Determination of the nature of distinct catalytic sites in hydrodenitrogenation by competitive adsorption

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The inhibitive effect of nitrogen-containing compounds on hydrodenitrogenation was studied over NiMo(P)/Al_2O_3 catalysts. From the differences in the adsorption constants it is concluded that at least four distinct catalytic sites are involved in the elementary hydrodenitrogenation steps. The catalytic site for the cleavage of aliphatic C(sp^3)–N bonds is acidic and most probably an SH species on a surface Mo or Ni site. The catalytic site for the hydrogenation of a phenyl group is different from that for alkene hydrogenation, the former being more coordinately unsaturated than the latter, with two or three sulphur vacancies. A fourth site is responsible for the hydrogenolysis of the C(sp^2)–N bond of anilines. It is characterised by a more reduced environment of Mo and by phosphorus promotion.

Keywords: hydrodenitrogenation, catalytic sites, competitive adsorption

1. Introduction

Hydroprocessing ranks among the most important processes in the petroleum industry. The main hydroprocessing reactions are hydrodesulphurization, hydrodenitrogenation, hydrodeoxygenation, and hydrodemetalization [1,2]. A variety of chemically different reactions are involved in the hydrodenitrogenation (HDN) process, namely: hydrogenation of alkenes, hydrogenation of carbocyclic or heterocyclic aromatic rings, hydrogenation of the phenyl group of aniline molecules, aliphatic C(sp^3)–N bond cleavage, and aromatic C(sp^2)–N bond cleavage. There are clear indications in the literature that these reactions take place on different catalytic sites. Thus, Satterfield and co-workers observed that the presence of H_2S in the feed substantially enhanced the C(sp^3)–N bond cleavage in the HDN of quinoline, but slightly inhibited the hydrogenation of the quinoline ring over a sulphided NiMo/Al_2O_3 catalyst [3,4]. In a comparative HDN study of aniline, cyclohexylamine, and N-methylaniline over a NiMo/Al_2O_3 catalyst, Shanthi et al. concluded that distinct catalytic sites are needed for C(sp^3)–N and C(sp^2)–N bond cleavage [5]. They found that H_2S had a promotional effect on the breaking of the C(sp^3)–N bond, but an inhibitive effect on the cleavage of the C(sp^2)–N bond.

The necessity of different catalytic sites for C(sp^2)–N bond cleavage and hydrogenation of a phenyl group has been demonstrated by the HDN product composition, influence of reaction conditions, and catalyst composition in the HDN of alkylanilines [6,7]. A kinetic study of the hydrodeoxygenation of *p*-cresol which is similar to the HDN of *p*-toluidine, showed that the inhibitive adsorption constants of ammonia and *o*-cresol were higher on the active site for C(sp^2)–O bond cleavage than on the site for the phenyl ring hydrogenation, and the effect of H_2S on the two parallel reactions was different over NiMo/Al_2O_3 and CoMo/Al_2O_3 catalysts [8].

Due to the basic properties of the nitrogen-containing compounds in oil fractions, and the acidic properties of the hydrotreating catalysts, nitrogen-containing molecules adsorb strongly during the hydrotreating process. They occupy the active sites on the catalyst surface and inhibit their own as well as other hydrotreating reactions [9–13]. A well known inhibitive effect is that of quinoline-type compounds on the HDN of anilines: Pure anilines can be converted almost completely to nitrogen-free hydrocarbons under normal HDN conditions, while the presence of quinoline-type compounds strongly inhibits this reaction [14–16]. The much stronger inhibitive effect of quinoline-type compounds on the HDN of alkylanilines than on their own HDN, suggests that the two reactions take place on distinct catalytic sites. It explains that the concentration of alkylanilines can be much higher in the product of hydrotreatment than in the feed [17].

Notwithstanding all this evidence of different sites for different reactions, it has generally been ignored in kinetic studies. Almost all kinetic HDN studies lump the kinetic equations by assuming that all substrate and intermediate molecules have the same adsorption constants. Only a few studies have recognised the possibility that more adsorption constants may be needed, but even they do not go further than a maximum of two distinct adsorption constants [12].

In the present study we show that these simplified assumptions in the kinetic HDN schemes strongly distort the truth. In reality, every single step needs its own

adsorption constant, and thus its own catalytic site. These adsorption constants have been determined by studying the inhibitive effects of nitrogen-containing substrates on a variety of chemically different reactions which are part of the HDN network of quinoline. The nature of the catalytic sites is discussed and correlated with the catalyst properties.

2. Experimental

Catalysts used in this work had a composition of 3 wt% nickel, 8 wt% molybdenum and 0 or 2 wt% phosphorus. Details of the catalyst preparation can be found elsewhere [18]. The reactions were carried out in a continuous-flow microreactor. A sample of 0.1 g catalyst diluted with 9.5 g SiC was sulphided in situ with a mixture of 10% (mol) H_2S and H_2 at 643 K and 1.5 MPa for 4 h. After sulphidation the pressure was increased to 3.0 MPa and liquid reactant was fed to the reactor by means of a high pressure pump, with *n*-octane as the solvent. Dimethyldisulphide was added to the liquid reactant to generate H_2S in the reaction stream (usually P_{H_2S} = 6.5 kPa).

Reaction products were analyzed on-line with a Shimadzu GC-14A gas chromatograph equipped with a 30 m DB-5 fused silica capillary column (J&W, 0.32 mm ID, 0.25 μm film thickness) and a flame ionization detector. Samples were taken after 100 h on stream at 643 K when the activity of the catalyst was relatively stable, with *n*-nonane and *n*-dodecane as internal standards. The space time was changed by varying the liquid and gaseous reactant flow rates while keeping their ratio constant [19]. The reproducibility of the measurements is $\pm$10%.

3. Results

The adsorption constant of a molecule on a catalytic site provides a quantitative measure of its strength of adsorption on this site, and a comparison of such adsorption constants gives direct evidence of the similarity or difference of the sites for different reactions. When Langmuir–Hinshelwood adsorption is assumed, the reaction rate of substrate A in a heterogeneous catalytic reaction can be written as

$$-\frac{dP_A}{d\tau} = \frac{k_A K_A P_A}{1+\sum_i K_i P_i} = \frac{k_A K_A P_A}{1+K_A P_A^0}, \qquad (1)$$

where τ is the space time, P_A the partial pressure of reactant A (P_A^0 is the initial partial pressure), k_A the rate constant, and K_A the adsorption constant of A. K_i and P_i represent respectively the adsorption constant and partial pressure of compound *i* in the reaction stream which can adsorb on the surface site. Since the nitrogen-containing substrates adsorb much stronger than all other compounds, eq. (1) can be simplified by neglecting the adsorption terms of other substrates, and by assuming a constant adsorption term of reactant A in the denominator at low conversions ($x_A < 15\%$). The adsorption constant K_A can thus be easily calculated by regression analysis [7]. Since hydrogen adsorbs weakly and is in large excess, the effect of hydrogen has been lumped into the rate constant k_A.

Equation (1) can also be integrated to eq. (2):

$$\frac{\tau}{-\ln(1-x_A)} = \frac{1}{k_A K_A} + \frac{1}{k_A}\cdot P_A^0 . \qquad (2)$$

By measuring the conversion x_A at different initial reactant partial pressures P_A^0, the adsorption constant K_A can be calculated from the slope and intercept of the $-\tau/\ln(1-x_A)$ versus P_A^0 plot. Figure 1 gives an example for the HDN of ortho-propylaniline (OPA). The simplified equations (1) and (2) can only be used for relatively simple systems, however, for more complex cases, a complete regression analysis including variation of τ as well as P_A^0 has to be performed [20].

The inhibition adsorption constant of a nitrogen-containing substrate on the catalytic site on which another weakly adsorbing substrate reacts (such as alkenes) can be determined through simultaneous reactions. At low conversion of the inhibitor A ($x_A < 15\%$), the conversion of the alkene B can be written as

$$-\frac{dP_B}{d\tau} = \frac{k_B K_B P_B}{1+\sum_i K_i P_i} = \frac{k_B K_B P_B}{1+K'_A P_A^0}, \qquad (3)$$

$$-\ln(1-x_B) = \frac{k_B K_B}{1+K'_A P_A^0}\cdot\tau , \qquad (4)$$

where k_B, K_B, P_B, and x_B are the rate constant, adsorption constant, partial pressure, and conversion of the weakly adsorbing alkene B, respectively. K'_A is the adsorption constant of the strongly adsorbing molecule A on the catalytic site for the hydrogenation of alkene B.

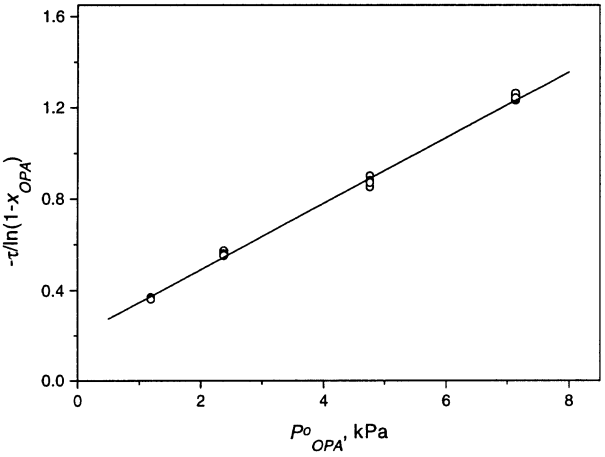

Figure 1. Determination of the kinetic parameters in the HDN of ortho-propylaniline over $NiMo/Al_2O_3$ at 623 K and 3.0 MPa by eq. (2).

Since $k_B K_B$ can be calculated from the reaction of pure B ($P_i = 0$ and $k_B K_B \ll 1$), K'_A is then calculated from the slope of the $-\ln(1 - x_{CHE})$ versus τ plot in the presence of inhibitor P_A. Examples are given in figure 2. This method can also be applied to determine the inhibitive adsorption constant of quinoline-type compounds on the conversion of OPA, an intermediate in the HDN network of quinoline whose HDN is strongly inhibited, and for which the inhibitive effect has never been quantified. The experimental results are shown in figure 3.

It proved impossible to distinguish the adsorption constants of quinoline (Q) and 1,2,3,4-tetrahydroquinoline (THQ1), as well as of 5,6,7,8-tetrahydroquinoline (THQ5) and decahydroquinoline (DHQ) in the above measurement due to fast (de)hydrogenation of the heterocyclic ring of quinoline. The linearity of figure 3 also indicates that the inhibition strengths of Q and THQ5 (and of THQ1 and DHQ) on the hydrogenation of the phenyl group of OPA differ hardly.

Once the inhibitive adsorption constant of DHQ on the catalytic site for C(sp^3)–N bond cleavage is obtained, the inhibitive adsorption constant of anilines on the C(sp^3)–N bond cleavage site can be calculated from eq. (6) by comparing the HDN results of DHQ with those of DHQ + OEA (OEA = ortho-ethylaniline, similar to OPA) at low conversions, and by assuming that all the quinoline-type compounds exhibit the same adsorption strength on the C(sp^3)–N bond cleavage site:

$$-\frac{dP_{DHQ,alone}}{d\tau} = \frac{k_{DHQ} K^{C-N}_{DHQ} \cdot P_{DHQ}}{1 + K^{C-N}_{DHQ} \cdot P^0_{DHQ}}$$

and

$$-\frac{dP_{DHQ,+OEA}}{d\tau} = \frac{k_{DHQ} K^{C-N}_{DHQ} \cdot P_{DHQ}}{1 + K^{C-N}_{DHQ} \cdot P^0_{DHQ} + K^{C-N}_{OEA} \cdot P^0_{OEA}}, \quad (5)$$

thus

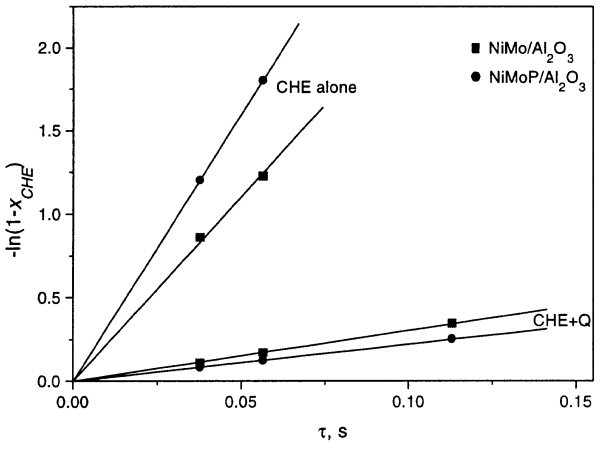

Figure 2. Hydrogenation of cyclohexene at 623 K, 3.0 MPa and $P_{H_2S} = 6.5$ kPa over $NiMo/Al_2O_3$ and $NiMoP/Al_2O_3$ catalysts in the presence and absence of quinoline ($P^0_Q = 4.8$ kPa, $\tau = 0.038$, 0.057 and 0.11 s).

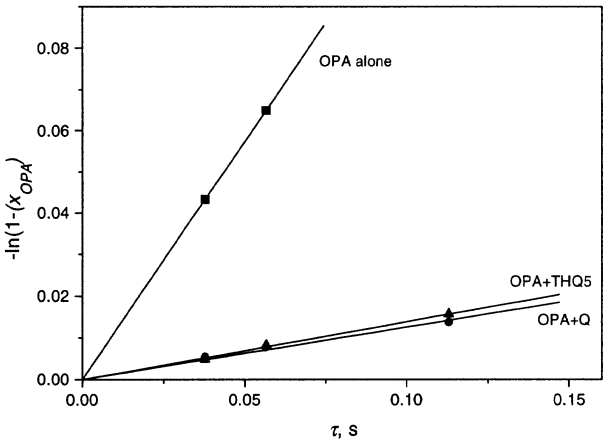

Figure 3. HDN of ortho-propylaniline over $NiMo/Al_2O_3$ at 623 K, 3.0 MPa and $P_{H_2S} = 6.5$ kPa in the presence and absence of quinoline and 5,6,7,8-tetrahydroquinoline ($P^0_Q = P^0_{THQ5} = 4.8$ kPa).

$$\frac{\ln(1 - x_{DHQ,alone})}{\ln(1 - x_{DHQ,+OEA})} = 1 + \frac{K^{C-N}_{OEA} \cdot P^0_{OEA}}{1 + K^{C-N}_{DHQ} \cdot P^0_{DHQ}}, \quad (6)$$

where $x_{DHQ,alone}$ and $x_{DHQ,+OEA}$ are the C–N bond cleavage conversions of DHQ in the HDN of DHQ alone and in the simultaneous reaction of DHQ and OEA, respectively; P^0_{DHQ} and P^0_{OEA} are the initial partial pressures of DHQ and OEA in the reactant, K^{C-N}_{DHQ} and K^{C-N}_{OEA} the inhibitive adsorption constants of OEA and DHQ on the catalytic site for the C(sp^3)–N bond cleavage, respectively; and k_{DHQ} is the rate constant of the C(sp^3)–N bond cleavage of DHQ. The adsorption constants obtained by the methods described above are presented in table 1. The 95% confidence ranges of these constants are all within ±20% of the reported values.

4. Discussion

4.1. The catalytic site for hydrogenation

Hydrotreating catalysts have usually been regarded as acidic and therefore gas phase proton affinities of nitrogen-containing substrates have been correlated with their adsorption constants on the catalysts. Nagai et al. reported a linear correlation between gas phase proton affinities of a series of nitrogen-containing compounds and their inhibitive adsorption constants on the hydrodesulphurization of dibenzothiophene over a $NiMo/Al_2O_3$ catalyst [21], although the measured adsorption constants of saturated amines were lower than expected on the basis of their gas phase proton affinities. A similar discrepancy exists for the quinoline-type compounds as indicated by figures 2 and 3: the adsorption constants of all four quinoline-type substrates are about equal, although the gas phase proton affinities of DHQ and THQ1 are much higher than those of Q and THQ5 [22]. To explain those differences, π-electron den-

Table 1
Adsorption constants (kPa^{-1}) of OPA and Q-type compounds for different HDN reactions on different catalytic sites over NiMo(P)/Al_2O_3 at 623 K and $P_{H_2S} = 6.5$ kPa

Reaction site	Catalyst:	$NiMo/Al_2O_3$		$NiMoP2/Al_2O_3$	
	Inhibitor:	OPA	Q-type	OPA	Q-type
$C(sp^3)$–N cleavage		0.1	0.5	0.1	0.5
alkene hydrogenation		0.4	1.6	0.9	3.4
phenyl ring hydrogenation		0.8	7	1.2	13

sity has been assumed to influence the adsorption strengths as well [23].

The adsorption constant of OPA is much smaller than those of quinoline-type compounds on the hydrogenation site, as expected from the gas phase proton affinities. La Vopa and Satterfield reported 5–20 times larger adsorption constants for quinoline-type compounds than for alkylanilines in the hydrodesulphurization of thiophene [22], which is in good agreement with the present results for the hydrogenation of the phenyl ring of OPA (table 1). The about ten times larger adsorption constant of quinoline-type compounds than of OPA, gives a quantitative explanation for the very low reactivity of anilines in the presence of quinoline-type compounds. The difference between the adsorption constants for quinoline-type compounds and alkylanilines is, however, much smaller for the catalytic site of alkene hydrogenation. The results in table 1 demonstrate that, although in both cases hydrogenation is the chemical reaction, the hydrogenation of alkene and phenyl groups takes place over different catalytic sites. The catalytic site for the latter is much more sensitive to poisoning than the former.

It is general accepted that the active sites for hydrotreating reactions consist of sulfur vacancies located at the edges and corners of the NiMoS and MoS_2 crystallites. Thus, Kasztelan et al. emphasized the role of three different coordinatively unsaturated Mo sites [24], and Eijsbouts et al. showed a correlation between the HDN activity of an industrial catalyst and the number of Mo atoms at corners and edges of the MoS_2 crystallites [25]. Since the unshared electron pair of the nitrogen atom is supposed to be involved in the adsorption on the active sites, the larger adsorption constants of OPA and quinoline-type compounds on the active site for phenyl group hydrogenation than on that for alkene hydrogenation suggests that the former site is more electrophilic. The metal atom in this site may be more uncoordinated, that is more depleted in sulphur ions. The catalytic site for the hydrogenation of a phenyl group may thus be a surface Mo or Ni entity with two or even three sulphur vacancies. This makes it very sensitive to poisoning, since a molecule adsorbing on one of the vacancies will completely incapacitate the active site for the hydrogenation of a phenyl group, although the remaining vacancy might still be an active site for alkene hydrogenation.

4.2. The catalytic sites for C–N bond cleavage

Based on the observation that H_2S promotes aliphatic $C(sp^3)$–N bond cleavage and inhibits hydrogenation, Yang and Satterfield proposed that hydrogenation occurs on a surface molybdenum vacancy and $C(sp^3)$–N bond cleavage on a Brønsted acidic site, and that dissociative adsorption of H_2S changes the former site into the latter [3,26]. This proposal is supported by the fact that sulphidic catalysts catalyse aliphatic C–N bond cleavage by NH_3 elimination or nucleophilic attack [13,27]. The transformation between the $C(sp^3)$–N bond cleavage site and the hydrogenation site is also in agreement with the fact that a high hydrogenation activity of a $NiMo/Al_2O_3$ catalyst is usually accompanied by a low $C(sp^3)$–N bond cleavage activity.

Table 1 shows that the adsorption constants of quinoline-type compounds on the aliphatic $C(sp^3)$–N bond cleavage site are much smaller than on the hydrogenation sites. This is understandable since a Brønsted SH group will be a weaker acid than a Lewis metal vacancy, thus the nitrogen-containing compounds will interact more stronger with the metal vacancy site. Table 1 also shows that the adsorption constants of alkylaniline on the $C(sp^3)$–N bond cleavage site is about 5 times smaller than that of quinoline-type compounds, and that introduction of phosphorus has no influence on the adsorption constants on this site, which is in contrast to that on the hydrogenation sites. This demonstrates the importance of SH groups for $C(sp^3)$–N bond cleavage. The adsorption of nitrogen-containing molecules occurs probably via these SH groups, and therefore, the other constituents of the catalyst (Ni, Mo, P) will not have a direct influence on the adsorption strengths.

The catalytic site for $C(sp^2)$–N bond cleavage of aromatic amines is different from that for aliphatic $C(sp^3)$–N bond cleavage, because H_2S was found to inhibit the former and to promote the latter, while phosphorus had the opposite effect. Furthermore, in the HDN of alkylanilines, the absence of Ni and presence of phosphorus in $NiMoP/Al_2O_3$ catalysts especially favoured the $C(sp^2)$–N bond hydrogenolysis path [5,6]. This indicates that the catalytic site for $C(sp^2)$–N bond hydrogenolysis is different from that for hydrogenation of a phenyl group as well. The favourable influence of phosphorus on the $C(sp^2)$–N bond cleavage activity of $NiMo/Al_2O_3$ cat-

alysts is explained by the replacement of some surface S^{2-} by P^{3-} ions, creating a more reduced metal site that is responsible for the $C(sp^2)$–N bond cleavage. This is in line with the HDN of quinoline over Mo_2N catalysts [28] and the HDS of benzothiophene over reduced sulphided $CoMo/Al_2O_3$ catalyst [29]. In the HDN over Mo_2N which has metallic properties, only $C(sp^2)$–N bond cleavage occurred, and reduction of a sulphided $CoMo/Al_2O_3$ catalyst favoured the direct hydrogenolysis of sulphur from benzothiophene. An EXAFS measurement showed that the Mo–S coordination number decreased after reduction of the sulphided $CoMo/Al_2O_3$ catalyst [29]. This suggests that sites active for hydrogenolysis are associated with metallic properties of the catalyst.

The necessity for distinct catalytic sites for hydrogenolysis and hydrogenation is especially clear in the hydrodesulphurization of dibenzothiophene, since the addition of a nitrogen-containing substrate was found to inhibit the hydrogenation path and to promote the hydrogenolysis path [21]. Unfortunately, under our reaction conditions it was not possible to determine the adsorption constants of nitrogen-containing compounds on the catalytic site for the $C(sp^2)$–N bond cleavage of OPA due to the relatively low contribution of this hydrogenolysis path ($< 10\%$) to the total HDN [7]. This information may be obtained in future by a careful design of experiment and catalyst.

5. Conclusions

At least four different catalytic sites involved in the HDN reactions over sulphided Mo-based catalysts could be distinguished from competitive adsorption experiments. One site is responsible for the $C(sp^3)$–N bond cleavage of saturated amines; it is promoted by H_2S and Ni, and impaired by phosphorus. This site can be an SH group created by dissociative adsorption of H_2S under the hydrotreating conditions. Another site is responsible for the hydrogenation of alkenes. It is promoted by Ni and phosphorus, but inhibited by H_2S.

A third site is required for the direct $C(sp^2)$–N bond cleavage of anilines. This site is promoted by phosphorus, impaired by H_2S, and is characterised by a more reduced environment of Mo site on the surface [6]. Hydrogenation of the phenyl ring needs still another site which resembles that of the NiMoS phase, is promoted by Ni and phosphorus, but poisoned by H_2S [7]. This site is different from that for the hydrogenation of alkenes, and may be a doubly or triply coordinatively unsaturated site.

Removal of nitrogen atoms from aromatic nitrogen-containing molecules takes place via a sequence of reaction steps: hydrogenation of the aromatic rings, NH_3 elimination or C–N bond hydrogenolysis, and olefin hydrogenation. The very different adsorption constants show that these reaction steps cannot be lumped together in one kinetic equation, because every reaction takes place on a different catalytic site which differ in its ability to bind reactant, intermediates and products.

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