NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES

Type of report	Seminannual
Reporting Period:	November 1, 1995-July 17, 1996 (Second semiannual)
Principal Investigators:	S. Ted Oyama & David F. Cox
Date of Report:	April 30, 1996
DOE Award Number:	DE-FG22-95PC95207
Institute:	Virginia Polytechnic Institute & State University Department of Chemical Engineering Blacksburg, VA 24061-0211
Grant Date:	July 17, 1995
Contracting Officer's Rep:	Udaya Rao

NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES
SECOND SEMIANNUAL REPORT

S. Ted Oyama & David F. Cox
Virginia Tech

Disclaimer

Abstract

Work involving the synthesis of monometallic transition metal carbides supported on alumina is described. The catalysts have excellent initial activity in the hydrodechlorination of CCl_2F_2 (CFC 12), but deactivate with time by the deposition of carbon. Initial work on the preparation of unsupported bimetallic oxynitrides is also described.

Table of Contents

Title Page 1
Disclaimer 2
Abstract 2
Table of Contents 2
Executive Summary 3
Introduction 3
Results and Discussion 3
Conclusion 4

References 5

Executive Summary

Several supported transition metal carbides and nitrides were prepared and tested in the catalytic dechlorination of the freon CFC 12 (CCl2F2). The catalysts had excellent initial activity compared to noble metal catalysts, but deactivated due to the deposition of carbon. Good progress was made with the preparation of bimetallic oxynitrides, and several stable compositions were obtained.

Introduction

In the previous quarterly report we described the synthesis and characterization of a series of unsupported transition metal carbides and nitrides. The catalysts had excellent activity in hydrodenitrogenation (HDN) of a model coal-liquid feed. Because of the exceptional hydrogenation activity it was decided to test them for the dechlorination of CC_2F_2 (freon 12), a chlorofluorocarbon. Dechlorination of freons to hydrofluorocarbons is an important environmental objective which warranted examination.

In the first quarterly report it was shown that the best catalysts were molybdenum and tungsten carbide. It was decided to prepare these compounds in supported form on an alumina substrate. Also, because of the positive initial results and the good prospects for developing the carbides and nitrides, it was also decided to prepare new compositions based on combining two different metals. Such bimetallic alloys could be prepared by the same temperature-programmed techniques used to synthesize the monometallic compounds.

Results and Discussion

Preparation of Supported Compounds

Supported carbide catalysts were prepared by temperature-programmed reaction of supported oxide precursors. These precursors were made by impregnating Al_2O_3 (Degussa Aluminum Oxid C) with ammonium molybdate and ammonium metatungstate (20% loading of oxide). The precursors were pelletized and reacted with a stream of 20% CH_4 in H_2. X-ray diffraction analysis of the compounds showed the presence of Mo_2C and W_2C. These supported carbides were also themselves impregnated with 1% Pd, to test for synergy between the carbides and a noble metal. The catalysts were characterized by chemisorption of CO and BET measurements.

Testing of Catalysts

The catalysts were tested for the conversion of CCl_2F_2 (CFC 12) in a medium pressure reactor system consisting of two stainless steel reactors in parallel. The reaction products were analyzed by on-line gas-chromatography (Varian, Model 3700) using a PoraPLOT Q column (Chrompack, Inc.). The catalysts were compared to a standard palladium catalyst. The results are summarized in Table 1. It was found that the initial activities of the carbides were high, rivaling those of the palladium catalyst, but that the activity deteriorated with time. Examination of the spent catalysts by XPS indicated that they had substantially contents of carbon. Evidently, some cracking had occurred to cause coke deposition. The work has been published and is reported in Ref. *1*.

Table 1
Initial Activities of Catalysts at a Space Velocity of 1800 h^{-1}

Catalyst	Temp (K)	Conv of CFC (%)	Selectivity to HFC 32 (%)	Turnover rate (s^{-1})
0.1% Pd-Mo_2C/Al_2O_3	573	13	100	0.055
1% Pd-Mo_2C/Al_2O_3	623	43	100	0.183
Mo_2C/Al_2O_3	623	46	100	0.196
W_2C/Al_2O_3	623	73	100	0.310
Mo_2C	623	4	100	0.017
WC	623	6	100	0.026
1% Pd/activated C	523	47	45	0.200

Preparation of Bimetallic Compounds

A new class of materials, M_I-M_{II}-O-N (where M_I, M_{II} = V, Mo, W, and Nb) were synthesized by nitriding bimetallic oxide precursors with ammonia gas via a temperature programmed reaction. The oxide precursors were prepared by conventional solid state reaction between two appropriate monometallic oxides. The synthesis of the oxynitrides involved passing NH_3 gas over the oxide precursors at a flow rate of 6.80 x 102 μmol s^{-1} (1000 cm^3 min^{-1}) and raising the temperature at a rate of 5 K min^{-1} to a final temperature which was held constant for a short period of time. The oxynitrides thus obtained were pyrophoric and needed to be passivated before exposing them to air. All these new bimetallic oxynitrides had a face centered cubic metal arrangement and high values of surface area. They had good CO uptakes and are likely to be surface active. Their XRD patterns are reported in Figure 2 and indicate pure substances. The work has been published (Ref. *2*,*3*).

Conclusions

The supported carbides and nitrides show good activity in hydrodechlorination, but deactivate. This may be due to the acidity of the alumina support. The bimetallic oxynitrides can be made in a homologous series and are promising for hydroprocessing.

References

1. Novel Catalysts for Selective Dehalogenation of CCl_2F_2 (CFC 12)
B. Dhandapani and S. T. Oyama, *Catal. Lett.* **1995**, 35, 353.
2. Synthesis of New Bimetallic Transition Metal Oxynitrides V-Me-O-N (Me = Mo and W)
by Temperature Programmed Reaction
C. C. Yu and S. T. Oyama, *J. Solid State Chem* **1995**, 116, 205
3. Synthesis and Characterization of New Bimetallic Transition Metal Oxynitrides:
M_I-M_{II}-O-N (M_I, M_{II} = V, Mo, W and Nb)
C. C. Yu and S. T. Oyama, *J. Mat. Sci.* **1995**, 30, 4037.