## New Catalysts for Hydroprocessing:

## Molybdenum and Tungsten Phosphide

Paul Clark

Dissertation submitted to the faculty of Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

> Doctor of Philosophy in Chemical Engineering

S. Ted Oyama, Chairman

David F. Cox

Kimberly Forsten

Stephen L. Kampe

Uri Vandsburger

September 29, 2000

Blacksburg, Virginia

Keywords: hydrodenitrogenation, molybdenum, tungsten, phosphide

#### New Catalysts for Hydroprocessing:

#### Molybdenum and Tungsten Phosphide

by

Paul Clark

Committee Chairman: S. Ted Oyama

**Chemical Engineering** 

#### Abstract

This dissertation describes the preparation and application of a novel class of hydroprocessing catalysts, transition metal phosphides. Concentration was placed on molybdenum and tungsten monophosphides because of the importance of these elements in standard sulfidic hydrotreating catalysts. Transition metal phosphides exist over a wide range of stoichiometry, and their properties have a great deal of variation, ranging from phosphorus poor compounds with metallic electrical properties to phosphorus rich compounds with semiconducting or insulating properties. The x-ray diffraction patterns of the phosphides studied here were unchanged under the conditions of catalytic hydroprocessing, demonstrating their stability toward the hydroprocessing conditions and allowing study of their intrinsic catalytic properties. Materials were prepared in bulk form, supported on alumina, and supported on silica. The mechanism of hydrodenitrogenation on MoP/SiO<sub>2</sub> and WP/SiO<sub>2</sub> catalysts was investigated by comparison of hydrodenitrogenation reactions of pyridine, piperidine, *n*-pentylamine, *tert*-pentylamine, and *neo*-pentylamine.

#### Acknowledgments

This thesis is dedicated to Charles C. Clark, PhD.

I am grateful to my mother and father for their love and patience, and for teaching me responsibility.

I thank my wife, Ingrid, for her love and patience with me through these years. I am grateful for my children, Kathryn and Lucas.

I express my gratitude Professor S. Ted Oyama for the opportunity to do this work. I will always respect his teachings regarding how to work and how to think.

I thank my committee members for their time and insight.

I appreciate the support and companionship of my laboratory colleagues, Mark Abee, Chad Byrd, Bala Dhandhapani, Rajat Kapoor, Doohwan Lee, Wei Li, Toby Lucy, Anil Prabhu, Rakesh Radhakrishnan, Corey Reed, Celine Sayag, Viviane Schwarz, Todd St. Clair, Victor Teixiera da Silva, and Xianqin Wang.

I also thank the department and university staff, Wendell Brown, Diane Cannaday, Judy Coleman, Riley Chan, Frank Cromers, Chris Moore, Diane Patty, Carol Stables, Todd Solberg, and Dean Trindle, for their help in accomplishing many tasks.

## **Table of Contents**

## Chapter 1

#### Introduction

1.1.	Fuel Production by Hydroprocessing	1
1.2.	Introduction to Transition Metal Phosphides	5

## Chapter 2

## Synthesis and Activity of a New Catalyst for Hydroprocessing:

## **Tungsten Phosphide**

2.1. Introduction	16
2.2. Experimental	
<b>2.3.</b> Results	
2.3.1. Synthesis of Tungsten Phosphide	
<b>2.3.2.</b> Catalyst Characterization	
<b>2.3.3.</b> Catalytic Reaction	
2.3.4. X-ray Photoelectron Spectroscopy	
2.4. Discussion	
2.5. Conclusions	41

### Chapter 3

### Preparation and Hydroprocessing Properties of Molybdenum Phosphide

## Supported on y-Alumina

3.1. Introduction	
3.2. Experimental	46
<b>3.3.</b> Results and Discussion	
<b>3.3.1.</b> Synthesis of MoP/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	
<b>3.3.2.</b> Catalytic Activity of MoP/γ-Al <sub>2</sub> O <sub>3</sub> Catalysts	61
<b>3.3.3.</b> Relationship to Previous Results in the Literature	
3.4. Conclusions	70

# Chapter 4

### **Introduction to Hydroprocessing Reactions**

4.1.	Reactions of Alkyl Aliphatic Species	72
4.2.	Reactions of Aliphatic Ring Compounds	80
4.3.	Reactions of Aromatic Heterocyclic Hydrocarbons	84
4.4.	Heteroatom Exchange Reactions	88

# Chapter 5

# Push-pull Mechanism of Hydrodenitrogenation over

# Silica Supported MoP, WP, and MoS<sub>2</sub> Hydroprocessing Catalysts

<b>5.1.</b> Introduction	
5.2. Experimental	96
<b>5.3.</b> Results	100
<b>5.3.1.</b> Preparation and Characterization of Catalysts	
<b>5.3.2.</b> Pentylamine Study	
<b>5.3.2.1.</b> <i>n</i> -Pentylamine	
5.3.2.2. <i>tert</i> -Pentylamine	111
<b>5.3.2.3.</b> <i>neo</i> -Pentylamine	113
5.4. Discussion	115
<b>5.4.1.</b> Preparation of Silica Supported Phosphides	115
<b>5.4.2.</b> Reactivity in Hydroprocessing	118
<b>5.4.3.</b> Study of the Mechanism of HDN	119
5.5. Conclusions	131

# Chapter 6

# Pyridine and Piperidine Denitrogenation on

# Silica Supported Phosphides

<b>6.1.</b> Introduction	
6.2. Experimental	136
6.3. Results and Discussion	
<b>6.3.1.</b> Reaction of Piperidine	
<b>6.3.2.</b> Reaction of Pyridine	148
6.4. Conclusions	156

## List of Tables

<b>Table 1.1</b> : Structural trends in the first row transition metal monophosphides
Table 1.2: Densities, specific metal volumes, and average metal - metal distances for Mo
and W compounds relevant to this study10
<b>Table 1.3</b> : Structural parameters of transition metal compounds adopting the WC, NiAs,
MnP, and layered hexagonal structure types11
<b>Table 2.1</b> : Composition of liquid feed used for hydroprocessing reaction
<b>Table 2.2</b> : Variation in the temperature corresponding to the maximum rate in the
formation of WP as a function of heating rate24
Table 2.3: Comparison of ex situ measurements of BET surface area, CO chemisorption,
and site density characteristics of WP catalyst, before and after hydrotreating study25
Table 2.4: Summary of XRD results for tungsten phosphide catalyst before and after
reaction27
Table 2.5: Product distributions, reported as conversion and selectivity, in
hydroprocessing reactions using WP and WS <sub>2</sub> catalysts
<b>Table 2.6</b> : XPS atomic percentage results for tungsten phosphide catalyst
Table 2.7: XPS curve fit results for tungsten 4f and 4d regions and phosphorus 2p region.
Binding energies are reported in eV. Relative amounts are in parentheses
Table 3.1: Compositional characteristics of MoP/Al <sub>2</sub> O <sub>3</sub> catalysts
Table 3.2: X-ray diffraction results for MoP/Al <sub>2</sub> O <sub>3</sub> catalysts.    55
Table 3.3: Surface area and chemisorption properties of MoP/Al <sub>2</sub> O <sub>3</sub> samples

<b>Table 3.4</b> : Apparent first order activation energies of reduction events in the preparation
of 23% MoP/Al <sub>2</sub> O <sub>3</sub> 61
<b>Table 3.5</b> : Hydroprocessing conversions of MoP/Al <sub>2</sub> O <sub>3</sub> catalysts
Table 3.6: Comparison of specific hydroprocessing rates of 13 % MoP/Al <sub>2</sub> O <sub>3</sub> with 13 %
MoP/SiO <sub>2</sub> and bulk MoP64
<b>Table 4.1</b> : Reactions involving alkyl amines, thiols, and alcohols.    78
<b>Table 4.2</b> : Reactions of aliphatic ring compounds
<b>Table 4.3</b> : Reactions of aromatic heterocyclic compounds
<b>Table 4.4</b> : Exchange reactions of heteroatoms
Table 5.1: Compositional characteristics of silica supported catalysts101
<b>Table 5.2</b> : Preparation conditions of silica supported phosphides
<b>Table 5.3</b> : Physical characteristics of silica supported catalysts    107
<b>Table 5.4</b> : Olefin production and distribution for <i>n</i> -pentylamine HDN at 513 K111
Table 5.5: Quinoline hydrodenitrogenation, quinoline hydrogenation, and
dibenzothiophene hydrodesulfurization as % conversion, for silica supported catalysts
during hydroprocessing of model feedstock at 643 K and 3.1 MPa119
<b>Table 5.6</b> : Relative properties of pentylamines for HDN reaction
<b>Table 5.7</b> : Relative reactivities of pentylamines according to possible reactions
mechanisms122
<b>Table 6.1</b> : Conversion and selectivity of catalysts in piperidine HDN. (a) WP/SiO <sub>2</sub> ; (b)
MoP/SiO <sub>2</sub> ; and (c) MoS <sub>2</sub> /SiO <sub>2</sub> 144
Table 6.2: Constants derived from kinetic analysis of piperidine and pyridine HDN
reactions146

Table 6.3:	Conversion	and selectivity	of catalysts i	n pyridine HDN.	(a) WP/SiO <sub>2</sub> ; (b)	
MoP/SiO <sub>2</sub>	; and (c) Mos	S <sub>2</sub> /SiO <sub>2</sub>				.152

# List of Figures

Figure 1.1: Adapted structural model of an oil shale molecule 2
Figure 1.2: Structural models of naphtha and gas oil
<b>Figure 1.3</b> : Production of synthetic crude oil from bitumen
Figure 1.4: Methods of preparation of transition metal phosphides
Figure 1.5: Structural types of transition metal monophosphides
Figure 2.1: Water evolved during the synthesis of tungsten phosphide from tungsten
phosphate glass. Samples were preheated to 773 K at 0.0833 K s <sup>-1</sup> , then ramped at
0.0167 K s <sup>-1</sup> to their final temperature. In situ surface area ( ) and CO uptake values
( $\clubsuit$ ) of quenched intermediates are compared to the reaction progress. The letters $b - h$
also correspond to XRD spectra of quench intermediate samples noted in Figure 2.222
Figure 2.2: X-ray diffraction patterns of intermediate samples quenched at various
temperatures after reduction in hydrogen at 0.0167 K s <sup>-1</sup> . The letters $b - h$ also
correspond to BET surface area and CO chemisorption values of intermediate samples
noted in Figure 2.1
Figure 2.3: X-ray diffraction patterns of the WP catalyst before and after catalytic
reaction

Figure 2.4: Hydrotreating performance of tungsten phosphide with time. Definitions:
HDS is dibenzothiophene conversion, HDN is the quinoline conversion minus HYD, and
HYD is the sum of anilines and tetrahydroquinolines
Figure 2.5: Comparison of quinoline HDN and dibenzothiophene HDS conversions of
(a) $WS_2$ , (b) $W_2N$ , (c) WC, (d) WP, and (e) $NiMoS(P)/Al_2O_3$
Figure 3.1: Temperature programmed reduction profiles for various MoPO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>
samples reduced to 1223 K at 5 K min <sup>-1</sup>
<b>Figure 3.2</b> : Evolution of MoP during the reduction of $MoPO_x/Al_2O_3$ (13 % MoP).
Samples were reduced to intermediate temperatures, quenched in helium, and
characterized by <i>in-situ</i> CO uptake before passivation. (o) $MoO_3$ , (y) $MoO_2$ , (+) $Mo^\circ$ ,
(x) MoP, and (*) Al <sub>2</sub> O <sub>3</sub>
Figure 3.3: Evolution of <i>in-situ</i> CO uptake sites of quenched intermediates during the
preparation of 13 wt% MoP/Al <sub>2</sub> O <sub>3</sub> 53
Figure 3.4: Reduction profiles for 'blank' alumina samples reduced to 1223 K at 5 K
min <sup>-1</sup> . (a) 1.16 mmol g <sup>-1</sup> PO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> ; (b) AlPO <sub>4</sub> ; (c) 1.16 mmol g <sup>-1</sup> MoPO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> ; and (d)
$1.16 \text{ mmol g}^{-1} \text{ MoO}_x/\text{Al}_2\text{O}_3.$
Figure 3.5: X-ray diffraction results showing increased amounts of MoP with loading for
samples reduced to 1223 K at 5 K min <sup>-1</sup> . (x) MoP, and (*) $Al_2O_3$
Figure 3.6: Development of <i>in-situ</i> CO uptake as a function of loading. The samples
were reduced to 1223 K at 5 K min <sup>-1</sup> in hydrogen flow at 1 dm <sup>3</sup> min <sup>-1</sup> g <sup>-1</sup> 59
Figure 3.7: Effect of heating rate on the temperature programmed reduction forming
23% MoP/Al <sub>2</sub> O <sub>3</sub>

Figure 3.8: X-ray diffraction of fresh and spent 13% MoP/Al <sub>2</sub> O <sub>3</sub> catalyst prepared at
1123 K. MoP is the only crystalline phase of Mo, and is not significantly affected by
reaction study
Figure 3.9: X-ray diffraction of fresh and spent 13 wt% MoP/Al <sub>2</sub> O <sub>3</sub> catalyst prepared at
1023 K. MoP and Mo are both present in the material, and are not significantly affected
by reaction study67
<b>Figure 5.1</b> : Temperature programmed reduction profiles in the preparation of $MoP/SiO_2$
and MoP at 0.0833 K s <sup>-1</sup> (5 K min <sup>-1</sup> )103
<b>Figure 5.2</b> : Temperature programmed reduction profiles in the preparation of WP/SiO <sub>2</sub>
and WP at 0.0833 K s <sup>-1</sup> (5 K min <sup>-1</sup> )104
Figure 5.3: X-ray diffraction spectra for fresh and spent MoP/SiO <sub>2</sub> samples105
Figure 5.4: X-ray diffraction spectra for fresh and spent WP/SiO <sub>2</sub> samples106
Figure 5.5: Time dependence of hydroprocessing reactivity of MoP/SiO <sub>2</sub> and WP/SiO <sub>2</sub>
catalysts in the conversion of a model feed at 643 K and 3.1 MPa108
<b>Figure 5.6</b> : Product distribution in the hydrogenolysis of $n$ -pentylamine on MoP/SiO <sub>2</sub> ,
WP/SiO <sub>2</sub> , and MoS <sub>2</sub> /SiO <sub>2</sub> catalysts. $\times$ = Conversion, $\blacksquare$ = Dipentylamine, $\nabla$ = <i>n</i> -Pentane,
= Tripentylamine, O = Pentenes, = Pentanethiol
<b>Figure 5.7</b> : Product distribution in the hydrogenolysis of <i>tert</i> -pentylamine on MoP/SiO <sub>2</sub> ,
WP/SiO <sub>2</sub> , and MoS <sub>2</sub> /SiO <sub>2</sub> catalysts. $\times$ = Conversion, $\blacksquare$ = 2-Methyl-2-butene, = 2-
Methyl-1-butene, $\nabla = n$ -Pentane
Figure 5.8: Product distribution in the hydrogenolysis of <i>neo</i> -pentylamine on MoP/SiO <sub>2</sub> ,
WP/SiO <sub>2</sub> , and MoS <sub>2</sub> /SiO <sub>2</sub> catalysts. $\times$ = Conversion, $\blacksquare$ = Di( <i>neo</i> -pentyl)amine, $\nabla$ =
Dimethylpropane, = 2,2-Dimethylpropylnitrile114

Figure 5.9: Total conversion of pentylamines over MoP/SiO <sub>2</sub> , WP/SiO <sub>2</sub> , and MoS <sub>2</sub> /SiO <sub>2</sub>	$O_2$
catalysts	123
Figure 6.1: Conversions and product distributions from piperidine HDN on: (a)	
MoP/SiO <sub>2</sub> ; (b) WP/SiO <sub>2</sub> ; and (c) MoS <sub>2</sub> /SiO <sub>2</sub> .	139
Figure 6.2: Second order kinetic curve fits of piperidine HDN data	143
Figure 6.3: Conversions and product distributions from pyridine HDN on: (a) MoP/Sid	O <sub>2</sub> ;
(b) WP/SiO <sub>2</sub> ; and (c) MoS <sub>2</sub> /SiO <sub>2</sub>	149
Figure 6.4: Kinetic curve fits of pyridine HDN data.	154

### List of Schemes

Scheme 4.1: Reactions of alkylamines74
Scheme 4.2: Reactions of aliphatic ring compounds
Scheme 4.3: Reactions of aromatic heterocyclic compounds
Scheme 4.4: Exchange reactions of heteroatoms
Scheme 5.1: Potential mechanisms of alkylamine HDN reactions
Scheme 5.2: Push - pull mechanism in the HDN of an alkylamine
Scheme 5.3: Push - pull mechanism in the isomerization of an olefin
Scheme 6.1: Main reaction pathway for pyridine HDN135
Scheme 6.2: Side reactions encountered in pyridine HDN
Scheme 6.3: Second order analysis for the decomposition of piperidine142
Scheme 6.4: Zero <sup>th</sup> order kinetics in the decomposition of pyridine