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

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ABSTRACT

OBJECTIVE

The overall objectives of this project are to explore the potential of novel supported bimetallic carbide catalysts for coal/waste coprocessing, and to understand the fundamental chemistry related to the reaction pathways of coprocessing and the role of the catalysts in the conversion of coal/waste into liquid fuels. The catalysts to be tested include supported monometallic and bimetallic carbides based on molybdenum and tungsten. Four specific tasks have been defined:

Task 1. Preparation of monometallic and bimetallic carbides

Task 2. Characterization of the materials

Task 3. Measurement of catalytic activities

Task 4. Determination of surface composition and adsorption properties

ACCOMPLISHMENT TO DATE

The novel carbide catalyst Mo_2C was prepared at Virginia Polytechnic Institute & State University and shipped toPenn State in closed ampoules. Three metal sulfide catalysts have been used as the benchmark catalysts in this work, including commercial alumina-supported catalysts, Co-Mo/Al_2O_3 (CR344TL) and Ni-Mo/Al_2O_3 (CR424TL) from Criterion, and one dispersed catalyst MoS_2 derived from ammonium tetrathiomolybdate [ATTM, $(NH_4)_2MoS_4$].

In order to clarify the catalytic functionalities of novel molybdenum carbide catalyst, five model compounds were examined both as individual reactants and as 5-component mixture in this work, including (1) 4-(1-naphthylmethyl)bibenzyl (100%), abbreviated as NMBB, (2) pyrene (99%), (3) dibenzothiophene (98%), (4) quinoline (99%), and (5) eicosane (99%). For the purpose of screening tests, 3-compound mixtures (pyrene, dibenzothiophene, and quinoline) have also been conducted under the same reaction conditions.

The single-compound experiments indicated that the degree of conversion can be approximately ranked as, NMBB > quinoline > DBT > pyrene > eicosane. All catalytic runs gave substantially higher conversion than the thermal runs. The experiments with 5-component mixture showed 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 conversion of NMBB ranges widely, from 50% to 96%. Quinoline seemed to be the easiest to convert, but the product is dominated by 1,2,3,4-THQ over Mo_2C catalyst, and by 2-propylbenzamine and HDN products over CR424 catalyst. In general, pyrene and eicosane were hardest to convert in the mixtures. While Mo_2C catalyst was equally active for pyrene and NMBB conversion, CR424 was much more active for NMBB conversion than for pyrene conversion. Overall, CR-424 TL catalyst appears to be the most effective on HDS, HDN and on hydrogenolysis of C-C bond in NMBB.

Based on CO chemisorption measurements for Mo_2C, and the oxygen chemisorption measurements for metal sulfide catalysts (MoS_2 from ATTM, sulfided CR344 and CR424), the numbers of active sites per gram of these catalysts are similar to each other.

PLANS FOR THE COMING YEAR

- To complete the model compound test using different catalysts to explore the catalytic activities, including the bimetallic metal carbide catalysts to be prepared at VirginiaTech and shipped to Penn State.

- To conduct the real coprocessing of coal with waste plastics and waste tires using the novel catalysts

- To test the surface composition and adsorption properties of fresh and used catalysts

- To understand the radical reaction chemistry in catalytic coprocessing

Articles and Presentations Crediting Grant DE-FG26-97FT97265

Papers

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. New Catalysts for Hydroprocessing: Bimetallic Oxynitrides M_I-M_{II}-O-N (M_I, M_{II} = Mo, W, V, Nb, Cr, Mn, and Co) Part I: Synthesis and Characterization.
   C. C. Yu, S. Ramanathan and S. T. Oyama
   J. Catal. 1998, 173,1.

3. New Catalysts for Hydroprocessing: Bimetallic Oxynitrides M_I-M_{II}-O-N (M_I, M_{II} = Mo, W, V, Nb, Cr, Mn, and Co) Part II: Reactivity Studies..
   C. C. Yu, S. Ramanathan and S. T. Oyama
   J. Catal. 1998, 173, 10

Presentations

1. "Synthesis and Reactivity of Niobium Molybdenum Oxycarbide, a New High Activity Hydroprocessing Catalyst", 215 th ACS National Meeting, Dallas Texas, Symposium on Advances in Heteroatom Removal, U.S. Ozkan, M. Daage, G. Antos, H. Topsoe, Organizers. March 29-April 2, 1998.

2. "Studies on Single Crystal Molybdenum Carbide", Tristate Catalysis Meeting, Charleston, West Virginia, April 20, 1998.

Students Supported under this Grant

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