

## ETHYLATION OF TETRAHYDROQUINOLINE USING Ru/Mo BIMETALLIC CATALYST PRECURSORS SYSTEM.

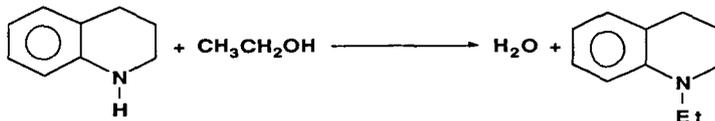
Sang-Man Koo, D. Ryan, and R. M. Laine  
The Department of Materials Science and Engineering and  
the Department of Chemistry, University of Michigan,  
Ann Arbor, MI. 48109-2136

Keywords: Ethylation ; Tetrahydroquinoline ; Bimetallic Catalyst Precursors.

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.<sup>1</sup> They are easily modified to contain other transition metals such as Co, Ni or Ru and, can be made soluble in organic solvents.<sup>1-3</sup> The protic forms exhibit extremely high acidities with  $pK_a$ 's  $\approx$  0-2.<sup>1</sup> In addition, selectively modified HPAs can function as low temperature hydrogenation catalysts that exhibit microporosity.<sup>4</sup> HPAs are multi-functional catalysts that could be used to promote both hydroliquefaction and hydrotreating. The overall goal of the work reported here concerns our efforts to evaluate HPAs as soluble liquefaction and hydrotreating catalysts, with the goal of developing soluble analogs of surface confined catalysts.<sup>5,6</sup>

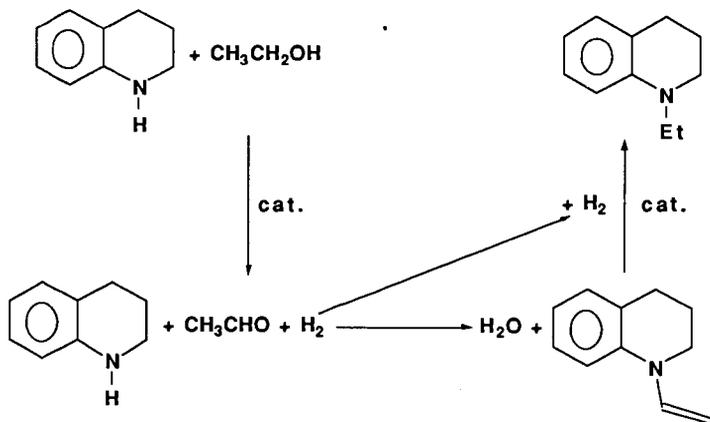
The primary purpose of the work reported here is to carefully delineate the reactivity patterns of RuMo bimetallic precatalysts. In particular, efforts were made to understand the reactivity of tetrahydroquinoline (THQ) at moderate temperatures. We have previously shown that bimetallic RuMo and trimetallic RuCoMo organometallic derived, supported catalysts will promote HDN of THQ at temperatures of 350°C.<sup>5,6</sup> Thus, we were interested to determine whether or not our recently developed, unsupported RuMo catalysts would have sufficient activity to work at temperatures below 250°C.

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 40% completion in 25 h at 1000 psig H<sub>2</sub> using a standard bimetallic precatalyst system [4 mL EtOH stock solution, 4.39 x 10<sup>-4</sup> M in Mo-HPA:1 mL stock solution, 5.74 x 10<sup>-4</sup> M in RuCl<sub>3</sub>/1.96 x 10<sup>-4</sup> M Ru<sub>3</sub>(CO)<sub>12</sub>, 50 μL CS<sub>2</sub>] as shown in Figures 1 and 3. 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<sub>3</sub> [or Ru<sub>3</sub>(CO)<sub>12</sub>] stock solution, where no synergistic effects are possible, almost no product is observed. In baseline tests, the Mo-HPA derived catalyst appears to function slightly better than the RuCl<sub>3</sub> derived catalyst [or nearly the same as Ru<sub>3</sub>(CO)<sub>12</sub>]. Apparently, it is necessary to have the bimetallic catalyst form in order to observe ethylation.

Another unexpected result comes from the observation that, for RuCl<sub>3</sub>/Mo-HPA catalyst precursor system, dropping the initial H<sub>2</sub> pressure from 1000 psig to 400 psig does not affect the rate of reaction at all (Figure 2). At least under the two pressures measured, it appears that H<sub>2</sub> 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:<sup>7</sup>



In this reaction scheme, the first step involves dehydrogenation of ethanol to form acetaldehyde which condenses with THQ to form the enamine, shown in the lower right hand

corner. The enamine is then readily hydrogenated to **N-Et-THQ**.

In contrast to the RuCl<sub>3</sub>/Mo-HPA precatalyst system, the Ru<sub>3</sub>(CO)<sub>12</sub>/Mo-HPA system exhibits significant H<sub>2</sub> pressure dependence (Figure 4). The percent conversion rate (also TF value) reaches a maximum at 600 psig H<sub>2</sub> (~296 for TF and 32 for TF') as shown in Figure 4 and Table 1). The inhibition in catalyst activity observed above 600 psig H<sub>2</sub> is somewhat unexpected and further study will be needed.

Figure 5 and Table 2 show the effects of relative concentrations of bimetallic precatalyst on catalyst activity for **THQ** ethylation. Except at the lowest value of [Ru<sub>3</sub>(CO)<sub>12</sub>]/[Mo-HPA], increasing the relative concentration of Ru<sub>3</sub>(CO)<sub>12</sub> results in a decrease in percent conversion and lower TF (and TF') values. Maximum TF (or TF') values are obtained when a 1 mL/4 mL(Ru/Mo) precatalyst stock solution mixture is used.

Initial rates of reaction were determined for each temperature from 220 to 250°C with initial H<sub>2</sub> pressures of 600 psig. Raw reaction rate data are used to calculate initial TFs which are used as k<sub>obs</sub>.<sup>8</sup> These data allow us to calculate the energy of activation, E<sub>a</sub> = 27 ± 3 kcal/mole. When the reaction temperature was below 210°C, the percent conversion on to **N-Et-THQ** is much less than 1 %, even after 24 hours.

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 reverse. 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.

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.

### **Acknowledgements**

We wish to thank the Department of Energy and the Pittsburgh Energy and Technology Center for generous support of this work through contract no. DE-FG22-90PC90313.

### **References**

1. Heteropoly and Isopoly Oxometalates, M. T. Pope, Springer-Verlag Pub., Berlin, GDR,

1983.

2. R. F. Renneke and C. L. Hill, *J. Am. Chem. Soc.*, (1988) **110**, 5461.
3. R. K.C. Ho, W. G. Klemperer, *J. Am. Chem. Soc.*, (1978) **100**, 6774.
4. A. R. Siedle, R. A. Newmark, M. R. V. Sahyun, P. A. Lyon, S. L. Hunt, and R. P. Skarjune, *JACS* (1989) **111**, 8346.
5. "Bulk Ruthenium as an HDN Catalyst", A. S. Hirschon and R. M. Laine, *J. Energy and Fuels* (1988) **2**, 292-295.
6. "Use of Promoters to Enhance Hydrodenitrogenation and Hydrodeoxygenation Catalysis", A. S. Hirschon, L. L. Ackerman, R. M. Laine, and R. B. Wilson, Jr. *Proc. of the 1989 Internat. Conf. on Coal Science, Tokyo.* Vol. **II**, p. 923.
7. "Homogeneous Catalytic Cleavage of Saturated Carbon-Nitrogen Bonds." Y. Shvo, M. Abed, Y. Blum, and R. M. Laine, *Isr. J. Chem.* (1986) **27**, 267-275.
8.  $k_{obs}$  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  $k_{obs} = A e^{(-E_a/RT)}$ .

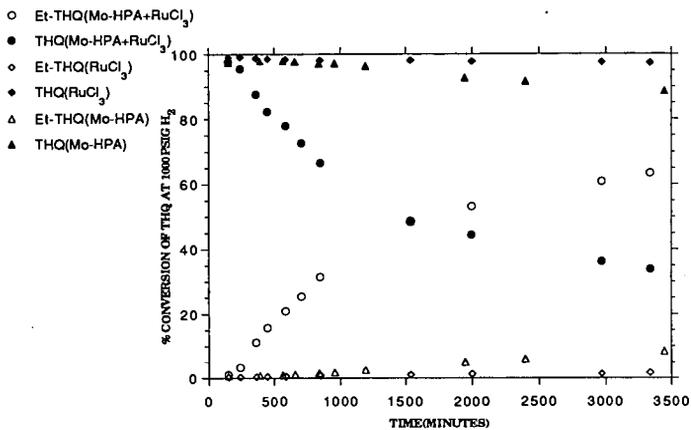


Figure 1. Percent Conversion of THQ to N-Et-THQ for Individual and Mixed Bimetallic Catalyst Precursors at 1000 Psig H<sub>2</sub> and 220 °C.

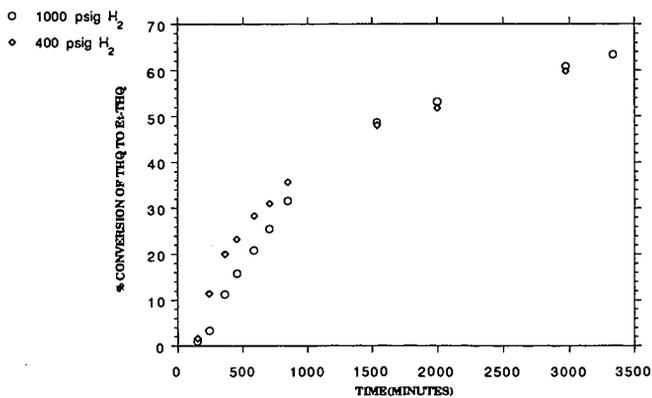


Figure 2. Percent Conversion of THQ to N-Et-THQ for Mo-HPA/RuCl<sub>3</sub> Bimetallic Catalyst Precursors in two different H<sub>2</sub> pressure at 220 °C.

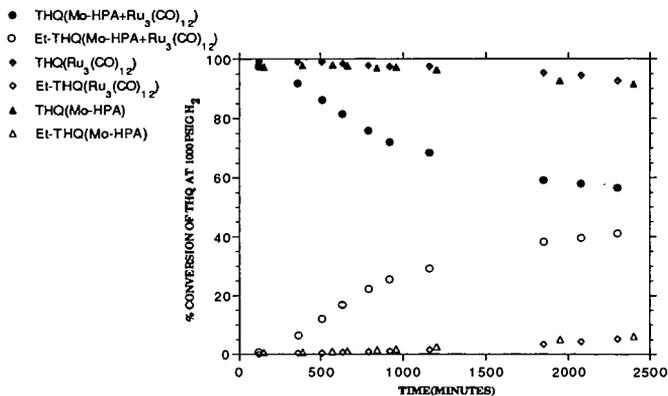


Figure 3. Percent Conversion of THQ to N-Et-THQ for Individual and Mixed Bimetallic Catalyst Precursors at 1000 Psig H<sub>2</sub> and 220 °C.

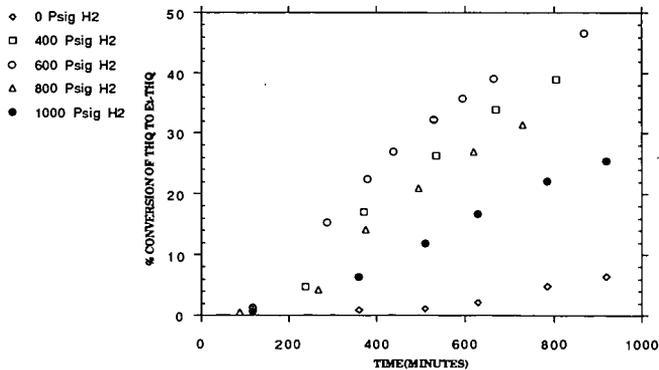


Figure 4. Percent Conversion of THQ to C<sub>2</sub>H<sub>5</sub>-THQ for Bimetallic Mo-HPA/Ru<sub>3</sub>(CO)<sub>12</sub> Precatalyst at Various Pressures.

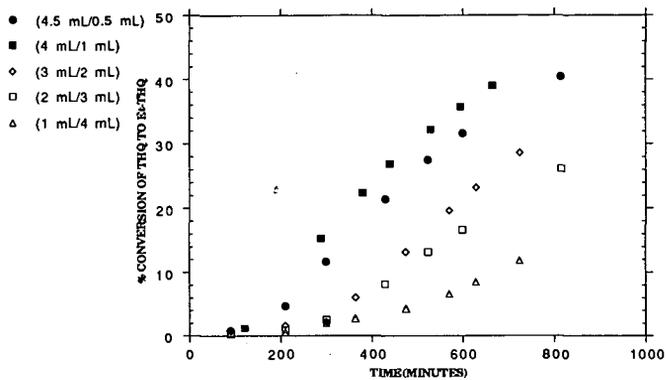


Figure 5. Percent Conversion of  $C_6H_2$ -THQ at Different Relative Concentration of Bimetallic Catalyst Precursors.  
 (Mo-HIPA/Ru<sub>3</sub>(CO)<sub>12</sub> = v/v, 1 mL Mo-HIPA =  $1.1 \times 10^{-4}$  M and 1 mL Ru<sub>3</sub>(CO)<sub>12</sub> =  $1.98 \times 10^{-4}$  M)

**Table 1. Turnover Frequencies of Mixed Bimetallic Catalyst Precursors at different H<sub>2</sub> Pressure and 220 °C.**

H <sub>2</sub> Pressure	TF(Total no. of moles of catalyst precursor)	TF(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, N-Et-THQ/no. of moles of catalyst (or metal atoms)/h

\*The total no. of moles of catalyst precursor is  $6.34 \times 10^{-6}$  moles [Mo-HPA/Ru<sub>3</sub>(CO)<sub>12</sub> =  $4.38 \times 10^{-6}$ /1.96 x 10<sup>-6</sup>].

\*The total no. of moles of metal atoms is  $5.85 \times 10^{-5}$  moles (Mo/Ru = 5.26 x 10<sup>-6</sup>/5.87 x 10<sup>-6</sup>).

**Table 2. Turnover Frequencies of Mixed Bimetallic Catalyst Precursors at different Relative Concentration. (600 psig H<sub>2</sub> and 220 °C)**

Relative volume (Ru/Mo) of catalyst precursor soln	Concentration	no. of moles of Ru <sub>3</sub> (CO) <sub>12</sub> catalyst precursor (x 10 <sup>-6</sup> moles)	no. of moles of Mo-HPA catalyst precursors (x 10 <sup>-6</sup> moles)	Total no. of moles of metal atoms (x 10 <sup>-5</sup> 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	236 ± 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 as in table 1.