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STUDIES IN COAL LIQUEFACTION WITH APPLICATION TO
THE SRC AND RELATED PROCESSES

Quarterly Report for the Period May—July 1983

By
A. R. Tarrer
James A. Guin
Christine W. Curtis

Work Performed Under Contract No. AC22-79ET13397

Auburn University
Auburn University, Alabama

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WITH APPLICATION TO
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Quarterly Report for the
Period May, 1983 - July, 1983

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. DE-AC01-79ET13397

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would results from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives are being carried out in cooperation with the Southern Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

The research program is divided into three major tasks with several sub-tasks within each area. An outline of the program by tasks and subtasks is presented on the following page.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- C. Direct Visual Observation of In-situ Particle Dissolution

Task 2. Catalysis by Coal Mineral Matter

- A. Process Variable and Kinetics
- B. Characterization of Coal Minerals
- C. Regeneration/Pretreatment of Coal Minerals and Residue
- D. Effect on Individual Species in Coal Liquefaction Products
- E. Continuous Reactor Studies

Task 3. Analytical Support

- A. Fourier Transform Infrared Spectroscopy of Coal and SRC
- B. Energy Dispersive X-Ray Fluorescence of Coal and SRC

Dates: May, 1983 - July, 1983

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PROJECT TITLE: Studies in Coal Liquefaction with Application to the
SRC and Related Processes

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Summary

This report examines liquid-phase adsorption as a possible method of studying the interactions between coal liquids and hydrotreating catalysts. The dual purposes of this work are to develop a method to determine specific surface areas of porous catalysts and to examine how compounds commonly found in coal liquids are adsorbed on hydrotreating catalysts.

The liquid-phase adsorption studies were performed at room temperature in tubing bomb reactors. Adsorption isotherms obtained from these experiments were assumed to follow Langmuir-type behavior.

Compounds used in these studies included PNA compounds, a basic nitrogen containing compound, and an acidic oxygen containing compound. Various commercial grade catalysts as well as presulfided CoMo/Al₂O₃ and presulfided iron oxide were used as adsorbents.

Experiments have shown that quinoline, a basic nitrogen containing compound, appears to be an excellent compound for surface area determination via liquid-phase adsorption. Adsorption of compounds such as pyrene, a PNA

compound, and phenol, an acidic oxygen containing compound, may be used to determine the relative areas of different types of sites on catalyst surfaces.

The sensitivity of this liquid-phase adsorption technique was evaluated by adsorbing different solutes on various catalyst surfaces. This technique shows that the adsorptivity of different coal liquids is a distinct function of the individual properties of the adsorbate as well as the properties of adsorbent used.

Comparison of the adsorption properties of these coal liquids on various adsorbents may give insights as to how they adsorb on hydrotreating catalysts, how they compete for the active catalyst sites, and what types of sites the adsorbed molecules occupy.

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I. INTRODUCTION

Numerous types of compounds are found in coal derived liquids. Gates et al. (1) and Shridharani (2) have found that some of these compounds inhibit hydrogenation reactions that are desirable for coal liquefaction (e.g., the hydrogenation of naphthalene to form tetralin). This inhibition is believed to be the controlling mechanism for oil (pentane soluble) production from coal.

Shridharani (2) has observed the catalytic hydrogenation of naphthalene to be inhibited by several compounds. This inhibition is believed to be due to preferential adsorption of the inhibiting compound on the catalyst surface. He has used the Langmuir-Hinshelwood model to describe this inhibition. The Langmuir-Hinshelwood model is used to describe processes in which competitive reactions occur; it accounts for reaction selectivity due to differences in adsorptivity of the reactants on the catalyst surface. Naphthalene is used to model a certain class of compounds found in coal liquids.

To better understand the importance that preferential adsorption has in coal liquefaction reactions, the work described herein was initiated to develop a technique to measure the relative adsorptivity of a compound. The relative adsorptivity of a compound was then to be correlated with its physical and chemical properties and with its apparent inhibition characteristics.

Adsorption studies may be performed either in the gas-phase or in the liquid-phase. Liquid-phase adsorption studies are usually concerned with characterizing the properties of the adsorbate rather than those of the adsorbent as is commonly the case when gas-phase adsorption is used. For example, gas-phase adsorption is typically used to characterize catalysts and liquid-phase adsorption is often used to determine the ease by which a compound can be separated by means of liquid chromatography (3,4,5,6). An extensive investigation of gas-phase adsorption is presented by Brunauer (7).

Liquid-phase adsorption was chosen over gas-phase adsorption for these studies for the following reasons: (1) the equipment required was not complicated and was relatively inexpensive, and (2) many of the compounds of interest had a low volatility and thermal degradation that might result when volatilizing for gas-phase analysis could be avoided.

Adsorption is a function of the properties of both the adsorbate and the adsorbent. Three important properties of the adsorbate in adsorption are basicity, acidity, and the type of bond that it forms with the adsorbent surface.

Appleby et al. (8) have developed a correlation between basicity of PNA molecules and their coking propensity. It was originally thought that a similar correlation between basicity and adsorptivity of compounds found in coal liquids could be developed. Correlations such as this one were attempted by Klemm et al. (6). They investigated the effect of the chemical structure of aromatic hydrocarbons on adsorptivity

and found that adsorptivity could not be correlated to only one parameter such as basicity (as is illustrated in Table 1). The adsorptivity of different compounds was observed to vary directly with their following properties: (a) number of double bonds, (b) approach to coplanarity, (c) symmetry number, (d) extent of conjugation, and (e) number of sterically unhindered methyl or alkylene groups. For the wide diversity of chemical groups found in coal liquids, it appears that the only effective means for rating their adsorptivity is by direct measurement.

Adsorptivity may be characterized in several ways. In the field of chromatography, relative adsorption may be compared on a basis of retention time or retention volume. Relative adsorption is usually compared on the basis of unit mass of adsorbed material per unit mass of adsorbent.

Snyder (3-5) has performed several characterizations of different groups of compounds using linear elution chromatography with alumina as an adsorbent. Snyder rates the adsorptivity of a compound using elution chromatography in terms of its retention volume, that is, the volume required to elute 50% of the solute per total weight of the adsorbent (the column packing).

Other investigators such as Klemm et al. (6) have used elution time as a measure of a compound's adsorptivity. Typically, a binary mixture of two components are passed through a column using a standard carrier solvent (e.g. pentane). The components elute at different times giving a relative measure of their adsorptivity. By sequential cross comparison of the adsorptivity of different binary groups, the adsorptivity of the

Table 1

Attempted Correlation of Adsorptivity With
Increasing Basicity Constant

Solute	Equivalent Retention Volume, Log R°	Log Basicity Constant
Naphthalene	0.92	-4.0
Phenanthrene	2.05	-3.7
Chrysene	3.05	-2.0
Pyrene	2.37	2.0
Anthracene	2.12	3.5

compounds can be rated. This has been done for a large number of compounds using alumina as the column packing. The relative adsorptivity of typical compounds found in coal liquids on catalysts like $\text{CoMo/Al}_2\text{O}_3$ is compared in this work to that determined by chromatographic-type techniques such as those used by Synder and Klemm.

Giles et al. (9), Kagiya et al. (10), and Smith et al. (11) have shown how liquid-phase adsorption can be used to estimate the surface area of the adsorbent. In the study presented here, surface areas of adsorbents are estimated in a manner similar to the methods used by these investigators. The surface area coverage by different compounds is used in this study to rate their relative adsorptivity.

II. ADSORPTION

Background

Liquid-phase adsorption has been utilized for many years as a means of separating components, of purifying liquids, and for stabilizing dispersions. For centuries, liquids such as drinking water, oils, and wines have been purified using solid adsorbents such as charcoal.

Adsorption is also a very important aspect of catalysis. Extensive research has been performed on gas-phase adsorption of reactants on solid surfaces since the early 1900's. Liquid-phase adsorption has received more limited attention as applied to reaction kinetics and catalysis. These limited studies may be attributed to the lack of a complete theory, which is applicable to a wide range of systems, for liquid-phase adsorption. The theory of liquid-phase adsorption, as applicable to these studies, is discussed here.

Literature Review

Previous investigators such as Klemm et al. (6) and Synder (3,4,5) have attempted to correlate chromatographic adsorptivity with structural factors of the adsorbing molecules, adsorbent deactivation, and eluent structure. Klemm has used alumina as an adsorbent to separate binary mixtures of PNA molecules by adsorption chromatography. These binary mixtures are eluted through the chromatographic column by means of the eluent, petroleum ether or petroleum ether-benzene. The results of these studies show that adsorptivity increases with increasing the (a)

number of double bonds, (b) approach to coplanarity, (c) symmetry number, (d) extent of conjugation, and (3) number of sterically unhindered methyl or alkylene groups (Appendix D).

Snyder (3,4,5) has investigated the possible use of a theoretical model capable of interrelating solute chromatographic separability. He has used linear elution adsorption chromatography with alumina as an adsorbent to rate the adsorptivity of classes of compounds such as PNA, phenols, nitrogen containing, and sulfur containing molecules (Appendix D). Because of the various chemical properties of the classes of compounds used, the elutents required to carry the solute through the chromatographic column varied with the class of solutes. The relative adsorptivities reported by Snyder in Appendix D may deviate significantly if another eluent is used for that class of compounds. This phenomenon is illustrated in Table 2.

Snyder has proposed a theoretical model which will correlate adsorptivity for systems which use different elutents and adsorbent deactivation. This model is based on parameters such as solute separation factors, eluent polarity factor, and adsorbent surface volume. Equivalent retention volumes, R^o , calculated by this model correlate well with experimental values for alkyl-substituted benzenes and alkyl-substituted thiophenes. Comparison of calculated and experimental equivalent volumes for alkyl-substituted pyridines and quinolines show that deviations as large as 55% may be obtained. Even when a small deviation between calculated and experimental values is obtained for a class of compounds, the order of adsorptivity among the compounds may be reversed if adsorptivity is based on the calculated values.

Table 2
Order of Adsorptivity for Solutes Using
n-Pentane and Benzene as Eluents*

Solute	Order of Increasing adsorptivity	
	n-pentane	Benzene
Methyl ethyl sulfide	1	1
Anisole	2	2
Benzaldehyde	3	4
Benzpyrene	4	3

*Reference 4.

This failure of the model proposed by Synder to predict adsorptivity tends to indicate that adsorptivity must be determined by experimental means. An exception to this rule is the adsorptivity for PNA molecules as determined by Klemm et al. (6) and Synder (4). These results show good agreement even though different elutents and different types of alumina adsorbent were employed. For systems using different elutents (solvents) and adsorbents than those used by Klemm and Synder, it should be noted that the prediction of adsorptivity based on their experimental results should be undertaken with caution.

Theory of Adsorption

The term adsorption is generally defined as the concentration of one component at an interface relative to an adjacent bulk phase.

The theory of liquid-phase adsorption was initially interpreted based on the theory developed for gas-phase adsorption. Kipling (12) has written a textbook on liquid-phase adsorption in which he presents the results of studies conducted by him as well as other researchers. In his book, he summarizes the progression of liquid-phase adsorption. These studies, for the most part, consisted of adsorption in the presence of adsorbents such as silica, silica-gel, alumina, and charcoal. Literature in the area of liquid-phase adsorption on commercial catalysts such as $\text{CoMo/Al}_2\text{O}_3$ or $\text{NiMo/Al}_2\text{O}_3$ is rare.

Kipling (12) has shown that in the case of liquid-phase adsorption the definition of adsorption as given above is insufficient. The reason is that the study of gas-phase adsorption has usually been confined to a single component system whereas liquid-phase adsorption as applied in this study involves at least two components. In this study of liquid-

phase adsorption all components in contact with the adsorbent may be adsorbed.

Two methods are commonly used in determining the quantity of a component adsorbed. The first consists of computing the concentration of the component in the bulk phase before and after adsorption. Adsorption studied in this manner is referred to as preferential adsorption. The amount of material adsorbed as determined in this manner can be very misleading because the bulk concentration changes as a result of the adsorption of one or more of the components in solution. In the second method, the actual quantity of material that is present in the adsorbed phase is calculated. Adsorption studied in this manner is referred to as absolute adsorption. Most studies have been performed using components which do not show strong competitive adsorption. Thus, preferential adsorption and absolute adsorption are approximately equal.

Competitive adsorption occurs as a result of differences in the strengths of interaction between the solid surface and the components in solution. The strength of interaction between the solid adsorbent and the adsorbate is governed by the chemistry of components in solution as well as the surface chemistry of the solid. These two factors have the most influence on the extent and selectivity of adsorption (2). According to Kipling (12), physical properties such as surface area, porosity, and heterogeneity may effect the extent and selectivity of adsorption. The extent of adsorption may be affected by steric hinderances due to the presence of side chains or substitutions (2). An increase in reaction temperature usually increases adsorption selectivity. Kipling has also shown that pressure has little effect on adsorption.

Surface Chemistry of Adsorbents. The extent and selectivity of adsorption is strongly influenced by the distribution of charge at the solid surface. Highly polar solids such as silica gel, preferentially adsorb polar compounds such as alcohol in preference to non-polar compounds such as iso-octane or benzene; conversely charcoal, which is non-polar, adsorbs benzene in preference to alcohol (12).

Kiselev and Yashin (13) have classified solid adsorbents as follows:

1. Nonspecific: No functional groups or exchangeable ions at the adsorbent surface. Examples of these types of adsorbents are carbon black and saturated hydrocarbons (polymers). Adsorbents of this kind can interact with any type of molecule.
2. Specific With a Localized Positive Charge: These types of adsorbents have a localized positive charge and are acidic in nature. The charge arises due to the presence of a functional group on the solid surface. Examples of adsorbents of this type are $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and alumina.
3. Specific With a Localized Negative Charge: These types of adsorbents have a localized negative charge due to the presence of a functional group on the adsorbent surface. Functional groups which fall into this category include esters, carbonyl groups, and nitrites.

Chemical Properties of Adsorbates. The extent and selectivity of adsorption are a function of surface chemistry of the adsorbent as well as chemical properties of the adsorbate. For example, piperidine is more

strongly adsorbed on gels than cyclohexane. The reason for this is that piperidine has a strong polar center (12).

Kiselev and Yashin (13) have classified adsorbates into four groups as follows:

Group A. This group is composed of inert gases and saturated hydrocarbons. Because these molecules have no accumulation of electrons, they do not interact with other molecules chemically but do so nonspecifically.

Group B. This group is composed of compounds whose molecules have a high electron density because of π -bonding or the presence of unshared electrons. Examples of these types of compounds are unsaturated and aromatic hydrocarbons.

Group C. The molecules of this group have a positive charge which is localized on small links. The corresponding excess electron density is distributed over adjacent links. Organometallic compounds probably fall in this category.

Group D. Molecules of this group contain a chain of small links alternating between net positive and net negative charge. Examples are water, alcohols, and primary and secondary amines.

Important Aspects of Adsorption Studies

Shridharani (2) has cited the most interesting and important aspects of liquid-phase adsorption studies. They are:

- (1) Investigation of the shape of the adsorption isotherm.
- (2) Determination of the appropriate equation to fit the isotherm.

- (3) Studies of the significance of the adsorption limit, or plateau, found in isotherms.
- (4) Determination of the extent to which the solvent is adsorbed.
- (5) Consideration of whether the adsorption involves a monolayer or a multilayer coverage.
- (6) Determining the orientation of the adsorbed molecule.
- (7) Consideration of whether the adsorption is due to physical forces or chemical interactions.

Some of the above-mentioned topics are discussed below:

Classification of Adsorption Isotherms. Adsorption isotherms are represented by plots of the quantity of material adsorbed with respect to the equilibrium concentration of the preferentially adsorbed species in the liquid-phase at constant temperature. Adsorption isotherms can be divided into different classes based on their shapes.

Giles et al. (14) classified isotherms into four main classes based on the shape of their initial slopes. These are: (1) S ("S" shaped), (2) L ("Langmuir" type), (3) H ("high affinity"), and (4) C ("constant partition"). Each class was divided into sub-groups based on the upper portions of the adsorption isotherms.

According to Giles et al. (4) the S-type isotherm usually appears when the solute molecule (a) is monofunctional (the orientation of adsorbed molecules is either edge-on or end-on to the substrate surface, (b) has moderate intermolecular forces of attraction, causing it to pack

vertically in a regular array in the adsorbed layer, and (c) is capable of withstanding strong competition from the solvent molecules for the substrate sites.

L class curves show that as more sites of the adsorbent are filled, less sites become available for adsorption by the bombarding solute. Adsorbates which exhibit these types of curves are usually adsorbed flat to the adsorbent surface. If there is little competition from other molecules for vacant sites, the adsorbate may adsorb end-on to the adsorbent surface.

H class adsorption isotherm curves are a special case of the L type curves. The solute in this class has such a great affinity for the adsorbent that in dilute solutions it is completely adsorbed. An extreme case of this type of isotherm is a horizontal line that intersects the vertical axis.

C curves are characterized by the constant partition of solute between solution and adsorbed phase up to the point of maximum possible adsorption. At the point of maximum adsorption there is an abrupt transition in the trend of the curve resulting in a horizontal plateau. The linearity in the shape of the curve indicates that the number of adsorption sites remains constant with an increase in equilibrium concentration of the solute in solution.

Significance of Plateau. A plateau or an inflection ("knee") is observed on most complete isotherms (14). The plateau or the linear portion of the isotherm above the "knee" represents monolayer coverage of adsorbent by the solute. This plateau is characteristic of both liquid-phase and gas-phase adsorption. A rise in the isotherm after the

plateau usually indicates multilayer coverage. Caution should be exercised in assuming that monolayer coverage exists unless a plateau or "knee" is distinctly observed (2).

Orientation of the Adsorbed Molecule. The orientations adapted by molecules of the adsorbate are of extreme importance in adsorption studies. For example, stearic acid, when adsorbed in a direction parallel to the surface of the adsorbent occupies five times the area it occupies when adsorbed in a direction perpendicular to the adsorbent surface.

The orientations of adsorbate molecules are a function of chemical properties of the adsorbent and adsorbate as well as symmetry of the adsorbate molecules. For example, stearic acid is adsorbed parallel to the adsorbent surface if the adsorbent is polar in nature. The same kind of orientation occurs when the acid is chemisorbed onto the solid surface.

The orientation of adsorbed molecules is of great importance in the separation of liquids. Perpendicular adsorption is desirable because it allows a larger quantity of material to be adsorbed for a given quantity of adsorbent. Orientation also plays an important role in catalysis. The orientation of the adsorbed molecule may account for the formation of different products upon reaction.

Type of Adsorption. An important parameter in catalysis is the type of adsorption on the catalyst surface, i.e. chemical or physical. In many cases there is a simultaneous occurrence of both phenomena which makes the distinction between chemisorption and physical adsorption

difficult. Listed below are some criteria which differentiate the two types of adsorption.

- **Bonding Forces:** Chemisorption is characterized by intramolecular forces and physical adsorption by intermolecular forces (15).
- **Enthalpy Effect:** Chemisorption is virtually always exothermic; the heat of adsorption is comparable to heats of reaction in magnitude. Physical adsorption is always exothermic; the heat of adsorption is comparable in magnitude to heats of condensation (15).
- **Shape of Adsorption Isotherm:** Adsorption of fatty acids on nickel and platinum catalysts from a benzene solution was studied by Smith and Fuzek (11). The adsorption of palmitic acid on Adams platinum catalyst illustrates that the amount of adsorption is independent of equilibrium concentration of solute in solution. If the amount of acid used is less than that required to saturate the surface, then all the acid is adsorbed from the solution. This is an example of irreversible chemisorption.
- **Desorption:** In most cases, physical adsorption occurs on top of the chemisorbed components. An increase in the equilibrium concentration of solute in the liquid-phase results in an increase in the amount of adsorption.

Cook and Hackerman (16) studied the adsorption of organic acids on powdered steel. Desorption studies were also performed by washing the equilibrated solid with a large excess of benzene several times.

The quantity of acid remaining on the surface of the steel was measured. This measured amount is the quantity of material chemisorbed.

- **Special Techniques:** Sophisticated instruments account for special techniques currently being devised to determine the nature of adsorption. Leftin and Hobson (17) have described how spectrophotometry may be used to study physical and chemical adsorption on catalyst surfaces. Welder (18) also described several methods such as work function, electrical and magnetic measurements, photoelectron spectroscopy, and ion mass spectrometry to study chemisorption.

Isotherm Models

For adsorption from dilute solutions, L2 type isotherms are the most common (14). These isotherms are the same as Type 1 isotherms for adsorption of vapors on solids.

Davies and Rideal (19) have derived an equation for the L2 type isotherm. Kinetic treatment of the adsorption-desorption process at equilibrium is the basis for their equation. A simplified version of the equation of Davies and Rideal is derived here. The following assumptions are applied in the derivation of this simplified equation (2).

1. There is no competition between component A and solvent B for the adsorption sites. There is a specific interaction between adsorbate A and the solid adsorbent, but the interaction between the solvent B and adsorbent is nonspecific. Therefore, the kinetic treatment is applied to the adsorption and desorption of the adsorbate A.

2. Adsorption occurs solely on the adsorption sites, and only one molecule can be adsorbed per site.
3. The maximum amount of adsorption corresponds to monolayer coverage.
4. The rate of desorption depends on the number of molecules adsorbed and the energy of adsorption.
5. The rate of adsorption of A on the surface is proportional to the number of molecules striking the vacant sites; also the rate of collision of A molecules on the sites is proportional to the concentration of A in the bulk solution.

Let θ_A denote the fraction of sites covered by species A; then the rate of adsorption of A is given by

$$r_{\text{adsorption}} = k_{\text{ad}} C_A (1 - \theta_A) \quad (1)$$

where k_{ad} is the pseudo rate constant for adsorption which is defined as $(\text{constant})e^{-\omega/kT}$, and C_A is the concentration of component A in solution.

The rate of desorption for a first-order reaction is given by

$$r_{\text{desorption}} = k_{\text{des}} \theta_A e^{-\omega/kT}$$

where k_{des} is the pseudo rate constant for desorption, ω is the energy of desorption and T is the absolute temperature.

At equilibrium,

$$r_{\text{adsorption}} = r_{\text{desorption}}$$

and,

$$k_{\text{ad}} C_A^E (1 - \theta_A) = k_{\text{des}} \theta_A e^{-\omega/kT} \quad (2)$$

rearranging,

$$\theta_A = \frac{k C_A^E e^{\omega/kT}}{1 + k C_A^E e^{\omega/kT}} \quad (3)$$

k is the ratio k_{ad}/k_{des} , and C_A^E is the concentration of species A in solution at equilibrium. By definition,

$$\theta_A = \frac{\Psi_{AR}}{\Psi_{AR}^M} \quad (4)$$

where Ψ_{AR}^M is the theoretical amount of A adsorbed reversible when there is monolayer coverage, and Ψ_{AR} is the actual amount of A adsorbed reversibly. Substituting into Equation (3)

$$\frac{\Psi_{AR}}{\Psi_{AR}^M} = \frac{k C_A^E e^{\omega/kT}}{1 + k C_A^E e^{\omega/kT}} \quad (5)$$

Equation (5) is similar to the equation derived by Davies and Rideal (19).

If the amount of adsorption energy per unit area of surface is constant and no lateral interactions between adsorbed molecules occurs, the energy of adsorption, ω , is independent of the fraction of active sites covered. Assuming this to be true, Equation (5) simplifies to give

$$\frac{\Psi_{AR}}{\Psi_{AR}^M} = \frac{k_A C_A^E}{1 + k_A C_A^E} \quad (6)$$

where k_A is a constant which is usually referred to as the adsorption equilibrium constant.

An equation that is linear in terms of C_A^E may be obtained by the rearrangement of Equation 6.

$$\frac{C_A^E}{\Psi_{AR}} = \frac{1}{\Psi_{AR}^M} \left[C_A^E + \frac{1}{k_A} \right] \quad (7)$$

From a plot of C_A^E/Ψ_{AR} versus C_A^E , Ψ_{AR}^M and k_A can be determined from the slope and intercept.

Everett (20) derived the following equation based on the Law of Mass Action:

$$\frac{X_A X_B}{n_0 \Delta X / m} = \frac{1}{n^S} \left[X_A + \frac{1}{\alpha - 1} \right] \quad (8)$$

Where X_A and X_B are the mole fractions of the solute and solvent respectively in the bulk phase; M_0 , the initial number of moles in contact with the catalyst; ΔX , the change in mole fraction of A and B combined in solution due to adsorption; n^S , the total number of moles (A and B) adsorbed for monolayer coverage; m , the amount of catalyst contacted with the solution; and α , the separation factor.

Equation 8 may be written in a form analogous to Equation 7 by making the following assumptions:

1. The number of moles of solvent adsorbed on the solid is negligible ($n_B^S \approx 0$ therefore, $n^S \approx$ moles of component A adsorbed for monolayer coverage).
2. The bulk solution is dilute in solute A ($X_B \approx 1.0$).
3. If $X_A < 0.01$; then according to Kipling (12) $n_A^S \approx \frac{n_0 \Delta X}{m}$

With these assumptions, Equation 8 becomes

$$\frac{X_A}{n_S} = \frac{1}{n_S} \left[X_A + \frac{1}{\alpha - 1} \right] \quad (9)$$

Equations 7 and 9 are similar except that Equation 9 is expressed in terms of mole fractions, whereas equation 7 is expressed in terms of concentration. Also, Equation 9 is expressed in terms of the separation factor α instead of the adsorption constant k_A .

III. DEVELOPMENT OF ADSORPTION PROCEDURE

Comparison Between Liquid-Phase and Gas-Phase Adsorption

As mentioned in Chapter II, the liquid phase adsorption studies done in this work differ from typical gas phase adsorption studies in that gas-phase adsorption usually involves only one component, whereas here, the liquid-phase adsorption involves at least two components (12). In liquid-phase adsorption all components may be adsorbed by the adsorbent. The concentration of each component in the adsorbed phase is very difficult to measure directly (12). As is done in most cases, the concentration of the adsorbed phase is approximated in this work by the change in concentration of the components in the bulk liquid-phase.

Solvent for the Adsorbate

If component A (solute) is adsorbed by the adsorbent preferentially over component B (solvent), the change in concentration of component A in the bulk liquid-phase gives a good approximation of its concentration in the adsorbed phase. Therefore, it is desirable to perform liquid-phase adsorption studies with a solvent whose adsorption on the solid surface is minimal. Two solvents were evaluated on this basis.

Cyclohexane

Cyclohexane was considered as a solvent for the following reasons:

- (1) Cyclohexane has only σ -bonds between its carbon atoms; therefore, it has no electron cloud parallel to the plane of the ring. Electron clouds formed from π -bonds in unsaturated hydrocarbons are thought to be a main localized area for adsorption.
- (2) Saturated compounds such as cyclohexane are good solvents for use in UV analysis (2). They do not adsorb in the same range of wavelengths as the unsaturated compounds being studied.
- (3) Several investigators (10,21,22) have used cyclohexane in their studies of liquid-phase adsorption. The work of Kagiya et al. (10) tends to indicate that the degree of adsorption for cyclohexane is small in comparison to the degree of adsorption for solutes such as toluene or benzene.

Experimental Studies. Quinoline was used as the solute and CoMo/Al₂O₃ catalyst (Harshaw 0402T) was used as the adsorbent to test the potential of cyclohexane as a solvent. Details of the experimental procedure will be outlined in a later section. The isotherm for this system is shown in Figure 1.

Assuming monolayer coverage of the CoMo/Al₂O₃ surface by quinoline, the calculated area of catalyst covered by quinoline (Table 3) indicates that the adsorbed phase contains no cyclohexane. This supports the hypothesis that unsaturated hydrocarbons are preferentially adsorbed over saturated hydrocarbons, and thus, cyclohexane appears to be a good solvent for adsorption studies.

Hexadecane

Hexadecane was also considered as a solvent for liquid-phase adsorption studies. Hexadecane, like cyclohexane, is a saturated hydrocarbon

Figure 1. Comparison of the Adsorption of Quinoline on $\text{CoMo}/\text{Al}_2\text{O}_3$ using Hexadecane and Cyclohexane as the Solvent.

Table 3
Comparison of Estimated Surface Areas When Using
Cyclohexane and Hexadecane as Solvents for
Liquid-Phase Adsorption

Solvent	$\frac{M}{W}$ (mg/g)	Calculated Surface Area (m ² /g)	BET Surface Area # (m ² /g)
Cyclohexane	66.2	213 ± 20	200 ± 20
Hexadecane	74.3	238 ± 20	200 ± 20

#Reported BET surface area of CoMo/Al₂O₃ (Harshaw 0402T).

and should show minimal adsorption as compared to unsaturated hydrocarbons. High temperature studies are possible with hexadecane because of its high boiling point. This solvent would be advantageous in collecting a set of isotherms for the adsorption of a component at different temperatures. These isotherms can provide insight with regard to the type of adsorption that occurs (chemical or physical).

Experimental Studies. Again quinoline was used as the solute and $\text{CoMo/Al}_2\text{O}_3$ (Harshaw 0402T) was used as the adsorbent. The isotherm of this system is depicted in Figure 1. Monolayer coverage of the adsorbent by quinoline in solution with hexadecane indicates minimal adsorption of the solvent. Quinoline is adsorbed onto the entire catalyst surface as shown in Table 3. Thus, hexadecane also appears to be a good solvent for liquid-phase adsorption studies.

Comparison of Cyclohexane and Hexadecane

Comparison of the isotherms obtained for both solvents (Figure 1) shows that their adsorption properties are nearly identical. Therefore, either solvent appears to be suitable for use in liquid-phase adsorption studies.

For this work, cyclohexane was chosen as the solvent because it is more convenient to use. Hexadecane is a more viscous liquid than cyclohexane which makes it more difficult to use for diluting the solutes because it adheres to the walls of the volumetric vessels. This tends to increase errors in preparing solutions for the adsorption studies. Hexadecane also presents problems for UV analysis because of difficulties confronted in cleaning the cuvettes after use.

Analysis of Adsorbate

Since cyclohexane shows minimal adsorption as compared to the adsorbate (solute), the amount of adsorbate in the adsorbed phase may be determined from the amount of adsorbate remaining in the bulk liquid-phase. Equilibrium was established between the bulk liquid-phase and the adsorbed phase with the use of an experimental procedure developed by Shridharani (2).

Experimental Procedure

Equipment. The adsorption studies were performed using tubular vessels constructed of 4-inch sections of 316 stainless steel tubing having an O.D. of 0.5 inches and a wall thickness of 0.035 inches (Figure 2). The tubes were sealed at each end with Swagelok caps.

To insure that the rate of adsorption was not limited by diffusion, the tubes were rotated at approximately 50 rpm on a roto rack (Fisher Scientific Co.).

The speed of rotation was kept at a minimum to prevent adsorbent size reduction. Mechanical breakdown of the adsorbent increases its specific surface area and thus its adsorptive capacity (23).

Procedure. Solutions of the solute were prepared in batch quantities from stock solutions by diluting with cyclohexane. The adsorbents were prepared in advance and stored in a dessicator until use. A clean and dry tube was carefully sealed at one end with a Swagelok cap. A specified amount of adsorbent was weighed out and placed in the tube. 5.0ml of solution were transferred to the tube with the use of a pipette. The other end of the bomb was then sealed with another Swagelok cap and the bomb was placed on a rotating shaker.

Figure 2. Schematic for Reactor used in Adsorption Studies.

All reactions were performed at room temperature and rotation of the bombs was continued until equilibrium was reached.

For analysis, the tubes were opened and the solution was decanted into 4.0 ml vials and centrifuged at 3000 rpm for 5 minutes to separate any adsorbent which may have been suspended in the solution.

The final concentration of the solution was determined via UV analysis. A Beckman DK-2A Ratio Recording Spectrophotometer was used for this. The solution concentrations were determined by comparison to a calibration curve of absorption versus concentration (Appendix C). If the solution was too concentrated for UV analysis, then it was diluted with cyclohexane until its concentration was in the range of the calibration curve.

Cyclohexane was used as the reference liquid in the UV analysis. The absorbance of the sample was determined at two wavelengths. These two values of absorbance were used to calculate an average concentration of the sample. The concentrations determined from each wavelength usually agreed within 2% of each other.

The tubes were then completely dismantled, cleaned with THF, and dried in an oven.

Exploratory Experiments. Shridharani (2) performed preliminary experiments to examine the resistance of the stainless steel tubes to adsorption. 5.0 ml of a 250 mg/l naphthalene solution were charged into two tubes which contained no adsorbent. The tubes were rotated at 50 rpm for 24 hrs. at room temperature. The concentrations of the samples were determined to be 249.3 ± 1.7 mg/l. This indicates that the stainless steel walls did not act as an adsorbent.

In another set of experiments, stainless steel tubes as well a glass cell were used as vessels for adsorption. In each vessel, 5 ml of a 250 mg/l naphthalene solution and one gram of calcined $\text{CoMo/Al}_2\text{O}_3$ catalyst were charged. The concentration of the sample obtained from the stainless steel tube was determined to be 44.3 mg/l. The concentration of the sample obtained from the glass cell was found to be 44.0 mg/l. This further confirmed that a relatively small amount of adsorption occurs on the walls of the stainless steel tubes.

Analytical Procedure

Rate of Adsorption

Experiments were performed to determine the magnitude of the rate of adsorption and the time required for adsorption to reach equilibrium. In these experiments the contact time between the adsorbents and the solution was varied. The time required for the solution to reach a steady concentration was taken as the time required for the solution to be in equilibrium. Four different compounds were used as adsorbates for these experiments: naphthalene, pyrene, phenol, and quinoline. $\text{CoMo/Al}_2\text{O}_3$ (Harshaw 0402T) was used as the adsorbent. The results of the experiments are presented in Table 4.

These results show that the magnitude of adsorption for naphthalene and pyrene is at least an order of magnitude less than that of phenol and quinoline. The rate of adsorption is very rapid during the initial 10 minutes of contact. After this period, the rate of adsorption decreases drastically and the amount of adsorbate adsorbed increases only slightly with an increase in adsorption time. The results indicate that the adsorption is close to equilibrium within 24 hours.

Table 4
Rate of Adsorption of Naphthalene, Pyrene, Phenol, and
Quinoline on CoMo/Al₂O₃ Catalyst

Compound	Amount Adsorbed, Ψ_A (mg/g)*				
	10	20	60	120	1440
	Time(min)				
Naphthalene	0.91	---	0.97	1.00	1.03
Pyrene	1.88	1.94	1.95	1.96	1.99
Phenol	23.81	24.08	24.09	24.30	24.61
Quinoline	34.58	34.57	34.86	---	35.36

*Results reported are an average of two experiments.

Initial Concentrations: Naphthalene - 250 mg/l
Pyrene - 500 mg/l
Phenol - 5000 mg/l
Quinoline - 7150 mg/l

Rate studies were also performed using presulfided iron oxide (pyrite) as an adsorbent. The results of these experiments are inconclusive because adequate duplication of Ψ_A values could not be achieved. The time required to approach an equilibrium value of adsorption was difficult to determine with pyrite. To insure that near equilibrium values were obtained for adsorbents with high and low affinities for the adsorbing material, contact time of three days was selected.

Interpretation of Data

Adsorption isotherms were determined by varying the initial concentrations of the solutions that were charged into the tubes. The concentration of the bulk liquid-phase, which is in equilibrium with the adsorbed phase, was found to increase with increasing initial solution concentration. The amount of adsorbate adsorbed, Ψ_A , was calculated for each final equilibrium concentration using the following equation:

$$\Psi_A = \frac{(C_A - C_A^E) (V)}{(1000 \text{ ml/l}) (W)} \quad (10)$$

where C_A is the initial concentration of the solution (mg/l), C_A^E is the concentration of the bulk liquid at equilibrium (mg/l), V is the initial volume of solution transferred to the tube (5.0 ml), and W is the weight of catalyst added to the tube.

Adsorption parameters were determined by plotting the values of Ψ_A as a function of the corresponding values of C_A^E (e.g. Figure 3).

Both irreversible and reversible adsorption were assumed to occur. Also, it was assumed that the reversible adsorption could be treated as

Figure 3. Example of Adsorption Isotherm.

being linearly superimposed onto the irreversible adsorption. This implies that

$$\Psi_A = \Psi_{AR} + \Psi_{AIR} \quad (11)$$

where Ψ_{AR} is the reversible amount of component A adsorbed and Ψ_{AIR} is the irreversible amount adsorbed.

Langmuir-type adsorption which is described by Equation 6, was assumed to occur.

$$\frac{\Psi_{AR}}{M} = \frac{k_A C_A^E}{1 + k_A C_A^E} \quad (6)$$

This equation is correct only for the reversible portion of an adsorption curve. Upon rearrangement, Equation 6 can be expressed in the following linear form:

$$\frac{C_A^E}{\Psi_{AR}} = \frac{1}{\frac{M}{\Psi_{AR}}} \left[C_A^E + \frac{1}{k_A} \right] \quad (12)$$

Using Equation (11), Equation (12) can be expressed in terms of the total amount of adsorption, Ψ_A .

$$\frac{C_A^E}{\Psi_A} = \frac{1}{\frac{M}{\Psi_A}} \left[C_A^E + \frac{1}{k_A} \right] \quad (13)$$

where the term

$$\frac{\Psi_{AIR}}{k_A \Psi_A}$$

is assumed to be negligible in comparison to the term $(C_A^E + \frac{1}{k_A})$ for large values of C_A^E .

The derivation of Equation (13) from Equation (12) is given in Appendix E. According to Equation (13), the total amount of adsorption with monolayer coverage, Ψ_A^M , is equal to the inverse of the slope of the curve $\frac{E}{C_A/\Psi_A}$ versus $\frac{E}{C_A}$.

Surface areas of the adsorbents can be calculated using the values of Ψ_A^M . The values of Ψ_A^M are calculated using equation 13. The surface area per unit mass of adsorbent is represented by the following equation:

$$S = \Psi_A^M \sigma N/M \quad (14)$$

where Ψ_A^M is the amount adsorbed for monolayer coverage (mg/g catalyst), σ is the cross-sectional area of the adsorbed molecule (m^2), N is Avogadro's number, and M is the molecular weight of the adsorbed molecule (mg/m mole).

Two important criteria must be met for equation 14 to be valid: The adsorbate must be adsorbed flat, and it must cover the entire surface of the adsorbent. Also, its molecular cross-sectional area must be known.

Error Analysis

Several measurements were made to evaluate the magnitude of the inherent errors involved in the experimental procedure used here for measuring adsorption. To this end, pyrene was adsorbed on CoMo/Al₂O₃ (Harsaw 0402T). Isotherms constructed using the results of these experiments showed a large amount of experimental scatter. Sources of possible errors are solution preparation, procedure discrepancies arising from dilution of solutions for UV analysis, and inconsistencies in the charging of the tubes.

The standard deviation in the concentration of the bulk-liquid at equilibrium was determined using a sample which required maximum dilution for UV analysis. For a final concentration of 55.0 mg/l, a standard deviation of ± 1.47 mg/l was obtained. Using these values, the amount of pyrene adsorbed was determined to be 7.73 mg/g with a standard deviation of ± 0.16 mg/g. These values correspond to an error in the value of C_{py}^E of $\pm 2.7\%$ and an error in the value of Ψ_{py} of $\pm 2.1\%$ (Appendix C).

Duplicate sets of data were used to construct two adsorption isotherms for pyrene. These two isotherms yielded Ψ_{py}^M values of 8.68 mg/g and 8.41 mg/g. The values of Ψ_{py}^M were found to have a maximum error of 3.2%.

These values indicate that the errors inherent in the experimental procedure are satisfactory. Duplication of the isotherms show that values of Ψ_A^M are highly reproducible.

Adsorbent Preparation

Commercial Catalyst

Commercially available catalysts were obtained in the form of pellets. These pellets were ground and sifted through a screen to obtain a mesh size of -35 to +60 so as to obtain adsorption equilibrium more expediently. The ground particles were placed in a pyrex tube of 1 inch O.D. and calcined in an oven overnight at 450°C. Calcining the catalyst at 450°C drives off chemisorbed water. This chemisorbed water strongly affects the adsorptive capacity of the catalyst (21).

Presulfided Iron Oxide

The method used for presulfiding iron oxide was developed by Shridharani (2). Anhydrous ferric oxide (Fe_2O_3) powder (Fisher Scientific Company) was used as the starting material for catalyst preparation. The iron oxide was sulfided using H_2S , +99.5% (Matheson Gas Company).

Approximately 20 grams of iron oxide were placed in the center of a 1-inch O.D. Pyrex tube. The tube was placed in a Lindberg Electric Furnace, Type 54032. An excess of H_2S was passed through the tube prior to heating. The furnace was then switched on and the reaction was performed for 150 min. at a temperature of 275°C . At the end of the reaction, the tube was removed from the furnace and allowed to cool. The flow of H_2S was continued until the catalyst cooled down to room temperature (See Figure 4 for apparatus used for sulfiding catalysts).

After the catalyst was prepared, known weights were placed in closed glass vials. This was done in an N_2 atmosphere in a glove bag to prevent oxidation of the catalyst.

Deviation of Batch Properties. Experiments performed using different batches of presulfided iron oxide were reproducible only to a limited extent. With the same initial solution concentration, triplicate runs were performed with catalyst from the same batch. Values of Ψ_A for the three runs were approximately equal in some cases. When another set of triplicate runs was performed with catalyst from a different batch, the values of Ψ_A did not correspond to those obtained for the catalyst from the previous batch. Deviations in the values of ϕ_A for different batches of catalysts were as large as 35%.

Figure 4. Apparatus for Sulfiding Ferric Oxide

The results of these experiments tend to indicate that the physical properties of the catalyst may vary from batch to batch and possibly even within the same batch. To overcome this problem, the following preparation procedure was adopted:

- (1) The Fe_2O_3 was sulfided at 275°C in a pure H_2S atmosphere for 3 hours.
- (2) The sulfided catalyst was allowed to cool and then ground with the use of a mortar and pestal until a uniform particle size was obtained.
- (3) The catalyst was then sulfided for an additional 3 hours.
- (4) The resulting catalyst was dried under vacuum for 1 hour to remove water formed during the reaction.
- (5) The catalyst was then stirred for 1 hour in a N_2 atmosphere.

This procedure was carried out to maximize the homogeniety of the physical and chemical properties of each batch of catalyst.

Presulfided $\text{CoMo}/\text{Al}_2\text{O}_3$

$\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst (Harshaw 0402T) was ground and screened to yield a mesh size of -35 to +60. The catalyst was sulfided using the procedure developed by Shridharani (2). The equipment used was the same as that described above for sulfiding Fe_2O_3 .

Approximately 30g of ground $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst were placed in the center of a 1-inch O.D. Pyrex tube. The tube was then placed in a Lindberg Electric Furnace, type 54032, and rubber stoppers with inlet and

outlet openings for gas flow were installed. The H_2S (Matheson Gas Company) flow rate was then adjusted to approximately 15cc/min. and the furnace was turned on.

The temperature was increased at a rate of approximately $4^\circ\text{C}/\text{min}$. The reaction was continued for 90 min. and a final temperature of 410°C was used. The furnace was then switched off and the catalyst was allowed to cool in the presence of a continuous flow of H_2S . After room temperature was reached, the H_2S flow was stopped and the catalyst was removed and stored in vials.

Importance of Cleaning Catalyst Surface. Initial adsorption experiments were performed using quinoline as the adsorbate. After equilibrium was obtained between the adsorbed phase and the bulk liquid-phase, the liquid solution was analyzed as described previously. The UV spectrum of the bulk liquid showed a distortion in the characteristic absorption peaks for quinoline. These distorted peaks were assumed to indicate that quinoline had interacted with contaminants present on the surface of the catalyst.

After sulfiding, the $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst retained a distinct odor of H_2S . It was thus assumed that the quinoline was reacting with residual H_2S adsorbed by the catalyst. To remove residual H_2S the catalyst was extracted with hot cyclohexane using a Soxhlet extractor (Figure 5).

Approximately 15g of catalyst were placed in the extraction thimble. The catalyst was washed using 250ml of cyclohexane in a 500ml flask. A heating mantle was used to heat the cyclohexane. The catalyst was extracted for approximately 1 hour and then it was allowed to cool. The

Figure 5. Soxhlet Extractor

cooled catalyst was placed in a 1-inch Pyrex tube in the presence of an N_2 atmosphere.

Experiments performed with the extracted catalyst yielded UV spectra which were distorted as before. These results were assumed to indicate that H_2S may be chemisorbed onto the catalyst surface. If it had only been physically adsorbed, it should have dissolved in the hot cyclohexane.

Chemisorption may be reversed by heating the catalyst to 400-450°C. In an attempt to accomplish this, the catalyst was placed in the same apparatus used for sulfiding the catalyst. N_2 was used to maintain an inert atmosphere for heating because sulfided $CoMo/Al_2O_3$ oxidizes to its original form when exposed to air. The catalyst was heated overnight at 410°C and then allowed to cool in the presence of an N_2 atmosphere.

Experiments performed using this "clean" catalyst showed that there was no significant distortion of the quinoline UV spectra. It was thus assumed that the surface of the catalyst was free of any contaminants.

IV. APPLICATIONS OF LIQUID-PHASE ADSORPTION

Surface Area Analysis

Specific surface area analysis has provided a useful means of characterizing the adsorptivity of certain compounds (24). In general, surface area measurements are commonly used to characterize solids in various technical fields such as kinetics, separations, metallurgy, bio-availability, effluent purification, and catalysis. Many experimental techniques such as volumetric and gravimetric gas adsorption, and fluid permeability have been developed over the past 40 years.

The method of Brunauer, Emmett, and Teller (BET) is the best known method for determining the specific surface area of powders. This method is based on the determination of the quantity of gas adsorbed on the surface of a solid when there is monolayer coverage. McClellan et al. (25) lists the limitations and the advantages of the BET method.

Specific surface area measurement via liquid-phase adsorption, has been attempted by several investigators. Smith et al. (11) performed adsorption experiments in which an attempt was made to calculate the surface areas of nickel and platinum catalysts through the adsorption of fatty acids. This method shows excellent agreement between the surface areas obtained experimentally and those calculated by the method of BET. Giles et al. (9) studied the adsorption of p-nitrophenol on granular solids and fibers. Water was used as a solvent for water-insoluble

granular materials. For materials which showed a tendency to dissolve in or to react chemically with water, non-aqueous solvents, e.g. xylene or n-hexane, were used. The three kinds of adsorbents used in these studies were non-porous powders, porous powders, and fibers.

p-Nitrophenol (PNP) was observed to adsorb with two different kinds of orientation relative to the adsorbent surface. Normally PNP molecules are adsorbed on the solid surface in a flat orientation, but on some polar solids it is adsorbed in an end-on orientation. If the orientation of the adsorbed molecule is not known it may lead to erroneous results in the calculation of the surface area.

The surface areas calculated using PNP as the adsorbate showed excellent agreement with the method of BET for the non-porous adsorbents considered by Giles et al. This method agreed poorly with BET measurements for porous solids; the deviation from BET values was as much as -95%. Giles attributed this deviation to the inability of PNP to fit into the pores of the solid and assumed that the surface area determined via PNP adsorption was the external surface area of the porous solid.

Kagiya et al. (10) have performed liquid-phase adsorption studies on various binary solutions on silica gel namely, cyclohexane and different aromatic compounds as well as cyclohexane and different cyclic ethers. Separation factors (α) and the number of moles in the adsorbed-phase per unit mass of silica gel were calculated based on the assumption that the adsorption followed the Langmuir model.

These studies indicated that aromatic hydrocarbons adsorb in an orientation which is flat to the surface and cyclic ethers adsorb in an orientation which is perpendicular to the adsorbent surface. The surface

areas calculated using chlorobenzene, benzene, toluene and p-xylene were found to be lower than those calculated by the BET method. Benzene and p-xylene yield values of $340 \text{ m}^2/\text{g}$ and $314 \text{ m}^2/\text{g}$, respectively. They deviate from the BET value ($383 \text{ m}^2/\text{g}$) by -11% and -18%, respectively. These deviations may possibly be attributed to errors in the approximation of the cross-sectional areas of the molecules.

As can be seen from the above three examples of surface area determination using liquid-phase adsorption, there is no generally accepted method which can be used for a wide range of adsorbents.

Objective

In this phase of the present study, the main objective was to find a solute which when adsorbed on an adsorbent could be used to calculate specific surface areas for various catalysts. In order for the solute to be acceptable it had to cover completely the catalyst surface. Monolayer coverage during adsorption was assumed to occur. The cross-sectional area of the solute molecules was approximated. The adsorbed solute molecule was assumed to have a flat orientation on the adsorbent surface. For molecules adsorbed in an end-on or side-by-side orientation, the surface area of the solid covered by the solute is difficult to approximate.

Preliminary Experiments. Preliminary experiments were performed using a polynuclear aromatic compound (pyrene), a basic nitrogen-containing compound (quinoline), and an acidic oxygen-containing compound (phenol). These compounds were adsorbed onto a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst (Harshaw 0402T). Adsorption isotherms were constructed for the three compounds. These are shown in Figures 6 and 7.

Figure 6. Adsorption Isotherm for the Adsorption of Pyrene on $CoMn/Al_2O_3$ Catalyst (Harshaw 0402T)

Figure 7. Adsorption Isotherms for the Adsorption of Quinoline and Phenol on CoMo/Al₂O₃ Catalyst

The amount of solute adsorbed for monolayer coverage, Ψ_A^M was calculated for each compound by plotting C_A^E/Ψ_A^E versus C_A^E as discussed previously (equation 7). The slope was determined by a least-squares computer routine which plots the best possible straight line through a given set of data points.

The cross-sectional area of quinoline, naphthalene, phenanthrene, and pyrene are based on the cross-sectional area of a benzene molecule ($34.4\text{\AA}^2/\text{molecule}$) as given by Brunauer (7). The cross-sectional-areas are determined from the following relationship:

$$\sigma = 34.4\text{\AA}^2 (\text{no. of Aromatic rings}) \quad (15)$$

Phenol was assumed to have approximately the same cross-sectional area as that of toluene which is reported as $42.9\text{\AA}^2/\text{molecule}$ (10).

The specific surface area of the catalyst covered by each compound was calculated using equation 14. These calculations are summarized in Table 5. Comparing these results with the reported BET value indicates that pyrene and phenol do not completely cover the catalyst surface.

Quinoline of 99.9% purity (Alfa Chemical Co.) appears to be the most promising compound for adsorption studies because the calculated surface area ($212.6 \text{ m}^2/\text{g}$) gives good agreement with the reported BET value of $200 \text{ m}^2/\text{g}$. Giles et al. (4) has developed a working hypothesis which states that whenever an S-type isotherm is obtained, the most likely orientation of the adsorbed solute molecule is end-on; whereas, when a flat orientation of solute molecules occurs, a curved isotherm that is concave to the equilibrium-concentration axis is usually obtained. Since the quinoline

Table 5

Comparison of the Surface Area Coverage of Pyrene, Phenol
and Quinoline on CoMo/Al₂O₃ Catalyst*

Compound	Surface Area of Catalyst Covered by Each Component (m ² /g)
Quinoline	212.6
Phenol	184.9
Pyrene	34.4

* Surface area (BET) of CoMo/Al₂O₃ (Harshaw 0402T) = 200 m²/g.

isotherm is concave to the equilibrium-concentration axis, which indicates a flat orientation, the surface area calculated using quinoline is assumed to give a "true" specific surface area.

Catalysts for Surface Area Determination

Several commercial grade catalysts possessing various chemical and physical properties were used as adsorbents to evaluate the method discussed in the previous section to determine surface areas using liquid-phase adsorption. BET surface areas of the catalysts tested ranged from 17 m²/g cat. to 320 m²/g cat.

CoMo/Al₂O₃. Adsorption isotherms were constructed for two types of CoMo/Al₂O₃ catalyst, Harshaw 0402T and AERO HDS 1442-B (American Cyanamid Co.). These isotherms are shown in Figure 8. A plot of $\frac{C_Q^E}{\Psi_Q}$ versus C_Q^E was prepared for each isotherm. A straight line fit was provided for the data using linear regression. The two plots are shown in Figure 9. From the slopes of these lines, Ψ_Q^M was calculated with the use of Equation 11. Specific surface areas of the catalysts were calculated with the use of Equation 14 and the calculated values of Ψ_Q^M . A comparison of the calculated values of surface area to the values determined by the BET method indicates good agreement between the two methods. These results and correlation coefficients determined for Figure 8 are summarized in Table 8. The surface areas calculated using this method for Harshaw 9492T and AERO HDS 1442-B deviated from those determined by the BET method of 6.3% and 0.47% respectively.

Table 6

Adsorption of Quinoline on CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W	Quinoline Concentration		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^o	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
0.9992	500	0	2
1.0013	1000	0	4.99*
1.0020	2000	0	9.98*
0.9999	4000	0	20.00*
1.0022	5000	0	24.95
0.9990	6000	0	30.03
0.9993	7000	0	35.03
1.0011	7150	6.25	35.33
1.0000±0.0011	7200	14.57±1.85	35.89±0.11
1.0006±0.0015	8000	47.16±6.76	39.23±0.01
1.0003±0.0009	9000	130.80±15.94	44.33±0.09
1.0008±0.0005	10,000	272.35±12.25	48.60±0.08
1.0010±0.0006	12,000	823.05±11.09	55.83±0.07
1.0009±0.0011	14,000	1707.83±38.67	61.41±0.20
1.0008±0.0007	16,000	2798.45±38.97	65.95±0.20
1.0005±0.0002	18,000	4115.65±403.76	69.39±2.01
1.0002±0.0003	20,000	5101.56±384.72	74.48±1.92

Table 7

Adsorption of Quinoline
on HDS 1442B Catalyst

Amount of Catalyst, W	<u>Quinoline Concentration</u>		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0001±0.0001	12,000	26.57±0.815	59.86±0.0
1.0007±0.0001	14,000	113.8±0.565	69.38±0.01
1.0008±0.0004	16,000	389.9±18.2	77.99±0.06
1.0002	18,000	723.0±78.0	86.37±0.39
1.0004±0.0001	20,000	1400.0±25.0	92.97±0.135
1.0002±0.0001	22,000	2212.6±18.75	98.91±0.12
1.0002	25,000	3906.3	105.44

Figure 8. Adsorption Isotherms for the Adsorption of Quinoline on CoMo/Al₂O₃ Catalysts.

Figure 9. Linear Forms of the Adsorption Isotherms for the Adsorption of Quinoline on CoMo/Al₂O₃ Catalysts.

Table 8

Comparison Between Surface Areas Calculated by the BET Method and
Surface Areas Obtained from the Liquid-Phase Adsorption of
Quinoline on CoMo/Al₂O₃ Catalysts

Catalysts	M 4Q (mg/g)	Surface Area (m ² /g)	Correlation Coefficient	BET Surface Area(4) (m ² /g)	Error (%)
Harshaw 0402T	66.2(1)±2.2(2)	212.6(1)±7.1(2)	0.999	200	6.3(3)
AERO HDS 1442-B 9.	100.2	321.5	0.999	320	0.47(3)

(1) Values reported are calculated from all data points obtained from duplicated isotherms.

(2) These values are the difference of the values calculated from each individual isotherm.

(3) Values reported are the deviation of BET values and calculated values.

(4) Micromeritics Instruments Corporation reports a surface area value of 183 m²/g for the Harshaw 0402T catalyst.

Note: Catalyst characteristics are summarized in Appendix A.

NiMo/Al₂O₃. The adsorption isotherm for the adsorption of quinoline on NiMo/Al₂O₃ (Shell 324) is given in Figure 10. ψ_Q^M was calculated from the initial slope of the curve C_Q^E/ψ_Q^E versus C_Q^E shown in Figure 11. The specific surface area of the catalyst was calculated with the use of Equation 14. The calculated value, 172 m²/g, and the BET value, 174 m²/g, show good agreement. Deviation of the calculated value from the BET value is -1.1%. These results along with the correlation coefficient calculated for the plot in Figure 11 are given in Table 10.

Catalyst Supports. In order to test the applicability of the method developed for surface area determination, adsorption isotherms were experimentally obtained for two types of catalyst supports, namely Al₂O₃ (Harshaw Al-1602) and MgO (Harshaw MgO-0601). Quinoline was used as the adsorbate for these catalysts. Plots of C_Q^E/ψ_Q^E versus C_Q^E were prepared for the two isotherms and values of ψ_Q^M were determined from their initial slopes. These plots are shown in Figure 13 and 15. The ψ_Q^M values were used to calculate the specific surface areas of the two supports. These results are compared to the BET values in Table 13. Errors in the surface areas based on the BET values for Harshaw Al-1602 and MgO-0601 are 4.7% and 8.2%, respectively. These results and the correlation coefficients for the two plots in Figures 13 and 15 are also summarized in Table 13.

Deactivated Catalyst. The surface areas of an activated and a deactivated catalyst were determined to assess the order-of-magnitude decrease in the surface area of the catalyst upon deactivation.

Table 9

Adsorption of Quinoline on NiMo/Al₂O₃ Catalyst
(Shell 324)

Amount of Catalyst, W	<u>Quinoline Concentration</u>		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.00	5000	0	25.0
1.00	6000	0	30.0
1.0006±0.0001	7200	29.44±1.69	35.8±0.01
1.0006±0.0004	8000	125.9±0.51	39.3±0.02
1.0010	9000	331.3	43.3
1.0004±0.0001	10000	600.6±10.6	47.0±0.06
1.0001±0.0001	12000	1440.7±31.5	51.8±0.01

Figure 10. Adsorption Isotherm for the Adsorption of Quinoline on $\text{NiMo}/\text{Al}_2\text{O}_3$ Catalyst (Shell 324).

Figure 11. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on NiMo/Al₂O₃ (Shell 324).

Table 10

Comparison Between Surface Areas Calculated by the BET Method
and Surface Areas Obtained from the Liquid-Phase Adsorption
of Quinoline on NiMo/Al₂O₃ Catalyst (Shell 324)

Catalysts	M φQ (mg/g)	Surface Area (m ² /g)	Correlation Coefficient	BET Surface Area (m ² /g)	Error (%)
Shell 324	53.6	172	0.999	174	-1.1 (3)

(3) See Table 8 for explanation.

Note: Catalyst characteristics are summarized in Appendix A.

Table 11.

Adsorption of Quinoline on MgO Catalyst
(Harshaw MgO-0601)

Amount of Catalyst, W	Quinoline Concentration		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0005	600	198.8	2.01
1.0008	800	302.5	2.49
1.0005	1000	527.5	2.36
1.0005±0.0006	2000	1396.3±16.2	3.02±0.080
1.0002±0.0002	3000	2271.9±3.10	3.64±0.010
1.0004±0.0004	4000	3187.5	4.06
1.0003±0.0001	5000	4046.9±15.6	4.77±0.070
1.0008	6000	5062.6±31.2	4.69±0.150
1.0002	8000	6984.4±15.6	5.08±0.080

Figure 12. Adsorption Isotherm for the Adsorption of Quinoline on MgO (Harshaw MgO-0601).

Figure 13. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on MgO (Harshaw MgO-0601).

Table 12

Adsorption of Quinoline on Al_2O_3 Catalyst
(Harshaw Al-1602T)

Amount of Catalyst, W	Quinoline Concentration		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0004±0.0003	7200	108.5±4.05	35.4±0.03
1.0004±0.0003	8000	183.2±44.4	39.1±0.21
1.0007±0.0006	9000	308.8±13.8	43.4±0.05
1.0001±0.0001	10000	444.8±7.25	47.8±0.04
0.9998±0.0001	12000	903.8±33.8	55.5±0.16
1.0000±0.0002	14000	1665.7±53.2	61.7±0.26
1.0001	16000	3020.8	64.9

Figure 14. Adsorption Isotherm for the Adsorption of Quinoline on Al_2O_3 (Harshaw Al-1602).

Figure 15. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on Al_2O_3 (Harshaw Al-1602).

Table 13

Comparison Between Surface Areas Calculated by the BET Method
and Surface Areas Obtained from the Liquid-Phase Adsorption
of Quinoline on Catalyst Supports

Catalysts	M ϕ Q (mg/g)	Surface Area (m ² /g)	Correlation Coefficient	BET Surface Area (m ² /g)	Error (%)
MgO-0601	4.94	17.8	0.990	17	8.2(3)
Al-1602	67.4	216.4	0.999	200	4.7(3)

(3) See Table 8 for explanation.

Note: Catalyst characteristics are summarized in Appendix A.

A NiMo/Al₂O₃ catalyst in its pellet form was used to experimentally study the adsorption of quinoline. These results were used to prepare an adsorption isotherm as described previously. The adsorption isotherm and a plot of C_Q^E/Ψ_Q versus C_Q^E are shown in Figures 16 and 17, respectively. From Figure 17, the surface area of the catalyst was determined to be 323.7 m²/g.

The deactivated catalyst was extracted with THF for approximately one month to remove all contaminants from its surface. The importance of a clean catalyst surface was emphasized in Chapter III. The catalyst was then calcined at 410°C overnight in the presence of a continuous N₂ flow. The adsorption isotherm for this process is shown in Figure 18. A plot of C_Q^E/Ψ_Q versus C_Q^E was also prepared. This is shown in Figure 19. Using this plot, the surface area of the deactivated catalyst was determined to be 192.8 m²/g.

It is interesting to note that the equilibrium concentration of quinoline approaches 7000 mg/l before apparent monolayer coverage of the deactivated catalyst occurs. For another catalyst which has approximately the same surface area, Harshaw 0402T, the equilibrium concentration approaches 3000 mg/l when apparent monolayer coverage is obtained. This indicates that adsorption of solute molecules on deactivated catalysts is slower than adsorption on activated catalysts.

The surface areas determined for the two catalysts indicate that there is a 40.4% decrease in the surface area of the deactivated catalyst. These results are summarized in Table 16. Cable et al. (26) have reported a surface area decrease of 50% for a different type of catalyst upon deactivation.

Table 14

Adsorption of Quinoline on ARMAK Catalyst

Amount of Catalyst, W	<u>Quinoline Concentration</u>		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0005	12000	10.38±0.19	59.92
1.0004±0.0002	14000	31.32±0.19	69.82±0.02
1.0005	16000	90.94±1.56	79.51±0.01
1.0005±0.0002	18000	222.8±0.3	88.84±0.02
1.0005	20000	1012.5±12.5	94.89±0.06
1.0002	22000	1806.3±12.5	100.96±0.07

Table 15

Adsorption of Quinoline on Deactivated ARMAK Catalyst

Amount of Catalyst, W	Quinoline Concentration		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0000±0.0005	5000	254.2±7.2	23.73±0.02
1.0005±0.0001	6000	475.1±11.3	27.61±0.05
1.0002±0.0003	8000	1111.3±31.3	34.43±0.17
1.0006±0.0002	10000	2065.7±46.9	39.65±0.25
1.0003±0.0004	12000	2862.5	45.67±0.02
1.0001±0.0005	14000	4015.7±46.9	49.92±0.16
1.0002±0.0001	16000	5500.0±62.5	52.49±0.32
1.0003±0.0001	18000	6703.2±78.2	56.47±0.40

Figure 16. Adsorption Isotherm for the Adsorption of Quinoline on ARMAK Catalyst.

Figure 17. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on ARMAK Catalyst.

Figure 18. Adsorption Isotherm for the Adsorption of Quinoline on Deactivated ARMAK Catalyst.

Figure 19. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on Deactivated ARMAK Catalyst.

Table 16

Comparison Between the Surface Areas of Activated and Deactivate
ARMAK Catalyst as Obtained from the Liquid-Phase
Adsorption of Quinoline

Catalyst	M Ψ Q (mg/g)	Surface Area (m ² /g)	Decrease in S.A. (%)
ARMAK	100.9	323.7	-
Deactivated ARMAK	60.1	192.8	40.4

*Both catalyst used were in pellet form.

The isotherms obtained using these commercial grade catalysts are of the "high affinity" (H_2) type as defined by Giles et al. (14). Cook et al. (16) have shown that isotherms of this type may occur due to a combination of reversible and irreversible adsorption. According to these results, the minimum amount of quinoline adsorbed irreversibly is indicated by the point at which the adsorption isotherm intersects the Ψ_Q axis.

The method developed for determination of specific surface areas appears to be comparable in accuracy to the method of BET (Figure 20). The various catalysts studied indicate that this method may be applicable to a wide variety of porous adsorbents. For catalysts used in coal liquefaction, which usually have specific surface areas between $150 \text{ m}^2/\text{g}$ and $350 \text{ m}^2/\text{g}$, this method gives excellent results.

Application to Catalytic Inhibition Studies

Background

In coal liquefaction, the rate limiting step has been postulated as the hydrogenation of process solvent to produce the H-donor species (27). Therefore, a good hydrogenation catalyst for coal liquefaction should provide a high concentration of H-donor species in the reactor leading to an increase in oil production during reaction. Shridharani (2) has studied the hydrogenation of naphthalene to obtain tetralin using different catalysts.

According to Shridharani (2) high affinity compounds, like phenol and quinoline, may be responsible for removing the active catalyst sites otherwise available for adsorption of polynuclear aromatic (PNA) compounds. This results in a reduction in the rate of hydrogenation of

Figure 20. Comparison Between the Method of BET and Liquid-Phase Adsorption for Surface Area Determination.

PNA compounds. This inhibition of PNA hydrogenation causes a reduction in the concentration of hydrogen donor species in coal liquefaction reactors.

Hydrogenation Inhibition

Shridharani (2) has studied the relative roles that different types of compounds present in coal liquids play in inhibiting the hydrogenation activity of a catalyst. For this purpose, naphthalene hydrogenation experiments were performed in the presence of nitrogen and oxygen containing compounds. The inhibition of naphthalene hydrogenation due to other PNA compounds was also studied to evaluate the selectivity of the catalyst used.

Inhibition Model. The inhibition of naphthalene hydrogenation was modeled using Langmuir-Hinshelwood kinetics (2). The model for naphthalene inhibition in the absence of inhibitors is

$$\frac{-W_S}{W_C} \frac{dC_N}{dt} = k \left[\frac{k_N C_N}{1 + k_N C_N + k_T C_T} \right] \text{Type 1} \left[\frac{k_H C_H}{1 + k_H C_H} \right] \text{Type 2} \quad (16)$$

where W_C is the amount of catalyst; W_S , the amount of solution; t , time; C_N , C_T , and C_H are the liquid-phase concentrations of naphthalene, tetralin, and hydrogen, respectively.

Assuming that the inhibitor adsorbs on Type 1 sites, Equation 14 becomes

$$\frac{-W_S}{W_C} \frac{dC_N}{dt} = k \left[\frac{k_N C_N}{1 + k_N C_N + k_T C_T + k_I C_I} \right] \text{Type 1} \quad (17)$$

Assuming that $k_N C_N + k_I C_I \ll 1$ and that the hydrogen concentration (C_H) remains constant during reaction, Equation 15 becomes

$$\frac{-dC_N}{dt} = \frac{k_0 C_N}{1 + k_I C_I} \quad (18)$$

where C_N = naphthalene concentration; C_I = inhibitor concentration; k_I = adsorption equilibrium constant for the inhibitor; and $k_0 = \frac{W_C k_N k_H C_H}{(1 + k_H C_H) / W_S}$.

Equation 18 was integrated using the assumption that C_I remains constant throughout the reaction. Upon rearranging, the following equation was obtained

$$\phi = \frac{t}{-\ln(1-x)} = \frac{1}{k_0} + \frac{k_I}{k_0} C_I \quad (19)$$

where x is the fractional conversion defined as $(C_{N0} - C_N) / C_{N0}$, and C_{N0} is the initial naphthalene concentration. This equation is linear with respect to ϕ and C_I . k_I is a measure of inhibition; the higher the value of k_I , the lower the rate of naphthalene hydrogenation.

Inhibition by Quinoline. Using the above model, Shridharani (2) found that the extent of inhibition of naphthalene hydrogenation by quinoline increased with an increase in initial quinoline concentration and a decrease in reaction time. Catalysts used for these experiments were presulfided iron oxide, presulfided CoMo/Al₂O₃, and molybdenum octoate. The decrease in inhibition with increased reaction time was attributed to the reaction of quinoline to form less inhibiting compounds.

The effect of inhibition is more pronounced with the presulfided iron oxide catalyst than with presulfided $\text{CoMo/Al}_2\text{O}_3$. These catalysts are compared on the basis of an initial quinoline concentration of 1.0% and a reaction time of 10 min. in Table 17.

Inhibition by Phenol. Shridharani (2) observed that naphthalene hydrogenation was not inhibited by the addition of phenol to the reactant solution. Phenol deoxygenation was obtained when both presulfided iron oxide and presulfided $\text{CoMo/Al}_2\text{O}_3$ were used as catalysts. Conversion of phenol was higher with presulfided $\text{CoMo/Al}_2\text{O}_3$ than with presulfided iron oxide. Even though phenol does not interfere with naphthalene hydrogenation, it is still adsorbed on the catalyst surface. If phenol conversion had occurred due to thermal effects only, there would not be a significant difference in the amount of phenol conversion obtained for each catalyst.

Inhibition by Pyrene. The extent of naphthalene hydrogenation was found to decrease with an increase in pyrene concentration (2). The extent of pyrene hydrogenation remained essentially constant with an increase in pyrene concentration. These results indicate that pyrene is adsorbed more strongly than naphthalene. This seems to be in accordance with the rule set forth by Klemm et al. (6): the adsorption of a compound increases with an increase in the number of double bonds.

Adsorption of Inhibiting Compounds

The main objective of this part of the study was to elucidate the interactions between catalyst surfaces and different types of inhibiting compounds. For this study, three different types of compounds were used:

Table 17

Comparison of Quinoline Inhibition of Naphthalene Hydrogenation
in the Presence of Different Catalysts*

Catalyst	Quinoline Concentration (wt%)	Naphthalene Conversion (%)
Presulfided Iron Oxide	1.02	5.8
Presulfided CoMo/Al ₂ O ₃	1.03	33.5

Reaction Conditions: 5g reaction mixture (10 wt% naphthalene in
hexadecane + quinoline), W_S catalyst, T°C,
1250 psig H₂ at room temperature, 860 rpm,
2 steel ball agitators, 15 ml reactor

Presulfided Iron Oxide: W_S = 0.5g, T = 410°C

Presulfided CoMo/Al₂O₃: W_S = 0.25g, T = 380°C

*Taken from reference (2).

(1) basic nitrogen-containing compounds, (2) acidic oxygen containing compounds, and (3) polynuclear aromatic compounds. Adsorbents used were presulfided iron oxide, $\text{CoMo/Al}_2\text{O}_3$, and presulfided $\text{CoMo/Al}_2\text{O}_3$.

Adsorption on Presulfided Iron Oxide Catalyst. Initially, naphthalene was chosen as a reference compound for these adsorption studies. The extent of naphthalene adsorption on presulfided iron oxide was found to be negligible as indicated in Table 18. It was decided at this point to use pyrene, which is also a PNA compound, because it is adsorbed more strongly than naphthalene (2). An adsorption isotherm was constructed for the adsorption of pyrene. This is shown in Figure 21. Duplication of the data points was very difficult to achieve as indicated by the scatter in the isotherm. The reasons for the poor reproducibility of these data points are unknown, but it is felt to be due to uncontrollable variations in the catalyst properties. These problems are discussed in more detail in Chapter III.

When the initial pyrene concentration was greater than 30 mg/l, a Langmuir type (L2) isotherm was observed. If an initial pyrene concentration of 30 mg/l or less was used, the amount of pyrene adsorbed was minimal ($\Psi_{\text{py}} < 0.06 \text{ mg/g}$) and a discontinuity occurred in the adsorption isotherm in this concentration range. It is possible that some type of interaction exists between either cyclohexane and pyrene or cyclohexane and the adsorbent which prevents the adsorption of pyrene. At higher concentration, pyrene may be adsorbed easily and these adsorbed molecules may permit more pyrene molecules to be adsorbed (i.e. cooperative adsorption).

Table 18

Adsorption of Naphthalene on Presulfided Iron Oxide

Amount of Catalyst, W	<u>Naphthalene Concentration</u>		Amount of Naphthalene Adsorbed per Gram of Catalyst, Ψ_N
	Initial C_N^0	Equilibrium, C_N^E	
(g)	(mg/l)	(mg/l)	(mg/g)
0.5047	100	101.3	-0.049
0.7496	100	102.3	-0.015
0.9877	100	102.9	-0.015
0.9978	100	93.3	0.033
1.4901	100	96.0	0.014
1.9901	100	95.00	0.013

Adsorption Test Conditions: 5 ml solution (naphthalene dissolved in cyclohexane), 10 ml stainless steel cell, 50 rpm, 3 days.

Table 19

Adsorption of Pyrene on Presulfided Iron Oxide

Amount of Catalyst, W	<u>Pyrene Concentration</u>		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_{PY}^0	Equilibrium, C_{PY}^E	
(g)	(mg/l)	(mg/l)	(mg/g)
2.0006±0.0004	15	6.1	0.022
0.4988±0.0011	30	24.0±0.2	0.061±0.030
0.6926±0.0684	30	24.1±0.4	0.044±0.010
0.0075±0.0058	30	17.6±3.2	0.062±0.020
1.5051±0.0060	30	17.2±0.2	0.043±0.005
2.0071±0.0048	30	14.4±0.4	0.039±0.001
1.0041±0.0013	45	26.3±4.6	0.093±0.020
1.0034±0.0034	60	4.9±0.1	0.27±0.002
1.0027	90	13.8	0.38
1.00182	120	33.8	0.43
1.00651	150	49.9	0.50
1.0024±0.0037	200	139.7±10.3	0.30±0.05
0.9981±0.0050	350	258.9±9.3	0.45±0.05

Figure 21. Adsorption Isotherm for the Adsorption of Pyrene on Presulfided Iron Oxide.

The value of Ψ_{py}^M was determined to be 0.419 mg/g from the initial slope of the plot of C_{py}^E/Ψ_{py}^E versus C_{py}^E which is given in Figure 22. Using Equations 13 and 14, the surface area of the adsorbed pyrene was found to be 1.7 m²/g.

The adsorption of phenol appears to follow a Langmuir-type (L2) isotherm over a wide range of concentrations as shown in Figure 23. Again, the data points show scatter indicating poor reproducibility. From the plot of C_{ph}^E/Ψ_{ph}^E versus C_{ph}^E (Figure 24) values of Ψ_{ph}^M and surface area of the adsorbed phenol were determined to be 2.36 mg/g and 8.4 m²/g, respectively.

The adsorption isotherm constructed for the adsorption of quinoline on presulfided iron oxide (Figure 25) yields a "high affinity" (H₂) type isotherm. The rise in the trend of the isotherm after the plateau is reached indicates that multilayer adsorption occurs in this region. These types of isotherms indicate that reversible and irreversible adsorption may be occurring simultaneously (7,17). A plot of C_Q^E/Ψ_Q^E versus C_Q^E is shown in Figure 26. This was used to calculate the values of Ψ_Q^M and surface area of the adsorbed quinoline. They were determined to be 8.20mg/g and 26.3 m²/g, respectively.

The three isotherms constructed using presulfided iron oxide as the adsorbent show significant scatter in the data. Shridharani (2) measured the surface area of the presulfided iron oxide using gas-phase adsorption. The surface area was determined to be 5.32 m²/g. Comparison between this value determined by Shridharani and the values determined for adsorption of quinoline and phenol tends to indicate that phenol and quinoline may not be adsorbed in an orientation which is flat to the

Figure 22. Linear Form of the Adsorption Isotherm for the Adsorption of Pyrene on Presulfided Iron Oxide.

Table 20

Adsorption of Phenol on Presulfided Iron Oxide

Amount of Catalyst, W	<u>Phenol Concentration</u>		Amount of Phenol Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_{PL}^0	Equilibrium, C_{PL}^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0076	300	85.0	1.07
0.4980	500	365.0	1.36
0.7574 $\pm$ 0.0081	500	268.7 $\pm$ 20.6	1.53 $\pm$ 0.15
1.0012 $\pm$ 0.0042	500	230.1 $\pm$ 36.4	1.30.18
1.5056 $\pm$ 0.0010	500	193.4 $\pm$ 5.95	1.02 $\pm$ 0.20
2.0072 $\pm$ 0.0171	500	138.0 $\pm$ 59.5	0.90 $\pm$ 0.11
2.5044	500	128.8	0.741
1.0003	1000	549.5	2.25
0.9973	1500	982.5	2.59
1.0066	2000	520.0	7.35
1.00177	2500	925.0	7.86
1.0033 $\pm$ 0.0051	3000	247.12 $\pm$ 79.2	2.62 $\pm$ 0.38
1.0085	3500	2987.5	2.54
0.9989 $\pm$ 0.0045	4000	3600 $\pm$ 203.2	21.00 $\pm$ 1.02

Figure 23. Adsorption Isotherm for the Adsorption of Phenol on Presulfided Iron Oxide.

Figure 24. Linear Form of the Adsorption Isotherm for the Adsorption of Phenol on Presulfided Iron Oxide.

Table 21

Adsorption of Quinoline on Presulfided Iron Oxide

Amount of Catalyst, W	Quinoline	Concentration	Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^o	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
0.5002	1000	345.4±3.4	6.54±0.03
0.7566	1000	197.3±2.3	5.31±0.02
1.0118±0.0073	1000	34.8±14.2	5.49±1.51
1.0017±0.0035	2000	416.0±156.2	7.90±0.75
1.5044	2000	181.9	6.04
1.9910	2000	151.3	4.64
2.5855	2000	128.8	3.62
0.5054	3090	1836.0	12.41
0.7631	3090	1600.0	9.76
1.0007±0.0081	3090	1601.5±119.5	7.36±0.53
1.5048±0.0002	3090	1009.0±8.05	6.92±0.03
2.0072±0.0066	3090	964.0±273.7	5.30±0.66
1.0004	4000	2300	8.50
0.9993	5000	3366.7	8.17
1.0026±0.0048	6372.5	4838.6±211.4	7.65±1.03
1.0043±0.0033	7650	6234.4±159.0	7.05±0.78
1.0007±0.0023	8000	6298.3±80.2	8.50±0.42
1.0011±0.0021	10000	7529.7±86.8	9.84±1.21
0.9988±0.0022	12000	9578.1±429.8	12.13±2.18

Figure 25. Adsorption Isotherm for the Adsorption of Quinoline on Presulfided Iron Oxide.

Figure 26. Linear Form of the Adsorption Isotherm for the Adsorption of Quinoline on Presulfided Iron Oxide.

adsorbent surface. If phenol and quinoline were adsorbed in an orientation which is flat to the catalyst surface, the surface areas predicted by phenol and quinoline would be no larger than the surface area obtained by Shridharani. Assuming some end-on adsorption occurs, then the shape of the phenol and quinoline isotherms would be contradictory with the hypothesis of Giles et al. (14) that an S-type isotherm is obtained when molecules are adsorbed in an end-on orientation to the catalyst. Most likely, the higher surface area values obtained via liquid adsorption (quinoline and phenol) can be attributed to the poor reproducibility of the adsorption isotherms. Because the adsorptivity of phenol and quinoline on presulfided iron oxide is small in relation to their adsorbability on catalysts such as $\text{CoMo/Al}_2\text{O}_3$, small errors in the data points obtained for their respective isotherms may result in significant errors in the prediction of surface area of catalyst covered by each component.

The results summarized in Table 22 indicate that the amount adsorbed for monolayer coverage depends on the type of compound studied. These results also indicate that Ψ_Q^M and Ψ_{Ph}^M are at least an order of magnitude greater than Ψ_{Py}^M .

Adsorption on $\text{CoMo/Al}_2\text{O}_3$ Catalyst. The adsorption behavior of three PNA compounds, naphthalene, phenanthrene, and pyrene as well as phenol and quinoline on $\text{CoMo/Al}_2\text{O}_3$ was studied. The isotherms obtained using these compounds are of the "high affinity" type as indicated in Figures 27, 29, 31, and 33. The shape of the quinoline isotherm at the higher concentration range tends to indicate multilayer coverage. As indicated by the isotherms, the apparent amounts of quinoline and phenol adsorption

Table 22

Comparison Between the Adsorption of Pyrene, Phenol, and
Quinoline on Presulfided Iron Oxide

Compound	Ψ^M (mg/g)	Correlation Coefficient	Surface Area (m ² /g)
Pyrene	0.419	0.968	1.7
Phenol	2.36	0.963	8.4
Quinoline	8.20	0.983	26.3

Table 23

Adsorption of Naphthalene on CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W	<u>Naphthalene Concentration</u>		Amount of Naphthalene Adsorbed per Gram of Catalyst, $\bar{y}$
	Initial C^0_{Nap}	Equilibrium, C_{Nap}	
(g)	(mg/l)	(mg/l)	(mg/g)
1.00015	250	39.0	1.05
1.0049	350	63.5	1.43
1.00066	500	107.0	1.96
1.00032	700	180.0	2.60
1.00046	900	268.0	3.16
1.00037	1100	325.0	3.87

Table 24

Adsorption of Phenanthrene on CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W (g)	<u>Phenanthrene Concentration</u>		Amount of Phenanthrene Adsorbed per Gram of Catalyst, Ψ Phen (mg/g)
	Initial C^E Phen (mg/l)	Equilibrium, C^E Phen (mg/l)	
0.99995	400	15.6	19.2
1.00108	600	33.0	2.83
0.99990	800	61.0	3.70
1.00015	1000	94.0	4.52
1.00042	1200	140.0	5.29
1.00020	1400	185.0	6.07

Figure 27. Adsorption Isotherms for the Adsorption of Naphthalene and Phenanthrene on CoMo/Al₂O₃ Catalyst (Harshaw 0402T)

Figure 28. Linear Form of the Adsorption Isotherms for the Adsorption of Naphthalene and Phenanthrene on $\text{CoMo}/\text{Al}_2\text{O}_3$ Catalyst (Harshaw 0402T).

Table 25

Adsorption of Pyrene on CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W	Pyrene	Concentration	Amount of Pyrene Adsorbed per Gram of Catalyst, Ψ_{Py}
	Initial C_{Py}^0	Equilibrium, C_{Py}^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0001±0.0003	400	1.09±0.486	2.00±0.0045
1.0004±0.0001	500	1.90±0.721	2.49±0.0024
1.0004±0.0002	600	3.28±0.868	2.99±0.0058
1.0003±0.0003	700	4.44±0.512	3.48±0.0050
1.0000±0.0004	800	7.30±1.17	3.97±0.0100
1.0005±0.0004	1000	11.6±2.15	4.94±0.0129
1.0006	1200	20.9±4.08	5.89±0.0183
1.0007±0.0003	1400	29.7±3.82	6.85±0.0206
1.0004±0.0002	1600	44.4±7.98	7.78±0.0404

Table 26

Adsorption of Pyrene on Presulfided CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W	Pyrene	Concentration	Amount of Pyrene Adsorbed per Gram of Catalyst, Ψ_{PY}
	Initial C_{PY}^0	Equilibrium, C_{PY}^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0004±0.0002	800	9.51±1.47	3.95±0.01
1.0002±0.0001	1000	16.13±2.36	4.92±0.02
1.0003±0.0002	1200	27.25±4.11	5.86±0.02
1.0005±0.0002	1400	44.50±2.48	6.18±0.01
1.0004±0.0002	1600	51.63±8.29	7.74±0.04
1.0001	1800	71.25±1.25	8.65±0.01
1.0002±0.0004	2000	95.0	9.53±0.01

Figure 29. Adsorption Isotherms for the Adsorption of Pyrene on CoMo/Al₂O₃ and Presulfided CoMo/Al₂O₃ Catalysts (Harshaw 0402T).

Figure 30. Linear Form of the Adsorption Isotherms for the Adsorption of Pyrene on $CoMo/Al_2O_3$ and Presulfided $CoMo/Al_2O_3$ (Harsahw 0402T).

Table 27

Adsorption of Phenol on CoMo/Al₂O₃ Catalyst
(Harshaw 0402T)

Amount of Catalyst, W	Phenol Initial C _{Ph} ^o	Concentration Equilibrium, C _{Ph} ^E	Amount of Phenol Adsorbed per Gram of Catalyst, Ψ_{Ph}
(g)	(mg/l)	(mg/l)	(mg/g)
0.9997	500	0	2.50
0.9995	1000	0	5.00
1.0009	2000	0	9.99
0.9998	4000	0	20.01
1.0003±0.0006	5000	28.00±9.83	24.85±0.06
1.0001±0.0012	6000	43.56±10.47	29.78±0.03
1.0007±0.0007	7000	75.56±22.80	34.60±0.12
1.0004±0.0003	8000	119.2±33.09	39.39±0.18
1.0003±0.0005	10000	374.2±36.80	48.11±0.20
1.0004±0.0007	12000	823.5±28.70	55.86±0.26
1.0006±0.0007	14000	1670.0±101.7	61.62±0.52
1.000±0.0004	16000	2726.6±109.1	66.35±0.54
1.007	18000	3943.8	70.22

Table 28

Adsorption of Phenol on Presulfided CoMo/Al₂O₃
(Harshaw 0402T)

Amount of Catalyst, W	<u>Phenol</u>	<u>Concentration</u>	Amount of Phenol Adsorbed per Gram of Catalyst, Ψ_{Ph}
	Initial C_{Ph}^o	Equilibrium, C_{Ph}^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0002±0.0004	5000	0	25.00±0.01
1.0005±0.0003	6000	9.72±5.16	29.95±0.03
1.0003±0.0004	8000	65.61±32.78	39.66±0.16
1.0002±0.0003	10000	358.5±45.6	48.20±0.23
1.0002±0.0001	12000	1238.1±71.5	53.98±0.66
1.0003±0.0003	14000	2418.8±88.0	57.89±0.42
1.0002±0.0003	16000	3900±40.5	60.49±0.21

Figure 31. Adsorption Isotherms for the Adsorption of Phenol and CoMo/Al₂O₃ and Presulfided CoMo/Al₂O₃ Catalysts

Figure 32. Linear Form of the Adsorption Isotherm for the Adsorption of Phenol on $CoMo/Al_2O_3$ and Presulfided $CoMo/Al_2O_3$ Catalysts (Harsahw 0402T).

Table 29

Adsorption of Quinoline on Presulfided CoMo/Al₂O₃ Catalyst

Amount of Catalyst, W	Phenol	Concentration	Amount of Phenol Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0001±0.0002	5000	8.63±1.50	24.96±0.01
1.0002±0.0001	6000	34.41±5.87	29.82±0.01
1.0001±0.0001	8000	277.8±64.0	38.61±0.32
1.0002±0.0001	10000	716.3±96.4	46.41±0.48
1.0004±0.0003	12000	1515.7±232.0	52.37±1.19
1.0004±0.0003	14000	2653.2±358.5	56.71±1.80
1.0000±0.0002	16000	3867.2±407.8	60.57±2.12

Figure 33. Adsorption Isotherms for the Adsorption of Quinoline on $\text{CoMo/Al}_2\text{O}_3$ and Presulfided $\text{CoMo/Al}_2\text{O}_3$ Catalysts

Figure 34. Linear Form of the Adsorption Isotherms for the Adsorption of Quinoline on CoMo/Al₂O₃ and Presulfided CoMo/Al₂O₃ Catalysts (Harshaw 0402T).

required for monolayer coverage are at least an order of magnitude greater than those of the PNA molecules. The order of adsorptivity of these PNA molecules, based on the surface area of the catalyst covered by the adsorbing molecule, correlate well with the order of adsorptivity of PNA compounds as determined by Klemm (6) and Synder (4).

The surface area of the catalyst covered by each component which is summarized in Table 30, indicates that quinoline is adsorbed on all types of catalyst sites but phenol and PNA molecules are adsorbed only on selective sites. Kim (28) believes that PNA molecules such as naphthalene, pyrene, etc. are adsorbed specifically on acid sites. The sum of the surface areas of phenol and pyrene is approximately equal to the total surface area of the catalyst surface. This may indicate that phenol and PNA molecules such as pyrene adsorb on different types of catalyst sites.

Adsorption of Presulfided $\text{CoMoAl}_2\text{O}_3$. "High affinity" type adsorption isotherms are obtained with quinoline, phenol, and pyrene. Quinoline is adsorbed much more strongly than pyrene and approximately to the same extent as phenol (Figures 29, 31 and 33). The surface area calculated for the adsorption of quinoline indicates that the surface area decreased slightly upon sulfiding (Table 31).

The surface area covered by phenol and pyrene indicate that less phenol but more pyrene is adsorbed for monolayer coverage of the presulfided catalyst (Table 31). This indicates that sulfiding increases the number of active pyrene sites and decreases the number of active phenol sites. The sum of the surface areas covered by phenol and pyrene

Table 30

Adsorption of Pyrene, Phenol, and Quinoline on CoMo/Al₂O₃*

Compound	Ψ_A (mg/g)	Surface Area (m ² /g)	Correlation Coefficient
Quinoline	66.2(1)±2.2(2)	212.5(1)±7.1(2)	0.999
Phenol	67.3(1)±0.5(2)	184.9(1)±1.4(2)	0.999
Pyrene	8.39(1)±0.27(2)	34.4(1)±1.1(2)	0.987
Naphthalene	4.85	15.7	0.997
Phenanthrene	7.63	26.6	0.993

*CoMo/Al₂O₃ (Harshaw 0402T); BET surface area = 200 m²/g

(1), (2) see Table 8 for explanation.

Table 31

Adsorption of Pyrene, Phenol, and Quinoline on Presulfided CoMo/Al₂O₃*

Compound	Ψ_A (mg/g)	Surface Area (m ² /g)	Correlation Coefficient
Quinoline	60.2(1)±5.7(2)	193.1(1)±18.3(2)	0.997
Phenol	60.4(1)±0.54(2)	165.8(1)±1.5(2)	0.999
Pyrene	11.0(1)±2.9(2)	44.9(1)±12.0(2)	0.983

(1) See Table 8 for explanation

(2) See Table 8 for explanation

*Presulfided CoMo/Al₂O₃ (Harshaw 0402T)

is approximately the same as the specific surface area calculated for quinoline, as shown in Table 31.

Comparison Between Inhibition and Adsorption Studies

Shridharani (2) has shown that quinoline severely inhibits the hydrogenation of naphthalene. From the liquid-phase adsorption studies, quinoline was found to adsorb on all types of sites on all the catalysts used. This is consistent with the results obtained by Shridharani.

Phenol was adsorbed to a lesser extent than quinoline on the three catalysts. Shridharani (2) has shown that phenol does not inhibit naphthalene hydrogenation but phenol deoxygenation occurs with each catalyst used. The observed adsorption of phenol may be due to hydrogen bonding which may be reversed while heating to the reaction temperatures used by Shridharani. This is one reason why no inhibition was observed with phenol and yet its apparent adsorptivity is very high at room temperatures. On the other hand, the phenol may be adsorbing on sites other than hydrogenation sites. More work is needed to discern why phenol does not appear to inhibit hydrogenation yet has an apparently high adsorptivity at room temperature.

Preliminary experiments, using presulfided iron oxide and CoMo/ Al_2O_3 , indicate that the amount of adsorption of pyrene is approximately twice as much as that of naphthalene. Shridharani (2) has found that pyrene is more selective than naphthalene in terms of hydrogenation.

Solvent Tailoring

Shridharani (2) performed experiments using a model solvent to explore the effect of the addition of quinoline on the product distribution

of coal liquefaction reaction products. The hydrogenation activity of the catalyst appears to effect the oil-yield of coal liquefaction reaction products. For this reason, the possible reduction of oil-yield through the inhibition of hydrogenation sites by quinoline was studied.

Shridharani (2) found that the addition of quinoline to a model process solvent resulted in only a marginal decrease in oil-yields and a marked increase in asphaltene production (Table 32). A suggested explanation as to why little inhibition occurred was that the quinoline was converted relatively early in the reaction to a form that is less inhibiting than quinoline.

Another explanation for the non-inhibiting effect of quinoline on coal liquefaction reactions is that quinoline may become incorporated into the bulk of the coal. This part of the study was aimed at determining the amount, if any, of quinoline which may adsorb on coal.

An adsorption isotherm for the adsorption of quinoline on coal (Elkhorn #3) was constructed and is shown in Figure 35. Ψ^M coal was calculated from a plot of $\frac{C^E \text{ coal}}{\Psi^E \text{ coal}}$ versus $C^E \text{ coal}$ and was found to be 4.16 mg/g. The value obtained for monolayer adsorption of quinoline on presulfided iron oxide is 8.20 mg/g.

In so much as 1.0 gram of catalyst and 3.0 grams of coal were used in the studies performed by Shridharani (2), the quinoline may have adsorbed on the coal instead of on the catalyst. Because the reaction temperature used by Shridharani (2) and the temperature at which the adsorption studies were conducted differ greatly, it is difficult to predict the amount of quinoline adsorbed on the catalyst and the amount adsorbed on the coal at the reaction temperature used.

Table 32

Effect of Quinoline on Catalytic Activity of Presulfided Iron
Oxide for Oil-Production in a Model Solvent*

Quinoline Concentration	<u>Products (wt%)</u>				
	Gases	Oils	Asphaltenes	Preasphaltenes	IOM
0	6	31	22	21	20
15	8	33	37	8	16

Model Solvent: 3g naphthalene and 3g pyrene + quinoline
 Reaction Conditions: 6g solvent, 3g Elkhorn #3 coal, 1g catalyst,
 425°C, 60 minutes, 1250 psig H₂ pressure at
 room temperature, 860 rpm, 2 steel balls
 agitators, 46.3 ml reactor.

*Taken from reference (2).

Table 33

Adsorption of Quinoline on Coal (Elkhorn #3)

Amount of Catalyst, W	<u>Quinoline Concentration</u>		Amount of Quinoline Adsorbed per Gram of Catalyst, Ψ_Q
	Initial C_Q^0	Equilibrium, C_Q^E	
(g)	(mg/l)	(mg/l)	(mg/g)
1.0000±0.0005	200	22.90±0.40	0.89±0.005
1.0007±0.0001	300	47.25±2.25	1.26±0.01
1.0005±0.0003	400	105.1±0.75	1.48±0.005
1.0000	800	310.8	1.86
1.0002±0.0002	2000	1381.3±6.25	3.09±0.03
1.0003±0.0001	3000	2268.8	3.66±0.005
1.0004±0.0001	4000	3168.8±56.3	4.10±.285

Figure 35. Adsorption Isotherm for the Adsorption of Quinoline on Coal (Elkhorn #3)

V. Summary and Conclusions

Surface Area Determination

Liquid-phase adsorption using a quinoline-cyclohexane system appears to be a reasonably accurate method for determining specific surface areas of porous catalysts. The surface areas calculated using this method show reasonable agreement with values calculated by the method of BET.

Competitive Adsorption and Inhibition

The adsorptive behavior of three types of compounds commonly found in coal liquids was studied: a basic nitrogen containing compound (quinoline), an acidic oxygen containing compound (phenol), and some PNA compounds (naphthalene, pyrene, and phenanthrene). Three catalysts were used as adsorbents: presulfided iron oxide, CoMo/Al₂O₃, and presulfided CoMo/Al₂O₃.

All adsorption isotherms appeared to be of the "high affinity" (H₂) type with the exception of isotherms for pyrene and phenol adsorption on presulfided iron oxide. Pyrene and phenol adsorption on presulfided iron oxide had an apparent Langmuir (L₂) type of isotherm. The "high affinity" isotherm are believed to indicate a strong interaction between the adsorbate and the adsorbent.

The amount of adsorbate adsorbed on various catalyst surfaces was found to be a function of the type of compound and the type of catalyst

used. The following order of adsorptivity of different compounds on the catalyst surface was observed:

Naphthalene < Phenanthrene < Pyrene << Phenol < Quinoline

This order of adsorptivity agrees with those of other investigators (4,6).

NOTATION

C_A	concentration of component A
C_A^0	initial concentration of component A
C_A^E	equilibrium concentration of component A
k_A	adsorption equilibrium constant of component A
k_{ad}	pseudo rate constant for adsorption
k_{des}	pseudo rate constant for desorption
M	molecular weight of adsorbing component (mg/mmole)
m, w	weight of catalyst contacted with the solution
N	Avogadro's number
n^S	total number of moles of all components adsorbed for monolayer coverage
n_A^S	moles of component A adsorbed for monolayer coverage
n_0	initial number of moles in contact with catalyst
S	surface area of adsorbent per unit mass of adsorbent
T	absolute temperature
V	volume of solution in contact with adsorbent (ml)
X_A	mole fraction of component A in contact with adsorbent at equilibrium
α	separation factor
θ_A	fraction of adsorbent sites covered by component A
σ	cross-sectional area of the adsorbed molecule
Ψ_A	amount of component A adsorbed

Ψ_{AR}	amount of component A adsorbed reversibly
Ψ_{AIR}	amount of component A adsorbed irreversibly
Ψ_A^M	calculated theoretical amount of component A adsorbed for monolayer coverage
ω	energy of adsorption

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Appendices*

*Appendices to this report are contained in ref (29) and are available from the Auburn University Library.