

HYDRODEOXYGENATION OF O-CONTAINING POLYCYCLIC MODEL COMPOUNDS USING NOVEL ORGANOMETALLIC CATALYST PRECURSORS

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INTRODUCTION

Oxygenated compounds are present in virtually all coals [1]. Phenols (and related hydroxyl compounds) have been identified as components of coal-derived distillates [2,3]. Ethers and related compounds, connecting structural units within the coal matrix, have been proposed as sites for the depolymerization of the coal [4] and also ethers, together with carboxyls and phenolics, have been implicated in the facilitation of retrogressive, crosslinking, repolymerization reactions [5,6].

Low-rank coals (i.e. lignites and subbituminous coals) include significantly more oxygen-containing groups than coals of higher rank [7]. With the increase in the extraction of lower rank coals in the U.S. and research into their use as liquefaction feedstocks [5,8,9], the importance of oxygen functionality removal from coal and coal-derived liquids is all the more apparent.

The removal of these 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 during the liquefaction process would be beneficial. This goal may be attainable with the use of sulphided bimetallic catalysts dispersed onto the coal using an organometallic precursor [10,11].

Model compound studies using multi-ring systems, or those of comparable molecular weight, were performed to investigate the capabilities of these catalysts. The model compounds selected represent a variety of oxygen functionalities, possibly present in coals of differing rank [12-14], 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).

EXPERIMENTAL

All experiments were performed in a 22ml capacity microreactor. A 0.5g sample of model compound was loaded into the reactor. Solvent was added in a 1:2 weight ratio to model compound and catalyst precursors were added at 2.46mol% concentration (unless otherwise stated). The catalyst precursors used were $(\text{NH}_4)_2\text{MoS}_4$ (ATTM), $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$ (Ni-Mo1) and $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (CoMo-T2).

Air was removed by flushing the reactor three times with H_2 to 1000psi. The reactor was then repressurized to 1000psi H_2 . Reactions were performed at 300°C, 350°C and 400°C for 30 minutes. All reactions were carried out in a fluidized sand bath equipped with a vertical oscillator driving at a setting of 55 (~250 strokes per minute). At the end of the reaction the microreactor was quenched in cold water.

Tridecane (0.25g) was added to the microreactor as an internal standard. The microreactor contents were then extracted with acetone and diluted for analysis.

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

RESULTS AND DISCUSSION

Product distributions have been grouped as oxygen-containing and deoxygenated for the purposes of this article. The conversions of anthrone, dinaphthyl ether, xanthene and 2,6-di-*t*-butyl-4-methylphenol are shown in Figures 1-4, and the product distribution of dinaphthyl ether is given in Figure 5.

Generally, the addition of any catalyst to a system under the conditions studied increases the total conversion. For example, at 400°C dinaphthyl ether undergoes 26% thermal conversion; this yield is increased to 72% in the presence of ATTM, 88.5% with Ni-Mo1, and 100% using CoMo-T2. However, any improvement in the product quality, especially deoxygenation and ring reduction, in the presence of these catalysts is also important, and the variation of these factors for the different oxygen functional groups will be the main focus of this discussion.

Anthrone

Under non-catalytic conditions anthrone converts to anthracene through thermal reaction of the carbonyl oxygen. Anthracene then reacts further to form a variety of hydrogenated ring species, such as di- and tetrahydroanthracene.

In the presence of ATTM, the formation of oxygen-containing compounds in the products at 350°C and 400°C (substituted naphthols and phenols) suggest hydrogenation of

the carbonyl oxygen to a hydroxyl group before extensive conversion to anthracene. Reduction in the yields of these oxygen functionalities in the ATTM reaction at 400°C may indicate the possibility of an increase in the conversion of these species to non-oxygenated products.

Conversion of anthrone to oxygen-free products is increased considerably using the CoMo-T2 catalyst precursor. This implies that CoMo-T2 has the capability to increase the conversion of carbonyls without additional 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. From the reactions of 2,6-di-*t*-butyl-4-methylphenol with CoMo-T2, it can be seen that this catalyst, although removing some hydroxyl functionality, does not promote the ready conversion of phenols to non-oxygen containing species.

Variations in the oxygen-free products of anthrone conversion are also apparent for the different catalyst precursors. Ni-Mo1 appears to promote the formation of 1,2,3,4-tetrahydroanthracene (THA), whereas CoMo-T2 demonstrates the facilitation of 9,10-dihydroanthracene (DHA) production. ATTM seems to have equal affinity for the formation of both products. Ni-Mo1 and ATTM both exhibit an increase in the formation of 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) at 400°C (0% under catalyst-free conditions to 11.8% and 11.3% respectively), which only appears in very low yields with CoMo-T2 (1.5%). This reduction in OHA yield for the CoMo-T2 precursor is comparable to increases in anthracene and DHA production, suggesting selective hydrogenation of the 9- and 10- positions (i.e. the carbonyl carbon).

Dinaphthyl Ether

Under non-catalytic conditions naphthalene is the major product of dinaphthyl ether (DNE) hydrogenation, with low yields of 2-naphthol, although total conversion is very small (26%). Oxygen functionality removal is increased in the presence of all the catalyst precursors, although to a lesser extent than for anthrone.

ATTM increases DNE conversion to oxygen-free products (63.6% at 400°C) with the balance of the products being phenols, naphthols (1.8%) and ring-reduced derivatives of the starting material. Phenol and naphthol yields decrease from 350°C to 400°C, again implying that ATTM facilitates hydroxyl group removal.

High conversions to tetralin and naphthalene are achieved in the presence of CoMo-T2 (51.6% and 40.2% respectively at 400°C). Phenols and naphthols are present in larger yields than for anthrone, suggesting the cleavage of a single C-O bond followed by hydrogenation of the phenoxy (or naphthoxy) group. Ring-reduced derivatives of DNE produced at 350°C are absent at 400°C and naphthol yields decrease across the same temperature range. These reductions in oxygen compound yields are accompanied by increases in tetralin, naphthalene and alkylbenzene formation.

The product distributions (O : non-O) of reactions of ATTM, Ni-Mo and CoMo-T2 with DNE (Figures 2 and 5) distinctly show the latter precursor to be the most favourable for C-O-C bond cleavage to oxygen-free products.

Xanthene

In the absence of a catalyst xanthene is totally unreactive. Addition of ATTM or CoMo-T2 produces noticeable reaction at 350°C and 400°C.

At 350°C the products from both precursors are phenols, cycloalkyl- and long-chain alkylbenzenes 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 (24.9%).

Increases in oxygen-free product yields are also achieved with CoMo-T2 at 400°C, but with accompanying increases in phenol formation. This gain in phenols may be attributed to the formation of short-chain (C1-C2) alkylphenols from longer chain alkylphenols, implying that CoMo-T2 favours C-C cleavage over C-OH.

The comparably large conversion to oxygen-free products and phenols reinforces the ability of CoMo-T2 to cleave ether linkages, and inability to remove hydroxyl groups. However, the low conversions of xanthene illustrate the unreactive nature of the starting material.

2,6-Di-*t*-butyl-4-methylphenol (DBMP)

Under non-catalytic reaction conditions the conversion of DBMP involves the cleavage of one, or both, of the *t*-butyl groups to produce 2-butyl-4-methylphenol (BMP) and ultimately 4-methylphenol (100% at 400°C). No reaction occurs at 300°C in the absence of a catalyst. When a catalyst is present the removal of the butyl groups becomes more favourable and formation of the above products takes place.

At 350°C with ATTM, almost all the starting material has reacted and only a small portion remains as BMP (13.5%). The major product, 4-methylphenol, then undergoes catalytic hydrogenation and hydroxyl removal to form toluene and methylcyclohexane. At 400°C these reactions proceed to a greater extent, resulting in greater yields of both products (46.5% and 20.2% respectively).

In the presence of CoMo-T2, DBMP appears to lose both butyl groups so rapidly that no 2-*t*-butyl-4-methylphenol is isolated, so 4-methylphenol is the only product at

300°C. At 350°C it exhibits some further conversion to methylcyclohexane (1.6%) and at 400°C toluene and methylcyclohexane are produced.

DBMP is a reactive compound through loss of its butyl groups. However, the hydroxyl group C-OH bond is very resistant to reaction and is only cleaved, to a substantial degree, in the presence of the ATTM precursor. CoMo-T2 removes the OH-group, but only to a small extent.

Investigations using the Ni-Mo1 precursor are not as advanced as those for ATTM and CoMo-T2. Presentation of these results is planned for future articles.

CONCLUSIONS

From the non-catalytic data shown there is a clear order of starting material reactivity : 2,6-di-*t*-butyl-4-methylphenol > anthrone > dinaphthyl ether > xanthene. However, the reactivity order of the oxygen functionalities in the presence of the various catalysts is different. For non-catalytic conditions the order appears to be : carbonyl > aryl-aryl ether » substituted phenol ≈ heterocyclic ether. In the presence of ATTM this sequence changes slightly to : carbonyl > substituted phenol ≈ aryl-aryl ether » heterocyclic ether and for reactions involving CoMo-T2 the reactivity order appears to be : carbonyl > aryl-aryl ether > heterocyclic ether > substituted phenol.

These differences in reactivity order emphasize the effect of the nature of the oxygen functionality on the deoxygenating capabilities of the catalysts and that different catalysts can have different roles in promoting hydrodeoxygenation and reduction, depending on the nature of the starting material. They also highlight the undesirability of phenolic and heterocyclic ether structures in liquefaction systems. Both these structures types are quite unreactive under liquefaction conditions and any reaction has a tendency to form high yields of single-ring phenols.

When applied to coals, these findings suggest that coals differing from each other in the form of which oxygen functional groups are dominant, may show quite different kinds of liquefaction products, depending on which catalyst precursor was chosen.

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Figure 1. Yield of oxygenated and deoxygenated products of anthrone as a function of temperature and catalyst precursor.

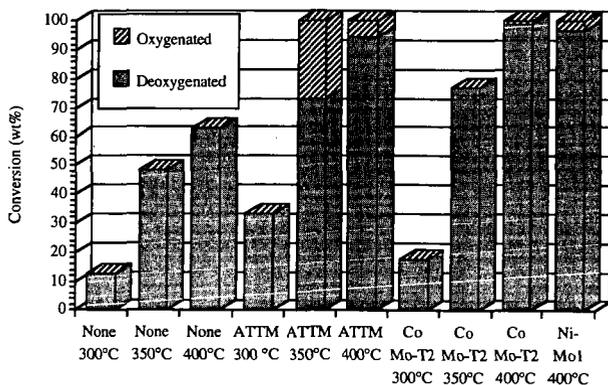


Figure 2. Yield of oxygenated and deoxygenated products from dinaphthyl ether as a function of temperature and catalyst.

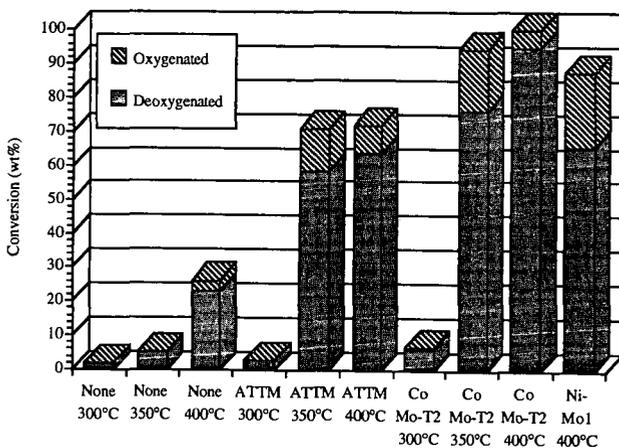


Figure 3. Yield of oxygenated and deoxygenated products of xanthene as a function of temperature and catalyst.

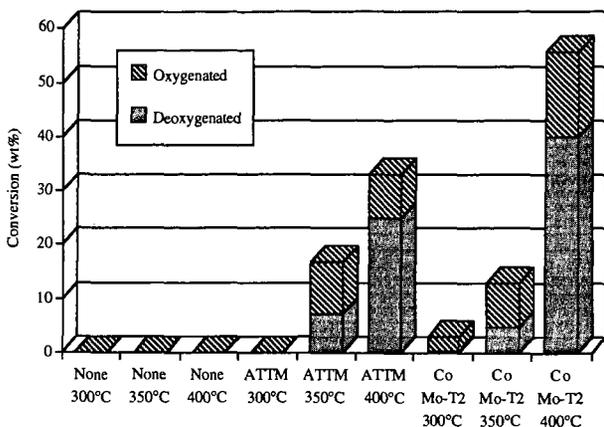


Figure 4. Yield of oxygenated and deoxygenated products of 2,6-di-*t*-butyl-4-methylphenol as a function of temperature and catalyst.

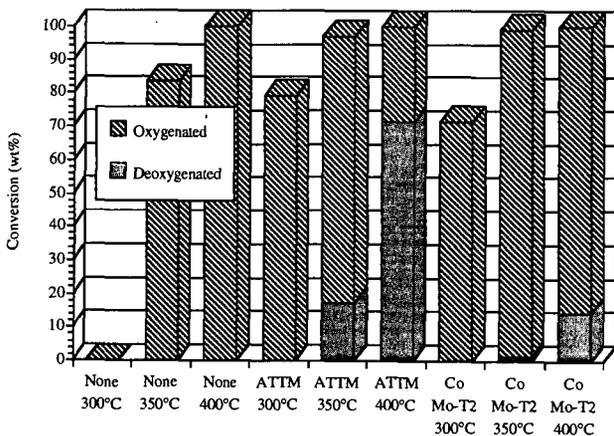


Figure 5. Product distribution of dinaphthyl ether under liquefaction conditions.

React. temp.(°C)	300	350	400	300	350	400	400	300	350	400
Cat. Precursors	None	None	None	ATTM	ATTM	ATTM	Ni-Mo	CoMo-T2	CoMo-T2	CoMo-T2
Products(wt%)										
Tetralin		1.2		1.3	30.5	24.4	24.6	4.4	47.2	51.6
Naphthalene	1.9	4.1	22.9	1.4	26.1	38.3	39.1	1.9	28.6	40.2
THDNE					7.4	6.3	12.0	0.3	7.5	0.3
OH DNE					1.7		3.2		2.6	
THnaphthol					2.3	1.0	4.1		5.9	3.5
2-Naphthol			3.2		0.6	0.8	2.1	0.3	1.5	0.5
Methylphenol					0.3		0.4		0.6	0.7
Alkylbenzenes					1.9	0.9	2.0		0.5	3.1
Conv. (wt%)	1.9	5.3	26.1	2.7	70.7	71.9	87.6	6.9	94.3	100