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 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 NH₃ (eqn. 1) [1, 2].

\[ \text{N} \boxtimes 3 \text{H}_2 \rightarrow \text{C}_5\text{H}_{11}\text{NH}_2 \rightarrow \text{C}_5\text{H}_{12} + \text{NH}_3 \]  \hspace{1cm} (1)

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 NiMo/γ-Al₂O₃ 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](image1.png)

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 \( \text{N} \)-heterocycles can have several different modes of coordination, such as \( \eta^1\text{-}(\text{N}) \), \( \eta^2\text{-}(\text{C},\text{C}) \), \( \eta^2\text{-}(\text{N},\text{C}) \), and \( \eta^6\text{-}(\text{C}_5\text{R}_5\text{N}) \). The \( \eta^2\text{-}(\text{N},\text{C}) \) 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 \( \eta^2-(N,C)(C_5H_2(t-Bu)_3N)Ta \) complex, eqn. 2 [16], and the thermal dealkylation of \( \eta^2-(N,C) \) iminoacyl tantalum complexes [17, 18]. Furthermore, the coordination of an imide in an \( \eta^2-(N,C) \) fashion may represent a possible intermediate in the dealkylation of imides [19].

![Image of chemical structures](image)

\[ \text{OR} = 2,6\text{-diisopropylphenoxide} \]

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


