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^aRichard M. Laine, ^bThomas Stoebe

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^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

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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.

As determined in initial studies, the HPAs act as catalyst precursors rather than catalysts. That is, under useful liquefaction conditions, they decompose to form high surface area bimetallic catalyst particles. The chemical makeup and catalysis behavior of these novel particles was examined with several extremely surprising results. For example (see below), bimetallic CoMo HPAs provided catalyst particles that were no more active (for quinoline hydrogenation) than monometallic Mo catalyst particles, despite the well known fact that CoMo is frequently found to exhibit superior hydrotreating activity when compared to simple Mo based catalysts. The superior behavior is thought to arise because Co provides better hydrogenation activities.

Another surprise was that ruthenium/molybdenum RuMo bimetallic particles were found to exhibit synergistic catalytic behavior for a set of quite different reactions over a wide range of reaction conditions.

The exploration of the novel properties of these catalyst particles has followed a specific research plan, consisting of three major tasks: (1) Preparation of candidate bimetallic HPA precatalysts; (2) Studies on the decomposition of the precatalyst HPAs to well defined catalyst particles, and (3) studies directed towards delineating the catalytic reactivity patterns of the resulting particles under a set of well defined reaction conditions. The major efforts in each Task are briefly described in the following.

The studies on the preparation, decomposition and catalyst particle characterization are presented in the following chapter which includes the preliminary work published as a Fuel Preprint. Note that we provide an original manuscript and Figures for the preprint as this is of better quality than a photocopy. The catalytic activity patterns for a series of monometallic and bimetallic catalyst particles for quinoline hydrogenation are also described.

Chapter 1.

- a. "Heteropolyanions, Soluble Precatalysts for Quinoline Hydrogenation," S-M. Koo, M.L. Hoppe, Prepr. Am. Chem. Soc. Div. Fuel Chem. (1992) 37, 290-297.
- b. "Heteropolyanions as Precursors to Quinoline Hydrogenation Catalysts," S-M. Koo, D. Ryan, G. Huess, R.M. Laine, Energy and Fuels (1993) 7, 981.

Preprints - removed

Once the particles produced by hydrogenative decomposition of ethanol soluble, polyoxoanions, heteropolyoxoanions and bimetallic heteropolyoxoanions were physically characterized and their quinoline hydrogenation reactivity patterns determined; the next step was to examine **THQ** reactions at higher temperatures. Because the decomposition and **Q** hydrogenation reactions were studied primarily in EtOH, it was assumed that in higher temperature studies, the fresh catalyst particles would be generated *in situ* at the higher reaction temperatures; however, these studies demonstrated that the surface areas produced at higher temperatures were lower than obtained at the original 170°C decomposition temperatures. Because our objective is to generate highly active catalysts, it was decided that 170°C, EtOH generated catalyst particles would be the benchmark catalysts.

The first goal was to seek the lowest temperature where **THQ** could be observed to react, as an approach to identifying the most promising catalysts for future development. Thus, initial studies examined **THQ** reactivity at temperatures ranging from 200-250°C. The results of these studies were quite surprising. Rather than effect **THQ** HDN it was observed that all of the catalysts promoted N-ethylation of **THQ**. Furthermore, the RuMo catalysts were again found to offer the most active systems pointing to novel and wider scope synergistic effects. The details of these studies are presented in Chapter 2 of this report, which follows. Chapter 2 again contains the preliminary work, which was described in a Fuel Division Preprint, and then a full paper, published in J. Appl. Organometallic Chemistry.

Chapter 2.

- a. "Ethylation of Tetrahydroquinoline Using Ru/Mo Bimetallic Catalyst Precursors," S-M. Koo, D.Ryan, R.M. Laine, Prepr. Am. Chem. Soc. Div. Fuel Chemistry (1992) 37, 275-282.
- b. "Sulfided Heterogeneous, Bimetallic RuMo Catalysts Derived from Mixtures of $\text{Ru}_3(\text{CO})_{12}$ (or RuCl_3) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Reactions of EtOH with **THQ**," S-M. Koo, D. Ryan, R.M. Laine, Appl. Organomet. Chem. 6,437-448 (1992).

The observation of Mo, RuMo and Ru catalyzed ethylation of **THQ** made it obvious that true studies of **THQ** HDN could not be run in EtOH. Consequently, a decision was made to prepare larger quantities of catalysts ex-situ in EtOH, characterize these catalysts, and then perform **THQ** HDN studies in hexadecane solvent, a solvent we had previously used for our supported catalyst studies. This method proved to work quite well. We now report studies on the use of hexadecane solvent with undecane or decane as the GC standard. The catalysts used are the same as prepared in bulk quantities for the ethylation studies. The following studies were run using a MoS_x catalyst with a BET determined surface area of 7.3 m²/g. Likewise, the RuMoS_x catalyst was found to have a specific surface area (SSA) of 3.5 m²/g. Preliminary comparative studies were performed with a RuS_x with a SSA of ≈ 17 m²/g.

Experimental

These reaction conditions typically involved the addition of a known amount of **THQ**, propylaniline, or propylbenzene to a hexadecane solution containing a known amount of decane or undecane as an internal standard for GC analysis.

For example, RuMo catalyst particles with 1:11 Ru:Mo, generated under conditions identical to the Q hydrogenation reactions, at 175°C, but in the absence of Q, as noted in chapter 1 were used. Studies were done with two 250 mg batches of catalyst which were mixed to obtain a uniform catalyst.

Product analyses for all the kinetic studies were performed on a temperature programmed Hewlett-Packard 5890A reporting GC equipped with FID using a 12 m 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 (4 min) followed by ramping at 5°C/min to 100°C and then at 40°C/min to 250°C. The eluting gas mixture was H₂/He.

GC-MS studies were performed using an HP 5890 Series II GC, an HP 5970 mass spectrometer, and the HP 5940 MS Chemstation. The capillary column used for product separation was a 12 m x 0.12 mm x 0.33 μ m film thickness HP-5 (crosslinked 5% phenyl methyl silicone) capillary column. The temperature for the analysis was held at 50°C for 5 min, then ramped at 4°C/min to 275°C. The eluting gas used was H₂/He. < ?

THQ HDN Kinetic Runs

Typically, 18-20 mg of catalyst are added to a solution of 1.0 ml (8.5 mmol) of **THQ** (or mmol equivalents of **PA**, or **PB**) mixed with 9.0 ml of hexadecane and 50 μ l of decane as internal standard in a quartz lined, Parr General Purpose Bomb reactor with a 34 ml internal volume. The reaction solution is then pressurized to 400 psig with N₂ at RT and depressurized. The process is repeated and then 400 psig with H₂ at RT is added and the reaction is heated, with magnetic stirring, to the 370°C for the studies shown below. At the appropriate times (typically 0, 10, 20, 30, 60 and 300 min) the reactor is cooled in flowing water, depressurized and a sample is taken for GC analysis. The reactions are run to less than 25% conversion so that the initial rates of product formation correspond essentially to zero order in reactant concentration. Note that the reaction times used here are much shorter than used at lower temperatures as the rates of reaction are relatively high.

The work reported in the following pages was fraught with analytical problems that required 4 months to resolve and were a consequence of a distorted gold leaf disc located (hidden) in the GC injection system that led to irreproducible results. Hewlett Packard was able to fix this problem but only after a significant

effort was made in-house to troubleshoot the problem.

THQ HDN produces a wide variety of primary, secondary and tertiary products including decahydroquinoline, propylaniline, propylbenzene, propylcyclohexene, and propylcyclohexane as shown in the following HDN network:

To best characterize the catalytic reactivity patterns of each type of catalyst with each component of the reaction network, we sought to examine the reactivities of the individual catalysts with selected components of the above reaction network. Thus, we examined the reactivities of the RuMo and Mo sulfided catalysts for: (1) HDN of **THQ**, (2) propylaniline-**PA**, and (3) propylbenzene-**PB**.

In general, the reactivity of the RuMo catalyst for effecting specific types of reactions was higher than that found for the Mo catalyst. Initial studies with the Ru catalyst alone suggest that it has relatively lower reactivities than either the RuMo or Mo catalysts. A more complete study can only be completed after this final report has been submitted.

The exact reactivities for each catalyst were determined by selecting individual components of the above **THQ** HDN reaction network to determine their particular reactivity patterns with the two types of catalysts. In the following sections, we present some of our primary findings about product disappearance rates and formation rates [as $TFs = (\text{moles reacted or formed})(\text{sec} \cdot \text{m}^2/\text{g})^{-1}$] for disappearance and appearance for selected products as shown in the series of schematics.

We are particularly interest in the reactivity pattern of propylbenzene as it (1) represents aromatics in coal liquefaction, (2) is a sink for hydrogen and (3) thereby controls to some extent H_2 consumption during hydrotreating:

Propylbenzene Hydrogenation

Note that this study is incomplete in part because of the problems with the GC and in part because only one undergraduate has been working on the project part-time.

The primary observation is that **PB** hydrogenation by both catalysts ($TFs = -6.4x$ and $1.5E-9$ for RuMo and Mo respectively) are comparable to the **PB** appearance rates found during **PA** HDN as shown in the following network fragment:

Reactions of Propylaniline

Recall that these appearance rates are still concentration dependent and the disappearance rates measured are for relatively high concentrations by comparison with quantities of **PB**, that will form during **PA** and **THQ** HDN. Thus, we do not need to consider them in discussions that concern the reactivity profiles of the various products formed in these last two processes.

In the **PA** HDN studies the primary products formed are those commonly observed, **PB**, **PC** (propylcyclohexene) and **PCH** (propylcyclohexane). The **RuMo** catalyst exhibits slightly less than 2 x the activity of the **Mo** catalyst for HDN of **PA**, as might be predicted based on the lower temperature Chapters 1 and 2 studies. The **PB:PC:PCH** product selectivities for both catalysts are:

$$\begin{array}{lcl}
 \text{RuMo} & \text{PB:PC:PCH} & = \begin{array}{ccc} .4 & .5 & .1 \\ 3.2 : 4.7 : 1.1 \end{array} = 9.0 \\
 \text{Mo} & \text{PB:PC:PCH} & = \begin{array}{ccc} .4 & .4 & .2 \\ 1.7 : 1.8 : 0.9 \end{array} = 4.4
 \end{array}$$

These results are quite interesting for two reasons, the product selectivities are nearly identical, however, the **RuMo** rates are ≈ 6 times higher based on **PA** disappearance and 2 times higher based on rates of product appearance; however, we have not included several minor products in detailing the product selectivity pattern. We conclude that the rate differences are real.

We have also begun to examine the complete **THQ** HDN process and find that (see complete HDN network above) **THQ** rates of disappearance for **RuMo** (2.5×10^{-8}) and **Mo** (1.3×10^{-8}) are 50% higher than the rates of product appearance. The selectivities to two of the expected products, **Q** and **PA**, are 15:1 for **RuMo** and 5.5:1 **RuMo** respectively, these are what might be expected based on the similarity in the **PA** studies. These will have to be examined in more depth at a later date.

Recall that both catalyst systems use approximately the same amount of metal, but the **RuMo** system replaces 0.08% of the total **Mo** with some **Ru**. Thus, there appears to be an increase in reactivity obtained by including **Ru** in the system. This is still better than expected based on **Ru** baseline studies presented in our recent Fuel Preprint--see Chapter 3, below.

The obvious general conclusion that can be made is that like all of the other reactions studied, the **RuMo** catalyst exhibits more activity than a simple **Ru** or **Mo** catalyst made from essentially the same starting materials. This points to a rather broad synergistic behavior for this bimetallic catalyst. At this time, it is not possible to delineate all of the important features of the **RuMo** sulfided catalyst; however, in the opinion of this research group, there is much to be learned through continued exploration of this catalyst system for HDN, HDS and HDO.

We thank the DOE/PETC for generous support and patience during the performance of this work.

A portion of the above work was published as Chapter 3.

3. "Bimetallic **Ru/Mo** Catalyst Particles for HDN of Tetrahydroquinoline," D.B. Ryan, T. Hinklin, G. Heuss, S.-M. Koo, R.M. Laine, Prepr. Am. Chem. Soc. Div. Fuel Chemistry, (1993) 38, 542-545.

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