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Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts

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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°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. $[EM_{12}O_{40}]^{4-}$ 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 $pK_a \approx 0\text{-}2$.[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 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 of 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 Fifth Quarter

In this quarter, standard reaction conditions for characterization of quinoline (**Q**) hydrogenation at low temperatures (<250°C) were completed and culminated in a paper being submitted to J. Catalysis (see Appendix 1). Construction of a high temperature heater for studies at temperatures >250°C) was initiated. Efforts towards establishing baseline reaction conditions for tetrahydroquinoline (**THQ**) hydrodenitrogenation (**HDN**) were begun.

As will be discussed in the following sections, we have determined that in ethanol solution, at 225°C, **THQ** does not undergo HDN reactions when exposed to the bimetallic Mo-HPA/Ru precatalyst system found to be exceptionally active for **Q** hydrogenation. Surprisingly, this catalyst does effectively promote the ethylation of **THQ** directly to N-ethyl-**THQ**. Indeed, the bimetallic catalyst significantly outperforms the individual Mo-HPA and Ru precatalysts. This side reaction could hamper efforts to hydrotreat coal, coal liquids and petroleum materials.

Experimental Section

General Methods. Quinoline (Q) was purchased from Aldrich and distilled from CaH_2 under N_2 before use. 1,2,3,4-tetrahydroquinoline (**THQ**) was purchased from Fluka and used without further purification. Absolute ethanol was used as received. Molybdophosphoric acid ($H_3PO_4 \cdot 12MoO_3 \cdot xH_2O \equiv H_3PMo_{12}O_{40} \cdot xH_2O$, Mo-HPA) and $Ru_3(CO)_{12}$ were purchased from Strem Chemicals and used as received. $RuCl_3 \cdot xH_2O$ (x=1-3) was obtained from Johnson Matthey Electronics and stored in a Dri-Box under N_2. Stoplight compound, $(NH_4)_6[Co_2Mo_{10}O_{38}H_4] \cdot 7H_2O$, was prepared as described elsewhere.[11] Phosphotungstic acid ($H_3PW_{12}O_{40} \cdot xH_2O$, W-HPA), ammonium metavanadate (NH_4VO_3), and ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] were purchased from Aldrich, British Drug House Ltd., and Allied Chemical Company, respectively and used as received.

Analytical Procedures. Product analyses for all the kinetic studies were performed on a temperature programmed[12] Hewlett-Packard 5890A reporting GC equipped with FID using a 5 m x 0.53 mm x 2.65 μm capillary column packed with 100 % dimethyl polysiloxane gum.

General Reaction Procedures for Kinetic Studies. Stock solutions of Mo-HPA were prepared before use by dissolving 0.1 g (5.5×10^{-2} mmol) of molybdophosphoric acid (Mo-HPA) in 50 mL of ethanol to form a 1.1×10^{-3} M solution. In a typical reaction for bimetallic catalyst precursors, an amount of stock solution (e.g. 4 mL) containing 4.4×10^{-3} mmol of Mo-HPA ,and 1 mL (5.7×10^{-3} M, 5.7×10^{-3} mmol) of stock solution of $RuCl_3 \cdot xH_2O$ [prepared by dissolving 0.06 g (0.23 mmol) of $RuCl_3 \cdot xH_2O$ in 40 mL of absolute ethanol] and 5 mL (0.04 moles) of **THQ** are placed in a magnetically stirred, 34-mL quartz lined, bomb reactor with 50 μL of CS_2. For monometallic catalyst precursors, 1 mL of $RuCl_3 \cdot xH_2O$ stock solution and 4 mL of EtOH or 4 mL of Mo-HPA stock solution and 1 mL of EtOH were used. The reactor was sealed and degassed via three pressurization/depressurization cycles using 1000 psig N_2 and H_2 and then pressurized to the desired pressure (**1000 psig or 400 psig**) with H_2. The reactor was heated in an oil bath thermostatted to ± 2°C of the appropriate temperature (**220°C**), and samples were taken at selected times by cooling the reactor in cold water bath, depressurizing, and removing a 0.1 mL sample. The reaction was then restarted following the above procedure. In all of the experiments described throughout this report, the reported H_2 gas pressures are presented as psig, at room temperature.

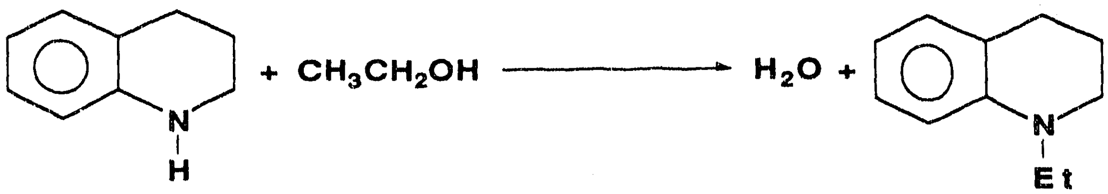
GC-MS studies for product of bimetallic catalyst precursor at 1000 psig H_2 after 48 % product conversion were performed using an Finnegan Quadrapole, ion trap instrument. The temperature program used was: 50°C for 2 min, 15°C/min ramp to 275°C as the final temperature. The elution gas used was H_2/He.

Catalyst Activity. In all instances, catalyst activity is measured as a function of the turnover frequency (TF). TF is defined as: No. moles of product (N-Et-**THQ**)/total moles of metal (or moles of precatalyst where noted)/ hour. Activities were always determined based on less than 25% conversion of **THQ** to **N-Et-THQ**. Thus, no falloff effects were included in the TF calculations.

Results and Discussion

The purpose of the work carried out this quarter was to establish whether or not the superior catalyst system developed for **Q** hydrogenation to **THQ**, would also be capable of promoting **THQ** HDN at low temperatures. We have previously shown that bimetallic (Ru/Mo) and trimetallic (RuCoMo) organometallic derived supported catalysts were capable of promoting HDN at temperatures of 350°C.[5,6] Thus, we were interested in determining whether or not the currently developed, unsupported bimetallic catalysts would have sufficient activity to work at 220°C, the highest temperature that we can safely work with using our silicone oil heating baths. This work was done as a bridge study while we finish constructing a high temperature heating system.

The preliminary results of this study are quite surprising and warrant further, more detailed studies. First, we find that **THQ** does not undergo HDN to products such as propylaniline, propylbenzene, propylcyclohexane, nor is it hydrogenated to decahydroquinoline. However, it does undergo a surprising reaction with the ethanol solvent wherein the nitrogen is ethylated according to the following reaction:



At 220°C, this reaction goes to 50% completion in 25 h at 1000 psig H_2 using the standard bimetallic catalyst (4 mL stock solution Mo-HPA:1 mL stock solution $RuCl_3$, 50 µL CS_2; see experimental and Appendix) as shown in Figure 1. *What is extremely surprising about this reaction is that when this same reaction is run either with 4 mL of Mo-HPA stock solution or only 1 mL of $RuCl_3$ stock solution, that is where no synergistic effect is possible, almost not product is observed (see Figure 2).* In the baseline tests, the Mo-HPA derived catalyst appears to function somewhat better than the $RuCl_3$ derived catalyst. Apparently, it is necessary to have the bimetallic catalyst form in order to observe ethylation.

Another unexpected, but not surprising, result comes from the observation that dropping the initial H_2 pressure from 1000 psig to 400 psig does not effect the rate of reaction at all (see Figure 3). At least under the two pressures measured, it appears that H_2 pressure plays no role in the rate limiting step. Based on our previous work in this area, we can suggest a mechanism that explains this observation:[14]

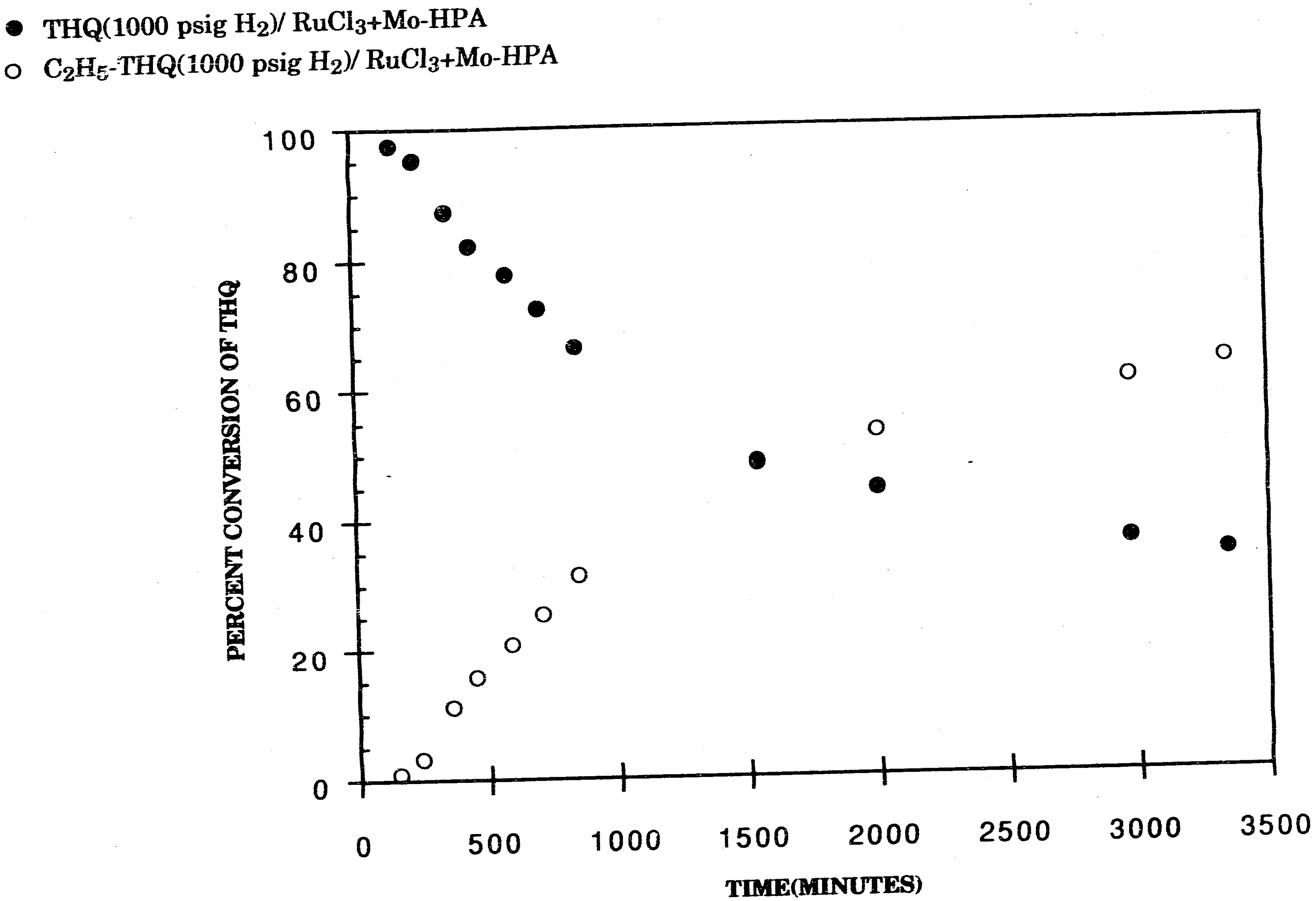


Figure 1. Percent Conversion of THQ to Et-THQ using Bimetallic Catalyst Precursors at 1000 psig H_2 and 220 °C.

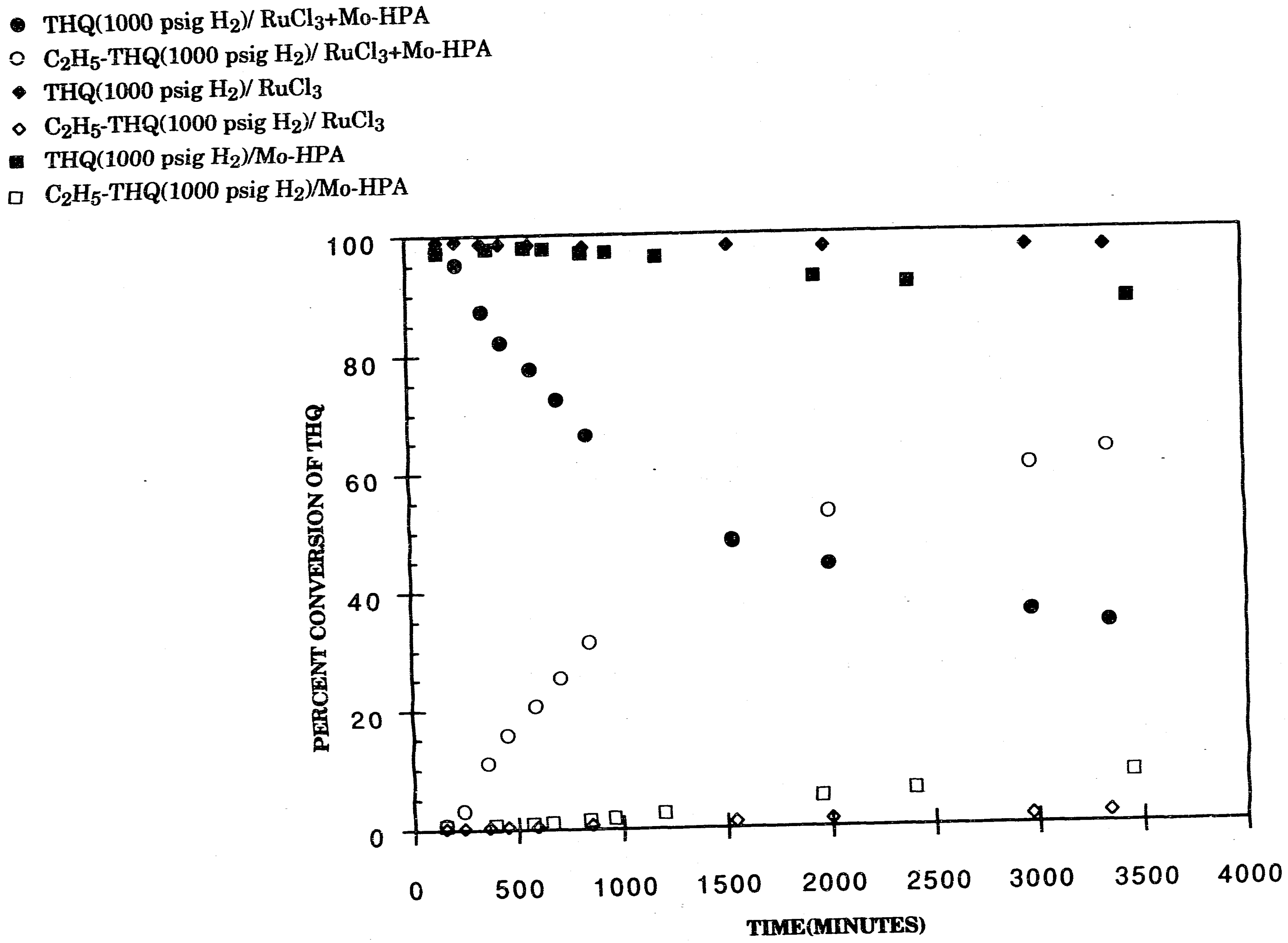


Figure 2. Percent Conversion of THQ to Et-THQ using several Catalyst Precursors at 1000 psig H_2 and 220 °C.

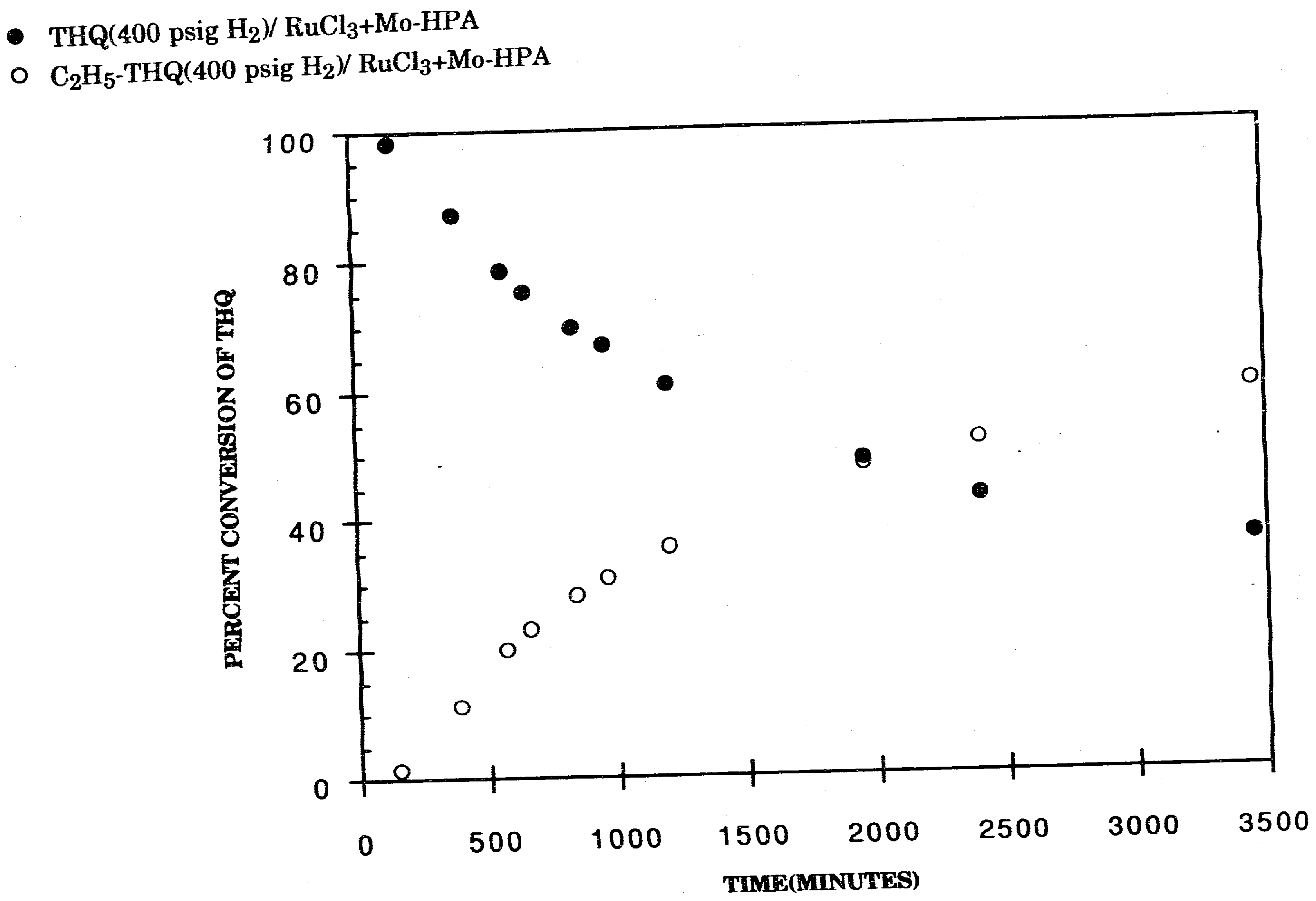
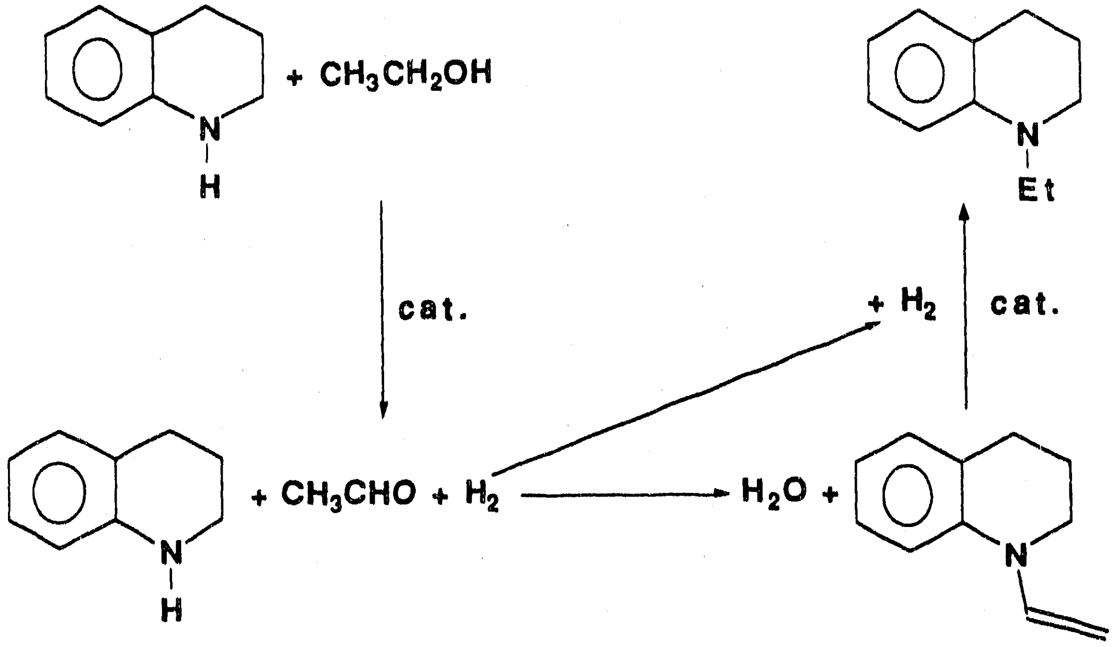


Figure 3. Percent Conversion of THQ to Et-THQ using Bimetallic Catalyst Precursors at 400 psig H_2 and 220 °C.



In the above reaction scheme, the first step involves dehydrogenation of ethanol to form acetaldehyde which reacts readily with **THQ**, to form the enamine shown in the lower right hand corner. Enamines are very susceptible to hydrogenation. Thus, once formed the enamine is very susceptible to conversion to **Et-THQ**.

Typically, the dehydrogenation step is the slow step. In addition, one would normally consider it to be sensitive to H_2 pressure. The fact that the reaction is not H_2 pressure sensitive suggests either that we are running the reaction under pseudo-first order conditions with respect to H_2 pressure--or another step is rate limiting. We will have to determine this in the future.

One possible conclusion as to why the bimetallic system is so much better than the individual metals is that one metal does one of the above catalytic operations well and the other poorly. The second metal then does the the first operation poorly and the second well. If this is the case, then from our hydrogenation studies, we would conclude that Mo catalyst sites are responsible for dehydrogenation and the Ru catalyst sites are responsible for hydrogenation. This again will be work planned in the next quarter.

If the Mo sites are indeed responsible for dehydrogenation, then the above observed ethylation reaction is of importance for several reasons: (1) it is the first example wherein sulfided Mo catalysts promote dehydrogenation of alcohols; (2) alkylation of amines by alcohols may occur during hydrotreating, and (3) it represents another example of a synergistic interaction between Mo and Ru.

Point number 2 deserves further discussion. In hydrotreating crude oil, oil shale and coal liquids; it is certain that primary and secondary alcohols will form during the process. Given that standard HDN catalysts contain sulfided Mo sites and Co sites, it is likely that these intermediate alcohols will alkylate any amine sources produced coincidental. Although, Co is not as good a hydrogenation catalyst as Ru, at the elevated temperatures currently used for hydrotreating, it is possible that alkylation will occur quite readily.

Because the resulting amines will be more alkylated, it then becomes that much harder to remove the nitrogen centers that are catalyst poisons for reforming catalysts. Clearly, it is of importance to understand this reaction to develop an understanding of the consequences of its occurrence in coal liquefaction and hydrotreating studies.

Future Work

As noted in the last paragraph in the previous section, it appears quite worthwhile to develop a more in-depth picture of the THQ ethylation reaction. Thus, we plan to undertake more detailed studies of the order of those described in the Appendix. Thus, we will:

- verify the H_2 pressure independence at lower pressures,
- develop a clearer understanding of the metal concentration dependencies, and
- examine the use of different solvents with EtOH, e.g. CH_3CN

We will also continue efforts to get our high temperature heating units online to explore HDN reactions of **THQ** with the bimetallic catalysts. Following successful implementation, we will pursue coal liquefaction and hydrotreating with Wyodak coal.

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12. The conditions for the GC heating program used in this study are: Initial temperature; 35°C, initial time; 30 sec., final temperature; 180°C, Final time; 1 min., Rate; 15 deg./min, oven temperature; 35°C, injection temperature; 200°C, detector temperature; 250°C, equilibrium time; 1 min.
13. k_{obs} at each temperature is obtained from the slope of the equation, $d[THQ]/dt = k_{obs}[Q]^{o}$, assuming zero order reaction from data obtained. The activation energy, E_a, is calculated from the expression $k_{obs} = Ae^{(-Ea/RT)}$.
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