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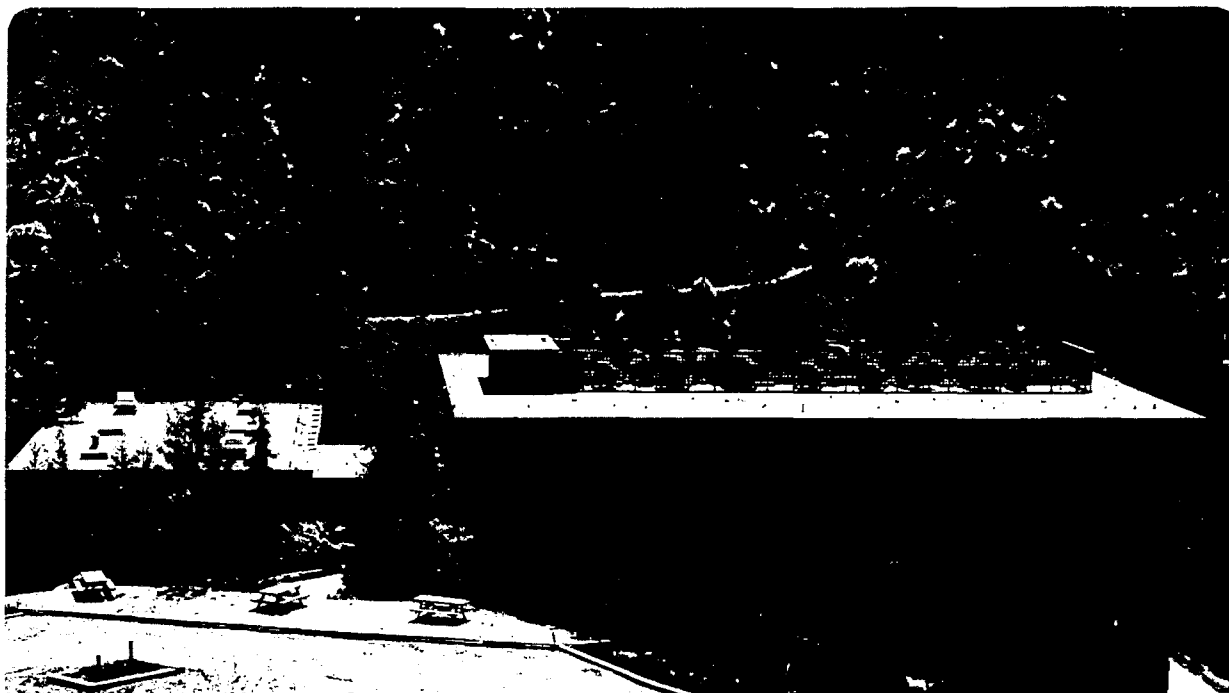
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CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
QUARTERLY REPORT

Heinz Heinemann

June 1982

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QUARTERLY REPORT

April 1 to June 30, 1982

Chemistry and Morphology of Coal Liquefaction

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II Technical Program for Fiscal 1982

Task 1 - Selective Synthesis of Gasoline Range Components from Synthesis Gas - A. T. Bell

Analytical methods will be developed to better define product distribution in each carbon number product (n/i ratio, paraffin/olefin ratio) and to test the Schultz-Flory theorem for each hydrocarbon type. This will also permit distinction between primary and secondary products. The extent of olefin saturation and hydrogenolysis will be investigated. Tests will be conducted with iron catalysts prepared on either ZSM-5 type zeolites or carbon molecular sieves. The emphasis of this work will be on determining the effect of the support structure and composition on the distribution of products obtained. The degree to which the formation of high molecular weight products can be curtailed by this means will be examined as a function of support pore size and composition, as well as reaction conditions.

Task 2 - Electron Microscope Studies of Coal During Hydrogenation - J. W. Evans

The major research activity in 1982 will be the use of the environmental cell in the Hitachi 650kV transmission electron microscope to observe reactions between carbonaceous materials (with and without catalysts present) and gases. Plans are to start with oriented graphite then later use coal char and finally coal. Gaseous atmospheres would be water vapour, hydrogen or mixtures of the two. Reaction products will be identified by analysis of the gas leaving the cell using the mass spectrometer. This will also permit a semi-quantitative measurement of reaction rate by simultaneously measuring the flow rate of gaseous reactant into the cell.

Some additional investigations of coal microstructure may be carried out as time permits.

Task 3 - Catalysed Low Temperature Hydrogenation of Coal - G. A. Somorjai

Exploration of the mechanism of alkali catalyzed reactions of carbon and steam will include attempts to detect CH_x and COH intermediates by electron spectroscopy and exploration of the possibility of alkali intercalation into the graphite that may be an important reaction step needed to break the C-C bonds of the reactant efficiently. The use of alkaline earth compounds as possible catalysts will be investigated to optimize the activity of the carbon-water ($\text{C-H}_2\text{O}$) reaction. The combination of transition metals and alkali-metal compounds as catalysts should be explored in order to aid the formation of hydrocarbon molecules larger than CH_4 .

Task 4 - Selective Hydrogenation, Hydrogenolysis and Alkylation of Coal and Coal Liquids by Organo-Metallic Systems - K. P. C. Vollhardt

The Lewis acid catalyzed cleavage and alkylation of benzene will be investigated in great detail. Scope and limitations will be explored with a variety of substrates, particularly substituted benzenes and higher condensed aromatic molecules. Heteroaromatic systems will be exposed to similar reaction conditions. The mechanism of the reaction will also be subjected to scrutiny, using kinetic and labeling techniques.

An investigation of the potential use of transition metals as catalysts and/or reagents in the cleavage of aromatic carbon-carbon bonds with the particular aim to effect hydrogenation and hydrogenolysis will be begun.

Work will continue concerned with delineating mechanism and scope of transition metal mediated hydrogen shifts of organic π ligands.

Task 5 - Chemistry of Coal Solubilization and Liquefaction - R. G. Bergman,
T. Vermeullen, and R. H. Fish

Plans for FY 1982 are to move into the area of metal-catalyzed transfer hydrogenation. We intend to begin by investigating metal complexes which serve either as hydrogenation or dehydrogenation catalysts, and determine whether they will function as transfer hydrogenation agents. If we are successful in finding workable systems, we will then investigate their mechanisms with an eye toward understanding the transfer hydrogenation in general, and improving the efficiency of the catalysts which are uncovered.

Further work will be done on the important selective hydrogenation of N-containing rings in polynuclear aromatic hydrocarbons with homogeneous catalysts, discovered in 1981. In particular, the question of catalyst recovery, e.g., by heterogenizing the metallo-organic complex will be investigated.

Task 6 - Coal Conversion Catalysts - Deactivation Studies - A. V. Levy and
E. E. Petersen

Short term plans are a series of experiments similar to those already carried out, but at much more stringent conditions; i.e., higher metal concentrations, higher temperatures, and longer times. The objective of these studies is to deactivate the catalyst sufficiently to observe changes in the global rates of demetallation and desulfurization. The deactivated catalysts will be subjected to electron microprobe measurements, and transient diffusion measurements as well as more traditional surface area, porosimetry, and pore volume measurements to evaluate the chemical and physical factors contributing to deactivation.

All of the results to date have been obtained using vanadyl naphthenate. We envision a series of runs using vanadyl tetraphenylporphyrin to compare with the naphthenate results. We also envision a similar series using analogous titanium compounds. Although these metalloporphyrins are more representative of the metal constituents of residua and coal derived liquids, their solubility in hydrocarbon solvents is limited. Steady-state experiments rather than semi-batch will be used. Also, to make the desulfurization global activity measurements easier, we plan to add dibenzothiophene as the sulfur component.

III Highlights

1. All tasks of this project were active in the third quarter of fiscal 1982. Two papers based on this work were submitted for publication and one publication issued (J. Catal. 75, 7-22 (1982)).
2. The formation of C₁ to C₄ hydrocarbon gases during Fischer-Tropsch synthesis over iron catalysts can be suppressed by operation at low H₂/CO ratios and high total pressure. This means that the formation of C₅₊ products can be enhanced by controlling reaction conditions.
3. In the hydrogenation of polynuclear nitrogen compounds, it has been found that heterogenized "Wilkinson's Catalyst" works as well as the homogeneous material with 100% selectivity to hydrogenation of the nitrogen containing ring only. It has also been found that the partially hydrogenated nitrogen compounds are excellent hydrogen donor materials. Life of the catalyst appears to be reasonable.
4. From activation energies obtained for the graphite-water reaction promoted by KOH, it appears that the same mechanism prevails at temperatures above 300°C as below 300°C.

Differences between calcium oxide and potassium oxide promotion were confirmed. Hydrogen is required (in addition to water) to produce methane in the presence of CaO, but water alone is sufficient for KOH. Intercalation of graphite with potassium showed no advantage over impregnation. In fact it appears that reaction proceeds only when potassium is on the surface of the graphite.

The remarkable first step conversion of graphite to "carbide" carbon, which in turn is converted to hydrocarbons was further elucidated and found to exist for potassium as well as calcium promoted reactions.

5. Vanadyl- and titanyl porphorins have been synthesized and are being used in demetallation studies. It appears that metal porphorins in petroleum or coal liquids behave differently on hydrogenation catalysts than non-porphorin metals.

IV Progress of Studies

Task 1 - Selective Synthesis of Gasoline Range Components from Synthesis Gas - A. T. Bell

The synthesis of hydrocarbons from syn-gas over a fused Fe catalyst, promoted with potassium, has been studied in a well-stirred autoclave. Products were analyzed on stream using gas chromatography. The product distribution changes with time and approaches a Schulz-Flory distribution asymptotically. Each product approaches the steady-state distribution with a time constant which depends on the molecular weight and Henry's Law constant of the product in the paraffin wax used to suspend the catalyst. A mathematical model of the evolution of the product distribution was found to describe the observed results very successfully and to explain many anomalies in the published literature.

The dependence of the synthesis rates on H_2 and CO partial pressures, and temperature, have been determined. It is observed that the H_2 dependence is unity for all products. The CO dependence is -0.42 for methane and increases to zero for C_4 . This suggests that the formation of light hydrocarbons can be reduced at low H_2/CO ratios and high total pressures. The activation energies for all products were nearly the same, lying between 26 and 29 kcal/mole. At low conversions the primary C_{2+} hydrocarbons are α -olefins and the primary oxygenates are C_{2+} aldehydes. As conversion increases, the olefin to paraffin ratio decreases slightly and the aldehydes are converted increasingly to alcohols. Very little methanol is produced at any conversion level.

The effects of olefin readsorption and reaction on the distribution of synthesis products has been examined in a fixed bed reactor. Addition of 2% C_2H_4 to the synthesis gas passed over an Fe catalyst increases the formation of C_3 and C_4 olefins and paraffins slightly but has no effect on the distribution of C_{5+} products. Propylene addition causes a slight increase in the formation of C_5 products but has no further effect. These results indicate that olefin readsorption has relatively little effect on product distribution.

Task 2 - Electron Microscope Studies - J. W. Evans and D. J. Coates

In-situ experiments utilizing the environmental cell of a high voltage transmission electron microscope have been continued for the study of the graphite-steam reaction. Previous work has shown that potassium hydroxide acts catalytically in ~ 1 Torr water vapor at 500-600°C by a channeling mode. Kinetic studies have indicated that a similar activation energy for the reaction occurs throughout the temperature range 200-600°C and recent environmental cell work has investigated the reaction at the lower temperatures (200-300°C).

As the temperature of a thin film graphite specimen previously immersed in a solution of KOH is raised to 300°C in the environmental cell, a distinct solid film on both surfaces becomes apparent. The film is not continuous, with cracks apparent in some regions, while in others the solid material is separated into discrete particles so that it can no longer be described as a film. Water vapor, at a partial pressure of ~ 1 Torr was passed over the specimen and periodic observations were made. No significant change in the morphology of the graphite or the film have been detected, even after exposures of a number of hours. Further experiments at higher partial pressures of water vapor (~ 20 Torr) have yielded similar results and indicate that, on the microscopic level, the catalytic reaction mode is apparently different at 300°C to that at 500°C, although rate measurements would indicate the contrary.

Further experiments will investigate the reaction at intermediate temperatures and will utilize other alkali hydroxides as catalyst material in order to clarify the findings.

Task 3 - Catalysed Low Temperature Hydrogenation of Coal - G. A. Somorjai with A. L. Cabrera and R. Casanova

Studies this quarter have been directed to gain more insights into the fundamental mechanisms of the methanation of graphite using water vapor and/or hydrogen. Our main goal remains to produce high molecular weight hydrocarbons. Potassium hydroxide and calcium oxide have been used as catalysts for the methane synthesis.

The activation energies for the methane production from the graphite-water reaction was determined at temperatures $T > 300^\circ\text{C}$ when potassium hydroxide was used as a catalyst, as well as for the graphite-hydrogen reaction catalyzed by calcium oxide. A preliminary experiment on potassium intercalated graphite revealed some important information.

a) KOH-Graphite System

The activation energy for the potassium hydroxide catalyzed graphite-water reaction was calculated from the rates of CH_4 production as a function of the temperature T for the case $T > 300^\circ\text{C}$. The value obtained for this energy is 11 ± 1 Kcal/mole which is very similar to that determined earlier for $T < 300^\circ\text{C}$. This fact indicates that the activation energy for this reaction is temperature independent and perhaps that the catalytic mechanisms involved in this reaction are the same for all temperatures. An Arrhenius plot is shown in Fig. 1.

The sample's surface was inspected by means of ESCA immediately after a reaction at 500°C that lasted more than 20 hours. ESCA showed the presence of a peak at 290 eV which we have attributed to a transformation from graphitic to "carbide" carbon. This peak was not present before the reaction. Energy shifts of $\sim 2\text{eV}$ and $\sim 4\text{eV}$ were also observed for the C_{1s} and K_{2p} peaks.

b) CaO-Graphite System

Methane production with this system was achieved by the following procedure: The sample was first heated in 22 Torr of H_2O and in 1 atm of He at the temperature of interest; the sample was then heated at the same temperature in only 1 atm of He. Methane was detected only after the last step. In contrast to the KOH-graphite case, no CH_4 was detected for temperatures lower than 300°C. An activation energy of 25.5 Kcal/mole was determined for the temperature range $350^\circ\text{C} \leq T \leq 600^\circ\text{C}$. An Arrhenius plot for this reaction is shown in Fig. 2. The CH_4 concentration, produced for the temperature range under study was approximately one order of magnitude higher than for the KOH-graphite system. However, the CH_4 production in stationary state lasted for a much shorter time than the KOH-graphite system. A typical plot of the CH_4 concentration vs. time is presented in Fig. 3 for the CaO-graphite system.

The sample surface was monitored with ESCA before the exposure to H_2O , after the heating in H_2O and after the reaction with H_2 for the temperature of interest. We have confirmed once more, a striking feature that was reported earlier in a preliminary study. ESCA revealed the presence of a peak at 290eV after the heating in 22 Torr of H_2O . The intensity of the peak decreased by more than 70% after heating in 1 atm of H_2 , when CH_4 was produced. These observations indicate that one needs to "activate" the graphite surface first, in order to produce methane. The ESCA peak at 290 eV can be attributed to an active carbon which can be easily reduced with H_2 to produce methane. This peak is shown in Fig. 4. In the ESCA spectrum we can also observe the presence of a potassium peak. This potassium was found as a contamination in the CaO powder used to prepare the dipping solution. According to AES the amount of potassium is only ~ 0.2 monolayers.

The duration of the stationary state for the methane production with the system may be linked with the disappearance time of the 290 eV peak. Our results show that the duration of the stationary state is inversely proportional to the temperature T.

We conclude from our studies that the catalytic effects of KOH and CaO are different. However, it seems that there is one step in common, the transformation of graphite to a reactive carbon by these catalysts.

c) Potassium-Intercalated Graphite

A preliminary study has been undertaken to gain information about intercalation as a possible catalytic mechanism in the methanation of graphite. For this study a C_8K sample was used. A reaction at 300°C of the potassium-intercalated graphite with 20 Torr of H_2O was followed for approximately 20 hours. The CH_4 concentrations observed were slightly lower than for the KOH-graphite system. A striking physical change was observed. The sample thickness

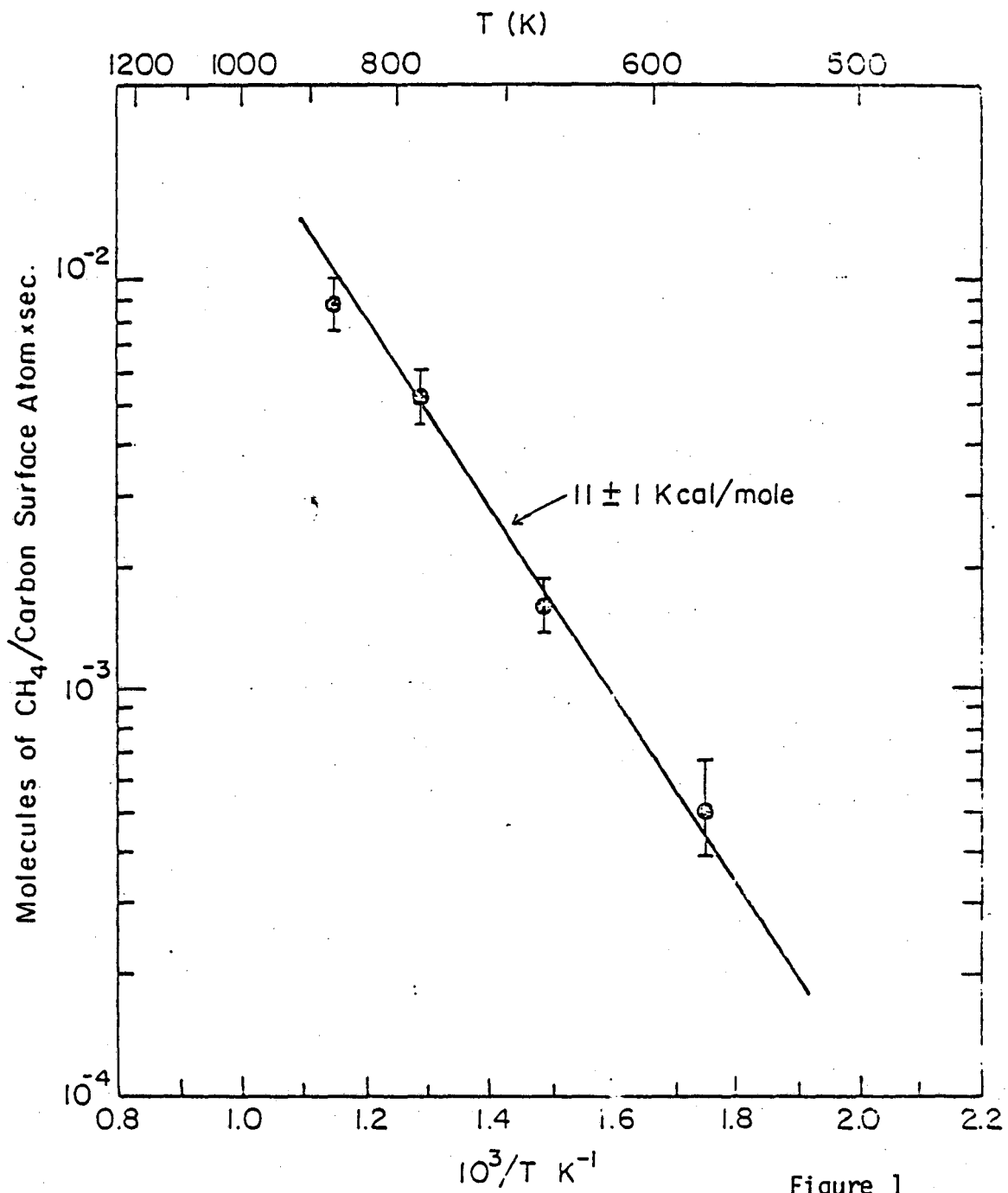


Figure 1

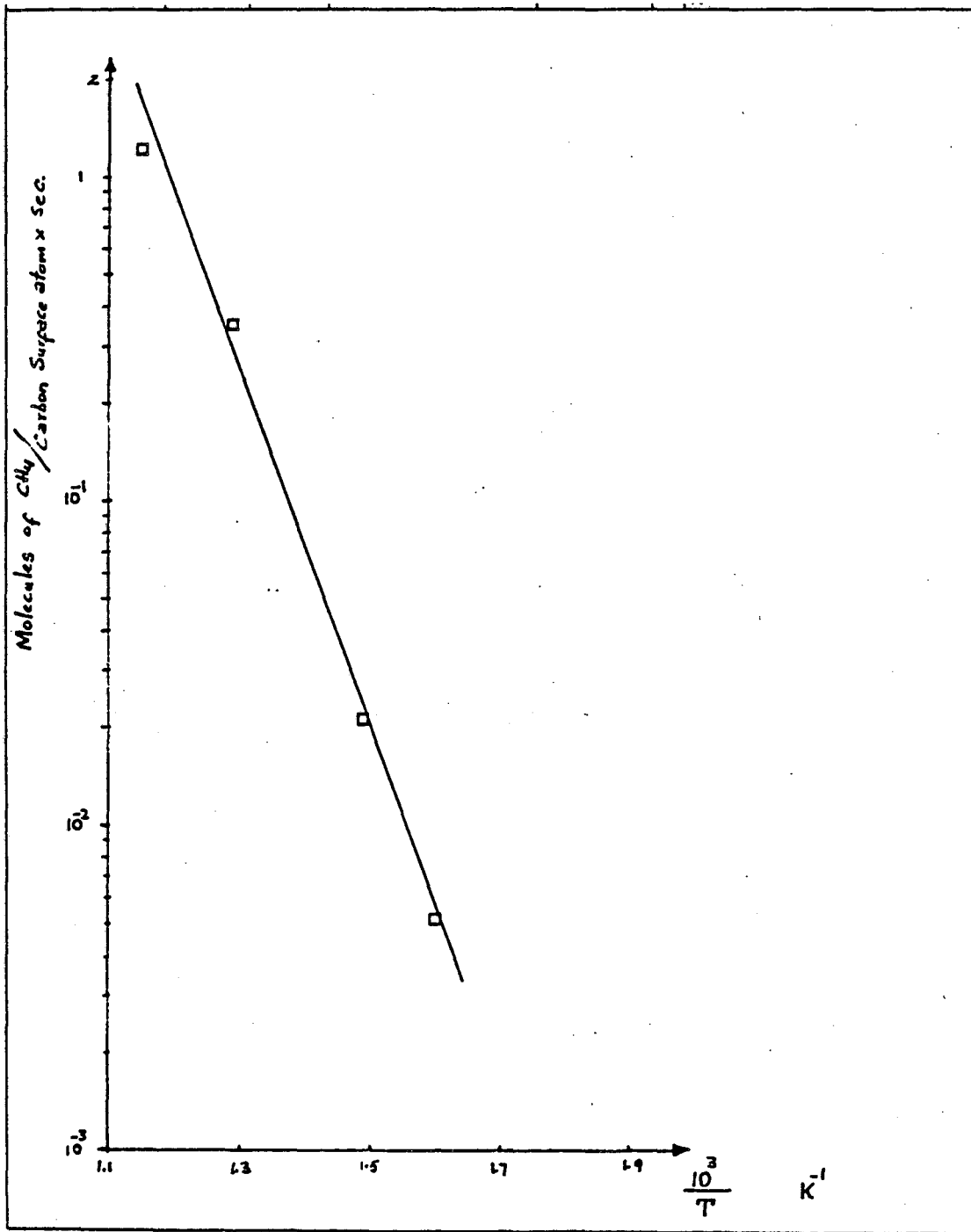


Figure 2

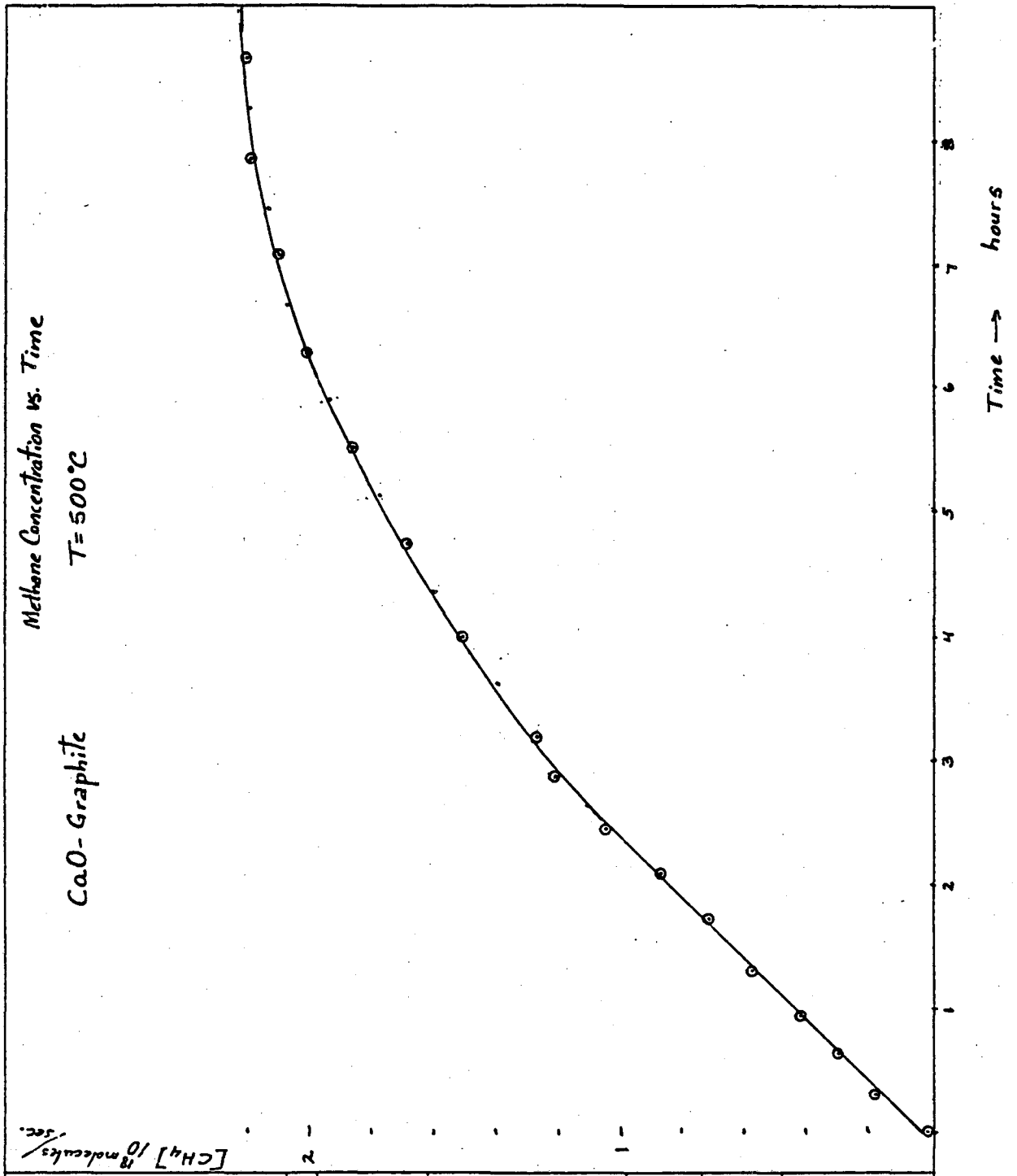


Figure 3

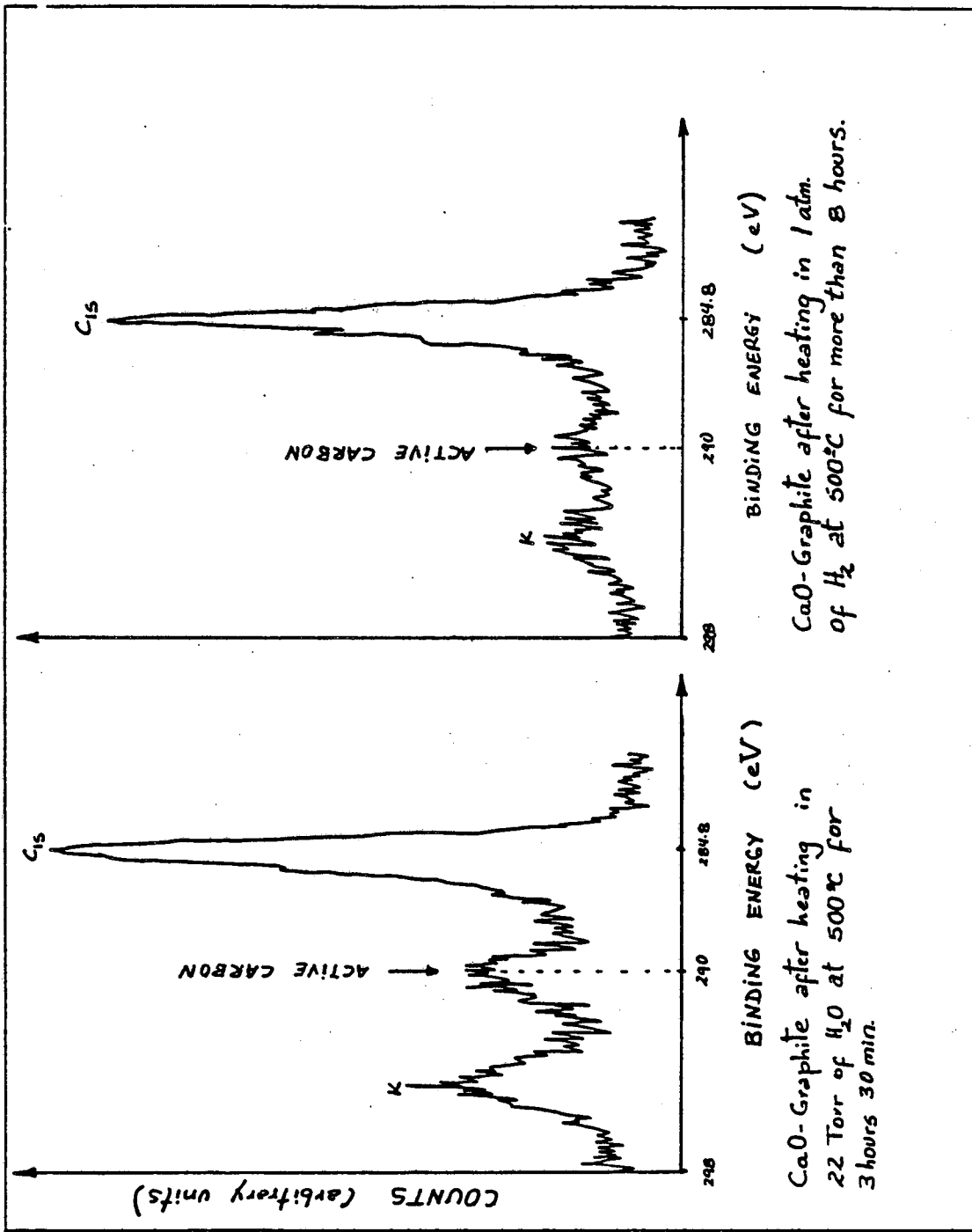


Figure 4

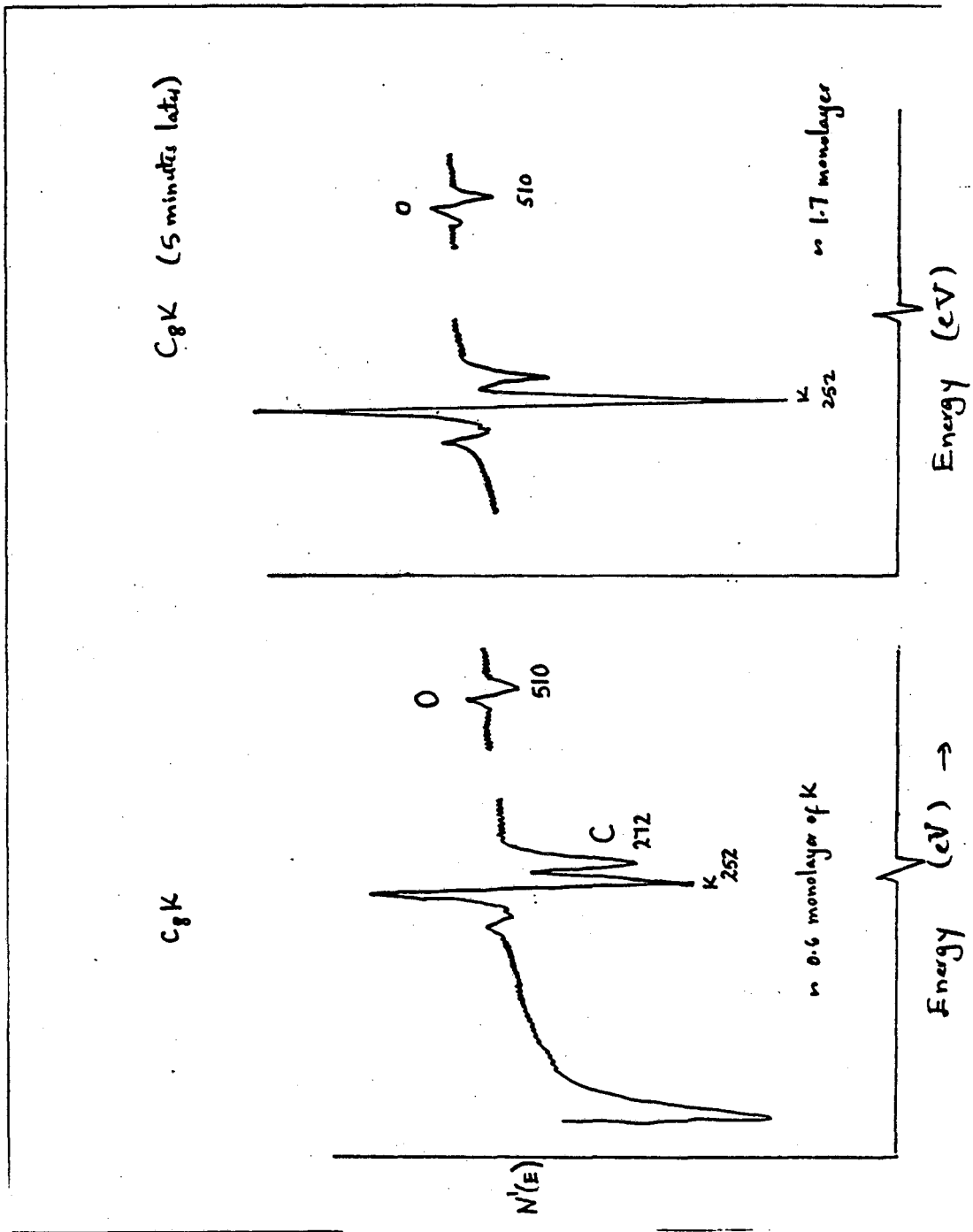


Figure 5

increased by a factor of 7 or 8, probably due to water absorption between the constituent aromatic layers of graphite. Another remarkable effect was observed by means of Auger spectroscopy. The intensity of the potassium peak increased after the electron beam had impinged on the sample for 5 minutes (see Fig. 5). This effect may be due to local heating produced by the electron beam that causes some potassium to diffuse to the surface from the lower layers.

It seems that the change in thickness rules out intercalation as a fundamental step in the methanation of graphites.

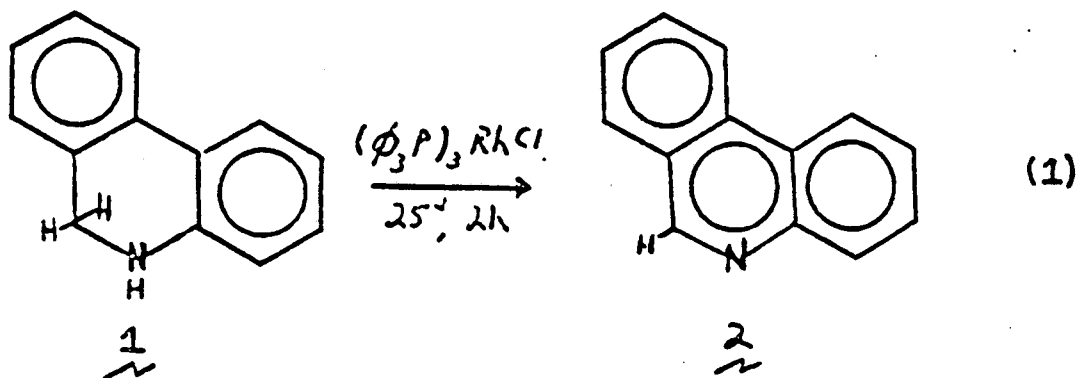
Task 4 - Selective Hydrogenation, Hydrogenolysis, and Alkylation of Coal and Coal-Related Liquids by Organometallic Systems - K. P. C. Vollhardt

Work has been completed and terminated on the reaction of benzene with aluminum trichloride in the presence and absence of catalytically activated hydrogen. The results of this study, some of which have already been published in preliminary form, have now been submitted for publication with full experimental details and mechanistic discussion.

For budgetary reasons, progress in this task has been curtailed. Further mechanistic details of a remarkable low-energy transition metal mediated hydrogen shift have been investigated, particularly kinetic parameters have been determined, and one labeling study completed, and a second started. A limited study has begun of the scope of this reaction using early transition metals. This might also allow the detection of a postulated but presently unknown ring opening reaction involving six-membered carbocycles.

Task 5 - Chemistry of Coal Solubilization - T. Vermeulen and R. H. Fish

A facile dehydrogenation reaction (eq 1) was discovered when 9, 10-dihydrophenanthridine was reacted with $(\phi_3P)_3RhCl$ at room temperature. This dehydrogenation reaction could be important in the catalytic transfer of hydrogen from donor to acceptor molecules in the coal liquefaction process.



Reaction of 1 with $(\text{O}_3)_3 \text{RhCl}$ in the presence of Quinoline provided a small conversion to 1, 2, 3, 4-tetrahydroquinoline. This represents an example of catalytic transfer hydrogenation and will be studied further.

Reaction of 2. with catalytic amounts of $(\text{O}_3\text{P})_3 \text{RhCl}$ (10:1 substrate to catalyst ratio) in the presence of deuterium gas (D_2) provided 1 with two deuteriums on the carbon alpha to nitrogen (C_{10}) as well as partial deuteration of the ring position at C_8 .

The dehydrogenation of 9, 10-dideutero phenanthridine with $(\text{O}_3\text{P})_3 \text{RhCl}$ gave 1 with a deuterium on the C_{10} position (alpha to nitrogen).

We had previously studied the homogeneous catalyzed hydrogenation reactions of several polynuclear heteroaromatic nitrogen compounds using $(\text{O}_3\text{P})_3 \text{RhCl}$ and have now extended these to the "heterogenized" $(\text{O}_3\text{P})_3 \text{RhCl}$, bonded to polystyrene. Reactions of the heterogenized Wilkinson's catalyst under hydrogenation conditions provided a 100% conversion of quinoline to 1, 2, 3, 4-tetrahydroquinoline after 24 hours at 80°C and 800 psi H_2 .

These reactions were repeated for three turnovers of the same filtered catalyst with 2 hr. reaction times at 80°C and 240 psi H_2 to provide a 14%, 26% and 32% conversion of quinoline to 1, 2, 3, 4-tetrahydroquinoline. These exciting results will be extended to other polynuclear heteroaromatic nitrogen compounds and we hope to heterogenize the ruthenian catalyst we previously found active.

Task 6 - Coal Conversion Catalysts - Deactivation Studies - A. V. Levy
and E. E. Petersen with M. West and M. Smith

We have synthesized both vanadyl tetraphenylporphyrin (VOTPP) and titanyl tetraphenylporphyrin (TiOTPP). We have begun experiments on VOTPP in mineral oil as a model liquid containing dibenzothiophene as a model sulfur compound, but have not yet fully analyzed the results of these runs. Work on a program calculating the rate of deposition of metal by finite difference approximation of the diffusion with reaction equations within the pellet has been completed. The program corrects the diffusivities and the surface area within the catalyst as the deposits form and the pore distribution is altered.

Analysis of previously taken vanadyl naphthenate experiments has lead to several interesting conclusions. First, an overall material balance shows that vanadyl naphthenate can be demetallized exterior to the catalyst, the amount increasing significantly with increasing temperature. Similar behavior of the analogous iron compounds found in coal-liquids could result in serious bed plugging. Second, analysis of local demetallation rates and local metal concentrations shows that the product of the demetallation reaction, vanadium sulfide, is an active demetallation catalyst itself.

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