particle.

With the above ideas in mind, an attempt to more realistically represent the diffusion behavior in spent catalyst extrudates was made by development of a model which included a nonuniform distribution of coke deposits. In a

nonuniform deposit model, the corresponding local coke deposit distribution along the particle radius is needed. Because the exact radial distribution of deposits in the spent catalyst is generally unknown, as was the case here, a postulated distribution of deposits with adjustable parameters was assumed. In accord with the discussion for diffusion of the spent extrudates and crushed particles, it is apparent that the deposits are located increasingly near the surface of catalyst particles. For simplicity, it was assumed that the *local* porosity in the spent catalyst could be represented by a step function of the particle radius having three adjustable parameters, b , c and c_0 , viz.,

$$\frac{\epsilon}{\epsilon_0} = \begin{cases} c, & \xi < b \\ c_0, & b \leq \xi \leq 1 \end{cases} \quad (5.8)$$

A better physical understanding of the postulated deposit distribution may be obtained by referring to Figure 5.7. In equation (5.8), parameter b locates the step, c and c_0 are the ratios of ϵ/ϵ_0 in the inner and outer regions of the particle, respectively. The values for b , c and c_0 must be in the range 0 to 1, with c greater than c_0 . We should emphasize here that the purpose of this deposit postulation is to provide a rational explanation for the observed diffusivities in the spent catalysts and that the actual deposit distribution is probably not the same as the simple step model assumed here. However, it is required, as shown in the following, that our postulated distribution of ϵ/ϵ_0 conform to the experimentally measured macroscopic properties of the spent catalysts.

In order to have physically realizable values of surface area, pore volume and tortuosity in the spent catalyst, the parameter values in the postulated ϵ/ϵ_0 distribution are restricted to a fairly narrow range. By trial and error it was determined that allowable values of parameter b were around 0.75 for catalyst A

Figure 5.7 Step model for nonuniform coke deposit profiles in spent catalysts. (not to scale)

and 0.90 for catalyst B. The other two deposit parameters, c and c_0 were determined by matching the experimentally measured changes in two average properties of the spent extrudates, namely, specific surface area and pore volume, as compared to their values in the fresh extrudates. By assuming a capillary pore model, we have

$$\frac{\langle \epsilon \rangle}{\epsilon_0} = \frac{\rho_p V_p}{\rho_{p0} V_{p0}} = \frac{\int_0^R \epsilon 4\pi r^2 dr}{\int_0^R \epsilon_0 4\pi r^2 dr} = 3 \int_0^1 \frac{\epsilon}{\epsilon_0} \xi^2 d\xi \quad (5.9)$$

$$\frac{S}{S_0} = \frac{\int_0^R \alpha A_p^{\frac{1}{2}} r^2 dr}{\int_0^R \alpha A_{p0}^{\frac{1}{2}} r^2 dr} = 3 \int_0^1 \sqrt{\frac{A_p}{A_{p0}}} \xi^2 d\xi = 3 \int_0^1 \sqrt{\frac{\epsilon}{\epsilon_0}} \xi^2 d\xi \quad (5.10)$$

Equation (5.9) assumes that during the deposition process, the pores maintain geometric similarity, as their cross sectional area, i.e., pore diameter, is reduced. Insertion of the deposit model equation (5.8) into the integrals in equations (5.9, 5.10) together with the experimental values for S/S_0 and $\rho_p V_p / \rho_{p0} V_{p0}$ from Table 5.2 yields the c and c_0 parameter values for spent A and B, as shown in Table 5.5. The resulting deposit distributions are shown in Figure 5.7. These distributions indicate that catalyst A is more severely clogged at the particle surface than catalyst B.

For a cylindrical pore model, the local pore diameter is related to the local porosity in the catalyst particle by

Table 5.5 Fitted Effective Diffusivities and other Parameters with Step
Nonuniform Particle Model for Spent Catalysts Extrudates ^(a)

catalysts	b	c	c_0	ϵ	λ	K_p	K_r	$\tau^{(b)}$	$D_e * 10^6$ cm ² /s
A	0.75	0.95	0.014	0.009	0.47	0.28	0.21	4.1	0.0015
B	0.90	0.70	0.038	0.029	0.26	0.55	0.49	3.7	0.024

(a). Calculated based on the outer surface of the particle

(b). Constant value

$$D_p = D_{p0} \sqrt{\frac{\epsilon}{\epsilon_0}} \quad (5.11)$$

and the ratio of molecule diameter to local pore diameter λ can be expressed as

$$\frac{\lambda}{\lambda_0} = \sqrt{\frac{\epsilon_0}{\epsilon}} \quad (5.12)$$

Based on the above equations, functions g_1 and g_2 can be evaluated at any particle radial position. With these values of g_1 and g_2 , the diffusion model with nonuniform deposit distribution can be solved numerically, as discussed in the model development section. The resulting fit parameters for spent catalysts A and B extrudates with the nonuniform particle model are shown in Table 5.5. From Table 5.5 it can be seen that with the nonuniform particle model, the porosity ϵ and hindrance factors K_p and K_r at catalyst particle exterior surface are decreased substantially as compared to the uniform particle model. These reduced hindrance factors at the particle surface are a consequence of the lower porosity and pore diameter near the outer particle surface as depicted by the porosity distribution in Figure 5.7. The tortuosity factors τ are now physically reasonable values of 4.1 and 3.7 for spent A and B respectively, as compared to the unrealistic values of 1080 and 116 obtained from the uniform particle model fit. These results show that by allowing for nonuniform coke deposition within the spent catalyst particles, a reasonable fit of the diffusional uptake data is possible, with physically realistic values of the parameters, including the tortuosity.

The proceeding results indicate that reliable estimates of pore diffusivities in spent catalyst extrudates can not be made a-priori from experimentally measured *average* physical properties, e. g., pore volume, surface area, pore

diameter, etc. without taking into account the possible nonuniformity of particle deposits. By adopting a model which allows for nonuniformity of coke deposition within the catalyst particle, a reasonable description of the intrapore diffusion process can be obtained.

Conclusions

The pore volumes, porosities, surface areas and adsorption capacities for both spent unimodal and bimodal direct coal liquefaction catalysts were much less than those for the fresh catalysts. The equilibrium adsorption isotherms of quinoline in cyclohexane with fresh, spent and regenerated unimodal and bimodal catalysts were all nonlinear, and were well represented by the Freundlich isotherms. The loss in active sites during the coal liquefaction process, as indicated by reduced adsorption of the basic N compound quinoline, was much greater than would be estimated from the loss in BET surface area. Carbonaceous deposits, rather than metals, were the dominant factor causing a decrease in the effective diffusivity for the spent catalysts, and this decrease was much greater than would be estimated from the decrease in *average* pore diameter calculated based on surface area and pore volume of the spent catalysts. Regeneration by controlled oxidation of spent unimodal and bimodal catalysts significantly restored the effective diffusivities, although not completely to the levels for the fresh catalysts, with the regeneration extent for the bimodal catalyst exceeding that of the unimodal catalyst.

A diffusion model based on uniform particle properties satisfactorily fit the experimental data with both fresh catalysts, with the effective diffusivity for the bimodal catalyst being greater than that for the unimodal catalyst. The uniform

particle model was not valid for spent catalyst extrudates as was evident from unrealistically high tortuosity factors. Experiments with crushed spent particles indicated a nonuniform coke deposit in both spent unimodal and bimodal catalyst extrudates. A diffusion model incorporating a nonuniform deposit distribution gave a satisfactory fit of the observed data for the spent catalyst extrudates, including reasonable tortuosity factors, and indicated that nonuniformity of pore deposits should be considered when modeling intrapore diffusion in spent catalyst extrudates.

VI EFFECT OF SOLUTE ADSORPTION ON HINDERED DIFFUSION

Introduction

Configurational or hindered intrapore diffusion can significantly influence overall catalytic reaction rates when the reactant size is comparable to the pore size of the catalyst. Many investigators have observed intrapore diffusion effects, and several mathematical diffusion models have been applied to describe the diffusion process (Guin et al., 1986; Lee et al., 1991; Limback and Wei, 1990; Haynes, 1988). Hindered diffusion effects include both steric exclusion and hydrodynamic restriction phenomena (Deen, 1987). Steric exclusion accounts for the fact that the center of mass of a molecule, if assumed to be a hard sphere, can not be closer to the pore wall than a distance equal to the molecular radius. Hydrodynamic effects arise from the increased drag resistance due to the confinement of the fluid by the pore walls and corresponding reduction in solute mobility in the pores. When adsorption of solute molecules occurs during a hindered diffusion process, as in heterogeneous catalysis, the adsorbed molecules may indirectly affect the intrapore diffusivity by modifying the catalyst pore structure. Along these lines, Hossain et al. (1986) studied the immobilization of enzymes in porous materials and developed a model incorporating constriction of pore mouths due to the adsorbed layer of immobilized enzymes. A better understanding of adsorptive hindered diffusion behavior in catalyst pores will aid

in designing better catalysts for the treatment of macromolecular feedstocks, such as occurs in the hydrotreatment of petroleum resids and coal-derived liquids.

In this work, a mathematical model for an adsorptive hindered diffusion system was developed and experimentally tested. The model was used to simulate the diffusion controlled uptakes of quinoline and polystyrene from cyclohexane in experiments with a porous NiMo/Al₂O₃ catalyst.

Experimental

Chemicals and Catalysts

Quinoline (99+%, Aldrich Chemical Company) and Polystyrene ($M_w=2514$, $M_w/M_n=1.09$, Aldrich Chemical Company) were used as solutes, HPLC grade cyclohexane (99.9+%, Fisher Scientific) was used as solvent. Quinoline and cyclohexane were pretreated with 4A molecular sieves prior to use to remove impurities and water. A commercial NiMo/Al₂O₃ catalyst, Criterion 324, developed by Criterion Catalyst Company, was used in this study. Catalyst samples were calcined at 673 K for 12 hours prior to use in diffusion experiments.

Apparatus and Procedures

Catalyst pore volume, particle density and porosity were measured by pycnometry. Catalyst surface area was determined by the single point BET method using N₂. Pore size distribution was obtained by Hg porosimetry to 60,000 psia.

Equilibrium adsorption experiments were performed at the same manner as described in chapter 5, except that the temperature was controlled at 303 and 308 K for quinoline and polystyrene systems, respectively. Equilibrium concentrations of quinoline and polystyrene were determined by UV spectrophotometry at 274 nm and 262 nm, respectively.

Diffusion experiments were performed as described in chapter 5.

Shrinking Pore Model for Adsorptive Diffusion

Generally, in studies of hindered diffusion in fresh catalysts, properties of the porous solid are considered to be uniform throughout the particle during adsorptive diffusion process. This assumption is valid if the adsorbed layers of solute do not significantly change the pore diameter, e. g., with small solute molecules and/or low amounts of adsorption. However, in the extended model developed here, it is assumed that the values of porosity and pore size in the porous particle may be functions of time and radial position throughout the particle during adsorptive diffusion process. This assumption, motivated by experimental results to be discussed later, results in an effective diffusivity which is also a function of time and radial position inside the particle. Thus, the model developed here is somewhat more general than previously used models which assumed constant average values for catalyst properties and a resulting constant effective diffusivity.

In hindered diffusion studies, if a significantly thick layer of solute molecules adsorbs on the pore walls, this process will modify the pore structure through which the remaining molecules diffuse. In another words, the adsorbed solute molecules will further hinder the diffusion process by decreasing the local

pore size. The effects of adsorption on hindered diffusion are embodied in the functions g and h , as discussed in the model development chapter. In this case, g and h are functions of time and position inside the particle. The mathematical diffusion model based on these assumptions is termed the *shrinking pore model* (SPM).

To obtain local expressions for g and h in the SPM, the following assumptions were made. For simplicity, the pores were modeled as short cylindrical capillaries with locally uniform cross sections, with the pore cross-sectional area being linearly dependent on the amount of solute adsorption, viz.,

$$A_p = A_{p0} - (A_{p0} - A_{pm}) \frac{q}{q_m} = A_{p0} \left(1 - \left(1 - \frac{A_{pm}}{A_{p0}} \right) \frac{q}{q_m} \right) \quad (6.1)$$

A similar assumption has been made by Hossain et al. (1986) in modeling enzyme immobilization. In equation (6.1), A_{pm} represents the pore cross-sectional area with an adsorbed monolayer of solute molecules q_m . For a monolayer of spherical molecules of diameter d_m in a pore of diameter d_{p0} , we have

$$A_{pm} = \frac{\pi}{4} (d_{p0} - 2d_m)^2 \quad (6.2)$$

Therefore, according to equation (6.1), the *local* pore diameter can be expressed as,

$$d_p = d_{p0} \left(1 - 4\lambda_0 (1 - \lambda_0) E_m \theta_q \right)^{\frac{1}{2}} \quad (6.3)$$

where

$$E_m = \frac{q_i}{q_m} \quad (6.4)$$

The parameter E_m reflects the ratio of equilibrium adsorption capacity to monolayer adsorption capacity, evaluated at the initial bath concentration.

Thus, the local ratio of molecule size to pore size will be given by

$$\lambda = \lambda_0 [1 - 4\lambda_0(1 - \lambda_0)E_m \theta_q]^{-\frac{1}{2}} \quad (6.5)$$

where λ_0 is a constant without the consideration of adsorption effects. The ratio of local to initial porosity is

$$\frac{\epsilon}{\epsilon_0} = \frac{\lambda_0^2}{\lambda^2} = 1 - 4\lambda_0(1 - \lambda_0)E_m \theta_q \quad (6.6)$$

Whereby, functions g and h can be expressed with respect to the adsorption amount, as shown in chapter 5,

$$g = \frac{K_p \epsilon}{K_{p0} \epsilon_0} = \frac{(1 - \lambda)^2}{(1 - \lambda_0)^2} \frac{\lambda_0^2}{\lambda^2} \quad (6.7)$$

$$h = \frac{K_p K_R \epsilon}{K_{p0} K_{r0} \epsilon_0} = \frac{1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5}{1 - 2.104\lambda_0 + 2.089\lambda_0^3 - 0.948\lambda_0^5} \frac{(1 - \lambda)^2}{(1 - \lambda_0)^2} \frac{\lambda_0^2}{\lambda^2} \quad (6.8)$$

and the partial derivative of g with respect to θ_q will be

$$\frac{\partial g}{\partial \theta_q} = \frac{\partial}{\partial \theta_q} \left(\frac{(1 - \lambda)^2}{(1 - \lambda_0)^2} \frac{\lambda_0^2}{\lambda^2} \right) = -4E_m \lambda_0 \frac{1 - \lambda}{1 - \lambda_0} \quad (6.9)$$

where subscript "0" represents the catalyst properties without the effects of the solute adsorption layer.

If one assumes that the tortuosity factor τ is independent of the solute adsorption layer, the value of which is equal to that of fresh catalyst without the effect of adsorption, the local pore diffusivity can be given by

$$D_e = \frac{K_p K_r \epsilon}{\tau_0} D_{\infty} = h D_{e0} \quad (6.10)$$

and the dimensionless time will be

$$t^* = \frac{D_{e0}}{K_{p0} \epsilon_0 R^2} t = \frac{K_{r0} D_{\infty}}{\tau_0 R^2} t \quad (6.11)$$

By substituting the expressions for functions g and h together with the adsorption isotherm into the diffusion model equations shown in chapter 3, the mathematical model can be solved numerically.

In the case of the Freundlich adsorption isotherm, where

$$\theta_q = \theta^{\frac{1}{n}}, \quad \frac{\partial \theta_q}{\partial \theta} = \frac{1}{n} \theta^{\frac{1-n}{n}} \quad (6.12)$$

the solution of the dimensionless bath concentration for SPM can be given by

$$\theta_b = \theta_b(t^*, E, F, n, E_m, \lambda_0) \quad (6.13)$$

On the other hand, if it is assumed that the pore structure of the catalyst is uniform and unchanged during the diffusion-adsorption process, as is the case in most hindered diffusion studies, we have,

$$\lambda = \lambda_0, \quad K_p = K_{p0}, \quad K_r = K_{r0}, \quad \epsilon = \epsilon_0, \quad D_e = D_{e0} \quad (6.14)$$

and thus,

$$g=1, \quad h=1 \quad (6.15)$$

In this case, the solution for dimensionless bath concentration can be expressed as

$$\theta_b = \theta_b(t^*, E, F, n) \quad (6.16)$$

The diffusion model for this case is termed the *uniform pore model* (UPM).

Comparison of the solutions for the SPM and the UPM, as shown in equations (6.13) and (6.16), respectively, shows that two additional model parameters are required for the SPM, namely, E_m and λ_0 . It is informative to examine the influence of these two additional parameters on the uptake rates. In a diffusion experiment, the maximum value of adsorbed solute q_i occurs at $t=0$ when the bath concentration is greatest. When the monolayer adsorption capacity q_m is much larger than this amount, i.e., $E_m \ll 1$, the SPM reduces to the UPM. Similarly, when the solute molecule size is very small compared to the pore size, i.e., $\lambda_0 \ll 1$, the effects of solute adsorption on the pore structure are negligible, and the SPM approaches the UPM. These trends are evident in Figures 6.1 and 6.2 which show the numerical solutions for typical values of E , F and n at different E_m and λ_0 values, respectively. From Figure 6.1 it can be seen that the solute uptake rate is decreased by adsorption on the pore walls as reflected by the SPM. As E_m decreases, the SPM approaches the UPM. Likewise, as shown in Figure 6.2, when λ_0 is small, the SPM approaches the UPM. Both Figures 6.1 and 6.2 show that the effect of an adsorbed layer of solute molecules acts to slow the diffusional uptake of solute from the bath, i.e., C_b/C_{bi} declines at a slower rate, depending on the amount of adsorption and the relative size of the adsorbed molecules.

In order to explore these effects experimentally, two adsorptive solute molecules, quinoline and polystyrene, with λ_0 values of 0.055 and 0.19 and E_m values of 0.70 and 1.22, respectively, were chosen.

Figure 6.1 Effect of Adsorption Parameter E_m (numbers on the lines) on Uptake Rates for the Uniform and Shrinking Pore Models with $\lambda=0.2$.

Figure 6.2 Effect of Molecule/Pore Size Ratio λ_0 (numbers on the lines) on Uptake Rates for the Uniform and Shrinking Pore Models with $E_m=0.67$.

Results and Discussion

Adsorption Isotherms and Model Parameter Estimation

To obtain experimental values for model parameters, adsorption isotherms and certain properties of the diffusion system were measured. Adsorption isotherms were obtained by fitting equilibrium data with the Freundlich equation (3.8). Figure 6.3 shows the isotherms for the adsorption of quinoline and polystyrene from cyclohexane, and Table 6.1 gives the corresponding Freundlich isotherm parameters m and n for these systems.

For simulation studies, the quinoline molecule was modeled as a hard sphere, with a critical diameter of 0.69 nm, as described in chapter 5. Several investigators have used different methods to estimate the molecular size of polystyrene in hindered diffusion studies. Colton et al. (1975) suggested that the size of the monomer unit, instead of the randomly coiled polymer, might be used in fitting hindered diffusion data. More recent studies by Bishop et al. (1989) and Dimino (1994) indicated that a hard sphere model for the randomly coiled polystyrene gave good agreement of experimental data with the hindered diffusion theory. Thus, based on the more recent studies, the randomly coiled polystyrene was treated as a hard sphere, and the hydrodynamic diameter in cyclohexane at 308 K was estimated by the Mark-Houwink equation (Sperling, 1992) to be 2.32 nm.

Molecular diffusivities of quinoline and polystyrene in cyclohexane were calculated by the Wilke-Chang and Stokes-Einstein equations, respectively, as shown in Yang (1996). The monolayer adsorption capacity q_m was estimated geometrically by the assumption of a complete random deposition of spherical

Figure 6.3 Equilibrium Adsorption Isotherms for Quinoline and Polystyrene in Cyclohexane with Criterion 324 Catalyst.

Table 6.1 Measured and Estimated Parameters of Diffusion Systems

Properties of Criterion 324 catalyst	
shape	cylindrical
diameter, cm	0.15
length/diameter	1.0
support	unimodal Al_2O_3
metals, wt%	
Ni	3.7
Mo	13.2
average pore diameter $d_{p0}^{(a)}$, nm	12.5
porosity ϵ_0 , cc/cc	0.66
pore volume V_{p0} , cc/g	0.47
particle density ρ_p , g/cc	1.40
surface area S , m^2/g	150
Properties of quinoline/cyclohexane/Criterion 324 system at 303 K	
molecular diameter d_m , nm	0.69
molecular diffusivity D_∞ $\cdot 10^5$ cm^2/s	1.16
monolayer adsorption q_m , mg/g	45.5
Freundlich isotherm constant m	52.4
Freundlich isotherm constant n	7.03
Properties of polystyrene/cyclohexane/Criterion 324 system at 308 K	
molecular diameter d_m , nm	2.32
molecular diffusivity D_∞ 10^6 cm^2/s	2.42
monolayer adsorption q_m , mg/g	67.5
Freundlich isotherm constant m	97.7
Freundlich isotherm constant n	5.34
Diffusion conditions	
temperature, K	$(303 \pm 1)/(308 \pm 1)$
bath volume, cc	150
stirring speed, rpm	> 800

a. $d_{p0} = 4V_{p0}/S$

molecules on the pore surface of the catalyst, as schematically shown in Figure 6.4. In this random packing process, the surface is assumed to be covered by adsorbate molecules, deposited at random, until there remains no space large enough to accommodate another molecule. At this point the coverage is considered to be a complete monolayer. Mathematical simulations of this random deposition process have shown that, at completion, the fraction of surface occupied by molecules, referred to as the packing density, is about 0.56 (Hall, 1988). Based on this model, the monolayer adsorption capacity q_m can be estimated by

$$q_m = \frac{M_w}{6.023 \times 10^{23}} \frac{0.56S}{\frac{\pi d_m^2}{4}} \frac{d_{p0} - d_m}{d_{p0}} \quad (6.17)$$

Diffusion Experiments and Model Simulation

Two adsorptive solutes were chosen for the experiments, quinoline (0.69 nm diameter) and polystyrene (2.32 nm diameter). Table 6.2 gives the dimensionless model parameter values for these systems as calculated from equations (3.16), and (6.4). It can be seen that the values of λ_0 for quinoline and polystyrene are 0.055 and 0.19, respectively, and the values of E_m are 0.70 and 1.22, respectively. According to equation (6.4), the values of E_m indicate that in our experiments, the amount of adsorption at the initial bath concentration is larger than a monolayer adsorption amount for the polystyrene system, but not for the quinoline system. According to discussions in the theoretical section and as shown in Figures 6.1 and 6.2, these values of E_m and λ_0 show that for the

Figure 6.4 Model for Estimation of Monolayer Adsorption Capacity in a Cylindrical Catalyst Pore.

Table 6.2 Dimensionless Model Parameters for the Diffusion Systems

diffusion model parameters	solute	
	quinoline	polystyrene
n	7.03	5.34
E	2512	658
F	2357	473
λ_0	0.055	0.19
E_m	0.70	1.22

polystyrene system, the effects of adsorption on catalyst pore structure during the uptake process are expected to be considerably more significant than for the quinoline system. In another words, the uptake rate of polystyrene should be hindered to a greater degree by the adsorbed layer of molecules on the pore walls of the catalyst.

Figure 6.5 shows experimental data for quinoline uptake from the bath as a function of time, together with the curves fitted from both the UPM and the SPM. It can be seen that both the UPM and the SPM fit the experimental data fairly well, with little difference between the curves. The agreement with both the UPM and the SPM results from the fact that the values of $\lambda_0(0.055)$ and $E_m(0.70)$ are small in the quinoline system. As noted in the theoretical section, when the values of λ_0 and E_m are small, the SPM approaches the UPM. Physically, this result derives from the fact that quinoline is a small molecule, and the amount of adsorption at the concentration level used in the experiment is much less than the estimated monolayer adsorption capacity.

Figure 6.6 shows the same data for both the UPM and the SPM with the quinoline system, plotted as dimensionless time t^* vs. dimensional time t . According to the t^* - t relation in equation (6.11), a plot of t^* vs. t should be straight line through origin with slope dependent on the effective diffusivity. As shown in Figure 6.6, the fitted data points with both the UPM and the SPM give a reasonable single straight line, with an error of less than 10%. From the slope of this straight line, the tortuosity was calculated to be 1.9 according to the t^* - t relation in equation (6.11). This value of tortuosity is in satisfactory agreement with other experimentally observed values for the type of pore structures in alumina supported catalysts (Tsai et al., 1991; Satterfield, 1980; Froment and Bischoff, 1990).

Figure 6.5 Comparison of Experimental Data with the Uniform and Shrinking Pore Models for the Uptake of Quinoline in Cyclohexane on Criterion 324 Catalyst.

Figure 6.6 Plot of t^* vs. t According to the Relation in Equation (6.11) with the Uniform and Shrinking Pore Models for the Uptake of Quinoline in Cyclohexane on Criterion 324 Catalyst.

Figure 6.7 shows the polystyrene uptake data and the simulated uptake rates predicted from both the UPM and the SPM. To simulate the experimental data in Figure 6.7, a tortuosity value is required. Since the same catalyst was used for both quinoline and polystyrene systems, it seems reasonable to a first approximation that the tortuosity would be about the same for both cases. Therefore in Figure 6.7, the tortuosity value of 1.9 determined from the quinoline system was used. It can be seen that the UPM predicts a too fast uptake rate, when in reality, as shown by the experimental data points, the uptake of polystyrene is much slower, taking about 3 times as long as the model predicted value to decline to a C_b/C_{bi} value of 0.5.

It is possible to obtain a better fit of the experimental data in Figure 6.7 with the UPM by adjusting the tortuosity value, thereby admitting the use of two different tortuosity values for the quinoline and polystyrene systems. However, to obtain a good fit with the UPM would require that a tortuosity value of 7.6 be used for the polystyrene system, which is approximately 4 times greater than the 1.9 value obtained with quinoline and at the upper limit of observed values for catalysts of this type (Tsai et al., 1991; Satterfield, 1980; Froment and Bischoff, 1990). In other words, the increased hindrance effects caused by the adsorbed solute layer would be reflected in an increased tortuosity value in the UPM. Tsai et al. (1991) considered the experimental variation of tortuosity with molecule/pore size ratio and concluded that the use of a single average value of tortuosity up to $\lambda_0=0.35$ was justified by their data. Smith (1986) has studied theoretically the effect of molecule/pore size on the tortuosity, finding the tortuosity variation to be a complex function of a pore constrictivity parameter. The degree of pore constrictivity is difficult to measure; although, Smith pointed

Figure 6.7 Comparison of Experimental Data with the Uniform and Shrinking pore models with $\tau=1.9$ for the Uptake of Polystyrene in Cyclohexane on Criterion 324 Catalyst.

out that an indication can be obtained from the difference in the pore diameter based on the ratio of pore volume to surface area and the Hg injection pore diameter, the latter being more indicative of the smallest pore openings. The close agreement of catalyst pore diameters obtained from both the ratio of pore volume to surface area and mercury injection shown in Figure 5.1 in our work indicates that the pores in the Criterion 324 catalyst are not highly constricted and that the tortuosity values for both quinoline and polystyrene systems should be roughly the same, i.e., about 1.9. In light of the preceding considerations, it is more plausible that the slower than UPM predicted uptake rate observed with the larger polystyrene solute results from a relatively thicker layer of adsorbed solute molecules on the pore walls, with associated increased hindrance factors, rather than simply an increase in pore tortuosity. These suggestions are strengthened by the application of the SPM with tortuosity of 1.9, as shown in Figure 6.7, which yields an excellent prediction of experimental uptake as compared to the UPM. The slower uptake rate predicted with the SPM as compared to the UPM is a direct consequence of the fact that polystyrene is a larger molecule, with $\lambda_0=0.19$, and having in addition a larger adsorption parameter value of E_m (1.22). As compared to the quinoline results in Figure 6.5, the larger values of λ_0 and E_m cause the SPM and the UPM predictions in Figure 6.7 to be further apart, as discussed in the theoretical section. Physically, this result stems from the fact that for polystyrene with larger molecule size, the adsorbed layer of solute molecules significantly decreases the pore size, thereby further increasing the hindrance effects and decreasing the diffusion rate, particularly at the outer surface of the catalyst particle during the early stage of the uptake process.

Table 6.3 compares the fitted effective diffusivities and other

Table 6.3 Parameters for the Uniform and Shrinking Pore Models

parameters	quinoline system		polystyrene system	
	UPM	SPM ^(a)	UPM	SPM ^(a)
ϵ	0.66	0.56	0.66	0.17
λ	0.055	0.060	0.19	0.36
K_p	0.89	0.88	0.66	0.41
K_r	0.88	0.88	0.62	0.33
$D_e, *10^6, \text{cm}^2/\text{s}$	3.1	2.7	0.35	0.029

(a) Local values evaluated at outer surface of the catalyst particle at $t=0$.

parameters from the UPM and the SPM. For the quinoline system, the initial values of λ and ϵ at the outer surface of the catalyst particle are nearly the same for the SPM as compared to those for the UPM, with differences of less than 15%, and the effective diffusivities are close, 2.7 and $3.1 \times 10^6 \text{ cm}^2/\text{s}$, respectively. However, in the case of polystyrene, due to its larger λ_0 and E_m values, the *local* porosity ϵ at the outer catalyst surface with the SPM decreased substantially, from 0.66 to 0.17 . The increased λ value also yields locally decreased K_p , K_r factors. Locally decreased values of these three parameters reflect the increased hindered diffusion effects at the outer surface of the particle during the initial uptake process, causing the *local* effective diffusivity for polystyrene to decrease from $0.35 \times 10^6 \text{ cm}^2/\text{s}$ with the UPM to $0.03 \times 10^6 \text{ cm}^2/\text{s}$ with the SPM.

Conclusion

A mathematical model, termed the *shrinking pore model*, was developed and applied to the diffusion controlled adsorptive uptake of a solute from a finite bath into a porous medium. The model extends previous generally used models by incorporating the enhanced restrictive effect of an adsorbed solute layer of finite thickness on the pore walls. This layer tends to further restrict the solute uptake rate by decreasing the effective *local* pore size and porosity and increasing hindrance effects. Comparison of model simulations with experimental data showed that although both the shrinking and the uniform pore models fitted the experimental uptake data of quinoline well, the shrinking pore model was required to obtain a satisfactory representation of adsorptive uptake for the larger polystyrene solute.

VII DIFFUSIONAL UPTAKES OF COAL AND PETROLEUM ASPHALTENES INTO A HYDROTREATING CATALYST

Introduction

In the catalytic upgrading and hydrotreatment of asphaltenes, heavy oils, coal derived liquids, and other macromolecular feedstocks, reaction rates are often limited by the rate at which the molecules can negotiate the catalyst pore structure (Ho and Weller, 1979; Eigenson et al., 1977; Song et al., 1991; Sooter and Crynes 1975; Yen et al. 1976; Kang, 1983; Guin et al., 1986; Curtis et al., 1883; 1986; 1987; Spry and Sawyer, 1975). Because the sizes of reactant molecules and catalyst pores are comparable, the intrapore diffusion process is often in the hindered diffusion regime. In spite of the importance of this problem in the processing of fossil fuels, measurements of asphaltene intrapore diffusion in porous catalysts are recent and few in number. In one study, Baltus and Anderson (1983) studied the hindered diffusion of petroleum asphaltenes through membranes, in which several fractions were defined by SEC (size exclusion chromatography) according to their elution characteristics. They found that the diffusivities of asphaltenes were only about half the values of the equivalent polystyrene molecules at the same elution volumes. Mieville et al. (1989) measured the diffusion of petroleum asphaltenes through porous materials by adsorptive uptake experiments, in which the asphaltenes were treated as monodispersed. In their study, a linear adsorption isotherm was obtained.

The paucity of investigations regarding asphaltene diffusion probably stems in part from the difficulty of asphaltene characterization and quantification, from a fundamental viewpoint. Due to the complexities of asphaltene molecules as well as the pore structure of typical heterogeneous catalysts, numerous approximations and estimations must be made if a reasonably practical description of the diffusion process is to be obtained. With this in mind, we have investigated the hindered diffusion of coal and petroleum asphaltenes into a commercial NiMo/Al₂O₃ catalyst immersed in THF using adsorptive uptake experiments. The uptake process was monitored by SEC as the asphaltenes were removed from the solution by diffusion into the catalyst. A simplified adsorption-diffusion model was developed for the uptake process. The overall objective of the work was to determine if the diffusion-controlled adsorptive uptakes for both coal and petroleum asphaltenes could be represented by a simple unified mathematical model using reasonable parameter values, e. g. diffusivities, such as could be estimated from literature correlations.

Experimental

Materials

HPLC grade THF (tetrahydrofuran, Fisher Scientific) and toluene (Fisher Scientific), respectively, were used as solvents in the uptake experiments. Polystyrenes (Aldrich) with narrow molecular weight distributions, as well as styrene, TPP (tetraphenylporphrine), 1-methynaphthlene, undecane, and heptane, were used as SEC calibration standards. A commercial unimodal catalyst, Criterion 324, with an average pore diameter of 125 Å, was used in this study. The

pore size distribution was shown in Figure 5.1. The catalyst samples were crushed to -12+16 mesh size (-1.0+1.4 mm in diameter), dried at 673 K for 12 hours, and kept in sealed bottles prior to use in uptake experiments.

Two coal residues (257 K and 258 D) and three petroleum asphalts, California Valley (AAD-1), California Coast (AAG-1), and Boscan (AAK-1), were used as asphaltene sources in this study. The coal residues were from the Wilsonville Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama. The 257 K sample was a Solvent Refined Coal (SRC) from run 257 K using Black Thunder mine coal from Powder River Basin, while the 258 D sample was from run 258 using Illinois No. 6 Coal from the Burning Star mine #2. The three petroleum asphalt samples, California Valley, California Coast, and Boscan, were used as received. Tables 7.1 and 7.2 show the elemental analysis of the coal residues and properties of the petroleum asphalts, respectively.

Apparatus and Procedures

Diffusional uptakes of asphaltenes in a solvent into porous catalyst particles were performed in a magnetically stirred glass diffusion cell containing a screen wire basket for holding catalyst particles at different temperatures. Two different solvents, THF and toluene respectively, were used in this study. The uptake equipment has been previously tested for mass transfer characteristics, and external transport limitations to the uptake process have been shown to be negligible, as shown in chapter IV. For each diffusion run, 150 cm³ of asphaltene solution was used, with an initial asphaltene concentration of 0.05 mg/cm³. The catalyst particles were presaturated with the corresponding solvent (THF or toluene) used in uptake experiment before diffusion runs. During the diffusional

Table 7.1 Elemental analysis of coal asphaltene source materials

code	258D	257K
source	Wilsonville coal resid	Wilsonville coal resid
C, %	89.5	88.4
H, %	6.48	7.46
O, %	2.50	2.99
N, %	1.26	0.89
S, %	0.10	0.22

Table 7.2 Properties of petroleum asphaltene source materials ^a

Asphalt	AAD-1	AAG-1	AAK-1
Crude	CA Coast	CA Valley	Boscan
Viscosity			
140°C, poise	1055	1862	3256
275°C, cSt	309	243	562
Penetration, 0.1 mm			
77°C, 100g, 5s	135	53	70
39.2°C, 100g, 5s	9	2	2
Ductility, cm (39.2°C, 1cm/min)	150+	150+	27.8
Softing Point (R & B), °F	118	120	121
Component Analysis, wt%			
Asphaltenes (n-heptane)	23.0	5.8	21.1
Asphaltenes (iso-octane)	3.4	3.3	2.8
Polar Aromatics	41.3	51.2	41.8
Naphthene Aromatics	25.1	32.5	30.0
Saturates	8.6	8.5	5.1
Elemental Analysis			
C, wt%	81.6	85.6	83.7
H, wt%	10.8	10.5	10.2
O, wt%	0.9	1.1	0.80
N, wt%	0.77	1.10	0.70
S, wt%	6.90	1.30	6.40
V, ppm	310	37	1480
Ni, ppm	145	95	142
Fe, ppm	13	48	24
Aromatic C, wt%	23.7	28.8	31.9
Aromatic H, wt%	6.81	7.27	6.83

a. From the Materials Reference Library, Asphalt Institute.

uptake process, 3 cm³ samples were withdrawn periodically from the diffusion cell, filtered through a 0.1 μ m filter, and analyzed via SEC using 50 μ l injections. The remaining sample solution was returned to the diffusion cell in order to maintain an essentially constant bath volume during the uptake process.

An SEC device was used to analyze the asphaltene samples. The SEC consists of a solvent delivery system (Waters Associates, Model 590), a sample injector (Waters, Model U6K), a variable wavelength UV detector (Waters, Model 484), four μ -styragel columns (nominal pore sizes of 1000 Å, 1000 Å, 500 Å and 500 Å respectively, each of tube size 300 x 7.8 mm) in series, and a computer data acquisition system. The temperature of the columns was controlled by a temperature control module at 30 °C. The wavelength of the UV detector was chosen as 262 nm. HPLC grade THF was used as a mobile phase with a flow rate of 1.0 ml/min. The THF reservoir was purged with helium gas to keep THF from forming peroxides and to eliminate moisture. Each sample for SEC analysis was filtered through a 0.1 μ m syringe filter before injection.

Hindered Diffusion Model for Asphaltenes

In the experiments conducted herein, the porous catalyst particles are surrounded by a well-stirred bath containing asphaltenes and solvent. The asphaltene molecules diffuse into the porous particles where they are adsorbed onto the solid catalyst surface. As a result of this diffusion-adsorption uptake process, the concentration of asphaltenes in the surrounding bath is depleted. The uptake rate of an individual asphaltene fraction in the bath is determined largely by two factors, namely the equilibrium adsorptivity and the effective diffusivity of the fraction. Thus, the uptake rates for the individual asphaltene

fractions will be different, depending on their individual adsorption and diffusion characteristics.

The hindered diffusion model developed to describe the diffusion-controlled uptake of asphaltenes into the porous catalyst particles incorporates several simplifying assumptions including negligible solute transport by surface diffusion, spherical catalyst particle geometry, uniform pore size distribution along the particle radius, negligible external fluid-solid mass transfer resistance, and local adsorption equilibrium inside the particle pores. These assumptions have been found to give a good description of the uptake process with model compounds, as shown in the preceding chapters. Using data obtained by the SEC analysis the polydisperse asphaltenes are grouped into different individual fractions according to molecular weight increments. As a first approximation, it was assumed that the properties of each asphaltene fraction, e.g., molecular size, diffusivity, and adsorptivity, were independent of every other fraction during the adsorption-diffusion process. This is obviously an oversimplification for a continuous polydisperse, multicomponent system such as presented by asphaltenes; however, in view of the limited characterization of such species, combined with the complexities of multicomponent diffusion/ adsorption, such an approach seemed reasonable, in keeping with the objective of developing a simple, tractable model for the uptake process. While the multicomponent aspects of the diffusion and adsorption processes for the asphaltenes are undoubtedly present, the essentially infinite number of species seem to make such a detailed approach infeasible at the present time. For the same reasons we have also neglected any change in the catalyst pore diameter due to the adsorbed layer of asphaltene molecules. A model which considers this factor has been developed and tested with a single component adsorbing solute, as discussed in Chapter VI; however,

extension of this model to a multicomponent system would be very complex, and has not been performed at this time.

With the above assumptions, the adsorption-diffusion mathematical model for each asphaltene fraction can be developed, as discussed in Chapter III. In this work, we have also assumed that the adsorption isotherm is linear for each individual molecular weight fraction. Each individual fraction can, however, have a different adsorption constant, viz.,

$$q_j = K_j C_j \quad (7.1)$$

Mieville et al. (1989) also showed that the adsorption of quasi-monodispersed asphaltenes was linearly dependent on the concentration. In this case, the diffusion model equations can be solved analytically for the dimensionless bath concentration of asphaltene fraction j , as shown in Chapter III, which can be expressed as a function of dimensionless time by,

$$\theta_{bj} = \frac{B_j}{1+B_j} + 6B_j \sum_{k=1}^{\infty} \frac{\exp(-b_k^2 t_j^*)}{B_j^2 b_k^2 + 9(1+B_j)} \quad (7.2)$$

where, the b_k 's are the non-zero roots of

$$\tan(b_k) = \frac{3b_k}{3+B_j b_k^2} \quad (7.3)$$

and

$$\theta_{bj} = \frac{C_{bj}}{C_{bj0}}, \quad B_j = \frac{V_b \rho_p}{W} \frac{1}{K_{pj} \epsilon + \rho_p K_j}, \quad t_j^* = \frac{D_{ej}}{R^2} \frac{1}{K_{pj} \epsilon + \rho_p K_j} t \quad (7.4)$$

In above equations, D_{ej} is the effective diffusivity expressed as,

$$D_{ej} = \frac{K_{pj}K_{rj}\epsilon}{\tau}D_{\infty j} \quad (7.5)$$

in which K_{pj} and K_{rj} factors are hindered diffusion parameters due to steric and hydrodynamic effects, respectively, being estimated by,

$$K_{pj} = (1-\lambda_j)^2 \quad (7.6)$$

$$K_{rj} = 1 - 2.104\lambda_j + 2.089\lambda_j^3 - 0.948\lambda_j^5 \quad (7.7)$$

The molecular diffusivity $D_{\infty j}$ is related to the solute size by the Stokes-Einstein equation,

$$D_{\infty j} = \frac{kT}{6\pi\eta r_{mj}} \quad (7.8)$$

For a typical adsorptive diffusion experimental system, the values for most parameters appearing in the model are known from the experimental setup, except for the adsorption constants K_j and diffusivities D_{ej} . The values of these two parameters can be estimated either from literature correlations, or by fitting the mathematical model to the experimental asphaltene uptake data. In our study we used a combination of these two approaches wherein the diffusivity values were estimated using correlations developed from previous literature data, while the adsorption constants for the different asphaltene fractions were determined from fitting our experimental uptake data.

Results and Discussion

Preparation of Asphaltenes

In this work, two coal asphaltenes and three petroleum asphaltenes, denoted as C-257K, C-258D and P-AAD, P-AAG, P-AAK, were prepared from coal residues and petroleum asphalts, respectively. The asphaltenes in our work were defined as THF-solubles and pentane-insolubles. The following solvent extraction procedures were used to prepare the asphaltenes.

- (1). A coal solid or petroleum asphalt was first dissolved in THF solvent in a beaker, with an asphalt/THF ratio of 0.5 g/ml, and filtered through a 1 μ m filter paper (with solubility in THF of larger than 99 % as indicated by the amount of insolubles on the filter paper);
- (2). An excess amount of solvent n-pentane was added to the asphalt/THF solution with a pentane/THF ratio of 10. The pentane-insoluble and THF-soluble solid was precipitated during this solvent extraction process;
- (3). The above mixture was centrifuged in a centrifuge bottle for 10 minutes;
- (4). After decanting the supernatant, the precipitate was transferred to the beaker;
- (5). Steps (2) to (4) were repeated for two more times;
- (6). The precipitate was transferred to a bottle, washed with pentane for several times until the pentane solution in the bottle was clear, dried in a hood at room temperature overnight to remove solvent, and then dried again in a vacuum oven at 110 °C for 10 hours;
- (7). The dried precipitate (solid powder) was weighed and the mass yield of the precipitate from the original resid or asphalt was calculated;

- (8). The precipitate (asphaltene) was ground to fine particles and sealed in a bottle for later use.

Table 7.3 shows the mass yields of the asphaltenes prepared by the solvent extraction method. It can be seen that the yields for the two coal asphaltenes are 38 wt% and 54 wt% respectively, whereas the mass yields for the petroleum asphaltenes are relatively smaller, particularly for P-AAG asphaltenes (2.2 wt%). These results indicated that asphaltene contents in petroleum asphalts are less than those in coal liquefaction residues. For the three petroleum asphalts, the relative asphaltene contents obtained in this work are consistent with those shown in Table 7.2, which were defined as n-heptane insolubles rather than n-pentane insolubles. It should be noted that in Table 7.3 the three petroleum asphaltenes are black, whereas the coal asphaltenes are brown, possibly due to the higher metal contents, e.g., Fe, in the coal asphaltenes than in the petroleum asphaltenes.

Calibration of SEC Columns

SEC is a chromatographic technique in which molecules are separated on the basis of their ability to penetrate a porous gel. As the mixture passes through the SEC column in the mobile phase, smaller molecules enter the stationary solvent trapped within the gel pores. However, large molecules cannot enter the gel pores and are therefore excluded, being confined to the mobile phase. This results in large molecules travelling through the column at the same speed as the mobile phase, whereas small molecules are retarded by the gel. Molecules of intermediate sizes are held back to an extent depending on their molecular sizes and the distribution of pore sizes within the gel.

Table 7.3 Yields of asphaltenes from coal residues and petroleum asphalts

asphaltenes	source	yield, wt%	color
C-257K	coal liquid 257 K	38.4	brown
C-258D	coal liquid 258 D	53.7	brown
P-AAD	petroleum asphalt AAD-1	16.0	black
P-AAG	petroleum asphalt AAG-1	2.2	black
P-AAK	petroleum asphalt AAK-1	12.5	black

SEC analysis of asphaltenes requires the use of calibration standards to determine the average molecular weights of the fractions from elution volume. Therefore a calibration curve was first obtained by the use of calibration standards including polystyrenes and styrene monomer, as well as TPP (tetraphenylporphrine), 1-MN (1-methynaphthlene), undecane, and heptane. The standards were first dissolved in THF, then the solutions were analyzed via SEC. Table 7.4 shows the molecular weights of the standards and the corresponding SEC elution volumes, and Figure 7.1 plots the molecular weights vs. SEC elution volumes of the standards. As seen from this figure, the data points for polystyrenes and styrene monomer fit a straight line, being expressed as,

$$\log(M_{PS}) = 7.328 - 0.128V_R \quad (7.9)$$

It may be noted that the data points for the other standards are not on this straight line, with the multi-ring standards (TPP and 1-methynaphthlene) being eluted at slower rates, while the paraffinic compounds (n-heptane and undecane) are eluted at faster rates. These results are consistent with those of Bartle et al. (1984) and can be explained by the fact that the condensed multi-ring compounds have higher molecular weights than the randomly coiled polystyrenes, while the paraffinic standards possess smaller molecular weights, for the same hydrodynamic volumes.

Asphaltene Molecular Weight Distribution

According to the theory of hindered diffusion, as embodied in equations (7.5-7.8), the diffusivity of an asphaltene molecule in a catalyst pore depends on the ratio of the molecule to pore size, i. e. the size of the asphaltene molecule.

Table 7.4 Molecular weights and elution volumes of SEC standards

standards	M_w^a	M_n^a	M_v^a	M_w/M_n	V_R, cm^3
polystyrene	568	503	/	1.13	35.7
polystyrene	794	700	687	1.13	34.5
polystyrene	1306	1221	/	1.07	32.8
polystyrene	2514	2300	2727	1.09	30.7
polystyrene	4136	3967	4075	1.04	28.8
polystyrene	10000	9600	9800	1.04	26.3
polystyrene	13502	12910	12860	1.05	25.6
styrene	104	104	104	1.00	42.0
1-methynaphthlene	142	142	142	1.00	43.3
TPP	615	615	615	1.00	37.3
n-heptane	100	100	100	1.00	40.1
undecane	156	156	156	1.00	38.4

a. Weight, number, and volume average molecular weights of polystyrenes were obtained from Aldrich product description sheets.

Figure 7.1 Calibration of SEC columns by using different standards.

While the molecular weight itself does not appear explicitly in the preceding diffusion model, the size of the asphaltene molecule is a function of its molecular weight. A literature review shows that extensive efforts have been made over the years to define asphaltene molecular weights, using a variety of analytical methods such as VPO, SEC, and mass spectrometries. Based upon its success and ease of use in polymer analysis, the SEC method has been widely applied to asphaltene characterization. However, SEC analysis of asphaltenes is limited by the requirement of appropriate calibration standards to determine the molecular weights of the fractions from elution volumes. Several investigators have used polystyrenes (PS) with narrow molecular weight distributions as calibration standards to obtain the equivalent molecular weight distributions of heavy oils and asphaltenes (Song et al., 1991; Baltus and Anderson, 1983; Sanchez et al., 1984; Dark and McGough, 1978). However, it is now fairly well accepted that, in many cases and especially for the higher molecular weight ranges, the SEC equivalent polystyrene molecular weights are different from the actual asphaltene molecular weights. Vapor pressure osmometry (VPO) is thought to be a more accurate method for asphaltene molecular weight determination provided appropriate care is taken to minimize association effects. Realization of this situation has prompted several investigators to make comparisons of the number average molecular weights obtained from VPO and polystyrene calibrated SEC for coal liquids (Wong and Gladstone, 1983), petroleum asphaltenes (Nali and Manclossi, 1995), and prefractionated subfractions (Brule, 1981; Bartle et al., 1984; Reerink and Lijzenga, 1975; Kiet et al., 1977). In a recent comparative study using a different method, Larsen et al. (1994) have compared the PS calibrated SEC molecular weights with molecular weights obtained by plasma desorption mass spectrometry for a large number of nondistillable residual coal-derived materials

(850°F+ "resids") from the Wilsonville pilot plant, very similar to the 258D material used in our study. These investigators found that the PS calibrated SEC molecular weights agreed quite well with the mass spectrometry molecular weights and with the field ionization mass spectrometry molecular weights from another study using the same materials, especially in the lower molecular weight region. This good agreement was suggested to be due to the fact that the coal "resids" were of relatively low molecular weight, and had a relatively low heteroatom content.

Using data from the above comparative studies we have constructed Figure 7.2, which shows a comparison of the actual molecular weights (M_A) of coal and petroleum derived samples, as measured by VPO and mass spectrometry methods, with molecular weight measurements on the same samples using polystyrene calibrated SEC, termed PS equivalent molecular weights (M_{PS}). The solid line in Figure 7.2 is the best fit of all the data points, while the dashed line assumes equality of the actual and PS equivalent molecular weights. It can be seen that even though the data points are scattered, there is a systematic trend between the asphaltene and the PS equivalent molecular weights in that the actual molecular weights are generally somewhat greater than the PS equivalent SEC values, i. e. most data points fall above the dashed line. In other words, at the same SEC elution volume, the asphaltenes have a greater molecular weight than the corresponding PS standard, i. e. an asphaltene molecule of the same molecular weight would have a longer SEC elution time. This trend is usually attributed to the fact that the planer asphaltene molecules have more condensed molecular structures than the randomly coiled linear polystyrene standards used for SEC calibration. Standards other than polystyrenes have been suggested as a remedy to this situation and this approach certainly has merit (Bartle et al., 1984; Kiet et

Figure 7.2 Comparison of actual molecular weights of asphaltenes and heavy oils with polystyrene equivalent SEC molecular weights. Data points are obtained from different investigators.

al., 1977; Nali and Manclossi, 1995), although the PS calibrated SEC method continues to enjoy widespread use as an analytical tool for asphaltene and resid characterization, because of its ease of use and wide availability of the PS standards. The regression (solid) line in Figure 7.2 is expressed by the following equation,

$$\log(M_A) = -5.354 \times 10^{-2} + 1.067 \log(M_{PS}) \quad (7.10)$$

In our study, based on the above analysis, we have used the above best-fit regression equation to estimate the asphaltene molecular weights of our coal and petroleum asphaltenes, from the corresponding polystyrene calibrated SEC chromatogram.

Combination of equations (7.9) and (7.10) gives the following expression for asphaltene molecular weight as,

$$\log(M_A) = 7.765 - 0.137V_R \quad (7.11)$$

Based on this equation, the molecular weights of the asphaltenes can be estimated from their SEC elution volumes.

Figure 7.3 shows SEC chromatograms of the coal and petroleum asphaltenes in THF. There are two x-axes in this figure, one being the elution volume, the other being the estimated asphaltene molecular weight calculated from equation (7.11). It is observed that the molecular weights of the coal asphaltenes, 50-2000 for C-258D and 50-3000 for C-257K, are much smaller than those of the petroleum asphaltenes (300-30000, 200-20000 and 300-30000 for P-AAD, P-AAG and P-AAK, respectively). Computation of number average molecular weights using the following equation

Figure 7.3 Comparison of molecular weights for coal and petroleum asphaltenes in THF

$$M_n = \frac{\sum_j h_j}{\sum_j \frac{h_j}{M_j}} \quad (7.12)$$

gives values of 490, 320, 2200, 1250 and 2390 for the asphaltenes C-257K, C-258D, P-AAD, P-AAG and P-AAK, respectively. Again, these values indicate that the number average molecular weights for the coal asphaltenes are much smaller than those for the petroleum asphaltenes.

Experimental Results of Diffusional Adsorptive Uptake Experiments

In uptake experiments, one coal and two petroleum asphaltenes (C-258D, P-AAG and P-AAK, respectively) were used as solutes. Samples taken periodically from the adsorptive uptake experiments were analyzed by SEC to obtain the molecular weight distributions of the nonadsorbed asphaltenes remaining in the bath during some time period. Figures 7.4, 7.5 and 7.6 shows the resulting molecular weight distributions for the three asphaltenes in THF during uptake on the Criterion 324 catalyst. It is seen from these figures that as diffusion time increases, the UV absorbances, assumed proportional to concentrations of the individual asphaltene fractions, generally decrease as the asphaltenes are removed from the bath by adsorption on the catalyst surface. However, the rates of decrease for asphaltenes having different molecular weights vary, depending on their diffusion rates and adsorption capacities, as discussed in the model development section.

It is interesting that for the two petroleum asphaltenes, as shown in Figures 7.5 and 7.6, some crossovers of the SEC data were observed at highest molecular weights (greater than approximately 10000). In other words, the molecular weight

Figure 7.4 SEC chromatograms of samples taken during uptake of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 35 °C.

Figure 7.5 SEC chromatograms of samples taken during uptake of petroleum asphaltenes P-AAG in THF into Criterion 324 catalyst at 35 °C.

Figure 7.6 SEC chromatograms of samples taken during uptake of petroleum asphaltenes P-AAK in THF into Criterion 324 catalyst at 35 °C.

distribution shifted to higher values during the uptake process, resulting in an apparent increase in bath concentrations for these fractions. A possible speculation for this phenomenon might be the agglomeration of smaller asphaltene species into larger ones during the uptake process; although, the exact reason for this observation is not clear and this aspect of the work needs further investigation.

Effective Diffusivities and Adsorption Constants for Individual Asphaltene Fractions

In order to perform the model simulation for uptake of each asphaltene fraction, the effective diffusivities D_{ej} and the adsorption parameters K_j are required. One method for determination of the molecular diffusivities of asphaltene fractions is to assume that they are the same as those of the polystyrene standards with the same SEC elution volumes. However, Baltus and Anderson (1983) found that these two values were different, with the molecular diffusivities of polystyrenes being roughly twice those of petroleum asphaltene fractions. In a related study, Nortz et al. (1990) measured hydrodynamic properties of prefractionated heavy oils and obtained the following relationship between the molecular radius in Å and asphaltene molecular weight,

$$r_m = 0.36 M_A^{0.50} \quad (7.13)$$

In equation (7.13) the molecule radius was calculated from the Stokes-Einstein equation (7.8) using the molecular diffusivity experimentally determined by Taylor dispersion measurements. Since the above equation was based on experimentally measured asphaltene diffusivities, we have assumed that it is applicable to our

coal and petroleum asphaltenes, and have used it to estimate the molecular diffusivity of the individual asphaltene fractions eluted from the SEC. Application of this procedure for some asphaltene fractions yields the results shown in Table 7.5. Comparison of the molecular weight ranges in Figure 7.3 with Table 7.5 shows that the estimated effective diffusivities for the coal asphaltenes (C-258D) are in a relatively narrow range of $2\text{--}40 \times 10^{-7}$; while the ranges for the petroleum asphaltenes (P-AAG and P-AAK) cover a broad range from less than 5×10^{-10} to $1 \times 10^{-6} \text{ cm}^2/\text{s}$. These values indicate that the uptake rates will vary widely for the various individual asphaltene fractions, depending on their molecular weights.

Due to the instability of asphaltenes in THF solvent at long time periods, e.g. several days, it is difficult to obtain the adsorption constants K_j from long term equilibrium adsorption experiments; therefore, this remaining model parameter value was determined by fitting the experimental diffusional uptake data with the model solution given by equation (7.2).

Model Simulation of Asphaltene Diffusional Uptake into the Porous Catalyst

For the numerical simulation of the experimental uptake results of the three asphaltenes, shown in Figures 7.4, 7.5 and 7.6 respectively, we first grouped the SEC data into individual fractions, each with an elution volume of 0.5 cm^3 . Estimated effective diffusivities for some of these fractions were shown previously in Table 7.5. For each fraction, the dimensionless bath concentration θ_{bj} was obtained by the ratio of the area under the SEC curve at time t to that at time $t=0$. That is, it was assumed that Beer's Law was obeyed by each individual narrow SEC fraction during the uptake experiment. The adsorption constants K_j were then obtained by fitting the experimental (θ_{bj}, t) uptake data with the model

Table 7.5 Estimated effective diffusivities and other parameters for asphaltenes in THF at 35 °C

V_R cm ³	M_A^a g/mol	r_m^b Å	D_∞^c cm ² /s	D_e^d cm ² /s
25	21900	53.2	9.62E-07	3.42E-10
27	11600	38.8	1.32E-06	4.40E-09
29	6190	28.3	1.81E-06	2.65E-08
31	3300	20.7	2.48E-06	9.18E-08
33	1750	15.1	3.40E-06	2.24E-07
35	933	11.0	4.66E-06	4.46E-07
37	497	8.0	6.38E-06	7.83E-07
39	264	5.9	8.75E-06	1.27E-06
41	141	4.3	1.20E-05	1.96E-06
43	75	3.1	1.64E-05	2.92E-06
45	40	2.3	2.25E-05	4.25E-06
47	21	1.7	3.09E-05	6.08E-06

a. Determined by equation (7.11).

b. Estimated from equation (7.13).

c. Calculated from equation (7.8) with THF viscosity of 4.42×10^{-3} g/cm-s (Reid et al., 1977).

d. Determined by equation (7.5) with $\tau=3.0$ and $\epsilon=0.66$ (Yang and Guin, 1996a).

solution for each fraction. Figure 7.7 shows the resulting values of adsorption constants K_j for the three asphaltenes as a function of molecular weight of the asphaltene fractions. It is interesting that even though the properties of the coal and the petroleum asphaltenes are quite different, the values of adsorption parameters for the fractions of these asphaltenes have the same trend and lie in a relatively narrow band; with increasing the molecular weight, the adsorption constant monotonically increases. This observation seems reasonable in light of the fact that it has also been found that the adsorption of polymers increases as the molecular weights increase (Takahashi et al., 1980; Dimino, 1994). Because of the narrow band of data in Figure 7.7 a single best fit line for all three asphaltenes was obtained with a second order polynomial regression,

$$K_j = 24.00 + 7.74 \times 10^{-2} M_{Aj} + 5.95 \times 10^{-5} M_{Aj}^2 \quad (7.14)$$

It should be noted that for the two petroleum asphaltenes P-AAK and P-AAG in above equation, we used fractions with molecular weights less than 10000. Beyond this value, as noted earlier, some of the experimental bath concentrations increased as discussed above and obviously could not be fitted by the uptake model, which will always have a decreasing concentration. For this reason, adsorption constants K_j for fractions of molecular weights larger than 10000 were obtained by extrapolation of equation (7.14).

Having obtained the adsorption constants K_j and the effective diffusivities D_{ej} , the diffusion equation (7.2) can be solved for the uptake of any asphaltene fraction. Figures 7.8, 7.9 and 7.10 show the resulting simulated model solutions (lines), together with experimental data (points), for the three asphaltenes, respectively. It is observed that for the coal asphaltene C-258D, the model fits experimental data quite well, as seen from Figure 7.8. As shown in Figures 7.9

Figure 7.8 Simulation of experimental uptake data with mathematical model for diffusion of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 35 °C.

Figure 7.9 Simulation of experimental uptake data with mathematical model for diffusion of petroleum asphaltenes P-AAG in THF into Criterion 324 catalyst at 35°C.

Figure 7.10 Simulation of experimental uptake data with mathematical model for diffusion of petroleum asphaltenes P-AAK in THF into Criterion 324 catalyst at 35°C.

and 7.10 the two petroleum asphaltenes have contrasting uptake SEC profiles, due to differences in the initial molecular weight distributions. Generally, however, in spite of the differences in shapes, the mathematical model fits the experimental data fairly well in the molecular weight region below about 10^4 , as shown in Figures 7.9 and 7.10 respectively; however, in higher molecular weight regions ($M_A > 10^4$), some departures of the simulation from experiments were observed due to the crossovers of the experimental uptake data, particularly at longer diffusion times.

Effects of Experimental Conditions on the Uptake of Asphaltenes

1. Effects of Initial Concentration

As shown in equation (7.2), if the equilibrium adsorption for each asphaltene fractions is linearly dependent on its concentration, then the plot of $\theta_{bj} = C_j/C_{j0}$ vs. t during the uptake process is independent of the initial concentration. In other words, the numerical solution of the mathematical model for asphaltene fractions with linear adsorption isotherms is independent of the initial concentration.

To study the effect of initial concentration on the uptake process, two initial concentrations, 0.05 and 0.5 mg/cm³ respectively, were used for the diffusion of coal asphaltenes (C-258D) in THF into Criterion 324 catalysts. The uptake results (data points) at these two initial concentrations are shown in Figures 7.8 and 7.11 respectively, and the adsorption constant vs. molecular weight is plotted in Figure 7.12. As can be seen from Figure 7.12, the adsorption constants at $C_0 = 0.5$ mg/cm³ are less than those at $C_0 = 0.05$ mg/cm³. These results seem to show that the equilibrium adsorption for asphaltene fraction is not

Figure 7.11 Simulation of uptake data with math model for diffusion of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 35°C. $C_0 = 0.5 \text{ mg/cm}^3$.

Figure 7.12 Effect of initial concentration on adsorption constant for the uptake of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 35°C.

strictly linear because of the dependence of adsorption constant on initial concentration. However, as stated before, due to the instability of asphaltenes in solvent, it is difficult to obtain the adsorption isotherm by using equilibrium experiments. In this case, we still assumed that the equilibrium adsorption of asphaltene fraction is linearly dependent on its concentration, keeping in mind that the linear adsorption constant obtained by fitting experimental data with mathematical model is an average value due to the concentration change during the uptake process. The fact that the adsorption constant changes with concentration might also be due to some agglomeration phenomena, e.g. self-assemblies, in the adsorption process, as a result of the change in asphaltene concentration.

2. Effects of Temperature

To investigate the effects of temperature on the adsorption-diffusion behavior, uptake experiments of one coal asphaltene (C-258D) and one petroleum asphaltene (P-AAG) in THF into Criterion 324 catalyst were performed at three different temperatures, 20°C, 35°C, and 50°C respectively. The adsorption constants K_j for the asphaltene fractions at different temperatures were obtained by fitting the experimental data with the mathematical model. The results for coal (C-258D) and the petroleum (P-AAG) asphaltenes are shown in Figures 7.13 and 7.14 respectively, plotted as adsorption constant vs. molecular weight. It should be noted that both the effective diffusivities and the adsorption constants are dependent on the temperature used in the uptake experiments. Therefore, the effective diffusivities of asphaltene fractions were estimated at different temperatures using the Stokes-Einstein equation 7.8, with the solvent viscosities being determined at the corresponding temperatures, as shown in Yang (1996).

Figure 7.13 Effects of temperature on adsorption constant for the uptake of coal asphaltenes C-258D in THF into Criterion 324 catalyst.

Figure 7.14 Effects of temperature on adsorption constant for the uptake of petroleum asphaltenes P-AAG in THF into Criterion 324 catalyst.

For an equilibrium system, one would expect that as temperature increases, the adsorption constant, thus the equilibrium adsorption amount, should decrease if one considers the exothermic behavior observed in most adsorption processes. However, for coal asphaltene fractions of less than 1000 in molecular weight, as shown in Figure 7.13, the maximum adsorption constants were observed at 35°C rather than at 20 °C, while the adsorption constants at 50 °C are smaller than those at both 35°C and 20°C. For the petroleum asphaltenes, as shown in Figure 7.14, it seems that the adsorption constants at three temperatures (20°C, 35°C, and 50°C respectively) are about the same.

Figures 7.15, 7.8 and 7.16 show the simulated results for the coal asphaltenes at 20°C, 35°C, and 50°C respectively, and Figures 7.17, 7.9 and 7.18 show those for the petroleum asphaltenes respectively. It can be seen from these figures that the mathematical model fits the uptakes of both coal and petroleum asphaltenes fairly well at different temperatures.

3. Effects of Solvent Composition

To investigate the effects of solvent on asphaltene adsorption-diffusion process, uptake experiments were performed for the diffusion of coal asphaltenes (C-258D) into Criterion 324 catalyst using two solvents, THF and toluene, respectively. Different solvents result in varied viscosities and thus diffusivities in the diffusion process, as shown in equation (7.8). Figure 7.19 compares the adsorption constants obtained using THF and toluene as solvents in the uptake experiments, and Figures 7.8 and 7.20 show the simulated results for the two solvents, respectively. It can be seen that the adsorption constants with toluene solvent are at least 1 order of magnitude larger than those with THF solvent. This may be related to the fact that toluene is not as "good" a solvent as THF for

Figure 7.15 Simulation of experimental uptake data with mathematical model for diffusion of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 20°C.

Figure 7.16 Simulation of experimental uptake data with mathematical model for diffusion of coal asphaltenes C-258D in THF into Criterion 324 catalyst at 50°C.

Figure 7.17 Simulation of experimental uptake data with mathematical model for diffusion of petroleum asphaltenes P-AAG in THF into Criterion 324 catalyst at 20°C.

Figure 7.18 Simulation of experimental uptake data with mathematical model for diffusion of petroleum asphaltenes P-AAG in THF into Criterion 324 catalyst at 50°C.

Figure 7.19 Effects of solvent on adsorption constant for the uptake of coal asphaltenes C-258D into Criterion 324 catalyst at 35°C.

Figure 7.20 Simulation of experimental uptake data with mathematical model for diffusion of coal asphaltenes C-258D in toluene into Criterion 324 catalyst at 35°C.

the asphaltenes and may indicate the presence of agglomeration or "self-assemblies" of asphaltenes with the toluene solvent.

Conclusion

Both the coal and petroleum asphaltenes used in this study have very broad molecular weight distributions, with the molecular weights of the coal asphaltenes (50-2000) being much smaller than those of the petroleum asphaltenes (300-30000 for P-AAK and 200-20000 for P-AAG). Examination of prior literature data showed that SEC elution data, based on polystyrene calibration standards, could be used to develop a correlation for estimating the molecular weights of asphaltene fractions. The coal asphaltene fractions have estimated effective diffusivities which span 1 order of magnitude, whereas these spans are more than 3 orders for the two petroleum asphaltenes. The uptake rates for individual asphaltene fractions with different molecular weights are different, depending on their diffusion rates and adsorption constants. Even though the properties of the asphaltenes used were quite different, the values of model parameters for the fractions of the three asphaltenes had the same trend; with increasing molecular weight of the fraction, the adsorption constant increased and the effective diffusivity decreased monotonically. The experimental diffusion controlled uptake data for the three asphaltenes was represented fairly well in most molecular weight regions by the same mathematical model using appropriate parameter values, although some departures were observed in the high molecular weight region. While only three asphaltenes were tested in the current study, it might be speculated that the uptake of additional asphaltenes as a function of molecular weight could be estimated using the present model.

The adsorption constants for coal asphaltene fractions at 0.5 mg/cm^3 initial concentration are less than those at 0.05 mg/cm^3 , indicating the non-linearity of coal asphaltene adsorption on the porous catalyst. Comparison of uptake results using different solvents showed that the adsorption constants with toluene solvent are much larger than those with THF solvent. The effect of temperature on the adsorptive uptake was complex, with the adsorptivity for coal asphaltenes at 35°C exceeding that at 25°C in the lower ($<10^3$) molecular weight region; while the adsorptivities for petroleum asphaltenes were about the same at 20 , 35 , and 50°C .

NOMENCLATURE

Letters

A_e	effective cross sectional area of capillary pore in catalyst particle, cm^2
A_p	cross sectional area of capillary pore in catalyst particle, cm^2
A_{pm}	cross sectional area of capillary pore with monolayer adsorption, cm^2
A_t	total cross sectional area of capillary pore in catalyst particles, cm^2
b	constant in nonuniform porosity model for spent catalyst
B	dimensionless diffusion model parameter
c	constant in nonuniform porosity model for spent catalyst
c_0	constant in nonuniform porosity model for spent catalyst
C	solute pore concentration, g/cm^3
C_b	solute bath concentration, g/cm^3
C_s	solute bath concentration at particle surface, g/cm^3
d_m	solute diameter, cm
d_p	average catalyst pore diameter, cm
D	diameter of cylindrical catalyst extrudates, cm
D_∞	solute molecular diffusivity, cm^2/s
D_e	effective diffusivity in the pores, cm^2/s
D_{ep}	effective diffusivity for ordinary diffusion in the pores, cm^2/s
D_K	Knudsen diffusion coefficient, cm^2/s
D_s	surface diffusion coefficient, cm^2/s

E	dimensionless diffusion model parameter
E_m	dimensionless diffusion model parameter
F	dimensionless diffusion model parameter
F_N	confinement free energy of molecules in the pores, erg
g	dimensionless function in nonuniform particle model
G	dimensionless function in Langmuir isotherm
h	dimensionless function in nonuniform particle model
k'	number of catalyst particles in diffusion experiment
k	Boltzmann constant, 1.38×10^{-16} erg/K
K	linear adsorption constant, $\text{cm}^3\text{-solution/g-cat}$
k_c	mass transfer coefficient, cm/s
K_L	Langmuir adsorption constant, $\text{g-solute/cm}^3\text{-solution}$
K_p	partition factor
K_r	restriction factor
L	length of cylindrical catalyst extrudate, cm
L'	length or angle factor of the pores
m	Freundlich adsorption constant
M	molecular weight, g/mol
M_w	weight average molecular weight of a polymer, g/mol
M_v	volume average molecular weight of a polymer, g/mol
M_n	number average molecular weight of a polymer, g/mol
n	Freundlich adsorption constant
N_A	mass flux in porous particle, $\text{g/cm}^2\text{-s}$
N_{Ac}	external mass flux around porous particle, $\text{g/cm}^2\text{-s}$
N_{Ap}	mass flux in porous particle without hindered effects, $\text{g/cm}^2\text{-s}$
N_{As}	surface mass flux in porous particle, $\text{g/cm}^2\text{-s}$

$N_{A\infty}$	ordinary mass flux in bulk solution, $\text{g}/\text{cm}^2\text{-s}$
Nu	Nusselt number
P	pressure, atm
q	amount of equilibrium adsorption, $\text{g-solute}/\text{g-catalyst}$
q_m	amount of monolayer adsorption, $\text{g-solute}/\text{g-catalyst}$
Q_t	total amount of solute entered catalyst particle at time t, g
Q_e	total amount of solute entered catalyst particle at equilibrium, g
r	radial position of catalyst particle, cm
r_m	solute radius, cm
r_p	pore radius, cm
R	catalyst particle radius, cm
	universal gas constant, $82.06 \text{ cm}^3\text{-bar}/\text{mol-K}$
Re	Reynolds number
S	surface area of porous catalyst, m^2/g
S_{ext}	external surface area of catalyst particle, cm^2
S'	shape factor of the pores
Sc	Schmidt number
Sh	Sherwood number
t	diffusion time, s
t^*	dimensionless time
t_1^*	dimensionless time with linear adsorption isotherm
T	absolute temperature, K
u_∞	fluid linear velocity around catalyst particle, cm/s
V	catalyst pellet volume, cm^3
V_b	bath volume, cm^3
V_R	SEC elution, cm^3

V_p	catalyst pore volume, cm^3/g
W	catalyst weight, g
z	constant in Beck-Schultz's power law in equation (2.20)

Greek

α	geometric constant for capillary pore
ϵ	catalyst porosity
$\langle \epsilon \rangle$	average porosity in spent catalyst
η	solvent viscosity, $\text{g}/\text{cm}\cdot\text{s}$
θ	dimensionless concentration in the pores, C/C_{bi}
θ_b	dimensionless concentration in the bath, C_b/C_{bi}
θ_q	dimensionless adsorption in catalyst particle, q/q_i
θ_s	dimensionless bath concentration at particle surface, C_s/C_{bi}
λ	ratio of solute molecule diameter to catalyst pore diameter, d_m/d_p
ξ	dimensionless radial position, r/R
ρ	solvent density, g/cm^3
ρ_p	catalyst particle density, g/cm^3
τ	tortuosity factor

Subscripts

i	initial time
j	j th component in asphaltenes
0	fresh catalyst
∞	infinite time or equilibrium

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