ELSEVIER

Catalysis Today 31 (1996) 121–135

CATALYSIS TODAY

Hydrodeoxygenation of O-containing polycyclic model compounds using a novel organometallic catalyst precursor

Stephen R. Kirby *, Chunshan Song, Harold H. Schobert

Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Abstract

Compounds containing oxygen functional groups, especially phenols, are undesirable components of coal-derived liquids. Removal of these compounds from the products of coal liquefaction is required. A beneficial alternative would be the removal of these compounds, or the prevention of their formation, during the liquefaction reaction itself, rather than as a separate processing step. A novel organometallic catalyst precursor containing Co and Mo has been studied as a potential hydrogenation catalyst for coal liquefaction. To ascertain the hydrodeoxygenation activity of this catalyst under liquefaction conditions, model compounds were investigated. Anthrone, 2,6-di-*t*-butyl-4-methyl-phenol, dinaphthyl ether, and xanthene were reacted in the presence of the Co-Mo catalyst precursor and a precursor containing only Mo over a range of temperatures, providing a comparison of conversions to deoxygenated products. These conversions give an indication of the hydrodeoxygenating abilities of organometallic catalyst precursors within a coal liquefaction system. For example, at 400°C dinaphthyl ether was converted 100% (4.5% O-containing products) in the presence of the Co-Mo organometallic precursor, compared to 76.5% conversion (7.4% O-products) in the presence of the Mo catalyst.

Keywords: Hydrodeoxygenation; O-Containing polycyclic model compounds; Novel organometallic catalyst precursor

1. Introduction

Oxygen-containing functional groups are present in virtually all coals [1]. Phenols (and related hydroxyl compounds) have been identified as components of coal-derived distillates [2,3], and oxygenated compounds have been connected to the instability of these distillates [4]. Ether linkages, connecting structural units within the coal matrix, have been proposed as sites for the depolymerization of the coal [5], and together with carboxyls and phenolics, have been implicated in facilitating retrogressive, crosslinking, repolymerization reactions [6,7].

Low-rank coals (i.e. lignites and subbituminous coals) include significantly more oxygen-containing groups than coals of higher rank [8]. With the increase in the extraction of low-rank coals in the US and research into their use as liquefaction feedstocks [6,9,10], the ability to remove oxygen functional groups from coal and coal-derived liquids becomes even more important. The removal of these oxygen functionalities from the distillate products of coal liquefaction can be both complicated and expensive, and often leads to substantial reductions in distillate yields [3]. Therefore, deoxygenation dur-

---

* Corresponding author.

0920-5861/96/$32.00 Published by Elsevier Science B.V.
PII S0920-5861(96)00083-1

ing the liquefaction process itself would be beneficial.

Sulfided metal catalysts have been considered desirable for liquefaction processes, because they are not readily poisoned by the oxygen-, nitrogen- or sulfur-containing compounds produced from the coal. Sulfided molybdenum catalysts are particularly active for coal liquefaction. Unfortunately, MoS_2 is insoluble in all common solvents, and because of this is difficult to disperse onto the coal particles. A strategy to mitigate this problem is the use of so-called catalyst precursors, which are soluble salts that presumably can be readily dispersed onto coal. The catalyst precursors may have little or no catalytic activity themselves, but decompose into an active form at the temperatures of the liquefaction reaction.

Supported mixed-metal catalysts of cobalt-molybdenum (CoMo) and nickel-molybdenum (NiMo) have been studied in some detail for both liquefaction reactions and the upgrading of the resulting products. This application is extensively treated in the literature; recent reviews have been published by Anderson [11] and by Mochida and Sakanishi [12]. Both these catalysts have been shown to facilitate hydrodeoxygenation reactions. However, the traditional, supported heterogeneous catalysts might be suitable for downstream processing of coal-derived liquids, but could not intervene in the primary liquefaction reactions nearly as effectively as a catalyst dispersed onto the coal particles. It seemed to us that it would be neither easy nor efficient to obtain the promoting effect of nickel or cobalt by sequential dispersion of a molybdenum-containing catalyst precursor followed by application of a nickel or cobalt precursor. Instead, we hypothesized that this goal may be attainable with the use of bimetallic catalysts dispersed onto the coal using an appropriate precursor in which both the molybdenum and the promoter were simultaneously present [13,14].

Two distinct reaction pathways have been discussed in the catalytic removal of phenolic oxygen [15]: (A) the direct elimination of the hydroxyl group (deoxygenation); and (B) thermal dehydration of a saturated or partially saturated cyclic alcohol (hydrogenation). Both mechanisms were reported to occur on the same catalytically active sites, pathway (A) being preferred by the supported CoMo catalyst and pathway (B) by the supported NiMo catalyst [4].

Temperature can drastically affect the balance between these mechanisms. Reactions of phenyl ether and of benzofuran, under hydrotreating conditions in the presence of a supported CoMo catalyst, produced hydrogenation products at temperatures $< 400°C$ and direct deoxygenation products at temperatures $> 400°C$ [4]. Substituents can also affect the kinetics of both mechanisms [16]. Pathway (A) is sensitive to steric hindrance of the reacting oxygen functionality, whereas pathway (B) is affected by the electronic characteristics of the substituent and their effect on the delocalized resonance of the aromatic ring.

Coal liquefaction using dispersed catalysts has certain advantages over non-catalytic liquefaction or liquefaction in the presence of a supported catalyst. A highly dispersed catalyst can be distributed throughout the mass of coal particles, creating (in the presence of hydrogen) the reducing conditions required for liquefaction, within close proximity to the coal molecule. Such dispersion could remove the need for a good hydrogen-donating solvent [17]. Recent work in our laboratory has shown that, for reactive low-rank coals, high conversions can be achieved at temperatures $\leq 400°C$ with either a good donor solvent or an active dispersed catalyst; it is not necessary to have both [18]. Stoichiometry of the sulfide phase is also important [19]. Upon decomposition the precursor should produce the most active form of the catalyst (i.e. MoS_2 for sulfided molybdenum). For example, ammonium tetrathiomolybdate (ATTM) only decomposes to MoS_2 at high temperatures ($\geq 350°C$); at lower temperatures the less active form, MoS_3, is produced [17]. These decomposition temperatures are lowered under hydrogen. In addition, the use of an organometallic precursor permits the formation of the active sulfide catalyst at much lower temperatures [13].

Model compound studies using multi-ring systems, or single-ring compounds of comparable molecular weight, were performed to investigate the capabilities of these catalyst precursors. The model compounds selected represent a variety of oxygen functionalities, possibly present in coals of differing ranks [20–22], contained within polycyclic systems. They include anthrone (carbonyl); dinaphthyl ether (aryl-aryl ether); xanthene (heterocyclic ether); and 2,6-di-*t*-butyl-4-methylphenol (hydroxyl). In this paper we report an investigation of the effect of ATTM and a bimetallic organometallic precursor (CoMo-T2) on the conversion and product distribution of these model compounds under liquefaction conditions. In addition, for comparison purposes we have conducted the same reactions under non-catalytic conditions, and in the presence of ATTM, which is a commonly used catalyst precursor in liquefaction research.

2. Experimental

All experiments were performed in 22 ml capacity microautoclave reactors made of stainless steel. A 0.5 g sample of model compound was loaded into the reactor. 1-Methylnaphthalene was added as solvent in a 1:2 weight ratio to model compound and catalyst precursors were added at 2.5 mol% concentration (unless otherwise stated). Tridecane (0.25 g) was added to the reactor as an internal standard. The catalyst precursors used were $(NH_4)_2MoS_4$ (ATTM), and $Cp_2Co_2Mo_2(CO)_2S_4$, which for convenience we call CoMo-T2. (The symbol Cp represents the cyclopentadienyl group.) This precursor has a thiocubane structure (Fig. 9).

Anthrone (97%), xanthene (99%), 2,6-di-*t*-butyl-4-methylphenol (99 + %), 1-methylnaphthalene (98%), tridecane (99 + %) and ammonium tetrathiomolybdate (99.97%) were purchased from Aldrich. 2,2′-Dinaphthyl ether was purchased from TCI America. All compounds were used as received. CoMo-T2 was synthesized in our laboratory [23].

Air was removed by flushing the reactor three times with H_2 to 7 MPa. The reactor was then repressurized to 7 MPa H_2. Reactions were performed at 300, 350 and 400°C for 30 min. All reactions were carried out in a fluidized sand bath preheated to the desired reaction temperature and equipped with a vertical oscillator driving at ≈ 250 strokes per minute. At the end of the reaction the reactor was quenched in cold water. The reactor contents were then extracted with acetone and diluted for analysis.

Capillary gas chromatography (GC) connected to a flame ionization detector (Perkin-Elmer model 8500) and gas chromatography/mass spectrometry (Hewlett-Packard model 5890) were used for the quantitative and qualitative analysis of the product distribution, respectively.

3. Results and discussion

Figs. 1–4 show reaction schemes proposed as possible pathways to the product distributions observed. These schemes are derived from the analyses of reaction products. We have not determined kinetic constants for the various reactions, nor conducted detailed mechanistic studies. Therefore, while Figs. 1–4 are consistent with the observation of the formation of various products, it should be recognized that other mechanisms may be possible. Tables 1–4 provide the product distributions for the respective model compounds under conditions of varying temperature and catalyst precursor. For the purposes of discussion, products have been grouped by the types of reaction involved in their formation, such as, for example, hydrogenation or deoxygenation. Figs. 5–8 are plots illustrating the conversion of the starting materials into products grouped as reaction types.

Generally, the addition of any catalyst precursor to a system, under the conditions studied, increases the total conversion to all products. For example, at 400°C dinaphthyl ether undergoes 26% conversion in non-catalytic reactions; this yield is increased to 72% in the presence of ATTM and 100% using CoMo-T2 (structure is given in Fig. 9). However, any improvement in the product quality, which in these cases would be indicated by oxygen removal, ring hydrogenation, or both, in the presence of these precursors is also important. As discussed in the introduction, oxygen removal may occur by either of two major mechanisms: direct deoxygenation or oxygen removal after ring hydrogenation. The variation of all these factors, for the various oxygen functional groups and different catalysts, will be the main focus of the discussion that follows.

3.1. Anthrone

For anthracene and related compounds hydrogenation and dehydrogenation reactions are most favourable at the 9- and 10-positions [24]. Therefore the most likely product of hydrogenation of anthrone is 9,10-dihydroanthracene (DHA).

Oxygen removal occurs readily for anthrone, even under non-catalytic conditions. Although the hydrogenation of anthrone in the absence of a catalyst is difficult, considerable oxygen removal is achieved through direct deoxygenation, forming anthracene. Hydrogenated products are only observed at higher temperatures and in low yields.

Hydrogenation reactions in general increase with temperature in most cases, but are enhanced considerably in the presence of a cata-

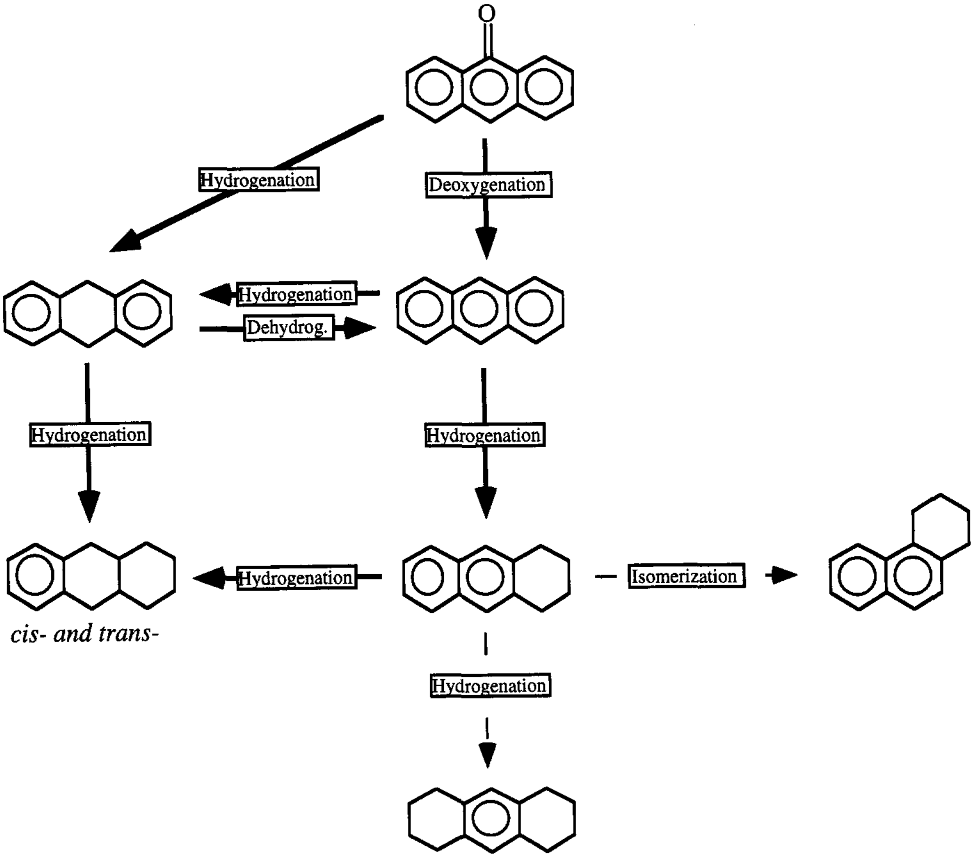

Fig. 1. Conceptual reaction scheme for the product distribution of anthrone.

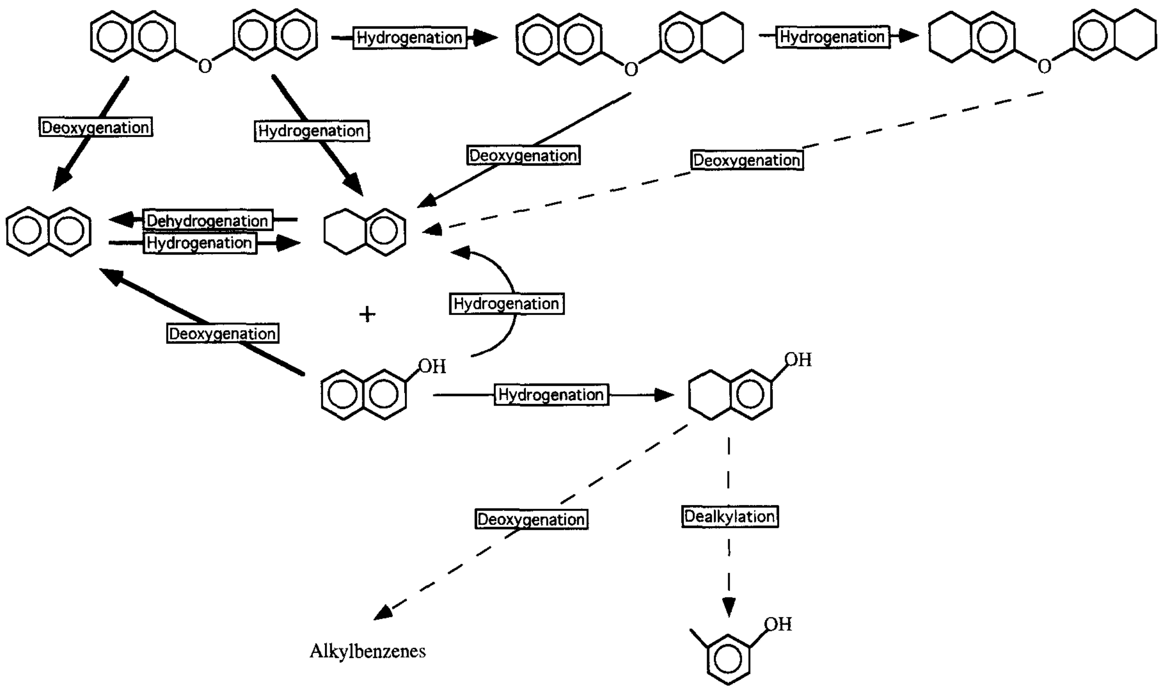

Fig. 2. Conceptual reaction scheme for the product distribution of dinaphthyl ether.

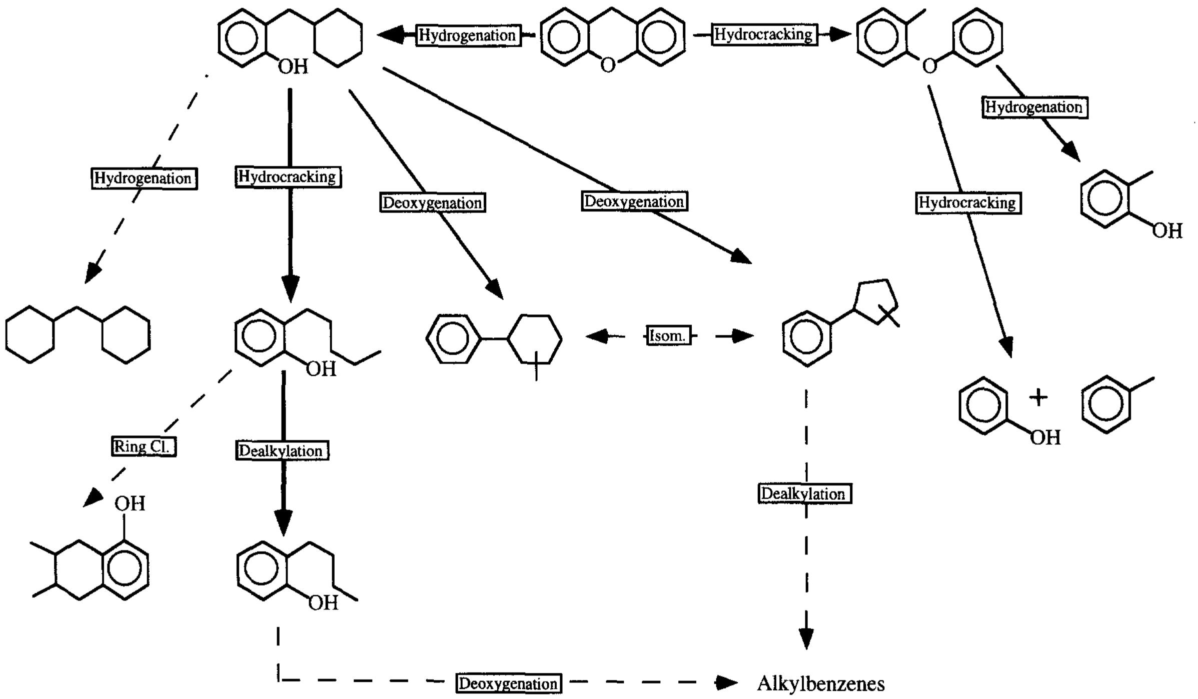

Fig. 3. Conceptual reaction scheme for the product distribution of xanthene.

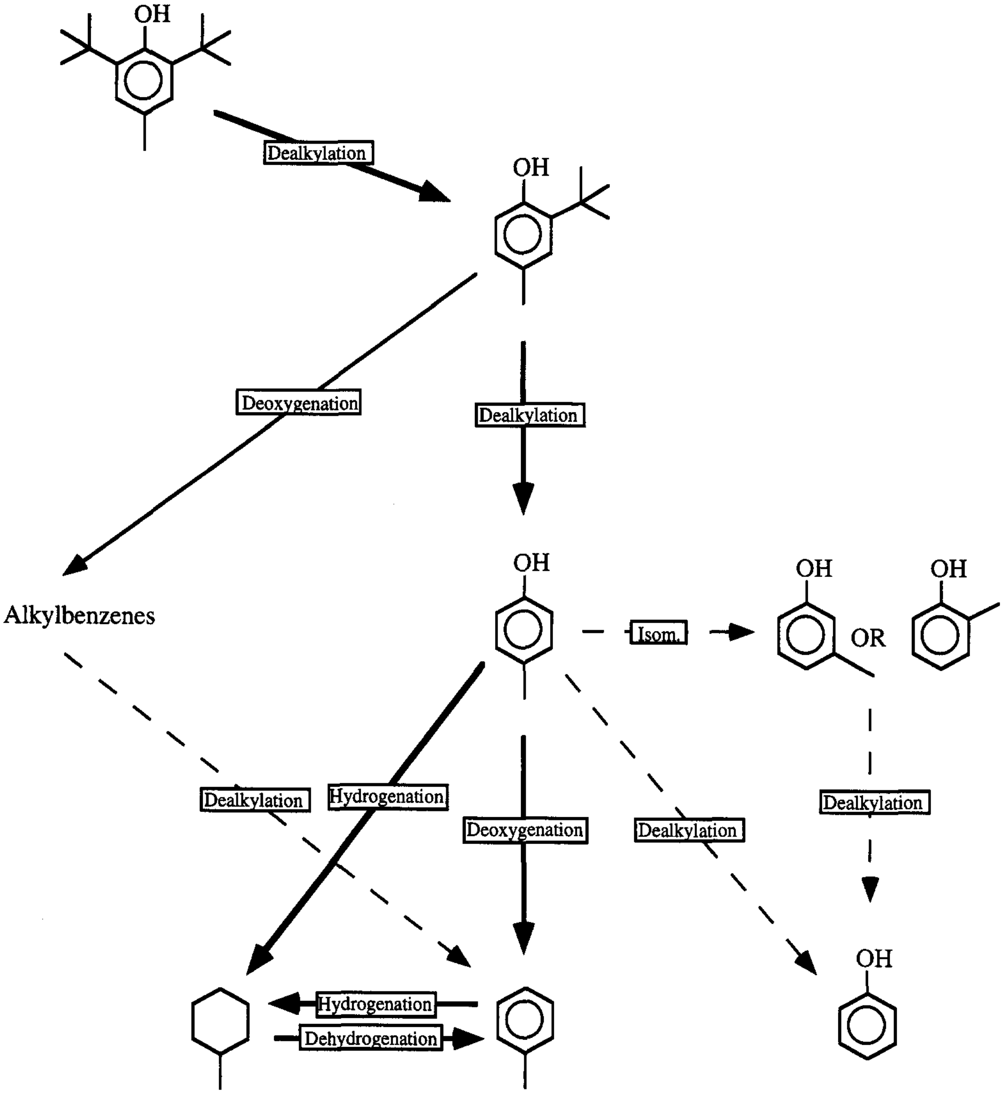

Fig. 4. Conceptual reaction scheme for the product distribution of dibutylmethyl phenol.

Table 1
Effect of catalyst precursors on conversion and product distribution of anthrone

Reaction temperature (°C)	300	350	400	300	350	400	300	350	400
Catalyst precursors	None	None	None	ATTM	ATTM	ATTM	CoMo-T2	CoMo-T2	CoMo-T2
Products (wt%)									
Anthracene	12.3	40.3	39.4	16.1	0.0	10.3	7.0	20.7	10.4
DHA	0.3	7.3	17.2	16.5	5.1	41.4	10.8	51.1	63.6
THA		0.9	6.2	0.6	27.8	30.6		4.9	23.5
THP			0.3		1.4	0.8			
sym-OHA						11.3		0.3	1.5
unsym-OHA (*cis*- or *trans*-)					9.6	1.4			0.3
unsym-OHA (*trans*- or *cis*-)					17.2	4.2			0.6
Conversion (wt%)	12.6	48.4	63.1	33.2	100	100	17.8	77.0	100

Table 2
Effect of catalyst precursors on conversion and product distribution of dinaphthylether

Reaction temperature (°C) Catalyst precursors	300 None	350 None	400 None	300 ATTM	350 ATTM	400 ATTM	300 CoMo-T2	350 CoMo-T2	400 CoMo-T2
Products (wt%)									
Tetralin		1.2		1.3	30.5	24.4	4.4	47.2	51.6
Naphthalene	1.9	4.1	22.9	1.4	26.1	38.3	1.9	28.6	40.2
THDNE					7.4	6.3	0.3	7.5	0.3
OHDNE					1.7			2.6	
THnanphthol					2.3	1.0		5.9	3.5
2-Naphthol			3.2		0.6	0.8	0.3	1.5	0.5
Methylphenol					0.3			0.6	0.7
Alkylbenzenes					1.9	0.9		0.5	3.1
Total conversion (wt%)	1.9	5.3	26.1	2.7	70.7	71.9	6.9	94.3	100

Table 3
Effect of catalyst precursors on conversion and product distribution of xanthene

Reaction temperature (°C) Catalyst precursors	300 None	350 None	400 None	300 ATTM	350 ATTM	400 ATTM	300 CoMo-T2	350 CoMo-T2	400 CoMo-T2
Products (wt%)									
Methylene-biscyclohexane					0.5	1.0			3.3
CyclopentylMecyclohexane						0.7			3.1
Benzene (cyclohexylMe/Et)					1.0	8.4			2.1
Phenol (2-cyclohexylmethyl)					4.6	12.5	0.3	4.9	25.8
Benzene (1-Me-2-phenoxy)					0.6				1.1
Phenol						0.4			1.8
Methylphenol						0.9			2.7
Butylphenol					4.2	2.9	1.7	1.8	2.5
Pentylphenol					3.2	2.7	1.1	4.1	3.2
Dimethylnaphthol					1.6	1.2		2.0	4.2
Toluene						1.1			2.3
Alkylbenzenes					1.1	1.2			3.3
Conversion (wt%)	0	0	0	0	16.9	33.0	3.1	12.8	57.7

Table 4
Effect of catalyst precursors on conversion and product distribution of 2,6-di-*t*-butyl-4-methylphenol

Reaction temperature (°C) Catalyst precursors	300 None	350 None	400 None	300 ATTM	350 ATTM	400 ATTM	300 CoMo-T2	350 CoMo-T2	400 CoMo-T2
Products (wt%)									
2-Butyl-4-methylphenol		44.6		55.5	13.5	0.9			
4-Methylphenol		38.8	100	23.7	66.5	24.3	71.6	97.6	85.4
Methylcyclohexane					8.2	20.2		1.6	8.5
Toluene					7.0	46.5			6.1
Phenol/other Mephenols						3.5			
Alkylbenzenes					2.1	4.7			
Conversion (wt%)	0	83.4	100	79.1	97.3	100	71.6	99.2	100

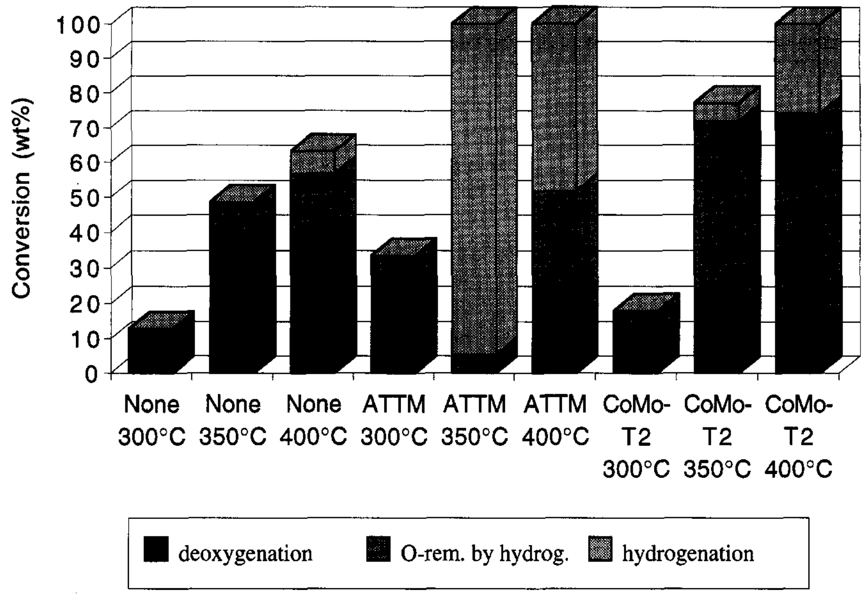

Fig. 5. Quantitative representation of anthrone reaction distribution.

lyst. Reaction at 350°C in the presence of the ATTM precursor is an exception to this trend, showing considerably more extensive hydrogenation than the reaction at 400°C. This particular experiment was performed at a later date with a new batch of ATTM to that used for previous reactions. In conjunction with other observations recently made in our laboratory, this result implies that ATTM undergoes severe changes in activity during aging. Therefore, the result obtained at 350°C is incomparable to the other results, and shall be excluded from the

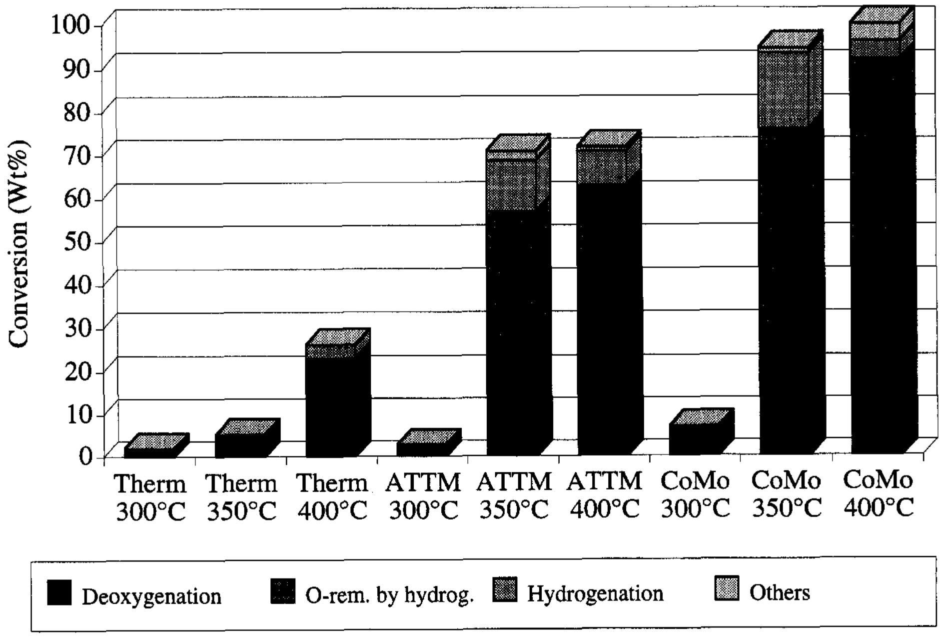

Fig. 6. Quantitative representation of dinaphthyl ether reaction distribution.

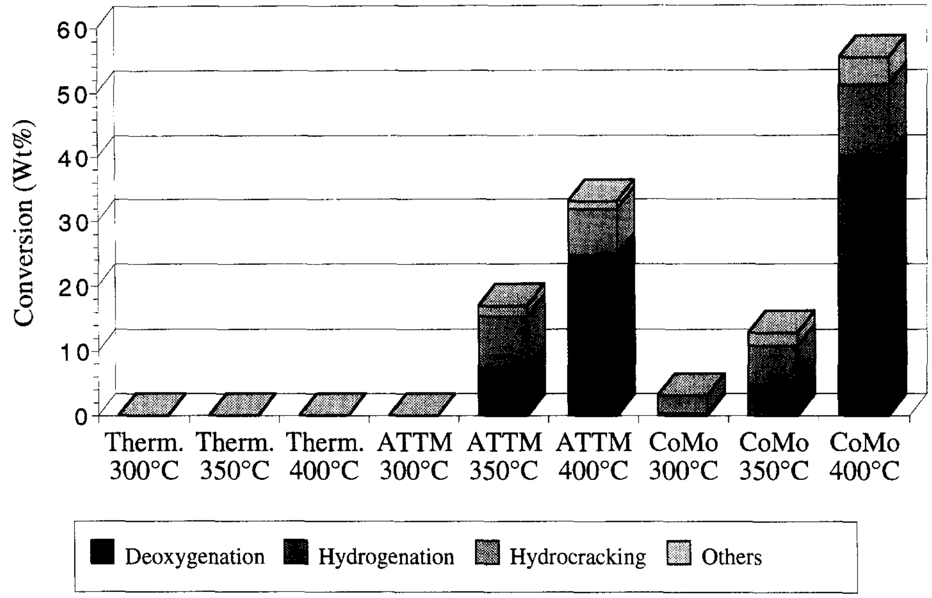

Fig. 7. Quantitative representation of xanthene reaction distribution.

discussion. Studies in the effects of storage and aging on the activity of this catalyst precursor will be the subject of future work.

In the absence of a catalyst, the yield of anthracene is larger and no decrease from 350 to 400°C is observed. This may be attributed to

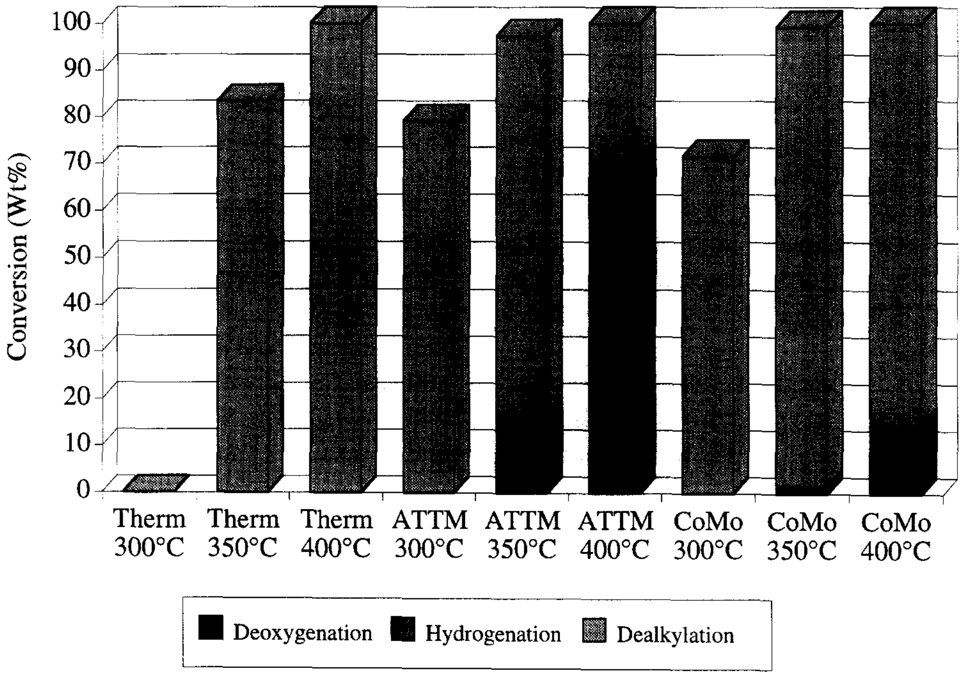

Fig. 8. Quantitative representation of dibutylmethyl phenol reaction distribution.

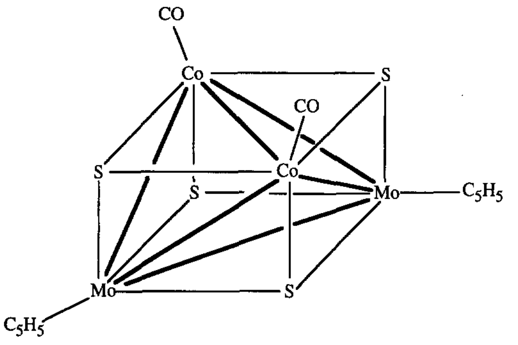

Fig. 9. Structure of $Cp_2Co_2Mo_2(CO)_2S_4$ (CoMo-T2).

an equilibrium between anthracene and DHA, which favours the increased stability of the dehydrogenation product at higher temperatures, when the enhanced hydrogenation effect of a catalyst is not available.

Both precursors provide similar activities toward oxygen removal and ring hydrogenation, although the distribution of these hydrogenated products is quite different depending on the catalyst precursor used. CoMo-T2 appears to favour the formation of DHA, whereas use of ATTM results in greater yields of the products of more extensive hydrogenation. At 400°C, for example, the yield of total hydrogenated anthracenes is 89.7% using ATTM and 89.6% with CoMo-T2. The difference is seen in that the yields of tetra- and octahydroanthracenes are much higher with ATTM. In this case, dihydroanthracene accounts for just under half of the total yield of hydrogenated anthracenes, while with CoMo-T2, dihydroanthracene makes up approximately three-quarters of the hydrogenated anthracenes.

Assuming an equilibrium between anthracene and DHA, all the oxygen-free products observed can be accounted for by the hydrogenation of anthracene and consequently are products of direct deoxygenation of anthrone. This explanation accounts for the lower yields of anthracene at 400°C in the presence of a catalyst, coinciding with increased yields of its hydrogenated products. Also, no hydrogenated products that still contain oxygen are observed, again suggesting that all hydrogenated products are formed from anthracene.

Further evidence of such a mechanism is provided by the percentage of oxygen-free products that are hydrogenated. At 350°C, hydrogenated compounds represent 73% of the total oxygen-free products from CoMo-T2. However, at 400°C, hydrogenated compounds represent 90% of the total oxygen-free products obtained with both catalysts. This suggests that oxygen removal is easier or faster, and hydrogenation then has to 'catch up'. If so, this would be quite consistent with the data from non-catalytic reactions that show oxygen removal by direct deoxygenation is fairly facile, but hydrogenation is not.

These results could also be achieved, however, if DHA is formed directly from anthrone by hydrogenation. In this case, the reduced anthracene yields would be attained by formation of 1,2,3,4-tetrahydroanthracene (THA) and its hydrogenation products, as well as by shifting the equilibrium reaction toward DHA formation. This would suggest that, in the presence of either ATTM or CoMo-T2, oxygen removal accompanied by hydrogenation would be favourable over direct deoxygenation. This may be a result of the location of the carbonyl group at the 9-position, so that the product of the hydrogenative deoxygenation of anthrone would be the favoured 9,10-dihydroanthracene.

Both of these processes may occur at the same time, but in competition for the catalytic sites. If so, the product distributions imply that in the presence of CoMo-T2 hydrogenation is the dominant pathway for oxygen removal from anthrone (as shown by the higher yield of DHA), whereas in the presence of ATTM both mechanisms occur to similar extents (as indicated by roughly comparable yields of DHA and THA).

Both ATTM and CoMo-T2 have the capability to increase the conversion of carbonyls without phenol or naphthol production. This may be achieved by either rapid C = O cleavage prior to ring hydrogenation, rapid phenol conversion to oxygen-free products, or by the prevention of initial hydroxyl group formation or oxygen removal after initial ring hydrogenation. From the reactions of 2,6-di-*t*-butyl-4-methyl phenol (DBMP) with CoMo-T2, it can be seen that this precursor, although removing some hydroxyl functionality, does not promote the ready conversion of phenols to non-oxygen containing species. Therefore, it is likely that CoMo-T2 facilitates rapid carbonyl removal, either before or after ring hydrogenation.

3.2. 2,2′-Dinaphthyl ether

Dinaphthyl ether is substantially less reactive than anthrone with respect to both oxygen removal and ring hydrogenation. Again, hydrogenation reactions do not readily occur in the absence of a catalyst. However, in contrast to anthrone, hydrogenation can occur without prior oxygen removal. Naphthalene and 2-naphthol increase in yield as temperature increases in the absence of a catalyst precursor.

Hydrogenation products decrease as reaction temperature is increased from 350 to 400°C under catalytic conditions. For ATTM all hydrogenation products decrease in yield from 350 to 400°C, but in the presence of CoMo-T2, the reduction in the total yield of hydrogenation products is nevertheless accompanied by a slight increase in tetralin yield. With both precursors, a substantial increase in naphthalene yield (by 12 percentage units in both cases) is observed at the higher reaction temperature.

If direct deoxygenation reactions increase at higher temperatures then the larger naphthalene yields suggest an enhancement of direct deoxygenation of dinaphthyl ether and 2-naphthol. In the absence of a catalyst, tetralin formation is negligible. Under catalytic conditions, the equilibrium between naphthalene and tetralin should favour hydrogenation under the temperatures studied. Also, the deoxygenation of dinaphthyl ether and 2-naphthol would be accompanied by the direct deoxygenation of any previously hydrogenated compounds (i.e. 5,6,7,8-tetrahydrodinaphthyl ether (THDNE) and 5,6,7,8,5′,6′,7′,8′-octahydrodinaphthyl ether (OHDNE)), to form both naphthalene, tetralin, 2-naphthol and 5,6,7,8-tetrahydronaphthol (THnaphthol).

Naphthol yields diminish due to either hydrogenation to tetralin and THnaphthol or direct deoxygenation to naphthalene. In the presence of ATTM, decreases in naphthol yield are accompanied by increases in naphthalene yield, although clearly most of the naphthalene produced in these experiments derives from sources other than naphthol deoxygenation. In the presence of CoMo-T2, increases in tetralin and lower molecular weight products are observed when naphthol yields decrease. We noted above that tetralin was the only hydrogenated product of reactions with CoMo-T2 to increase in yield when temperature is increased from 350 to 400°C. The increase in tetralin yield, 4.4 percentage units, is very nearly accounted for by the corresponding reductions of yields of 2-naphthol and THnaphthol (which total 3.4 percentage units). These results suggest a difference in the process of oxygen removal depending on which catalyst precursor is used.

With regard to total conversion to all products, CoMo-T2 is considerably superior to ATTM at all temperatures. The yields of naphthalene for the two catalyst percursors are comparable at all temperatures, suggesting the differences in total conversion are due to increased hydrogenation activity by CoMo-T2. Indeed, this is clearly shown by the substantially higher yields of tetralin from reactions with CoMo-T2.

3.3. Xanthene

Xanthene is very unreactive in our experiments. It does not react in the absence of a catalyst and undergoes little, or no, reaction at 300°C in the presence of a catalyst. Even under catalytic conditions at 400°C limited oxygen removal occurs. For both catalyst precursors, the products of direct deoxygenation increase with temperature. Products of oxygen removal by hydrogenation are only observed at higher temperatures (400°C), although C–O bond cleavage following ring hydrogenation is observed at 300°C.

At 350°C the products from reactions in the presence of both precursors are alkylphenols and cycloalkylbenzenes formed by C–O and C–C bond cleavage. However, at 400°C ATTM produces an increase in oxygen-free products with no increase in phenols, although conversion to non-oxygen containing species is low (12.3%).

Yields of oxygen-free products are observed with CoMo-T2 only at 400°C (14.1%), but with accompanying substantial increases in phenol formation. This gain in phenols may be attributed to the production of 1-methyl-2-phenoxybenzene, which reacts readily to form phenol, toluene and possibly 2-methylphenol.

For both precursors, the formation of C–C bond cleavage products (i.e. pentyl- and butylphenol) is a prominent reaction pathway at 350°C. However, at 400°C in the presence of ATTM the yields of these products decrease. An increase in those products formed through the cleavage of C–O bonds does occur. Reactions with CoMo-T2 also show an increase in C–O bond cleavage and direct deoxygenation products at 400°C, yet this increase is accompanied by a rise in C–C bond cleavage and hydrogenation products. Comparatively little ring hydrogenation occurs using either precursor, except at 400°C. For example, with ATTM, reaction products containing cyclohexyl or cyclopentyl rings comprise about a third of the total product yield at 350°C, but account for about two-thirds of all products at 400°C. ATTM is superior to CoMo-T2 in providing deoxygenation of the products formed from xanthene conversion, though for both precursors oxygenated products dominate the product slate at all reaction temperatures.

3.4. *2,6-Di-t-butyl-4-methylphenol*

2,6-Di-*t*-butyl-4-methylphenol (DBMP) is highly reactive. Previous work from this laboratory has demonstrated a very rich thermally induced chemistry of highly alkylated phenols at 350°C and above [25,26]. Even under non-catalytic conditions, 100% conversion can be achieved (by *t*-butyl cleavage) at 400°C, although no reaction occurs at 300°C. Removal of the hydroxyl group is much more difficult to accomplish than is dealkylation, since no C–OH bond cleavage occurs in the absence of a catalyst. Ring hydrogenation also does not occur without a catalyst.

In the presence of either catalyst precursor, both hydrogenation and direct deoxygenation increase with temperature. The sequential removal of both *t*-butyl groups becomes more favourable under catalytic conditions, although aromatic C–OH cleavage appears to be substantially more facile than aromatic C–CH_3 cleavage. In fact, it is noteworthy that the methyl group survives virtually all reactions while debutylation occurs very easily even without a catalyst.

At 350°C using ATTM, almost all the starting material reacted and only a small portion remains as 2-*t*-butyl-4-methylphenol (BMP). The major product 4-methylphenol, then undergoes catalytic hydrogenation and direct deoxygenation to form methylcyclohexane and toluene, respectively. At 400°C these reactions proceed to a greater extent, resulting in greater yields of both products. Methylcyclohexane can be produced by hydrogenation of toluene, as well as ring hydrogenation of methylphenol followed by deoxygenation.

In the presence of CoMo-T2, DBMP loses both butyl groups so rapidly that no BMP is isolated. Consequently, 4-methylphenol is the only product at 300°C. At 350°C some further conversion to methylcyclohexane occurs and at 400°C toluene and methylcyclohexane are produced. Although rapid dealkylation is achieved, hydroxyl removal is only slight using CoMo-T2. This suggests that CoMo-T2 may remove oxygen by hydrogenation and this pathway cannot occur rapidly until removal of other ring substituents is complete. Therefore, the presence of the stable *p*-methyl group retards the hydrogenation reaction.

4. Summary and conclusions

Our interest in this work was primarily to examine the hydrodeoxygenation ability of the novel catalyst precursor CoMo-T2. To evaluate the behavior of this material, we compared its reactions at three temperatures with four model compounds having different oxygen functional groups. Further, to have benchmarks for comparison, we conducted the same reactions with ATTM, which is extensively used in a number of laboratories for liquefaction research, and without added catalyst. Except for some reactions of the very reactive 2,6-di-*t*-butyl-4-methylphenol, conversions at 300°C were relatively low, and in some cases even zero. Thus, we confine our concluding remarks to data obtained at 350 and 400°C. Table 5 summarizes the results, and consolidates the data presented in Tables 1–4 into information on the yield of all deoxygenated products and on the percentage of the total products that are also deoxygenated.

Clearly, deoxygenation in the absence of a catalyst is very difficult. Only dinaphthyl ether provided noticeable yields of deoxygenated products in non-catalytic reactions.

For reactions of anthrone, both precursors provide comparable yields of deoxygenated products. The apparent differences are, first, that the total conversion is lower with CoMo-T2 than with ATTM at 350°C, and, second, that ATTM affords a greater degree of hydrogenation, as shown by the higher yields of tetra- and octahydroanthracenes. Because all reactions were run for 30 min, we cannot say whether CoMo-T2 would ultimately reach 100% conversion at 350°C if allowed a longer reaction time.

With dinaphthyl ether, CoMo-T2 not only gives higher conversions than ATTM, but also the yield of deoxygenated products is much higher with CoMo-T2. This is potentially a very significant finding, to the extent that aryl ether linkages represent an important contribution to the crosslinks or bridging groups holding aromatic moieties in the macromolecular structure of the coal. Therefore, the use of the CoMo-T2 catalyst precursor offers the prospect of both increased conversion of the coal and simultaneous deoxygenation in the liquefaction reactor. This is the behavior we had hoped to find by using bimetallic catalyst precursors. In addition, with this compound it is CoMo-T2 that provides the greater yield of hydrogenated products, mainly accounted for by the much greater yields of tetralin than those obtained with ATTM.

Table 5
Summary of deoxygenation results at 350 and 400°C

Reaction temperature (°C)	Model compound	350	400	350	400	350	400
Catalyst precursors		None	None	ATTM	ATTM	CoMo-T2	CoMo-T2
Total conversion	Anthrone	48.4	63.1	100	100	77	100
Yield of deoxygenates		48.4	63.1	100	100	77	100
Deoxygenates as percentage of total conversion		100	100	100	100	100	100
Total conversion	DNE	5.3	26.1	70.7	71.9	94.3	100
Yield of deoxygenates		5.3	22.9	67.6	69.9	86.4	95.2
Deoxygenates as percentage of total conversion		100	87.7	95.6	97.2	91.6	95.2
Total conversion	Xanthene	0	0	16.9	33	12.8	57.7
Yield of deoxygenates		0	0	2.6	12.4	0	14.1
Deoxygenates as percentage of total conversion		N/A	N/A	15.4	37.6	0	24.4
Total conversion	DBMP	83.4	100	97.3	100	99.2	100
Yield of deoxygenates		0	0	17.3	71.4	1.6	14.6
Deoxygenates as percentage of total conversion		0	0	17.8	71.4	1.6	14.6

Xanthene is the least reactive of the compounds we studied. At 400°C, CoMo-T2 provides higher conversion than ATTM, and comparable yield of deoxygenated products. (Of course, this means that the yield of deoxygenated products expressed as a percentage of all products is lower for CoMo-T2 than for ATTM).

In contrast, 2,6-di-*t*-butyl-4-methylphenol is the most reactive compound, at least in terms of total conversion to other products. Two general features of its chemistry are noteworthy: first, the methyl group is extraordinarily refractory, essentially surviving intact into all products of all reactions; and, second, the phenolic –OH group is also fairly resistant to reaction. With this compound it is noteworthy that the best deoxygenation by far is provided by ATTM, at 400°C. The yield of deoxygenated products is 71.4%. This result provides an interesting dilemma that needs to be addressed in future work. Phenolic groups abound in many coals, and it appears from the present results that ATTM would be the catalyst precursor of choice if it were desired to have deoxygenation occur simultaneously with liquefaction. But as we indicated above, CoMo-T2 would be the precursor of choice if the main objective were to cleave aryl ether bridging groups with attendant deoxygenation.

These differing results obtained with dinaphthyl ether and 2,6-di-*t*-butyl-4-methylphenol show that a careful matching of the catalyst precursor to the specific coal is necessary to achieve the desired liquefaction conversions and product qualities.

From the perspective of the types of oxygen compounds examined, there are some differences evident between the two catalyst precursors. In terms of simple reactivity, as measured by conversion to total products at 400°C, the reactivity order with ATTM is anthrone ≈ 2.6-di-*t*-butyl-4-methylphenol > dinaphthyl ether > xanthene. With CoMo-T2 the general ranking is nearly the same: anthrone ≈ 2.6-di-*t*-butyl-4-methylphenol ≈ dinaphthyl ether > xanthene. However, when comparing the yields of deoxygenated products at 400°C, we find with ATTM anthrone > 2.6-di-*t*-butyl-4-methylphenol ≈ dinaphthyl ether > xanthene, whereas with CoMo-T2 anthrone ≈ dinaphthyl ether ≫ 2.6-di-*t*-butyl-4-methylphenol ≈ xanthene. This again highlights the important fact that there are differences in the ability of a catalyst precursor to effect conversion (that is, to cause a compound to react simply to form some other product) compared to its ability to effect deoxygenation. Again, this also suggests that different catalyst precursors can have different roles in promoting oxygen removal by hydrogenation or direct deoxygenation and enhancing hydrogenation reactions, depending on the nature of the starting material. At 400°C CoMo-T2 exhibits comparable, and in some cases superior, total conversion with all the model compounds and also appears to show a greater activity for oxygen removal, except in the case of the substituted phenol.

The differences in reactivity order also highlight the undesirability of phenolic and heterocyclic ether structures in liquefaction systems. Both these structure types are quite resistant to deoxygenation under liquefaction conditions and any reaction has a tendency to form high yields of single-ring phenols. This observation with the model compounds is consistent with the literature we have cited above [2,3] on the prevalence of phenols and related hydroxyl compounds in coal-derived distillate liquids.

Our work so far has focused on cobalt-molybdenum catalyst precursors. Nickel and iron bimetallic precursors are now under study in our laboratory, and those results will be reported in due course.

Acknowledgements

The authors wish to express their appreciation to the US Department of Energy, Pittsburgh Energy Technology Center for supporting this work, Dr. E. Schmidt for synthesizing the catalyst precursors and Mr. R.M. Copenhaver for the fabrication of the microreactors.

References

[1] C. Song, L. Hou, A.K. Saini, P.G. Hatcher and H.H. Schobert, Fuel Process. Technol., 34 (1993) 249–276.
[2] R.E. Pauls, M.E. Bambacht, C. Bradley, S.E. Scheppele and D.C. Cronauer, Energy Fuels, 4 (1990) 236–242.
[3] C. Burgess, Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1994.
[4] P.C. Wailes, Fuel, 61 (1982) 1038–1044.
[5] L. Artok, O. Erbatur and H.H. Schobert, in press.
[6] C. Song, H.H. Schobert and P.G. Hatcher, Energy Fuels, 6 (1992) 326–328.
[7] M.A. Serio, E. Kroo, S. Charpenay, R. Bassilakis, P.R. Solomon, D.F. McMillen, A. Satyam, J. Manion and R. Malhotra, Proc. Contractors' Review Conference: Coal Liquefaction and Gas Conversion, Pittsburgh, PA, 1993, pp. 15–44.
[8] S.M. Solum, R.J. Pugmire and D.M. Grant, Energy Fuels, 3 (1989) 187–193.
[9] C. Song and H.H. Schobert, Am. Chem. Soc., Div. Fuel Chem. Prepr., 37 (1992) 42.
[10] L. Huang, C. Song and H.H. Schobert, Am. Chem. Soc., Div. Fuel Chem. Prepr., 37 (1992) 223.
[11] L.L. Anderson and Y. Yürüm, Editor, Clean Utilization of Coal, Kluwer Academic, Dordrecht, 1992, pp. 207–212.
[12] I. Mochida and K. Sakanishi, D.D. Eley, H. Pines and W.O. Haag, Editors, Advances in Catalysis, Academic Press, San Diego, Vol. 40, 1994, pp. 39–85.
[13] C. Song, D.S. Parfitt and H.H. Schobert, Catal. Lett., 21 (1993) 27–34.
[14] C. Song and H.H. Schobert, Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction, Department of Energy DE-AC22-92PC92122-TPR-1, 1993.
[15] H. Weigold, Fuel, 61 (1982) 1021–1025.
[16] S.B. Gevert, M. Eriksson, P. Eriksson and F.E. Massoth, Appl. Catal. A, 117 (1994) 151–162.
[17] A.S. Hirschon and R.B.W. Jr, in H.H. Schobert, K.D. Bartle and L.L. Lynch, Editors, Coal Science II, ACS Symp. Ser., 1991, 461.
[18] L. Huang, Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1995.
[19] F. Derbyshire, Energy Fuels, 3 (1989) 273.
[20] L.M. Stock, Acc. Chem. Res., 22 (1989) 427–433.
[21] R. Hayatsu, R.E. Winans, R.G. Scott, L.P. Moore and M.H. Studier, Fuel, 57 (1978) 541.
[22] J.H. Shinn, Fuel, 63 (1984) 1187.
[23] D.S. Parfitt, C. Song and H.H. Schobert, Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction, Department of Energy DE-AC22-92PC92122-TPR-2, 1993, pp. 7.
[24] R.T. Morrison and R.N. Boyd, in Organic Chemistry, Allyn and Bacon, Newton, MA, 1983, p. 1252.
[25] S. Eser, C. Song, R.M. Copenhaver, J. Perison and H.H. Schobert, Thermal stability of coal derived jet fuels, US Air Force Rep. AFWAL-TR-87-2042, 1990, pp. 127.
[26] S. Eser, J. Perison, R.M. Copenhaver, J. Shiea and H.H. Schobert, Am. Chem. Soc., Div. Pet. Chem. Prepr., 37 (1992) 540–547.