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CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN FRESH AND AGED CATALYST EXTRUDATES

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Statement of Work

Configurational Diffusion of Asphaltenes in Fresh and Aged Porous Catalyst Extrudates

Objective: The objective of this research is 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, how do the effective intrapore diffusivities depend on molecule configuration and pore geometry.

Task 1. Relationship Between Effective Intrapore Diffusion Coefficients, Molecular Size and Pore Geometry.

Finite bath-type diffusion experiments will be performed using both coal and petroleum-derived macromolecular species, e.g. asphaltenes, as well as model compounds, e.g. porphyrins, polymers, of known molecular size. By monitoring the concentration of solute macromolecules in the bath, the effective intrapore diffusion coefficients will be determined through application of the appropriate diffusion equations. Macromolecular species concentrations will be monitored by size exclusion chromatography (SEC). Relationships will be sought between the size, and shape, e.g. planar, coil, of the diffusing solutes and the pore geometry (pore size distribution) of the catalyst support. The effects of molecule configuration and catalyst pore size distribution on the effective intrapore diffusivity will be examined. Specially prepared laboratory catalysts with very narrow pore size distributions and other model porous media, e.g. porous Vycor glass, will be utilized in the experiments. Pore structures of all catalysts and other porous media will be characterized by mercury porosimetry and surface area (BET) analysis.

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.

Diffusion experiments such as in Task 1 will be performed with varying solvent compositions, i.e., paraffinic-aromatic mixtures, to examine the effects of the state of molecular

aggregation (self-assemblies) on the rates of diffusion of coal and petroleum asphaltenes in the catalyst pores. Similar experiments will be performed to study the effect of *temperature* and solute (macromolecule) *concentration* on the state of molecular configuration and aggregation on the resulting pore diffusivity.

Task 3. Assessment of Diffusional Limitations in Aged Catalysts

Diffusivity measurements such as conducted in Task 1 will be performed with both model compound and coal-derived macromolecular species using extrudate-type aged catalysts from laboratory experiments as well as aged catalysts obtained from actual coal liquefaction pilot plants such as the Wilsonville, AL Advanced Coal Liquefaction R & D Facility. From the experimental diffusivities so obtained, an evaluation of effects of changes in catalyst pore structure, e.g. tortuosity, pore plugging, shall be made. The changes in pore diffusivities associated with the pore structural changes caused by coke and metals deposition will be investigated, as compared with the fresh catalysts. As assessment of the relationship of increased diffusional limitations to coke and metals deposition in the catalyst pores will be made based on the results of the diffusivity measurements. The degree to which pore diffusivities can be restored to their original values by carefully controlled oxidation and/or extractive catalyst regeneration techniques also will be explored. The practical importance of these findings to coal liquefaction technology will be evaluated.

Summary

This quarter we performed some initial scoping experiments dealing with the diffusive adsorption of petroleum/asphalt and coal molecules on alumina catalysts. In these experiments, the concentration of solute molecules in a bath exposed to the adsorbing solid (alumina) was monitored as a function of time. Because these are only preliminary scoping experiments, no quantitative calculations of diffusivity or adsorption equilibria were made; however, these experiments do demonstrate the feasibility of the finite bath technique for diffusivity determination.

Planned Work

A new PhD student has joined the project, Mr. X. Yang. He will begin his work this next quarter. The M.S. student currently working on the project, Mr. C. C. Chen, will graduate in June, 1992.

Detailed Progress

Desorptive Diffusion of Petroleum Asphalt Molecules from Pores of Alumina A-202 Catalyst into a Large Bath of Pure THF

Objective

The purpose of these preliminary experiments was to study the diffusion of asphalt molecules in liquid-filled pores of alumina. The study focused on asphalt molecule diffusion rates by measuring the concentration of asphalt solutions at different time intervals in a bath containing alumina aggregates.

Experiments

Alumina catalyst A-202 was used as a matrix through which a concentrated asphalt solution diffused into a surrounding bath of pure THF. The pore size distribution of the alumina catalyst is shown in Figure 1. The asphalt used in this experiment was an AR-4000 grade petroleum asphalt with an asphaltene content of 23 %. About five grams of alumina A-202 spheres (average diameter 0.6 cm) was placed in a vacuum oven at 100°C for one day to remove the moisture. The dried alumina was then placed in a wire basket and immersed in an asphalt solution. After saturation, the basket with the alumina was lifted from the concentrated asphalt solution and quickly rinsed with pure THF to remove any excess asphalt solution from the outer surface of the alumina as well as the basket. The basket with alumina then was placed in a bath with 200 ml of pure

THF, and the solution was well stirred with a magnetic stirrer to insure a uniform concentration in the cell. One milliliter samples of the solution in the cell were withdrawn for GPC analyses at time intervals of 1, 6, and 20 minutes, and 2, 4, 6, 10, and 28 hours.

Results and Discussion

Results of GPC analyses are shown in Figure 2. As seen in the chromatograms, the absorbances of the solutions increased with time. The increase is about the same for the large molecule fraction and the small molecule fraction of the asphalt molecules. The fact that the large and small molecules diffuse out of the aggregate at about the same rate is probably the result of a combination of both adsorption and diffusive factors.

Adsorptive Diffusion of Coal Molecules in THF into Alumina A-202 Catalyst Pores

Experiments

A solid coal residue (Rose Residue, From Run 258D, Sample No. 97500) from the Southern Clean Fuel Division (Wilsonville, AL) was utilized in this experiment. A 0.5 wt. % coal residue solution in THF was prepared. A part of the dried alumina was ground and sieved with 35 and 48 mesh screens, so that sizes of all the particles collected were between 0.417 mm and 0.295 mm. Two sets of five serum bottles containing five grams of 0.6 cm alumina spheres and -35+48 mesh particles, respectively, with 5 grams of coal

solution were placed in a shaker at 250 rpm, and 25°C. These samples were analyzed by GPC at various time intervals: 0.5, 1, 2, 17.5, and 24 hours for alumina spheres and 0.25, 0.5, 1, 2, and 17.5 hours for -35+48 mesh particles. Another two bottles containing the same amount of materials were placed in a shaker at 250 rpm, and 50°C and analyzed with the same procedures to examine the effect of temperature on adsorption. In order to examine the effect of particle size on the equilibrium adsorption, alumina pellets were crushed into fine powder and sieved through a 100 mesh screen so that the diameters of the particles obtained were smaller than 0.015 cm. Two serum bottles containing 5 grams of alumina powder and 5 grams of coal solution were placed in a shaker at 250 rpm, and 25°C. The solution was then filtered and analyzed by GPC after 24 hours.

The stability of coal molecules in THF was also examined by GPC analysis in a control experiment (no catalyst) 24 hours after the solution was made.

Results and Discussion

Results for the time dependence of adsorption are shown in Figures 3 and 4. As seen in Figure 3, the equilibrium adsorption is reached in less than 17.5 hours, and half of the maximum uptake is reached in a half hour. The large molecules are adsorbed to a much greater extent than the small molecules. The results for small particles shown in

Figure 4 shows that the equilibrium adsorption is almost reached in 15 minutes. The fact that this is much faster than the previous results (Figure 3) is indicative of a diffusion controlled adsorption process. The particle size of the alumina, therefore, plays an important role on the adsorption rate of coal molecules from THF solutions. Comparisons of the effect of particle size and temperature on equilibrium adsorption are shown in Figure 5 and Figure 6, respectively. The effects of temperature and particle size however do not appear to have a very significant effect on coal molecule adsorption at equilibrium. As was the case with petroleum asphalt molecules, the large size molecules appear to be more strongly adsorbed. Results of the stability test are shown in Figure 7. The coal molecules are quite stable in THF for one day, as shown by the results of the GPC analysis after 24 hours.

Figure 1. Pore Size Distribution for Alumina A-202

Figure 2. Time Dependence of Asphalt AAD-1 Diffusion from A-202 Alumina Aggregate

Figure 3. Time Dependence of Coal Molecule Adsorption on 0.6 cm Alumina A-202 Spheres

Figure 4. Time Dependence of Coal Molecule on Adsorption on -35 +48 Mesh Alumina A-202 Particles

Figure 5. The Effect of Particle Size on Coal Molecule Adsorption on Alumina A-202 after 24 Hours

Figure 6. The Effect of Temperature on Coal Molecule Adsorption on Alumina A-202 after 2 hours

Figure 7. Comparison of the Original Coal Molecules and Coal Molecules after 24 Hours in THF

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