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Inhibition of the Hydrogenation and Hydrodesulfurization Reactions by Nitrogen Compounds over $NiMo/Al_2O_3$

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Abstract The inhibiting effect of nitrogen compounds on the hydrogenation of aromatic compounds and on the hydrodesulphurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6 DMDBT), has been systematically investigated over a commercial NiMo hydrotreating catalyst. Amongst the different nitrogen compounds considered, interestingly ammonia was found to have the strongest inhibition effect on hydrogenation as well as on hydrodesulfurization reactions. The inhibiting effects were found to increase in the order quinoline < tetrahydroquinoline < indole < indoline < ammonia for phenanthrene/tetralin hydrogenation and HDS reactions. The molecules with nitrogen atoms having higher negative Mulliken charges showed higher adsorption constants.

Key words Inhibition · Aromatic hydrogenation · Nitrogen · Hydrodesulfurization

1 Introduction

Due to stringent clean fuel regulations [1–6], there is considerable interest in investigating the different hydrotreating reactions such as hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HYD). From the viewpoint of meeting on-road diesel specifications it is important to achieve very high efficiencies for the HDS and HYD reactions. Nitrogen-containing compounds inhibit HDS and HYD through competitive adsorption. Although interesting information about the inhibition effect from nitrogen compounds has been forwarded by previous studies [7–9], the inhibition effect from the ubiquitous ammonia has not been adequately investigated and is not well understood with respect to other nitrogen compounds. Moreover, the majority of the studies have focused on the nitrogen inhibition effect on the HDS reaction and therefore systematic information related to the inhibition effect on HYD reactions is scarce [7].

From a practical viewpoint, it is very important to obtain a more complete picture about the inhibiting effect from nitrogen species (i.e. the relative inhibition by ammonia with respect to basic and non-basic nitrogen compounds on HYD and HDS). With this objective in mind, herein we have undertaken systematic studies to investigate the effect of different nitrogen compounds on HYD and HDS reactions under practically relevant reaction conditions. The inhibiting effect of quinoline, 1,2,3,4-tetrahydroquinoline, indole, indoline and ammonia has been individually investigated on the hydrogenation of aromatic compounds as well as on the hydrodesulphurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6 DMDBT) over a commercial NiMo hydrotreating catalyst. Theoretical calculations have been used to explain the experimental results.

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2 Experimental Section and Kinetics

2.1 Reactor Tests

The commercial NiMo/alumina hydrotreating catalyst *Criterion 424* used for all the experiments contained 6 wt%

Table 1 Feeds investigated

	Feed-0	Feed-Q	Feed-THQ	Feed-IN	Feed-HIN	Feed-NH_3
Quinoline		1000				
Tetrahydroquinoline			1000			
Indole				1000		
Indoline					1000	
Ammonia						85

Concentrations of added nitrogen containing molecules in ppm

Note: In all feed, Dodecane (DO) was used as a solvent, while 5 wt% tetralin (TL), 2 wt% phenanthrene (PHE), 500 ppmw dibenzothiophene (DBT) and 500 ppmw 4,6- dimethyldibenzothiophene (4,6-DMDBT) were used as the feed matrix

Ni and 18 wt% Mo. The catalytic activity was measured in a continuous flow reactor at a temperature of 345 °C and a total pressure of 70 atm, with a H_2/HC molar ratio in the range 20–130 and at different contact times. Before each run, the catalyst sample was physically mixed with 5 cc of inert alumina and placed in the center of the reactor, between layers of 3 mm glass beads. The catalyst was pre-sulfided in flow of 10% H_2S in H_2 at 200 and 370 °C. Several different feeds were used in this work (see Table 1) A model feed was prepared by blending 5 wt.% of tetralin (TL; Acros, +98%) and 2 wt.% of phenanthrene (PHE; Aldrich, 98%), 500 ppm of dibenzothiophene (DBT; Aldrich, 99%) and 500 ppm of 4,6-dimethyldibenzothiophene (4,6-DMDBT; Aldrich, 99%) in 90 wt.% of dodecane (DO; Aldrich, 99%). Nitrogen compounds containing feeds were prepared by adding 1,000 ppm of quinoline (Q; molar fraction = 0.00176); 1,2,3,4-tetrahydroquinoline (THQ; molar fraction = 0.00171); Indole (IN; molar fraction = 0.00194), Indoline (HIN; molar fraction = 0.00191) and 85 ppm NH_3 (molar fraction = 0.00114), respectively, to the model feed, respectively. The products were trapped with chilled water and analyzed online by a HP6890 gas chromatograph with an FID detector using an HP-5 column. The data were collected at Time-on-stream (TOS) = 5 h, because of the stability and reproducibility of the data at this TOS. Experiments were undertaken at pre-determined conditions (flow-rate = 10 cc/h and particle diameter <0.64 mm) where no significant mass transfer effects were expected.

2.2 Kinetics

The generalized Langmuir–Hinshelwood model for hydrogenation suggested by Kiperman [9] was used to fit the data obtained in this study.

$$r_{ij} = \frac{k_{ij} K_i K_{H_2} (P_i^{n_1} P_{H_2}^{n_2} - P_j / K_{\mathrm{eq}})}{(1 + \sum_m K_m P_m^{n_3})^Z} \quad (1)$$

where r_{ij} (mol g_{cat}^{-1} h^{-1}) is the rate of conversion of compound i to compound j, P (atm) is the partial pressure, k_{ij} (mol $gcat^{-1}$ h^{-1}) is the kinetic rate constant, K_{eq} is the equilibrium constant and K_m (atm^{-1}) is the adsorption parameter of individual compounds. Usually n_1 can be taken equals to 1, Z represents the number of surface sites required for reaction, n_3 is ½ for atomic adsorption of H_2, and m is 1 for molecular adsorption. The equilibrium constants were obtained using HSC-Chemistry-5.0® software (Reg. USPTO, Outotec). The nonlinear parameter estimation of the kinetic model was performed with the Powell version of the Levenberg-Marquardt algorithm. The differential equations were solved using the EPISODE package of Scientist®.

2.3 Theoretical Calculations

The electronic structures of the studied organonitrogen compounds were calculated using density-functional theory (DFT) and the Mulliken charges were calculated using Gaussian 03W (DFT/B3LYP/STO-3G) [11].

3 Results and Discussion

The inhibition from the different nitrogen compounds for tetralin and phenanthrene hydrogenation is shown in Fig. 1. The nitrogen compounds showed a very strong inhibiting effect on the hydrogenation reaction and the inhibiting effect was found to increase in the following order: quinoline < tetrahydroquinoline < indole < indoline < ammonia. Tetralin and phenanthrene hydrogenation both showed the same trend. Figure 2 shows the HDS of DBT and 4,6 DMDBT for the same experimental test runs shown in Fig. 1. Even in case of the HDS reaction, the inhibiting effect of the nitrogen compounds was found to increase in the same order: quinoline < tetrahydroquinoline < indole < indoline < ammonia. A stronger inhibiting effect of indole as compared to quinoline has also been previously observed for the HDS reaction over a Co-based hydrotreating catalyst [12]. It is interesting to note that in our present study ammonia exhibited the strongest inhibition effect for HYD as well as for HDS reactions. Although significant inhibition

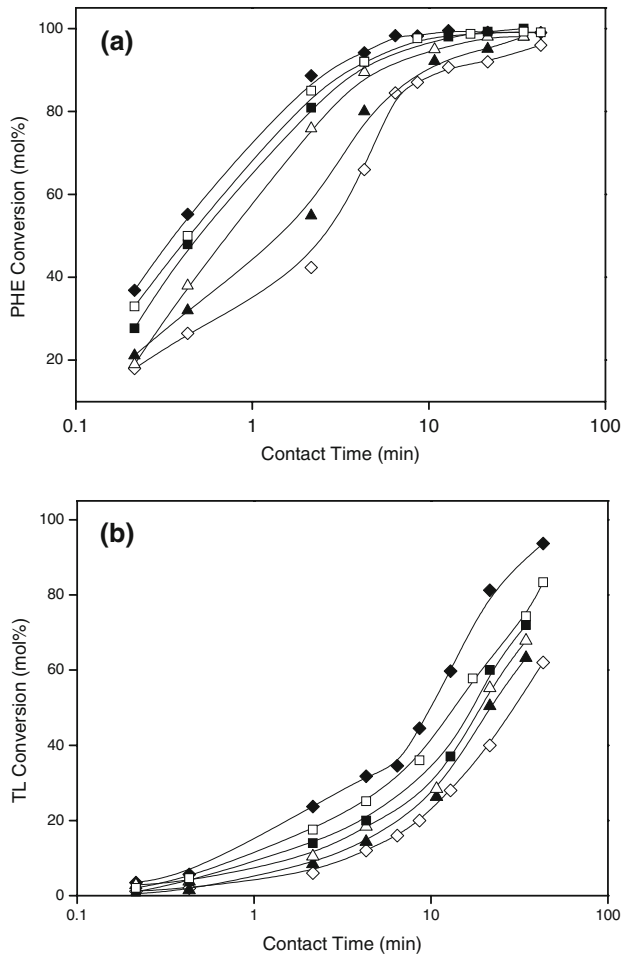

Fig. 1 Nitrogen compounds inhibition effect on the (**a**) PHE Hydrogenation and (**b**) TL Hydrogenation. Feed-0 (♦); Feed-Q (□); Feed-THQ (■); Feed-IN (Δ); Feed-HIN (▲); Feed-NH_3 (◇). *Note*: Log scale used for clarity

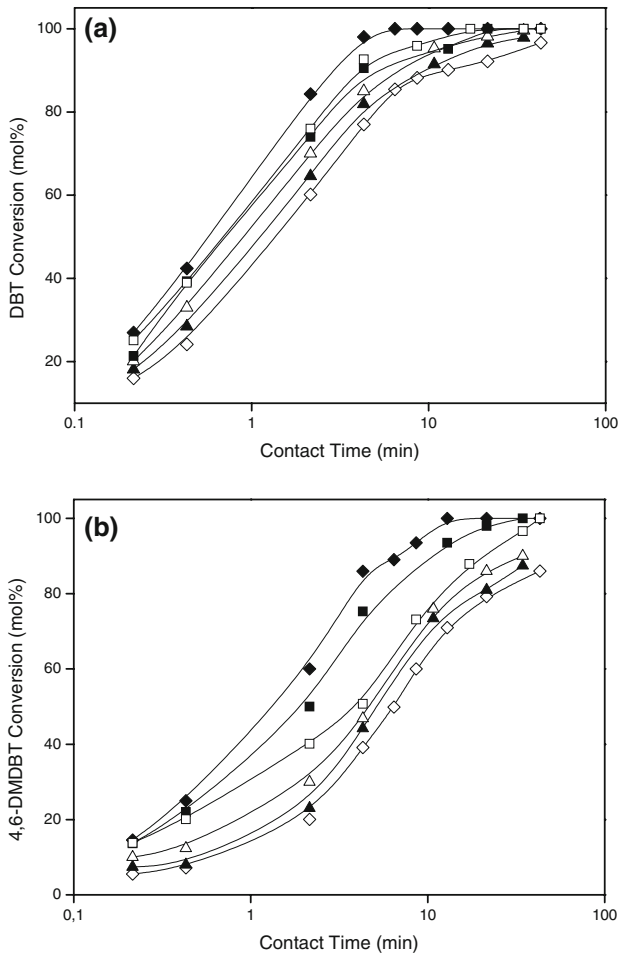

Fig. 2 Nitrogen compounds inhibition effect on the (**a**) DBT HDS and (**b**) 4,6-DMDBT HDS. Feed-0 (♦); Feed-Q (□); Feed-THQ (■); Feed-IN (Δ); Feed-HIN (▲); Feed-NH_3 (◇). *Note*: Log scale used for clarity

from NH_3 has been reported in some previous studies [13], there has been no systematic study comparing its relative effect with other nitrogen compounds for the HYD and HDS reaction.

A generalized Langmuir–Hinshelwood rate equation (described in the Experimental section) was used to represent the inhibiting effect of the nitrogen compounds on the tetralin and phenanthrene hydrogenation. The inhibition effect from ammonia as a by-product was included in the parameter calculations. The adsorption parameters were estimated using molar fraction versus *W*/*F* (g_{cat} h/mol TL+PHE) data, and solving simultaneously for all experiments involving a particular compound, i.e.; Feed-Q and Feed-THQ were fitted simultaneously to obtain *K* values for quinoline, tetrahydroquinoline and *o*-propylaniline. Similarly Feed-IN and Feed-HIN were fitted simultaneously to obtain *K* values for indole, indoline and *o*-ethylaniline. For illustrative purpose, the results for the case of Feed-IN are shown in Fig. 3. Similar curves were obtained for each of the feeds investigated. The Langmuir adsorption constants resulting from the fitting for each of the inhibiting nitrogen compounds are listed in Table 2. It is clear that the adsorption strength increases in the order quinoline < indole < tetrahydroquinoline < indoline < ammonia. The strong inhibiting effect of ammonia is in qualitative agreement with previous studies [14, 15].

The inhibiting strength also seems to be affected by the conversion of the parent nitrogen compound, the formation or disappearance of basic compounds and the degree of organic nitrogen removal. For example, the inhibiting effect of indole is higher than tetrahydroquinoline, despite the fact that tetrahydroquinoline has higher adsorption constant than indole. This apparent disparity may be explained by taking into account that indole is probably quickly converted into indoline and *o*-ethylaniline, which in turn are more basic compounds and possess higher adsorption constants than tetrahydroquinoline. The basic and non-basic organonitrogen compounds have distinct electronic structures and properties that determine their

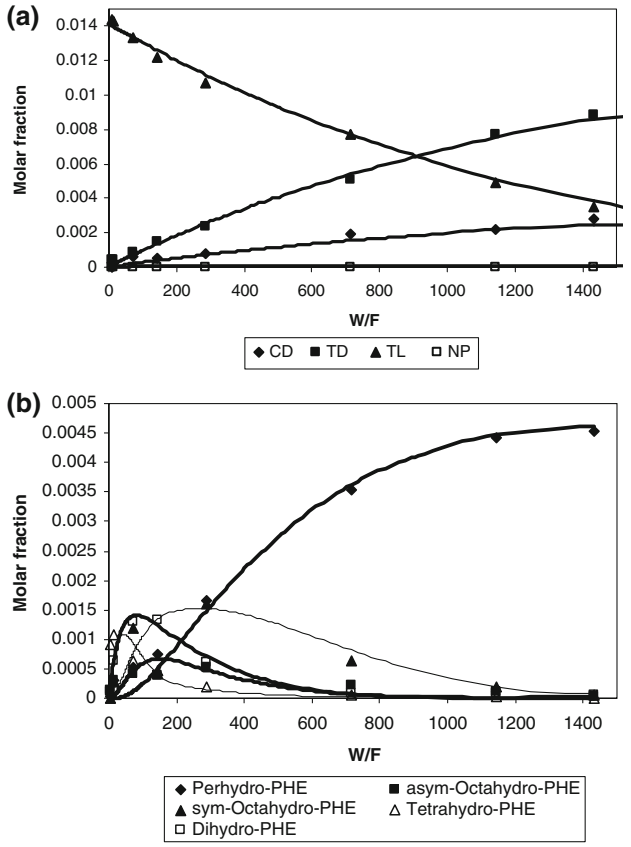

Fig. 3 Molar fraction versus *W/F* (g h mol^{-1} of TL+PHE) for the reactions involving Feed-IN. (**a**) TL hydrogenation products; (**b**) PHE hydrogenation products. The lines were obtained by fitting the kinetic curves derived from the model to the experimental data

Table 2 Adsorption constants for the different nitrogen compounds derived from the kinetics analysis

Compound	Adsorption constant (atm^{-1})
Quinoline	500
TetrahydroQuinoline	1,450
Indole	1,200
Indoline	1,500
Propylaniline	2,000
Ethylaniline	2,000
Ammonia	3,129

HDN reactivities on hydrotreating catalyst surfaces. The inhibiting effect can be correlated to the Mulliken charges on the nitrogen atoms of the organonitrogen molecules.

Figure 4 shows the correlation of the adsorption constant of the organonitrogen compounds and the negative Mulliken charges on the nitrogen atom of the corresponding molecules, calculated by using Gausian 03 W. An excellent correlation was observed between the Mulliken

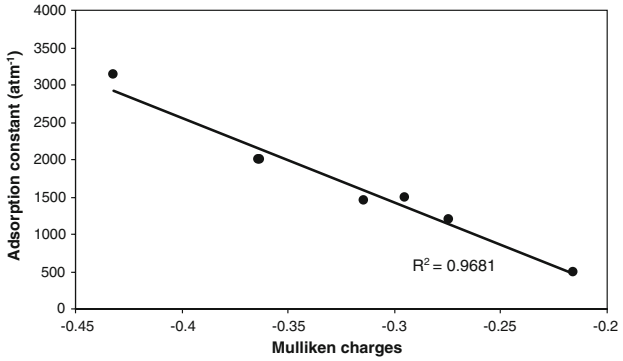

Fig. 4 Correlation between the adsorption constant of the organonitrogen compounds and the negative Mulliken charges on the nitrogen atom

negative charge on the nitrogen atom and the relative adsorption constant of the studied nitrogen species (derived from the kinetics analysis). A higher negative charge on the nitrogen atom of a saturated nitrogen molecule would lead to stronger adsorption of the molecule on the catalyst surface and correspondingly a higher surface coverage [16]. This is probably the reason for the excellent correlation observed in Fig. 4 and also the strong inhibiting effect on the HYD and HDS reactions.

4 Conclusions

The main findings of the study are summarized below:

a. The experimentally observed inhibiting effect of the nitrogen compounds increases in the order quinoline < tetrahydroquinoline < indole < indoline < ammonia for the HYD and HDS reactions.
b. The calculated adsorption strength of the nitrogen compounds increases in the order quinoline < indole < tetrahydroquinoline < indoline < ethylaniline ~ propylaniline < ammonia.
c. The adsorption constant of the organonitrogen compounds derived from the kinetics analysis correlated well with the negative Mulliken charges on the nitrogen atom of the corresponding molecules.

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