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Materials & Molecular Research Division

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
QUARTERLY REPORT, OCTOBER 1 to DECEMBER 31, 1981

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Quarterly Report

October 1 to December 31, 1981

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. In the presence of hydrogen and the absence of base, using the catalyst $\text{RuCl}_2(\text{CO})_2(\text{O}_3\text{P})_2$, excellent yields of reduced polynuclear heteroaromatic nitrogen compound were produced with 100% selectivity for the N-containing ring.
2. A careful gas chromatographic analysis of Fischer-Tropsch products has shown that major peaks, previously thought to be single compounds are composites of two or more compounds. Resolution of these peaks will enable one to establish a rational grouping of n/i and paraffin/olefin ratios.
3. Addition of iron or rhodium to potassium impregnated graphite did not result in the production of heavier hydrocarbons than methane from the graphite-steam reaction at low temperature. However, small amounts of iron enhanced the methane production.

IV Progress of Studies

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

During the past quarter, emphasis was placed on refining the chromatographic system used to characterize the products attained by Fischer-Tropsch synthesis. A 50m capillary column, coated with OV101, was installed and operated from -80 to 250°C , at a programmed heating rate of $10^\circ\text{C}/\text{min}$. Using this technique, it has proven possible to resolve completely the products containing between four and twenty carbon atoms. Comparison of the new chromatographs with those obtained previously has revealed that a number of the major peaks originally thought to be single compounds are really composites of two or more products, and in several a single peak was found to be composed of an olefinic and a paraffinic product. Identification of the peaks now defined is being carried out using GC/MS. Once this has been achieved, it will be possible to establish rational groupings of products at a given carbon number. It is also expected that the new chromatographic system will greatly facilitate the study and identification of which products are produced via CO hydrogenation and which are formed via isomerization of primary products or via the scavenging of CH_x ($x = 2,3$) groups from the catalyst surface in secondary processes.

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

Further work on the catalyzed low temperature gasification of carbon (discussed in Task 3) has been carried out. In-situ gasification experiments in the residual gases in the HVEM have been conducted at temperatures in the range 200-400°C using KOH as a catalyst. Observations clearly show the enhanced gasification of carbon in contact with KOH, although the mechanism is not yet clear.

Further experiments using an environmental cell in the high voltage electron microscope will provide clearer data. The temperature response of the e-cell furnace has been calibrated using a number of gas mixtures. Experiments are proceeding using water vapour in a carrier gas to catalytically gasify graphite specimens.

Task 3 - Catalyzed Low Temperature Hydrogenation of Coal - G. A. Somorjai with A. Cabrera

Following the surprising discovery, reported in the last report, that alkali coated graphite reacts with steam at as low a temperature as 225°C to produce methane and CO₂, the ultra high vacuum equipment was modified by installation of an X-ray source. This now allows us to perform X-ray photoelectron spectroscopy (XPS) along with Auger electron spectroscopy. A new BET surface area unit was also installed to permit surface area (S.A.) measurements of catalyst samples.

New combinations of catalysts were tested for the production of hydrocarbons at low temperature from graphite and water. The major purpose, thus far unsuccessful, was to attempt the formation of hydrocarbons higher than C₁.

Since LiOH had been the most active catalyst for the production of methane from graphite and water, study of this system was extended to the temperature range 525-671K. The logarithm of the rate of CH₄ production as a function of the increase in absolute temperature is plotted in Fig. 1. An activation energy of 4.2 ± 0.5 Kcal/mole is derived from this plot. CH₄ is produced from water vapor in a helium as well as in a hydrogen atmosphere.

Iron or rhodium was deposited on graphite either before or after alkali (KOH) deposition. There was no difference between iron being deposited before or after alkali deposition. In all cases, the only products of the reaction of water vapor with the graphite containing both potassium hydroxide and iron, resp. rhodium were methane and CO. Light deposits of iron enhanced the steady state methane production, while heavy iron deposits inhibited CH₄ formation, as shown in Figure 2). The data in Figure 2 were obtained with 0.1 of a monolayer of Fe or Rh, resp. AES reveals that Fe and Rh were in an oxidized state during the experiments. These metal oxides may keep the KOH dispersed, resulting in greater activity.

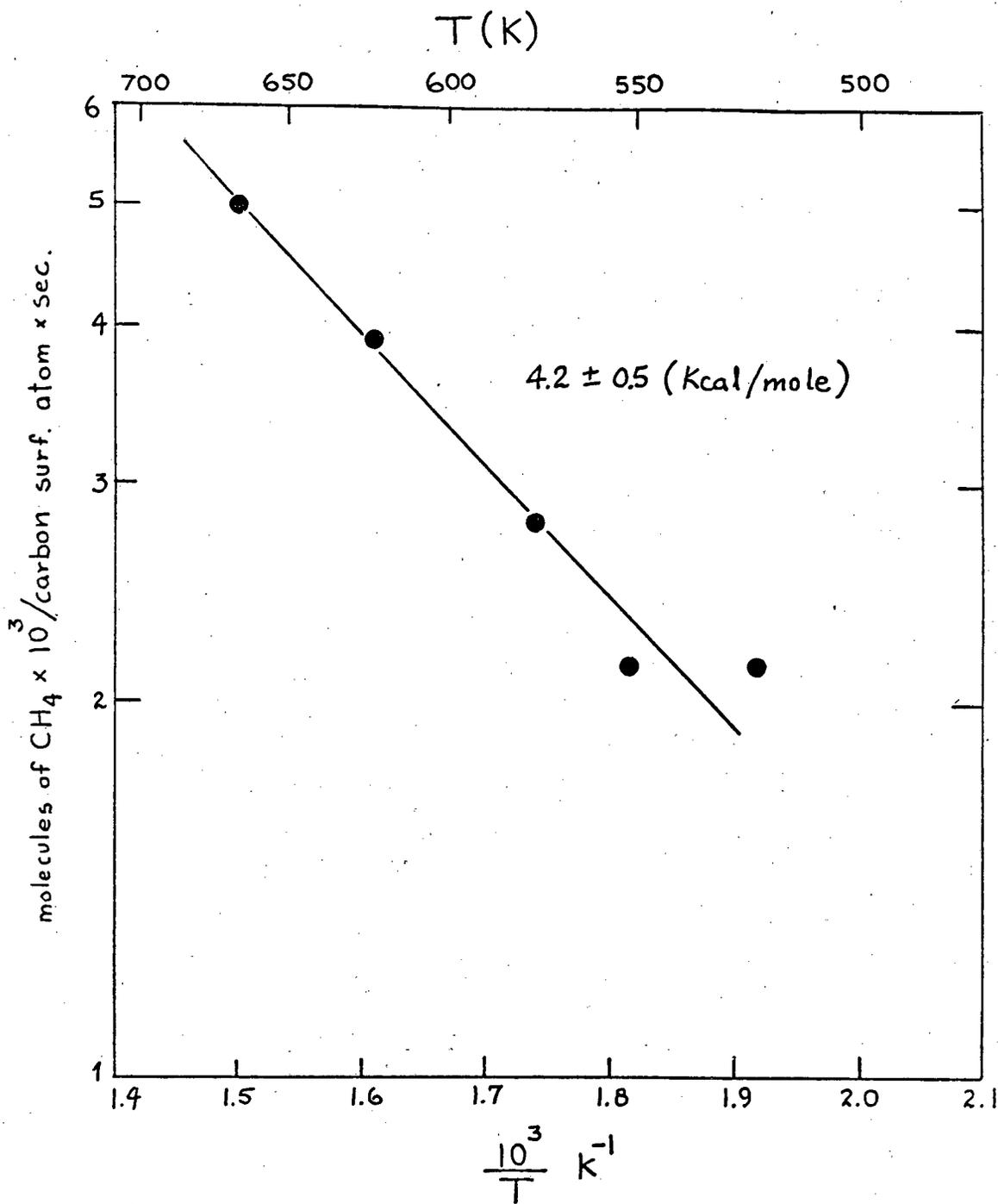


Fig. 1

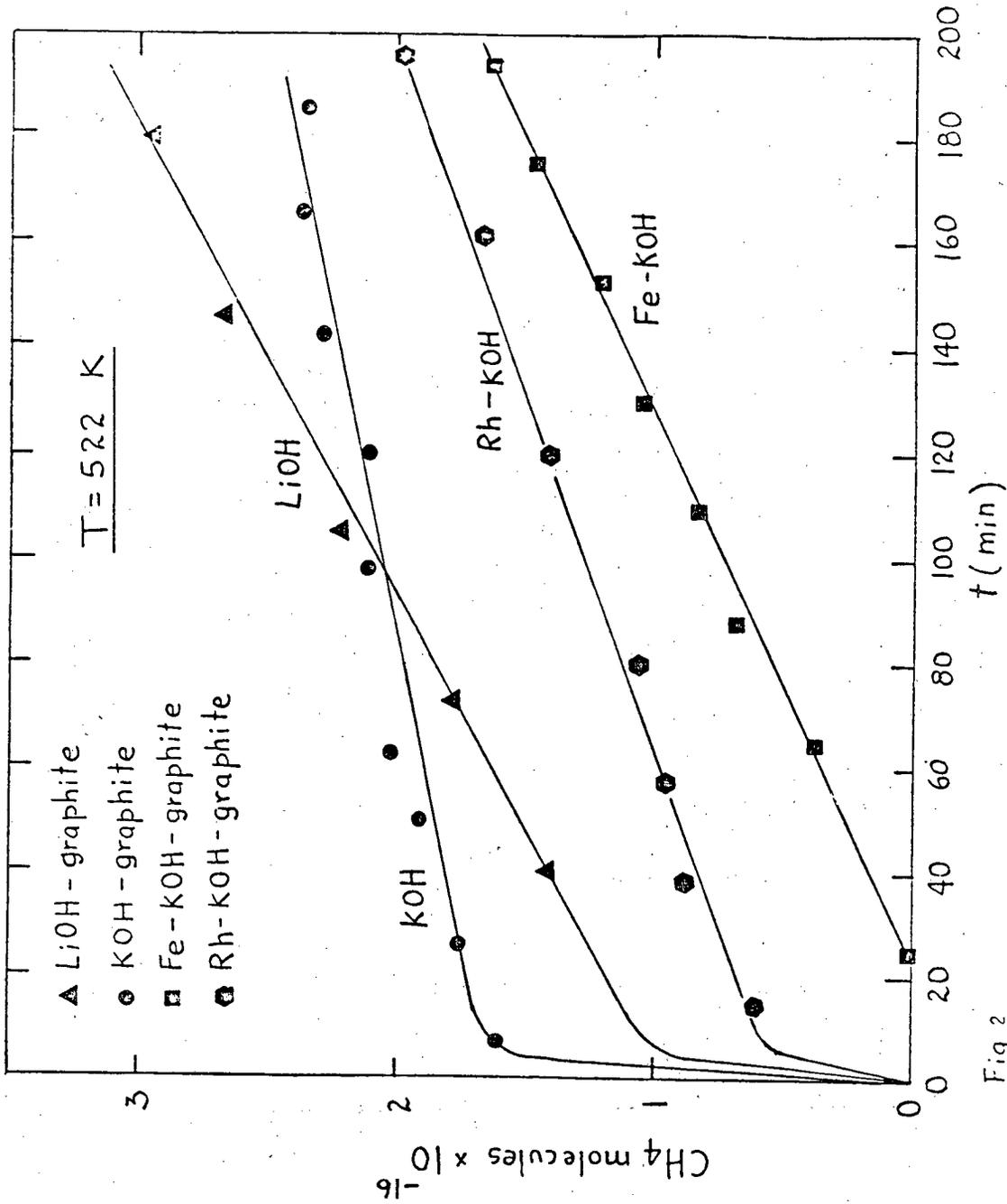


Fig 2

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

A study has been undertaken of the reaction of benzene and aluminum chloride in the presence of hydrogen and a heterogeneous platinum catalyst. It was hoped that the previously investigated cracking-disproportionation products of benzene could be intercepted by hydrogen. Indeed hydrogen uptake was observed, the product distribution being significantly different from that obtained in the absence of hydrogen and platinum. A typical result is shown in Table 1. On prolonged exposure increasing amounts of hydrogenated aromatics are obtained which subsequently undergo hydrogenolysis. The latter is also observed when cyclohexane or biphenyl is reacted under the same conditions. The major products from the reaction of biphenyl were methylcyclopentane and cyclohexane. Minor products were benzene, methylcyclohexane, and dimethylcyclohexanes.

Table 1: Yields of major aromatic products in the reaction of AlCl_3 and benzene with and without PtO_2/H_2

<u>Products</u>	<u>Rxn Time = 48 h Without PtO_2/H_2</u>	<u>Rxn Time = 7 h With PtO_2/H_2</u>
Toluene	2.19	0.49
Ethylbenzene	2.68	1.98
n-Propylbenzene	0.18	0.03
i-Propylbenzene	0.33	0.21
Butylbenzenes	0.11	0.23
Tetralin	0.73	1.20
Phenylcyclohexane	0.06	1.50
Biphenyl	1.55	0.37
Diphenylmethane	0.23	trace
Diphenylethane(s)	0.34	0.21
<u>TOTAL</u>	8.40	6.22

Work has been continued concerned with the activation of vinyl-hydrogen bonds by cobalt. Kinetics, labeling experiments, and scope and limitations are being studied.

Publications

G. Ville, K. P. C. Vollhardt, and M. J. Winter, On the Reversibility of η^4 -Cyclobutadiene Metal Formation From Complexed Alkynes: Unimolecular Isomerization of Labelled Racemic and Enantiomerically Enriched η^5 -Cyclopentadienyl- η^4 -cyclobutadiene Cobalt Complexes, J. Am. Chem. Soc. 103, 5267 (1981).

Y.-Y. Lai, W. Tam, and K. P. C. Vollhardt, Transition Metal Activation of π -Complexed Benzene: Double Nucleophilic Addition, J. Organometal. Chem., 216, 97 (1981).

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

We have found that in the presence of hydrogen and the absence of base, using the catalyst $\text{RuCl}_2(\text{CO})_2(\text{P}_3)_2$, excellent yields of reduced polynuclear heteroaromatic nitrogen compounds were produced. This is shown with quinoline as the model coal compound in Table 1.

Interestingly, in the presence of base, we find that quinoline reacts to not only give 1, 2, 3, 4 tetrahydroquinoline (35%), but surprisingly, 5,6,7,8-tetrahydroquinoline (4%) as well. This latter product does not form in the absence of base and moreover higher yields of reduced 1,2,3,4-tetrahydroquinoline (~100%) are produced when base is removed.

A control experiment further substantiates the role of base in the aromatic ring reduction of quinoline, where added water provided no 5,6,7,8-tetrahydroquinoline. The reduction of 5,6,7,8-tetrahydroquinoline was also studied and reduction of the pyridine ring only occurred in the absence of base.

We have investigated Wilkinson's catalyst ($\text{RhCl}(\text{P}_3)_3$) and found it to be an excellent hydrogenation catalyst for polynuclear nitrogen heterocyclic compounds. Table 2 demonstrates this with quinoline and 5,6-benzoquinoline. In experiments to determine some mechanistic aspects, we added excess triphenylphosphine and observed a small reduction in the yield (from 100% to 84%) of 1,2,3,4-tetrahydroquinoline.

Moreover, the addition of carbon monoxide produced the known $\text{RuCl}(\text{P}_3)_2\text{CO}$, which is not a good reducing agent for nitrogen heterocyclic compounds.

We are presently studying some sulfur model coal compounds to determine their reactivity with both $\text{RuCl}_2(\text{CO})_2(\text{P}_3)_2$ and $\text{RhCl}(\text{P}_3)_3$.

Publications For J. Amer. Chem. Soc. (Submitted)

Richard H. Fish and Gregg A. Cremer

Homogeneous Catalytic Hydrogenations 1.

Reductions of Polynuclear Aromatic and Heteroaromatic Nitrogen Compounds Utilizing Carbon Monoxide with Water or Hydrogen. (LBL 13734)

Homogeneous Catalytic Hydrogenations 2.

Regiospecific Reductions of Polynuclear Aromatic and Heteroaromatic Nitrogen Compounds Catalyzed by Ruthenium Carbonyl Hydrides. (LBL 13735).

Table 1 Homogeneous Catalytic Hydrogenations
with $\text{RuCl}_2(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ as Catalyst

Catalyst	H_2 (Psi)	Substrate	Temp.	Time	Results	Conditions
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi (init)	Quinoline	180°C	2 hr.	96.7% 1,2,3,4 tetrahydro	H_2 only
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi	Quinoline	180°C	2 hr.	34.8% 1,2,3,4 tetrahydro 3.6% 5,6,7,8 tetrahydro	3 ml of 0.2M KOH solution added
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi	Quinoline	180°C	2 hr.	100% 1,2,3,4 tetrahydro	3 ml of H_2O added
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi	5,6,7,8-Tetra hydroquinoline	180°C	2 hr.	12.1% decahydroquinoline	H_2 only
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi	5,6,7,8-Tetra hydroquinoline	180°C	2 hr.	no rxn.	3 ml 0.2M KOH added to catalyst before adding substrate
$\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$	240 psi	Quinoline	180°C	2 hr.	20.5% 1,2,3,4 tetrahydro 2.1% 5,6,7,8 tetrahydro	Same as above.

Table 2 Homogeneous Catalytic Hydrogenations
with $\text{RhCl}(\text{PPh}_3)_3$ as Catalyst

Catalyst	H_2 (Psi)	Substrate	Temp.	Time	Results	Notes
$\text{RhCl}(\text{PPh}_3)_3$	240 psi	Quinoline	180°C	2 hr.	100% 1,2,3,4 tetrahydro	
$\text{RhCl}(\text{PPh}_3)_3$	240 psi	Quinoline	150°C	1 hr.	100% 1,2,3,4 tetrahydro	
$\text{RhCl}(\text{PPh}_3)_3$	240 psi	Quinoline	150°C	1 hr.	84.8% 1,2,3,4 tetrahydro	XS PPh_3 added to reaction
$\text{RhCl}(\text{PPh}_3)_3$	240 psi	Quinoline	180°C	2 hr.	17.7% 1,2,3,4 tetrahydro	XS CO added to reaction $\text{RhCl}(\text{PPh}_3)_2\text{CO}$ formed in Situ
$\text{RhCl}(\text{PPh}_3)_2\text{CO}$	240 psi	Quinoline	180°C	2 hr.	13.5% 1,2,3,4 tetrahydro	
$\text{RhCl}(\text{PPh}_3)_3$	240 psi	5,6 benzoquinoline	180°C	2 hr.	35.0% 1,2,3,4 tetrahydro -5,6-benzoquinoline	

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

During this quarter we completed a series of runs at 325C, 375C, and 400C with metal concentrations between 200 and 400 ppm to extend the previous work at 350C. At 400C the gas oil cracks considerably. Very little metal deposits, probably due to heavy carbon buildup on the catalyst exterior. At 375C there was no noticeable cracking or coking. The vanadium levels at the surface were much higher but the penetration was shallower than for a comparable 350C run. At 325C the vanadium levels were lower but the penetration was two to three times greater than at the higher temperatures. These results convince us that future experiments should be conducted at 325C where the greater depth of penetration will make the electron microprobe analysis of deposited metals more accurate. Reproducibility of the microprobe analysis for several pellets from the same experiment substantiate the experimental technique. It is important to note that the trend of shallower penetration at higher temperatures agrees with the well established model of a diffusion-controlled reaction in a porous pellet.

We have also worked on a model to predict the metal distribution profile inside the catalyst pellet and compared it with published data. The metal deposition reaction is assumed to be proportional to the product of the metal and hydrogen sulfide concentrations in the liquid. Deposit profiles can be fit by adjusting the reaction kinetics and reactant diffusivity.

The experimental and theoretical results obtained so far give us confidence in our approach and point us towards running a more well-defined experiment to gather parameters more accurately for the model.

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