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Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts

Quarterly Report No. 8

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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 temperature. 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 H₂ consumption using quinoline as a model substrate. Solvent will be hexadecane and/or H₂O. 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 (H₂ or CO/H₂O) and temperatures on conversions, H₂ consumption and the quality of the coal liquids will be used to evaluate catalyst ability.

Progress For Eighth Quarter

In this quarter, we spent considerable efforts to prepare the [PRuMo₁₁O₃₉]⁴⁻ cluster to test its properties vis a vis the properties of the bimetallic, RuMo catalysts made by mixing stock solutions of the two metals. The procedure used is that noted in the paper by C. Rong and M. T. Pope in J. Am. Chem. Soc. **114**, 2932-2938 (1992). To our surprise, the catalyst particles prepared using the bimetallic HPA gave essentially the same size particles and activities as those found for the mixed metal systems. In reflection, this is not as surprising as it might seem given that our studies on the optimum ratios of Ru to Mo for catalyst activity give a roughly 1:9 ratio. This may correspond to the preformation of the RuMo-HPA. We will need to undertake further work on this subject.

During this period, we also used our two high temperature heating systems to explore the utility of the RuMo bimetallic catalyst for catalysis of tetrahydroquinoline (THQ) HDN. We now find that we can indeed make the catalyst work as an HDN catalyst. We have had to revamp the GC analysis methodology because of the new set of products that we are now getting. This has taken some time as Mr. Dan Ryan, the graduate student on the project has left to become an officer in the Air Force.

Future Work

We anticipate conducting detailed studies on THQ HDN in the following two quarters.

Personnel Working On the Project this Quarter:

Students:

Mr. Daniel Ryan

Mr. Tom Hinklin (Undergrad.)

Postdoctoral Fellows and Visiting Scientists:

Dr. Sang-Man Koo

Dr. Brian Mueller

Papers

One paper, entitled: " Sulfided heterogeneous, bimetallic Ru/Mo catalysts derived from....) was published. ~~A copy is attached.~~ *Applied Organometallic Chemistry, 1992, v. 6, 437-448.*

Edited Journal

Volume 6, issue 5 of the Journal of Applied Organometallic Chemistry consists of six papers on modeling hydrotreating catalysis. This issue was edited by R. M. Laine.

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