Chapter 5

Push-Pull Mechanism of Hydrodenitrogenation over Silica Supported MoP, WP, and MoS\textsubscript{2} Hydroprocessing Catalysts

5.1. Introduction

Silica supported molybdenum phosphide, MoP/SiO\textsubscript{2}, and tungsten phosphide, WP/SiO\textsubscript{2}, were employed to study the mechanism of liquid phase catalytic hydrodenitrogenation at 3.1 MPa using a series of pentylamines of different structures. Removal of nitrogen occurred primarily by an E2 elimination mechanism involving acidic and nucleophilic species on the surface in a push-pull process. Similar results were obtained with a reference MoS\textsubscript{2}/SiO\textsubscript{2} sample tested at the same conditions. This indicated that sulfur was probably present on the active surface and assisted in the mechanism of HDN. The Mo and W phosphides, however, showed higher activity in quinoline HDN than the MoS\textsubscript{2}/SiO\textsubscript{2}, indicating that their surface composition was unique.

Transition metal phosphides have recently been reported to be active hydroprocessing catalysts, extending the range of known active compounds for this class of reactions. In particular MoP (1, 2), WP (3), Ni\textsubscript{2}P, and Co\textsubscript{2}P (4) have been shown to give high conversions in hydrodesulfurization (HDS) and especially hydrodenitrogenation (HDN) of model petroleum feedstocks. Little is known about the nature of these catalytic materials, and studies to elucidate their behavior are of practical and fundamental interest. We have undertaken the present investigation to assess the performance of MoP and WP
when deposited on a neutral support, and to understand the mechanism by which they
carry out the HDN reaction.

Elucidation of the mechanism of HDN is complicated for several reasons. Not only is
the reaction affected by the conditions at which it is run, such as hydrogen pressure,
delivery rate, and the presence of H₂S, but also the catalyst may be complex and posses
multiple functionalities, such as hydrogenation and hydrogenolysis sites (5). It is likely
that the mechanism and rate of reaction will depend ultimately on the nature of its
interaction with the reacting molecule. The classical mechanism of denitrogenation is the
Hofmann degradation of amines (6), but there are a number of other possibilities (7, 8, 9)
such as Sₙ₁, E₁, Sₙ₂, E₂, and metallacycle or metal alkyl formation pathways These
pathways are displayed diagrammatically in Scheme 5.1. The mononuclear pathways
(Sₙ₁ and E₁) start with the generation of a carbocation by quaternization of an amine
followed by cleavage of ammonia. Nucleophilic substitution occurs by attack of a
nucleophile (HS⁻) on the carbonium ion (the original α-carbon), while elimination occurs
by abstraction of a proton by the nucleophile (from the original β-carbon). The binuclear
pathways (Sₙ₂ and E₂) begin with the formation of the quaternized ammonium
compound as in the mononuclear case, but without scission of ammonia. Nucleophilic
substitution occurs by attack of a nucleophile on the α-carbon while elimination (E₂)
occur by attack on the β-carbon to abstract a proton and form an olefin. The pathways
involving reactions with metals (metallacycle and metal alkyl formation) require
activation of the α-carbon to the nitrogen (10). These pathways likely occur with
metallic catalysts like Ir or Os, but are not preferred with the phosphide or sulfide
catalysts considered here.
**Scheme 5.1:** Potential mechanisms of alkylamine HDN reactions.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction</th>
</tr>
</thead>
</table>
| Protonation        | \[
\begin{align*}
\text{H} & \text{C} - \text{C} - \text{N}^- + \text{H}^+ \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- \\
\text{H} & \text{C} - \text{C} - \text{N}^- + \text{H}^+ \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{NH}_3 \\
\text{S}_\text{N}^1 & \text{HS} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{SH} \\
\text{E}_1 & \text{HS} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{H}_2\text{S} \\
\text{S}_\text{N}^2 & \text{HS} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{NH}_3 \\
\text{E}_2 & \text{HS} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{NH}_3 + \text{H}_2\text{S} \\
\text{Metallacycle} & \text{NH} + \text{M} \rightarrow \text{NH}_2\text{M} \\
\text{Metal Alkyl} & \text{H} - \text{C} - \text{C} - \text{N}^- + \text{M} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{M} \\
\text{Aziridinium Ring} & \text{H} - \text{C} - \text{C} - \text{N}^- + \text{M} \rightarrow \text{H} - \text{C} - \text{C} - \text{N}^- + \text{M} + \text{H}^- \\
\end{align*}
\]   |
hydroprocessing catalysts has not been widely studied because weak interactions with the active phase generally lead to low dispersions (11). However, it has been found that low loading (2 – 4 wt %) samples of MoS$_2$/SiO$_2$ can perform better than their Al$_2$O$_3$ counterparts (12, 13). In the present study, the low interactions expected with SiO$_2$ are ideal for studying the intrinsic properties of MoP and WP compared to MoS$_2$.

5.2. Experimental

Silica supported phosphides were prepared by incipient wetness impregnation with aqueous metal phosphate precursors, followed by controlled reduction in flowing hydrogen. The silica support (Cabot, Cabosil L90, 99.8%) consisted of 0.2 - 0.3 µm aggregates of spherical particles of ~30 nm diameter prepared by vapor phase hydrolysis of SiCl$_4$ in a H$_2$ – O$_2$ flame (14). Stoichiometric amounts of ammonium paramolybdate, (NH$_4$)$_6$Mo$_7$O$_{24}$$\cdot$4H$_2$O (Aldrich, 99%) or ammonium metatungstate (NH$_4$)$_6$W$_{12}$O$_{39}$$\cdot$xH$_2$O (Aldrich, 90%) were combined with ammonium phosphate (NH$_4$)$_2$HPO$_4$ (Aldrich, 99%) in distilled water, and the solution was used to impregnate the silica support. The moist paste was calcined in air at 773 K for 6 h, ground and mixed, then pressed, broken, and sieved between 650 and 1180 µm screens to form pelletized supported phosphate materials. These precursor phosphates were loaded in quartz glass u-tube reactors, and were reduced to phosphides using linear temperature ramps in flowing hydrogen. Hydrogen flow was set at 650 µmol s$^{-1}$ g$^{-1}$ starting material (e.g. 300 cm$^3$(NTP) min$^{-1}$ H$_2$ flow for a 0.300 g sample) for all syntheses. Species in the effluent were identified
periodically (2-5 s) by a mass spectrometer (Dycor/Ametek MA100) to follow the progress of the reaction. Water was the principle gaseous reaction product detected. Occasionally, small amounts of a yellow insoluble deposit were formed downstream in the reactor following higher temperature reactions of WP/SiO₂. After reduction, the phosphide was cooled to room temperature under 65 µmol s⁻¹ helium and typically was passivated progressively by flowing 78 µmol s⁻¹ 0.1 % O₂/He overnight, followed by 13 µmol s⁻¹ of 0.5 % O₂/He for 2 h. The reactor was then disconnected from the flow system, and oxygen, carbon dioxide, and water from ambient air were allowed to diffuse in for 24 h before collecting the sample from the tube.

MoS₂/SiO₂ samples were prepared by sulfiding 5 % MoO₃/SiO₂ for 2 h in a stream of 10 % H₂S/H₂ at 678 K and a heating rate of 0.0833 K s⁻¹ (5 K min⁻¹). The sulfide samples used for hydroprocessing were sulfided directly from the oxide within the catalytic reactor at a flow rate of 98 µmol s⁻¹ (150 cm³ (NTP) min⁻¹) at atmospheric pressure. The characterization of the sulfide samples by O₂ chemisorption also directly followed sulfidation of the oxide. For the chemisorption measurements, 0.3 g of oxide were sulfided in 650 µmol s⁻¹ g⁻¹ (300 cm³ (NTP) min⁻¹) of 10 % H₂S/H₂ using the same temperature program noted for the catalyst samples.

All gases were supplied by Air Products. Hydrogen, helium, and carbon monoxide were all 99.999% pure, and were passed through a water trap (Alltech) before contacting the sample. Specialty mixtures, including 0.5 % O₂/He, 30 % N₂/He, and 10 % H₂S/H₂ were used as received.

The total dynamic CO and O₂ uptakes were measured by passing pulses of CO or O₂ (5.6 µmol) in a stream of 40 µmol s⁻¹ helium over samples at room temperature.
Measurements performed on freshly reduced samples following cooling in helium are termed here *in situ* uptakes, while measurements on air exposed samples rereduced to 723 K for 2 h are denoted *ex situ*. The O\textsubscript{2} uptake was modified by a factor of 2 to account for dissociative adsorption on the surface. Surface area measurements were performed with a Micromeritics 2000 sorption unit.

X-ray diffraction (XRD) spectra were collected with a Scintag XDS-2000 X-ray diffractometer using Ni-filtered Cu K\textsubscript{α} (\(\lambda = 0.1541\) nm) radiation. Scans were collected at a rate of 0.035° 2θ s\(^{-1}\) and in increments of 0.03° 2θ.

Two types of hydrotreating reactions were investigated. The first was to assess the activity of the catalysts, the second was used to study the mechanism of HDN. Activity was measured by hydrotreating of a model liquid containing quinoline and dibenzothiophene at 643 K (370 °C) and 3.1 MPa (450 psig) in an upward-flow, fixed-bed reactor as described in chapter 2. Compositional characteristics of the model feed liquid were summarized previously in Table 2.1. With the exception of tetradecane, which was purchased from Fisher (99%), chemicals were obtained from Aldrich, and had a purity level of 97+%.

The mechanism of HDN was studied by hydrodenitrogenation of solutions containing 2000 ppm N as *n*-pentyamine (C\textsubscript{5}H\textsubscript{13}N, Acros, 99%), *tert*-pentyamine (Acros, 98%), or *neo*-pentyamine (TCI) dissolved in tetradecane (Fisher, 99%). These reactions were carried out at 3.1 MPa and as a function of temperature for each catalyst. The pentyamine feed solutions also contained 3000 wppm S as dimethyldisulfide (C\textsubscript{2}H\textsubscript{6}S\textsubscript{2}, Aldrich, 99%), as well as 2000 wppm *n*-octane (C\textsubscript{8}H\textsubscript{18}, Aldrich, 99%) as an internal standard.
The basis set of catalytic reaction results used was the percent of reactant converted to a given product, counting all of the detected species as 100%. Only the liquid phase products were analyzed. The carbon balances on the amine reactants and their products were typically 90% ± 10%. Gas-liquid equilibria were considered in the atmospheric pressure samples (after collection) to help account for the volatility of the C\textsubscript{5} hydrocarbons and amines (15). Small amount of light products were found in dry-ice temperature condensate from the hydrogen (vapor) effluent, but it was not possible to accurately quantify this material, as complications arose from carryover of the liquid phase solvent tetradecane in the gas stream. Thus the slightly low carbon balances can be explained as either due stripping of the light molecules in the gas phase, or from coke formation from nitrogen molecules, as noted in the literature (16).

The composition of hydroprocessing liquids was identified with a Hewlett Packard 5890A gas chromatograph (equipped with a CP Sil 5B column) on samples collected at 2-3 h intervals. Steady state was typically achieved after about 60 h of reaction time at a given condition. Reaction products were identified through matching of retention times with commercially available molecules, as well as by GC/MS analysis. The GC/MS combined a Fisons Carlo Erba 8060 series gas chromatograph, using a HP-5MS 5% phenylmethylsiloxane stationary phase, with a VG Quattro triple quadrupole mass spectrometer operated in the electron impact – positive ion mode.

To start a catalytic reaction, phosphide catalysts were pretreated in 100 µmol s\textsuperscript{-1} hydrogen at 723 K and 1 atm pressure for 2 h, while the sulfide catalyst was presulfided with a 10% H\textsubscript{2}S/H\textsubscript{2} mixture at 678 K and 1 atm pressure for 2 h. After the pretreatment, the conditions were set to 3.1 MPa (450 psig), a hydrogen flow rate of 100 µmol s\textsuperscript{-1} (150
sccm), a liquid feed rate of 0.0833 cm$^3$ s$^{-1}$ (5 cm$^3$ min$^{-1}$), and the desired temperature. For amine reactions, the amounts of catalysts used were 3.3 g of MoS$_2$/SiO$_2$, 1.4 g of MoP/SiO$_2$, and 3.1 g of WP/SiO$_2$. These amounts corresponded to roughly similar quantities (56, 70, and 58 µmol, respectively) of chemisorption sites. In the case of activity measurement for the MoS$_2$ reference, two experiments were conducted. In the first, the conditions were changed directly from amine HDN to model feed hydroprocessing, generating results similar to the blank. Thereafter, a new 5% MoO$_3$/SiO$_2$ sample was prepared, characterized, and tested for hydroprocessing. This material had O$_2$ uptake equal to 27 µmol g$^{-1}$, and 2.59 g were loaded to the reactor, corresponding to 70 µmol of sites. For the SiO$_2$ blank, an arbitrary amount of 3 g was employed, as the material had negligible chemisorption of CO. Once started, the individual catalysts were used for extended sets of conditions (i.e. different molecules and temperatures). The duration of the total set of experiments was lengthy, requiring several months, but standard conditions were repeated periodically to verify that no deactivation occurred. Results from repeated conditions were similar, and were averaged to obtain the reported values.

5.3. Results and Discussion

5.3.1. Preparation and Characterization of Catalysts

Silica supported molybdenum phosphide, tungsten phosphide, and molybdenum sulfide catalysts were prepared by incipient wetness impregnation of silica support with
ammonium salts of Mo, W, and P dissolved in distilled water. Compositional characteristics of each sample are summarized in Table 5.1. The surface depositions of molybdenum and tungsten monophosphide were held constant at 1.156 mmol each of Mo, W, and P per gram of silica, leading to 12.8 wt% MoP/SiO$_2$ and 19.9 wt% WP/SiO$_2$, respectively. Sulfidation of a sample containing 5 wt% MoO$_3$ on SiO$_2$ led to 5.6 wt% MoS$_2$/SiO$_2$.

Table 5.1: Compositional characteristics of silica supported catalysts.

<table>
<thead>
<tr>
<th>sample</th>
<th>wt%‡</th>
<th>mmol metal g$^{-1}$ SiO$_2$</th>
<th>metal atom nm$^{-2}$ SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/SiO$_2$</td>
<td>5.6</td>
<td>0.368</td>
<td>2.44</td>
</tr>
<tr>
<td>MoP/SiO$_2$</td>
<td>12.8</td>
<td>1.156</td>
<td>7.67</td>
</tr>
<tr>
<td>WP/SiO$_2$</td>
<td>19.9</td>
<td>1.156</td>
<td>7.67</td>
</tr>
</tbody>
</table>

‡ wt% MoP, WP, or MoS$_2$

Oxidic catalyst precursors were reduced to phosphide form by temperature-programmed reduction in hydrogen, and were subsequently passivated. Conditions used in the prereduction of samples from their respective phosphate precursor materials are summarized in Table 5.2. Prior to the reactivity measurements and ex situ CO uptake characterization, passivated phosphides were pretreated in hydrogen at 723 K for 2 h to remove the surface oxide layer.
Table 5.2: Preparation conditions of silica supported phosphides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H$_2$ flow $^*$</th>
<th>Heating rate K min$^{-1}$</th>
<th>Temperature max K</th>
<th>Soak time $^\dagger$ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP/SiO$_2$</td>
<td>650</td>
<td>5</td>
<td>850</td>
<td>2</td>
</tr>
<tr>
<td>WP/SiO$_2$</td>
<td>650</td>
<td>5</td>
<td>1000</td>
<td>2</td>
</tr>
</tbody>
</table>

$^*$ µmol H$_2$ g$^{-1}$ oxide s$^{-1}$

$^\dagger$ at maximum temperature

The temperature programmed reduction (TPR) trace at 5 K min$^{-1}$ of MoP/SiO$_2$ is compared to that of bulk MoP in Figure 5.1. The predominant reduction features appeared at high temperatures, 680 K and 820 K for the supported sample, and 770 K and 920 K for the unsupported reference. The TPR traces of WP/SiO$_2$ and WP are shown in Figure 5.2. Again, the predominant reduction peaks occur at high temperatures, 890 K and 970 K for the supported material, and 1010 K for the unsupported reference.

X-ray diffraction patterns of the MoP/SiO$_2$ samples are shown in Figure 5.3. The patterns showed features of bulk MoP both before and after reaction. XRD patterns of the WP/SiO$_2$ samples are shown in Figure 5.4. Again, the patterns corresponded to those of bulk WP both before and after reaction in hydrotreating.
**Figure 5.1:** Temperature programmed reduction profiles in the preparation of MoP/SiO$_2$ and MoP at 0.0833 K s$^{-1}$ (5 K min$^{-1}$).
Figure 5.2: Temperature programmed reduction profiles in the preparation of WP/SiO$_2$ and WP at 0.0833 K s$^{-1}$ (5 K min$^{-1}$).
Figure 5.3: X-ray diffraction spectra for fresh and spent MoP/SiO$_2$ samples.
**Figure 5.4:** X-ray diffraction spectra for fresh and spent WP/\(\text{SiO}_2\) samples.
The chemisorption and surface area properties of the catalysts are summarized in Table 5.3. The time course of the reaction in hydroprocessing dibenzothiophene and quinoline at 643 K and 3.1 MPa of MoP/SiO$_2$ and WP/SiO$_2$ are shown in Figure 5.5.

**Table 5.3**: Physical characteristics of silica supported catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area$^a$</th>
<th>CO uptake$^b$ fresh</th>
<th>CO uptake$^b$ spent hdt$^c$</th>
<th>CO uptake$^b$ spent amine$^d$</th>
<th>Dispersion$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ blank</td>
<td>91</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$/SiO$_2$</td>
<td>93$^f$</td>
<td>18(27)$^g$</td>
<td>-</td>
<td>-</td>
<td>4.7(7.0)</td>
</tr>
<tr>
<td>MoP/SiO$_2$</td>
<td>50</td>
<td>50</td>
<td>26</td>
<td>26</td>
<td>3.8</td>
</tr>
<tr>
<td>WP/SiO$_2$</td>
<td>62</td>
<td>19</td>
<td>6.5</td>
<td>10.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^a$ m$^2$ g$^{-1}$ catalyst; passivated catalysts; degassed in vacuum at 273 K for 24 h
$^b$ CO uptake at 298K in μmol g$^{-1}$; sample pretreated at 723 K in H$_2$
$^c$ following hydroprocessing of model feedstock
$^d$ following hydrodenitrogenation of pentylamines
$^e$ number of sites g$^{-1}$ / number of moles of metal g$^{-1}$ * 100%
$^f$ as oxide: MoO$_3$/SiO$_2$
$^g$ O$_2$ uptake at 78 K; sample presulfided at 678 K in 10% H$_2$S/H$_2$

(Value in parentheses is for second sample)
Figure 5.5: Time dependence of hydroprocessing reactivity of MoP/SiO$_2$ and WP/SiO$_2$ catalysts in the conversion of a model feed at 643 K and 3.1 MPa.
5.3.2. Pentylamine study

A study of the reactivity of a series of pentylamines was carried out to explore the effect of amine structure on the HDN reaction. The results for each individual amine are presented below.

5.3.2.1. \textit{n}-Pentylamine

The product distributions for \textit{n}-pentylamine HDN on silica supported MoP, WP, and MoS\textsubscript{2} are presented in Figure 5.6. The species favored at the lowest temperature in each case was dipentylamine. As temperature increased, pentane appeared along with small amounts of pentenes, pentanethiol, and tripentylamine. Total \textit{n}-pentylamine conversions at all temperatures except 513 K increased in the order MoP/SiO\textsubscript{2} < MoS\textsubscript{2}/SiO\textsubscript{2} < WP/SiO\textsubscript{2}, however, the production of hydrocarbons increased in the order MoP/SiO\textsubscript{2} < WP/SiO\textsubscript{2} < MoS\textsubscript{2}/SiO\textsubscript{2}. The MoP/SiO\textsubscript{2} catalyst was the least active by both measures. Comparatively, the WP/SiO\textsubscript{2} had a higher propensity for condensation than MoS\textsubscript{2}/SiO\textsubscript{2}, while the MoS\textsubscript{2}/SiO\textsubscript{2} had better hydrocarbon production.

The amounts and distributions of olefins at 533 K are summarized in Table 5.4, along with equilibrium concentrations estimated by thermodynamic calculations for this temperature. The predominant olefin formed on all catalysts was 1-pentene. Cis and trans 2-pentenes were observed for the WP/SiO\textsubscript{2} and MoS\textsubscript{2}/SiO\textsubscript{2} catalysts at higher temperatures (513 K). In no cases were iso-pentene isomers observed.
Figure 5.6: Product distribution in the hydrogenolysis of \( n \)-pentyamine on MoP/SiO\(_2\), WP/SiO\(_2\), and MoS\(_2\)/SiO\(_2\) catalysts. \( \times \) = Conversion, ■ = Dipentylamine, ▽ = \( n \)-Pentane, ▲ = Tripentylamine, ○ = Pentenes, □ = Pentanethiol.
Table 5.4: Olefin production and distribution for n-pentylamine HDN at 513 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Olefins %</th>
<th>1-Pentene % selectivity</th>
<th>trans-2-Pentene % selectivity</th>
<th>cis-2-Pentene % selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoP/SiO$_2$ *</td>
<td>3</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>WP/SiO$_2$</td>
<td>6</td>
<td>42</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>MoS$_2$/SiO$_2$</td>
<td>12</td>
<td>39</td>
<td>39</td>
<td>22</td>
</tr>
<tr>
<td>equilibrium</td>
<td>7</td>
<td>69</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

% = % of n-pentylamine converted to olefins
% selectivity = % of total olefin as olefin i
* note that MoP results are from 533K. Total hydrocarbons for MoP at 513 K = 0.

Overall, the hydrocarbon distribution was consistent with the occurrence of an elimination reaction followed by dehydrogenation. However, significant amounts of pentanethiol were also found at 493 K on the MoS$_2$/SiO$_2$ catalyst, demonstrating the presence of N-S exchange as well.

5.3.2.2. tert-Pentylamine

The product distributions for n-pentylamine HDN on silica supported MoP, WP, and MoS$_2$ are presented in Figure 5.7. Hydrocarbons are the only products of tert-pentylamine HDN, with olefins being preferred at lower temperatures, and the alkane 2-methylbutane becoming more important at higher temperatures. The order of activity of the catalysts increased as MoP/SiO$_2$ < WP/SiO$_2$ < MoS$_2$/SiO$_2$, with the MoP catalyst being significantly less active than either the WP or MoS$_2$ catalysts. The relative amount of 2-methyl-2-butene was always greater than 2-methyl-1-butene on each catalyst.
Figure 5.7: Product distribution in the hydrogenolysis of tert-pentylamine on MoP/SiO$_2$, WP/SiO$_2$, and MoS$_2$/SiO$_2$ catalysts. $\times =$ Conversion, $\blacksquare =$ 2-Methyl-2-butene, $\square =$ 2-Methyl-1-butene, $\triangledown =$ n-Pentane.
Di(tert-pentyl)amine was not observed, in agreement with previous results (7), and its absence is attributed to steric effects.

5.3.2.3. neo-Pentylamine

The product distributions for neo-pentylamine HDN on silica supported MoP, WP, and MoS₂ are presented in Figure 5.8. The initial product formed at low temperatures/conversions was di(neo-pentyl)amine. This molecule was the only product detected on the MoP catalyst. On WP and MoS₂, 2,2-dimethylpropane was observed at higher temperatures and was the only hydrocarbon product detected. The order of reactivity of the catalysts in terms of both total conversion and the formation of hydrocarbons increased in the order MoP/SiO₂ < WP/SiO₂ < MoS₂/SiO₂. Small amounts of nitrile were detected in products produced by WP and MoS₂ containing catalysts. Thus, neo-pentylamine is the only molecule for which a nitrile product was observed in this study.
Figure 5.8: Product distribution in the hydrogenolysis of neo-pentylamine on MoP/SiO$_2$, WP/SiO$_2$, and MoS$_2$/SiO$_2$ catalysts. $\times$ = Conversion, ■ = Di(neo-pentyl)amine, ▼ = Dimethylpropane, $\equiv$ = 2,2-Dimethylpropynitrile.
5.4. Discussion

5.4.1. Preparation of silica supported phosphides

The preparative reduction profile for the MoP/SiO₂ catalyst is presented in Figure 5.1, and is compared to the reduction profile of bulk MoP taken under similar conditions. The reduction trace of MoP/SiO₂ shows a feature at low temperature (370 K) and two peaks at high temperature (680 K and 820 K). The low temperature feature is due to the dehydration of the sample, while the high temperature peaks are indicative of the reduction stages of the phosphate. The TPR trace of MoP/SiO₂ resembles that of MoP at lower heating rates, with the first peak producing no crystalline phase, and the second peak forming MoP. It can be seen that the synthesis reaction is substantially over at 850 K and this was used as the final reduction temperature for the preparation of the MoP/SiO₂ catalyst. A holding time of 2 h was used at this temperature to ensure completion of the reduction.

The bulk MoP reduction profile also shows these two high temperature reduction processes. However, because of the higher metal oxide content (the hydrogen flow rate was based on the weight of starting material), the first peak is unresolved and both peaks are shifted to higher temperature (770 K and 920 K). This is likely due to inhibition of the reduction process by the gas phase water vapor generated by reduction and the presence of larger particles (17).

The XRD spectra of the bulk MoP and supported MoP samples prepared at 850 K, before and after the hydrotreating reactions, are shown in Figure 5.3. The bulk MoP has
a pattern which corresponds exactly to that reported in the literature (powder diffraction file 24-771). MoP has a hexagonal WC type structure (strukturbericht designation $B_h$) with space group $P_{6_3}m2$ and lattice parameters $a_o = 322$ pm and $c_o = 319$ pm (18). The supported MoP/SiO$_2$ shows a broad feature at $\sim 22^\circ$ 2$\theta$ produced by the amorphous silica support, and several distinct peaks which match those of the bulk MoP phase.

The preparative reduction profile for the WP/SiO$_2$ catalyst is presented in Figure 5.2, and is compared to the reduction profile for bulk WP taken under similar conditions. The reduction trace of WP/SiO$_2$ shows a slight feature at 370 K, a slight rise at 630 K, and a large peak at 890 K with a high temperature shoulder at 970 K. The feature at 370 K is due to dehydration of the sample, while the high temperature peaks are due to formation of phosphide. The slight rise at low temperature may be due small quantities of highly dispersed species, while the shoulder at high temperature may be due to small quantities of larger particles which reduce more like the bulk WP. It is clear from the figure that the reduction process is essentially completed at 1000 K, which was used as the maximum temperature in the preparation of WP catalyst. Again, a hold time of 2 h was used to ensure complete reduction of the sample.

The reduction profile of the bulk WP also shows the slight dehydration feature at 370 K, and a high temperature reduction peak at 1010 K. Again, the largest peak is shifted to higher temperature, likely as a result of inhibitive action of water vapor and the presence of larger particles in the bulk material. The assymetry in the shapes of the MoP and WP reduction profiles are due to the use of relatively high heating rates. This asymmetry disappears at lower heating rates (3).
The XRD spectra of the bulk WP and supported WP samples prepared at 1000 K, before and after hydrotreating reactions, are shown in Figure 5.4. The bulk WP has a pattern corresponding exactly to that reported in the literature (powder diffraction file 29-1364). WP adopts the orthorhombic MnP type structure (strukturbericht designation B31) with space group P\textit{nma} and lattice parameters $a_0 = 571$ pm, $b_0 = 325$ pm, and $c_0 = 623$ pm (19). The supported WP/SiO\textsubscript{2} shows a broad feature at $\sim 22^\circ$ 2\theta of the silica support, and several distinct peaks which match those of the WP phase.

The \textit{ex situ} chemisorption characteristics and BET surface areas of samples reduced according to the specifications in Table 5.2, are summarized in Table 5.3. The surface area of the MoS\textsubscript{2}/SiO\textsubscript{2} catalyst (93 m\textsuperscript{2} g\textsuperscript{-1}) precursor was close to that of the support (91 m\textsuperscript{2} g\textsuperscript{-1}) as its loading was low. The surface areas of the MoP/SiO\textsubscript{2} (50 m\textsuperscript{2} g\textsuperscript{-1}) and WP/SiO\textsubscript{2} (62 m\textsuperscript{2} g\textsuperscript{-1}) samples were significantly decreased from that of the support, a common finding for phosphorus promoted, supported catalysts (20, 21, 22). This is presumably an effect of pore blocking by phosphorus compounds. The use of elevated temperatures during sample reduction, 850 K for MoP/SiO\textsubscript{2} and 1000 K for WP/SiO\textsubscript{2}, may also have contributed to the decrease in surface area by sintering the silica support.

Chemisorption quantities of O\textsubscript{2} and CO for the fresh catalysts were moderate and were found to decrease somewhat after reaction for the phosphides. Measurements taken after reaction were carried out on recovered samples washed in hexane and rereduced at 723 K for 2 h. The CO uptakes of MoP/SiO\textsubscript{2} and WP/SiO\textsubscript{2} and O\textsubscript{2} uptake of MoS\textsubscript{2}/SiO\textsubscript{2} were used to calculate dispersions based on stoichiometries for adsorption of 1 CO molecule and 1 O atom per surface metal atom. The dispersions are reported in Table 5.3. They
were low, 4.9 % for MoS$_2$/SiO$_2$, 4.3 % for MoP/SiO$_2$, and 1.6 % for WP/SiO$_2$, consistent with the observation of crystalline phases visible in the XRD patterns of the phosphides.

5.4.2. Reactivity in Hydroprocessing

The activity of the catalysts in the HDS of dibenzothiophene and the HDN of quinoline was evaluated in a three phase flow reactor at 643 K and 3.1 MPa. Figure 5.5 shows the conversions as a function of time on the silica supported MoP and WP in HDS and HDN. Both materials demonstrated good stability in their activity levels. It should be noted that those results were obtained with 58 µmol of sites of WP/SiO$_2$ and 70 µmol of sites of MoP/SiO$_2$ loaded in the reactor. The conversions were corrected to an equal sites basis, for WP/SiO$_2$, WP, and MoP, according to a first order kinetic expression as follows. Denoting $X_1$ as the conversion corresponding to a quantity of sites $S_1$, and $X_2$ as the conversion corresponding to $S_2$ sites, then the quantities are related by:

$$
\ln(1 - X_2) = \left(\frac{S_2}{S_1}\right) \times \ln(1 - X_1)
$$

The corrected results for the supported MoP/SiO$_2$, WP/SiO$_2$, and MoS$_2$/SiO$_2$ are summarized in Table 5.5, along with results from bulk MoP and WP and the silica support. The MoP/SiO$_2$ catalyst was similar to the bulk MoP (1), while the WP/SiO$_2$ sample differed from its unsupported counterpart (3) having lower HDS activity and higher HDN hydrogenation. Importantly, note that hydroprocessing on MoS$_2$/SiO$_2$ was carried out on a separate, freshly prepared, sample from that used for the amines. The MoS$_2$/SiO$_2$ sample used for the amine study yielded results for the hydroprocessing of
quinoline and dibenzothiophene similar to the blank, when the conditions were switched directly from amine hdn to quinoline hdn.

**Table 5.5**: Quinoline hydrodenitrogenation, quinoline hydrogenation, and dibenzothiophene hydrodesulfurization as % conversion, for silica supported catalysts\(^a\) during hydroprocessing of model feedstock at 643 K and 3.1 MPa.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% HDN</th>
<th>% HYD(^b)</th>
<th>%HDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>2</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>MoS(_2)/SiO(_2)</td>
<td>11</td>
<td>45</td>
<td>31</td>
</tr>
<tr>
<td>MoP/SiO(_2)</td>
<td>31</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td>WP/SiO(_2)(^c)</td>
<td>46</td>
<td>46</td>
<td>16</td>
</tr>
<tr>
<td>MoP(^c)</td>
<td>54</td>
<td>34</td>
<td>24</td>
</tr>
<tr>
<td>WP(^c)</td>
<td>88</td>
<td>33</td>
<td>92</td>
</tr>
</tbody>
</table>

\(^a\) Loading equals 70 µmol of sites for supported samples except WP/SiO\(_2\) (58 µmol), or 30 m\(^2\) for bulk samples.

\(^b\) % HYD = Hydrogenation of quinoline to N-containing products.

\(^c\) Value adjusted according to first order equation given in text.

### 5.4.3. Study of the Mechanism of HDN

It is well accepted that HDN is more difficult than HDS in hydroprocessing because of the higher strength of C-N bonds by 3-9 kcal mol\(^{-1}\) versus C-S bonds (23). The high activity of the phosphide catalysts for HDN was unusual and prompted investigation of the mechanism of HDN. A method described by the group of Breysse (7, 8, 9) utilizing a series of pentylamines of different structure was adapted to high-pressure, liquid-phase
conditions in our study. The amines consisted of \( n \)-pentlyamine, \( tert \)-pentlyamine, and \( neo \)-pentlyamine and their structure and properties are described in Table 5.6.

The expected relative reactivities of the pentlyamines are summarized in Table 5.7, as described by Cattenot et al. (7). \( neo \)-Pentlyamine contains no \( \beta \)-hydrogen atoms and is sterically hindered, so is expected to be the least reactive molecule in the series. \( tert \)-Pentlyamine has the greatest number of \( \beta \)-hydrogen atoms, and forms the most stable carbocation counterpart, so it is the most reactive molecule in the series. \( n \)-Pentlyamine has an intermediate number of \( \beta \)-hydrogen atoms, is the least sterically hindered, and is expected to have intermediate activity. Carbocations of \( neo \)-pentlyamine and \( n \)-pentlyamine are expected to have similar stability.

The conversions to hydrocarbons of each catalyst for each of the three amines are plotted in Figure 5.9. The trend for the three pentlyamine HDN reactions over MoP/SiO\(_2\), WP/ SiO\(_2\), and MoS\(_2\)/SiO\(_2\) catalysts is for increased reactivity from \( neo < n < tert \). Overall, this order is consistent with C-N bond scission occurring primarily by an E2 mechanism on all three catalysts (Table 5.7).

Temperature programmed desorption studies show that this species decomposes to release ammonia and ethylene in equal proportions, but in a nonconcerted manner. A possible sequence of steps for the transformation is depicted in Scheme 5.2.
<table>
<thead>
<tr>
<th>Reactant</th>
<th>Structure</th>
<th># α-Hydrogen</th>
<th># β-Hydrogen</th>
<th>steric hindrance</th>
<th>carbocation stability</th>
<th>carbanion stability</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-Pentylamine</td>
<td>[\text{H}_3\text{C} \equiv \text{CH}_2 \equiv \text{C} \equiv \text{NH}_2]</td>
<td>2</td>
<td>2</td>
<td>low</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td><em>tert</em>-Pentylamine</td>
<td>[\text{H}_3\text{C} \equiv \text{CH}_2 \equiv \text{C} \equiv \text{NH}_2]</td>
<td>0</td>
<td>8</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td><em>neo</em>-Pentylamine</td>
<td>[\text{H}_3\text{C} \equiv \text{CH}_2 \equiv \text{C} \equiv \text{NH}_2]</td>
<td>2</td>
<td>0</td>
<td>med</td>
<td>med</td>
<td>med</td>
</tr>
</tbody>
</table>
Table 5.7: Relative reactivities of pentylamines according to possible reaction mechanisms.

<table>
<thead>
<tr>
<th>Reactant</th>
<th># β-Hydrogen</th>
<th>S_N1</th>
<th>S_N2</th>
<th>E1</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentylamine</td>
<td>2</td>
<td>very low</td>
<td>high</td>
<td>very low</td>
<td>medium high</td>
</tr>
<tr>
<td>tert-Pentylamine</td>
<td>8</td>
<td>high</td>
<td>very low</td>
<td>very high</td>
<td>high</td>
</tr>
<tr>
<td>neo-Pentylamine</td>
<td>0</td>
<td>very low</td>
<td>very low</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>
Figure 5.9: Total conversion of pentylamines over MoP/SiO₂, WP/SiO₂, and MoS₂/SiO₂ catalysts.
Scheme 5.2: Push - pull mechanism in the HDN of an alkylamine.

In this scheme we have taken the surface of the phosphide catalyst to be populated with sulfur species which provide Brøsted acidity in the form of sulfhydryl groups, as well as nucleophilic centers. The exact structure of these groups is uncertain, and the forms shown in Scheme 5.2 should be considered illustrative, as other possibilities exist. However, the main features of the mechanism are otherwise consistent with the known observations. The amine first interacts with a Brøsted site on the surface to adsorb as an alkylammonium species. This then undergoes a β-hydride elimination by attack by a surface nucleophilic center. This is exactly an E2 elimination (Scheme 5.1) with the role of the surface now explicitly indicated, and results in the release of ammonia, as found in
the TPD experiments. The olefin interacts with the coordinatively unsaturated site on the surface to be released in a subsequent step.

The reactivity patterns of \( n \)-pentylamine and tert-pentylamine are consistent with the above mechanisms. In particular, for \( n \)-pentylamine it is likely that 1-pentene was the primary reaction product as it was the major olefin product formed at low temperatures (Figure 5.6, Table 5.4). At higher conversions the 1-pentene intermediate was hydrogenated to form \( n \)-pentane or isomerized by double bond migration to form cis and trans 2-pentenes. Importantly, no iso-pentenes were observed, indicating that carbonium ion intermediates such as those formed by \( S_N1 \) or E1 pathways were not formed. The lack of skeletal isomerization of the hydrocarbon suggests that the double bond migration step also occurred by a push-pull type mechanism, as proposed in Scheme 5.3.

Again, in Scheme 5.3 the surface structures are pictorial representations. Thermodynamic calculations show that 2-pentene is favored over 1-pentene, and trans-2-pentene is favored over cis-2-pentene. In the case of \( n \)-pentylamine the cis-trans distribution in the catalyst effluent was skewed toward 1:1 suggesting a kinetic control over the double bond migration step.

In the case of tert-pentylamine, the products of reaction were exclusively olefins and paraffins. The formation of 2-methyl-2-butene was preferred over 2-methyl-1-butene over each catalyst. This result shows preference for the thermodynamically favored triply substituted olefin product compared to the kinetically favored product having 3 times more available \( \beta \)-hydrogen atoms (6:2) for E2 elimination. Since E1 elimination is unlikely (as concluded earlier), this suggests that the pentenes can isomerize readily.
The reactions of neo-pentylamine fall in a different category from those of \textit{n}-pentylamine and \textit{t}-pentylamine because the molecule doesn’t have any $\beta$-hydrogen, making standard E1 and E2 elimination reactions impossible. Similarly, there is no $\gamma$-elimination as indicated by the absence of methylbutenes (24). As far as nucleophilic substitutions are concerned, the S$_{N}$1 route is unlikely because the intermediary primary carbonium ion is unstable, while the S$_{N}$2 pathway is partially blocked by steric hindrance. There is a possibility of hydride attack to displace the amine group, as the existence of hydride species associated with metal centers has been suggested before (25), as charged
species in spillover on neutral silica support (26), and organometallic HDN reactions involving lithium aluminum hydride (27). However, again this route appears unlikely because the hydride is likely to be held strongly. Finally, a homolytic reaction pathway can be considered involving H radicals (28, 29). This probably does not occur because of the lack of skeletal isomerization and β-scission products.

The more likely scenario in the case of neo-pentylamine is activation of an alpha carbon by one of the metal-centered reactions noted in Scheme 5.1. This would be followed by a series of hydrogenation and reductive elimination steps to produce the neo-pentane or the 2,2-dimethylpropylnitrile species. Nitriles have been reported before in the reactions of primary amines, nitrile formation being favored by lower pressures (30), and the absence of hydrogen (31, 32). In this case, the reactive channel involving a metal type reaction is likely opened up at the higher temperatures of reaction needed to convert neo-pentylamine.

Comparison of the product distributions for the three amines shows that a significant amount of condensation products and thiols are found with n-pentylamine and neo-pentylamine. Thus, substitution is an important pathway for these molecules, especially at low temperature. In contrast, no condensation or thiol products occur for the tert-pentylamine HDN, indicating that elimination and hydrogenation are the only relevant reactions. In fact, the E1 mechanism is possible on tert-pentylamine because of the stability of the carbocation. This point is highlighted by 22% conversion of tert-pentylamine in the blank run at 513 K. This was the only significant background reaction noted in this study.
The results of this study are different from the results reported for bulk sulfides by Cattenot et al. (8) because they were taken at high pressure. Hence, we have a greater propensity for hydrogenation in this study, resulting in pentanes as well as pentenes. Interestingly, earlier results for NiMo/Al₂O₃ operating at 2.0 MPa yielded no condensation products (9). In particular, we operate at the same temperature (523 K), and with sulfur, but also find 2,2-dimethylpropane and condensation products in the effluent. This could be due to the presence of liquid solvent or to the nature of the catalysts.

In comparing our results for quinoline HDN to those for the amine conversion we find that MoS₂ is competitive for hydrogenolysis reactions at low temperatures, but has limited capacity for quinoline HDN at higher temperatures. It is possible that the MoS₂ has poor hydrogenation properties at the elevated temperature, or is affected by the presence of the more complicated feedstock. Our results for MoS₂/SiO₂ resembled those of bulk MoS₂ used by Cattenot et al. (7). In particular, both had good activity for neopentylamine conversion, and had similar product distributions for n-pentylamine conversion, including di(n-pentyl)amines.

The results for WP were somewhat different. Here, moderate performance at low temperature for hydrogenolysis was contrasted by good performance at high temperature for both hydrogenation and hydrogenolysis. Thus, the WP catalyst was able to provide a balance of HDN functionalities, including elimination, condensation, and aromatic hydrogenation, which allowed it to survive the shift to higher operating temperature and greater aromatics content. However, compared to the bulk WP sample, the SiO₂
supported WP sample seems to be less capable of hydrogenolysis, as shown by the large amount of hydrogenated products in the effluent (Table 5.4).

The presence of acid sites alone does not lead to active hydroprocessing catalysts, as demonstrated by the inactivity of alumina and silica-alumina supports, acting alone, in hydrodenitrogenation reactions of aromatic heterocycles (20, 33, 34, 35). It is relevant, though, that alumina has been reported as a catalyst for denitrogenation reactions of aliphatic amines leading to olefins, including amines and piperidine (35, 36). The authors of the study on alklamine HDN over the alumina catalyst (36) found that methyl substitution at the $\alpha$ carbon increased the amine reaction rate, while methyl substitution at the $\beta$ carbon decreased the rate. This is in complete agreement with our findings. Thus, acid-base chemistry alone can explain the results for aliphatic amines.

The origin of the need for hydrogenation activity is related to the requirement of saturation of both the $\alpha$ and $\beta$ carbon atoms in order to allow the C-N hydrogenolysis reaction to take place. It was on this basis that Nelson and Levy (6) proposed that an E2 mechanism is responsible for the C-N bond cleavage reaction. Thus the activity of catalysts toward aromatic molecules in real feedstocks, such as quinolines, is limited by the ability of the catalyst for hydrogenation of the C$_6$ ring. Our results confirm independently that C-N bond cleavage is dominated by E2 elimination. Furthermore, our interpretation of results in conjunction with acid-base chemistry is in substantial agreement with the suggestion of Tops$^{\square}$ et al. that the active centers of hydrodenitrogenation catalysts involve Brønsted acid sites (37).
It has been found in the literature that MoS\textsubscript{2} is active for hydrogenolysis reactions, while is not as active for hydrogenation reactions. Our finding that MoS\textsubscript{2}/SiO\textsubscript{2} was active for C-N bond hydrogenolysis reactions, but was inactive for quinoline HDN seem to support this established conclusion.

As seen in schemes 5.2 and 5.3, our picture of the catalyst involves an amphoteric surface in which HDN elimination reactions operate by a push-pull mechanism. The amine is pictured adsorbing by hydrogen bonding to a sulfhydryl Br\textsuperscript{\textdegree}sted acid site. A nearby bridging sulfide group provides the basic site necessary for elimination reaction. The bridging sulfide can be viewed as the conjugate base of the sulfhydryl acid site. The sulfhydryl site, as pictured, is intimately associated with a coordinatively unsaturated site. Thus measurements of unsaturated sites by CO and O\textsubscript{2} uptake correlate indirectly to the active acid-base sites, but are effective nonetheless.

It has been suggested in the literature that the essential competing reaction for E2 elimination of amines involves nucleophilic substitution of sulfur upon amine groups (7, 8, 9, 38). The resulting thiol is then reported to react quickly by direct hydrogenolysis with hydrogen, forming H\textsubscript{2}S and a saturated hydrocarbon. However, this does not properly explain the case of aliphatic thiol decomposition on MoS\textsubscript{2}, in which 83\% of the product of desulfurization of \textit{n}-butanethiol was found to be olefinic, and butadiene was a major product in the decomposition of tetrahydrothiophene (39). Thus, it is likely that thiols also decompose primarily by E2 elimination, similar to the case for aliphatic amines.

In the case of benzylamine or isoquinoline HDN reactions reported in the literature, HDN proceeds without prior hydrogenation of the C6 ring, but is slower (occurs at higher
temperature) than in the case of aliphatic amines. This suggests that an alternate mechanism, such as one of the metal mediated routes (metal alkyl, aziridinium ring), is available for HDN in cases where the β-carbon is not fully saturated (5, 43). This is verified by the production of hydrocarbons from neo-pentylamine found in this study. Thus these metal mediated routes are possible, but the condensation and elimination reactions are easier and thus dominate the reaction pathways of most molecules.

5.5. Conclusions

MoP and WP were prepared on a silica support. They were moderately active catalysts for hydrodenitrogenation of quinoline in a complex mixture. Conversion of a series of amines with different structure confirmed the predominance of the E2 mechanism in the conversion of primary amines to hydrocarbons on these catalysts. The reaction involved formation of adsorbed alkylammonium species and reorganization of bonds by a push-pull mechanism involving acid and nucleophilic species on the surface.
References


