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REVIEW

Use of organometallic chemistry for hydrotreatment catalyst development

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This paper describes our use of organometallic chemistry to develop enhanced hydrotreatment catalysts. The approach involves (1) identifying the most active catalytic metals, (2) choosing precursors that will be easily activated into these materials under mild conditions, and (3) then increasing the surface area to provide a highly active catalyst. We describe our efforts in studying hydrodenitrogenation (HDN) reactions, including homogeneous reaction chemistry of the C—N bond, development of enhanced HDN catalysts for coal liquids, and some applications of organometallic chemistry towards coal liquefaction.

Keywords: Hydrotreatment, catalysis, transition metals, coal liquids

INTRODUCTION

Conventional hydrotreatment has focused on petroleum feedstocks that are relatively easy to process, but with petroleum more difficult to find the focus has now shifted to utilizing heavy oils and coal-derived liquids. These feedstocks, especially those of coal liquids, are much harder to refine than the light-petroleum products. In the past, CoMo- and NiMo-based catalysts on alumina refractory support have been satisfactory as hydrotreatment catalysts. However, the heavy oils and coal liquids are much higher in heteroatom content, with the latter also having a high aromatic content. These heteroaromatic compounds are extremely difficult to hydrotreat, and require strenuous reaction conditions. Such conditions are especially difficult when using highly aromatic feedstocks since concurrent hydrogenation will also occur, wasting large amounts of expensive hydrogen. What is needed is a more selective catalyst, that will perform hydrogenolysis reactions selectively over hydrogenation reactions. If such a catalyst could hydrotreat at lower temperatures and pressures than are currently used, then not only would there be energy savings, but there would be less sintering and deactivation of catalysts so that the overall process would give a better-quality product and the cost of catalyst would be decreased.

In order to improve these catalysts, a thorough understanding of the mechanism of the hydrotreatment reaction and the roles of the metals for hydrogenation and hydrogenolysis reactions need to be established. However, conventional means of catalyst preparation lead to catalytic metals in a variety of physical and chemical states. The correct active site is not always obvious, and with the utilization of novel supports, recent work has shown that many of the 'well-known' facts about the roles of catalytic metals are incorrect. Thus an important role of organometallic chemistry techniques is the ability to form well-defined catalytic materials. In the following sections we describe how research groups at SRI have used organometallic methods to model HDN catalysis and then apply these methods to both hydrotreatment and coal liquefaction.

2 DETERMINATION OF ACTIVE CATALYSTS

Based on the rationale that an understanding of the HDN process, at the molecular level, will provide valuable information of use in the development of new or improved HDN catalysts, the C—N bond cleavage was studied using the transalkylation reaction [1].[1-7] The objectives of the transalkylation studies were to provide experimental evidence that homogeneous cluster catalysts could be used to model the catalytic reactions of heterogeneous catalysts. A high correlation between the catalytic reactivity patterns of homogeneous cluster catalysts and

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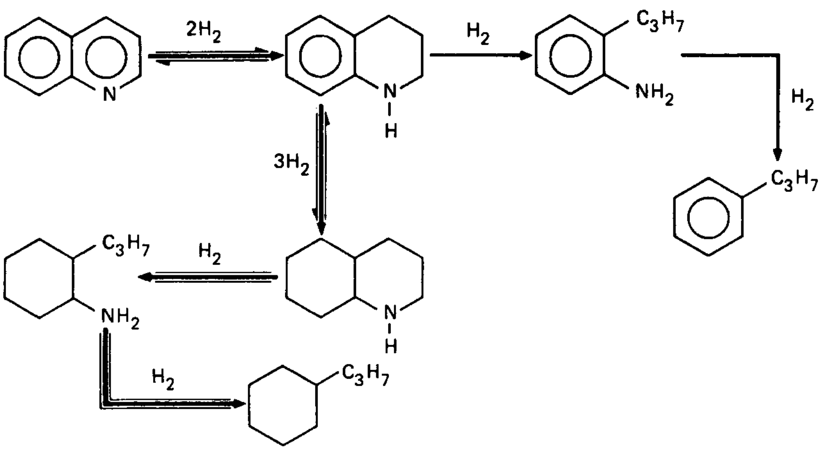

Figure 1 Quinoline HDN reaction network.

several heterogeneous catalysts was observed in their reactions with tertiary amines.

$$Et_3N + Pr_3N \xrightarrow{\text{catalyst}} Et_2NPr + Pr_2NEt \qquad [1]$$

Numerous homogeneous catalyst systems were evaluated for both C—H and C—N activation, with the order of reactivity being Os > Ru > Ir > Rh ≫ Fe,Co,Mo. Thus, both ruthenium and osmium catalyst systems were found to be optimal catalysts for transalkylation, and we predict that these metals would also be optimal for HDN catalysis.

In order to verify this prediction when applied to heterogeneous HDN catalysis, we examined the activity of a series of bulk metals on quinoline or tetrahydroquinoline.[8] These nitrogen molecules are useful HDN models because, as shown in Fig. 1, there are two routes to the HDN products. The bold-face route, which leads to propylcyclohexane (PCH), consumes 7 mol of hydrogen, compared with the aromatic route which leads to propylbenzene (PB), and consumes only 4 mol of hydrogen. Thus the two routes present a measure of selectivity of catalyst. A catalyst that selectively gives a higher ratio of PB over PCH would most likely also consume less hydrogen from the hydrogenation of the other aromatic components in the coal liquid or petroleum feedstock. The bulk ruthenium was found to be exceptionally effective for HDN catalysis at temperatures of 200–300 °C and hydrogen pressures of 500 psig (3450 kPa). However, as shown in Fig. 2, mainly aliphatic products and indiscriminate C—C and C—N bond-cleavage products were produced. Rhodium and platinum were less active and nickel, molybdenum, rhenium and osmium were inactive. A commercial sulfided and activated CoMo or NiMo catalyst does not show significant HDN activity under these conditions until temperatures of 350 °C are reached. The reactivity profile, with the exception of osmium, correlates directly with what might be expected based on the publications of Sinfelt,[9] Pecoraro and Chianelli,[10] and Harris and Chianelli,[11] as well as the results predicted from the amine transalkylation.[1–7] Chianelli and Sinfelt present evidence that ruthenium and osmium exhibit superior catalytic activity for a variety of bond-cleavage reactions, including C—C and C—S bond hydrogenolyses and ammonia decomposition, relative to the majority of the transition metals.

However, the bulk metal studies showed that the presence of sulfur poisons the bulk ruthenium, and deactivates it both for aromatic ring hydrogenation and for C—N bond hydrogenolysis,[8] and therefore a commercial sulfided CoMo hydrotreatment catalyst, which is sulfur-tolerant, was modified with organometallic ruthenium complexes (i.e. ruthenium carbonyl). The objectives of this experiment were to determine (1) whether the ruthenium would increase the HDN activity and selectivity of the CoMo catalyst and (2) whether the CoMo catalyst would make the ruthenium sulfur-tolerant.[12, 13] Some results of this modification to form a RuCoMo catalyst are listed in Tables 1 and 2. Other metals were added to the CoMo catalyst in the form of their respective carbonyls, and the HDN activity of the resulting promoted catalysts showed a similar range of activities as with the bulk metals, with the

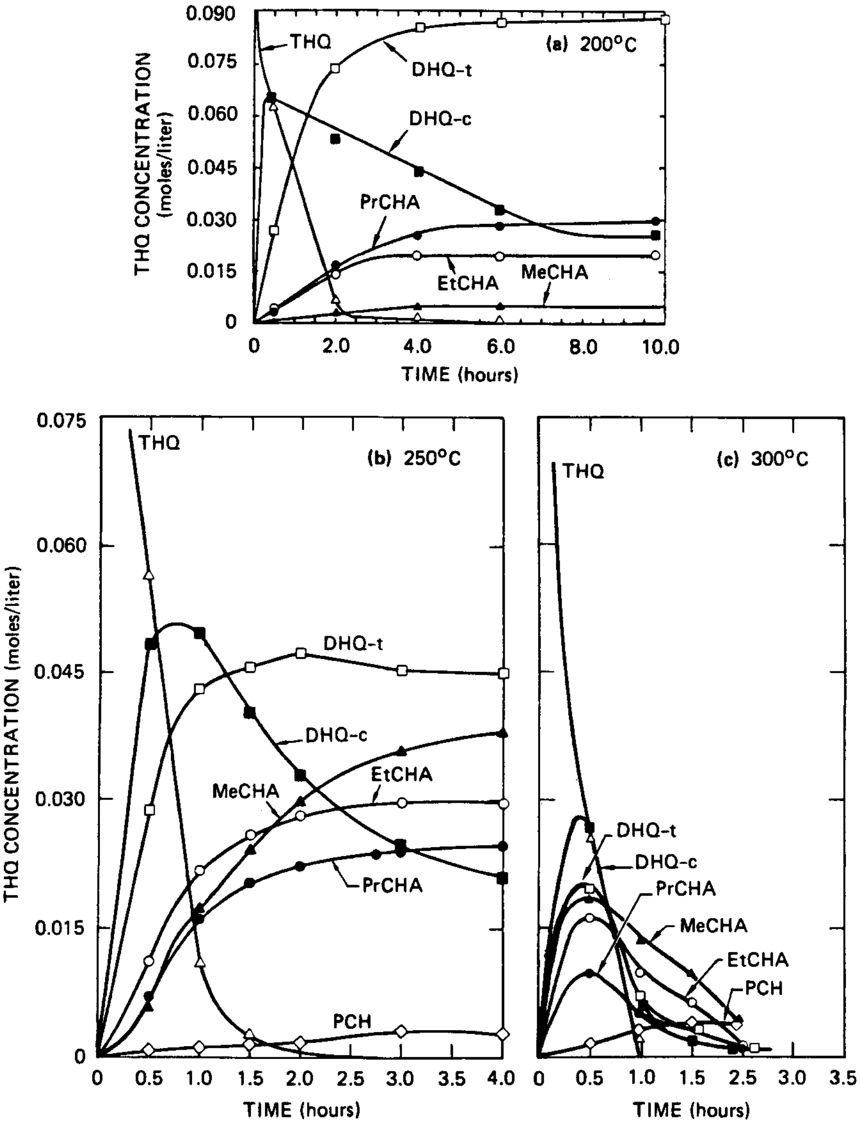

Figure 2 Product distribution from reactions of THQ with bulk ruthenium at 500 psig hydrogen as a function of temperature ($10\,cm^3$ of $0.151\,mol\,dm^{-3}$ THQ and 0.1 g ruthenium in hexadecane). THQ, tetrahydroquinoline; DHQ, decahydroquinoline; MeCHA, EtCHA and PrCHA, methyl-, ethyl- and propyl-cyclohexane; PCH, propylcyclohexane.

ruthenium-promoted catalyst being the most active. HDN activities of the catalysts were compared by calculating the turnover frequencies (TF) for the disappearance of tetrahydroquinoline (THQ) and formation of PB and PCH. Selectivities were determined from the relative distribution of PCH, PB and propylcyclohexene (PCHE) when 5% of the quinoline had been converted into these hydrocarbon products. In contrast to the bulk ruthenium, this catalyst promoted with ruthenium gives products similar to those from conventional hydrotreatment catalysts, but is extremely selective and highly active toward the production of aromatic products. For instance, the ruthenium-modified catalyst increased PCH production by a factor of three and the PB production by a factor of more than 20 over that of the non-promoted catalyst. Furthermore, it had less of the intermediate propylcyclohexene (PCHE) which is found in the HDN reactions of quinoline as an intermediate. This catalyst was very active and selective, even in

Table 1 Turnover frequencies for quinoline HDN using promoted catalysts[a]

	TF[b]		
Catalyst	THQ	PCH	PB
CoMo	54.0	8.9	0.5
RuCoMo	141	26.9	8.0
FeCoMo	54.6	6.8	1.3
RhCoMo	104.9	12.6	0.8

[a] 10 cm^3 of hexadecane solution and 0.10 g catalyst at 350 °C and 500 psig hydrogen. [b] Moles substrate/total moles metal in catalyst per h.

the presence of excess sulfur as H_2S. Interestingly, in the presence of excess sulfur, an increase in the amount of PCHE was observed. PCHE has been postulated to arise from the catalytic route; however, in a separate experiment we also examined the effect of the support, aluminum oxide, at 350 °C on cyclohexylamine and found that it loses ammonia to form cyclohexene as an acid-catalyzed deamination. Thus, an additional possibility for the formation of PCHE is an acid-catalyzed route, which is consistent with the acidic properties of H_2S.

The effects of hydrogen pressure on the HDN of quinoline with the RuCoMo catalyst is shown

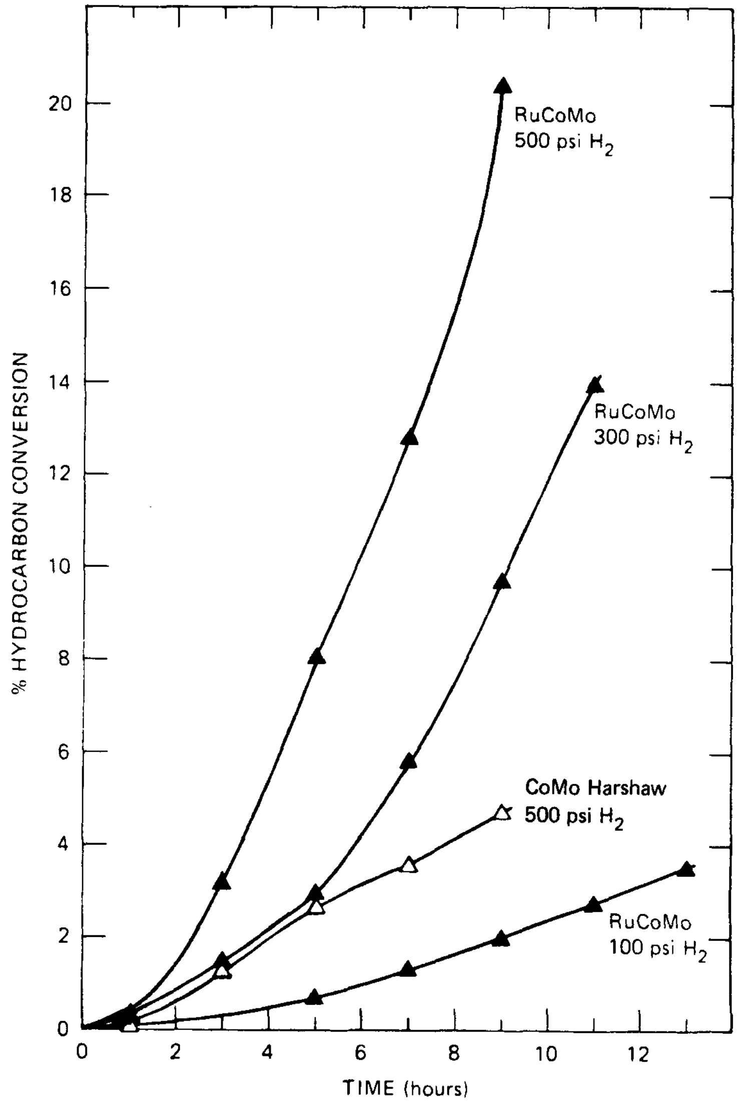

Figure 3 Total hydrocarbon conversion as a function of hydrogen pressure

Table 2 Selectivity at 5 mol% conversion[a]

	Hydrocarbon products (mol %)			
Catalyst	PCH	PB	PCHE	PCH/PB
CoMo	82.2	4.6	13.2	17.8
RuCoMo	76.6	23.4	0	3.3
FeCoMo	63.0	17.0	20.0	3.7
RhCoMo	90.0	4.0	6.0	23.0

[a] 5% conversion of quinoline into hydrocarbon products.

Table 3 Selectivity at 5 mol % conversion[a]

	Hydrocarbon products (mol %)			DHQ present at 5% conversion (mol %)
	PCB	PB	PCHE	
CoMo (Harshaw)	82.2	4.6	13.2	18
RuCoMo				
500 psig H_2	76.6	23.4	0	24
300 psig H_2	75.3	24.7	—	6
100 psig H_2	50.0	50.0	—	<1

[a] 5% conversion of quinoline into hydrocarbon products.

in Fig. 3 for the RuCoMo and the CoMo catalyst. The activities at 500 and 300 psig (3450 and 2070 kPa) are both superior to that of the CoMo, and the 100 psig (690 kPa) reaction is about one-half as active. The selectivity data, tabulated in Table 3, show that the distribution changes from 76.6% PCH and 23.4% PB at 500 psig to 75.3% PCH and 24.7% PB at 300 psig to 50% PCH and 50% PB at 100 psig for the RuCoMo catalyst. In comparison, the CoMo catalyst yields 82.3% PCH to 4.6% PB at 500 psig, and at 100 psig the CoMo catalyst is almost inactive. Also as seen in this table, at 5% HDN conversion there is 24%, 6% and <1% DHQ at 500, 300, and 100 psig, respectively, for the RuCoMo catalyst, compared with 18% for the CoMo catalyst at 500 psig. The lower DHQ formation at reduced pressure may reflect less concurrent hydrogenation, indicating an even greater saving in hydrogen consumption.

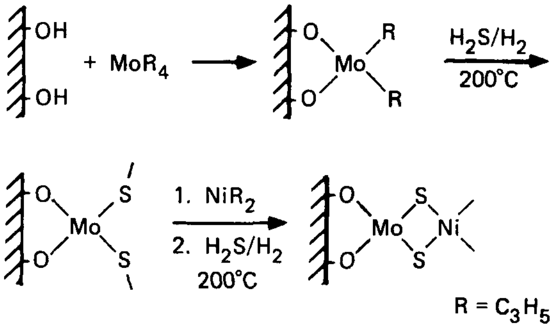

Figure 4 Preparation of surface-supported catalysts.

3 SUPPORTED ORGANOMETALLIC CLUSTERS

The second approach utilized to improve HDN catalysts, based on the work of Yermakov, involves the synthesis of a highly dispersed metal bound on the surface of the support through reactions of organometallic compounds with support hydroxyl groups.[14,15] The metal is then sulfided, and a second metal is then added to form the bimetallic surface-confined catalyst, as illustrated in Fig. 4. In contrast, a conventionally made catalyst, such as one made by the incipient wetness technique, involves heating metal salts at high temperatures under oxygen to form metal oxides, and then treating the metal oxides at high temperatures under hydrogen sulfide/hydrogen to form the reduced metal sulfides. The high-temperature preparations cause sintering of the metals to form large metal particles. Thus only a small portion of the total metal is on the surface and available for catalysis.

The advantage of the Yermakov method is that the catalyst is highly dispersed, can be activated at low temperatures (<250 °C), and forms relatively small metal particles. Measurements from electron microscopy has shown that molybdenum and tungsten sulfides, when activated at temperatures of 350 °C, give particle sizes of less than 10 Å (1 nm) compared with a range of 10–2000 Å (1–200 nm) when prepared by conventional means. Bimetallic catalysts such as sulfided NiMo prepared by the Yermakov method have been shown to form filaments of approximately 25 Å in length, and XPS data suggest a bimetallic alloy. These catalysts may be exceptionally active because of the high surface area of the metals. Another possible advantage of these dispersed 'surface-confined catalysts' is that, because they can be prepared from metal clusters, they may have some of the properties of homogeneous catalysts; that is, they may be more selective.

Table 4 compares the HDN activities of a NiMo catalyst prepared by the organometallic

Table 4 Turnover frequencies for quinoline HDN[a] (Organometallic vs Conventional Catalysts)

		TF[b]		
Catalyst	Precursor	THQ	PCH	PB
NiMo	Conventional	67.4	8.2	0.3
NiMo	$Mo_2(allyl)_4$ $Ni(COD)_2$	111	26.5	1.4
NiMo	$Mo_2(OAc)_2$ $Ni(COD)_2$	40.6	3.4	0.5
RuNiMo	$Mo_2(allyl)_4$ $Ru_3(CO)_{12}$	155	22.2	2.4
RuMo	$Mo_2(allyl)_4$ $Ru_3(CO)_{12}$	260	40.8	12.1

[a] 10 cm^3 of hexadecane solution and 0.10 g catalyst at 350 °C and 500 psig H_2.

[b] Moles substrate/total moles metal in catalyst per h.

approach, using molybdenum(II) allyl dimer, with that prepared by a conventional incipient wetness approach (conv.) Here the TF for formation of PCH has increased from 8.2 to 26.5 and the TF for formation of PB has increased from 0.3 to 1.4. The increased activity is due to a highly dispersed organometallic complex, yielding a high-surface-area catalyst and using the minimum amount of metal. Also note that when a less active catalyst precursor is used, $Mo_2(OAc)_4$, the HDN activity is far less. The methods of preparation and activation of both these complexes were similar, and most likely could not explain the differences in reactivity. We believe the difference in this case is due to a low dispersion of $Mo_2(OAc)_4$ on the alumina support due to its lack of reactivity with the surface OH molecules. The last examples show a combination of both surface-confined catalyst and promoted ruthenium to form RuMo and RuNiMo catalysts. Note that the reactivity and selectivity for the RuMo catalyst are far greater than those of any other catalysts, with a TF of 40.8 and 12.1 for formation of PCH and PB, respectively, showing a 25-fold increase in reactivity towards PB over a conventional-type catalyst.

4 NON-SUPPORTED CLUSTERS

Hydrotreatment catalysts are very often good coal liquefaction catalysts, and therefore high-dispersion techniques were also investigated for coal liquefaction applications. Dispersed catalysts are sometimes used to provide a means of rapidly hydrogenating the coal molecules and possibly removing heteroatoms during the initial stages of coal liquefaction. These catalysts help prevent thermal polymerization reactions (retrogressive reactions) which limit the conversion of coal to soluble products. Generally, efforts to use dispersed catalysts during coal liquefaction utilize precursors that are not activated except at high temperatures.[16–19] For instance, molybdenum is often added as either the oxide, the thiolate water-soluble salt, or molybdenum naphthenate. In the latter case the molybdenum must be transformed from the oxide first to the trisulfide, and finally to the disulfide, the most active form of the catalyst (Eqn [2]). However, the conversion of the trisulfide to disulfide occurs only under high temperatures, in excess of 350 °C.[20] Thus these types of dispersed catalysts would not be active during the low-temperature regime where most of the retrogressive reactions are thought to occur.

$$MoO_4^{2-} \rightarrow MoS_4^{2-} \rightarrow MoS_3 \rightarrow MoS_2 \qquad [2]$$

A more desirable precursor would be one which decomposed to the desired product under mild conditions. For these types of precursors we followed the work of DuBois *et al.* and Curtis *et al.*, who have intensively investigated the preparation and reactivities of molybdenum thiolato complexes and molybdenum bimetallic thiolato complexes (i.e. $Cp_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$, and $Cp_2Mo_2Co_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)(CO_4)$.[21-25] These types of complexes are intriguing in that they are soluble in organic solvents and active catalysts at room temperatures, and when used as catalytic precursors, are of the correct stoichiometry to form directly the desired catalyst (for instance, MoS_2 rather than MoS_3). For our purposes we expect that these complexes in organic solvents will impregnate the coal structure and under liquefaction conditions will decompose to MoS_2 within the coal pores to form a highly dispersed catalyst. For these investigations we compared the water-soluble MoS_4^{2-}, referred to as Mo(Aq), which is often used in coal liquefaction experiments as a dispersed catalyst, with $Cp_2(Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$, referred to as Mo(OM).[26–28] Data from coal conversions in tetralin and hexadecane solvent systems using these systems are presented in Tables 5 and 6, respectively. The first three liquefaction experiments listed in Table 5 were conducted at 400 °C and include a non-catalyzed conversion, as well as conversions using both molybdenum catalysts. The remaining three experiments were conducted at 425 °C. The Illinois no. 6 coal gave quite high conversions to toluene-soluble material even under the mild conditions of 500 psig hydrogen pressures and 400 °C when tetralin was used for the coal liquefaction, as expected for a high-volatile bituminous coal in a good hydrogen-donor solvent. For example, the conversion to toluene-soluble material in the absence of catalyst in tetralin was 48%, compared with 53% when impregnated with aqueous molybdenum, and 61% when the coal was impregnated with organometallic molybdenum. A similar trend was observed when the conversion temperature increased to 425 °C, with the molybdenum organometallic-catalyzed reactions giving a 15% increase over the non-catalyzed conversions.

Since the tetralin appeared to moderate the effects of the catalysts, so that the range of conversions was only about 15%, n-hexadecane was utilized as a non-reacting, non-donor conversion medium that would not interfere with the study of the catalysts. The results of these conversions are shown in Table 6. Most of the conversions are quite low, as expected. For instance in the absence of catalyst the Illinois no. 6 coal was converted to 25% toluene-soluble material, compared with 48% in tetralin. However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. The aqueous molybdenum impregnation gave a conversion of 41% and the organometallic molybdenum impregnation resulted in a conversion of 54%, which is nearly as great as when tetralin was used as the conversion medium.

Thus dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen-donating solvent. Dramatic evidence of this is the extent of the conversions in the non-donor solvent hexadecane, showing that the catalyst itself is effective at hydrogenating the coal from molecular hydrogen without relying upon a donor solvent as a hydrogen shuttler.

Table 5 Conversion to toluene soluble products in tetralin[a]

Catalyst	Temp. (°C)	TS (mol %)
None	400	48
$MoS_4(Aq)$	400	53
$MoS_2(OM)$[b]	400	61
None	425	69
$MoS_2(OM)$[b]	425	84
$MoS_4(Aq)$	425	76

[a] Reaction conducted in 300 cm^3 autoclave: 5 g Illinois no. 6 coal in 30 g solvent; H_2 at 500 psig for 20 min. [b] OM refers to organometallic precursor.

Table 6 Conversion to toluene-soluble products in hexadecane[a]

Catalyst	TS (mol %)
None	25
$MoS_4(Aq)$	41
$MoS_2(OM)$[b]	54

[a] Reaction conducted in 300 cm^3 autoclave with 5 g coal in 30 g solvent and 500 psig H_2 for 20 min. [b] OM refers to organometallic precursor.

Differences in particle size and dispersion due to the method of preparation have been well documented. For instance, Thompson and Carvill recently estimated the particle size of MoS_2 formed from an organometallic molybdenum thiolate precursor to be less than 15 Å.[29, 30] In contrast, estimates of particle sizes from aqueous impregnation techniques have been in the hundreds of Angstroms (tens of nanometers).[31] Thus the effective surface area and therefore the effective reactivity must be far greater for catalysts formed from the proper organometallic precursors.

EXPERIMENTAL

A typical preparation of surface-confined catalyst for hydrotreatment applications supported on alumina is as follows. The alumina was dried under flowing air at 400 °C to remove excess water before being treated by organometallic molybdenum clusters such as molybdenum(II) acetate and molybdenum(II) allyl dimer, synthesized by the methods of Wilkinson[32] and Cotton,[33] respectively. These low-valent reactive metal clusters react with the free OH groups of supports such as alumina, as shown in Fig. 4. These supported metals are then sulfided under an atmosphere of hydrogen sulfide and hydrogen to prepare the thiolato forms of the metals. To make the bimetallic catalyst, a second organometallic metal such as $Ni(COD)_2$ was added in solution to the thiolato molybdenum, to form the mixed-metal cluster. This cluster was then activated under hydrogen and hydrogen sulfide to form the surface-supported catalyst. In order to determine the effect of various promoters to these catalysts, or to conventionally prepared catalysts, we impregnated the fully sulfided bimetallic catalysts with the desired metal carbonyl, and then further sulfided the catalyst. We have also prepared catalysts utilizing the organometallic metal thiolato complexes such as $Cp_2(Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$, Mo(OM), which is easily made by the addition of sulfur to the corresponding molybdenum complex.[23] we have used this catalyst primarily as a non-supported catalyst for direct coal liquefaction.

CONCLUSIONS

We have taken two approaches to understand and develop enhanced hydrotreatment catalysts. The first is to use homogeneous reaction chemistry to help determine the most promising catalysts, and the second approach is to use surface-confining techniques to form the heterogeneous catalysts in a well-defined manner. The advantages of these techniques are that the active catalyst can be identified without interferences from supports, or other forms of the metal catalyst. The homogeneous and surface-confined catalysts are more easily characterized and observed during their reactions, and thus more fundamental information can be obtained than with conventional types of catalysts.

Thus the use of organometallic chemistry is potentially a very powerful tool to understand better and to help develop heterogeneous catalysis. For instance, a thorough investigation of bi- and multi-metallic clusters as models to study these relationships in terms of the transalkylation reaction and effects of potential poisons such as hydrogen sulfide will aid us in the design of enhanced HDN catalysts with the optimal catalytic metal sites to give a catalyst which is both active and selective.

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