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Existence of different catalytic sites in HDN catalysts

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Abstract

The hydrodenitrogenation (HDN) of *ortho*-propylaniline (OPA) has been studied over NiMoP/Al_2O_3 catalysts with 0–4 wt% phosphorus, 0–3 wt% nickel and 0–12 wt% molybdenum. The HDN reaction was found to proceed via two reaction paths: hydrogenation of the phenyl ring followed by NH_3 elimination to propylcyclohexene, which further (de)hydrogenated to propylcyclohexane and propylbenzene, and direct C(sp^2)–N bond hydrogenolysis to propylbenzene. The first denitrogenation path was promoted by Ni and inhibited by the presence of H_2S, where hydrogenation of the phenyl ring was suggested to be the rate-limiting step. The second denitrogenation path was promoted by phosphorus and inhibited by the presence of H_2S and Ni.

It is suggested that at least two different kinds of catalytic sites are acting in the HDN of OPA over a sulphided Mo-based catalyst. The first site bears the characteristics of the Ni–Mo–S phase, is strongly promoted by Ni and is responsible for the hydrogenation reaction. The second site is a site associated with Mo, its activity is enhanced by phosphorus, but diminished by Ni and H_2S, and it is specially active for the C(sp^2)–N bond cleavage reaction. Both sites are different from the catalytic site which is responsible for the aliphatic C(sp^3)–N bond cleavage.

Keywords: Hydrodenitrogenation of *ortho*-propylaniline; NiMoP/Al_2O_3 catalysts; Catalytic sites; Effect of Ni, Mo, P and H_2S

1. Introduction

Although hydrotreating catalysts have received a wide commercial acceptance in the oil industry, there is still a lack of fundamental understanding about the nature of the active sites on the catalyst. Several models have been advanced to account for the catalytic activity of sulphided Ni(Co)Mo(W) catalysts, amongst others the monolayer model, the pseudo-intercalation model, the remote-control model and the Co–Mo–S phase model [1]. The most recent and well accepted Co–Mo–S phase model which has initially been proposed for the HDS reaction over CoMo catalysts [2], has also been extended to NiMo catalysts and to the HDN reaction [3]. In the Ni–Mo–S phase model, Mo is assumed to be present in the form of MoS_2 with a layer structure, Ni is located at the edges of the MoS_2 crystallites, and the promoted edge sites are responsible for the hydrotreating reactions [2]. In a recent work, it was suggested that edge sites at the top and bottom of a multilayer MoS_2 structure have a different reactivity than those at the middle of such a structure [4]. It has also been suggested that introduction of phosphorus to a NiMo/Al_2O_3 catalyst can change the geometry of the layered MoS_2 structure and therefore the relative amounts of the different sites [5,6].

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In contrast to the general agreement on the active phase structure of the NiMo/Al_2O_3 catalyst, the question whether Ni or Mo is the catalytic centre in the catalyst is still under discussion. Since pure molybdenum sulphide is much more active in hydrotreating reactions than pure nickel sulphide, over the years Mo has been recognised as the active component and Ni (Co) as the promoter. However, from a HDS study of carbon-supported catalysts, it was shown that a Co/C catalyst can be as active as a CoMo/C catalyst, and therefore Co has also been proposed as the active component [7,8].

In the present work the effect of Ni, Mo and P in the HDN of *ortho*-propylaniline (OPA) over supported NiMoP/Al_2O_3 catalysts was studied both in the presence and absence of H_2S. Simultaneous hydrogenation of cyclohexene (CHE) and HDN of *ortho*-ethylaniline was studied as well, in order to elucidate the reaction mechanisms and the nature of the active sites. The presence of different catalytic sites which are responsible for the direct C(sp^2)–N bond hydrogenolysis, hydrogenation and C(sp^3)–N bond cleavage during the HDN reaction has been evidenced.

2. Experimental

Catalysts were prepared by means of the incipient wetness impregnation method. Aqueous solutions containing the required amount of nickel nitrate and/or ammonium heptamolybdate and/or *ortho*-phosphoric acid were prepared to impregnate the γ-Al_2O_3 support which had a particle size of 0.25–0.45 mm. The samples were impregnated at room temperature for 4 h, dried at 393 K for 12 h and then calcined at 773 K for 4 h. Details of the catalyst preparation can be found elsewhere [9]. The catalysts used in this work usually had a composition of 3 wt% Ni and/or 8 wt% Mo and/or 2 wt% P, unless stated otherwise.

The HDN reactions were carried out in a continuous-flow microreactor. A sample of 0.5 g catalyst (0.1 g catalyst for kinetic studies) diluted with 9.5 g SiC was first 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 a gas/liquid ratio of 3600 (v/v). The initial reactant concentration (A_0) was set at 4.76 kPa. In the simultaneous reaction of decahydroquinoline (DHQ), *ortho*-ethylaniline (OEA), and cyclohexene (CHE), the initial reactant concentration of DHQ and OEA was 4.76 kPa, and that of CHE was 1.59 kPa. Dimethyldisulphide was added to the liquid reactant to generate H_2S in the reaction stream ($H_2S/H_2 = 3.0 \times 10^{-3}$ mol/mol). Reaction products were analysed by on-line gas chromatography with a Shimadzu GC-14A gas chromatograph equipped with a 50 m CP Sil-5 fused silica capillary column and a flame ionisation detector. Samples were taken after 25 h (50 h for kinetic studies) on stream when the activity of the catalyst was stable, with n-nonane as the internal standard. Space time was defined as $\tau = \epsilon \cdot V_{cat}/v_{gas}$, where ϵ is the void fraction of the catalyst bed ($\epsilon = 0.4$), V_{cat} is the volume of the catalyst, and v_{gas} is the volume flow rate of the gas phase reactant. The space time (τ) was changed by varying the liquid and gaseous reactant flow rates while keeping their ratio constant.

3. Results and discussion

3.1. Reaction pathways and product compositions

The HDN reaction network of *ortho*-propylaniline is shown in Fig. 1. The C–N bond cleavage reaction can proceed via two reaction pathways: hydrogenation of OPA to propylcyclohexylamine (PCHA) followed by a C(sp^3)–N bond cleavage to propylcyclohexene (PCHE) which can be further hydrogenated to propylcyclohexane (PCH) or dehydrogenated to propyl-

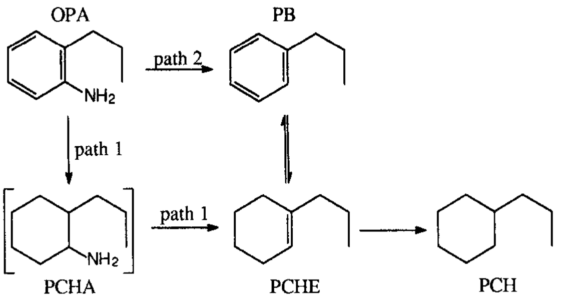

Fig. 1. HDN reaction network of *ortho*-propylaniline.

benzene (PB) (path 1), and direct C(sp^2)–N bond cleavage of OPA to PB (path 2). In the literature, it has been suggested that the HDN of anilines proceeds predominantly through path 1 [10–12].

To study the HDN reaction network of OPA we have carried out a simultaneous reaction of cyclohexene (CHE) and *ortho*-ethylaniline (OEA, same reactivity as OPA). The reaction was performed at 643 K, since at lower temperatures hardly any aromatic product benzene (B) could be observed from the dehydrogenation of CHE. However, since the conversions of pure OPA and CHE were too high at 643 K, we introduced decahydroquinoline (DHQ, $A_0 =$ 4.76 kPa) to the reaction stream as an inhibitor. The results are given in Table 1.

Table 1 shows that in the reaction product of OEA, the ratio of ethylcyclohexane to ethylbenzene (ECH/EB) decreases as the space time decreases, while in the reaction of CHE the ratio of CH/B (CH = cyclohexane) stays more or less constant. If the aromatic EB product in the HDN of OEA would only be produced by the dehydrogenation of ethylcyclohexene (ECHE), as in the case of B from CHE, the ratio of ECH/EB would stay constant as the space time changed. Because in that case the formation of ECH and EB would only depend on the rate constants of ECHE → ECH and ECHE → EB, which will not be influenced by the space time.

The simultaneous reaction of OPA and EB was also performed at 643 K. Even at the highest space time the conversion of EB was only 1.5%. This proves that under our reaction conditions EB can hardly be further converted, once formed. This result excludes the possibility that the changes of the ECH/EB ratios are due to the further conversion of EB after it is formed, and indicates that there must be other reaction pathways to account for the formation of EB. This can only be the direct C(sp^2)–N bond cleavage of OEA. The decreased ECH/EB ratio at smaller space time confirms that EB is formed as a primary HDN product.

3.2. HDN of *ortho-propylaniline at 623 K*

The results of the HDN of OPA at 623 K over a phosphorus-containing and a phosphorus-free catalyst both in the presence and absence of H_2S are given in Table 2.

In contrast to the negative effect of phosphorus in the HDN of piperidine and decahydroquinoline [9,13], it is evident from Table 2 that phosphorus has a promotional effect on the HDN of OPA both in the presence and absence of H_2S over the $NiMo/Al_2O_3$ catalyst. When a

Table 1
Simultaneous reaction of OEA and CHE over $NiMo/Al_2O_3$ at 643 K in the presence of DHQ and H_2S

Space time (τ, ms)	CHE		OEA			
	conv. (%)	CH/B	ECH	ECHE	EB	ECH/EB
380	99.6	45	84.6	0	13.7	6.2
231	99.3	45	15.3	3.4	2.5	6.1
114	94.4	46	8.3	3.4	1.7	4.9
56	68.6	46	3.7	2.5	1.0	3.7
38	–	–	2.6	1.8	0.9	2.9

Table 2
HDN of OPA at 623 K and 3.0 MPa (τ = 0.57 s)

Catalyst	H_2S	DN (%)	HDN products				PCH/PB ratio
			< C9	PCH	PCHE	PB	
$P(2)/Al_2O_3$	yes	0	0	0	0	0	–
$Ni(3)Mo(8)/Al_2O_3$	yes	65.8	0.4	55.5	4.3	5.3	10.5
$Ni(3)Mo(8)P(2)/Al_2O_3$	yes	90.9	0.5	75.3	2.9	12.2	6.1
$P(2)/Al_2O_3$	no	0	0	0	0	0	–
$Ni(3)Mo(8)/Al_2O_3$	no	82.3	0.2	68.4	1.6	12.1	5.6
$Ni(3)Mo(8)P(2)/Al_2O_3$	no	96.0	0.3	75.3	1.0	19.4	3.9

$P(2)/Al_2O_3$ sample was used as the catalyst, no HDN conversion was observed at all. The function of phosphorus in the catalyst thus must arise from its influences on Ni and Mo.

One may argue that in the HDN of OPA, reaction path 1 is predominant and that the rate-limiting reaction step is the hydrogenation of the phenyl ring, different from that of the HDN of DHQ and piperidine. However, the results of the simultaneous reaction of piperidine and cyclohexene have already demonstrated that phosphorus has an inhibiting effect on the hydrogenation reaction [9]. Therefore, we have to assume that different catalytic sites are present in the sulphided catalyst in order to understand the different behaviours of phosphorus in the HDN of OPA on the one hand and piperidine and DHQ on the other hand.

Table 2 also shows that the introduction of phosphorus to a $NiMo/Al_2O_3$ catalyst changes the HDN product selectivity, P-containing catalysts favour the formation of PB. The formation of PB was especially favoured in the absence of H_2S. A kinetic study shows that as space time approaches zero (Fig. 2), the HDN product selectivity of PB does not approach zero, confirming that at least part of the PB in the product is a primary HDN product, especially in the absence of H_2S.

3.3. *The function of Ni and Mo in the catalyst*

Table 3 shows that $Ni(3)/Al_2O_3$ alone has almost no HDN activity. Even a $Ni(3)/Al_2O_3$ catalyst which was not calcined (to avoid the loss of surface Ni through its interaction with the Al_2O_3 support) had a very low activity. $Mo(8)/Al_2O_3$ alone exhibits a substantial HDN activity which is further promoted by phosphorus and inhibited by H_2S, as in the case of the

Table 3
HDN of OPA at 623 K and 3.0 MPa (τ = 0.57 s)

Catalyst	H_2S	DN (%)	HDN products				PCH/PB ratio
			< C9	PCH	PCHE	PB	
$Ni(3)/Al_2O_3$	yes	1.2	0	0.1	0.9	0.1	1.5
$Ni(3)/Al_2O_3$ (uncalcined)	yes	0.7	0	0	0.7	0	–
$Mo(8)/Al_2O_3$	yes	13.7	0	6.5	4.7	2.5	2.6
$Mo(8)P(2)/Al_2O_3$	yes	17.2	0	8.6	3.9	4.7	1.8
$Mo(12)P(2)/Al_2O_3$	yes	27.2	0	15.0	4.7	7.5	2.0
$Ni(3)/Al_2O_3$	no	2.3	0	0.1	2.1	0.1	1.4
$Ni(3)/Al_2O_3$ (uncalcined)	no	1.7	0	0	1.7	0	–
$Mo(8)/Al_2O_3$	no	37.7	0	12.2	5.6	19.9	0.61
$Mo(8)P(2)/Al_2O_3$	no	52.5	0	14.2	6.9	31.4	0.45
$Mo(12)P(2)/Al_2O_3$	no	74.1	0	20.5	9.5	44.1	0.46

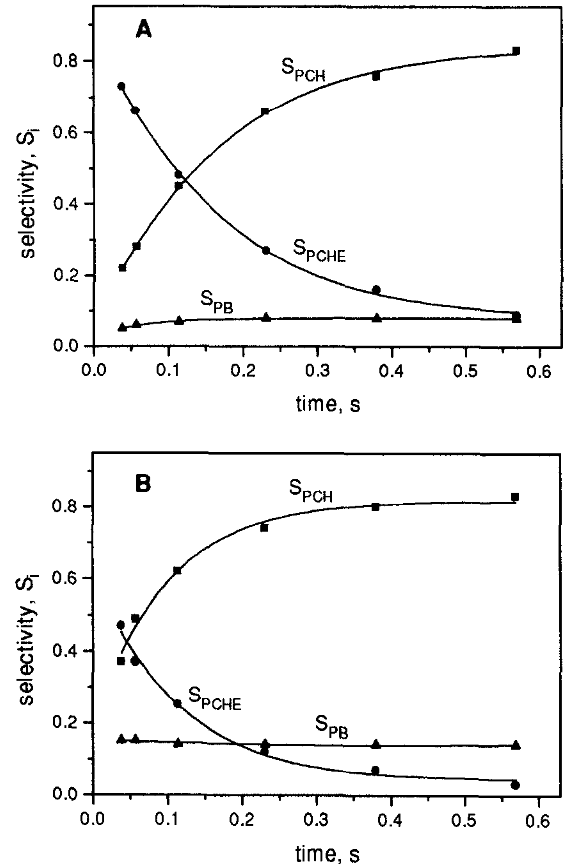

Fig. 2. Product selectivity in the HDN of OPA over NiMo/Al_2O_3 ($S_i = C_i / \Sigma C_i$) in the presence (A) and absence (B) of H_2S.

Ni(3)Mo(8)/Al_2O_3 catalyst. It thus looks as if molybdenum (not nickel) is responsible for the HDN reaction of OPA.

Table 3 also shows that in the absence of H_2S, the concentration of PB changes greatly while the concentration of PCH hardly changes between the Mo(8)/Al_2O_3 and Mo(8)P(2)/Al_2O_3 catalysts. The concentration of PB from the Mo(P)/Al_2O_3 catalysts was even higher than that produced by the corresponding NiMo(P)/Al_2O_3 catalysts in the absence of H_2S, although the total HDN conversion was higher for the latter catalyst. This suggests that the majority of the HDN reaction took place through the direct C(sp^2)–N bond cleavage (path 2) over the Ni-free catalysts in the absence of H_2S, considering that dehydrogenation of PCHE to PB occurs to a much lesser extent.

Therefore, Mo(8)/Al_2O_3 and Mo(8)P(2)/Al_2O_3 catalysts are better catalysts for the direct C–N bond hydrogenolysis than the corresponding Ni-containing catalysts. Introducing Ni diminishes the direct hydrogenolysis activity but creates new hydrogenation activity. As a consequence, most of the HDN reaction takes place through hydrogenation to a saturated amine intermediate (PCHA), followed by an elimination reaction to PCHE, and further hydrogenation to PCH or dehydrogenation to PB (path 1) over the Ni-containing catalysts.

When increasing the Mo content in a MoP/Al_2O_3 catalyst from 8 to 12%, the HDN conversion also increases by about 50%, both in the presence and absence of H_2S (Table 3), while the product selectivities for PB (path 2) and PCHE + PCH (path 1) stay unchanged (Table 4). This implies that increasing the Mo content in the catalyst just increases the number of the catalytic sites, without changing their nature.

Table 4
Selectivities of the HDN products of OPA at 623 K and $\tau = 0.11$ s

Catalyst	With H_2S			Without H_2S		
	S_{PCH}	S_{PCHE}	S_{PB}	S_{PCH}	S_{PCHE}	S_{PB}
Ni(3)Mo(8)/Al_2O_3	0.45	0.48	0.07	0.62	0.25	0.14
Ni(3)Mo(8)P(2)/Al_2O_3	0.39	0.51	0.10	0.56	0.24	0.20
Mo(8)/Al_2O_3	0.24	0.52	0.24	0.10	0.32	0.58
Mo(8)P(2)/Al_2O_3	0.15	0.58	0.27	0.07	0.33	0.60
Mo(12)P(2)/Al_2O_3	0.23	0.49	0.28	0.12	0.27	0.61

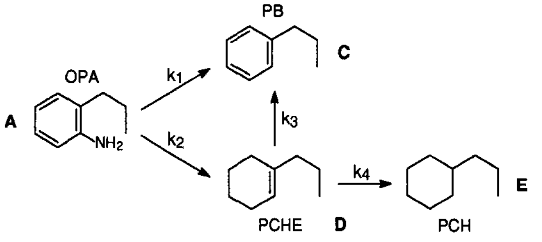

Fig. 3. Simplified HDN reaction network of OPA.

3.4. Kinetics analysis

Since the PCHA intermediate between OPA and PCHE was not observed under our reaction conditions and the hydrogenation of PB to PCH and PCHE hardly proceeds, a simplified reaction network can be drawn as follows (Fig. 3):

Assuming that the HDN reactions follow a first order Langmuir–Hinshelwood mechanism and that both catalytic sites have the same adsorption constant for OPA (K_A), then

$$\frac{dA}{dt} = -(k_1 + k_2)K_A A/\Sigma(1 + K_i I)$$

$$\frac{dC}{dt} = k_1 K_A A/\Sigma(1 + K_i I)$$

where A and C represent the OPA and PB concentrations, respectively, I stands for the concentration of all other components in the reaction stream, k_i is a rate constant and K_i is an adsorption constant. This gives:

$$1 - x_A = \frac{k_1 + k_2}{k_1} \cdot x_C$$

(x_C and x_A are the conversions of OPA and PB, respectively)

The ratio of k_2/k_1 can be calculated from the concentrations of OPA and PB in the reaction product at time zero, when the direct $C(sp^2)$–N bond cleavage was the only source of PB formation. The results obtained from analyzing data as in Fig. 4 are given in Table 5.

The ratios of the rate constants clearly show that reaction path 1 is favoured by the presence of Ni, and path 2 is favoured by the presence of phosphorus and absence of H_2S. Independent of the presence or absence of Ni, introducing phosphorus to the catalyst shifts the HDN reaction of OPA from hydrogenation of the phenyl ring to hydrogenolysis of the $C(sp^2)$–N bond. This means that the nature of the catalytic sites must have changed. In addition, the ratio of k_2/k_1 stayed constant while the total HDN conversion increased when the Mo content was increased in a $MoP(2)/Al_2O_3$ catalyst, confirming the qualitative results obtained in the foregoing section that an increase of the Mo content only changes the number of the catalytic sites.

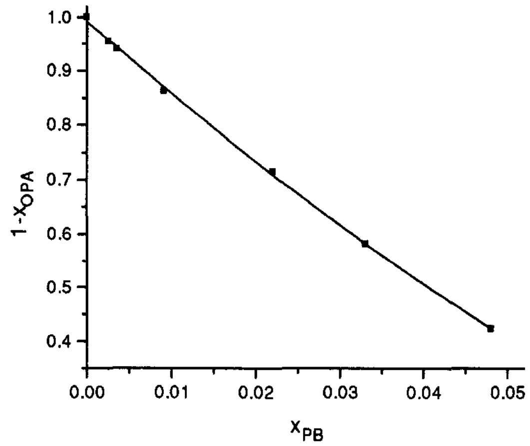

Fig. 4. HDN of OPA at 623 K over $NiMo/Al_2O_3$ in the presence of H_2S.

3.5. Nature of the catalytic sites

The catalytic sites of sulphided Co(Ni)Mo(W) catalysts have often been assumed to be sulphur vacancies at the surface of the MoS_2 crystallites. Yang and Satterfield [14] suggested that the surface Mo vacancy is responsible for the

Table 5
Relative reaction rate constants (k_2/k_1) in the HDN of OPA at 623 K

Catalyst	With H_2S	Without H_2S
$Ni(3)Mo(8)/Al_2O_3$	14.3	8.6
$Ni(3)Mo(8)P(2)/Al_2O_3$	9.7	4.6
$Mo(8)/Al_2O_3$	2.7	0.60
$Mo(8)P(2)/Al_2O_3$	2.0	0.52
$Mo(12)P(2)/Al_2O_3$	2.0	0.54

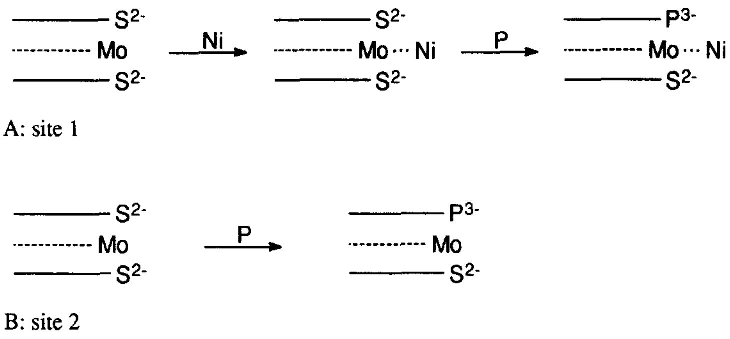

Fig. 5. Models of the catalytic sites on supported (Ni)Mo(P)/Al_2O_3 catalysts.

hydrogenation reaction, H_2S adsorbs on this vacancy and changes it into a Brønsted acid site which is active in the cleavage of an aliphatic C–N bond. From the above results it can be concluded that there are two kinds of catalytic sites on the NiMoP/Al_2O_3 catalysts in the HDN of OPA: the Ni-associated site (Ni–Mo–S) and the Mo-associated site. The activity of the former catalytic site is enhanced by the presence of Ni, and diminished by H_2S. This first kind of site is responsible for the hydrogenation of the phenyl group of an OPA molecule which is the rate-limiting reaction step in the HDN of OPA through path 1. The latter site, poisoned by H_2S and promoted by phosphorus, is especially suited for C(sp^2)–N bond cleavage and might have special affinity for aniline-type compounds. Both sites are different from the catalytic site in the HDN of piperidine and DHQ (C(sp^3)–N bond cleavage by elimination), which is promoted by H_2S and Ni, and diminished by phosphorus. The very low conversion of piperidine over Mo(P)/Al_2O_3 catalysts [9] (only C(sp^3)–N bond cleavage involved) compared with that of OPA also supports such a suggestion.

Both active sites are functioning in the HDN of OPA. In the presence of H_2S, where the first kind of active site is dominating, introduction of Ni to a MoP/Al_2O_3 catalyst not only increases the overall HDN activity, but also increases the concentration of PB in the product (reaction path 1, PB is formed from PCHE). In the absence of H_2S, where the contribution from the second kind of active site becomes dominating, introduction of Ni still increases the overall HDN activity (path 1 + path 2), but the concentration of PB in the product decreases, implying that the reaction path 2 is inhibited by Ni. In accordance with this, coverage of Mo ions by Ni (Co) has been reported in the literature [5].

From the results presented above, a picture of the catalytic sites on a sulphided Mo-based catalysts can be drawn (Fig. 5).

In the layered structure of MoS_2, Mo at the edges is responsible for the C(sp^2)–N bond hydrogenolysis reaction. Replacement of a sulphur anion by a phosphorus anion makes the environment of the Mo atom more electron rich, which helps to break the C(sp^2)–N bond. Evidence for such a P–S exchange reaction over sulphided catalyst surface has been presented [15]. In accordance with our suggestion, it has been reported from the reaction of a series of C_6H_5X molecules (X = R, Cl, NH_2, etc.) over NiMo/Al_2O_3 catalysts that the catalytic site for the direct hydrogenolysis of the C(sp^2)–X bond is associated with an electron-donating character and that the site for the hydrogenation reaction is associated with an electron-withdrawing character [12,16].

Since the Mo site is blocked in the nickel promoted catalyst, direct hydrogenolysis of the C(sp^2)–X bond is limited in the Ni-containing catalysts. In turn, a new Ni-promoted catalytic site is created which is very active in the hydrogenation reaction. The HDN of OPA proceeds via different reaction pathways over different catalysts.

4. Conclusions

At least three different kinds of catalytic sites are present in the sulphided NiMo/Al_2O_3 catalysts. One of them (site 3) is acidic and arises from the adsorption of H_2S on the metal sulphide surface in the reaction stream [14]; this site is active for C(sp^3)–N bond cleavage in the HDN reaction. It is promoted by H_2S and Ni, but diminished by phosphorus.

The two other catalytic sites prevail in the HDN of OPA, where the reaction proceeds via two reaction paths: hydrogenation of the phenyl group followed by a C(sp^3)–N bond cleavage, and direct C(sp^2)–N bond cleavage. In the first reaction path hydrogenation is rate-limiting and a catalytic site with the characteristics of the NiMoS phase is needed (site 1), it is strongly promoted by Ni and diminished by H_2S. In the second reaction path, a catalytic site which is only associated with Mo is required (site 2). This site is enhanced by phosphorus, but diminished by Ni and H_2S.

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