

Sulfided heterogeneous, bimetallic Ru/Mo catalysts derived from mixtures of $\text{Ru}_3(\text{CO})_{12}$ (or RuCl_3) and a molybdenum heteropolyanion: The reactions of ethanol with tetrahydroquinoline

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Efforts have been made to develop Ru/Mo bimetallic catalyst systems for hydrodenitrogenation (HDN) of tetrahydroquinoline (THQ). In the course of these studies, it was discovered that in ethanol, under hydrogen and in the presence of carbon disulfide (CS_2), precatalyst solutions containing ruthenium [as $\text{Ru}_3(\text{CO})_{12}$ or RuCl_3] and molybdenum [as the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ heteropolyanion (HPA)] decompose to form bimetallic, sulfided particles. Particle diameters run from 0.1 to 5 μm depending on the rate of stirring. Catalyst particles with sizes ranging from 0.1 to 1 μm can be prepared reproducibly. BET-measured surface areas for these size particles ranged from 2 to 20 m^2g^{-1} . These sulfided particles were found to catalyze, at temperatures of 200–250 °C and hydrogen pressures of 200–1000 psig (1.4–6.9 MPa) hydrogen, the *N*-ethylation of THQ to form *N*-ethyltetrahydroquinoline (*N*-Et-THQ), rather than the formation of propylcyclohexane or propylbenzene, reaction products expected for HDN of THQ. Monometallic heterogeneous catalysts prepared from the individual precatalyst complexes, under identical conditions, show minimal activity for *N*-ethylation by comparison with the bimetallic catalyst.

In the absence of hydrogen, the reaction proceeds so that THQ is converted to quinoline, *N*-Et-THQ, *N*- C_4H_9 -THQ and *N*- C_6H_{13} -THQ. The latter products appear to arise via acetaldehyde, formed as an intermediate by dehydrogenation of ethanol. Acetaldehyde either condenses with THQ to form *N*-Et-THQ, or self-condenses (aldol condensation) prior to reaction with THQ, thereby giving higher-homolog alkylation products.

Keywords: Alkylation, hydrodenitrogenation, clusters, ruthenium, molybdenum, heteropolyanion, coal liquefaction, hydrotreating

INTRODUCTION

We have previously shown that 'surface-confined' bimetallic (Ru/Mo) and trimetallic (Ru/Co/Mo) heterogeneous catalysts, prepared by reaction of organometallic precursors with alumina supports or via modification or sulfided Co/Mo catalysts by reaction with an organometallic precursor, show exceptional activity for hydrodenitrogenation (HDN) of quinoline.¹⁻⁶ Typical surface-confined Ru/Mo and Ru/Co/Mo catalysts were found to produce 1:1 propylbenzene/propylcyclohexane product ratios (at 350 °C/100–500 psig hydrogen). (Note: 1 psig \approx 6.9 kPa.) By comparison, surface-confined sulfided Co/Mo catalysts were found to produce propylbenzene/propylcyclohexane product ratios of 1:18 (at 350 °C/100–500 psig hydrogen), which is typical of commercial Co/Mo catalysts operating without transport limitations.

The Ru/Mo and Ru/Co/Mo catalysts were found to be sulfur-tolerant and actually exhibited enhanced activity in the presence of sulfur-containing species (CS_2 or H_2S). In addition, Ru/Mo and Ru/Co/Mo catalysts were shown to provide superior HDN/HDO for coal model compounds under specific conditions.⁶ Efforts to translate this exceptional synergistic catalyst activity to coal liquefaction using the Ru/Co/Mo catalyst and Wyodak coal led to only slight improvements in THF solubles over commercial, sulfided CoMo catalysts. In neither case was the catalyst activity as exceptional as that witnessed under modelling conditions.

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We believe that the exceptional behavior in the modelling studies does not translate to coal 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 rate of reaction obtained in the coal studies is thermodynamically controlled whereas, in the model studies, kinetic control exists.

To remedy this problem, we are seeking to develop unsupported, homogeneous bimetallic HDN (and liquefaction) catalysts that will not be diffusion-limited. Alternately, we seek to develop homogeneous bimetallic 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 Ru/Mo catalysts, with respect to the steps in the HDN process that are enhanced by the bimetallic system.

We have recently conducted a survey study wherein certain HPAs [$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Mo-HPA), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (W-HPA), and $(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4] \cdot 7\text{H}_2\text{O}$] and polyoxoanions [$(\text{NH}_4)\text{VO}_3$ and $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O})$] were screened for catalyst activity for hydrogenation of quinoline (Q) to tetrahydroquinoline (THQ) under a set of standard conditions [200 °C, 600 psig hydrogen, ethanol solvent].^{8,9} The activities of these precatalysts in the presence of added $\text{Ru}_3(\text{CO})_{12}$ and RuCl_3 were also studied. It was

found that all of the precatalysts are activated by conversion to heterogeneous, submicron sulfided particles. Of the systems screened, the Mo-HPA/Ru bimetallic catalysts exhibited enhanced Q hydrogenation activities (as anticipated) relative to the other precatalysts.

These studies suggest that the synergy obtained with supported (surface-confined) bimetallic Ru/Mo and Ru/Co/Mo HDN catalysts derives at least in part from enhanced hydrogenation of Q. However, the improved product ratios noted above must also come from enhanced activation/cleavage of the C–N bonds in THQ relative to hydrogenation of THQ to decahydroquinoline;^{4,5} otherwise, the product ratios would be those obtained with typical sulfided Co/Mo catalysts. Consequently, it is important to delineate the mechanisms whereby Ru/Mo promotes C–N bond cleavage and activation. It is also important to understand the interactions of the nitrogen center with catalyst sites.

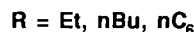
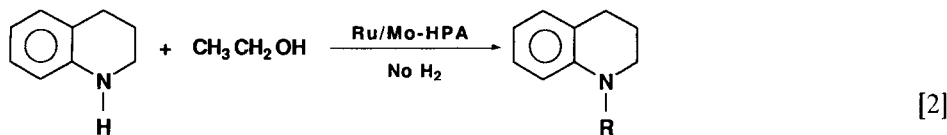
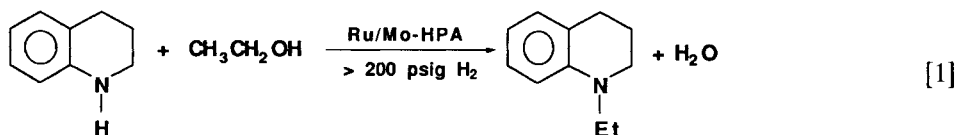
The following study was originally designed to explore, at low temperatures, the activation of the C–N bond in THQ, using Ru/MoHPA precatalyst systems. However, several unusual reactions of potential importance to coal catalysis chemistry were observed⁸ that warranted further study. These reactions include the ethylation and alkylation of THQ with ethanol as suggested by reactions [1] and [2].

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



from Midwest Grain Products Co. Molybdophosphoric acid [Mo-HPA, $\text{H}_3\text{PO}_4 \cdot 12(\text{MoO}_3) \cdot x\text{H}_2\text{O}$] was purchased from Johnson Matthey. $\text{Ru}_3(\text{CO})_{12}$ was 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 Vacuum Atmospheres Dri-Box under nitrogen. These precatalyst complexes were used as received.

Analytical procedures

Product analyses for all the kinetic studies were performed on a temperature-programmed Hewlett-Packard 5890A reporting GC equipped with a flame ionization detector (FID) using a $5 \text{ m} \times 0.53 \text{ mm} \times 2.65 \mu\text{m}$ capillary column packed with 100% dimethylpolysiloxane gum. The GC heating schedule used in this study was: hold at 35°C for 30 s, ramp to 180°C at $15^\circ\text{C min}^{-1}$, hold for 1 min. The injection temperature was 200°C and the detector temperature was 250°C .

Surface-area measurements

The BET surface areas were measured by the flow method using a Quantasorb model QS-17 sorption analyzer. The amount of nitrogen removed from the flowing gas mixture (29.3% nitrogen in helium, Scott) and physisorbed on the surface was determined using a thermal conductivity detector. Accurately measured pulses ($\pm 2\%$) of purified nitrogen (99.998%, Air Products) were used to calibrate the amount of adsorbed nitrogen. The BET surface area, S_g , was determined (in $\text{m}^2 \text{g}^{-1}$) from

$$S_g = \frac{\left(1 - \frac{P_N}{P_0}\right) \left(\frac{A_d}{A_c}\right) 4.03 V_c}{\text{sample mass (g)}}$$

where P_N is the partial pressure of nitrogen in the nitrogen-helium mixture, P_0 is the ambient pressure at 0% relative humidity (estimated from ambient pressure $P_a + 15$), A_d is the average desorption count, A_c is the average calibration count, and V_c is the volume of carrier gas injected during calibration. Desorption and calibration counts from three separate runs were averaged in determining S_g .

Elemental composition studies

Energy dispersive spectroscopy (EDS) spectra were obtained on a JEOL 2000 FX STEM equipped with a Tracor Northern detector (model 5502) adapted with an ultra-thin beryllium window, using an accelerating voltage of 200 keV. The catalyst sample was dispersed in isopropanol and pipetted onto a holey-carbon-coated beryllium grid.

GC-mass spectroscopy (GC MS)

Studies to identify products formed in the reaction run with bimetallic precatalyst at 0 and 1000 psig hydrogen after 50% product conversion were performed using a Finnegan Quadrupole ion-trap instrument. The temperature for the analysis was held at 50°C for 2 min, then ramped at $15^\circ\text{C min}^{-1}$ to 275°C . The elution gas was hydrogen-helium. The $1 \text{ cm}^3 : 4 \text{ cm}^3$ $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ (1:4) system was used for these studies.

General reaction procedures for kinetic studies

Stock solutions of Mo-HPA were prepared before use by dissolving 0.1 g (5.33×10^{-2} mmol) molybdophosphoric acid (Mo-HPA) in 50 cm^3 of ethanol to form a $1.07 \times 10^{-3} \text{ mol dm}^{-3}$ 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 cm^3 ethanol to form a $5.74 \times 10^{-3} \text{ mol dm}^{-3}$ 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 cm^3 ethanol to give a $1.96 \times 10^{-3} \text{ mol dm}^{-3}$ solution. In a typical reaction using a bimetallic precatalyst system, an amount of Mo-HPA stock solution (e.g. 4 cm^3), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ or $\text{Ru}_3(\text{CO})_{12}$ stock solution (1 cm^3), and 5 cm^3 (0.04 mol) THQ are placed in a magnetically stirred, 34 cm^3 quartz-lined bomb reactor with $50 \mu\text{l}$ CS_2 . An example of a ruthenium monometallic precatalyst solution would be 1 cm^3 of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ or $\text{Ru}_3(\text{CO})_{12}$ stock solution and a make-up volume of 4 cm^3 of ethanol. An example of a molybdenum monometallic precatalyst solution would be 4 cm^3 of Mo-HPA stock solution and 1 cm^3 of ethanol.

The reactor was sealed and degassed via three pressurization/depressurization cycles using 1000 psig nitrogen followed similarly with hydrogen, and then pressurized to the desired level with hydrogen. The reactor was heated in an oil bath

thermostated to $\pm 4^\circ\text{C}$ of the appropriate temperature (220°C in the current studies). Samples were taken at selected times by cooling the reactor in cold water, depressurizing, removing approx. 0.25 cm^3 for a GC sample, and repressurizing. The reaction was then restarted. The time required for the entire sampling procedure is *ca* 10 min. The time required to come to full reaction temperature is approximately 10 min, as has been determined previously.¹⁻⁴ The minimum time between samples was always at least 40 min, not including heat-up time. In all experiments described throughout this report, hydrogen gas pressures are presented as psig, at 20°C .

The bomb reactors were always placed above the center of a magnetic stirrer and care was taken to ensure a rapid, but constant, rate of stirring to minimize irregular growth patterns during precatalyst decomposition. The most important measure of the reproducibility in catalyst particle size is that the kinetic data reported below are typically reproducible to $\pm 10\%$ when care is taken to create effective stirring conditions.

Procedure A

In the hydrogen pressure and temperature dependence studies, 4 cm^3 of the stock Mo-HPA solution, 1 cm^3 of Ru stock solution, and 5 cm^3 (39.7 mmol) of THQ were used with $50\ \mu\text{l}$ 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 precursors or added THQ were varied over a selected range (see below).

Catalyst activity

In all instances, catalyst activity is measured as a function of the turnover frequency (TF). TF is defined as moles of *N*-Et-THQ/total moles of metal per hour. Activities were always determined at THQ conversions below 25%. No fall-off effects are included in the TF calculations.

Hydrogen pressure studies

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

Bimetallic precatalyst concentration studies

Reactions were run as described for procedure B. Experiments were conducted in ethanol using an initial hydrogen pressure of 600 psig. The reaction temperature was held at 220°C . Total concentrations of $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ were varied between 5.80×10^{-4} and $8.91 \times 10^{-4}\text{ mol dm}^{-3}$ with total reaction volumes of bimetallic precatalyst solution maintained at 5 cm^3 . Typically, a known volume (e.g. 1.0 cm^3) of the $\text{Ru}_3(\text{CO})_{12}$ stock solution was syringed into the reactor, followed by Mo-HPA stock solution (4.0 cm^3) to maintain constant solvent volume of catalyst solution, and then 5.0 cm^3 of THQ. Note that at this temperature the individual catalysts were almost inactive. At higher Mo-HPA concentrations (e.g. 4 cm^3 stock solution), TFs were typically $< 10\text{ mol } N\text{-Et-THQ/mol Mo metal per hour}$. The ruthenium catalysts were even less active.

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 $6.24 \times 10^{-4}\text{ mol dm}^{-3}$. The $1\text{ cm}^3:4\text{ cm}^3$ $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ (1:4) system was used for these studies. THQ concentrations were varied from 0.79 to 3.97 mol dm^{-3} . Ethanol was added to maintain the standard 10 cm^3 reaction mixture volume.

Temperature studies

Reactions were run as in the hydrogen pressure studies, with the exception that the initial hydrogen pressure was always 600 psig. Rates were recorded at 220, 235, and 250°C , the range bounded at low temperature by minimal catalyst activity, and at high temperature by the flammability/decomposition point of the oil baths ($\sim 250^\circ\text{C}$).

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 improvements in HDN catalysis would be immediately obvious. Because our previous studies were conducted in ethanol, the use of ethanol for the current studies was a natural extension.

The nature of the catalytic reaction

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 used here is 220 °C and THQ is used in place of Q. The choice of 220 °C instead of 200 °C is a result of our inability to detect any HDN reaction products when the Q hydrogenation reactions were run to ~100% conversion at 200 °C. However, even at 220 °C, 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 hydrogen using two bimetallic precatalyst systems (4 cm³ ethanol stock solution 1.07 × 10⁻³ mol dm⁻³ in Mo-HPA, 1 cm³ ethanol stock solution 5.74 × 10⁻³ mol dm⁻³ in RuCl₃ or 1.96 × 10⁻³ mol dm⁻³ in Ru₃(CO)₁₂, and 50 μl CS₂) as shown in Figs 1 and 2.

What is extremely surprising about N-ethylation is that when it is run with either 4 cm³ of Mo-HPA or 1 cm³ of RuCl₃ [or Ru₃(CO)₁₂] stock solution and a make-up volume of ethanol, where no synergistic effects are possible, almost no product is observed. In baseline tests (Figs 1 and 2), the Mo-HPA-derived catalyst appears to function slightly better than the RuCl₃-derived catalyst [or

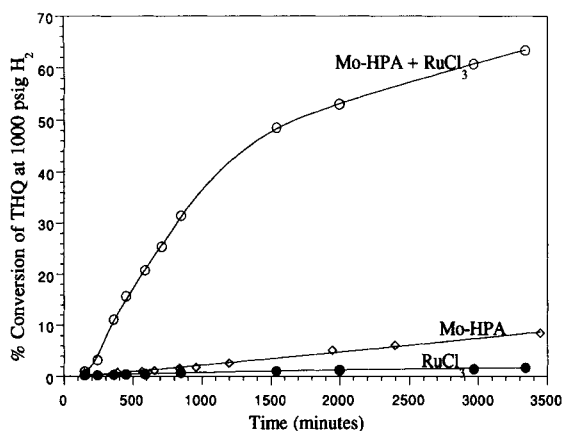


Figure 1 Conversion of THQ to *N*-Et-THQ for the RuCl₃ and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C with stock precatalyst solutions (1 cm³ RuCl₃ + 4 cm³ Mo-HPA, 4 cm³ Mo-HPA, or 1 cm³ RuCl₃).

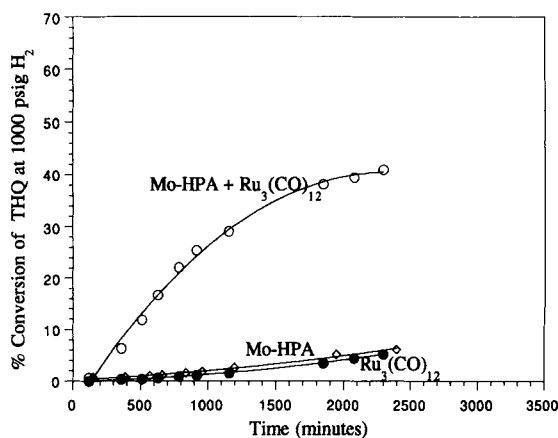


Figure 2 Conversion of THQ to *N*-Et-THQ for the Ru₃(CO)₁₂ and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C with stock precatalyst solutions (1 cm³ Ru₃(CO)₁₂ + 4 cm³ Mo-HPA, 4 cm³ Mo-HPA, or 1 cm³ Ru₃(CO)₁₂).

nearly the same as Ru₃(CO)₁₂]. Apparently it is necessary to form a bimetallic catalyst in order to observe ethylation.

THQ concentration studies

The pattern of reaction of THQ is nearly identical to that found for Q hydrogenation. The results shown in Fig. 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 (TF = 62) at [THQ] = 1.59 mol dm⁻³ using the 1 cm³:4 cm³ Ru₃(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 explanation is that the active catalyst sites can successfully bind both THQ and ethanol. At high THQ concentrations, THQ competes successfully with ethanol for active catalyst sites, thereby limiting the rate of ethanol dehydrogenation (reactant starvation) and slowing the rate of ethylation. This possibility is supported by the zero hydrogen-pressure studies, wherein THQ is partially dehydrogenated to Q at reasonable rates. Thus, THQ can indeed compete for active catalyst sites.

The second explanation is that at these high THQ concentrations, the composition of the reaction solution is considerably changed—there is much less ethanol. Consequently, the solubility of THQ or the solvation of the precatalyst changes

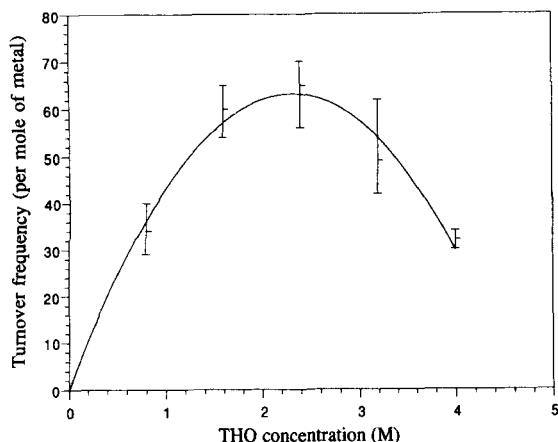


Figure 3 Turnover frequency dependence on THQ concentration for the $\text{Ru}_3(\text{CO})_{12}$ and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C under 600 psig hydrogen with 1 cm^3 $\text{Ru}_3(\text{CO})_{12}$ and 4 cm^3 Mo-HPA stock solutions. TFs based on initial rates.

and the surface area of the active produced is diminished, thereby reducing overall catalyst activity. We have no support for this possibility at present.

Activation energy

Initial rates of reaction were determined for each temperature from 220 to 250 °C with initial hydrogen pressures of 600 psig. Raw reaction rate data are used to calculate initial TFs which are used as k_{obs} . k_{obs} at each temperature is obtained from the slope of the curve

$$k_{\text{obs}}[\text{Q}]^0 = \frac{d[\text{N-Et-THQ}]}{dt}$$

assuming zero-order reaction from the data obtained. The activation energy, E_a , is calculated from the expression $k_{\text{obs}} = A \exp(-E_a/RT)$. The data thus allowed us to calculate the apparent energy of activation, $E_a = 27 \pm 3 \text{ kcal mol}^{-1}$. (Note: 1 kcal = 4.2 kJ.) The limited temperature range used to determine E_a arises because, at reaction temperatures below 220 °C, the percentage conversion of Q to N-Et-THQ is much less than 1%, even after 24 h. The upper temperature limit was determined by the flammability of the oil used in the thermostated oil bath. The value $E_a = 27 \pm 3 \text{ kcal mol}^{-1}$ found for the ethylation reaction is considerably higher than that found for the Q hydrogenation reaction, where $E_a = 16 \pm 3 \text{ kcal mol}^{-1}$.

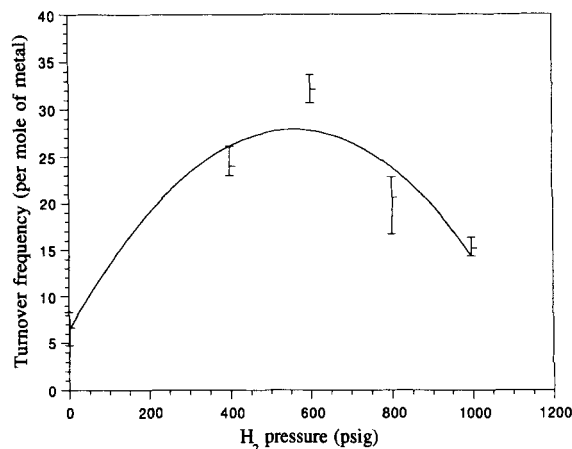


Figure 4 Turnover frequency dependence on hydrogen pressure for the $\text{Ru}_3(\text{CO})_{12}$ and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C with 1 cm^3 $\text{Ru}_3(\text{CO})_{12}$ and 4 cm^3 Mo-HPA stock solutions. TFs based on initial rates.

The nature of the active catalyst

Hydrogen pressure dependence

Figure 4 indicates that the $\text{Ru}_3(\text{CO})_{12}$ /Mo-HPA precatalyst system has the same pressure dependence as the RuCl_3 /Mo-HPA system (Fig. 5), within the limits of analytical error. The percent conversion rate (also TFs) for both catalysts reaches a maximum at approximately 600 psig hydrogen (TF $\approx 30 \pm 3$ for the $\text{Ru}_3(\text{CO})_{12}$ /Mo-HPA system and 55 ± 3 for the RuCl_3 /Mo-HPA system) as seen in Figs 4 and 5. Note that the concentration of the $\text{Ru}_3(\text{CO})_{12}$ stock solution is one-third that of the RuCl_3 stock

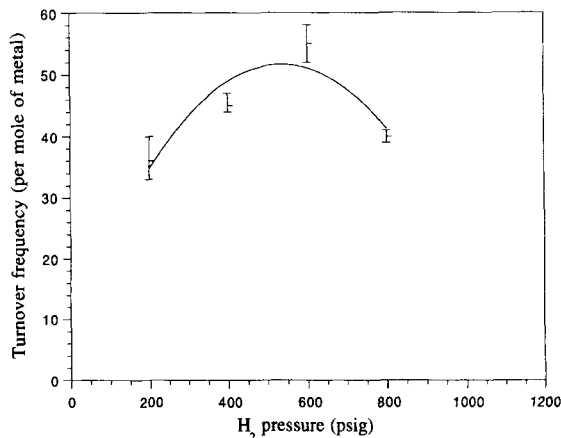
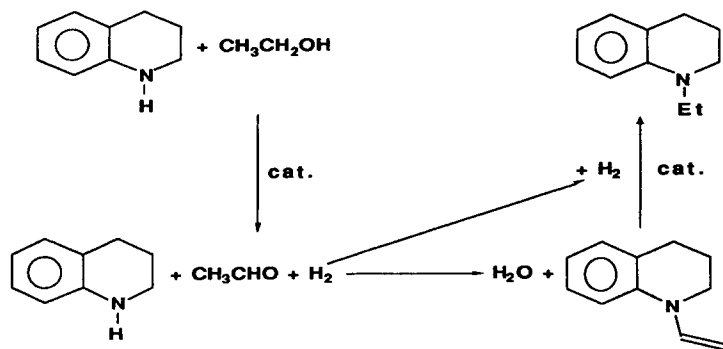


Figure 5 Turnover frequency dependence on hydrogen pressure for the RuCl_3 and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C with 1 cm^3 RuCl_3 and 4 cm^3 Mo-HPA stock solutions. TFs based on initial rates.



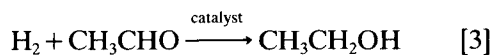
Scheme 1

solution so the total moles of Ru metal used in both bimetallic precatalyst solutions are the same. Therefore, it appears that the catalysts produced using either ruthenium source are essentially identical. Note that the slightly better rates for the chloride system appear to result from slightly higher surface areas obtainable with the chloride system as opposed to the carbonyl system (see below).

The inhibition in catalyst activity observed above 600 psig hydrogen is likely the result of hydrogen competing with one of the reactants (or intermediates) for catalyst sites. We, and others, have previously shown that homogeneous ruthenium and rhodium catalysts are very effective for alkylamine hydrolysis, alcohol dehydrogenation, and for reductive alkylation of amines with aldehydes.¹⁰⁻¹³ Based on this body of work, we can suggest a mechanism that can be used to explain these observations (Scheme 1).

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

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



reaction [3], limiting the rate of formation of acetaldehyde (CH_3CHO). This will lead to reduced rates of ethylation. An alternate explanation would be one in which hydrogen successfully competes with either ethanol or enamine for an

active catalyst site. By displacing ethanol, 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 (pH) conditions employed in the reaction, the enamine would 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 hydrogen does not displace enamine from the catalyst site. The most likely explanation is that the rate of reaction [3] is enhanced with higher hydrogen pressures, and/or hydrogen competes with ethanol for the active catalyst site. In contrast, low hydrogen pressure reactions should provide increased amounts of acetaldehyde which should be visible, and in a negative way provide support for [3]. The low-pressure results do indeed support this, as noted below.

Catalyst concentration studies

Efforts to delve into the nature of the bimetallic systems focused initially on basic catalyst concentration studies of the individual metal complexes. Unfortunately, catalyst activities were sufficiently low for good correlation of concentration versus rates of *N*-ethylation not to be possible for low metal concentrations, and high metal concentrations resulted in low-surface-area, large-diameter catalyst particles. Thus, efforts were made solely to determine the effects of relative metal ratios for one precatalyst system [where ruthenium 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 percentage conversion and lower TF (and TF') values as shown in Figs 6 and 7, and Table 1. The

maximum TF (or TF') values are obtained when a 1 cm³:4 cm³ (Ru/Mo) precatalyst stock solution mixture is used. This corresponds to a Ru/Mo atomic ratio of ~1:9.

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 ruthenium 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 that each reaction is catalyzed most effectively by one of the two metals. If this is correct, the question becomes: what metal promotes which reaction?

Both the ruthenium catalyst and the Mo-HPA catalyst are quite active for Q hydrogenation, with the most active ruthenium and Mo-HPA catalysts exhibiting TFs ≈ 20 (at 200 °C) as compared with maximum rates of 55 ± 3 for the ethylation reaction at 220 °C. (The 1 cm³:4 cm³ RuCl₃/Mo-HPA system was used for these studies.) Hydrogenation of Q to THQ is nearly identical in nature to enamine hydrogenation. Thus, Q hydrogenation must be at least as fast as ethylation given the TFs at 200 °C and an apparent activation energy of $E_a = 16 \pm 3$ kcal mol⁻¹, which allows us to predict the rate of hydrogenation at 220 °C should be 40–50.

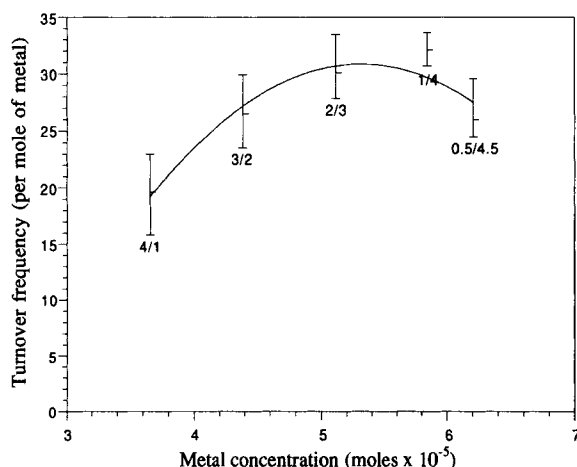


Figure 6 Turnover frequency dependence on relative metal concentration for the Ru₃(CO)₁₂ and Mo-HPA precatalyst system. Reactions run in ethanol at 220 °C under 600 psig hydrogen with Ru₃(CO)₁₂ and Mo-HPA stock solutions. Labels indicate the volume ratio of Ru₃(CO)₁₂ to Mo-HPA stock solutions (cm³/cm³). TFs based on initial rates. See also Table 1.

Therefore, we must conclude that the slow step in ethylation is ethanol dehydrogenation. However, if (1) only one metal is a good ethanol dehydrogenation catalyst, (2) both are good hydrogenation catalysts, and (3) enamine formation and hydrogenation are not involved in the rate-determining step, then one of the two metals should be able to catalyze ethylation almost as well as the bimetallic system. Since this does not occur, we must conclude that there is only one type of active catalyst site and that site contains both molybdenum and ruthenium atoms. The similarity in the rates of catalysis found using either RuCl₃ or Ru₃(CO)₁₂ with Mo-HPA, and the similarity in the catalyst particles formed on decomposition, suggests that the same catalyst site is generated in both systems.

Nature of the catalyst particles

Decomposition reactions were conducted to characterize the catalyst particles formed and identify problems of reproducibility. In this and earlier studies, catalysts surface areas ranged from 2 to 20 m² g⁻¹,⁹ although without stirring decomposition occurred on the walls of the quartz liner with the formation of massive fragments. Efforts were made to optimize stirring as a prerequisite to obtaining reproducible particle sizes. The scanning electron micrographs shown in Figs 8 and 9 reveal the formation of particles with size distributions in the range of 0.1–3 μm. The surface area of the chloride-derived particles was found to be 4.5 m² g⁻¹. By comparison, the carbonyl-derived particles have a correspondingly lower surface area of 2.4 m² g⁻¹. This surface area ratio of 4.5:2.4 correlates very well with the catalytic activities of 55:33 of the two systems, and supports the idea that the catalysts produced by the two routes are very similar or identical. It is important to note that grain growth in solution leads to irregular particles.

The SEM images show that the carbonyl-derived particles are smaller (0.1–1 μm) than the chloride-derived particles (0.3–1.5 μm); however, the apparently higher dispersity of the carbonyl particles is less than for the chloride particles. This must account for the differences in surface area and reactivity.

One might conclude that the irregular particle shapes are indicative of preferred growth along crystallographic planes; however, X-ray powder diffractometry does not provide any evidence of a crystalline phase, not even evidence of X-ray line broadening. Thus, the decomposition process

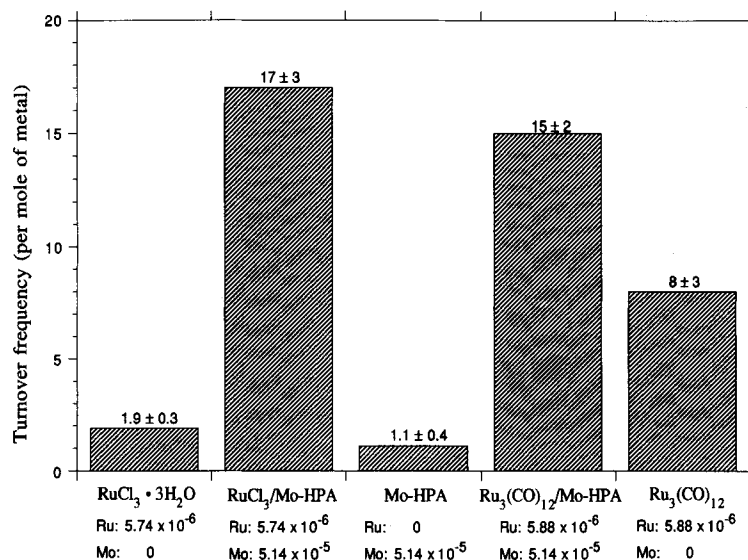


Figure 7 Turnover frequency (based on total moles metal in precatalysts) of individual and mixed bimetallic precatalysts. Reactions run in ethanol at 220 °C under 1000 psig hydrogen. Reactions run to less than 25% conversion of THQ to *N*-Et-THQ. Numbers beneath legends indicate total moles of each metal atom present.

leads to amorphous materials. The amorphous nature of the particles is confirmed by transmission electron microscope studies, where efforts were made to obtain small-area electron diffraction patterns, again without success.

Energy-dispersive spectroscopy (EDS) analyses of the particles, shown in Figs 10 and 11, suggest that the particles are chemically very similar. Sulfur is not directly seen in these EDS analyses because the sulfur line overlaps with molybdenum lines and is difficult to resolve.

A second alkylation reaction

Attempts to extend the hydrogen pressure dependence studies to 0 psig hydrogen were rewarded with additional reaction products. When a standard reaction solution consisting of a 1 cm³:4 cm³ mixture of the $\text{Ru}_3(\text{CO})_{12}$ and Mo-HPA stock solutions and 5 cm³ of THQ is heated under nitrogen at 220 °C for four days, GC MS analysis of the reaction solution reveals unreacted THQ (58%), Q (9%)^{16,17} and

Table 1 Turnover frequencies of $\text{Ru}_3(\text{CO})_{12}/\text{Mo-HPA}$ -derived catalysts at various relative concentrations and 600 psig hydrogen/220 °C

Relative volume (Ru/Mo, cm ³ /cm ³) of catalyst precursor solution	Ratio $\text{Ru}_3(\text{CO})_{12}/\text{MoHPA}$ (10^{-6} mol/ 10^{-6} mol)	Total metal atoms (10^{-3} mol)	Total catalyst precursors (10^{-6} mol)	TF (metal) ^a	TF' (catalyst) ^a
0.5/4.5	0.98/4.82	6.07	5.80	26 ± 3	273 ± 38
1/4	1.96/4.28	5.72	6.24	32 ± 2	296 ± 14
2/3	3.92/3.21	5.03	7.13	30 ± 3	214 ± 24
3/2	5.88/2.14	4.33	8.02	27 ± 3	144 ± 19
4/1	7.84/1.07	3.64	8.91	20 ± 4	81 ± 15

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

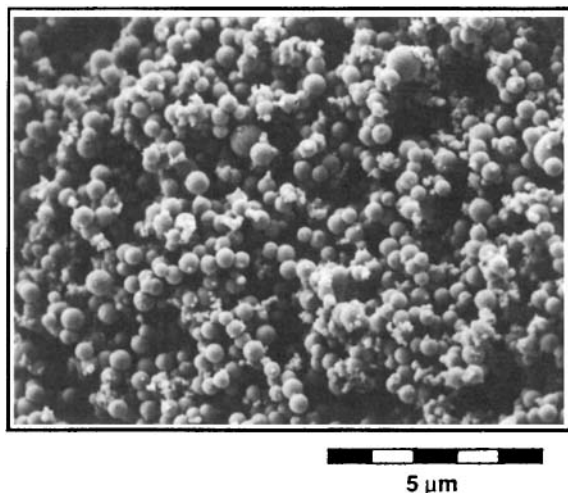


Figure 8 Scanning electron micrograph (SEM) of the $\text{Ru}_3(\text{CO})_{12}/\text{Mo}$ -HPA-derived catalyst.

N-R-THQ where R = Et (19%), *n*Bu (5%) and small amounts of R = nC_6H_{13} (2.5%). For Q, typical fragments are $m/z = 129$ (100), 128 (20), 102 (29) and 51 (21). The values in parentheses are relative to the highest ion current (assigned a peak height of 100). THQ typically fragments to $m/z = 132$ (100), 133 (82), 118 (24), 117 (23), 77 (20) and 65 (29). For *N*-Et-THQ, typical fragments are $m/z = 161$ (42), 146 (100), 131 (15), 130 (19), 118 (17), 91 (18) and 77 (14), and for *N*-*n*Bu-THQ, $m/z = 189$ (40), 175 (17), 174 (100), 161 (20), 146 (57) and 132 (24). Trace amounts of

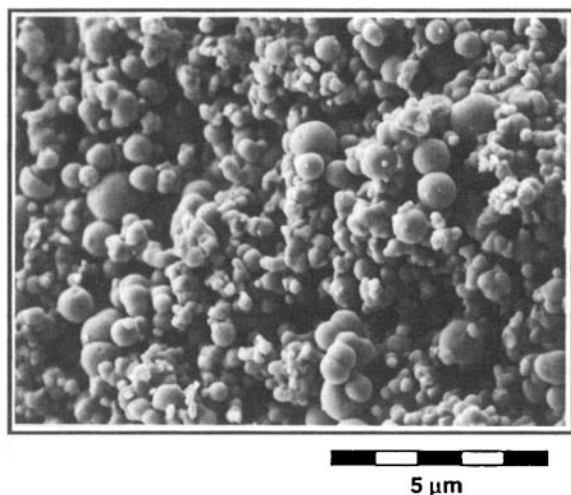


Figure 9 Scanning electron micrograph of the RuCl_3/Mo -HPA-derived catalyst. Note that the particle size distribution is larger than that of the $\text{Ru}_3(\text{CO})_{12}/\text{Mo}$ -HPA-derived catalyst.

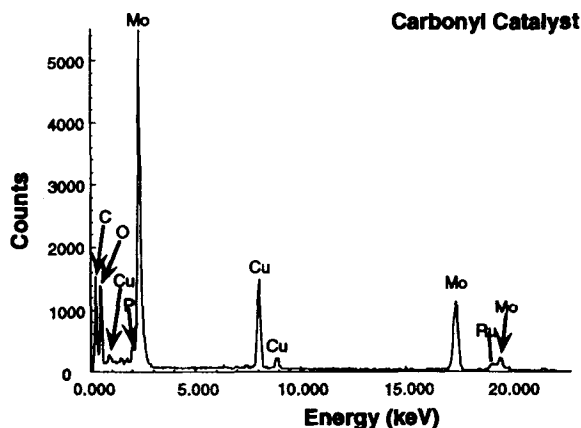


Figure 10 Energy dispersive spectroscopy (EDS) spectrum of the $\text{Ru}_3(\text{CO})_{12}/\text{Mo}$ -HPA-derived catalyst. See the Experimental section for conditions.

what is most likely *N*- nC_6H_{13} -THQ are observed and identified by fragments at $m/z = 207$ (23), 206 (72), 205 (90), 204 (100), 203 (70), 202 (37), 146 (5). There is also GCMS evidence for what appears to be *N*-propenyl-THQ with fragments $m/z = 187$ (31), 172 (100), and 144 (27).

Catalytic THQ dehydrogenation to Q is expected to occur readily in the absence of hydrogen.¹⁵ The additional *N*-alkylation products can be readily explained by increased rates of ethanol dehydrogenation in the absence of hydrogen. If we assume that reaction [3] becomes insignificant at 0 psig hydrogen, then acetaldehyde (which elutes with the solvent peak and was not identifiable by GC MS) must increase in concentration and can undergo a series of reactions as summarized in Scheme 2. Acetaldehyde can react normally with THQ to form an anamine, as

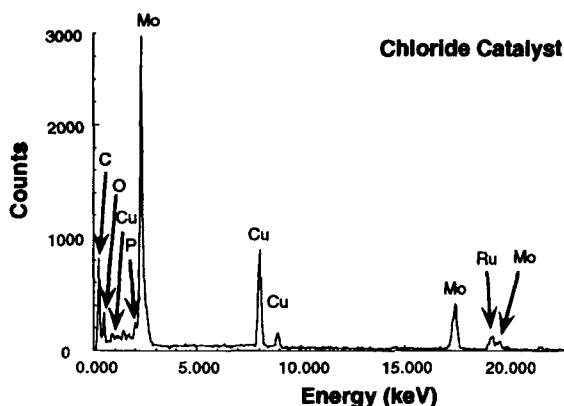
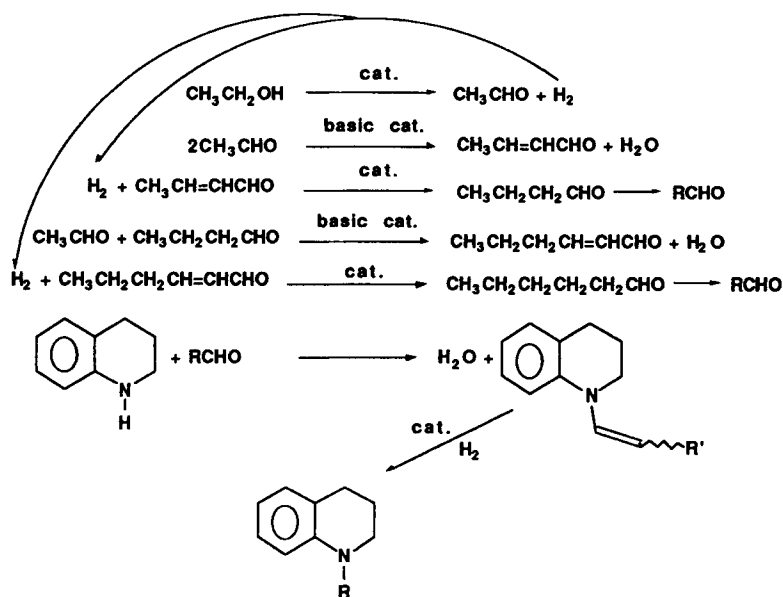


Figure 11 Energy dispersive spectroscopy (EDS) spectrum of the RuCl_3/Mo -HPA-derived catalyst. See the Experimental section for conditions.



shown above, which subsequently undergoes hydrogenation to *N*-Et-THQ as in reaction [1]. If acetaldehyde reaches sufficient concentration, it will undergo classic aldol condensation to 2-butenal and eventually can form 2-hexenal.

Given that aldol condensation is a bimolecular reaction, the presence of significant quantities of the longer-chain alkylation products (*N*-*n*Bu-THQ accounts for 15% of products) is indicative of relatively high concentrations of acetaldehyde in the reaction solution. This observation provides indirect support for high-pressure hydrogen inhibition occurring via reaction [3]. One might anticipate seeing some aldol-condensation-derived alkylation products if another inhibition mechanism were operating. Further work on this system will be necessary to detail the kinetics and mechanisms of ethanol dehydrogenation apart from its role in THQ alkylation.

CONCLUSIONS

In liquefaction of coal and hydrotreating of crude oil, oil shale and coal-derived liquids, it is certain that primary and secondary alcohols form. Since standard HDN catalysts contain sulfided molybdenum and cobalt sites, it is likely that these intermediate alcohols will alkylate any amine sources produced coincidentally. Although cobalt

is not as good a hydrogenation catalyst as ruthenium, at the elevated temperatures currently used for hydrotreating it is possible that alkylation will occur quite readily. Given that tertiary amines (e.g. *N*-Et-THQ) undergo HDN with a great deal more difficulty than unalkylated amines, it is important to understand and control the processes identified above.

Future studies are planned in which we will contrast the current results with the catalytic activity of the RuMo-HPA, $H_4PMO_{11}RuO_{39}$.¹⁴ This should prove the key to understanding the value, or lack thereof, of using two-component versus single-component precatalyst solutions.

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