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ADSORPTION AND DESORPTION OF HYDROCARBONS AT LOW CONCENTRATIONS

FINAL TECHNICAL REPORT

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NOTICE

CONTENTS

ABSTRACT

Research accomplishments during the report period include the following: (i) Experimental measurements of the time-dependent transmission of hydrocarbons and their mixtures at low concentrations through activated carbon and polystyrene adsorber beds, (ii) theoreticl and experimental studies of dynamics of adsorbates (including radioactive gases) in adsorber beds, (iii) formulation of the theory of adsorption of single gases and their mixtures on heterogeneous microporous solids, (iv) initial studies of adsorption from solutions on heterogeneous microporous solids, and (v) study of the influence of adsorbent heterogeneity on the pressure swing adsorption process. During the report period, the chromatographic dynamic method for measuring transmission of gases and gas mixtures through adsorbent beds was improved and modified in order to cover very low adsorbate concentrations and low temperatures. The transmission measurements were utilized to study diffusion effects for gases and gas mixtures flowing through adsorber beds and to calculate equilibrium adsorption isotherms for single gases and gas mixtures. Significant progress has been achieved in the theory of gas adsorption on heterogeneous microporous solids and in the characterization of structural and energetic heterogeneities of these solids.

1. Introduction

Research accomplishments during the research period (from 1 June 1984 through 31 August 1989) are reported in the publications and presentations listed and attached in Appendices A and B, respectively. A general summary of the research and a comprehensive evaluation of the progress in the area of the research supported by the Department of Energy (DOE) is given below.

2. Experimental Measurements

We measured the time-dependent transmission of hydrocarbons and their mixtures at low concentrations through adsorber beds at low temperatures in the range from 273 to 303 K. The beds were packed with solid adsorbents [viz., (Columbia 4LXC 12/28) activated carbon and crosslinked polystyrenes]. We obtained adsorption capacities and adsorption isotherms for methane (A32), ethane (A4,A5,A29), propane (A4,A5,A18,A31), n-butane (A4,A18,A31), 1,3-butadiene (A9), acetaldehyde (A32), acetylene (A16,A32) and acetone (A21) on the above-mentioned adsorbents. Details concerning the transmission measurements and the calculations of adsorption isotherms are described in papers A5 and A6.

We measured also the time-dependent transmission of stable argon (A7) and the radioactive isotope argon-41 on activated carbon at 273 K (A8). The transmission of radioactive argon-41 was carried out at the two-megawatt research reactor at University of Michigan.

3. Dynamics of Adsorbates in Adsorber Beds

Studies of dynamics of adsorbates in adsorber beds were published in papers A1, A7, A8, A16, A17, and A32. Papers A7 and A8 present the moment analysis of transmission curves measured for various concentrations of argon in helium on Columbia activated carbon. In paper A8, equations for the first-order moment of a transmission curve, the propagation time, and the steady-state transmission are extended to the transport of a radioactive gas (argon-41) through an (activated carbon) adsorber bed. The theory used to describe the transport of gases and gas mixtures through adsorber beds takes into account both solid- and gas-phase diffusion, mass-transfer resistance, and a first-order chemical reaction. An analytical solution of the mass balance equation for a first-order

reaction in a packed bed with diffusion was discussed in paper A1. The longitudinal and interparticle diffusions of hydrocarbons in activated carbon and crosslinked polystyrene is discussed in papers A16 and A17. We provided additional experimental verification of the theory of dynamics for adsorbates in adsorber beds (A7,A16,A17,A32), and extended this theory to the transport of a radioactive gas through an adsorber bed (A8).

4. Formulation of the Theory of Gas Adsorption on Heterogeneous Microporous Solids and its Experimental Verification

Significant progress has been achieved in the area of adsorption of gases and vapors on heterogeneous microporous solids (A3,A11,A12,A13,A14, A19,A20,A21,A22,A23,A24,A25,A26,A27,A29,A30,A31). Previously, the Polanyi-Dubinin adsorption potential theory was used to describe gas adsorption on microporous solids including activated carbons. In papers A3 and A19, we modified this theory and presented a rigorous physical interpretation of the energy parameters. We showed also that the classical adsorption potential theory is not sufficient for describing gas adsorption on microporous activated carbons because it does not take into account the structural and energetic heterogeneities of these important adsorbents. In papers A12, A14, A20, A26, and A27, we formulated the theory of gas adsorption on heterogeneous microporous solids. These papers extend the Dubinin-Radushkevich equation (A14, A20, A26) and the Dubinin-Astakhov equation (A27) to adsorption on structurally-heterogeneous microporous solids. The energy distribution function that characterizes the energetic heterogeneity of the microporous structure, and the energy parameters were discussed in papers A12, A20, and A27. The thermodynamics of adsorption on structurally heterogeneous microporous solids was discussed in papers A23 and A25. Papers A24, A29, and A30 present a successful application of the above mentioned theory for characterizing the structural and energetic heterogeneities of microporous activated carbons.

5. Studies of Mixed-Gas Adsorption Equilibria on Heterogeneous Solids

Mixed-gas adsorption was discussed in papers A5, A6, and A13. In papers A5 and A6, we discussed adsorption interference in gas mixtures

flowing through activated carbon adsorber beds and its influence on equilibrium adsorption isotherms. In paper A13, we showed that a correct description of mixed-gas adsorption equilibria on activated carbons should include the energetic heterogeneity of these solids; accordingly, we proposed an equation for predicting multicomponent adsorption equilibria. This equation is associated with a Gaussian energy distribution function that characterizes the heterogeneities of activated carbons.

6. Adsorption from Solutions on Microporous Solids

In paper A22, we presented the results of our initial studies dealing with description of adsorption from dilute solutions on heterogeneous microporous solids. There is no rigorous theory of liquid-solid adsorption on heterogeneous microporous solids. Our achievements in the theory of gas adsorption on heterogeneous microporous solids obtained under the present research grant provide foundations for elaborating a theory of adsorption from solutions on these solids and for characterizing liquid-solid adsorption systems. Because our initial studies presented in paper A22 are promising, we submitted a proposal to continue this important research.

7. Pressure Swing Adsorption

In papers A10, A28, A34, and A35, we extended the equilibrium theory of the pressure swing adsorption (PSA) process for a system with a linear adsorption isotherm to systems with non-linear adosorption isotherms. We presented analytical equations for pressure swing adsorption systems with Freundlich and Langmuir-Freundlich isotherms; because these isotherms take into account the energetic heterogeneities of the adsorbents, we were able to study the influence of adsorbent heterogeneity on the PSA process. These studies are important because the PSA process is applied widely in gas separation processes that utilize heterogeneous solids.

Appendix A

Publications

reprints removed to

A1. "Analytical Solution for a First-Order Reaction in a Packed Bed with Diffusion," J.C. Huang, D. Rothstein, and R. Madey, AIchE J. 30, 660-662 (1984).

A2. "Free-Volume Effect in the Thermodynamics of Gas-Liquid Chromatography," J.C. Huang, R. Madey, J. of Chromatogr. 298, 494-498 (1984).

A3. "Correlation of Adsorption Isotherms of Hydrocarbon Gases on Activated Carbon," T.V. Lee, J.C. Huang, D. Rothstein, and R. Madey, Carbon 22, 493-495 (1984).

A4. "Adsorption Isotherms and Isosteric Heats of Adsorption for Ethane, Propane, and n-Butane on Polystyrene," D. Rothstein, J.-C. Huang, B.-G. Wu, T.V. Lee and R. Madey, Journal of Colloid and Interface Science 106, 399-409 (1985).

A5. "Adsorption Equilibria for Ethane and Propane Gas Mixture on Activated Carbon," T.V. Lee, R. Madey and J.-C. Huang, Separation Science and Technology 205 (5&6), 461-479 (1985).

A6. "Adsorption Interference in Mixtures of Adsorbate Gases Flowing Through Activated Carbon Adsorber Beds," R. Madey, P.J. Photinos, D. Rothstein, R. Forsythe and J.-C. Huang, Langmuir 2, 173-178 (1986).

A7. "Gas-Solid Chromatography of an Argon-Helium Mixture: Moment Analysis of a Transmission Curve," A. Bhairi, D. Rothstein, R. Madey, J.-C. Huang, and K.B. Lee, J. of Chromatogr. 361, 3-11 (1986).

A8. "Moment Analysis of the Time-Dependent Transmission of a Step-Function Input of a Radioactive Gas Through an Adsorber Bed," T.V. Lee, D. Rothstein, and R. Madey, Sep. Sci. & Tech. 21, 689-700 (1986).

A9. "Binary Adsorption of Propane, n-Butane and 1,3-Butadiene on Cross-Linked Polystyrene," D. Rothstein, R. Madey, and J.-C. Huang, Langmuir 2, 613-615 (1986).

A10. "Pressure Swing Adsorption for a System with a Freundlich Isotherm," X. Lu, J.-C. Huang, and R. Madey, Sep. Sci. & Tech. 22, 1547-1556 (1987).

A11. "Determination of the Micropore Volume of Activated Carbon from the Adsorption Isotherms of Light Hydrocarbons," T.V. Lee, R. Madey, D. Rothstein, and M. Jaroniec, Materials in Chemistry and Physics 16, 583-586 (1987).

A12. "The Energy Distribution Function Associated with Dubinin's Description of Gas Adsorption on Heterogeneous Microporous Solids," M. Jaroniec and R. Madey, Carbon 25, 579-582 (1987).

A13. "Correlation of Heterogeniety Parameters for Adsorption of Single Gases and Gas Mixtures on Solids," M. Jaroniec, R. Madey, and D. Rothstein, Chem. Engin. Sci. 42, 2135-2141 (1987).

A14. "Gas Adsorption on Structurally Heterogeneous Microporous Solids," M. Jaroniec and R. Madey, Sep. Sci. & Tech. 42, 2367-2373 (1987).

A15. "Adsorption of a Radioactive Gas," R. Madey, A. Bhairi, D. Rothstein and J.-C. Huang, in Fundamentals of Adsorption, A. Liapis, Editor, Engineering Foundation, New York, pp. 371-380 (1987)

A16. "Gas-Solid Chromatography: Longitudinal and Intraparticle Diffusion in Acetylene in Activated Carbon," R. Forsythe, R. Madey, P.J. Photinos, D. Rothstein, and J.C. Huang, Sep. Sci. & Tech. 23, 2319-2328 (1988).

A17. "Diffusion Coefficients in Crosslinked Polystyrene," D. Rothstein, B.G. Wu, R. Madey, and J.C. Huang, Sep. Sci. & Tech. 23, 2309-2318 (1988).

A18. "Sorption Properties of Polystyrene Adsorbents from Isotherms of Propane and n-Butane", X. Lu, R. Madey, D. Rothstein, and M. Jaroniec, Materials Chem. Phys. 19, 247-254 (1988).

A19. "Physical Interpretation of the Energy Parameters in the Dubinin-Raduskevich Equation," M. Jaroniec and R. Madey, Carbon 26, 107-108 (1988).

A20. "Adsorption Theory of Volume Filling of Micropores for Structurally Heterogeneous Solids," M. Jaroniec and R. Madey, J. Chem. Soc., Faraday Trans. 2, 84, 1139-1148 (1988).

A21. "Adsorption of Acetone on Activated Carbon", R. Forsythe, R. Madey, D. Rothstein, and M. Jaroniec, Carbon 26, 98-100 (1988).

A22. "Solute Adsorption from Dilute Solutions on Structurally-Heterogeneous Solids," M. Jaroniec, R. Madey, J. Choma, and J. Piotrowska, J. Colloid and Interface Science 125, 561-566 (1988).

A23. "Enthalpy of Immersion of a Microporous Solid," M. Jaroniec and R. Madey, Journal of Physical Chemistry 92, 3986-3988 (1988).

A24. "Characterization of Energetic and Structural Heterogeneities of Activated Carbons", M. Jaroniec, R. Madey, X. Lu, and J. Choma, Langmuir 4, 911-917 (1988).

A25. "Thermodynamic Functions Associated with the Exponential Isotherm Equation for Gas Adsorption on Heterogeneous Microporous Solids," M. Jaroniec, R. Madey, and J. Choma, J. Colloid and Interface Science 126, 69-73 (1988).

A26. "Gas Adsorption on Solids with Gaussian Micropore-size Distributions", M. Jaroniec, X. Lu, and R. Madey, Monatscheffe für Chemie 119, 889-901 (1988).

A27. "Physical Adsorption of Gases and Vapors on Structurally Heterogeneous Microporous Solids", M. Jaroniec, X. Lu, and R. Madey, Chemica Scripta 28, 369-374 (1988).

A28. "Pressure Swing Adsorption for a System with a Langmuir Isotherm," X. Lu, D. Rothstein, R. Madey, and J.C. Huang, Sep. Sci. & Tech. 23, 281-291 (1988).

A29. "Adsorption of Ethane on Microporous Activated Carbon," X. Lu, M. Jaroniec, R. Madey and D. Rothstein, Materials Chem. Phys. 21, 427-436 (1989).

A30. "Comparison of Adsorption Methods for Characterizing the Microporosity of Activated Carbons," M. Jaroniec, R. Madey, J. Choma, B. McEnaney, and T. Mays, Carbon 27, 77-83 (1989).

A31. "Adsorption of Propane and n-Butane on Polystyrene Adsorbents," X. Lu, M. Jaroniec, R. Madey, D. Rothstein, and J.C. Huang, Monatschefte für Chemie 120, 401-411 (1989).

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A32. "Transport of Methane, Acetylene, and Acetaldehyde through Activated Carbon," R. Forsythe, R. Madey, and P.J. Photinos, Sep. Sci. Tech. (submitted July 1989).

A33. "A New Description of Gas Adsorption on Microporous Solids and its Comparison with the Dubinin Formulation", M. Jaroniec, R. Madey, and D. Rothstein, Polish Journal of Chemistry 63, (1989), in press.

A34. "Pressure Swing Adsorption for a System with a Langmuir-Freundlich Isotherm," X. Lu, R. Madey, D. Rothstein, M. Jaroniec, and J.C. Huang, Chem. Eng. Sci. (in press).

A35. "Pressure Swing Adsorption for a System with a Non-Linear Isotherm," X. Lu, R. Madey, D. Rothstein, M. Jaroniec, and C. Huang, Proceedings of 2nd Int. Conf. on "Separation Science and Technology" Hamilton, Ontario, Canada, Oct. 1-4, 1989 (accepted).

These preprints were not attached

Appendix B

Presentations

B1. "Diffusion Coefficients of Methane, Ethane and Acetylene Adsorbed on Crosslinked Polystyrene by the Method of Moments," D.P. Rothstein, J.C. Huang, B.G. Wu and R. Madey, Meeting of the Ohio Section of the American Physical Society, Cleveland, Ohio (October 12-13, 1984); Bull. Am. Phys. Soc. 30, 1044 (1985).

B2. "Adsorption Interference in Mixtures of Adsorbate Gases Flowing Through Activated Carbon Adsorber Beds," R. Madey, D. Rothstein, P.J. Photinos, R. Forsythe, and J.-C. Huang, Fifth International Conference on Surface and Colloid Science, Clarkson University, Potsdam, N.Y. (24-28 June 1985).

B3. "Adsorption Equilibria for Ethane and Propane Gas Mixtures on Activated Carbon at 25°C," T.V. Lee, D. Rothstein, J.C. Huang and R. Madey, Meeting of the Ohio Section of the American Physical Society, Cleveland, Ohio (October 12-13, 1984) Bull. Am. Phys. Soc. 30, 1044 (1985).

B4. "Adsorption of a Radioactive Gas," R. Madey, A. Bhairi, D. Rothstein and J.C. Huang, Second International Conference on Fundamentals of Adsorption, Santa Barbara, CA (4-9 May 1986).

B5. "Pressure Swing Adsorption for a System with a Freundlich Isotherm," X. Lu, D. Rothstein, R. Madey, and J.-C. Huang, Ohio Section, American Physical Society, Akron, Ohio (May 1987).

B6. "The Adsorption of Radioactive Argon-41 on Activated Carbon," D.P. Rothstein, A. Bhairi, and R. Madey, Ohio Section, American Physical Society, Akron, Ohio (May 1987).

B7. "Thermodynamic Analysis of Gas Adsorption Measurements on Microporous Activated Carbons," M. Jaroniec, X. Lu, and R. Madey, 19th Biennial Conference on Carbon, Penn. State Univ., PA, June 25-30, 1989.

B8. "Pressure Swing Adsorption for a System with a Non-linear Isotherm," X. Lu, R. Madey, D. Rothstein, M. Jaroniec, and J.C. Huang, International Conference on Separation Science and Technology, Hamilton, Ontario, Canada, Oct. 1989.