CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
Quarterly Report
January 1, 1984 - March 31, 1984

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April 1984

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
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QUARTERLY REPORT

January 1, 1984 - March 31, 1984

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

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This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.
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1. Technical Program for FY 1984

Task 1: SELECTIVE SYNTHESIS OF GASOLINE-RANGE COMPONENTS FROM SYNTHESIS GAS

A. T. Bell, Task Manager

It is planned to complete the objectives of the present project during FY 1984. The experimental results obtained for Fischer-Tropsch synthesis over α-Fe, Fe₂O₃, and Fe₃C will be compared to establish patterns in catalytic activity and selectivity as a function of catalyst composition. X-ray diffraction patterns will be taken of the fresh and spent catalysts to determine whether bulk composition changes with time on stream. In particular it would be desirable to know whether these materials achieve a common bulk composition, catalytic activity, and selectivity after extended use.

Efforts will also be made to interpret the rate data obtained for α-Fe, Fe₂O₃, and Fe₃C in the light of mechanistic models of the reaction kinetics.

The work on supported Fe catalysts will be concluded by obtaining data on the performance of Fe/Al₂O₃, Fe/TiO₂, and Fe/MgO for comparison with the data already available for Fe/SiO₂ and zeolite-supported Fe. All catalysts will be examined both in a calcined and in a reduced state to determine the influence of pretreatment. Additional work will also be done with Fe/ZSM-5 to understand better why the zeolite appears to influence the product distribution so little at temperatures below 300°C. It is conceivable that for the zeolite to have an effect, the temperatures must exceed 300°C by a substantial margin.
Task 2: CATALYZED LOW TEMPERATURE REACTION OF CARBON AND WATER

G. A. Somorjai, Task Manager

Leads to make the production of higher hydrocarbons from carbon and water truly catalytic will be pursued. It appears possible to catalytically decompose phenolates formed, preventing stoichiometric limitations.

Attempts will be made to greatly increase rates and volume of hydrocarbon formation. This may be accomplished by operation at higher water partial pressure and by catalytic promoters. Further, the addition of CO, resp. CO₂, to the reaction offers indications of producing liquid hydrocarbons.

Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION

R. H. Fish, Task Manager

The FY84 program will concentrate on the use of polymer-supported catalysts and their mechanistic implications in the selective catalytic hydrogenation of model coal compounds. This will include experiments with deuterium rates, and competitive reaction to better define potential catalyst poisoning as well as enhancement of rates of selected model coal compounds.

Catalytic cracking of partially hydrogenated nitrogen containing ring compounds will be investigated to determine the total savings of hydrogen in nitrogen removal over conventional hydrocracking.

In addition, we will attempt to define the important parameters in the catalytic transfer of hydrogen from saturated nitrogen heterocyclic compounds to other coal liquid constituents. This will include scope, rates and a perusal of polymer-supported catalysts capable of dehydrogenation-hydrogenation reactions.
11. Highlights

Task 1: SELECTIVE SYNTHESIS OF GASOLINE-RANGE COMPONENTS FROM SYNTHESIS GAS

Rate expressions were developed for four different iron catalysts (promoted and unpromoted). Data for all four catalysts can be correlated by a semi-empirical expression.

Task 2: CATALYZED LOW TEMPERATURE REACTIONS OF CARBON AND WATER

The catalytic activity for the production of hydrocarbons from graphite and water over KOH plus a co-catalyst was investigated for several first row transition metals. NiO showed the greatest activity.

Several samples of $^{13}$CO, $^{13}$CO$_2$ and H$_2$O adsorbed on graphite and on catalyst-graphite systems after reaction with steam were prepared for NMR investigation.

Surface science investigations suggest the presence of four distinct oxygen containing species following CO or CO$_2$ exposure of KOH containing graphite. Potassium deposition on graphite leads to the formation of an over-layer as well as to intercalation.

Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION

Rate studies of quinoline reduction to tetrahydroquinoline in the presence of the homogeneous catalysts ($\phi_3^P$)$_3$RhCl have provided definitive evidence that benzothiophene, indole, pyrrole, carbazole, thiophene, p-cresol and dibenzo-thiophene enhance the initial rate of hydrogenation of quinoline by a factor greater than 1.5.

P-cresol was found to enhance the initial rate of hydrogenation of quinoline (1.6 to 2 fold) in a model coal liquid with polymer-supported (2% cross-linked) ($\phi_3^P$)$_3$RhCl.
The binding of quinoline to the rhodium hydride, \((\phi_3 P)_3 \text{RhCl}\)
was successfully established by 200 MHz H nmr experiments.
III. Progress of Studies

Task 1: SELECTIVE SYNTHESIS OF GASOLINE RANGE COMPONENTS FROM SYNTHESIS GAS
A. T. Bell

The majority of the work carried out during this quarter has focused on the development and testing of rate expression for correlating the experimental results obtained with potassium-promoted fused iron, unpromoted iron oxide, potassium-promoted iron oxide, and iron carbide catalysts. It was found that the rate data obtained for the potassium-promoted fused-iron and iron oxide catalysts could be described by power-law expressions in the partial pressures of $H_2$ and CO. Similar expressions cannot be used, though, to describe the rate data obtained with the unpromoted catalysts. Log-log plots of the rate of product formation versus $P_{H_2}$ or $P_{CO}$ for these catalysts exhibit curvature—the extent of which increases with increasing chain length. Rate expressions were developed based on a reaction mechanism that involves $C$ and $CH_x$ ($x=1-3$) as principal surface intermediates. The four parameters involved in the final expressions are identified by fitting the theoretical rate expressions to a portion of the data. The analysis also revealed that the data over all four catalysts are correlated well by the semi-empirical expression

$$\frac{R_{C_n}}{\alpha^n} = K P_{H_2} P_{CO}^{-0.5} \quad (1)$$

where $R_{C_n}$ is the rate of synthesis of a product containing $n$ carbon atoms and $\alpha$ is the probability of chain growth. For the two promoted catalysts, $\alpha$ is virtually independent of $P_{H_2}$, $P_{CO}$, and $T$. and hence eqn. 1 provides the overall dependence of the rate for each product on $P_{CO}$ and $P_{H_2}$. For the unpromoted catalyst, $\alpha$ is a complex function of $P_{H_2}$ and $P_{CO}$ and $T$. Since $R_{C_n}$ is proportional to $\alpha^n$, this explains the chaining dependence of $R_{C_n}$ on $P_{H_2}$ and $P_{CO}$ with $n$ observed for these catalysts.
The balance of the effort for this quarter has been devoted to the preparation of manuscripts for submission to journals. A paper describing all of the work with the fused-iron catalyst is being completed, and two papers dealing with promoted and unpromoted iron oxide are currently drafted.
Task 2: CATALYZED LOW TEMPERATURE REACTIONS OF CARBON AND WATER

W. T. Tysoe, J. Carrazza, G. A. Somorjai

Work was continued trying to identify a suitable catalyst system for the study using the flow reactor. The investigation of graphite surface chemistry using the high pressure/low pressure reactor also continued.

Mixtures of different oxides along with KOH on graphite have been studied to try to decrease the steam gasification temperature of graphite. First row transition metal oxides and KOH have been studied. The activity of the NiO/KOH catalyst is higher than any of the other mixtures.

Experiments are being done to compare KOH/Fe$_2$O$_3$ and KOH/NiO catalysts. Figure 1 shows the activity of the two systems compared with KOH alone, plotted versus temperature in a temperature programmed reactor. The activity of the NiO/KOH system is twice that of the Fe$_2$O$_3$/KOH system and comparable with KOH alone in the stoichiometric region.

Production of hydrocarbons is the major difference between the two. In the case of the NiO/KOH system, the methane production was followed at 850K up to three turnovers (around two hours). Even though the initial methane proportion in the gas products is lower than with KOH alone (0.08% vs 0.2%), it remains constant. With the KOH/Fe$_2$O$_3$ catalyst, the initial methane proportion is lower by a factor of 10 compared with KOH above (0.03% vs 0.2%) and drops to zero after half of a turnover.

More experiments will be done to completely characterize both systems.
Various solid state NMR samples have been prepared to try to identify reaction intermediates. The samples are prepared in quartz reactors and sealed in situ under vacuum, to avoid air contamination. A summary of samples prepared is as follows: $^{13}\text{CO}$ and $^{13}\text{CO}_2$ were adsorbed onto graphite at 560 and 925 K in order to try to characterize the surface species. The results will be compared with XPS experiments described previously (1).

Samples were prepared to study the water/carbon interaction. An overlayer of C was deposited over graphite by $^{13}\text{CO}_2$ reaction at 900 K (2 $^{13}\text{CO}_2 +^{13}\text{CO} + \text{C}$) and subsequent annealing at 1200 K. Water was adsorbed at room temperature. Samples were sealed after water adsorption and after heating up to 418 K and 723 K. The temperatures were chosen to examine surface species before and after the major water TDS peaks.

Samples of KOH, LiOH, Fe$_2$O$_3$/LiOH and NiO/LiOH deposited on graphite were prepared after reaction with steam. $^3\text{Li}$, $^{19}\text{K}$ and $^1\text{H}$ NMR signals will be taken to study the interaction between the catalysts and the reactants, (water and carbon).

The samples will be analyzed using Professor J. Reimer’s facilities at U. C. Berkeley Chemical Engineering Department.

**UHV/High Pressure Cell Experiments**

In order to decide whether peaks in the TDS spectra after CO and CO$_2$ adsorption (fig. 4, ref. 1) were indeed due to desorption from a graphite surface, a graphite single crystal with an exposed edge plane was dosed with either CO or CO$_2$ ($>10^8$ L) and the O KLL Auger peak-to-peak height measured as a function of annealing temperature. The results are shown in figure 2.
Rapid decreases are observed that correspond to either CO or CO\textsubscript{2} desorption.

These data further confirm that peaks below 400 K are indeed due to desorption from the graphite surface.

Four distinct surface species arising from either CO or CO\textsubscript{2} adsorption may therefore be identified as follows:

(i) A species that desorbs at ~380K to yield CO, and may be assigned to an adsorbed CO molecule.

\[
\text{\begin{tikzpicture}
  \node (o) at (0,0) {O};
  \node (c) at (0,1) {C};
  \node (h1) at (1,1) {H};
  \node (h2) at (2,1) {H};
  \node (h3) at (1,2) {H};
  \draw (o) -- (c) -- (h1); \draw (c) -- (h2); \draw (c) -- (h3);
\end{tikzpicture}}
\]

(ii) The peak at 400K in the 44 amu TD spectrum may similarly be assigned to an adsorbed CO\textsubscript{2} molecule.

\[
\text{\begin{tikzpicture}
  \node (o1) at (0,0) {O};
  \node (c) at (0,1) {C};
  \node (o2) at (0,-1) {O};
  \node (h1) at (1,1) {H};
  \node (h2) at (2,1) {H};
  \node (h3) at (1,2) {H};
  \draw (o1) -- (c); \draw (o1) -- (h1); \draw (o1) -- (h2); \draw (o1) -- (h3);
\end{tikzpicture}}
\]

(Where the lines in the CO\textsubscript{2} molecule are not meant to imply a single bond).

(iii) The peak at 730K in the 44 amu spectrum is associated with a carbonyl group. Comparison with data obtained using
high surface area graphite (2) suggests that this may be due to a lactone group.

(iv) Finally, the 28 amu peak at 1230K, which XPS suggests contains a carbonyl group may be assigned as:

Results of measurements of the pressure dependence of the reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ at 890K are shown in figure 3, showing a negative order in CO pressure of 1.3 indicating an inhibition of CO$_2$ formation by CO. This may be explained if a step in the surface reaction is postulated to be

which requires an adjacent adsorbed CO molecule and carbonyl group at an edge plane. Thus, a high CO pressure is likely to lead to a preponderance of one type of molecule over the other thus leading to an inhibition of the reaction.

The adsorption of potassium on graphite has also been studied. Fig. 4 shows a XP spectrum of potassium on graphite exhibiting the C1S peak and the K2P spin-orbit coupling split doublet.
Figure 5 shows a 39 amu TD spectrum after exposure to potassium at room temperature. This exhibits a sharp peak at 440K and a broad peak centred at 730K. Loss of surface potassium during a desorption sweep can be monitored by Auger spectroscopy, and figure 5 also shows the amount of potassium remaining on the surface as a function of temperature. Figure 5 also is the same data obtained from thermal desorption (i.e. by integrating the TDS). There is evidently divergence between the two curves above 600 K. Below this temperature the agreement is good. This suggests that the low temperature peak is due to surface potassium while the high temperature peak is due to bulk potassium (i.e. intercalation).

This view is supported by the data of figure 6, which shows the amount of potassium on the surface as a function of exposure. There is a break in both potassium and carbon curves indicative of the completion of one monolayer. Subsequently, the potassium signal indicates the deposition of several monolayers of potassium with only minimal attenuation of the carbon substrate signal. This result can be explained by assuming that potassium intercalates.
REFERENCES

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2. S. S. Barton and B. H. Harrison, Carbon 13 283 (1975)

FIGURE CAPTIONS

Figure 1. Gas production as a function temperature for the reaction of steam with graphite catalyzed by KOH, KOH/Fe$_2$O$_3$ or KOH/NiO.

Figure 2. O KLL Auger peak-to-peak height as a function of sample temperature after CO or CO$_2$ adsorption.

Figure 3. Pressure dependence of CO$_2$ formation rate on the reaction between CO and graphite.

Figure 4. XP spectrum of potassium on graphite showing the C1S peak at 285ev and K2p peaks at 272 and 275 ev.

Figure 5. Thermal desorption of K from graphite (__________). Potassium loss from the graphite surface as a function of temperature, obtained from thermal desorption data, xxxxx obtained from AES.

Figure 6. K AES signal (.) and C AES signal (x) as a function of potassium exposure.
Figure 1

Temperature (K)

KOH alone
KOH/FeO
KOH/NiO

n mol/min KOH

n g/s in KOH

102

10

5
Figure 2

Oxygen Auger p-p height

5 \times 10^8 \text{L of CO}_2

CO

Annealing temperature (K)

XBL 842-733
Figure 3

\( \ln(CO_2 \text{production rate}) \) (arb. units) vs \( \ln(\text{pressure}) \)

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C}, 890\text{K} \]
Figure 4 C 1s, K 2p XP Spectra
Figure 5

- Thermal desorption
- - - K loss from TD
×××× K loss from AES

Desorption rate (arb. units)

Remaining potassium

T/K

300  500  700  900
Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION
R. H. Fish, A. D. Thormodsen and M. B. Simmons

Rate Enhancement Studies of Quinoline Hydrogenation with Homogeneous \( \Phi P \) \( \frac{3}{3} \) RhCl as a Catalyst

We studied the relative rates of hydrogenation of quinoline in the presence (1:1) of other heteroaromatic compounds to ascertain the scope of the rate enhancement phenomena we discovered previously. We found that benzothiophene, indole, pyrrole, carbazole and thiophene had enhanced the relative rate of quinoline hydrogenation by a factor of 1.5 (quinoline alone = 1.0), while dibenzothiophene and p-cresol increased the quinoline hydrogenation relative rate by a factor of 1.8 and 2.5 respectively. We believe this increase in relative rate is caused by either a more favorable pathway for oxidative addition of quinoline to rhodium metal center in the presence of the above mentioned compounds or alternatively that they act as ligands to stabilize electron deficient rhodium metal centers.

Studies of Polymer-Supported \( \Phi P \) \( \frac{3}{3} \) RhCl in Model Coal Liquids. Rate Enhancement of p-Cresol

We have been able to confirm that p-cresol, a constituent in a model coal liquid containing pyrene (30% by wt.), tetralin (5%), methyl-naphthalene (38%), p-cresol (17%), quinoline (7.5%), and methylpyridine (2.5%), enhances the rate of quinoline hydrogenation by a factor of approximately two. In addition, 2-methylpyridine had no effect on the quinoline reduction rate, which is in contrast to its effect when using a homogeneous catalyst. Thus, p-cresol might be useful in the hydroprocessing of coal liquids.
Quinoline Binding to (\(\phi_3 P\)) RhClH

In order to provide information concerning the binding of quinoline to a rhodium metal center, we utilized a 200 MHz H nmr spectrometer for these studies and found that indeed quinoline failed to bind to (\(\phi_3 P\))\(_3\)RhCl. However, if we performed the rhodium hydride, (\(\phi_3 P\))\(_3\)RhClH\(_2\), we found that the protons at the 2 and 8 positions of quinoline were shifted to lower field by 0.13 and 0.09 ppm (Figure 1). This experiment provides definitive evidence that the "hydride route" is favored, i.e., H oxidatively adds first, followed by loss of triphenylphosphine, and then quinoline oxidatively adds to the rhodium metal center. These results confirm our previously postulated binding mechanism in the total scheme of quinoline hydrogenation.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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