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Acknowledgements

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Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts

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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.

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 Sixth Quarter

In this quarter, standard reaction conditions for characterization of tetrahydroquinoline (THQ) ethylation at $220^\circ C$ were almost complete. The results of these studies are detailed in the draft manuscript attached that will be sent to the Journal of Applied Organometallic Chemistry (see Appendix). Construction of a high temperature heater for studies at temperatures ($>250^\circ C$) is progressing. Efforts towards establishing baseline reaction conditions for tetrahydroquinoline (THQ) hydrodenitrogenation (HDN) were begun.

The majority of the work completed in this quarter is detailed in the attached draft manuscript. As such, it is incorporated here as the primary part of the report.

Future Work

As noted in the Appendix, it appears quite worthwhile to develop a more in-depth picture of the THQ/Q ethylation. We are particularly intrigued by the alkylation of Q with ethanol as this may prove to serve as a model system for a novel, inexpensive way of alkylating coal and thereby solubilizing it. Thus, we plan to undertake more detailed studies of the order of those described in the Appendix for THQ ethylation. Thus, we will:

- verify the products derived from the reaction
- develop a clearer understanding of the HPA concentration dependencies, and
- examine the use of different solvents e.g. iPrOH

We anticipate finishing the high temperature heater this next quarter. Thus, we plan to explore HDN reactions of THQ with the bimetallic catalysts. Following successful implementation, we will pursue coal liquefaction and hydrotreating with Wyodak coal.

**Heterogeneous, Bimetallic RuMo Catalysts Derived from Mixtures of
 $\text{Ru}_3(\text{CO})_{12}$ (or RuCl_3) and a Molybdenum Heteropolyanion.
The Reactions of Ethanol with Tetrahydroquinoline.**

Sang-Man Koo, D. Ryan, and R. M. Laine*

The Department of Materials Science and Engineering and
the Department of Chemistry, University of Michigan,
Ann Arbor, MI 48109-2136

Abstract:

Efforts have been made to develop ruthenium/heteropolyanion catalysts for HDN of tetrahydroquinoline. In the process of these studies, it was discovered that the use of ethanol (EtOH) as solvent leads to a set of very unusual products. In a hydrogen atmosphere, the products obtained show no relation to those expected for HDN, instead the bimetallic catalyst promotes N-ethylation of THQ to form N-Et-THQ. The reaction does not go very effectively if either the Ru precursor [RuCl_3 or $\text{Ru}_3(\text{CO})_{12}$] or the Mo heteropolyanion are used separately in an attempt to catalyze the same reaction. Only when a bimetallic system is created is effective catalysis observed.

In the absence of hydrogen, the reaction proceeds such that THQ is converted to Q, Q-Et, Q- C_3H_7 , Q- C_4H_9 , Q- C_6H_{13} and N-Et-THQ. These results are possibly the result of HPA acting as a strong acid catalyst to promote alkylation of dehydrogenated THQ.

Introduction:

We have previously shown that "surface confined" bi- (RuMo) and trimetallic (RuCoMo), heterogeneous catalysts prepared using organometallic precursors show exceptional activity for hydrodenitrogenation (HDN) of quinoline.¹⁻⁵ Typical "surface confined" RuMo and RuCoMo catalysts were found to produce almost equal quantities of propylbenzene and propylcyclohexane (350°C/100 psig H₂) as opposed to "surface confined", sulfided CoMo catalysts where the ratio is that typical of commercial catalysts: 1:18 propylbenzene to propylcyclohexane (350°C/100 psig H₂). The RuMo and RuCoMo catalysts were found to be sulfur tolerant and actually exhibited enhanced activity in the presence of sulfur containing species (CS₂ or H₂S). While this was exceptional behavior for quinoline (Q) HDN, it could not be translated to improved catalysis of HDO or for HDN under coal liquefaction conditions.⁵ Catalyst activities for HDN of a Wyodak coal were the same (on a per mole of metal basis) for "surface confined", sulfided RuCoMo, CoMo and a commercial CoMo catalyst.

We believe that the reason that the exceptional behavior in the modeling studies does not translate to coal arises because coal is actually a three-dimensional, crosslinked polymer and the use of a supported heterogeneous catalyst will be transport (diffusion) limited in its reactivity. That is, the rate of reaction is most likely dependent on the rate at which the coal molecules diffuse to the heterogeneous catalyst surface. As a consequence, it is possible that the product distributions obtained in the coal studies are thermodynamically controlled whereas in the model studies, kinetic control exists.

To remedy this problem, we are seeking to develop unsupported, homogeneous HDN (and liquefaction) catalysts that will not be diffusion limited. Alternately, we seek to develop homogeneous precatalysts that can be introduced to solvent swollen coal polymer and generate very small, active heterogeneous catalyst particles within the coal, again defeating the diffusion limitation problem. To this end, we are exploring the use of heteropolyanion (HPA) catalysts modified by the introduction of ruthenium containing species.

We are simultaneously attempting to develop a detailed understanding of the nature of the synergistic behavior of RuMo catalysts, with respect to what steps in the HDN process are enhanced by the bimetallic system.

We have recently described a survey study wherein the HPAs: H₃PMo₁₂O₄₀ (**Mo-HPA**), H₃PW₁₂O₄₀ (**W-HPA**), (NH₄)₆[Co₂Mo₁₀O₃₈H₄]·7H₂O and the polyoxoanions, (NH₄)VO₃ and (NH₄)₆Mo₇O₂₄·6H₂O were screened for catalyst activity for hydrogenation of quinoline (Q) to tetrahydroquinoline (THQ) under a set of standard conditions.^{6,7} The activities of these precatalysts, in the presence of added Ru₃(CO)₁₂ and RuCl₃, were also studied. It was found that all of the precatalysts are activated by conversion to heterogeneous, submicron sized particles. Of the systems screened, the Mo-HPA/Ru bimetallic catalysts exhibited enhanced Q hydrogenation activities relative to the other catalysts and with respect to catalysts generated from the individual metal precatalysts Mo-HPA or Ru₃(CO)₁₂/RuCl₃.

These studies led to the conclusion that the synergy obtained with bimetallic RuMo catalysts de-

rives at least in part from enhanced hydrogenation of **Q**. However, the improved ratios of propylbenzene to propylcyclohexane described above must also come from better activation/cleavage of the C-N bonds in **THQ** relative to the hydrogenation of **THQ** to decahydroquinoline;^{3,4} otherwise, the product ratios would be those obtained from typical sulfided CoMo catalysts. Consequently, it is important to delineate the mechanisms whereby RuMo promotes C/N bond cleavage and activation. It is also important to understand the interactions of the nitrogen center with catalyst sites.

The following study was originally designed to examine, at minimum temperatures, the activation of the C-N bond in **THQ**, using the Mo-HPA /ruthenium catalyst systems. However, several unusual reactions of potential importance to coal catalysis chemistry were observed,^{6,7} that warranted further study. These reactions include the ethylation of **THQ** and **Q** with ethanol as suggested by the following reactions.

The emphasis of the work reported here is on reaction (1). We will only provide preliminary data on reaction (2), which will be explored in-depth in a later paper.

Experimental

General Methods. 1,2,3,4-tetrahydroquinoline (**THQ**) was purchased from Fluka and used without further purification. Absolute ethanol was used as received. Molybdophosphoric acid (Mo-HPA, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) and $\text{Ru}_3(\text{CO})_{12}$ were purchased from Strem Chemicals. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ($x=1-3$), obtained from Johnson Matthey, was stored in a Dri-Box under N_2 . Catalysts were used as received.

Analytical Procedures. Product analyses for all the kinetic studies were performed on a temperature programmed⁸ 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. Stock solutions of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were prepared by dissolving 0.06 g (0.23 mmol) of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in 40 mL of absolute ethanol to form a 5.74×10^{-4} M solution. Alternately, stock solutions of $\text{Ru}_3(\text{CO})_{12}$ were prepared by dissolving 0.05 g (0.078 mmol) of $\text{Ru}_3(\text{CO})_{12}$ in 40 mL of absolute ethanol to give a 1.96×10^{-4} M solution. In a typical reaction, using a bimetallic precatalyst system, an amount of stock solution (e.g. 4 mL) of Mo-HPA, and 1 mL of

stock solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, or of $\text{Ru}_3(\text{CO})_{12}$ 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 $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ stock solution, or 1 mL of $\text{Ru}_3(\text{CO})_{12}$ 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 or H_2 and then pressurized to the desired pressure with H_2 . The reactor was heated in an oil bath thermostatted to $\pm 2^\circ\text{C}$ of the appropriate temperature (220°C in the current studies). Samples were taken at selected times by cooling the reactor in cold water, depressurizing, and removing a 0.1 mL sample. The reaction was then restarted following the above procedure. In all experiments described throughout this report, the reported H_2 gas pressures are presented as psig, at 20°C .

Procedure A. In the H_2 pressure and temperature studies, 4 mL of the stock Mo-HPA solution, 1 mL of Ru stock solution, and 5 mL (39.7 mmol) of **THQ** were used with 50 μL of CS_2 .

Procedure B. A slightly modified version of Procedure A was used to explore the effects of variations in Ru/Mo-HPA and **THQ** concentrations on **THQ** ethylation rates. In these studies, the concentrations of bimetallic catalyst or added **THQ** was varied over a selected range (see below).

GC-MS. Studies to identify products formed in the reaction run with bimetallic precatalyst at 0 and at 1000 psig H_2 after 50% product conversion were performed using an Finnegan Quadrupole, ion trap instrument. The temperature program used was: 50°C for 2 min, $15^\circ\text{C}/\text{min}$ ramp to 275°C as the final temperature. The elution gas used was H_2/He . The 1 mL to 4 mL $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ (1:4) system was used for these studies.

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

H_2 Pressure Studies. These reactions were run according to procedure A. The reactor was charged with H_2 using pressures from 0 to 1000 psig (at room temperature). The reaction temperature was held constant at 220°C .

Bimetallic Precatalyst Concentration Studies. Reactions were run as described for procedure B. Experiments were conducted in ethanol using initial H_2 pressures of 600 psig. The reaction temperature was held constant at 220°C . Total concentrations of $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ were varied between $5.91 \times 10^{-4} \text{ M}$ and $8.92 \times 10^{-4} \text{ M}$ with total reaction volumes of bimetallic precatalyst solution maintained constant at 5 mL. Typically, a known volume (e.g. 1.0 mL) of the $\text{Ru}_3(\text{CO})_{12}$ stock solution was syringed into the reactor, followed by Mo-HPA stock solution (4.0 mL) to maintain constant solvent volume of catalyst solution, and then 5.0 mL of **THQ**.

THQ Concentration Studies. Reactions were run as in the catalyst concentration studies with the exception that the total concentration of $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ was held constant at $6.34 \times 10^{-4} \text{ M}$. **Q** concentrations were varied from 0.79 to 3.97 M. In these instances, additional ethanol was added to The 1 mL to 4 mL $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ (1:4) system was used for these studies.

Temperature Studies. Reactions were run as in the H_2 pressure studies with the exception that the initial H_2 pressure was held constant at 600 psig. Rates were recorded at 220, 235, and 250°C , the range

bounded at low temperature by minimal catalyst activity and at the upper temperature by the flammability/decomposition temperature of the oil baths ($\approx 250^{\circ}\text{C}$).

Results and Discussion

The original object of the studies conducted here was to establish the minimum temperature at which the HPA derived catalysts could promote **THQ** HDN. In this way, modifications to the catalyst system (e.g. by substituting different types of HPAs) that generated significant improvement in HDN catalysis would be immediately obvious. Because our previous studies were conducted in EtOH, the use of EtOH for the current studies was a natural extension.

The nature of the catalytic reaction.

Although, the conditions used in the current study are nearly identical to those used in the **Q** hydrogenation studies, with the exception that the standard reaction temperature was 220°C and **THQ** is used as the substrate in place of **Q**, the products isolated are quite unexpected. Products resulting from HDN are not observed; rather, reaction (1) is observed to occur. At 220°C , reaction (1) goes to 40% completion in 25 h at 1000 psig H_2 using two bimetallic precatalyst systems (4 mL EtOH stock solution, 5.5×10^{-5} M in Mo-HPA and 1 mL of stock solution, 5.5×10^{-6} M in RuCl_3 or 1.96×10^{-6} M in $\text{Ru}_3(\text{CO})_{12}$, 50 μL CS_2) as shown in Figures 1 and 2. What is extremely surprising about this reaction is that when it is run either with 4 mL of Mo-HPA stock solution or only 1 mL of RuCl_3 [or $\text{Ru}_3(\text{CO})_{12}$] stock solution, where no synergistic effects are possible, almost no product is observed. In baseline tests (Figures 1 and 2), the Mo-HPA derived catalyst appears to function slightly better than the RuCl_3 derived catalyst [or nearly the same as $\text{Ru}_3(\text{CO})_{12}$]. Apparently, it is necessary to form a bimetallic catalyst in order to observe ethylation.

Insert Figures 1 and 2

THQ concentration studies.

The pattern of reaction of **THQ** is nearly identical to that found for **Q** hydrogenation. The results shown in Figure 3 indicate that under the reaction conditions studied, the rate of **THQ** ethylation is not linearly dependent on initial **THQ** concentration. The turnover frequency reaches its maximum ($\text{TF} = 62$) at $[\text{THQ}] = 1.59$ M using the 1 mL to 4 mL $\text{Ru}_3(\text{CO})_{12}$ /Mo-HPA precatalyst system. There are two likely explanations for the observed behavior, especially the decreases in activity with increasing **THQ** concentration. One is that at these high concentrations, **THQ** competes successfully with EtOH for active catalyst sites, thereby slowing the rate of ethylation. The second explanation is that at these high **THQ** concentrations, the composition of the reaction solution is considerably changed--there is much less EtOH. Consequently, the solubility of **THQ** or the solvation of the precatalyst changes and the surface area of the active catalyst produced is diminished thereby reducing overall catalyst activity. In this instance, it is likely that **THQ** is competing for the active catalyst sites given the fact that at 0 psig H_2 it undergoes dehydrogenation at reasonable rates (see below).

Insert Figure 3

Activation Energy. Initial rates of reaction were determined for each temperature from 220 to 250°C with initial H_2 pressures of 600 psig. Raw reaction rate data are used to calculate initial TFs which are used as k_{obs} .⁹ These data allow us to calculate the energy of activation, $E_a = 27 \pm 3$ kcal/mole. The limited temperature range used to determine E_a results because at reaction temperatures below 210°C, the percent conversion of **Q** to **N-Et-HQ** is much less than 1 %, even after 24 hours. The upper temperature limit was determined by the flammability of the oil used in the thermostatted oil bath. The $E_a = 27 \pm 3$ kcal/mole found for the ethylation reaction is considerably higher than that found for the **Q** hydrogenation reaction where $E_a = 16 \pm 3$ kcal/mole.

The nature of the active catalyst

H_2 pressure dependence. Another unexpected result comes from the observation that, for the $RuCl_3/Mo$ -HPA catalyst precursor system, dropping the initial H_2 pressure from 1000 psig to 400 psig does not affect the rate of reaction at all. At least under the two pressures measured, it appears that H_2 pressure plays no role in the rate limiting step. In contrast, the $Ru_3(CO)_{12}/Mo$ -HPA system exhibits significant H_2 pressure dependence (Figures 4 and 5). The percent conversion rate (also TF value) reaches a maximum at 600 psig H_2 (~296 for TF and 32 for TF', see Table 1) as shown in Figure 4. The inhibition in catalyst activity observed above 600 psig H_2 is likely the result of H_2 competing with one of the reactants (or intermediates) for catalyst sites. Based on our previous work in this area, we can suggest a mechanism that can be used to explain these observations:^{10,11}

In this reaction scheme, the first step involves dehydrogenation of ethanol to form acetaldehyde which condenses with **THQ** to form the enamine (or an imminium salt),¹¹ shown in the lower right hand corner. The enamine is then readily hydrogenated to **N-Et-THQ**.

Insert Figures 4 and 5

The hydrogen dependence results can be explained in two ways. If the dehydrogenation step is reversible, as suggested in reaction (3), then increasing the H_2 pressure will drive reaction (3), limiting

the rate of formation of CH_3CHO . This will lead to reduced rates of ethylation. An alternate explanation would be one in which H_2 successfully competes with either EtOH or enamine for an active catalyst site. By displacing EtOH, the rate of formation of CH_3CHO is again diminished. By displacing enamine, the rate of enamine hydrogenation would be diminished. However, under the basic conditions employed in the reaction, the enamine should be stable and would be observable by GC-MS if formed. Because GC-MS analyses do not reveal the presence of the enamine, we presume that H_2 does not displace enamine from the catalyst site. The most likely explanation is that the rate of reaction (3) is enhanced with higher H_2 pressures.

While the above discussion may successfully explain the case where there is a significant H_2 dependence, it offers no explanation for the lack of H_2 dependence in the $\text{RuCl}_3/\text{Mo-HPA}$ bimetallic. A reasonable explanation may be that the rate determining step has changed and is no longer (for example) EtOH dehydrogenation, but condensation of CH_3CHO with **THQ**. This leads to the question: Why should there be a change in mechanism given that the concentration of Mo-HPA is constant in both systems, and the concentration of the two ruthenium species in terms of moles of metal is essentially the same?

The only logical explanation is that two different types of catalyst sites are formed using the two precursors. Future studies are planned in which we will contrast the current results with the catalytic activity of the RuMo-HPA , $\text{H}_4\text{PMo}_{11}\text{RuO}_{39}$.¹² This may lead to a better understanding of the effects of changing from a Ru(III) cocatalyst to a Ru(0) cocatalyst.

Catalyst concentration studies. Further efforts to delve into the nature of the bimetallic systems focused on the effects of relative ratios of the two precatalyst metals [where Ru is added as $\text{Ru}_3(\text{CO})_{12}$] on the rates of **THQ** ethylation. Except at the lowest value of $[\text{Ru}_3(\text{CO})_{12}]/[\text{Mo-HPA}]$, increasing the relative concentration of $\text{Ru}_3(\text{CO})_{12}$ results in a decrease in percent conversion and lower TF (and TF') values as shown in Figures 6, 7 and Table 2. The maximum TF (or TF') values are obtained when a 1 mL/4 mL(Ru/Mo) precatalyst stock solution mixture is used. This corresponds to a Ru:Mo atomic ratio of 1:10.

Insert Figures 6,7 and Table 2

At this time, it is not possible to offer a concise explanation as to why this ratio is approximately optimal. However, it is important to recognize that the synergistic effect observed with both Ru compounds most probably reflects a coupling of two catalytic reactions. One is the ethanol dehydrogenation reaction and the other must be the enamine hydrogenation reaction. It is possible to suggest that each reaction is catalyzed most effectively by one of the two metals. But if this is correct, then what metal promotes which reaction.

Both the ruthenium catalyst and the Mo-HPA catalyst are quite active for **Q** hydrogenation, with

the most active Ru and Mo-HPA catalysts exhibiting TFs ≈ 20 (at 200°C) as compared with maximum rates of 32 ± 2 for the ethylation reaction at 220°C. Hydrogenation of Q to THQ is nearly identical in nature to enamine hydrogenation. Thus, Q hydrogenation must be faster than ethylation given the rates at 200°C and an activation energy of $E_a = 16 \pm 3$ kcal/mole which allows us to predict that the rate of hydrogenation at 220°C should be ≈ 50 .

Therefore, we must conclude that the slow step in ethylation is ethanol dehydrogenation. However, (1) if only one of the metals is a good EtOH dehydrogenation catalyst; (2) if both are good hydrogenation catalysts, and (3) because enamine formation is not catalytically controlled; then one of the two catalysts should be able to catalyze ethylation almost as well as the bimetallic system. Since this does not occur, we must conclude that there may only be one type of active catalyst site and that site contains both Mo and Ru atoms. We can also conclude that the ratio of Ru:Mo atoms at this site is important in determining the rate limiting step based on the observed differences in H_2 pressure dependencies. Without proof, we must assume that the Ru content of the site generated using $Ru_3(CO)_{12}$ is higher than that generated using $RuCl_3$. These observations offer important implications concerning other studies with these bimetallic systems.

A second type of ethylation reaction

One might presume to attempt to develop a kinetic and therefore mechanistic understanding of the EtOH dehydrogenation reaction by exploring the effects of running the reaction without added H_2 . Our efforts to do so were rewarded by a set of reaction products that have no bearing on the N-ethylation reaction.

When a typical reaction mixture consisting of 1 mL of $Ru_3(CO)_{12}$ stock solution, 4 mL Mo-HPA stock solution, and 5 mL of THQ is heated under N_2 rather than H_2 . The GC-MS indicates the formation of an almost entirely new set of products in addition to N-Et-THQ. These products include Q, Q-Et, Q- C_3H_7 , Q- C_4H_9 , Q- C_6H_{13} and N-Et-THQ. It is likely that without H_2 , Mo-HPA is not reduced or only partially reduced by EtOH (or THQ) under the reaction conditions. The partially reduced catalyst would then be expected to drive THQ dehydrogenation to Q.

Subsequently, the strongly protic nature of the unreduced part of the HPA may be expected to effect ethylation of the aromatic rings at the reaction temperatures used. This would permit a relatively simple explanation of the C_2 - (monoethylation) and C_4 (diethylation) products and even the C_6 - products; however, this does not account for the appearance of the C_3 - products. The reasons for the appearance of these unusual products must await further studies.

Comments

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 coincidentally. 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.

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8. The conditions for the GC heating program used in this study are: Initial temp.; 35°C, initial time; 30 sec., final temp.; 180°C, Final time; 1 min., Rate; 15 deg./min, oven temp.; 35°C, injection temp.; 200°C, detector temp.; 250°C, equilibrium time; 1 min.
9. k_{obs} at each temperature is obtained from the slope of the equation, $d[N-Et-THQ]/dt = k_{obs}[Q]^0$, assuming zero order reaction from data obtained. The activation energy, E_a , is calculated from the expression $k_{obs} = Ae^{(-E_a/RT)}$.
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Figure 1. % Conversion of THQ for Individual and Mixed Bimetallic Catalyst Precursors at 1000 Psig H₂ and 220 °C. ○ Et-THQ(Mo-HPA+RuCl₃), ● THQ(Mo-HPA+RuCl₃), ◆ Et-THQ(RuCl₃), △ THQ(RuCl₃), ▲ THQ(Mo-HPA)

Figure 2. % Conversion of THQ for Individual and Mixed Bimetallic Catalyst Precursors at 1000 Psig H₂ and 220 °C. ● THQ(Mo-HPA+Ru₃(CO)₁₂), ○ Et-THQ(Mo-HPA+Ru₃(CO)₁₂), ◆ THQ(Ru₃(CO)₁₂), ◇ Et-THQ(Ru₃(CO)₁₂), ▲ THQ(Mo-HPA), △ Et-THQ(Mo-HPA).

Figure 3. Changes in Turnover Frequency as a Function of THQ Concentration.
Conditions of $\text{Ru}_3(\text{CO})_{12}$ /Mo-HPA system ; Ru/Mo-HPA = 1 mL/4 mL (v/v), 220 °C, and 600 psig H_2

Figure 4. % Conversion of C_2H_5 -THQ from THQ at Various Pressures.

Conditions : $Ru_3(CO)_{12}/Mo-HPA = 1mL/4mL$ (v/v), $220^\circ C$.

◇ 0 Psig H₂, □ 400 Psig H₂, ○ 600 Psig H₂, △ 800 Psig H₂, ● 1000 Psig H₂

Figure 5. Changes in Turnover Frequency as a Function of H₂ Pressure for the Ru₃(CO)₁₂/Mo-HPA system. Conditions : Ru/Mo-HPA = 1 mL/4mL (v/v), 220 °C.

Figure 6. % Conversion of C_2H_5 -THQ at Different Relative Concentration of Bimetallic Catalyst

Precursors at 220 °C and 600 psig H_2 (Mo-HPA/ $Ru_3(CO)_{12}$, v/v); ● (4.5 mL/0.5 mL),

■ (4 mL/1 mL), ◇ (3 mL/2 mL), □ (2 mL/3 mL), △ (1 mL/4 mL).

Figure 7. Changes in Turnover Frequency as a Function of Relative Concentration of $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ system. Conditions : 220 °C and 600 psig H_2 .

Table 1. Turnover Frequencies of Mixed Bimetallic Catalyst Precursors at Different H₂ Pressure and 220 °C.

H ₂ Pressure	TF(based on the total no. of moles of catalyst precursor)	TF'(Based on the total no. of moles of metal atoms)
0 psig	61 ± 17	7 ± 2
400 psig	221 ± 20	24 ± 2
600 psig	296 ± 14	32 ± 2
800 psig	190 ± 20	21 ± 2
1000 psig	140 ± 10	15 ± 1

* TF(TF') = no. of moles of product/ no. of moles of catalyst (or metal atoms)/ h.

* The total no. of moles of catalyst precursor is 6.34×10^{-6} moles.

* The total no. of moles of metal atoms is 5.75×10^{-5} moles.

* Ru₃(CO)₁₂/Mo-HPA = 1 mL/4 mL (v/v).

Table 2. Turnover Frequencies of Mixed Bimetallic Catalyst Precursors at Different Relative Concentration. (600 psig H₂ and 220 °C)

Relative volume (Ru/Mo) of catalyst precursor soln	no. of moles of Ru ₃ (CO) ₁₂ no. of moles of Mo-HPA (x 10 ⁻⁶ moles)	Total no. of moles of catalyst precursors (x 10 ⁻⁶ moles)	Total no. of moles of metal atoms (x 10 ⁻⁵ moles)	TF(Catalyst)	TF'(Metal)
0.5 mL/4.5 mL	0.98/4.93	5.91	6.21	273 ± 38	26 ± 3
1 mL/4 mL	1.95/4.38	6.34	5.85	296 ± 14	32 ± 2
2 mL/3 mL	3.91/3.29	7.19	5.12	214 ± 24	30 ± 3
3 mL/2 mL	5.87/2.19	8.06	4.39	144 ± 19	27 ± 3
4 mL/1 mL	7.82/1.1	8.92	3.66	81 ± 15	20 ± 4

* TF and TF's are defined same as in table 1.

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