



Performance evaluation of catalyst supports used in the hydrotreating of solvent refined coal
by Thomas Irving Insley, Jr

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
Montana State University
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Abstract:

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IN THE HYDROTREATING OF SOLVENT REFINED COAL

by

THOMAS IRVING INSLEY, JR.

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of the requirements for the degree

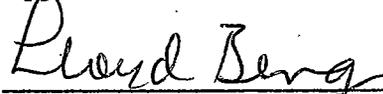
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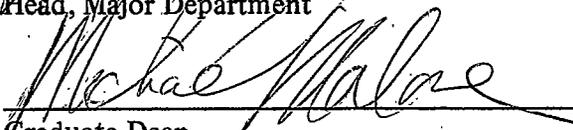
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MONTANA STATE UNIVERSITY
Bozeman, Montana

July 1982

ACKNOWLEDGMENTS

I wish to thank the staff of the Chemical Engineering Department at Montana State University for their assistance and support.

My appreciation is extended to Dr. Lloyd Berg and Dr. F. P. McCandless for the opportunity to be associated with such an interesting and challenging project.

The United States Department of Energy is to be thanked for their financial support that made this research possible.

My deepest gratitude goes to my wife, Carol, who encouraged and assisted me throughout this undertaking.

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ABSTRACT

A series of commercial catalyst supports impregnated on an equal weight per unit surface area basis were tested for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity on SRC II, a coal-derived liquid. The surface area distribution in the pore diameter range of 40-200 angstroms (\AA) was compared to relative catalytic activity of the supports. A correlation was found between relative HDS and/or HDN activity and the surface area attained in the 60-80 \AA pore diameter range. The significance, and supporting evidence, of the correlation between activity and surface area distribution is discussed.

Chapter I

INTRODUCTION

Late in World War II, pressed by reduced availability of conventional fuels, the German Reich turned to fuels derived from coal, so that they could continue their effort.

The technology they used was developed over many years of intense research in both Europe and America. This research was sparked by the discovery, in the 1800s, of the nature of coal's complex molecular structure, and of the possibilities of rearranging its components into useful products.

Working with hydrogenating catalysts at high temperatures and elevated pressures, Friedrich Bergius succeeded in liquefying coal. In the years after the war, little attention was directed to the development of coal-derived liquids, although, directly after the war a team of more than one hundred scientists was sent into Germany to collect synfuel technology.

In the late 1960s and early 1970s, rekindled by the threat of limited availability of conventional fuels, the United States, like other high energy consumers, turned its interests to synthetic fuels.

One aspect of current research is to reduce nitrogen and sulfur content of coal-derived liquids so that they can be used in either conventional refineries or as a boiler fuel.

The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of coal-derived liquids, generally performed by supported catalysts, involves the intraparticle mass transport of large molecules inside the catalyst. Since the diameter of reacting molecules is believed to be comparable to the pore size of the supported catalyst, partitioning of the molecules between the bulk liquid and the internal surfaces is a factor in catalyst perfor-

mance. To produce optimum rates of reaction the pore-size distribution of a catalyst should be such that the total of diffusional (pore size dependent) and reaction (surface area dependent) resistances be reduced to a minimum. One way to minimize the combined resistances is to optimize a pore-size and area relationship in terms of performance.

It is the object of this study to ascertain, for a given reaction system, what, if any, optimum pore-size and area relationships do exist.

Chapter II

BACKGROUND

The work presented in this study, that is, the activity of impregnated catalysts towards HDS and HDN of a coal-derived liquid with respect to the physical characteristics of the catalyst support, is based on three basic assumptions:

1. Catalyst support properties, in particular, pore size vs. cumulative surface area, can, in fact, be characterized.
2. Given the proper procedure and conditions, a catalytic component can be uniformly distributed over the entire surface area of the support, with the possible exception of the most minute realms; also, that these dispersions would not significantly alter relative support properties.
3. Diffusion and surface area limitations can both be factors when considering the global rate, and, in turn, degree of HDS and HDN of a coal-derived liquid.

A defense for these assumptions will now be outlined in the following section.

Surface Area Characterization

The relationship between supported catalyst surface area and pore size distribution is a key factor of influence in light of the reaction/transport scheme encountered in the catalytic upgrading of coal-derived liquids. Considering this, any inquiry into the relationship between catalytic performance and the physical nature of the support must include a basis for characterization of the materials' physical structures. Porous materials can be characterized in terms of several quantities; these generally include average pore diameter, pore volume, density, and surface area. Of these methods, surface area characterizations, that is, surface area which is greater than the observable geometric surface area, are of particular

utility. Porous materials differ greatly in their characteristic surface areas; for example, some activated carbons have surface areas 500,000 times the external geometric area, while a porous filter plate's surface area is only 1,000 times its geometric area. Many factors lend to this effect but one of particular interest is that of the pore size distribution within the materials.

Pores in different materials may vary greatly in their absolute dimensions, from those easily seen by the unaided eye, 10^6 angstroms (\AA) in diameter, to those of 4 to 5 \AA in diameter. Typically the surface area contributed by pores averaging 20 \AA in diameter is on the order of 1500 sq. meters per gram, while the surface area contributed by a practically equal volume of pores averaging 20,000 \AA in diameter is only 1.7 sq. meters per gram [1]. While the larger macropores do not contribute significantly to the total surface area they nonetheless play an important role in that they act as arteries to the smaller micropores [2].

In this study, two standard methods were used by the vendors of the carriers in the surface area characterizations of the catalyst supports. While neither of these methods produces a detailed description of the actual size and shape of each void space in the carrier they do give an averaged representation of the carriers' geometric properties. Since the procedures are standardized and widely accepted, the key to their utilization lies not in the ability to accurately determine the actual void volume according to void size, but, in the ability to generate a representative description of structure for a broad range of porous materials.

In 1945 Wheeler [3] proposed a theory, a composite of BET multilayer adsorption and capillary condensation viewpoints, which has been used as the basis for much work involving techniques for estimating the volume and area of porous adsorbents available to

molecules of various sizes. Over the years several refinements were made on Wheeler's original model to the point that today catalysis researchers have available straightforward and reliable methods for characterizations of this type [4].

Pore distribution characterizations founded on Wheeler's model find as their basis an interpretation of the sigmoid-shaped sorption isotherms generated by varying the pressure in a condensable-vapor/carrier system. Experimentally, these isotherms are obtained by measuring the change in volume (relative to an incremental increase in system pressure) of a condensable vapor, generally N_2 at $-196^\circ C$, due to capillary condensation in the porous material. When the system pressure is increased to the point of saturation, 1 atm for N_2 at $-196^\circ C$, the void space of the material is completely filled with condensed vapor and at this point the adsorption branch of the isotherm is complete. By reversing the process, that is, by gradually lowering the system pressure, the desorption branch of the isotherm is obtained.

It is considered that capillary condensation in porous materials occurs as a result of lower vapor pressure over a concave meniscus formed by liquid in the material's void space. The Kelvin equation [5] which gives the relationship between vapor pressure and radius of the concave surface of a meniscus, is used in conjunction with a cylindrical pore model to give a distribution of interior surface area with respect to pore size. When the Kelvin equation (or some form particular to the condensable vapor employed) [6] is used to convert pressure to pore radius the original isotherm can be replotted in terms of volume sorbed (pore volume) vs. radius. Since the pores of the model are considered to be straight and cylindrical (for a given increment of length), the surface area corresponding to a particular volume can be determined through the simple relationship of volume to radius:

$$\text{surface area} = \frac{2 \cdot (\text{pore volume})}{\text{pore radius}}$$

From this information one can formulate a descriptive picture of the distribution of the material's surface area over a wide range of pore sizes.

In an analysis of this type five basic assumptions are made:

1. Pores are cylindrical.
2. Each pore space is connected with at least one larger pore.
3. The meniscus radius is that of the inside tube formed by multilayer adsorption.
4. Liquid nitrogen surface tension is the same regardless of pore size.
5. There exists thermodynamic equilibrium on the desorption branch of the isotherm and that it is this branch to which the Kelvin equation is generally applied. On the adsorption branch of the isotherm there is a question as to the need of a supersaturated state before the pores fill with capillary condensed vapor, and, therefore, the adsorption branch is usually not considered in determinations of this sort.

A direct method for determining the volume and area distributions, in terms of pore size, of porous adsorbents was developed by Ritter and Drake [7]. This method, which utilizes a high pressure mercury porosimeter, is entirely independent of the sorption isotherm method. The idea is based on the phenomenon that mercury does not "wet" most catalyst materials, and, that it will not penetrate the void spaces of the material unless forced in under pressure. Ritter and Drake correlated the force needed to keep mercury out of a pore due to surface tension, to the force applied to the mercury/catalyst system. Using this procedure data can be generated relating the intrusion volume vs. applied pressure, and, from this a volume vs. pore diameter curve can be developed. Pores down to the

40 Å range in diameter can be accessed using modern apparatus which can attain pressures upwards of 50,000 psi. The cylindrical model incorporated in this technique, like that for the isotherm method, allows one to obtain surface area distributions in terms of pore size.

Comparisons between the mercury porosimeter and nitrogen isotherm methods [8] indicate that the two methods give substantially the same distribution curves. When cumulative pore volume vs. pore radius curves are compared, for the same material, the shape of the curves is nearly identical but there is a shift of the porosimeter generated curve towards the higher end of the pore range. Effectively what this shift amounts to is a reduction in surface area vs. pore size in the range of 20%.

In summary, the foregoing experimental methods gives a means of modeling the distribution of void spaces in porous materials over a wide range of void sizes. Even though the pores may be in fact interstices between crystalline building-blocks, and most likely not cylindrical in shape, a useful picture can be developed to give an idea as to what size void a molecule must pass before it can access a given surface area.

Dispersion of Catalytic Components on Alumina-Silica Supports

Typically catalysts are materials that possess high surface areas whether they take the form of fine powders, supported and coprecipitated metals, or films. The focus of this work has been on supported metal catalysts. These catalysts, in which the catalytic component is distributed throughout a porous material's surface area, can be prepared in a number of ways [9]. One procedure for preparation commonly used is the incipient wetness technique. Here, the metallic dispersions are a result of a series of wetting, drying, and

activation steps. The procedure generally consists of saturating a porous support with a solution containing the catalytic component, then after drying and calcination a distribution of small crystallites of the metal oxide are produced in the support.

Optimum composition profiles in supported catalysts are usually dictated by service conditions. For the reaction system encountered in the upgrading of coal derived liquids, which is neither predominately mass-transfer limited nor surface reaction controlled, a uniform impregnation was considered to be desirable from not only the standpoint of performance but also evaluation. The point being that a uniform distribution, throughout the macro- and microsystems of void spaces, gives one the basis by which catalyst performance can be compared to available surface area. (This is a key point of consideration if impregnated catalysts are to be evaluated in terms of the supports' physical properties, as has been done in this work.)

The ability to attain a uniform distribution of the catalytic component throughout, including the fine porous structures of the support material, remains a matter of conjecture, but, several physical phenomena lend credence to the feasibility.

1. Large capillary forces, present in highly porous materials, provide a vehicle by which even the innermost realms of volume can be attained by liquids possessing the proper wetting characteristics. As an example of application of this effect one can consider water adsorption procedures, which are widely used to determine the pore volume of silica alumina supports and similar catalyst carriers [10].

2. When in solution, catalytic components (like those used in this study) maintained at the proper pH remain in the ionic form. These ions possess diameters on the order of angstroms. For example, when solution pH is maintained in the acidic range, the cobalt ion

is generally present in the Co (II) state which has a radius of 0.82 Å [11]. Considering the small ionic size, transport of the catalytic component in solution should only be restricted in the very smallest realms of the support.

3. Adsorption of the catalytic components onto the surface of the support can influence dispersion. If sorption effects during the wetting stage of the impregnation are low, the component in solution would be uniformly distributed in the material's volume [12]. Reason being that if in solution the component has a high affinity for the support material a rapid adsorption will occur, resulting in a drop of its concentration as the liquid front moves throughout the pellet. A low adsorbing component, on the other hand, would remain at a more constant concentration in the pellet.

Depending on the support/impregnating solution combination, the pH of the system can influence the degree of adsorption [13]. For support/solution combinations like those used in this work, it has been found that a lower pH will result in a lower degree of adsorption. For instance, only 5% of a 1.2×10^{-4} M Co (II) ion solution will adsorb onto an SiO₂ surface of 75 square meters per liter of solution when the solution pH is 4.5 [14]. (Solution pH's encountered in this investigation were 4.6 or lower.)

By slowly drying the pellet, impregnated throughout with a constant concentration solution, a finely dispersed phase of the catalytic component uniformly distributed in the volume, will result upon precipitation [15].

It is generally accepted that by manipulating certain aspects of the incipient wetness process of impregnation such as pH (support and solution), concentration of impregnating solution, wetting time, drying speed, and general handling procedures one can attain a good degree of control over the distribution of the catalysts within the support granule.

Diffusion

Liquid-phase diffusivity, in a pore which is of size comparable to that of the diffusing chemical species, may be limited by two independent phenomena. First, the hydrodynamic resistance (drag), above that in the free solution, would hinder the movement of diffusing molecules through the pore. Second, a geometric exclusion factor, which essentially excludes a species from a fraction of the pore volume, leads to equilibrium partitioning; wherein, the species concentration inside the pore is less than the bulk concentration outside the pore. Both of these effects arise as a result of proximity of the species to the pore wall but are also influenced by the degree of adsorption of either the solute or solvent onto the pore surface.

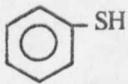
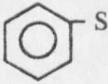
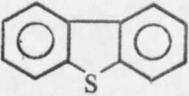
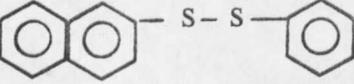
Various models have related these effects to the ratio of the relative size of the diffusing species to pore size [16,17,18,19]. Satterfield demonstrated, using silica-alumina catalysts, that in various solute/solvent combinations of hydrocarbons (saturated and aromatic) the logarithm of the ratio of effective to bulk diffusivity decreases linearly with increasing ratio of solute critical molecular diameter to pore diameter [20]. Another study, which used silica-alumina pellets, involved diffusion of similar solute/solvent systems (for example tetralin-benzene). There, it was shown that with a shift of average pore diameter from 66.4 to 56.9 Å the diffusivity of a component can be reduced by as much as 50% [21].

These and similar works of this nature, that is, the diffusion of a particular species in known solute/solvent systems, can not be directly related to the diffusional phenomena involving coal-derived liquids, which contain a host of components in undetermined concentrations.

There is, though, a general theme that comes forth: the concept that there occurs a rapid decrease in effective diffusivity of a chemical species, manifested with the narrowing of a pore through which the species must pass. Keeping this in mind and recognizing that coal-derived liquids are composed of molecular species with diameters between 25 and 150 Å [22] (comparable to the pore diameters which constitute the majority of surface area of the catalyst in this study) one can almost be assured that diffusional restrictions will play a major role in catalyst performance.

Chemistry of Coal-Derived Liquids

As a means of gauging catalytic performance, in terms of the pore size distribution of the carriers, HDN and HDS activity was followed. The kinetics, in particular the reaction sequences, in the hydrotreatment of coal-derived liquids is not well defined. Essentially when one is dealing with the chemistry of coal-derived liquids it must always be kept in mind that specific compounds in known concentrations are not encountered. Rather, models based on representative compounds, Fig. 1, are used to describe reactions that would likely occur. This is the case because, strictly speaking, there is no such thing as a coal molecule, from which these liquids are derived. Coal is a nonhomogeneous, bonded system of molecular groupings, most predominately benzene ring based, such as naphthalene, anthracene and larger-ring compounds. In addition, straight chained hydrocarbon subgroups are believed to be present in the infinitely interlinked system. Not only are large disseminations of chemical subgroups within particular classes of coals present, but, variations in composition between types of coals is notable [23].

<u>Sulfur Containing Structures</u>		<u>Boiling Point of Basic Structure</u>
Mercaptans		169.5°F
Sulfides		---
Thiophenes		183.5°F
Disulfides		---

Generally sulfides are the prevalent structures.

Nitrogen Containing Compounds

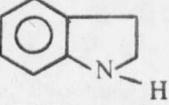
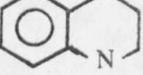
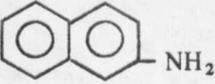
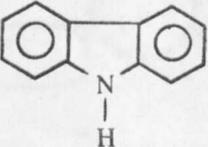
Pyridines		406°F
Indolines		445°F
Pyrroles		226°F
Quinolines		458°F
Amines		306°F
Carbazoles		670°F

Figure 1. Representative Structures of Coal-Derived Liquids.

