

# THE EFFECTS OF SUPPORT ACIDITY ON QUINOLINE AND INDOLE HYDRODENITROGENATION - A DETAILED KINETIC STUDY

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## Abstract

A detailed kinetic modeling including the liquid-vapor mass transfer was proposed to estimate kinetic and adsorption constants in complex reaction scheme and discriminate the support acidity effects on quinoline and indole HDN. The catalytic tests were carried out in a batch reactor, over two sulfide catalysts: NiMo(P)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo(P)/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (ASA). Over both catalysts, the hydrogenation of aromatic ring of nitrogen compounds is the rate determining step of the main reaction pathway. The NiMo(P)/ASA exhibited higher rate constants for this step and denitrogenation steps (without ring opening). The adsorption constants of all nitrogen compounds were compared. As expected, nitrogen compounds adsorbed more strongly on NiMo(P)/ASA than Al<sub>2</sub>O<sub>3</sub> counterpart. Quinoline showed a strong inhibiting effect on indole HDN whereas the inhibiting effect of indole on quinoline HDN was negligible over NiMo(P)/Al<sub>2</sub>O<sub>3</sub> and slightly more important over NiMo(P)/ASA.

## Keywords

Hydrodenitrogenation, NiMo(P)/ASA, Quinoline, Indole, Langmuir-Hinshelwood

## Introduction

The improvement of hydrodenitrogenation (HDN) catalyst activity is increasingly important because of an growing demand for upgrading heavy feedstocks and serious effects of nitrogen organic compounds, such as the poisoning of acid catalysts in hydrocracking and catalytic cracking processes as well as the inhibiting effect on hydrotreating reactions (Peeters *et al.*, 2000). Using quinoline and indole as model molecules is a way to understand how modifications of HDN catalysts act on the reaction network (Figures 1, 2). Our study of the effects of support acidity on the HDN of the molecules was carried out thanks to a detail kinetic analysis of reaction network and the characterizations of catalyst properties.

## Experimental

Two catalysts NiMo(P)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo(P)/ASA were synthesized by incipient wetness impregnation. The catalysts were sulfided with the mixture of 15 vol% of H<sub>2</sub>S in H<sub>2</sub>, at 400°C, for 4 hours. Catalytic tests were carried out in a batch reactor, at 7 MPa as total pressure, at 340-360°C, and the concentration 1-2 wt% for quinoline and 0.5-1 wt% for indole, over 0.75 g of sulfide catalyst. The

tests of mixture (quinoline and indole) were performed with 0.5 wt% of indole and 0.25 wt% of quinoline.

## Kinetic Modeling

The Langmuir-Hinshelwood kinetic model included the liquid-vapor (L-V) mass transfer, which was represented by a linear driving force model, and the competitive adsorption of all nitrogen compounds and H<sub>2</sub> on the same active site (Nguyen *et al.*, 2015). The L-V equilibrium of reaction mixture was simulated by ProSim (version 3.3). A set of 1000 experimental points corresponding to the concentrations of components in liquid samples at different reaction times, different initial concentrations and different temperatures were used to estimate 39 parameters including pre-exponential factors, activation energies ( $E_a$ ), adsorption enthalpies ( $\Delta H_{ads}$ ) and L-V mass transfer coefficient ( $k_{1a}$ ). The Levenberg-Marquard minimization method (Matlab, version 2015) was used for parameter's estimation.

## Results and Discussions

### Catalysts Characterizations

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The catalysts properties are summarized in Table 1. The Mo loading of the two catalysts was chosen so as to obtain a similar activity in toluene hydrogenation. The NiMo(P)/ASA was more acidic than NiMo(P)/Al<sub>2</sub>O<sub>3</sub>, as confirmed by cyclohexane isomerization conversion. The higher acidity of ASA supported catalyst led to the transfer of electrons of the sulfide phase towards the support, as proven by a shift of NiMoS band position in IR Spectroscopy of CO over this catalyst as compared to NiMo(P)/Al<sub>2</sub>O<sub>3</sub>. The X-ray Photoelectron Spectroscopy characterization showed also the higher content of promoted sulfide phase on NiMo(P)/Al<sub>2</sub>O<sub>3</sub>.

Table 1: Catalysts properties

Properties	NiMo(P)/Al <sub>2</sub> O <sub>3</sub>	NiMo(P)/ASA
wt% MoO <sub>3</sub> / NiO	18.6/3.84	14/2.97
NiMoS promoted phase content (mmol/g catal.)	0.326	0.205
Position of NiMoS band in IR Spectroscopy of adsorbed CO (cm <sup>-1</sup> )	2129	2134

#### Results of Kinetic Modeling

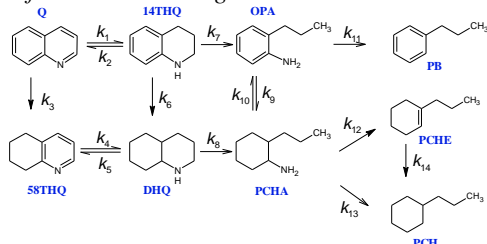


Figure 1: Reaction scheme of quinoline HDN

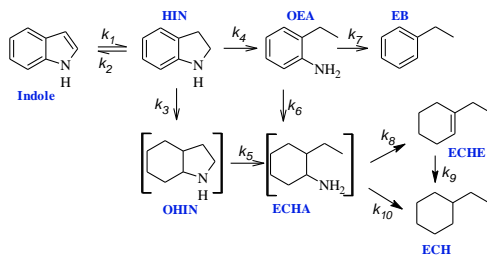


Figure 2: Reaction scheme of indole HDN

The estimated values of  $k_{1a}$  in the range of 0.05-0.25 s<sup>-1</sup> indicated the absence of L-V transfer limitation. As shown in Table 2, the adsorption constants of nitrogen compounds over NiMo(P)/ASA were higher than over NiMo(P)/Al<sub>2</sub>O<sub>3</sub>. This result was explained by the electronic effect of the acidic support on the sulfide phase.

As compared to NiMo(P)/Al<sub>2</sub>O<sub>3</sub>, the NiMo(P)/ASA favored the hydrogenation of 14THQ into DHQ and OEA into ECHA, and denitrogenation reactions (without ring opening reactions), including the C<sub>sp2</sub>-N bond breaking and the  $\beta$ -elimination (Table 3). However, the stronger adsorption of nitrogen compounds over NiMo(P)/ASA led to a stronger self-inhibition, and consequently the lower activity of this catalyst for quinoline and indole HDN. The HDN of the mixture showed that quinoline had

a strong inhibiting effect on indole HDN. The inhibiting effect of indole on quinoline HDN was negligible over NiMo(P)/Al<sub>2</sub>O<sub>3</sub> and slightly more important over NiMo(P)/ASA.

Table 2: Adsorption constants at 350°C

$K_i$ (l.mol <sup>-1</sup> )	NiMo(P)/Al <sub>2</sub> O <sub>3</sub>	NiMo(P)/ASA
Indole	0.3	0.9
14THQ/OEA	5.2	6.5
Q/58THQ	6.0	9.5
HIN/OEA	9.4	12.5
NH <sub>3</sub>	19.0	29.0
DHQ/PCHA	22.0	31.0
OHIN/ECHA	69.0	157.5

Table 3: Effective rate constants at 350°C

$k_i$ (s <sup>-1</sup> )	NiMo(P)/Al <sub>2</sub> O <sub>3</sub>	NiMo(P)/ASA
<b>Quinoline HDN</b>		
$k_6$	0.07	0.131
$k_7$	0.03	0.035
$k_8$	0.21	0.206
$k_{11}$	0.046	0.174
$k_{12}$	1.19	2.11
$k_{13}$	0.51	1.22
<b>Indole HDN</b>		
$k_3$	0.70	0.93
$k_4$	0.31	0.39
$k_5$	20.0	12.3
$k_6$	0.06	0.11
$k_7$	0.02	0.04
$k_8$	15.0	62.0
$k_{10}$	4.4	11.2

## Conclusions

Despite of the positive effect of NiMo(P)/ASA for the hydrogenation of aromatic ring and the denitrogenation reactions, the stronger adsorption of nitrogen compounds and the lower quantity of NiMoS phase over this catalyst decreased its global activity for quinoline. The higher intrinsic activity of NiMo(P)/ASA might be related to the modification of electronic properties of sulfide phase due to higher acidity of ASA support.

## Acknowledgments

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