

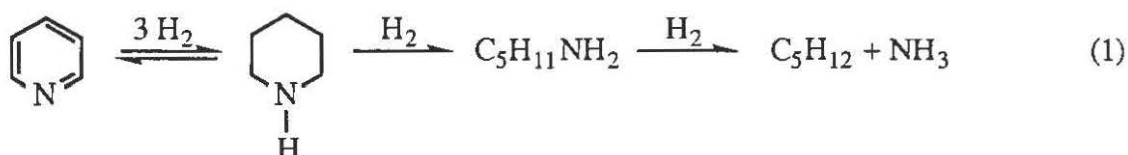
Heterogeneous and Homogeneous Aspects of Hydrodenitrogenation

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Hydrotreating, the removal of heteroatom impurities from crude oil, is an important step in the refining process. These impurities exist as organic compounds containing nitrogen, sulfur, oxygen and can occur as a mixture of free heterocycles and complexes of vanadium and nickel. Compounds such as these can poison the hydrocracking and reforming catalysts, resulting in major economic and processing problems. Furthermore, the combustion of organonitrogen and organosulfur compounds results in the emission of nitrogen and sulfur oxides. Hydrodenitrogenation, HDN, is one part of the hydrotreatment process in which nitrogen impurities are removed from petroleum feed stocks as NH_3 (eqn. 1) [1, 2].



The wide variety of substrates and intermediates in the process has made research in this area difficult. Thermodynamic studies indicate that the process is exothermic [3] and kinetic studies indicate that the hydrogenolysis of the C-N bond is the rate-limiting step [4]. While the mechanism for the process has yet to be determined, empirical studies indicate that hydrogenolysis occurs via two routes, a Hofmann type elimination or nucleophilic substitution [5, 6].

Although many transition metal sulfides are HDN active [7], the process is generally carried out over a sulfided $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Spectroscopic studies of the sulfided catalyst indicate that it exists as alternating layers of sulfur anions with molybdenum cations between the layers [8]. EXAFS of nickel in the catalyst suggest that the nickel is coordinated at edge sites, possibly in a square pyramidal fashion (Figure 1) [8, 9].

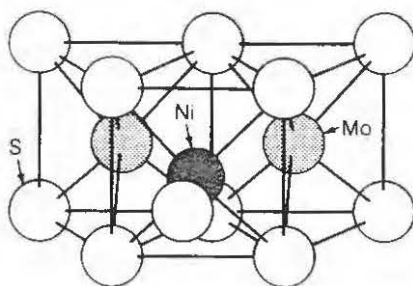
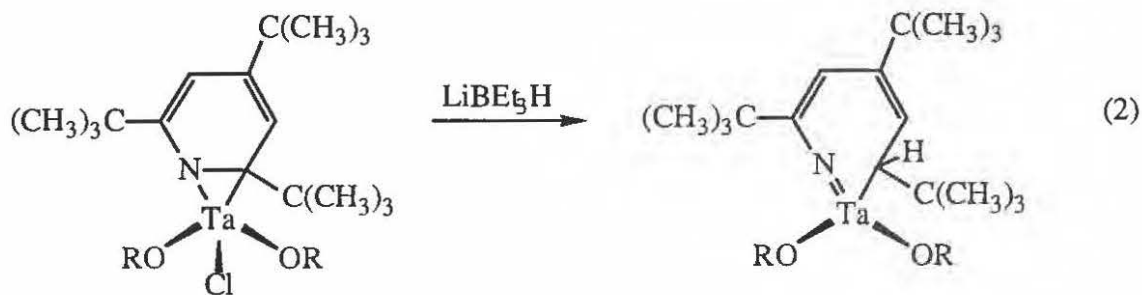


Figure 1

Homogeneous modeling of the HDN process could provide useful information on the structural, electronic, and chemical properties of the substrate. Organometallic compounds utilizing late transition metals have been observed to selectively hydrogenate the heteroaromatic ring under relatively mild conditions [10, 11]. Studies of transition metal complexes have shown that aromatic N-heterocycles can have several different modes of coordination, such as $\eta^1\text{-}(N)$, $\eta^2\text{-}(C,C)$, $\eta^2\text{-}(N,C)$, and $\eta^6\text{-}(C_5R_5N)$. The $\eta^2\text{-}(N,C)$ coordination can result in the activation of the C2 carbon, as seen in organometallic complexes of scandium in which the hydrogen on C2 can undergo deuterium exchange [12] and zirconium where alkyl groups

can be added at the C2 position [13]. In the case of tantalum, coordination of pyridine results in the disruption of aromaticity in the heteroaromatic ring as a result of π -backbonding [14, 15]. A possible intermediate in the HDN process could be the formation of a metal imide species. Although there are several methods to synthesize imide complexes, two methods applicable to HDN involve the hydrogenolysis of the C-N bond in an η^2 -(N,C)(C₅H₂(t-Bu)₃N)Ta complex, eqn. 2 [16], and the thermal dealkylation of η^2 -(N,C) iminoacyl tantalum complexes [17, 18]. Furthermore, the coordination of an imide in an η^2 -(N,C) fashion may represent a possible intermediate in the dealkylation of imides [19].



OR = 2,6-diisopropylphenoxide

Although much can be learned through homogeneous modeling, its relevance to the actual process is presently limited. Furthermore, direct information about the process is hampered by the complex environment for the catalytic sites and a complex reaction network which precludes the use of many spectroscopic techniques.

References

1. Ho, T. C., "Hydrodenitrogenation Catalysis," *Catal. Rev.-Sci. Eng.* **1988**, *30*, 117-160.
2. Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*, 2nd ed.; McGraw-Hill: New York, 1991.
3. Cocchetto, J. F.; Satterfield, C. N., "Thermodynamic Equilibria of Selected Heterocyclic Nitrogen Compounds with Their Hydrogenated Derivatives," *Ind. Eng. Chem., Proc. Des. Dev.* **1976**, *15*, 272-277.
4. Gultekin, S.; Satterfield, C. N., "Effect of Hydrogen Sulfide on the Catalytic Hydrodenitrogenation of Quinoline," *Ind. Eng. Chem., Proc. Des. Dev.* **1981**, *20*, 62-68.
5. Vivier, L.; Dominguez, V.; Perot, G.; Kasztelan, S., "Mechanism of C-N Bond Scission. Hydrodenitrogenation of 1,2,3,4-tetrahydroquinoline and of 1,2,3,4-tetrahydroisoquinoline," *J. Mol. Catal.* **1991**, *67*, 267-275.
6. Portefaix, J. L.; Cattenot, M.; Guerriche, M.; Breyse, M., "Mechanism of Carbon-Nitrogen Bond Cleavage During Amylamine Hydrodenitrogenation Over a Sulphided NiMo/Al₂O₃ Catalyst," *Catal. Lett.* **1991**, *9*, 127-132.
7. Shabtai, J.; Guohe, Q.; Balusami, K.; Nag, N. K.; Massoth, F. E., "Catalytic Functionalities of Supported Sulfides," *J. Catal.* **1988**, *113*, 206-219.

8. Bouwens, S. M. A. M.; Koningsberger, D. C.; de Beer, V. H. J.; Louwers, S. P. A.; Prins, R., "EXAFS Study of the Local Structure of Ni in Ni-MoS₂/C Hydrodesulfurization Catalysis," *Catal. Lett.* **1990**, *5*, 273-284.
9. Niemann, W.; Clausen, B. S.; Topsoe, H., "X-Ray Absorption Studies of the Ni Environment in Ni-Mo-S," *Catal. Lett.* **1990**, *4*, 355-364.
10. Sanchez-Delgado, R. A.; Gonzalez, E., "Selective Homogeneous Hydrogenation of Benzothiophene and Quinoline Catalysed by Ruthenium, Osmium, Rhodium, and Iridium Complexes," *Polyhedron* **1989**, *8*, 1431-1436.
11. Baralt, E.; Smith, S. J.; Hurwitz, J.; Horvath, I. T.; Fish, R. H., "Homogeneous Catalytic Hydrogenation. 6. Synthetic and Mechanistic Aspects of the Regioselective Reductions of Model Coal Nitrogen, Sulfur, and Oxygen Heteroaromatic Compounds Using the (η^5 -Pentamethylcyclopentadienyl)rhodium Tris(acetonitrile) Dication Complex as the Catalyst Precursor," *J. Am. Chem. Soc.* **1992**, *114*, 5187-5196.
12. Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E., "' σ Bond Metathesis' for C-H Bonds of Hydrocarbons and Sc-R (R = H, alkyl, aryl) Bonds of Permethylscandocene Derivatives. Evidence for Noninvolvement of the π System in Electrophilic Activation of Aromatic and Vinylic C-H Bonds," *J. Am. Chem. Soc.* **1987**, *109*, 203-219.
13. Jordan, R. F.; Guram, A. S., "Scope and Regioselectivity of Ligand C-H Activation Reaction of Cp₂Zr(CH₃)(THF)⁺," *Organometallics* **1990**, *9*, 2116-2123.
14. Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T., "Pyridine and Related Adducts, (silox)₃ML (M = Sc, Ti, V, Ta): η^1 -Pyridine-N vs η^2 -Pyridine-N,C Ligation," *Inorg. Chem.* **1990**, *30*, 2494-2508.
15. Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E., "Early-Transition-Metal-Mediated [2 + 2 + 2] Cycloadditions: Formation and Fragmentation of a Reactive Metallacyclopentadiene and Its Direct Conversion to η^6 -Arene and η^2 -Pyridine Complexes of Tantalum," *Organometallics* **1992**, *11*, 1275-1288.
16. Gray, S. D.; Smith, D. P.; Bruck, M. A.; Wigley, D. E., "Regioselective C-N Bond Cleavage in an η^2 (N,C)-Coordinated Pyridine and an η^1 (N) \rightarrow η^2 (N,C) Bonding Rearrangement in Coordinated Quinoline: Models for Hydrodenitrogenation Catalysis," *J. Am. Chem. Soc.* **1992**, *114*, 5462-5463.
17. Takahashi, Y.; Onoyama, N.; Ishikawa, Y., "Tantalum-Carbon Bond Formation in the Thermal Decomposition of Tantalum Diethylamide," *Chem. Lett.* **1978**, 525-528.
18. Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C., "Reactivity of Tantalum η^2 -Iminoacyl Groups: Intermolecular Coupling, Reduction, and Dealkylation," *J. Chem. Soc., Chem. Commun.* **1986**, 1203-1205.
19. Arney, D. J.; Bruck, M. A.; Huber, S. R.; Wigley, D. E., "Terminal vs Bridging Ligation in Complexes of Zirconium(IV) and Hafnium(IV): Structural Characterization of a μ -[η^1 (N): η^2 (N,C)] Imido Ligand," *Inorg. Chem.* **1992**, *31*, 3749-3755.