



# Comprehensive kinetic study for pyridine hydrodenitrogenation on (Ni)WP/SiO<sub>2</sub> catalysts

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## ABSTRACT

In this work the reaction kinetics for pyridine hydrodenitrogenation on (Ni)WP/SiO<sub>2</sub> catalysts were determined. The experiments were conducted at 17.2 bar and between 573 K and 633 K for various flow rates of hydrogen and pyridine. Adding Ni to the WP/SiO<sub>2</sub> catalyst enhanced the hydrogenation reaction and gave higher pentane and pentylamine yields. A trend in terms of selectivity was not evident on either catalyst. The results were fit to several models and a Bayesian approach was applied for parameter estimation and model discrimination. Adding Ni to the WP/SiO<sub>2</sub> catalyst did not change the reaction mechanism – both catalysts favor the same Langmuir–Hinshelwood model with different active sites for hydrogenation and C–N bond cleavage. Ni did, however, influence the type of adsorbed species, the heat of adsorption and the activation energies.

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## 1. Introduction

Because of more stringent environmental legislations, efforts have been made to lower the levels of nitrogen in fuels. Hydrodenitrogenation (HDN) is a hydrotreating process in which the nitrogen content of hydrocarbons is reduced during refining. Pyridine has traditionally been used as a model compound for studying the HDN of heteroaromatic nitrogen components commonly found in petroleum feedstocks [1]. The HDN of pyridine proceeds via the saturation of the heterocyclic ring to form piperidine ( $r_1$ ), followed by ring opening of piperidine to form pentylamine ( $r_2$ ) and then subsequent removal of nitrogen to form pentane and ammonia ( $r_3$ ) as illustrated in Scheme 1 [1–3]. Some authors have observed that pentylamine can react with piperidine to n-pentylpiperidine (not shown) [4,5].

Different catalysts and various process conditions have been used in the study of HDN kinetics of nitrogen containing hydrocarbons such as pyridine and various quinolines. These catalysts include conventional sulfided and unsulfided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts containing Ni and/or Co [3,6–15] and NiW/Al<sub>2</sub>O<sub>3</sub> [16,17]. Several unconventional catalysts have also been used to investigate the kinetics of pyridine HDN. For example, Schwartz and Oyama [4]

examined the reaction network of pyridine HDN over carbide and sulfide catalysts such as (Nb)MoC, NbC and MoS/SiO<sub>2</sub>.

The knowledge and understanding of how the HDN of pyridine occurs on the different catalysts not only helps in developing a better catalyst (i.e., higher conversion and selectivity), but also allows modeling the chemical reactor for design and process optimization purposes. Simple power law rates that are first order in pyridine, and Langmuir–Hinshelwood (LH) approaches have been used to study HDN kinetics [3,7,14,16,18]. Different modifications of the LH rate expression have been applied by authors to account for adsorption of pyridine, various intermediates, and ammonia on catalytic sites [3,7,17–19]. Some studies estimated rate coefficients and adsorption constants at one temperature only and, thus, no activation energies and heats of adsorption were reported [3,7,17,18]. Other authors have reported activation energies ranging from 55 to 134 kJ mol<sup>-1</sup> for the conversion of pyridine, but did not discuss the product distribution [14,16]. Shih and Yang [19] reported an activation energy of 59 kJ mol<sup>-1</sup> for the hydrogenation of pyridine over unsupported ruthenium taking into account the adsorption of piperidine.

A generalized form of a Langmuir–Hinshelwood rate equation based on the assumption of no competitive adsorption between hydrogen and N-compounds has been described in the review article by Furimsky and Massoth [1]. Other authors suggest that the hydrogenation reaction takes place on a different site than the C–N bond cleavage [6,20–24]. In general, there is little information on HDN kinetics as well as the influence of adding Ni to WP/SiO<sub>2</sub> catalysts. For alumina-based systems, it is known that Ni enhances the

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