

**NOVEL SUPPORTED BIMETALLIC CARBIDE
CATALYSTS FOR COPROCESSING OF COAL WITH WASTE
MATERIALS**

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Executive Summary

It is important to explore novel catalysts for producing clean synthetic fuels from heavy hydrocarbon resources including coal and waste organic substances such as plastics and tires. The overall objectives of this project are to explore the potential of novel monometallic and bimetallic Mo-based carbide catalysts for heavy hydrocarbon coprocessing, and to understand the fundamental chemistry related to the reaction pathways of coprocessing and the role of the catalysts in the conversion of heavy hydrocarbon resources into liquid fuels based on the model compound reactions.

A new family of bimetallic oxycarbide compounds $M^I-M^{II}-O-C$ ($M^I = Mo, W$; $M^{II} = V, Nb, Cr, Fe, Co, Ni$) has been synthesized by carburizing bimetallic oxide precursors using a temperature-programmed method. The catalysts were characterized by CO chemisorption, BET surface area measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine structure (NEXAFS). The NEXAFS spectra of the carbide catalysts indicate that surface contamination by oxygen and the presence of an oxycarbide instead of a pure carbide structure.

We have identified Nb-Mo-O-C as the most promising bimetallic carbide catalyst, and this catalyst together with Mo_2C , the most active single-metal carbide have been investigated for the model coprocessing reaction system. Comparative study was made with Mo-based monometallic and bimetallic sulfide catalysts. The model co-processing feedstock is a multi-component model mixture that simulates the combined feed of coal and waste materials. The idea is to use different compounds that are specific for each reaction type but have no overlapping products. Our proposed design involves a 5-component mixture containing 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB, (2) pyrene, (3) tetradecane, (4) dibenzothiophene and (5) quinoline. NMBB simulates the aromatic-aliphatic as well as aliphatic-aliphatic C-C bonds in coal and in some aromatic plastics such as polystyrene. Pyrene represents polyaromatic structures in coal, while tetradecane is representative of polyethylene-type plastics in chemical reactivity. Dibenzothiophene and quinoline provide sulfur and nitrogen content. Results from such model co-processing studies have revealed characteristic reaction pathways for bond cleavage and ring hydrogenation over monometallic and bimetallic metal carbide and sulfide catalysts.

Introduction

It is likely that the world will continue to rely on liquid hydrocarbon fuels for transportation. The largest source by far for such fuels today is crude oil, and the United States has found and used up a large amount of its cheap domestic oil reserves. The conversion of coal, waste materials and other heavy hydrocarbon resources and their upgrading to clean liquid fuels are important for a secure supply of clean transportation fuels and hydrocarbon sources in the future.

The simultaneous conversion of coal with tires or plastics is important as a new method for disposing of wastes, as well as utilizing an important energy resource. In this project we investigated a relatively new class of materials, transition metal carbides, which have excellent prospects for catalyzing the complex transformations of the solids.

The overall objectives of this project are to explore the potential of novel monometallic and bimetallic Mo-based carbide catalysts for heavy hydrocarbon coprocessing, and to understand the fundamental chemistry related to the reaction pathways of coprocessing and the role of the catalysts in the conversion of heavy hydrocarbon resources into liquid fuels based on the model compound reactions.

Results and Discussion

Synthesis and Characterization of Bimetallic Compounds

We have prepared a series of bimetallic oxycarbide compounds $M^I-M^{II}-O-C$ ($M^I = Mo, W$; $M^{II} = V, Nb, Cr, Fe, Co, Ni$) by a temperature-programmed method which consists of carburizing bimetallic oxide precursors. The oxide precursors were obtained by combining precursor oxides at high temperature. The synthesis involved passing a 20 mol% CH_4 in H_2 mixture over the oxide precursors while raising the temperature at a linear rate of $8.3 \times 10^{-2} \text{ K s}^{-1}$ (5 K/min) to a final temperature (T_{max}) which was held for a period of time (t_{hold}). The best

material among the nine synthesized is shown in Table 1 which summarizes its CO uptake, surface area and active site density.

Table 1. Characteristics of Bimetallic Carbides/Oxycarbides

Sample	CO up-take ($\mu\text{mol g}^{-1}$)	Surface Area ($S_g \text{ m}^2\text{g}^{-1}$)	Site Density ($\times 10^{15} \text{ cm}^{-2}$)
Nb-Mo-O-C	54	98	0.033
Nb-Mo/ Al_2O_3	30	77	-
Mo_2C	99	42	0.14

The catalysts were evaluated for hydroprocessing in a three-phase trickle-bed reactor operated at 3.1 MPa and 643 K. The feed was a model liquid mixture containing 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt% aromatics (tetralin), and balance aliphatics (tetradecane). The Nb-Mo-O-C showed higher HDN than a commercial sulfided Ni-Mo/ Al_2O_3 catalyst tested at the same conditions. X-ray diffraction of the spent catalyst indicated that it was stable at reaction conditions. The results are shown below.

Table 2. Summary of Catalyst Performance in Hydroprocessing at 3.1 MPa and 643 K

Catalyst	% QNL Conversion HYD + HDN	HDN %	HDS %
Nb-Mo-O-C	86	44	57
Mo_2C	86	43	46
Ni-Mo-S/ Al_2O_3	85	38	79

The molybdenum carbide material also showed good activity in HDN. In order to investigate its properties further, studies were conducted with a single crystal sample made available to us from a group in Japan (S. Otani, National Institute for Research in Inorganic

Materials). The structure and chemisorption properties were investigated using surface science techniques. It was found that the surface reconstructed into 3-fold rotated domains. The material chemisorbed CO in molecular form, in accordance to expectations.

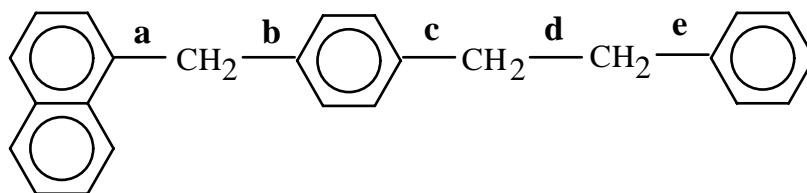
More details about work on the preparation and characterization of bimetallic carbide catalysts are described in related publications [Refs. 1-6].

Model Coprocessing Tests

Because of the high HDN activity found with Nb-Mo-O-C, various model co-processing tests were carried out with that compound. As references, Mo₂C and various sulfides were used. The unsupported monometallic (Mo₂C) and bimetallic (NbMo_{1.6}C) catalysts were prepared at Virginia Tech and sent to Penn State in sealed glass ampoules, which were examined in simulated coprocessing model tests at Penn State. Studies were carried out in 25-mL horizontal autoclave micro-reactors at 400 °C under 1000 psig initial H₂ pressure, with a residence time of 30 min plus 3 min for heat-up. The reactor was shook at a rate of 240 strokes/min. Results from such model co-processing studies in this project have revealed characteristic reaction pathways for bond cleavage and ring hydrogenation over monometallic and bimetallic metal carbide and sulfide catalysts.

The model coprocessing feed consisted of a 5-component mixture containing 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB, (2) pyrene, (3) tetradecane, (4) dibenzothiophene and (5) quinoline. The rationale and importance of using such compounds have been discussed in related publications [refs. 7-12]. Briefly, NMBB simulates the aromatic-aliphatic as well as aliphatic-aliphatic C-C bonds in coal and in some aromatic plastics such as polystyrene. Pyrene represents polyaromatic structures in coal, while tetradecane is representative of polyethylene-type plastics in chemical reactivity. Dibenzothiophene and quinoline provide sulfur and nitrogen content. The relevance of these types of model compounds to various hydroprocessing systems of heavy hydrocarbon resources has been discussed in related publications [Refs. 13-21].

Briefly, a multi-component model-feedstock was used to test catalytic functions for simultaneous hydrogenation, C-C bond hydrogenolysis, hydrodesulfurization, and hydrodenitrogenation. These reactions are precisely those involved in the conversion and processing of heavy hydrocarbon resources such as heavy oil, coal, and other residual materials. The multi-component feed includes 4-(1-naphthylmethyl)bibenzyl (NMBB), dibenzothiophene (DBT), quinoline, pyrene, and eicosane. An important question on catalytic functions is, whether and how does a catalyst promote simultaneous hydrogenation and C-C bond hydrogenolysis. NMBB (4-(1-naphthylmethyl)bibenzyl) is an unique model compound that can clarify this issue. There are five possible cleavage sites (C-C bonds) in NMBB, as shown in Scheme 1, but they are sensitive to the conditions. Purely thermal energy can cause cleavage of the aliphatic-aliphatic C-C bond in the bibenzyl portion of NMBB. Hydrogen atom transfer can induce the cleavage of the aromatic-aliphatic C-C bond in the naphthylphenylmethane portion of NMBB. There are two possible sites for such induced cleavage. If only hydrogenation occurs, partially hydrogenated NMBB would be the only product, as is the case with some metal carbonyl-derived catalysts. The information feedback from these types of model tests should be useful for selecting promising catalysts for hydroprocessing or coprocessing of coal and waste materials as well as petroleum resid in the future.



Scheme 1. Structure of 4-(1-naphthylmethyl)bibenzyl (NMBB).

It must be stressed that the comparison of the activities was carried out by loading equal number of active sites of each catalyst into the reactor. The active sites were titrated by chemisorption techniques, CO in the case of the carbides and low-temperature O₂ for the sulfides, as shown in table 3. Also, the catalysts were prepared *in situ* and transferred in sealed

ampoules to the autoclave reactors. The ampoules were broken mechanically, when the reactor was already purged by ultra-high-purity nitrogen three times and pressurized with hydrogen at room temperature.

Table 3 Active sites of catalyst by chemisorption

Catalyst	Catalyst/ Support	CoO (wt%)	NiO (wt%)	Mo (wt%)	Active Sites (micro-mol/g) on wt of catalyst used	Active Sites (micro-mol/g) on wt of catalyst recovered
ATTM	(NH ₄) ₂ MoS ₄	N/A	N/A	36.91	57.30	93.70
CR-344	Co-Mo/Al ₂ O ₃	2.90	N/A	9.0(13.5*)	82.40	85.90
CR-424	Ni-Mo/Al ₂ O ₃	N/A	3.00	8.7(13.0*)	92.30	95.00
Mo2C	Mo ₂ C	N/A	N/A	94.1	99.00	-
MoNb1.6C	NbMo _{1.6} C	N/A	N/A	59.4	22.00	-
Molyvan_L	Molyvan_L			8.1		

* The content of MoO₃ within the commercial catalysts

Single-Component Tests

Tables 4 and 5 show the results for hydrocracking of NMBB over Mo carbide and MoS₂-based sulfide catalysts at 400 °C and 375 °C, respectively. Reaction of NMBB without added catalyst provides a baseline for comparison of all catalytic reactions. Results are showed in Table 4.1 that naphthalene and 4-methylbibenzyl are the main products. They were derived from hydrocracking at bond *a*. The small amount of 1-(naphthyl)-4-tolyl-methane and toluene indicated that bond *d* would be another cracking site under non-catalytic atmosphere. Naphthyltolylmethane, which was not found in catalytic reactions, is believed to be a product in non-catalytic reactions at 400 °C. From Tables 4 and 5, the total yields of naphthalene and tetralin were almost over 70% and 4-methylbibenzyl close to or over 50% in most catalytic runs, indicating that the cleavage of NMBB mainly occurs on the aromatic-aliphatic bond *a*. Some further cracking products from 4-methylbibenzyl were also detected from the GC-MS spectroscopy, such as toluene, ethylbenzene, *p*-xylene. In addition, some amount of

methylnaphthalene, its hydrogenation isomers and bibenzyl also existed in the product pool, which represented that cracking also occurred on bond *b*. It is very obvious that no naphthyltolylmethane product were detected in all the catalytic reactions. In some catalytic runs, small amounts of hydrogenated NMBB products have been detected.

The results from reactions with single model component show that NMBB is a good model compound for examining the activity and selectivity of various catalysts. Compared to the product distribution of NMBB reactions over sulfided catalysts, the carbide catalysts showed different catalytic activity and selectivity. In case of NbMo_{1.6}C catalyst, more cracking products such as toluene, ethylbenzene and *p*-xylene were derived from further cracking of methylbibenzyl and bibenzyl products. The total yields of these secondary cracking products were up to 22.1% at 400°C, while those secondary cracking products only accounted for about 11.5% in case of Ni-Mo/Al₂O₃ catalysts at 400°C. This phenomenon is more obvious at low reaction temperature. It should be noted that the conversion values reported here are based on the mass of recovered products, and may be lower than true values. The true conversion value should be \geq sum of molar yields of naphthalene, methylnaphthalene, tetralin, decalin, hydrogenated methylnaphthalene isomers, naphthyltolylmethane, benzylnaphthalene (if any), and tetrahydro-NMBB because these products correspond to the starting material in a stoichmetric (molar) ratio of 1:1.

The results with single compound NMBB show that NbMo_{1.6}C catalyst exhibits higher activities than Mo₂C catalyst in terms of hydrogenation, and hydrogenolysis based on the same catalytic active sites charged. NbMo_{1.6}C has very high activity for hydrogenation of bibenzyl derivatives, as well as naphthalene. Compared to other MoS₂-based catalysts, Mo₂C and NbMo_{1.6}C carbide catalysts showed different catalytic functionalities on NMBB. NbMo_{1.6}C catalyst showed hydrogenation ability twice as high as sulfided Ni-Mo/Al₂O₃ based on the same active sites of catalyst per gram NMBB. More deep hydrogenated products such as decalin and hydrogenated products of 4-methylbibenzyl have been found in the presence of NbMo_{1.6}C.

An important phenomenon was observed that some new hydrogenated products derived from methylbibenzyl and bibenzyl were detected from catalytic reactions by those two carbide

catalysts. There were 1,2-dicyclohexylethane, 4-methylhexahydrobibenzyl, 4-methyl-1,2-dicyclohexylethane, which have never been reported in the previous literature.

Table 4 Hydrocracking of NMBB over Mo carbide and MoS₂-based sulfide catalysts at 400 °C

°	ATTM	Molyvan L	Co-Mo/Al ₂ O ₃	Ni-Mo/Al ₂ O ₃	Mo ₂ C	NbMo _{1.6} C	Thermal
Experiment No.	1-014	1-020	1-023	1-024	1-025	1-026	1-013
Catalyst Amount, g	0.1636	0.1500	0.0226	0.0203	0.1	0.125	
Active Sites, mcior-mol	9.37	NA	1.86	1.87	9.90	2.75	
Catalyst loading,micro-mol/g	9.37	NA	9.32	9.35	9.37	9.36	
Temperature, °C	400	400	400	400	400	400	400
g NMBB	0.9997	0.2000	0.1999	0.2003	1.0567	0.2939	0.2000
Yields, mol%							
Methylcyclohexane						5.5	
Toluene	4.6	1.1	5.1	6.2	6.6	8.7	2.2
Ethylbenzene			2.2	2.4	0.7	2.6	
p-Xylene	1.5		2.2	2.9	3.0	5.3	
Decalin					4.7	7.7	
Tetralin	62.9	25.7	43.7	41.5	64.7	46.9	
Naphthalene	8.2	57.1	28.9	42.8	4.6	3.6	2.0
MTHN isomers	5.1	4.3	4.6	4.8	1.8	2.3	
1-Methylnaphthalene		5.9	3.0	4.2	5.7	5.9	
Bibenzyl	9.9	22.7	8.7	9.8	5.9	3.4	
4-Methylbibenzyl	63.8	65.5	62.5	73.7	39.1	23.6	2.5
4-Methylhexahydrobibenzyl					18.6	16.8	
1,2-Dicyclhexylethane						5.9	
4-Methyl-1,2 -dicyclohexylethane					1.9	6.6	
1-Naphthyl-4-tolylmethane							0.7
NMBB Recovered							96.8
Conversion	100.0	100.0	100.0	100.0	100.0	100.0	3.2

Table 5. Hydrocracking of NMBB over Mo carbide and MoS₂-based sulfide catalysts at 375°C

°	ATTM	ATTM	Molyvan L	Co-Mo/Al ₂ O ₃	Ni-Mo/Al ₂ O ₃	Mo ₂ C	NbMo _{1.6} C
Experiment No.	1-016	1-016-2	1-019	1-021	1-022	1-017	1-018
Catalyst Amount, g	0.0326	0.0325	0.1500	0.0229	0.0203	0.1000	0.1140
Active Sites, mcior-mol	1.87	1.86	N/A	1.89	1.87	9.90	2.51
Catalyst loading,micro-mol/g	9.34	9.30	N/A	9.42	9.35	9.37	9.37
Temperature, °C	375	375	375	375	375	375	375
g NMBB	0.2001	0.2003	0.1998	0.2003	0.2005	1.0567	0.2678
Yields, mol%							
Methylcyclohexane							12.7
Toluene					1.4	1.9	5.4
Ethylbenzene							2.1
p-Xylene							6.0
Decalin							10.2
Tetralin	41.7	43.1	0.8	53.9	68.3	74.6	35.8
Naphthalene	34.3	35.1	64.9	31.6	2.9	7.8	6.8
MTHN isomers	1.8			1.4	1.6	3.7	4.0
1-Methylnaphthalene	3.6		8.3	1.9		1.1	
Bibenzyl	9.8	10.4	11.5	10.2	9.4	12.0	4.4
4-Methylbibenzyl	70.4	71.5	55.1	80.3	60.9	60.3	24.1
4-Methylbibenzyl isomer	-						
4-Methylhexahydrobibenzyl	9.4	8.4			2.3	7.0	11.1
1,2-dicyclohexylethane							10.0
4'-Methyl-1,2-dicyclohexylethane							8.9
Tetrahydro-NMBB-1				5.2	4.0	5.9	
Tetrahydro-NMBB-2			14.7				
NMBB Recovered	11.0	10.6	15.2			0.0	0.0
Conversion	89.0	89.4	84.8	100.0	°100.0	100.0	100.0

For example, the ratio of the total yields of hydrogenated products to the total yields of bibenzyl and methylbibenzyl were up to 1.28 at 400°C and 1.05 at 375°C over NbMo_{1.6}C catalyst.

It can be seen clearly that two monometallic and bimetallic carbide catalysts has different activity and selectivity on the reaction of NMBB from monometallic or bimetallic sulfided catalysts from the point view of product distribution. Differences were observed in the relative distribution of naphthalene, tetralin and decalin from the NMBB reactions over Mo₂C and NbMo_{1.6}C catalysts. These two carbide catalysts presented similar catalytic activity in terms of tetralin and naphthalene distribution. In addition, they both gave higher ratio of tetralin to naphthalene at 400°C than 375°C. However, it should be indicated that the amount of decalin was different from each other. No decalin was detected at all from the Mo₂C catalytic run at 375°C; instead 10.2% of decalin was hydrogenated from the NbMo_{1.6}C catalytic reaction. Similarly, 4.7% of decalin was hydrogenated by Mo₂C, while 7.7% of decalin was achieved from the bimetallic carbide NbMo_{1.6}C catalyst. From this point, we can see the bimetallic carbide NbMo_{1.6}C catalyst demonstrate high hydrogenation ability compared to the monometallic Mo₂C catalyst.

5-Component Model Tests

Table 6 and 7 list the results including conversion and product distribution of 5-component reactions over various Mo sulfide and carbide catalysts at 400°C and 375°C respectively. Generally speaking, all the molybdenum catalysts substantially enhanced conversion, hydrogenation, hydrodesulfurization and hydrodenitrogenation compared to the thermal non-catalytic reactions.

The results from 5-component reactions indicate that the patterns of product distributions strongly depend on the type of catalysts, and the trends do not always parallel with those for single-component tests, indicating the influence of co-reactants. The catalytic properties of Mo₂C are significantly inhibited in the 5-component reaction. ATTM performs as a better catalyst on HDN even than the two commercial Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. However, Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts show higher HDS ability on DBT than ATTM. NbMo_{1.6}C also shows high activity on hydrogenation and HDN.

The reaction temperature has a great effect on the product distribution. More hydrogenation products and very limited C-C cleavage products were obtained at 375°C, while higher yields of hydrocracking, and hydrogenated C-C cleavage products were detected at 400°C. Overall, the unique reactivities and selectivities of Mo₂C and NbMo_{1.6}C carbide in hydrogenation and its HDN and HDS performance make the Mo carbides promising catalysts for hydrocarbon processing.

Table 6. Results of 5-Component Model Co-processing Reactions at 400 °C

Catalyst	ATTM	Molyvan Co- L	Mo/Al ₂ O ₃	Ni- Mo/Al ₂ O ₃	Mo2C	NbMo1.6 C	Thermal
Experiment No.	5-017	5-021	5-024	5-025	5-028	5-029	5-013
Temperature, oC	400	400	400	400	400	400	400
Quinoline							
Propylcyclohexane	60.2	4.8	34.8	50.0	2.1	25.6	
PropylBenzene	3.9	1.5	2.4	3.9	0.4	3.1	
Propenylcyclohexene	0.8	3.4	3.1	3.3	2.6	4.3	
1,2,3,4-tetrahydroquinoline		39.0	13.8	3.2	50.3	12.4	11.3
5,6,7,8-tetrahydroquinoline		5.2	3.3	0.9	12.4	3.6	
Decahydroquinoline					7.0	1.5	
2-propylbenzenamine	6.0	3.2	19.7	20.6	3.0	5.4	
Quinoline recovered		3.3	1.0	0.9	7.0	1.3	89.0
Conversion	100.0	96.7	99.0	99.1	93.0	98.7	11.0
DBT							
Benzene, cyclohexyl-	10.6		4.8	4.7		4.7	
Biphenyl	6.3	1.9	72.1	80.5	5.4	40.7	
TH-DBT	15.6						
DBT recovered	53.9	98.1	24.1	14.8	95.1	52.3	100.0
Conversion	46.1	1.9	75.9	85.2	4.9	47.7	0.0
NMBB							
Methylcyclohexane	5.0			1.8			
Toluene	3.5		3.5	3.8		5.5	1.5
p-Xylene				1.3		2.8	
Tetralin	49.2		23.6	30.7	0.9	25.6	
Naphthalene	15.9	1.9	30.9	31.8	25.5	47.9	
1-Methylnaphthalene				0.8		1.5	
Bibenzyl	5.3		2.1	2.2	1.2	3.9	
4-Methylbibenzyl	64.1	2.9	47.3	51.6	21.7	64.7	
4-Methyldicyclohexylethane	5.6			2.9		1.2	
1-Naphthyltolylmethane							0.8
TH-NMBB-1			7.7	5.6		2.5	
TH-NMBB-2	9.3		21.9	21.5		8.0	
NMBB recovered	6.1	93.0	14.9	6.5	59.9	15.3	96.9
Conversion	93.9	7.0	85.1	93.5	40.1	84.7	3.1
Pyrene							
4,5,9,10-tetrahydropyrene	2.5		3.7	3.3	0.5	2.9	
1,2,3,3a,4,5-hexahydropyrene	9.7		6.4	6.7		6.3	
1,2,3,6,7,8-hexahydropyrene	10.7		6.1	7.3	0.8	8.3	
4,5-Dihydropyrene	20.5	12.1	29.2	27.2	15.2	24.4	1.8
Pyrene recovered	42.4	87.6	60.9	64.7	83.5	53.6	99.1
Conversion	57.6	12.4	39.1	35.3	16.5	46.4	0.9
Eicosane							
n-C20 recovered	97.7	95.2	91.5	90.1	91.9	88.7	99.5
Conversion	2.3	4.8	8.5	9.9	8.1	11.3	0.5

Table 7. Results of 5-Component Model Co-processing Reactions at 375 °C

Catalyst	ATTM	Molyvan L	Co- Mo/Al ₂ O ₃	Ni- Mo/Al ₂ O ₃	Mo ₂ C	NbMo _{1.6} C
Experiment No.	5-019	5-020	5-022	5-023	5-026	5-027
Temperature, °C	375	375	375	375	375	375
Quinoline						
Propylcyclohexane	30.4		10.9	20.2	0.6	13.6
PropylBenzene	2.1		0.4	0.7		2.0
Propenylcyclohexene	5.7		2.1	2.4	1.0	6.6
1,2,3,4-tetrahydroquinoline	16.9	45.0	54.0	46.7	77.7	30.3
5,6,7,8-tetrahydroquinoline	0.5	1.6	1.4	1.5	5.2	4.6
Decahydroquinoline					4.7	16.9
2-propylbenzenamine	13.1	3.4	12.5	17.1	1.8	1.0
Methylquinoline						0.3
Ethyl-THQ isomers					3.6	1.1
Ethylquinoline isomers					1.4	5.7
Quinoline recovered		2.1	2.3	1.3	5.7	2.0
Conversion	100.0	97.9	97.7	98.7	94.3	98.0
DBT						
cyclohexylbenzene	0.9		0.8	1.2		
Biphenyl	2.2	1.1	32.6	54.4	4.4	21.1
TH-DBT	8.8			0.3		
DBT recovered	88.1	98.7	66.3	44.7	95.8	78.9
Conversion	11.9	1.3	33.7	55.3	4.2	21.1
NMBB						
Methylcyclohexane						
Toluene						
p-Xylene						
Tetralin	6.7		2.4	4.8		3.3
Naphthalene	11.4		11.2	12.3	9.7	32.7
1-Methylnaphthalene			1.4	0.8	0.8	
Bibenzyl						1.3
4-methylbibenzyl	16.7		12.6	15.4	8.7	34.7
TH-NMBB-1	21.3		8.0	8.2		4.8
TH-NMBB-2	25.0		15.7	19.7		9.7
NMBB recovered	38.8	96.0	51.6	48.6	73.6	45.3
Conversion	61.2	4.0	48.4	51.4	26.4	54.7
Pyrene						
4,5,9,10-tetrahydropyrene	3.9		5.2	3.6	0.2	2.7
1,2,3,3a,4,5-hexahydropyrene	14.8		2.9	1.9		2.9
1,2,3,6,7,8-hexahydropyrene	21.0		2.2	1.9		4.1
4,5-dihydropyrene	27.4	5.5	36.1	32.3	7.6	26.8
1,3-dimethylpyrene						
Pyrene recovered	34.9	95.1	61.2	65.6	91.8	62.9
Conversion	65.1	4.9	38.8	39.7	8.2	37.1
Eicosane						
n-C ₂₀ recovered	90.0	97.5	93.9	98.3	98.8	90.4
Conversion	10.0	2.5	6.1	1.7	1.2	9.6

NMBB It is obvious that naphthalene, tetralin and 4-methylbibenzyl were the major cleavage products catalyzed by the molybdenum catalysts although product distributions were different from catalyst to catalyst, which will discuss the details in latter part. The conversions of NMBB are less than 100% in the multi-component reactions, not like the cases in the single component reactions, where all the reactions reached 100% conversion at 400°C.

Another obvious phenomenon is that a large amount of tetrahydro-NMBBs were detected from all the reaction except Molyvan L and Mo₂C catalytic runs at both 400°C and 375°C. Molyvan L and Mo₂C showed less activity on NMBB in the multi-component reactions, and no tetrahydro-NMBBs were observed in the final product slate. 4-metyldicyclohexylethane was also found in some catalytic runs at 400°C.

A small amount of bibenzyl and methylnaphthalene were also found in the product pool. Some secondary cracking products such as toluene, *p*-xylene, and methylcyclohexane were generated in the multi-component reactions.

Pyrene Seven types of hydrogenation products were detected from the 5-component catalytic reactions, which is consistent with the proposed network for pyrene hydrogenation described in literature [Ref. 22]. However, because of the very small amount of the decahydropyrenes and perhydropyrene, only 4,5-dihydropyrene, 4,5,9,10-tetrahydropyrene and 1,2,3,6,7,8-hexahydropyrene and 1,2,3,3a,4,5-hexahydropyrene were included in the calculation of the hydrogenation ability in the latter section.

Dibenzothiophene As described in the previous chapter, dibenzothiophene (DBT) would undergo two pathways to remove sulfur content in its structure under catalytic atmosphere. The major products include biphenyl, cyclohexylbenzyne (CHB) and tetrahydrodibenzothiophene (TH-DBT). There were very little of successive cracking products of benzene and cyclohexane in the 5-component catalytic system.

From the product distribution of specific catalytic runs, it can be observed that the hydrodesulfurization was implemented through different approaches for different catalyst. Biphenyl was the major HDS product for the two commercial bimetallic sulfide Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts, which indicates that sulfur was removed through direct C-S hydrogenolysis. For the ATTM catalytic run, the yield of cyclohexylbenzene is greater than that of biphenyl at 400°C, which indicates hydrodesulfurization via pathway II besides pathway I. DBT first undergoes hydrogenation to form tetrahydrodibenzothiophene (TH-DBT) and hexahydrodibenzothiophene (HH-DBT) followed by their desulfurization to form cyclohexylbenzene (CHB). Thus, a large amount of TH-DBT, the intermediate, was found in the ATTM catalytic runs. Almost 40% of converted DBT exists as the form of TH-DBT at 400°C and 75% of converted DBT exists as the form of TH-DBT at 375°C. The bimetallic NbMo_{1.6}C carbide catalyst presents high activity on DBT, and showed the similar catalytic mechanism on HDS as Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃. Mo₂C showed less HDS activity on DBT, and biphenyl is the major products.

Quinoline The reaction of quinoline yields many products, including hydrodenitrogenation product, such as propylcyclohexane, propylcyclohexene and propylbenzene, and hydrodenitrogenation intermediates, such as 1,2,3,4-tetrahydroquinoline (1-THQ), 5,6,7,8-tetrahydroquinoline (5-THQ), decahydroquinoline, 2-propylbenzenamine. It is worthily indicate that only the Mo carbide catalysts give decahydroquinoline in the final products compared to the Mo sulfide catalyst. It is also noticeable that some amount of alkylated quinolines, such as methylquinoline, ethylquinoline isomers and ethyl-THQ isomers, was detected in the reactions catalyzed by molybdenum carbides at 375°C.

We also can see from Tables 6 and 7 that propylcyclohexane is the major HDN product of quinoline. The ratios of propylcyclohexane to propylbenzene, which indicate the preference of HDN pathway, are around 15 for Mo sulfide catalysts, and 8 for NbMo_{1.6}C. From above information, we can assume that HDN of quinoline is considered to proceed mainly via the

saturated intermediates decahydroquinoline and propylcyclohexylamine to form propylcyclohexane.

Eicosane Because of the characteristics of its structure, eicosane is one of the most resistant compounds to cracking. All the catalysts do not show high activity for eicosane cracking and less than 15% of eicosane was cracked via these catalysts at 400°C.

From above product distribution analysis, we can see that different catalyst has different activity on certain compounds in the five-component mixture system; different catalyst also shows different selectivity on certain compound. Detail properties of hydrogenolysis, hydrodesulfurization and hydrodenitrogenation of those catalysts will be discussed in the following sections.

More details concerning model co-processing experiments and results are available in the Master Degree Thesis of Weilin Wang [Ref. 22] who was a graduate student working on this project as a part of his MS study.

Some real co-processing tests were conducted at Penn State by Jianli Yang (visiting scientist from Institute of Coal Chemistry, Chinese Academy of Sciences, China) using real coal sample and real samples of plastics (high-density polyethylene) and tires (real tire for automobile). The results at 400 °C showed that there are catalytic promoting effects by the carbide as well as sulfide catalysts for the co-processing reactions. However, it also appears that the temperature of 400 °C is relatively low for high-density polyethylene to break down. The tire sample was slightly more reactive than polyethylene at 400 °C.

Conclusions

1. A Nb-Mo bimetallic compound was synthesized by carburizing a bimetallic oxide precursor using a temperature-programmed method. The material had excellent activity in hydroprocessing.
2. The catalysts were evaluated for hydroprocessing in a three-phase trickle-bed reactor operated at 3.1 MPa and 643 K. The bimetallic oxycarbides had moderate activity for HDN of quinoline, with Nb-Mo-O-C showing higher HDN than a commercial sulfided Ni-Mo/Al₂O₃ catalyst tested at the same conditions.
3. The catalysts were examined in simulated co-processing tests with five model compounds. Similar results concerning relative activities were obtained as with the trickle-bed reactor. However, a number of mechanistic insights were gained from 5-component model tests.
4. For single-component tests with NMBB, compared to Mo sulfide catalysts, Mo carbide catalysts possess different catalytic functionality. Some new hydrogenation products derived from bibenzyl and 4-methylbibenzyl, such as 1,2-dicyclohexylethane, 4-methylhexahydrobibenzyl and 4-methyl-1,2-dicyclohexylethane, were formed in the catalytic runs over NbMo_{1.6}C catalyst.

Among the Mo sulfide catalysts, ATTM exhibits highest hydrogenation ability on NMBB reaction at 400°C, while Ni-Mo/Al₂O₃ showed high activity on hydrogenation at 375°C. In addition, Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ are more active to hydrocracking in terms of the yields of the secondary cracking products. Compared to Mo sulfide catalysts, Mo₂C and NbMo_{1.6}C carbide catalysts are extremely active to NMBB reaction in terms of hydrogenation ability. NbMo_{1.6}C catalyst shows hydrogenation ability twice as high as Ni-Mo/Al₂O₃ based on the same active sites of catalyst per gram NMBB. NbMo_{1.6}C also exhibits highest activity on hydrocracking among the examined Mo-based catalysts.

5. For the 5-component tests, on the basis of the thermal reactions of 5-component model compounds, we can rank the five compounds in the following sequence in terms of reactivity: quinoline > NMBB > pyrene > DBT > eicosane.

Among the Mo carbide catalysts and the Mo sulfide catalysts, NbMo_{1.6}C showed similar activity on quinoline and NMBB compared to the two commercial catalysts. Moreover, NbMo_{1.6}C exhibit slightly higher activity on the conversion of pyrene, which is consistent with its high hydrogenation ability. Co-reactants significantly influence NMBB conversion and the products derived. Many hydrogenation products from bibenzyl and 4-methylbibenzyl that were observed in single-component NMBB reaction in the presence of NbMo_{1.6}C, decline or disappear completely in the 5-component reaction. ATTM and Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ exhibit high activity for hydrogenolysis and hydrogenation reactions.

It is clearly noticed that Mo₂C, unlike in the single-component reaction, shows low activity on the model compounds, indicating Mo₂C was strongly affected by the existence of other co-reactants.

6. Given the same active sites per gram reactant charges, NbMo_{1.6}C showed slightly higher hydrogenation ability on pyrene than Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts at 400°C. Compared to the hydrogenation ability in single compound reactions, the co-reactants apparently change the catalytic activities of the various catalysts. The co-reactants significantly inhibit the hydrogenation of the products from NMBB cracking.

7. For all catalytic runs, quinoline is the most reactive among the 5 compounds, which was almost completely converted at 400°C. For DBT reaction, the two commercial Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts showed high activity compared to ATTM and Molyvan L catalysts. Molyvan L has almost no activity on DBT.

8. Significant effects of co-reactants were observed through comparative studies. NMBB conversion and product distribution in single-component and 5-component tests can be significantly different, indicating molecular interactions (competitive adsorption) in catalytic reactions. Nitrogen compounds may strongly affect cleavage of C-C bond in NMBB. In the case of 5-component mixture reactions, quinoline has higher probability to be adsorbed on more catalyst surface because of its competitive, preferential adsorption. Because of the competitive adsorption of quinoline, the number of active sites accessible for NMBB would decrease. Thus, hydrogenolysis of NMBB would decline remarkably compared to the single component reactions. Our experimental results support the above consideration. In addition, according to the experimental results, the effect of the absence of quinoline is equivalent to adding more catalyst in the reaction system. It can be explained that the other compounds are accessible to more catalytic active sites on the catalyst surface in the absence of quinoline than in the presence of quinoline.

List of Publications Related to This Project

1. Supported Bimetallic Nb-Mo Carbide: Synthesis, Characterization and Reactivity
V. Schwartz, S. T. Oyama, J. G. Chen
ACS Division of Petroleum Chemistry **1998**, 43, 72.
2. Transition Metal Bimetallic Oxycarbides: Synthesis, Characterization, and Activity Studies
S. T. Oyama, C. C. Yu, and S. Ramanathan
J. Catal. **1999**, 184, 535.
3. Cumene Hydrogenation Turnover Rates on Mo₂C: CO and O₂ as Probes of the Active Site
T. P. St. Clair, B. Dhandapani, S. T. Oyama
Catal. Lett. **1999**, 58, 169.
4. Preparation and Hydrodenitrogenation Performance of Rhenium Nitride
P. Clark, B. Dhandapani, S. T. Oyama
Appl. Catal. A: Gen. **1999**, 184, L175
5. Surface Characterization of α -Mo₂C(0001)
T. P. St. Clair, S. T. Oyama, D. F. Cox, S. Otani, Y. Ishizawa, R.-L. Ho, K. Fukui, Y. Iwasawa
Surf. Sci. **1999**, 426, 187.
6. Supported Bimetallic Nb-Mo Carbide: Synthesis, Characterization, and Reactivity
V. Schwartz, S. T. Oyama, J. G. Chen
J. Phys. Chem. B **2000**, 104, 8800
7. CO and O₂ Adsorption on α -Mo₂C(0001)
T. P. St. Clair, S. T. Oyama, D. F. Cox
Surf. Sci. **2000**, 468, 62
8. Simultaneous Hydrodesulfurization, Hydrodenitrogenation, Hydrogenolysis and Hydrogenation over MoS₂-based Catalysts
W. Wang, B. Wei, and C. Song
Proceedings of Sixteenth Annual International Pittsburgh Coal Conference, October 11-15, **1999**, Paper No. 18-5.
9. Model Reactions Simulating Hydroprocessing of heavy Hydrocarbon Resources over Mo Carbide and Sulfide Catalysts.
W. Wang.
Master Thesis, December **2000**, The Pennsylvania State University.

List of Students Supported under This Grant

- Weilin Wang, graduate student in Fuel Science Program, the Pennsylvania State University
- Viviane Schwartz, graduate student in Chemical Engineering, Virginia Polytechnic Institute and State University
- Xinqin Wang, graduate student in Chemical Engineering, Virginia Polytechnic Institute and State University.

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- 4). T. P. St. Clair, S. T. Oyama, D. F. Cox, S. Otani, Y. Ishizawa, R.-L. Ho, K. Fukui, Y. Iwasawa. Surface Characterization of $\alpha\text{-Mo}_2\text{C}(0001)$. *Surf. Sci.* 1999, 426, 187.
- 5). V. Schwartz, S. T. Oyama, J. G. Chen. Supported Bimetallic Nb-Mo Carbide: Synthesis, Characterization, and Reactivity. *J. Phys. Chem. B* 2000, 104, 8800

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