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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

**Technical Progress Report
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ABSTRACT

Coal liquefaction involves cleavage of methylene and dimethylene and ether-type bridges connecting polycyclic aromatic units. The selected compounds for model coal liquefaction reactions are 4-(1-naphthylmethyl)bibenzyl (NMBB) and several oxygen-containing compounds. This report mainly describes the synthesis and screening of selected iron and molybdenum compounds as precursors of dispersed catalysts for hydrocracking of NMBB and oxygen-containing compounds.

Experiments using NMBB were carried out at 400 °C for 30 min. under 6.9 MPa H₂ pressure. All catalyst precursors converted NMBB predominately into naphthalene and 4-methylbibenzyl. Small amounts of secondary products were formed by hydrogenation, isomerization and fragmentation of the primary products. Generally, ferrocene demonstrated very low activity as catalyst. Even sulfur addition did not increase activity. Hydrated iron sulfate FeSO₄ x 7 H₂O gave similar conversion like ferrocene. However, in an experiment with added sulfur, only iron sulfate became a more active catalyst. The same effect was observed in an reaction of CuZr₂P₃O₁₂ with added sulfur. The total sulfur concentration in the latter experiment was 3.4 wt %. In order to clarify the effect of sulfur alone on model compound conversion, NMBB was treated with sulfur in concentrations of 1.2 to 3.4 wt %, corresponding to conditions present in catalytic runs with sulfur. It was found that increasing sulfur concentrations lead to higher NMBB conversion. Furthermore, sulfur had a permanent influence on the reactor walls. It reacted with the transition metals in the steel to form a microscopic black iron sulfide layer on the surface, which could not be removed mechanically. Non catalytic runs after experiments with added sulfur yielded higher conversion than a normal run with a new reactor. This "wall effect" can be reduced by treating sulfided reactors with 6 N HCl for 5 min. and subsequent immersing into a base bath over night. However, repeated cleaning operations after sulfur runs leach out steel components in the reactors and shorten their life span considerably.

The objective of the work on oxygen-compounds is to investigate the utility of highly dispersed catalysts, from organometallic precursors, in the removal of heteroatom functionality from the products of a reaction performed under liquifaction conditions.

The bimetallic catalytic precursor CoMo-T2 exhibited a sizable increase in the yield of non-O-containing products, compared to the run using a standard inorganic catalyst precursor (ATTM) or a non-catalytic reaction. For the runs of both dinaphthylether and xanthene, total conversions at 400°C in the presence of the bimetallic precursor, CoMo-T2, are much higher than those with standard monometallic precursor ATTM. The lower reactivity of the model compounds dinaphthyl ether (DNE) and xanthene, relative to anthrone, under liquefaction conditions, assists to accentuate the superior bond cleavage capability of the bimetallic catalyst. The low yield of O-containing products, without sacrificing high conversion, may indicate a selectivity toward preferential C-O bond cleavage (i.e. removal of oxygen functionality).

Catalytic Hydrocracking of NMBB over Dispersed Catalysts

Introduction

Dwindling crude oil resources as feedstock for the chemical industry and for transportation fuel compel us to search for alternate sources. Coal (1), consisting of high molecular weight, via alkyl bridges interconnected, molecules and various functional groups like OH, CO, CO₂H, NH₂, CN, SH and S, provides the necessary material for further exploitation. Coal hydroliquefaction is the method of choice and has its roots in the work of Friedrich Bergius (2). Coal accounts currently as one of the main US energy sources (3). World's known coal reserves are double the known petroleum reserves. It becomes increasingly important to find an alternative feedstock for the crude oil based fuel- and chemical industry (4). Coal liquefaction is an important process for producing transportation fuels, useful aromatic chemicals and advanced materials from coal (5). Despite enormous efforts to reduce the cost of coal-derived distillates, coal-derived products are still not competitive with crude oil products. Typical reaction conditions in coal liquefaction involve the reactions of coal with reducing gas (H₂) in a solvent at high temperature and high pressure. The liquefaction process is extremely intricate and involves both chemical and physical transformations. It is known that direct coal liquefaction proceeds through two loosely defined stages, coal dissolution into solvent-soluble materials, followed by upgrading of the solubilized products. The distribution and quality of primary liquefaction products depend on the coal, catalyst, solvent and process conditions used in the first stage. The conversion of primary liquefaction products requires upgrading of heavy materials to distillate materials, followed by refining for use as transportation fuels including gasoline, jet fuels, and diesel fuels.

The classical coal liquefaction process breaks down the macromolecular coal molecules into smaller primary liquefaction products. These products consist mostly of polycyclic aromatic compounds, which need to be further processed for use as transportation fuel, or as source for chemical upgrading. Coal liquefaction is an intricate process in which complex compounds undergo different type of reactions. Depending on the sort of catalyst, major reaction paths are bond cleavage of larger molecules, hydrogenation and the reaction of heteroatoms like oxygen, sulfur and nitrogen with active catalyst sites. The complex structure of coal makes it very difficult to determine specific steps in the process of coal liquefaction. Our approach to understand the nature of coal liquefaction was to study a simplified model of coal. The complex molecular structure of coal consists mainly of interconnected polyaromatic

hydrocarbons. Our model compound 4-(1-naphthylmethyl)bibenzyl (NMBB) enabled us to focus on its particular structure and bonding pattern to quantitatively study its reactivity towards transition metal containing catalysts.

Bimetallic compounds turned out to be promising candidates for coal liquefaction. The primary objective of this research is to make novel bimetallic catalysts from organometallic precursors, that can be used in low concentrations but exhibit high activity for efficient conversion of our model compound NMBB. MoS₂-based heterometallic catalysts (6) have led to the preparation of several heterometallic thiocubanes. However, some novel Lewis acidic Ni and Mo catalysts also enhance coal pyrolysis at moderate (300 °C) temperatures (7). Recent work at Penn State has demonstrated the potential of using dispersed Mo and Fe catalysts (8). Especially hydrotreating reagents such as Co-Mo and Ni-Mo are most promising catalysts. Several reports have demonstrated the synergistic effects of acidic Zn-, Ni-, and Mo and Fe-Mo-based (9) catalysts for coal liquefaction model reactions. Even under severe reaction conditions (440 °C, 2000 PSI H₂), significantly higher yields of converted products were observed. The beneficial catalytic effect of multi component catalytic precursors will be used in our synthesis of a series of organometallic compounds. We can anticipate that synergistic effects of multicomponent catalysts could lead to improved catalytic activity for primary coal liquefaction products. In the earlier stages of cluster chemistry, the synthetic approach was spontaneous assembly. Advances in homometallic transition-metal sulfide chemistry have led to smaller clusters which are fragments of the thiocubane unit. Heteronuclear thiocubane clusters like Cp₂M₂S₄ and M₂M₂'(μ₃-S)₄ have been realized. A virtue of this type of compounds is the availability of a wide variety of M₂S₄²⁺ core compounds having sulfur. This flexibility of different ligands provides structural and electronic variations which are not present in the standard catalyst (NH₄)₂MoS₄ (ATTM). To gain a better understanding of the catalytic functions, the model reactions that are to be undertaken using thiocubane and inorganic complexes that contain Fe, Ni, Co, Mo and sulfur in either one molecule or varies combinations. The main question that arose from coal liquefaction research is what are the key functions of the catalyst leading to high oil yields and coal conversions. The present research is a fundamental study on catalytic model compound of bimetallic molecular precursors.

Numerous studies have been conducted to find out more about the nature of the decomposition process of catalyst precursors (10). The microstructure of a given catalyst has a decisive influence on its converting capabilities. Our only way to predetermine the appearance of the catalyst's surface is the choice of the catalyst precursor and under which physical and

chemical circumstances it can be thermally decomposed. Important factors are the catalyst formula (ratio transition metals/sulfur), functional groups, electronic structure (e.g. unpaired electrons) and the sort of bonding in the precursor molecule (metal-metal bonds). Even though detailed and exact models about active catalyst sites are missing, it turned out that heterometallic phases containing Mo, Co and sulfur are superior to homometallic phases such as Co_9S_8 and MoS_2 . With this in mind, it is apparent that a primary goal of catalyst precursor synthesis should be the search for methods that generate highly dispersed heterometallic sulfide phases. Two approaches towards highly dispersed heterometallic sulfide phases are imaginable. Method one requires thermal decomposition of molecules in which one, two or more metals are part of the sulfur-ligated cluster. Method two employs chemical alteration of existing MoS_2 -particles with Co-containing chemical reagents. The latter method is hard to realize. Not enough information is available about the structure of reactive edge sites of MoS_2 particles to apply selective chemical reactions. Hence our approach lies in the preparation of organometallic precursors which then will be thermally transformed into active catalyst particles.

The primary objective of this research is to explore the potential of bimetallic dispersed catalysts from heterometallic molecular precursors in their use in model compound liquefaction reactions. This quarterly report describes the use of several iron containing catalyst precursors in model compound reactions. The liquefaction process is intricate and involves hundreds of different coal components with various functional groups in interconnected aromatic systems. The complexity of coal liquefaction reactions makes it very difficult to study the reaction mechanisms. Therefore, it is extremely difficult to find optimum reaction conditions for selective bond cleavage. Furthermore, coals from different sources may react differently with different catalysts. We selected therefore the model compound 4-(1-naphthylmethyl)bibenzyl (NMBB), which consists of functionalities that are related to coal structures (11-15). Among these are alkyl groups which interconnect aromatic moieties and different ring systems. Of particular interest to our group was the fact that its reaction can give us information about the features of different catalysts. In a typical hydroliquefaction reaction, coal reacts at temperatures above 400°C with 7 MPa H_2 pressure for a period of ca. 30 min. to primary liquefaction products. Efficient conversion can only be achieved by transition metal containing catalysts and metal concentrations of 1 wt % or lower. Suitable catalytic systems contain Co, Ni, Mo or its combinations, either as inorganic complexes, or organometallic species. Good solubility of catalyst precursors generally leads to better catalyst dispersion and greater effectiveness for liquefaction reactions (16,17). One way to achieve better dispersion is the use of soluble organometallic precursors which produce in situ finely dispersed active catalyst particles at elevated temperatures. Greater catalyst surface area increases the yield of products dramatically,

due to greater hydrogen activation by augmented reactive catalyst sites. Hirschon and Wilson (18,19) demonstrated that highly dispersed catalysts from organometallic precursors can be effective for hydrogenating the coal with molecular hydrogen without relying upon a donor solvent.

This report describes our work on hydrocracking experiments of NMBB over different transition metal catalyst precursors. The effects of sulfur on conversion and product selectivity will also be investigated.

Experimental Section

Catalyst Precursors. Sulfur and ferrocene were purchased from Aldrich, the model compound NMBB from TCI America. GC-MS confirmed sufficient purity of NMBB (> 99 %) and it was used without further purification. $\text{CuZr}_2\text{P}_3\text{O}_{12}$ was prepared by Lynch and Brown of Pennsylvania State University. The sample is a green/grey dry powder that shows no thermal expansion even at high temperature and should keep its pore structure.

Model compound reactions. A stainless steel reactor (tubing bomb) with a capacity of 33 mL was loaded with ca. 0.25 g NMBB, 2.11 wt % catalyst precursor and 0.135 g solvent (tridecane; molar ratio NMBB/Tridecane 1:1). In experiments with added sulfur, the atomic ratio of Fe/S was 1:1. The reactor was purged three times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as heating source and the reactor agitated via an oscillator by vertical shaking of the horizontal micro reactor (about 240 strokes/min.) After the reaction the hot tubing bomb was quenched in cold water and the gaseous products collected in a gas bag for further analysis. The internal standard dodecane was added into the reactor after the reaction. The liquid contents were washed with 15 mL CHCl_3 through a low speed filter paper and stored in small glass bottles for qualitative and quantitative GC analysis. All runs were carried out at least twice to confirm reproducibility.

The compounds were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50 % phenyl - 50 % methyl polysiloxane with a coating film thickness of 0.25 μm . For quantification a Perkin Elmer 8500 capillary GC with a flame ionization detector and the same type of column (DB-17) was used. Both Perkin

Elmer 8500 GC and GC-MS were programmed from 40 to 280 °C at a heating rate of 4 °C/min. after a 5 min. isothermal holding at 40 °C and a final time of 15 min. The response factors of 10 pure compounds were determined. More experimental and analytical details may be found elsewhere (21-24).

Results and Discussion

Hydrocracking of NMBB: Catalyst activation takes place at elevated temperatures, depending on the type of catalyst precursor. Some inorganic salts require temperatures as high as 350 °C for this activation process. It is known (8,28-30) that catalyst precursors like metal carbonyls require the addition of sulfur for sufficient activity. The beneficial effect of sulfur addition to hydrogenation reactions was studied on the system molybdenum sulfide and oxide (7). There seems (27) to be consensus that the sulfides of the transition metals are more active in catalytic hydroliquefaction than their oxides. The reason for this remains unclear. Montano and co-workers (31,32) have emphasized the importance of correct stoichiometry between molybdenum oxides and sulfur in high temperature conversion reactions in order to generate catalytically active MoS₂ particles.

Among the tested catalyst precursors (Figure 1), ferrocene is more effective in hydrocracking reactions of NMBB than the inorganic iron complex FeSO₄ x 7 H₂O. Sulfur added to iron sulfate had the expected beneficial effect on NMBB conversion. But sulfur added to ferrocene had a negative effect on the catalysts activity. The only other iron containing organometallic complex that showed a similar trend in conversion, after sulfur addition was [Cp₂Fe(CO)₂]₂, as reported in TPR-7 and -8. Both complexes have cyclopentadienyl ligands as common features. Another precursor with Cp-functionalities and sulfur in the precursor molecule (Cp₄Fe₄S₄) showed very low activity too. There is apparently a negative correlation between the conversion of iron containing complexes and the presence of cyclopentadienyl/sulfur units. This is possibly due to the formation of iron carbide during the initial stage of the catalyst activation. It is known (24) that sulfur addition to iron oxide, or iron pentacarbonyl initiates the transformation into pyrrhotite (Fe_{1-x}S, where 0 ≤ x ≤ 0.125, because of Fe³⁺ impurities). This activation reaction is difficult to perform and iron carbonyls tend to form less reactive iron carbides and oxides during the activation process. Precursor molecules without CO ligands, but cyclopentadienyl groups are expected to form much more iron carbide. This might explain the low activity of certain iron containing catalyst precursors, compared with more active MoS₂ systems. Another reason for the low effectiveness of the iron-cluster in hydrocracking reactions may be that iron appears to function by removing oxygen

functionalities whereas Mo catalysts are good hydrogenation catalysts (9).

For the sulfur-free Fe catalyst precursor, the amount of added S to Fe in the atomic ratio of 1 to 1 may not be sufficient to produce a pyrrhotite phase. U. Rao suggested that it would be useful to study the literature or perform an experiment to establish the partial pressure of H_2S required to transform the precursor into pyrrhotite [personal communication with Dr. Udaya Rao, of U.S. DOE, PETC, March 16, 1995]. It is known that sulfur deficiency can result in the stoichiometric troilite, FeS which appears to be catalytically inactive. For a description of the role of sulfiding in catalyst activity, see Bacaud et al., ACS Fuel Chemistry Preprints, 38 (1), 1 (1993).

We also tested a copper zirconium phosphate $CuZr_2P_3O_{12}$, a material with stable pore structure, even at elevated temperatures. However, hydrocracking experiments at 400 °C gave no more conversion than a non-catalytic run. The beneficial effect of sulfur addition could once more be demonstrated in another experiment. Sulfur added to $CuZr_2P_3O_{12}$ led to an increase in conversion of about 50 %. The very low activity of the sulfur free copper zirconium phosphate stimulated our interest to study the influence of sulfur on hydrocracking reactions. A series of experiments was carried out to determine the impact of sulfur concentration on NMBB conversion. It was found that increasing sulfur concentration (starting at 1.2 wt %) led to increasing model compound conversion.

It was also found that sulfur had a permanent effect on the stainless steel reactor walls. Even new reactors turn after reactions with S black inside, depending on the sulfur concentration. We assume that added S reacts with iron on the surface of the reactor walls to form FeS. This black FeS layer can not be removed mechanically, or by leaving sulfided reactors in a KOH-base bath for an extended period of time (1 - 3 days). Further experiments of sulfided reactors with NMBB alone give dramatically higher conversion than an identical thermal run in a new reactor. This so called "wall effect" can be reduced by immersing sulfided tubing bomb reactors in a 6 N HCl bath for 5 min. Subsequent treatment of the same reactor in a base bath brings "background activity" down by more than 50 %. However, repeated acid washing leaches out steel components and shortens the lifetime of a reactor considerably. Furthermore, the surface area so treated reactors increases and changes therefore its catalytic activity permanently.

The influence of remaining catalyst, solvent and model compound in the upper part of our tubing bomb reactors was also investigated. The upper part of our reactor were washed subsequently with chloroform and ethanol to remove sublimed catalyst material and hydrocarbons. Experiments after this treatment revealed no difference compared to runs without washing of the upper reactor part. Our conclusion is that sulfur mainly controls the catalytic

behavior of used tubing bomb reactors. Treatment with hydrochloric acid partially removes unwanted FeS particles but does not restore the original low activity of a new reactor.

Product Distribution

Hydrocracking of NMBB yields three product categories that can be explained by the cleavage of the bonds between the aromatic moieties. The identified products can be classified into hydrocracking, hydrogenation and isomerization products. Those coming from hydrocracking reactions form the major pool of reaction products, followed by hydrogenation and isomerization products. Figure 2 shows the product distribution from catalytic hydrocracking experiments of NMBB. All iron containing catalyst precursors give a similar ratio of main products. It is apparent that ferrous catalysts cleave NMBB preferably in position a. Increasing conversion leads in most experiments to a proportional increase in the ratio of major products. The following compounds can be found as main products: tetralin, naphthalene, bibenzyl and 4-MBB.

Several studies, including the present work, have shown that NMBB tends to undergo cleavage of bond α connecting the naphthyl group to the remainder of the molecule when subjected to a variety of catalytic reactions under a variety of conditions. Farcasiu et al. (11-13) suggested a reaction mechanism in which the first stage consists of the formation of a radical cation. The loss of electron density leads to a weakened α -bond which can then be broken relatively easily. This is in contrast to model studies in which phenyl-containing compounds undergo preferably β -cleavage (15).

Scheme 1: Potential cleavage sites in 4-(1-naphthylmethyl)bibenzyl.

In the work of Penn and Wang (15) radical cations were generated in the mass spectrometer under a variety of conditions which had little impact on the bond cleavage pathway. Preference for β -cleavage was observed. It was explained by resonance stabilization of the intermediates formed via bond β cleavage. Both intermediates are resonance stabilized. Thermochemical calculations (33) show that reaction pathway β is 30 kcal/mol lower for both neutral and radical cationic species than pathway α . In contrast, neither of the intermediates resulting from bond α cleavage is stabilized. However, in the presence of a catalyst, the major reaction pathway mainly involves the cleavage of bond α (Scheme 1). These studies indicate that a new decomposition pathway mechanism must be developed to explain the results of bond cleavage involving model reactions on NMBB.

Catalyst Precursor Features: The previous report TPR-8 focused on the influence of various ferrous precursors in different structural environments on hydrocracking of NMBB. This report investigates the function of different ligand environments on the activity of several catalyst precursors in hydrocracking reactions over NMBB.

Ferrocene (scheme 2) is a 18 VE (valence electron) air stable orange complex with krypton electron configuration. The cyclopentadienyl ring are in a parallel arrangement. The complex decomposes above 173 °C and can be oxidized to its cation.

Iron sulfate $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ is a light green substance with 7 crystal waters. It oxidizes slowly on exposure with air to Fe(III). It is much more stable as ammonium salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \times 6 \text{H}_2\text{O}$.

Scheme 2: Structure of ferrocene.

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Hydrogenation of O-containing Model Compounds Using Novel Catalyst Precursors.

Introduction

Oxygenated compounds are present in some, if not all, coals [1]. Phenols (and related hydroxyl compounds) have been identified in coal derived distillates [2].

Ethers and related compounds, connecting structural units within the coal matrix, have been proposed as sites for the depolymerization of the coal [3] and also ethers, together with carboxyls and phenolics, have been implicated in the facilitation of retrogressive, crosslinking, repolymerization reactions [4, 5].

With the increase in the extraction of lower rank coals in the U.S. and research into their use as liquefaction feedstocks [5-7], the importance of oxygen functionality removal from coal and coal derived liquids is all the more apparent.

Further reduction of the phenol, carboxyl and ether-like oxygen containing compounds may be possible with the use of a selective bimetallic catalyst dispersed using an organometallic precursor (TPR1-8).

The model compounds used in this study were:

Anthrone

Dinaphthylether

Xanthene

Xanthenol

Experimental

Procedure

All experiments were performed in a 22 ml capacity microreactor. 0.5-1.0 g 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 2.46 mol% concentration (unless otherwise stated). The catalyst precursors used were ATTM ($(\text{NH}_4)_2\text{MoS}_4$), Ni-Mo1 ($[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$) and CoMo-T2 ($\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$). The latter two bimetallic precursors [Ni-Mo1; CoMo-T2] were synthesized in this laboratory, as described elsewhere^[8,9].

Air in the reactor was removed by flushing the reactor three times with H_2 to 1000psi. Reactions were performed at 300°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 cool water.

Analysis of Products

0.25g of tridecane was added to the microreactor as an internal standard. The microreactor contents were then extracted with acetone into a vial and diluted to 22 ml.

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

Results and Discussion

Conversion of Anthrone to Products

The effect of temperature and catalyst on the overall conversion of anthrone (i.e. the removal of the carbonyl oxygen) is illustrated in Figure 3. These results have been previously discussed in a previous report TPR-8, but have been included for comparison.

Conversion of Dinaphthylether to Products

Figure 4 illustrates the effect of a bimetallic dispersed catalyst precursor (CoMo-T2) compared to that of a monometallic inorganic counterpart (ATTM) at different temperatures. The conversion of dinaphthylether (DNE) was 100wt% at 400°C in the presence of CoMo-T2, with only 4.5wt% O-containing compounds remaining (comparative to that of the non-catalytic reaction). The equivalent reaction using ATTM gave a DNE conversion of 76.5wt%, with 7.4wt% O-compounds (excluding starting material) remaining.

Both catalysts produce dramatic increases in reactant conversion, compared to that of the non-catalytic run, at 400°C and smaller increases at 300°C. However, ATTM appears to increase the yield of O-containing species. This increase is primarily due to the conversion of DNE to THDNE (it's tetrahydro derivative). These results also demonstrated the superior catalytic activity of bimetallic precursor, CoMo-T2 (which was also called MoCo-TC2^[8] or CoMo-TC2^[9] in our

previous papers), as compared to the monometallic precursor ATTM.

Product distribution

In the non-catalytic experiment the oxygenated products are only naphthylacetate and unreacted DNE. So, ATTM does not actually increase the yield of O-containing products of a reaction without catalyst, but instead promotes O-removal from the products or simply hydrogenates the starting material (a preference for hydrogenation over bond cleavage). This results in the low yield of naphthylacetate (0.9wt%), a higher yield of THDNE (5.3wt%) and an intermediate yield of 2-tetrahydronaphthol (1.2wt%).

Reactions in the presence of the CoMo-T2 precursor, however, show a large proportion of the yield of O-containing species attributed to 2-tetrahydronaphthol (3.7wt%) and very small yields of naphthylacetate (0.6wt%) and THDNE (0.2wt%) (a sample chromatogram of CoMo-T2 @ 400°C, showing the product distribution, is given in Figure 5). This result suggests that the bimetallic catalyst favours bond cleavage over hydrogenation of aromatic ring systems.

This proposal is substantiated by the high yields of both naphthalene (35.1wt%) and tetralin (48.7wt%), in conjunction with a methyltetralin yield of 9.2wt%. Almost all substituent bonds are preferentially cleaved before hydrogenation of the ring system occurs. Further, in the absence of a catalyst the major product is naphthalene (11.6wt%) accompanied by a small tetralin yield (2.2wt%), implying slow cleavage of the C-O bonds and even slower hydrogenation of the ring system. Yet, ATTM, whilst having an equal yield of both naphthalene (35.2wt%) and methyltetralin (7.9wt%), has a much lower yield of tetralin (25.9wt%) hinting at a restriction in the hydrogenation ability of the catalyst.

Conversion of Xanthene to Products

Figure 6 illustrates the effect of temperature and catalyst precursor on the conversion of xanthene. This clearly shows the low reactivity of the starting material at 300°C and at 400°C in the absence of a catalyst. Total conversion at 400°C in the presence of CoMo-T2 (70.2wt%) is much higher than with ATTM (46.9wt%), although the proportion of O-containing compounds produced is also larger (19.6% of total products) compared with ATTM (11.3% of products). At 300°C, CoMo-T2 produces equal amounts of O-containing and non-O-containing species, although in very low yields (total 5.2wt%).

Product Distribution

Within the oxygenated compounds produced in the presence of CoMo-T2 (excluding unreacted xanthene), the relative amounts of phenols, >C4-alkylphenols, naphthols and ethers are

approximately the same, whereas for the reactions involving ATTM the major O-containing products are >C4-alkylphenols with little, or no, phenol, naphthol or ether production. This again attests the proposal that CoMo-T2 is a superior bond cleavage catalyst at 400°C than its inorganic, monometallic equivalent.

It follows therefore, that the lower total conversion of xanthene, in the presence of ATTM at 400°C, may be attributed to the catalysts inferior bond cleavage ability. The primary non-O-containing product in all reactions of xanthene was 1-methylheptylbenzene. The difference in yields of this compound, produced from reaction with CoMo-T2 (19.1wt%), and from reaction with ATTM (9.9wt%), is approximately equal to the difference in total yields of non-O-compounds (56.4 and 41.6wt% respectively). However, the yields of methyltetralins produced are comparable for both catalysts (~25wt%). This value is greater than the total alkylbenzene yield achieved with ATTM and approximately the same as that achieved using CoMo-T2.

This contrast may doubtlessly be attributed to the ability of CoMo-T2 to preferentially cleave bonds, especially C-O bonds, and ATTM's capacity for hydrogenation of ring systems. A sample chromatogram is depicted in Figure 7.

Conversion of Xanthenol to Products.

Work on this model compound are still ongoing, using both the catalysts discussed in this report.

Conclusions

The objective of this study is to investigate the utility of highly dispersed catalysts, from organometallic precursors, in the removal of heteroatom functionality from the products of a reaction performed under liquifaction conditions.

The catalytic precursor CoMo-T2 exhibited a sizable increase in the yield of non-O-containing products, compared to a non-catalytic reaction or one using a standard inorganic catalyst precursor (ATTM).

The lower reactivity of the model compounds DNE and xanthene, relative to anthrone, under liquefaction conditions, assists to accentuate the superior bond cleavage capability of the bimetallic catalyst. The low yield of O-containing products, without sacrificing high conversion, may indicate a selectivity toward preferential C-O bond cleavage (i.e. removal of oxygen functionality).

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Table 1: Effect of iron containing catalyst precursors on hydrocracking reactions of NMBB at 400 °C

Catalyst Precursors	Ferrocene	Ferrocene+S	FeSO ₄ x 7 H ₂ O	FeSO ₄ x 7 H ₂ O+ S
Products [mmol %]				
Benzene				
Toluene	1.6	1.1		1.3
p-Xylene				
Tetralin	0.4	0.3		0.6
Naphthalene	13.8	10.3	4.5	24.0
2-MTHN				
1-MTHN				
2-Methylnaphthalene				
1-Methylnaphthalene	5.6	0.5		1.5
Bibenzyl	2.6	0.6	0.6	2.5
Benzyl-naphthalene ^b				
4-Methylbibenzyl	9.4	7.4	2.6	19.1
TH-NMBB-derivatives				
Conversion [wt %]	15.8	9.6	3.7	23.9

^a Reactor residence time in preheated sand bath: 30 min. ^b Also called naphthyl phenyl methane.

Table 2: Effect of CuZr₂P₃O₁₂ and Sulfur addition on hydrocracking reactions of NMBB at 400 °C

Catalyst Precursors	CuZr ₂ P ₃ O ₁₂	CuZr ₂ P ₃ O ₁₂ + S	Sulfur 3.4 wt %	Sulfur 1.2 wt %	None [sulfided reactor]	None [reactor HCl treated]
Products [mmol %]						
Benzene						
Toluene	1.2	2.6	4.9	1.4	1.0	1.0
p-Xylene						
Tetralin	0.6	3.0	2.9	0.8	0.8	0.4
Naphthalene	13.8	50.3	74.4	24.8	19.1	10.8
2-MTHN			0.4			
1-MTHN						
2-Methylnaphthalene		0.6	7.8			
1-Methylnaphthalene	0.8	4.0	9.5	1.7	0.8	0.7
Bibenzyl	2.1	7.2	42.5	2.4	1.0	1.2
Benzyl-naphthalene ^b						
4-Methylbibenzyl	10.3	43.2	32.3	22.1	18.3	9.7
TH-NMBB-derivatives						
Conversion [wt %]	13.3	54.4	82.5	26.1	23.0	11.6

^a Reactor residence time in preheated sand bath: 30 min. ^b Also called naphthyl phenyl methane.

Scheme 3

Scheme 4

Scheme 5

Scheme 6

Scheme 7

Scheme 8

Catalytic Hydrocracking of NMBB

Figure 1

Effect of Ferrous Catalyst Precursors on Hydrocracking of NMBB

Figure 2

Figure 3 Conversion of Anthrone to Products.

Figure 4 Conversion of Dinaphthylether to Products.

Figure 5

Figure 6 Conversion of Xanthene to Products.

Figure 7