HINDERED DIFFUSION OF ASPHALTENES AT ELEVATED TEMPERATURE AND PRESSURE

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Abstract

During this final time period of the project, work was carried out in two areas. A major amount of effort was devoted to preparation of the final technical report for the project. The data taken on the project were organized and the asphaltenes, solvents, and catalysts used in the diffusional uptake experiments were organized into various systems. Since a large portion of the time for this report was spent on the preparation of the final technical report itself, the executive summary of the final technical report has been included in this semi-annual report as indicative of the effort during this time period. In addition to work on the final technical report for the project, a limited experimental study of dye adsorption into active carbon particles was performed by an undergraduate student in chemical engineering, Mr. Zachery Emerson. The objective of this study was to compare the diffusional uptake performance in two different types of vessels, a stirred glass cell and the tubing microreactor, for a simple dye-water-carbon diffusional uptake system. Due to time limitations, only qualitative conclusions were drawn from this study.

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Objectives

The overall goal of this project is to obtain a better understanding of the diffusion controlled uptake of model compounds and asphaltenes in porous catalysts at elevated temperatures. Generally past investigations have been restricted to uptake experiments at ambient temperatures and pressures. Thus we are seeking:

1. To investigate the hindered diffusion of both coal and petroleum asphaltenes in porous catalysts at elevated temperatures.
2. To examine the effects of temperature on the intraparticle diffusivity of asphaltenes.

Executive Summary

Our research project centers around obtaining a better understanding of the diffusion of model compounds and asphaltenes in porous catalysts at elevated temperatures. These matters are of interest in the design and tailoring of catalysts for reactions under elevated temperature and pressures such as may occur in coal liquefaction and petroleum resid upgrading, where diffusional influences often present themselves. Our efforts during the current reporting period have concentrated on preparation of the final technical report and a limited qualitative study of diffusion controlled adsorption of a dye from water with an activated carbon substrate. The purpose of the latter study was to compare the diffusional uptake performance in two different types of vessels, a stirred glass cell and a tubing microreactor, for a simple dye-water-carbon diffusional uptake system. Due to time limitations, only qualitative conclusions were drawn from this study.

Experimental

Introduction

The first part of the work done in this time period was a study, performed by Mr. Zachery Emerson, undergraduate student in chemical engineering, in which experiments were performed to analyze the adsorption of a dye, FD&C Blue #1, from an aqueous solution into active carbon particles. Two experimental setups were employed in the study, corresponding to the two uptake vessels used in the study, viz., a stirred glass cell and a tubing microreactor. The purpose of the study was to compare the diffusional uptake performance in the two different types of vessels for a simple dye-water-carbon diffusional uptake system.

The second phase of the work done during this time period was to prepare the final technical report for the project. In our preparation, we examined the data taken during the entire project and organized it into several systems depending on the particular catalyst, solute molecule, and solvent utilized. used in the uptake experiments. In our final technical report we included representative experimental data and results from each of the asphaltene-solvent-catalyst systems studied. Complete details are available for the interested reader in our series of semi-annual reports submitted during the course of the project.

Results and Discussion

Qualitative Study of Activated Carbon Adsorption:

One of the two uptake vessels used in this particular study was a glass diffusion cell utilized in earlier diffusion studies as described by Chen (1992). In this case, diffusional

uptakes of dye from water into porous catalyst particles were performed in a magnetically stirred glass diffusion cell containing a screen wire basket for holding catalyst particles. For each diffusion run, typically, 150 cm³ dye solution and 0.75 g active carbon were used. The carbon particles were presaturated with water before diffusion runs. During the diffusional uptake process, *ca.* 3 cm³ samples were withdrawn periodically from the diffusion cell, filtered through a 0.5 µm filter, and analyzed via spectrometry at 630 nm. A scan of the dye sample from 250 to 800 nm revealed that this absorbance peak was most useful for analysis of the dye concentration. The remaining sample solution following analysis was returned to the diffusion cell in order to maintain an essentially constant bath volume during the uptake process. A schematic diagram of the glass diffusion cell are given by Chen (1992). Using the glass diffusion cell, runs were performed at ambient temperature and 35 °C.

In a second set of experiments an approximately 20 cc microautoclave such as shown schematically by Joo (1996) was used in diffusional uptake experiments. In a typical run, where the diffusion-controlled adsorptive uptake of a solute from the solution onto carbon particles was carried out, the particles were supported on a wire mesh which avoided direct contact with the solution until the experiment was begun. Runs were made for various time intervals, following which the liquid phase was collected and analyzed to determine the concentration of solute remaining in the liquid. Generally, the microautoclaves used in this part of the study contained around 10 mL of the dye solution, and 0.05 g of carbon catalyst. The microautoclave experiments were carried out at agitation rates of 100 to 300 RPM speeds.

The dye used in the above uptake experiments was FD&C Blue number 1 (Merck Index, Vol. 11, number 1366) with a molecular weight of 793. The carbon used as an absorbent was a commercial active carbon catalyst, Calgon BPL 4x6, with an irregular shape, an equivalent

particle radius of 0.2 cm and a surface area of 1100 m²/g. This carbon was the same one used earlier in our work on asphaltene uptakes. There have been several dye adsorption studies on activated carbons of this type as reported in the literature (Leyva-Ramos and Geankoplis, 1994, McKay and Al-Duri, 1988, Walker and Weatherley, 2001, Yang and Al-Duri, 2001).

The results of the diffusional uptake study conducted by Mr. Emerson were qualitative in nature due to the limited amount of time for the study and the presence of significant scatter in the experimental data. Unfortunately, time did not permit us to determine the cause of the scatter in the data and thus we were only able to draw some qualitative conclusions from this limited study. Using the microautoclave reactor, the the average dimensionless dye concentrations, C/C_o , for four hour uptake periods were 0.51, 0.42 and 0.45 at agitation speeds of 100, 200, and 300 RPM. That is, the average dye uptake was slightly greater at the higher speed; however, the linear regression coefficient for the actual data as a function of agitation rate was only 0.076 indicating a low statistical significance for the correlation of uptake vs. agitation rate. Thus at this point, we can not discern any statistically significant trend of uptake rate with agitation rate for the microautoclave vessel. For the glass diffusion cell, similar uptake experiments were performed with uptake values that were only slightly greater than those in the microautoclave for the same time periods. Thus, based on the limited study performed, it was difficult to discern any significant degree of difference in the dye uptake rates in the two vessels used in our study, and we could only view the results in a qualitative sense. Additional studies would be required to develop a more quantative trend with greater statistical significance, however, due to the limited time and funds available during this final project period, such studies were not pursued.

Final Report Preparation. Following the preceeding studies, a major effort was made during the present time period to organize the work done on this project for presentation in an

overall final technical report. The executive summary from this part of the work is included herein as representative of the effort during this time period. The complete final technical report is available as desired as a separate document.

Executive Summary of Final Technical Report

Executive Summary

This project investigated the diffusion of large molecules termed asphaltenes and certain other model compounds into the pores of supported catalysts. The practical importance of this project stems from the need to upgrade heavy liquids from coal and petroleum in order to obtain clean transportation fuels such as jet, gasoline, and diesel. These heavy liquids contain a class of macromolecular species operationally defined, by solubility classification in various solvents, as asphaltenes. Because of their relatively large molecular sizes and micellar self-aggregative structure, these asphaltene moieties experience considerable diffusional resistance, or hindrance in the pores of the supported catalysts used for upgrading. Attempts to overcome this diffusional restriction have resulted in various catalyst pore size distributions, e. g., bimodal vs. unimodal, and pellet shapes, e. g., trilobe vs. cylindrical. However, because of a lack of fundamental understanding of diffusional mechanisms involving asphaltene species in the catalyst pores, the relative merits of these various catalyst modifications are many times unclear and contradictory results sometimes appear. Thus, this work was undertaken with the objective of providing some additional insight as to the manner in which asphaltenes diffuse into porous catalysts. Our approach was to study the diffusional uptake of asphaltenes in a finite bath system and then to model the experimental data with mathematical models based on literature research.

Most previous studies dealing with asphaltene diffusion have been those conducted at near ambient conditions and/or those conditions which involve idealized pore structures such as track-etch membranes with perfectly straight capillary pores. It is sometimes difficult to extrapolate these studies to other conditions in actual porous catalysts. Other studies have attempted to glean diffusional information from reaction rates using supported catalysts via extraction of the appropriate information from the apparent effectiveness factors during catalytic hydrotreatment. While this approach is certainly useful, reaction kinetics data is needed to extricate the diffusional parameters. By taking a somewhat different approach, this project entailed research to study asphaltene diffusion in actual catalyst pores, under elevated temperature and pressure conditions representative of catalytic upgrading, although using relatively inert supports, e. g. carbon, alumina, and atmospheres which would give a basically nonreactive environment to the asphaltenes. Along these lines, it is of interest that a 1999 article, relating to planning for the future research activities at DOE labs, has noted the need for increased understanding of the interactions between catalyst pore sizes and asphaltene sizes (Jacoby, 1999). Thus based on the above considerations, our project sought to investigate pore diffusion into actual catalyst pellets at various temperatures under nonreactive conditions.

Our project investigated asphaltenes from both coal and petroleum sources diffusing into alumina and porous carbon catalyst supports, at temperatures up to 325 °C. Both commercially available and laboratory produced catalyst supports were utilized in the experimental work. Catalysts were characterized by mercury porosimetry and by nitrogen adsorption (BET) surface area measurements. Some of the catalysts had broader pore size distributions than originally anticipated; however, this was allowed for by an average pore diameter based on the catalyst pore volume and specific internal surface area. Both diffusional uptake experiments and equilibrium adsorption experiments were performed. Uptake experiments used a finite bath

technique in which the concentration of the diffusing species, e. g. asphaltenes, was followed as the molecules were adsorbed onto the surface of the porous catalyst and thereby removed from the surrounding solution. Solvents which were used in the diffusion bath included compounds such as cyclohexane, mineral oil, toluene, and 1-methylnaphthalene, the latter being used predominately at higher temperatures due to its relatively low vapor pressure. A variety of diffusional vessels ranging in size from 1 L to 20 cm³ were used in the uptake experiments. Analytical techniques likewise were variable ranging from simple elemental compositional determinations to detailed liquid chromatographic (gel permeation chromatography) analysis. Throughout this experimental work, safety considerations were a primary concern, especially when dealing with large volumes of chemical solvents at elevated temperatures and pressures. These issues were mitigated to some extent through the utilization of small volume microreactor uptake vessels which minimized the amount of solvents in each experiment. In addition, the lumped-parameter modeling of the asphaltenes in which concentrations were determined from single UV-Vis spectrometry measurements rather than detailed liquid chromatographic analyses of each sample, helped to minimize usage of chromatographic solvents which have a tendency to form explosive peroxides, e. g. tetrahydrofuran.

During the course of the research, several problems were encountered. For example, the adsorption isotherms for the coal and petroleum asphaltenes were very complex, with temperature variations which did not follow the expected trends, i. e. the adsorption amount did not always decrease as temperature increased. This unexpected behavior was possibly due to aggregate formation by the asphaltenes in solution, a process which could vary with the temperature, or perhaps thermally induced chemical reactions. In some cases, where the pore diffusivity was found by direct nonlinear regression of the uptake data, these complex isotherms

yielded unreasonable values for the diffusivity in subsequent mathematical modeling, e. g. tortuosities less than unity. Generally, the mathematical treatment of asphaltenes as a multicomponent, diffusing and adsorbing system was found to be extremely challenging, as it was not clear how to model the complex multicomponent aspects of the system. To approach these problems in a tractable manner, a simplified lumped-parameter mathematical model was employed to analyze the experimental uptake data. The model accounted for factors such as molecule and pore diameter, solvent viscosity, catalyst loading, and temperature. In this lumped-parameter model, the diffusivity was estimated from the Stokes-Einstein equation and literature correlations for hindered diffusion, rather than direct nonlinear regression as originally planned. The literature correlations, based on the ratio of molecule to pore diameter, have a theoretical origin and have also been confirmed experimentally by membrane diffusion experiments with straight uniform pores. For complete estimation of the effective pore diffusivities, catalyst tortuosity factors were obtained from prior literature experiments using the same types of catalysts. The remaining model parameter, the adsorption equilibrium constant, was obtained via regression of the uptake data. Due to the extremely complex equilibrium adsorption behavior found for the asphaltenes, a linear isotherm was adopted to provide an approximate representation of this behavior. Experiments to investigate the effects of solvent aromaticity on the diffusional uptake process were performed using a mixture of mineral oil and 1-methylnaphthalene of various concentrations. Properties for the mixture were estimated from literature correlations and the mathematical model developed in the work was used to obtain the adsorption constant as a function of solvent aromaticity. Overall, the lumped-parameter mathematical model employed herein was found to provide a reasonably satisfactory description of the experimental data for the uptake of both coal and petroleum asphaltene species, as well as

certain model compounds, e. g. quinoline, into the porous catalysts at elevated temperature conditions. It is possible, however, that other models, not investigated herein would also fit the uptake data. In order to better delineate the applicability of various models, more definitive studies of multicomponent adsorption equilibria are recommended. This would allow the equilibrium parameters to be determined independently of the uptake data, thus giving these parameters a greater degree of confidence.

Conclusions.

Results of a limited study of adsorptive uptake using a dye medium adsorbed from an aqueous solution on activated carbon particles showed that there were little or no statistically significant differences in diffusion controlled adsorptive uptakes from two of the uptake vessels used in this study. A major effort was made in this time period on the preparation of the final technical report on this project, the executive summary of which is included in this semiannual report.

Planned Work.

This project has been concluded and the final technical report has been prepared. Thus no additional work is planned for the project.

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