Chapter 6

Pyridine and Piperidine Denitrogenation on Silica Supported Phosphides

6.1. Introduction

The objective of this investigation was to compare the denitrogenation behavior of molybdenum phosphide (MoP/SiO₂) and tungsten phosphide (WP/SiO₂) and molybdenum sulfide (MoS₂/SiO₂) in the reaction networks for piperidine and pyridine hydrodenitrogenation (hdn). The phosphide materials have recently emerged as a new type of hydrotreating catalyst (1, 2, 3)and understanding their properties in well studied model reactions is of fundamental interest, placing the properties of phosphides in context with the existing literature.

This study covers the hydrogenation reactions of pyridine and its hydrogenated intermediate piperidine. Pyridine hydrodenitrogenation has commonly been studied as a model test reaction for evaluation of hydroprocessing catalysts, requiring both hydrogenation and hydrogenolysis functionalities (4). The usual sequence described for pyridine hydrodenitrogenation, as shown in Scheme 6.1, is through hydrogenation to piperidine followed by sequential hydrogenolysis of C-N bonds to form *n*-pentylamine, then C_5 hydrocarbons (5).

Scheme 6.1: Main reaction pathway for pyridine HDN.



This reaction sequence has been described using both first order (6, 7, 8, 9, 10), and zero order (11, 12, 13, 14, 15) kinetic schemes. McIlvried (16) and Sonnemans et al. (17, 18, 19) both reported that the reaction is first order when evaluated by a contact time variation method, while it is found to be zeroth order when measured by a concentration variation method. They have described this effect as 'poisoned zeroth order' kinetics, in which the nitrogen molecules are strongly bound to the surface and have similar adsorption coefficients. A final type of analysis which has been successfully applied is a two site model, in which hydrogenation reactions are first order and occur on ' σ sites' (20, 21, 22).

Although the main pyridine HDN sequence shown in Scheme 6.1 is simple, side reactions forming larger molecules such as N-(*n*-pentyl)piperidine complicate the analysis from a kinetic and mechanistic standpoint. Side reaction products observed in this study are summarized in Scheme 6.2, while a more extensive description of products is contained in Chapter 4.

In this work we present a kinetic analysis that takes into account the influence of these side reactions. Considerable similarities were found between the phosphide and sulfide catalysts. Pyridine HDN was found to have zero order kinetics, while piperidine Scheme 6.2: Side reactions encountered in pyridine HDN.



HDN involved second order kinetics proceeding through the intermediate N-(*n*-pentyl)piperidine.

6.2. Experimental

The catalysts and equipment used in this study were the same as those reported in Chapter 5. Briefly, catalyst precursors were prepared by incipient wetness impregnation of a silica support (Cabosil L90) with a stoichiometric aqueous solution of a metal ammonium salt, (NH₄)₆Mo₇O₂₄•4H₂O (Aldrich, 99%) or (NH₄)₆W₁₂O₃₉•xH₂O (Aldrich, 90%), and ammonium phosphate, (NH₄)₂HPO₄ (Aldrich, 99%). The moist paste was calcined at 773 K for 6 h before mixing and pelletizing. These oxidic precursors (typically 1- 2 g) were reduced to phosphide form by temperature programmed reduction at 0.0833 K s⁻¹ in 650 μ mol s⁻¹ of hydrogen flow to temperatures of 850 K for MoP/SiO₂, and 1000 K for WP/SiO₂, where the temperature was held for 2 h before cooling and passivating. Surface loadings and chemisorption characteristics of the MoP/SiO₂, WP/SiO₂, and MoS₂/SiO₂ catalyst samples were summarized previously in Tables 5.1 and 5.3.

Hydrogenation of nitrogen containing molecules was carried out in tetradecane (Fisher, 99%) solvent at 3.1 MPa and temperatures between 453 K and 573 K. Pyridine (Mallinkrodt), piperidine (Aldrich, 99%), and *n*-pentylamine (Acros, 99%) were dissolved at 2000 wppm N, dimethyldisulfide (Aldrich, 99%) at 3000 wppm S, and octane (Aldrich, 99%) was included at 2000 wppm as an internal standard. The amounts of catalysts loaded to the catalytic reactors were reported previously in Chapter 5 (p. 99). The flow rate of liquid was set to 5 ml h⁻¹, yielding nitrogen delivery rates of 0.15 μ mol s⁻¹ and sulfur delivery equal to 0.10 μ mol s⁻¹. Reaction products were separated and quantified by gas chromatography (Hewlett-Packard, 5890A) using a 50 m polydimethylsiloxane column (Chrompack, CP Sil 5B). Products were identified by comparison of retention times with known standards and by GC/MS.

6.3. Results and Discussion

As shown in Scheme 6.1, pyridine HDN is typically reported to proceed through hydrogenation to piperidine followed by sequential ring cleavage of the C-N bonds to form *n*-pentylamine, C_5 hydrocarbons, and ammonia. The HDN of *n*-pentylamine was

reported in Chapter 5.3 (p. 108). In this chapter the hydrogenation of piperidine will be presented first, followed by pyridine. Kinetic analyses were applied using grouped product distributions, including condensation products, hydrocarbons, and reactants. Quinoline was grouped with the condensation products, while thiane was ignored.

6.3.1. Reaction of Piperidine

The product distributions as a function of temperature for piperidine HDN on silica supported MoP, WP, and MoS₂ are presented in Figure 6.1. At low temperatures and conversions, condensation to N-pentylpiperidine was the only significant reaction product. As temperature was increased, *n*-pentane and *n*-pentenes (1-pentene, trans-2pentene, and cis-2-pentene) were formed as the hydrocarbon products of denitrogenation. The activities for piperidine HDN increased in the order MoP/SiO₂ \approx WP/SiO₂ < MoS₂/SiO₂, with the sulfide catalyst showing an advantage over the phosphides, especially in terms of hydrocarbon formation.

One explanation for the formation of N-pentylpiperidine is that *n*-pentylamine is formed as a reaction intermediate (as seen in the main reaction pathway in Scheme 6.1), which subsequently condenses with piperidine. It is relevant that the production of the



Figure 6.1: Conversions and product distributions from piperidine HDN on: (a) MoP/SiO₂; (b) WP/SiO₂; and (c) MoS₂/SiO₂.

free alkyl hydrocarbon end in either compound, N-(n-pentyl)piperidine or *n*-pentylamine, requires elimination + hydrogenation (or direct hydrogenolysis). Thus it is apparent that the formation of N-pentylpiperidine is relatively complex, requiring both condensation and elimination reactions to form the molecule.

At intermediate temperatures, on the MoP/SiO₂ and WP/SiO₂ catalysts, quinoline and thiane (cyclopentylsulfide) were observed. The presence of thiane is evidence of N-S displacement, in a reaction similar to that leading to *n*-pentylsulfide as observed in the HDN of *n*-pentylamine reported in chapter 5. Thiane has been observed previously in piperidine HDN (23), and its formation is understood in terms of SN₂ exchange of amines with H_2S .

The formation of quinoline, although noted previously (24), is more complicated, as C-C bonds need to be formed at the 2 and 3 positions, and a C-C bond needs to broken to reduce the total number of carbon atoms from 10 to 9. No other compounds were identified which involved the formation of C-C bonds, but traces of N-butylpiperidine (i.e. a product of C-C bond scission) were noted under some conditions. Quinoline is resonance stabilized, so its formation is thermodynamically favored compared to other amines.

The relative abundance of pentane in the hydrocarbon products is evidence of the ease of olefin hydrogenation under reaction conditions, which is typical of piperidine HDN. In fact, the first elimination reaction on piperidine should ideally yield 4-pentenyl-1-pentylamine as the primary reaction intermediate. The hydrogenation of the double bond at the 4 position is observed to be very fast, a likely consequence of preferred

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bonding to the surface at the amine position. That is, the surface amine containing the 4pentenyl group, attached strongly at the nitrogen, probably has a long residence time on the surface giving the double bond at the dangling end opportunity for subsequent hydrogenation.

Equilibrium calculations of piperidine/pyridine hydrogenation (25) indicate that appreciable pyridine is not expected under our conditions of piperidine HDN. First order analysis methods of Prins (26), and others, did not give satisfactory fits to our data. Furthermore, the persistence of condensation products suggested that they be incorporated into the analysis.

The results of piperidine HDN agreed with a second order kinetic analysis according to Scheme 6.3. In this sequence, two piperidine molecules react to form Npentylpiperidine, which subsequently dissociates into hydrocarbon and piperidine. The reactant is regenerated in the process. The kinetic analysis is second order in piperidine content, and first order in N-pentylpiperidine. Dividing the rate of N-pentylpiperidine dissociation by the rate of piperidine disappearance yields Equation 8 of Scheme 6.3 (Equation 6.3.8).

The values, obtained by smoothing the curves and interpolating results, and/or extrapolating to zero conversion, yield linear fits for each catalyst when plotted according to Equation 6.3.8. These curves are presented in Figure 6.2. Meanwhile, the numerical values of conversion and selectivity are included in tabular form in Table 6.1. The numerically listed values suffer from two sources of error. The first is due to neglecting the thiols in the table (as they were not incorporated in the kinetic analysis). A mass

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balance should yield the selectivity of thiol as 100 % – (sum of % selectivities of other components). However, there is also scatter in the total mole balance introduced at

Scheme 6.3: Second order analysis for the decomposition of piperidine.





Figure 6.2: Second order kinetic curve fits of piperidine HDN data.

Table 6.1 : Conversion and selectivity of catalysts in piperidine HDN.	(a) WP/SiO ₂ ; (b)
MoP/SiO_2 ; and (c) MoS_2/SiO_2 .	

(a) WP/SiO₂

T/K	Conversion	Condensation Products	Hydrocarbons
473	0	_	-
493	2.1	100.0	0.0
503	2.2	100.0	0.0
513	4.9	100.0	0.0
533	19.5	74.9	0.0
538	24.2	82.6	4.1
544	30	76.7	11.3
548	34.2	72.5	15.5
553	39.3	52.9	22.6
558	44.5	60.7	29.9
564	51.2	52.7	39.1
568	55.8	47.7	43.5
573	61.3	22.7	49.8

(b) MoP/SiO₂

T/K	Conversion	Condensation Products	Hydrocarbons
493	0	-	-
500	2.0	100.0	0.0
513	6.4	100.0	0.0
518	8.8	90.9	4.5
520	10.0	88.0	8.0
524	12.0	88.3	10.0
528	14.2	83.1	12.7
533	17.2	79.1	12.8

T/K	Conversion	Condensation Products	Hydrocarbons
453	0.0	-	-
473	2.0	100.0	0.0
480	5.2	80.8	15.4
485	8.0	75.0	22.5
490	11.0	72.7	27.3
493	13.3	69.9	30.1
500	19.8	61.6	37.4
505	25.5	54.9	43.9
510	32.3	47.7	52.0
513	36.8	43.5	56.5
520	48.8	32.8	67.6
525	58.2	25.8	75.3
530	68.1	20.3	80.8
533	74.5	17.0	83.0

Table 6.1: cont... Conversion and selectivity of catalysts in piperidine HDN. (a) WP/SiO_2 ; (b) MOP/SiO_2 ; and (c) MOS_2/SiO_2 .

(c) MoS₂/SiO₂

interpolation/extrapolation points. As was noted in the experimental section, the total observed products in the GC traces were combined and normalized to 100% before calculating conversion and selectivity.

The numerical values for the ratio of rate constants calculated from the slopes of the lines in Figure 6.2 are summarized in Table 6.2. The results for MoP/SiO₂ and WP/SiO₂ are similar, whereas the MoS₂/SiO₂ has a lower value. This is consistent with either a slower N-pentylpiperidine decomposition, or a faster condensation process on the sulfide material. Second order kinetic fits have been found previously for reactions of amines (27), and piperidine (24). Additionally, di(*n*-pentyl)amine has been suggested to be a reaction intermediate in the HDN of *n*-pentylamine over MoS₂ (28).

Table 6.2: Constants derived from kinetic analysis of piperidine and pyridine HDN reactions

	Piperidine		Pyri	idine
Catalyst	A	В	$ln(A_1)$	E_1 / R
·			· -/	-
MoP/SiO ₂	-86	-52000	16.0	13500
WP/SiO ₂	-112	-67000	7.7	8500
MoS_2/SiO_2	-77	-43000	20.5	14500

$$A = \ln(Q * A_1 * A_{pip}^2 / A_2 * A_{cond}^2)$$
$$B = (E_1 + 2H_{pip} - E_2 - 2H_{cond}) / R$$

It is likely that the first order direct decomposition of piperidine is a competing reaction, but it alone could not fit the data. In contrast to other studies, *n*-pentylamine

was not observed in the reaction products. It is likely that this molecule is converted rapidly to either N-(*n*-pentyl)piperidine or hydrocarbons once formed.

The three catalysts tested here all yielded similar results, both in terms of product distributions and the kinetic fits. The similarity indicates that the mechanism of HDN is similar on the three catalysts, a finding that is corroborated by our studies of the effect of structure of the nitrogen species in chapter 5. The nitrogen bond cleavage reaction probably proceeds by a bimolecular elimination reaction (E2) assisted by sulfur species on the surface, as proposed in chapter 5.

It has been reported in the literature that the rate of C-N bond scission in di(*n*-pentyl)amine is easier than that in *n*-pentylamine (30), hence the increased difficulty in C-N bond scission in piperidine is related to its ring structure, and not to the presence of a second C-N bond on the nitrogen atom.

It is likely that fast condensation reactions (we observe in this study that condensation is the fastest of all observed reactions) can yield intermediate surface species, analogous to 5-amino-1-pentylamine, capable of bonding to the surface at two ends. Condensation reactions leading to heteroatomic exchange, as found in the literature, were reported previously in Chapter 4.4. Thiane can be explained by a double condensation reaction, the first is an attack of H₂S on piperidine to yield a surface species analogous to 5-thio-1-pentylamine. A second is an internal condensation attack of the thiol group on the amine group to yield thiane and ammonia.

In each of these proposed, yet unobserved intermediates, 5-amino-1-pentylamine and 5-thio-1-pentylamine, the molecule has two sites by which it can attach to the surface. As nitrogen species are well known to bond strongly to catalyst surfaces during

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hydroprocessing reactions, such bifunctional intermediates would be held twice, once at each end. This even holds true for olefin containing intermediates, such as 4-pentenyl-1pentylamine. Olefins are also known to be firmly adsorbed on hydroprocessing catalyst surfaces, yet we think that they are hydrogenated quickly in our high pressure conditions.

Although condensation reactions may yield partial removal of heteroatoms, the total number of C-N bonds is conserved. Thus, the true freeing of hydrocarbons does not begin until elimination reactions destroy C-N bonds. Thus, the rate limiting step of piperidine reaction is likely to be elimination (detailed in Chapter 5), which is required of both steps of the kinetic process outlined in Scheme 6.3.

6.3.2. Pyridine

The product distributions as a function of temperature for pyridine HDN on the silica supported MoP, WP, and MoS₂ catalysts are presented in Figure 6.3. For pyridine, the most abundant product on each catalyst at low temperatures and conversions is piperidine. The hydrogenation activity of the catalysts increases in the order MoP/SiO₂ < $MoS_2/SiO_2 < WP/SiO_2$. N-(*n*-pentyl)piperidine was observed at all temperatures on all of the catalysts, having maximum concentrations at 533 K on MoP/SiO₂ and WP/SiO₂, and 493 K on MoS₂/SiO₂. N-cyclopentylpiperidine was observed in small quantities at the mildest temperatures tested on WP/SiO₂ and MoS₂/SiO₂. This product is interesting because it displays conservation of hydrogen from the starting materials (via 2 piperidine molecules), assuming that the initial removal of N occurs by elimination, and that



Figure 6.3: Conversions and product distributions from pyridine HDN on: (a) MoP/SiO₂; (b) WP/SiO₂; and (c) MoS₂/SiO₂.

pyridine does not participate in the reaction directly. N-cyclopentylpiperidine has been observed in several previous studies (24, 29, 30). The C-N bond scission activity of the three catalysts, noted by the formation of hydrocarbons as pentane and pentenes, increases in the order WP/SiO₂ \approx MoP/SiO₂ < MoS₂/SiO₂. *n*-Pentylamine is not observed as a product from either piperidine or pyridine HDN, suggesting that it is rapidly converted once formed. The occurrence of thiane and quinoline (in the products from WP/SiO₂) was already discussed in conjunction with piperidine HDN.

The curves from Figure 6.3 were smoothed and values of conversion and selectivity were interpolated, or extrapolated to zero conversion, to give the data summarized in Table 6.3. The sources of error in the values are the same as those discussed in relation to the piperidine data. The data for the total appearance of hydrocarbon plus condensation products during pyridine HDN were found to match zero order kinetics according to the analysis presented in Scheme 6.4. The zeroth order log plots, shown in Figure 6.4, display reasonably good linear fits with the data. The combined quantity of condensation products plus hydrocarbons is possibly a manifestation of fast parallel reactions leading to each of these species from an (unseen and very reactive) *n*-pentylamine intermediate.

Scheme 6.4: Zeroth order kinetics in the decomposition of pyridine.



(7) $\mathbf{f}_{HYD} = \mathbf{f}_2 = \mathbf{Q}^* \mathbf{C}_{HYD}$

T/K	Conversion	Piperidine	Pyr/Pip	Condensation	Hydrocarbons
				Products	
320	0.0	-	-	-	-
340	0.3	100.0	332	0.0	0.0
360	1.5	100.0	65.7	0.0	0.0
380	3.5	100.0	27.6	0.0	0.0
400	7.5	100.0	12.3	0.0	0.0
420	14.5	100.0	5.90	0.0	0.0
440	23.0	100.0	3.35	0.0	0.0
453	29.4	95.2	2.52	4.8	0.0
473	37.3	88.5	1.90	11.5	0.0
493	41.9	86.4	1.60	13.6	0.0
513	47.0	79.8	1.41	17.7	0.0
533	56.2	73.5	1.06	21.4	1.6
540	60.5	68.4	0.95	18.8	8.3
548	65.0	61.2	0.88	15.2	18.2
553	67.1	56.0	0.88	14.2	23.8
560	68.8	48.0	0.95	15.1	30.5
568	69.6	38.9	1.12	16.7	38.4
573	69.8	32.2	1.34	20.8	41.8

Table 6.3: Conversion and selectivity of catalysts in pyridine HDN. (a) WP/SiO₂; (b) MoP/SiO₂; and (c) MoS_2/SiO_2 .

(a) WP/SiO₂

(b) MoP/SiO₂

T/K	Conversion	Piperidine	Pyr/Pip	Condensation	Hydrocarbons
				Products	
453	0.0	-	-	-	-
473	2.5	100.0	39.0	0.0	0.0
480	5.0	90.0	21.1	10.0	0.0
493	10.6	89.6	9.41	10.4	0.0
500	13.0	88.5	7.57	11.5	0.0
513	17.8	84.3	5.48	15.7	0.0
516	18.6	82.8	5.29	17.2	1.1
520	19.8	80.3	5.04	18.7	2.0
525	21.1	76.8	4.87	19.4	3.3
530	22.5	72.4	4.75	20.4	5.3
533	23.2	71.1	4.65	22.0	6.5

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T/K	Conversion	Piperidine	Pyr/Pip	Condensation Products	Hydrocarbon
433	0.0	-	-	-	-
453	5.0	80.0	23.8	20.0	0.0
460	8.5	78.8	13.7	22.4	0.0
468	13.6	79.4	8.00	23.5	0.0
473	17.1	77.8	6.23	22.2	0.0
480	22.1	75.1	4.69	22.2	2.3
485	25.7	73.9	3.91	21.4	4.7
490	29.4	70.7	3.39	21.1	9.5
493	31.8	67.9	3.16	20.4	11.6
500	36.8	60.6	2.83	18.5	21.7
505	41.0	53.7	2.68	17.1	29.3
510	45.0	46.7	2.62	15.6	37.8
513	47.4	42.8	2.59	14.8	42.4
518	51.5	35.9	2.62	13.6	50.9
524	56.6	27.4	2.80	12.7	60.4
528	60.5	21.8	2.99	12.2	65.3
533	64.7	16.4	3.33	11.7	71.9

Table 6.3: cont... Conversion and selectivity of catalysts in pyridine HDN. (a) WP/SiO₂; (b) MoP/SiO₂; and (c) MoS_2/SiO_2 .

(c) MoS₂/SiO₂



Figure 6.4: Kinetic curve fits of pyridine HDN data.

The zeroth order kinetic constants derived from the kinetic analysis in Figure 6.4 were summarized previously in Table 6.2 along with the results from piperidine HDN.

It is not clear why the kinetic analysis changes so much between piperidine and pyridine. On the one hand, kinetics of HDN reactions have been reported to be self inhibited by the N compound, in which increased concentration (feed rate) leads to zero order kinetics (31). However, piperidine and pyridine are thought to have similar adsorption strengths (13) and are delivered at the same rate. Thus, this explanation is inadequate.

The two-site (hydrogenation and hydrogenolysis sites) model discussed in the introduction may help explain this phenomenon. First of all, it has been found that alumina can catalyze piperidine HDN, while not affecting pyridine (32). This seems to be strong evidence for the existence of acid-base C-N bond cleavage sites, which are distinct from sites required to hydrogenate pyridine. If the two site model is adapted to include interconversion of sites, then the extra hydrogenation requirement of pyridine HDN could reduce the number of available hydrogenolysis sites for piperidine. This could lead to the observed site saturation. The presence of N-cyclopentylpiperidine in the pyridine reaction, but not in the piperidine reaction, suggests that the hydrogenation sites are more inhibited during pyridine HDN than piperidine HDN, probably due to their greater load.

It is reasonable to assume that the presence of liquid solvent eases desorption of larger hydrocarbon molecules. Thus, the significant role of condensation in this work, compared to other studies which are mostly in the vapor phase, could be due to the solvent.

Our kinetic analysis has the advantage that it considers all of the observed major compounds over a wide range of temperature and conversion. Several other methods were tried which failed to describe the processes accurately, thus our approach was one of trial and error using Arrhenius analysis of Langmuir-Hinshelwood type rate equations. Unfortunately, we could only obtain the reaction order and lumped kinetic constants from our analysis. Further experiments in which concentration and space velocity are varied are required to obtain activation energies and heats of adsorption for each species.

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6.4. Conclusions

WP/SiO₂, MoP/SiO₂, and MoS₂/SiO₂ catalysts were used for hydrodenitrogenation of *n*-pentylamine, piperidine, and pyridine in tetradecane solvent at 3.1 MPa and over a range of temperatures. Condensation products were important in each test. Piperidine HDN was fit to a second order kinetic analysis in which the condensation product N-pentylpiperidine was an intermediate in hydrocarbon formation. The conversion of pyridine into hydrocarbons plus condensation products was observed to follow zeroth order kinetics in each case.

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