AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100

Silver Spring, Maryland 20910

301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

JUN 01 1993

Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts

Quarterly Reports No. 10 and 11

For the period Jan 1, 1993 through May. 30, 1993

^aRichard M. Laine, ^bThomas Stoebe

May 19, 1993

Work Performed Under Contract No.

DE-FG22-90PC90313

^aDepartment of Materials Science and Engineering

H. H. Dow Building, North Campus

University of Michigan

Ann Arbor, MI 48109-2136

^bDepartment of Materials Science and Engineering

Roberts Hall, FB-10

University of Washington

Seattle, WA 98195

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

1 This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

BD

No Jones

JUN 01 1993

Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts

Quarterly Reports No. 10 and 11
For the period Jan 1, 1993 through May. 30, 1993

^aRichard M. Laine, ^bThomas Stoebe

May 19, 1993

Work Performed Under Contract No.
DE-FG22-90PC90313

^aDepartment of Materials Science and Engineering
H. H. Dow Building, North Campus
University of Michigan
Ann Arbor, MI 48109-2136

^bDepartment of Materials Science and Engineering
Roberts Hall, FB-10
University of Washington
Seattle, WA 98195

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PATENT STATUS

This technical report is being transmitted in advance of DOE patent clearance and no further dissemination or publication shall be made of the report without prior approval of the DOE Patent Counsel

TECHNICAL STATUS

This technical report is being transmitted in advance of DOE review and no further dissemination or publication shall be made of the report without prior approval of the DOE Project/Program Manager

Introduction

Present efforts to convert coal to fuels by direct hydroliquefaction suffer from being two stage direct processes, requiring high temperatures ($>400^{\circ}\text{C}$) and high hydrogen pressures (≈ 2000 psig) to effectively convert coal to a liquid and then to synfuels or petrochemical feedstocks. The need for high H_2 pressures results in excessive consumption of H_2 and an over-hydrogenated (lower quality) product. For a synfuels from coal process to be economical, all facets of the process must be made as efficient as possible. Improved control of reaction temperatures, H_2 pressures and consumption can provide significant improvements in efficiency and economy. All three areas are potentially controllable through careful selection of liquefaction catalysts.

Previous work in this group has shown that, surface confined, organometallic catalysts are exceptionally effective for hydrogenation and HDN of coal model compounds such as quinoline.¹⁻⁶ Unfortunately, surface confined catalysts have not proven to be particularly effective when used with coal itself. The problem derives from the fact that: (1) liquefaction is a solid (catalyst)-liquid (coal polymer) reaction system where, (2) diffusion of coal bonds to the heterogeneous catalyst surface is mass transport limited and controls liquefaction rates. Furthermore, heterogeneous catalyst mediated liquefaction is surface area dependent, placing another constraint on reaction rates.

The purpose of the present program is to develop soluble analogs of surface confined catalysts that can be impregnated directly into the coal structure at low temperatures. This approach should avoid problems related to surface area dependence, a two phase (surface-liquid) reaction system and, mass transport limitations.

Heteropolyanions (HPAs) offer the opportunity to develop soluble forms of surface confined catalysts. HPAs, are inexpensive, well-characterized, water soluble metal oxide clusters, e.g. $[\text{EM}_{12}\text{O}_{40}]^{4-}$ where E = Si or P and M = Mo or W.⁷ They are easily modified to contain other transition metals such as Co, Ni or Ru and, can be made soluble in organic solvents.⁷⁻⁹ The protic forms exhibit extremely high acidities $\text{pK}_a \approx 0-2$.⁷ In addition, selectively modified HPAs can function as low temperature hydrogenation catalysts that exhibit microporosity.¹⁰ HPAs are multi-functional catalysts that could be used to promote both hydroliquefaction and hydrotreating. In theory, these functions could be employed sequentially or simultaneously and could permit exceptional control of liquefaction reactions and reaction conditions. Thus, the current research program involves efforts to evaluate HPAs as soluble liquefaction and hydrotreating catalysts, with the goal of developing soluble analogs of surface confined catalysts.

Alternately, if HPAs decompose under useful liquefaction conditions, we will explore the utility of creating bimetallic HPAs that can be impregnated into coal and then decomposed to give high surface area heterogeneous catalyst particles that may still permit us to accomplish the above described goals.

The program consists of three major tasks: (1) Preparation of candidate HPA precatalysts; (2) HDN and HDO modeling studies and, (3) Direct liquefaction studies. The following sections outline the research planned in each area.

Task 1. Initially, we will prepare, according to literature procedure, a selected set of simple

monometallic heteropolyanions (HPAs) that will be screened in the Task 2 studies. Coincidentally, we will prepare more complex, bimetallic HPAs where the second metal is Ni, Co or Ru. We will prepare bimetallic HPAs wherein the cluster size, in terms of metal atoms, is varied as is the ratio of the two metals. We will also prepare trimetallic HPAs as the results in Tasks 2 and 3 warrant.

Task 2. The HPAs catalyst precursors prepared in Task 1 will be tested for HDN activities, selectivities, and H_2 consumption using quinoline as a model substrate. Solvent will be hexadecane and/or H_2O . We will further evaluate those catalysts found to have superior activity by conducting in-depth rate studies to optimize reaction conditions as a prelude to exploring their use in Task 3.

Task 3. Initially, we will test the efficiencies of selected monometallic and bimetallic HPAs to assess the value of the Task 2 screening studies. Superior HPAs will be tested for ability to promote Wyodak 2 liquefaction and to upgrade the resultant coal liquids. The effects of pressure, solvent, reducing system (H_2 or CO/H_2O) and temperatures on conversions, H_2 consumption and the quality of the coal liquids will be used to evaluate catalyst ability.

Progress For 10th and 11th Quarter

The progress in the past two quarters is described in the attached report

Future Work

We anticipate continuing detailed studies on THQ HDN in the next quarter. We hope to begin coal liquefaction studies in July or August.

Personnel Working On the Project this Quarter:

Students:

Mr. Gregory P. Heuss (Undergrad.)

Mr. Tom Hinklin (Undergrad.)

Postdoctoral Fellows and Visiting Scientists:

Dr. Cathy Scotto

Papers

See attached report

The objective of the project in the past two quarters was to develop unsupported, heterogeneous bimetallic catalysts for the hydrodenitrogenation (HDN) of liquids used as models of coal derived liquids and then to develop a homogeneous catalyst precursor designed to accomplish the HDN and liquefaction of coal in one step. The first of these objectives has been studied and the next part of the project will include studying the possibility of creating a homogeneous coal catalyst precursor that will perform the HDN and liquefaction of solid coal particles. Included in this report are the following, a description of the current reactions being performed, analysis of those reactions and future studies to be performed.

Experimental

Currently, studies of the HDN of three model compounds using three different catalysts are being conducted. The three compounds used to model products of coal liquefaction were tetrahydroquinoline (THQ), 2-propylaniline (PA), and propylbenzene (PB). The catalysts studied were the standard 1:11 ratio RuMo catalyst, a catalyst containing only Ru, and a catalyst containing only Mo. The catalysts had BET measured surface areas of 3.53 m²/g, 17 or 25 m²/g, and 7.30 m²/g, respectively.

Product analyses for the HDN studies were performed on a temperature programmed Hewlett-Packard 5890A reporting GC equipped with FID using a 12m x 0.53 mm x 2.65 μ m capillary column packed with 100 % dimethyl polysiloxane gum. The column heating schedule was initiated with a hold at 35°C (2 min) followed by ramping at 7°C/min to 250°C. The eluting gas mixture was H₂/He.

Formation of the Catalysts

For the preparation of each of the catalysts, one of the following reaction solutions listed below was syringed into a Parr General Purpose Bomb reactor. The catalyst containing only Ru was prepared by reacting 20 ml pre-catalyst solution (0.06g RuCl₃·xH₂O dissolved in 40 ml ethanol) and 100 μ l CS₂. The catalyst containing only Mo was prepared by reacting 10 ml pre-catalyst solution (0.100g Mo-HPA in 50 ml ethanol), 10 ml ethanol, and 100 μ l CS₂. The RuMo catalyst was prepared by the reaction of 8 ml pre-catalyst solution (Mo-HPA/EtOH), 2 ml pre-catalyst solution (RuCl₃·xH₂O/EtOH), 10 ml ethanol, 100 μ l CS₂. The reaction solution was then pressurized to 500 psig with N₂ at RT and depressurized. The process is repeated three times and then 600 psig H₂ at RT is added and the reaction is heated, with magnetic stirring at 180°C for one hour.

Chemical analyses of the catalysts are as follows:

	<u>Mo-HPA</u>	<u>RuMo</u>	<u>Ru</u>
SSA(m ² /g)	7.3	3.5	17.4
Mo (wt. %)	37.65	33.60	--
Ru (wt. %)	--	3.17	37.06
S wt %	33.53	34.16	29.71
M:S ratio	1: 2.7	1: 2.8	1: 2.5

HDN Reactions of Model Compounds

In each experiment, a low concentration of the model compound (1.59x10⁻³ mmol THQ, 1.42x10⁻³ mmol, or 1.43x10⁻³ mmol) and 10.0 mg of a catalyst (RuMo, Ru, or Mo) were added to a solution of 10

ml hexadecane, 20 μ l CS_2 , and 50 μ l decane as internal standard in a quartz lined, Parr General Purpose Bomb reactor with a 34 ml internal volume. The reaction solution was then pressurized to 500 psig with N_2 at RT and depressurized. The process is repeated three times and then 600 psig H_2 at RT is added and the reaction is heated, with magnetic stirring, to the desired temperature, 370°C. At time intervals of 1, 2, 3, 5, and 10 hours, the reactor is removed from the aluminum heating block, cooled under flowing water, depressurized and a .5 ml sample is then taken for later GC analysis.

Hexadecane is used as the solvent for the reaction. Decane is added as an unreactive internal standard used to calibrate the size of the peaks in the GC analysis. Carbon disulfide is added to show that the catalyst will function in the presence of sulfur. Resistance to poisoning by sulfur present during HDN is necessary for an effective catalyst.

These reactions were performed to analyze the mechanism of the HDN and to observe the differences in the behavior of the three catalysts.

The key products of the reactions are THQ (I) 2-propylaniline (PA, II), methylaniline, propylbenzene (PB, III), propylcyclohexadiene (PCD), propylcyclohexene (PCE) and propylcyclohexane (PCH). The numbers designate the three model compounds.

Analysis

Each of the samples taken was analyzed by gas chromatography. The analyses were organized on a spreadsheet. The integrated area of each peak was divided by the area of the standard (decane) peak and then normalized by dividing by the surface area. The resulting graphs gave display the number of moles per unit surface area vs. time of reaction.

From analyzing these graphs, conclusions can be drawn about the probable mechanisms of the reaction. The rate of disappearance of the starting compounds gives an indication of the rate and the change in rate of the formation of products over time.

In the majority of the reactions, the bimetallic RuMo catalyst is the most effective for HDN of THQ and propylaniline. From the chemical analysis, performed by Galbraith Laboratories, Inc., a ratio of 11 Mo: 1 Ru atoms form a complex in the standard RuMo catalyst. The RuMo catalyst appears to have a synergistic effect when compared to catalysts made of only one of the metals of the complex. In the reactions, the Ru only catalyst tends to break apart the carbon chain substituents on the ring. The ability of the Ru catalyst to break C-C bonds on the substituents of the hydrocarbon rings can be inferred from the products of the reactions. Analysis of the reactions performed with the model compounds, tetrahydroquinoline, 2-propylaniline, and propylbenzene are summarized:

Tetrahydroquinoline

The hydrogenation of THQ appears to reach an equilibrium in the reactions with each of the catalysts. This is clear from analysis of the chart below.

During the reaction, a relatively large amount of 2-propylaniline forms, some of which is converted to 2-methylaniline during the reaction.

Relatively small amounts of PCH, PB, and PCD form. These minor products appear to form approximately 4-5 hours into the reaction. For each of the compounds, the largest amount is formed in the presence of the RuMo catalyst. In the formation of PCH, 4-propylcyclohexene, and propylcyclohexadiene from decahydroquinoline, it is assumed that intermediates form, which cannot be isolated because of their instability. The instability is due to the easy with which the compound loses the amine group located at the number one position, adjacent to the propyl group.

2-propylaniline

In these reactions, the transformation of 2-propylaniline does not reach an equilibrium until a very small concentration remains. One of the major products, 2-methylaniline, forms at a constant rate. The RuMo catalyst continues to form 2-methylaniline up to 10 hours into the reaction.

2-methylaniline

The formation of PCH, PB, and 4-propylcyclohexene reaches equilibrium with each of the catalysts.

4-propylcyclohexene

Propylcyclohexane

Propylbenzene

Propylbenzene

From the reactions of PB with each of the catalysts, it is clear that only a small amount is converted to PCH under the conditions used. The RuMo catalyst leads to the hydrogenolysis of PCH faster than either of the mono-metallic catalysts. It hydrogenates, as the Mo catalyst is observed to do, as well as breaking C-C bonds in the propyl chain, which is typical of Ru catalysts. The H_2 hydrogenation activity is rather low when normalized for the high surface area, as shown in the following:

In future experiments, samples will be taken before the reaction is begun and immediately following, so the initial concentrations of the reagents can be recorded. This data will allow better assessment of the initial rates of reaction to be calculated.

Beause several of the reactions were observed to reach equilibrium, a technique for the removal of the products during the reaction would allow the full capabilities of the catalysts to be observed. Under the current reaction conditions, this is not possible (batch reactor), but development of a technique of a continuous feed reactor would prove helpful in analyzing the performance of the catalyst.

Several of the samples taken were analyzed by mass spectroscopy. From the resulting spectra, tabulation of the prominent peaks provided identification of the compounds present in the sample, which allows the determination of the mechanism of the catalyzed reaction.

Future Studies

After the studies on the Ru/Mo heterogeneous HDN of model compounds is finished, further studies will be performed. These studies will include analysis of the HDN of tetrahydroquinoline (DHQ). The development of a homogeneous catalyst precursor will also be studied. Solvent swollen solid coal

samples injected with the pre-catalyst solutions, used to form the heterogeneous Ru/Mo catalyst, will hopefully create a homogeneous catalyst precursor. A homogeneous catalyst precursor would conserve resources and time by allowing the liquefaction and HDN of coal to occur in one step.

**DATE
FILMED**

9 / 14 / 93

END