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

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Executive Summary

In this reporting period we have continued our investigation of bimetallic nitride and carbide compounds for use in coprocessing of coal and waste plastics or rubber. Following up on our finding of a class of bimetallic nitrides, reported in the last period, we now report on a new family of bimetallic oxycarbides M^I-M^{II}-O-C (M^I = Mo, W; M^{II} = V, Nb, Cr, Fe, Co, Ni). We have carried out a preliminary test of the compounds with a model coal liquid feed and find that, in general, these carbides are even more active than the nitrides. We have identified Nb-Mo-O-C as the most promising catalyst, and this catalyst together with Mo_2C, the most active single-metal carbide are being investigated for the coprocessing reaction. Comparison is made to standard sulfide catalysts. The latter reaction is carried out in batch autoclave systems, so that preliminary tests are first carried out with a simpler five-component feedstock.

The 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. This compound has been used as a probe molecule in previous studies [1,2]. 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.

Introduction

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

Results and Discussion

Synthesis and Characterization of Bimetallic Compounds

A new class 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 oxide precursors are prepared by conventional solid-state reaction between two appropriate monometallic oxides. The synthesis involves passing a 20 mol% CH_4 in H_2 mixture over the oxide precursors while raising the temperature at a linear rate of 8.3×10^{-2} K s^{-1} (5 K/min) to a final temperature (T_{max}) which is held for a period of time (t_{hold}). The synthesis, chemisorption properties, and reactivation of the materials indicate that the compounds can be divided into two groups of different reducibility (high and low). Table 1 summarizes the CO uptakes, surface areas and the active site density of the oxycarbides, together with their crystallite size and particle size.

Table 1. Characteristics of Bimetallic Carbides/Oxycarbides

Sample	in-situ			after passivation-reactivation		
	CO up-take (μmol g^{-1})	Surface Area (Sg m^{2}g^{-1})	Site Density (x 10^{15} cm^{-2})	CO up-take (μmol g^{-1})	Surface Area (Sg m^{2}g^{-1})	Site Density (x 10^{15} cm^{-2})
V-Mo-O-C	23	41	0.034	------	------	------
Nb-Mo-O-C	227	124	0.11	54	98	0.033
Cr-Mo-O-C	0	47	0	0	47	0
Fe-Mo-O-C	152	12	0.76	50	14	0.22
Ni-Mo-O-C	520	31	1.01	186	35	0.32
V-W-O-C	0	26	0	0	26	0
Nb-W-O-C	195	51	0.23	14	51	0.017
Mo-W-O-C	357	------	0.45*	141	48	0.18
Ni-W-O-C	95	5.6	1.02	80	6.3	0.76

* Assuming Sg = 48 m^{2}g^{-1}

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 bimetallic oxycarbides had moderate activity for HDN of quinoline, with Nb-Mo-O-C showing higher HDN than a commercial sulfided Ni-Mo/Al$_2$O$_3$ catalyst tested at the same conditions. X-ray diffraction of the spent catalysts indicated that the oxycarbides of the early transition metals were tolerant of sulfur, while those involving the late transition metals showed bulk sulfide phases. 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
Ni-Mo-O-C	70	20	40
Mo-W-O-C	65	10	3
Ni-W-O-C	50	0	20
Ni-Mo-S/Al$_2$O$_3$	85	38	79

Initial Tests with Model Coprocessing Mixture

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. Studies were carrried out in 25-mL horizontal autoclave micro-reactors at 400 ^{o}C under 1000 psig initial H_2 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.

Because of the high HDN activity found with Nb-Mo-O-C further tests were carried out with that compound. As references, Mo_2C and various sulfides were used. A blank run was carried out as well. 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 O_2 for the sulfides. Also, the catalysts were prepared *in situ* and transferred in sealed ampoules to the autoclave reactors. The ampoules were broken mechanically, when the feed was already at temperature.

The results are summarized in the table in the next page. The overall results are in good agreement with those obtained in the trickle-bed reactor. In HDN, Nb-Mo-O-C shows superior activity to Mo_2C, but similar performance to the sulfides. In HDS, the same occurs, but now the sulfides are more active. In the important NMBB reaction, Nb-Mo-O-C now shows the best conversion. In pyrene and eicosane conversion the performance of all the catalysts is comparable. These promising results will be followed up with further tests and analysis with NMBB to determine the reaction mechanism. This will be followed by the actual coprocessing of coal with plastic and rubber.

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, 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.

Table 3
Results of 5-Component Reactions

Catalyst	Thermal	Mo$_2$C	NbMo$_{1.6}$C	ATTM	Co-Mo/Al$_2$O$_3$	Ni-Mo/Al$_2$O$_3$
Experiment No.	5-013	5-014	5-018	5-017	5-002	5-003
Quinoline						
Propylcyclohexane	-	-	52.2	60.2	28.7	32.9
PropylBenzene	-	0.5	4.3	3.9	1.4	1.8
Propenylcyclohexene	-	-	13.6	0.8		
1,2,3,4-tetrahydroquinoline	11.3	9.0	7.4	-	17.7	9.4
5,6,7,8-tetrahydroquinoline	-	9.7	3.2	-	1.8	2.3
2-propylbenzenamine	-	0.5	10.2	6.0	18.8	21.0
Methylquinoline	-	1.4	-	-	-	-
Ethyl-THQ isomers	-	9.5	-	-	-	-
Ethylquinoline isomers	-	14.4	-	-	-	-
Quinoline recovered	89.0	13.3	-	-	1.0	1.0
Conversion	**11.0**	**86.7**	**100.0**	**100.0**	**99.0**	**99.0**
DBT						
Benzene, cyclohexyl-	-	-	3.8	10.6	3.4	1.9
Biphenyl	-	2.5	34.6	6.3	60.8	75.4
TH-DBT	-	-	-	15.6	0.6	0.5
DBT recovered	100.0	89.6	55.6	53.9	31.0	16.3
Conversion	**0.0**	**10.4**	**44.4**	**46.1**	**69.0**	**83.7**
NMBB						
Methylcyclohexane	-	-	3.2	5.0	1	1.0
Toluene	1.5	1.7	14.3	3.5	2.3	2.3
p-Xylene	-	-	4.1	-	1.2	1.2
Tetralin	-	1.8	24.2	49.2	15.0	14.2
Naphthalene	-	15.5	58.7	15.9	19.8	25.0
1-Methylnaphthalene	-	-	-	-	1.0	0.6
1-Ethylnaphthalene	-	2.0	-	-	-	-
Bibenzyl	-	1.2	3.5	5.3	1.6	1.0
4-methylbibenzyl	-	17.6	72.3	64.1	34.9	39.9
4-methyldicyclohexylethane	-	-	2.7	5.6		-
1-Naphthyltolylmethane	0.8	-	-	-		-
TH-NMBB-1	-	-	10.2	-	18.8	16.5
TH-NMBB-2	-	-	12.1	9.3	25.1	28.0
NMBB recovered	96.9	70.0	5.6	6.1	24.8	16.3
Conversion	**3.1**	**30.0**	**94.4**	**93.9**	**75.2**	**83.7**
Pyrene						
4,5,9,10-tetrahydropyrene	-	-	3.6	2.5	5.1	4.1
1,2,3,3a,4,5-hexahydropyrene	-	-	8.2	9.7	4.8	3.8
1,2,3,6,7,8-hexahydropyrene	-	-	9.3	10.7	6.5	5.3
4,5-dihydropyrene	1.8	3.8	20.9	20.5	28.5	27.1
1,3-dimethylpyrene	-	23.6	-	-	-	-
Pyrene recovered	99.1	54.6	37.3	42.4	48.7	56.2
Conversion	**0.9**	**45.4**	**62.7**	**57.6**	**51.3**	**43.8**
Eicosane						
n-C20 recovered	99.5	92.2	92.8	97.7	97.4	94.6
Conversion	**0.5**	**7.8**	**7.2**	**2.3**	**2.6**	**5.4**

Conclusions

1. 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.

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/Al_2O_3 catalyst tested at the same conditions.

3. The catalysts were examined in a simulated coprocessing test with five model compounds. Very similar results were obtained as with the trickle-bed reactor.

Future Work

We will continue the study of the new catalysts, this time concentrating on the actual coprocessing reaction. We will attempt reactions with both plastic and rubber reactions.

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2   E. Schmidt, C. Song and H. H. Schobert, *Energy Fuels* **1996**, 10, 597.