QUARTERLY PROGRESS REPORT
ON
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, uptake experiments of coal and petroleum asphaltenes into porous catalyst were performed using different initial concentrations, temperatures, and solvents. The adsorption-diffusion parameters were obtained by simulating the experimental data with the mathematical model. The results showed that the adsorption constants for coal asphaltene fractions at 0.5 mg/cm³ initial concentration are less than those at 0.05 mg/cm³, indicating the non-linearity of coal asphaltene adsorption on porous catalyst. Comparison of uptake results using different solvents showed that the adsorption constants with solvent toluene 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 (<10³) molecular weight region; while the adsorptivities for petroleum asphaltenes are about the same at 20, 35, and 50°C.

Effects of Experimental Conditions on the Uptake of Asphaltenes

Effects of Initial Concentration

As shown in the last quarterly report, if the equilibrium adsorption for each asphaltene fractions is linearly dependent on its concentration, then the plot of C_t/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 1 and 2 respectively. By using the same mathematical treatment as we did in the last quarterly report, the linear adsorption constants for asphaltene fractions were obtained by simulating the experimental data with the model solution. The results are shown in Figure 3, plotted as adsorption constant vs. molecular weight. As can be seen from Figure 3, the adsorption constants at $C_0=0.5$ mg/cm³ are less than those at $C_0=0.05$ mg/cm³. From these results it seems that the equilibrium adsorption for asphaltene fraction is not strictly linear because of the dependence of adsorption constant on initial concentration. However, 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 due to some agglomeration phenomena, e.g. self-assemblies, in the adsorption process, as a result of the change in asphaltene concentration.

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. The adsorption constants K_j for the asphaltene fractions were obtained by fitting the experimental data with the mathematical model, as discussed in the last quarterly report. The results for coal (C-258D) and the petroleum (P-AAG) asphaltenes are shown in Figures 4 and 5 respectively, plotted as adsorption constant vs. molecular weight. It should be noted that both the effective diffusivities and 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, with the solvent viscosities being determined at the corresponding temperatures, as shown in the last quarterly report.

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 4, 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 5, it seems that the adsorption constants at three temperatures (20°C, 35°C, and 50°C respectively) are about the same.

Figures 6, 1 and 7 show the simulated results for the coal asphaltenes at 20°C, 35°C, and 50°C respectively, and Figures 8, 9 and 10 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.

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 discussed in the last quarterly report. Figure 11 compares the adsorption constants obtained using THF and toluene as solvents in the uptake experiments, and Figures 1 and 12 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 the asphaltenes and may indicate the presence of agglomeration or "self-assemblies" of asphaltenes with the toluene solvent.

Conclusion

The adsorption constants for coal asphaltene fractions at 0.5 mg/cm³ initial concentration are less than those at 0.05 mg/cm³, 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 (<10³) molecular weight region; while the adsorptivities for petroleum asphaltenes were about the same at 20, 35, and 50°C.

Figure 1 Simulation of experimental data with mathematical model for the uptake of coal asphaltenes (C-258D) in THF into Criterion 324 catalyst at 35°C. $C_0=0.05$ mg/cm³

Figure 2 Simulation of experimental data with mathematical model for the uptake of coal asphaltenes (C-258D) into Criterion 324 324 catalyst at 35°C. $C_0=0.5$ mg/ml

Figure 3 Effect of initial concentration on adsorption constant for the uptake of coal asphaltenes (C-258D) in THF into Criterion 324 catalyst at 35°C.

Figure 4 Effects of temperature on the adsorption constants for the uptake of coal asphaltenes (C-258D) in THF into Criterion 324 Catalyst.

Figure 5 Effects of temperature on the adsorption constants for the uptake of petroleum asphaltenes (P-AAG) in THF into Criterion 324 catalyst at 35°C.

Figure 6 Simulation of experimental data with mathematical model for the uptake of coal asphaltenes (C-258D) in THF into Criterion 324 catalyst at 20°C.

Figure 7 Simulation of experimental data with mathematical model for the uptake of coal asphaltenes (C-258D) in THF into Criterion 324 catalyst at 50°C.

Figure 8 Simulation of experimental data with mathematical model for the uptake of petroleum asphaltenes (P-AAG) in THF into Criterion 324 catalysts at 20°C

Figure 9 Simulation of experimental data with mathematical model for the uptake of petroleum asphaltenes (P-AAG) in THF into Criterion 324 catalyst at 35°C.

Figure 10 Simulation of experimental data with mathematical model for the uptake of petroleum asphaltenes (P-AAG) in THF into Criterion 324 catalysts at 50°C

Figure 11 Effect of solvent on adsorption constants for the uptake of coal asphaltenes (C-258D) in Criterion 324 at 35°C.

Figure 12 Simulation of experimental data with mathematical model for the uptake of coal asphaltenes (C-258D) in toluene into Criterion 324 catalyst at 35 °C

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