

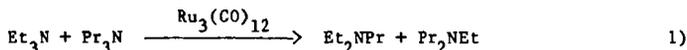
NEW CATALYSTS FOR HYDROTREATING COAL LIQUIDS

A. S. Hirschon, R. B. Wilson, Jr. and R. M. Laine*

SRI International, Menlo Park, CA 94025

The cost of hydrotreating coal liquids or heavy crudes is considerably higher than for light crudes because of the significantly higher amounts of sulfur, nitrogen and oxygen found in these hydrocarbon sources relative to light crudes. In particular, the current processes for the catalytic removal of nitrogen (HDN) and oxygen (HDO) consume excessive amounts of hydrogen due to concurrent hydrogenation of aromatics. The ideal HDN or HDO catalyst would be one that selectively cleaves C-N or C-O bonds with minimum consumption of hydrogen. This would reduce the overall hydrotreating costs for refining crude oil and could make synfuels a competitive energy source.

In this paper, we discuss the results of two approaches to the development of improved HDN catalysts. One approach focuses on the synthesis of high-activity, highly dispersed, "surface confined", catalysts using organometallic complexes. The other approach examines the hydrotreating activities of metals not currently used in HDN and HDO catalysis. This latter investigation arises as a consequence of our efforts to develop mechanistic models of HDN through studies of the homogeneous catalysis of the transalkylation reaction, (1,2) equation 1,



and through studies of quinoline HDN by bulk metals (3). In both the trans-alkylation and the bulk metal studies; ruthenium exhibits the highest activity for C-N bond cleavage. This suggests that it may be useful as an HDN catalyst.

We describe here the synthesis and HDN activities of catalysts prepared according to the principles established by these two separate approaches.

Experimental

Materials

The CoMo catalyst (HT-400, 3 wt% CoO, 15.1 wt% MoO₃, on Al₂O₃) was donated by Harshaw Chemical Company. The preparation of the sulfided catalyst has been described previously.⁴ γ-aluminum oxide was donated by Kaiser Aluminum and was made from Gibbsite (surface area = 210 m²/g and passed 400 mesh sieve.) The aluminum oxide was calcined at 400°C for 2h under flowing synthetic air. Ruthenium was obtained from Strem Chemical, and was heated at 400°C for 12 h first with flowing synthetic air to remove any surface sulfur, and then with flowing hydrogen to form the reduced metal. Ruthenium carbonyl [Ru₃(CO)₁₂] and nickel cyclooctadiene [Ni(COD)₂] were obtained from Strem Chemicals and used as received. Molybdenum(II) allyl dimer was prepared by modifying the method of Cotton and Pipal (5).

Preparation of a Conventional NiMo Catalyst

Ammonium molybdate tetrahydrate (2.10 g, 1.7 mol) and nickel nitrate hexahydrate (1.34 g, 4.6 mmol) were dissolved in 200 mL of water. Alumina, 10 g, was added to the metal salt solution and stirred for 24 h. The water was evaporated from the mixture, and the residue was slowly heated to 400 C under flowing synthetic air over a 2-h period. The heating was continued for 12 h. The process was repeated for another 12 h with flowing H₂S (10%)/H₂.

Preparation of Supported Organometallic Catalysts

Molybdenum Supported on Alumina. Molybdenum allyl dimer (1.0 g) dissolved in 10 mL of hexane was slowly added to a stirred slurry of 10 g of alumina in 20 mL of hexane. The mixture was stirred overnight, then washed with 20 mL of hexane to give a gray solid. The product was then heated at 200 C in flowing $H_2S(10\%)/H_2$ for 12 h.

Bimetallic Metal Supported Catalysts. An aliquot (1 g) of the sulfided supported molybdenum catalyst was suspended in 10 mL of hexane. The desired amount of Ni (as $Ni(COD)_2$) in THF was added to the suspension and the mixture stirred overnight, washed with hexane, dried, and sulfided at 200 C as described above.

Ruthenium doped CoMo Catalyst (RuCoMo). Under nitrogen, ruthenium carbonyl (0.053 g), dissolved in 5 mL of hexane, was added to a stirred slurry of 2.00 g of the sulfided CoMo catalyst in 10 mL of hexane. The mixture was allowed to stir for 72 h. The hexane was then evaporated and the residue heated under vacuum at 76°C for 6 h. A portion of the doped catalyst was sulfided by treating with a flowing mixture of $H_2S(10\%)/H_2$ at 200°C for 12 h.

Standard HDN Reaction Procedures

The following materials were placed in a quartz liner, under nitrogen in a 45-mL Parr bomb: the catalyst (0.100 to .250 g), a stirbar, and 10 mL of 0.197 M quinoline (0.151 M THQ for Ru reactions) and 0.098 M n-dodecane (as internal standard) in n-hexadecane. The bomb was pressurized with 500 psia of H_2 , and heated at the desired temperature.

Results and Discussion

The HDN activities of the catalysts prepared by the various synthetic techniques were compared using a quinoline/hexadecane solution for model studies. As shown in Figure 1, quinoline HDN leads to two major HDN products; propylcyclohexane (PCH) and propylbenzene (PB). In comparing the catalytic properties of the various catalysts, we use two criteria, rate of HDN and, as discussed above, hydrogen consumption. The production of PCH requires 7 moles of H_2 per quinoline and typifies aromatic hydrogenation, whereas the production of PB requires only 3 moles; thus the relative ratios of PCH to PB are an excellent measure of hydrogen consumption.

Comparison of Conventional NiMo and Organometallic Origin NiMo Catalysts

Table 1 lists the estimated turnover frequencies (TF = moles THQ reacted/mole of metal catalyst/hour \pm 10%) for THQ disappearance, and the appearance of PCH, PCHE, and PB, calculated based on initial rates. From this data we see that the organometallic origin or surface confined NiMo catalysts exhibit higher hydrogenation activity than a conventionally prepared NiMo catalyst. In a similar manner and from Figures 2a-c, it can be seen that the surface confined catalysts are superior in terms of C-N bond cleavage activity.

The total metal content in the catalysts is approximately the same, so that the activity and selectivity of these catalysts can qualitatively be compared. Figure 3 presents calculations of the total hydrocarbon conversion as a sum of PCH, PB and propylcyclohexene (PCHE) as a function of time.

To compare the relative PCH, PCHE and PB selectivities for the various catalysts, the relative distributions of these products, normalized to 5% total hydrocarbon conversion, were extracted from Figure 3 and are listed in Table 2. We see, in Table 2, that the product selectivities for the NiMo catalyst of organo-

metallic origin (surface confined catalyst) are essentially the same as those found with the conventionally prepared NiMo catalyst.

Table 1
TURNOVER FREQUENCIES^a

Catalyst	THQ	PCH	PB	PCHE
NiMo (conventional)	67.4	8.2	0.3	1.4
NiMo (0.83, 2.63)	111	26.5	1.4	--
NiMo (0.37, 2.81)	104	16.6	0.7	1.7
CoMo	54.0	8.9	0.5	0.8
RuCoMo	141	26.9	8.0	0

^aMoles product/moles metal catalyst/h.

Table 2
HYDROCARBON DISTRIBUTION AT 5 mol%
HDN CONVERSION^a

Catalyst	%PCH	%PB	%PCHE
NiMo (conventional)	76.2	5.2	18.6
NiMo (0.37% Ni, 2.81% Mo)	81.4	3.1	15.5
NiMo (0.83% Ni, 2.63% Mo)	76.0	5.0	19.0
CoMo	82.2	4.6	13.2
RuCoMo	76.6	23.4	0

^aReaction of 10 mL 0.197 M quinoline in n-hexadecane and catalyst at 350°C and 500 psig H₂.

Bulk Ruthenium HDN Catalysis

Figure 4 shows the product distribution from the reaction of bulk ruthenium with THQ at 200, 250 and 300°C. These results demonstrate ruthenium's high activity for C-N bond cleavage even at temperatures of 200°C. At 200 and 250°C the major HDN products are propyl- or ethyl- and methyl-cyclohexylamine, but at 300°C almost no nitrogen containing species remain after 3 hours of reaction time due to extensive

C-N and C-C bond hydrogenolysis. If the bulk ruthenium is exposed to sulfur in the form of CS₂ (20 µl to the standard reaction), then even at temperatures up to 350°C, no reaction of any type is observed. Thus, sulfur poisons bulk ruthenium's ability to catalyze both hydrogenation and C-N bond cleavage.

Ruthenium-Doped Harshaw CoMo Catalysts

In an attempt to overcome the difficulty of sulfur poisoning with the ruthenium, we doped a commercial CoMo catalyst with a ruthenium containing organometallic. Figure 5a and b show the product distribution after reaction with a sulfided Harshaw CoMo catalyst and the same catalyst doped with ruthenium. As seen in these figures, the doped catalyst is significantly more active, produces no PCHE, and gives a much higher ratio of propylbenzene to propylcyclohexane than does the "unpromoted" CoMo catalyst. As shown in Figure 3, the total hydrocarbon production is greater for the ruthenium-"promoted" catalyst than any of the other catalysts studied. This catalyst, as shown in Table 2, also produces the most propylbenzene of any of the catalysts studied. For instance, after 5% conversion, the fraction of propylbenzene in the hydrocarbon products has increased from 4.6% for the CoMo catalyst to 23.4% for the RuCoMo catalyst. Furthermore, when this catalyst was treated with carbon disulfide, as was the bulk ruthenium, the catalyst was even more active towards HDN activity.

Conclusions

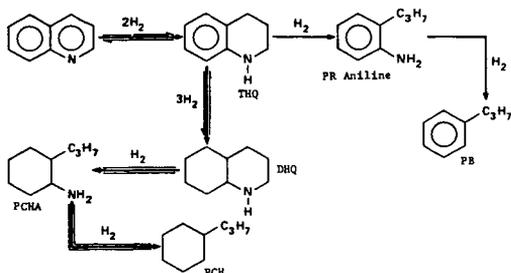
We have shown that the activity of HDN catalysts using conventional metals, such as nickel and molybdenum can be improved using organometallic precursors; although, in our hands, the selectivity of aromatic and aliphatic hydrocarbon products remained unchanged from that of conventional based catalysts. However, through the use of more active metals such as ruthenium, we can promote a conventional type catalyst to give a catalyst which is not only more active, but is more selective towards aromatic products, and remains sulfur tolerant.

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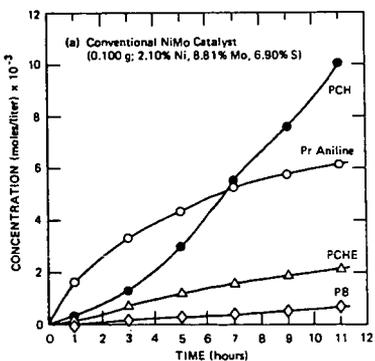
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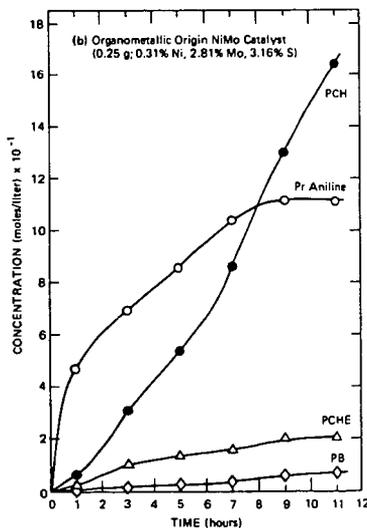
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FIGURE 1 QUINOLINE HDN REACTION NETWORK



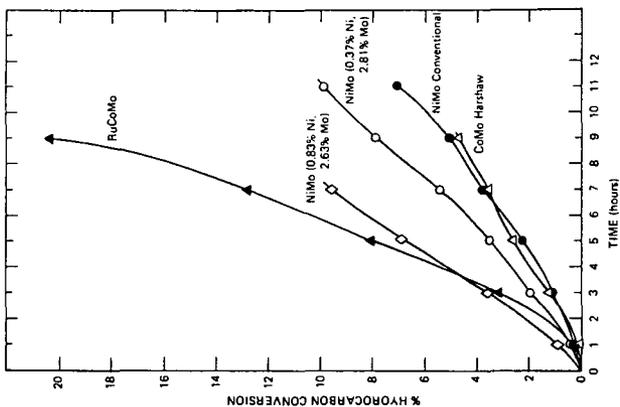
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FIGURE 2a PRODUCT DISTRIBUTION DUE TO CARBON-NITROGEN CLEAVAGE REACTIONS
10 mL of 0.197 M quinoline in *n*-hexadecane and sulfided NiMo catalyst at 350°C and 500 psia H₂.



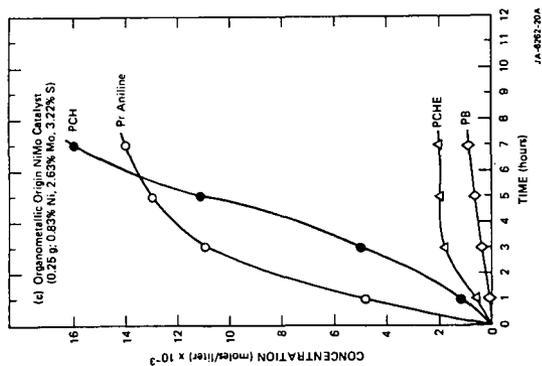
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FIGURE 2b PRODUCT DISTRIBUTION DUE TO CARBON-NITROGEN CLEAVAGE REACTIONS (Continued)
10 mL of 0.197 M quinoline in *n*-hexadecane and sulfided NiMo catalyst at 350°C and 500 psia H₂.



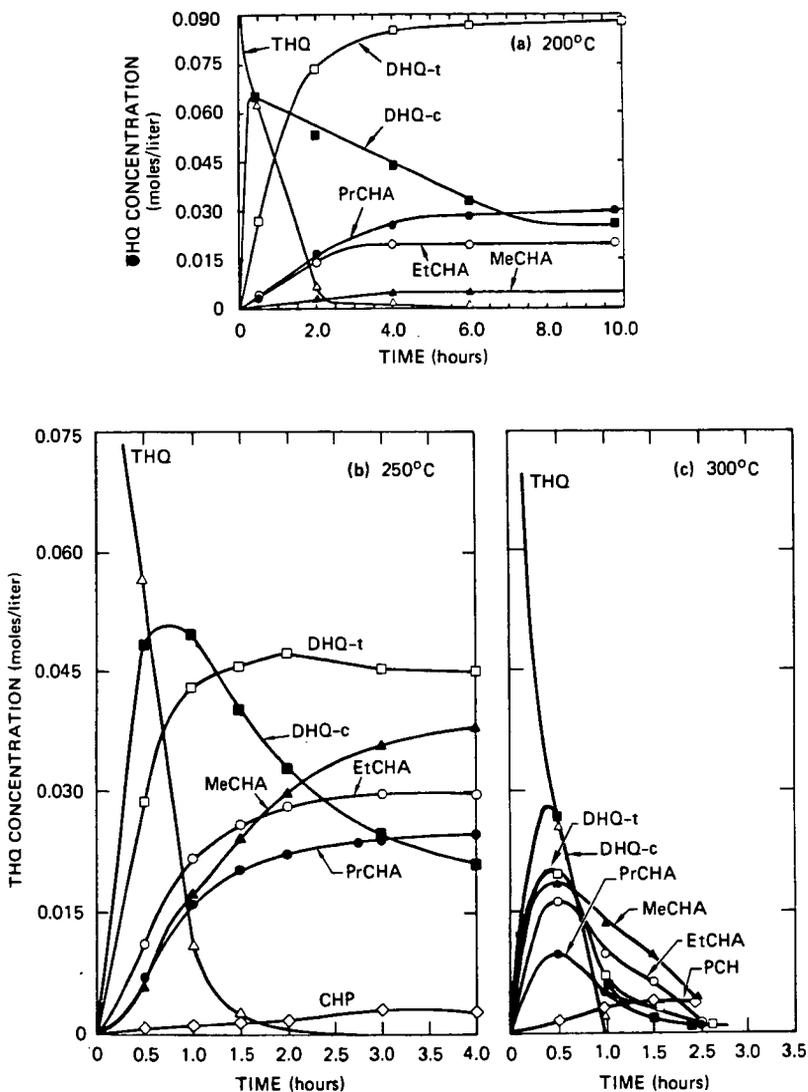
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FIGURE 3 TOTAL HYDROCARBON CONVERSION



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FIGURE 2c PRODUCT DISTRIBUTION DUE TO CARBON-NITROGEN CLEAVAGE REACTIONS (Concluded)
10 mL of 0.197 M quinoline in *m*-heptadecane and sulfided NiMo catalyst at 350°C and 500 psia H₂.



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FIGURE 4 PRODUCT DISTRIBUTION FROM REACTION OF THQ WITH RUTHENIUM AND 500 psi of H_2
 10 mL of 0.1506 M THQ and 0.100 g of Ru in hexadecane.

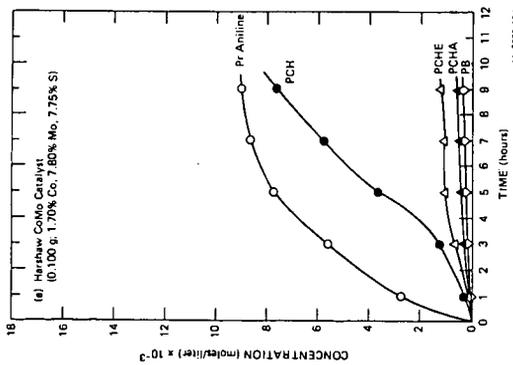


FIGURE 3a PRODUCT DISTRIBUTION DUE TO CARBON-NITROGEN CLEAVAGE REACTIONS WITH CoMo CATALYST
10 mL of 0.197 g/liter *m*-hexanamine and sulfided CoMo catalyst at 350°C and 500 psia H₂.

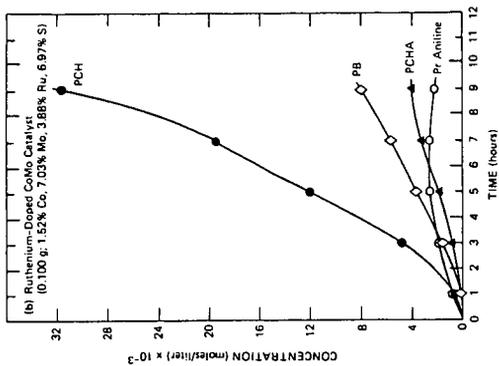


FIGURE 3b PRODUCT DISTRIBUTION DUE TO CARBON-NITROGEN CLEAVAGE REACTIONS WITH CoMo CATALYST (Continued)
10 mL of 0.197 g/liter *m*-hexanamine and Ru/CoMo catalyst at 350°C and 500 psia H₂.