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The effect of phosphorus on the HDN reaction of piperidine, decahydroquinoline and ortho-propylaniline over Ni–MoS_2/Al_2O_3 catalysts

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The hydrodenitrogenation (HDN) of piperidine, decahydroquinoline (DHQ) and ortho-propylaniline (OPA) has been studied over NiMo(P)/Al_2O_3 catalysts at 593 K and 3.0 MPa in order to understand the effect of phosphorus on the elementary HDN reaction steps. Phosphorus exhibited a negative effect on the HDN of piperidine and DHQ, both on the C–N bond cleavage reaction and on the subsequent hydrogenation reaction of alkene to alkane. A P/Al_2O_3 catalyst showed no HDN activity at all, neither with piperidine, nor with DHQ. A positive effect of phosphorus was observed in the HDN of OPA, where hydrogenation of the aromatic ring is needed and is rate limiting. It is suggested that introduction of phosphorus to NiMo/Al_2O_3 catalysts on the one hand decreases the available support surface area, and as a consequence the dispersion of the Ni-Mo-S phase and thus the capacity for C–N bond breaking and olefin hydrogenation. On the other hand, phosphorus induces either new or more active sites for the hydrogenation of aromatics.

Keywords: hydrodenitrogenation; piperidine; decahydroquinoline; ortho-propylaniline; C–N bond cleavage; NiMo(P)/Al_2O_3 catalyst; effect of phosphorus

1. Introduction

NiMoP/Al_2O_3 catalysts are widely used in industrial hydrodenitrogenation (HDN) of oil fractions. Phosphorus is a promoter which not only enhances the solubility of molybdate by the formation of phospho-molybdate complexes in the impregnation solution during catalyst preparation [1], but also increases the HDN activity of NiMoP/Al_2O_3 catalysts [2–4], both in model compound studies and in industrial performance. Several explanations have been advanced to account for this catalytic promotion effect of phosphorus, such as a decrease in the formation of coke [5] and thus in the deactivation, an increase in the dispersion of the active component [6,7], the formation of new catalytic active sites [3,8], and an increase in the acidity of the catalyst support thus increasing the capability to break the C–N bond [9]. The direct involvement of phosphorus in the C–N bond cleavage reaction of the saturated reaction intermediates was even proved in a dual bed HDN study of quinoline [3].

However, discrepancies exist in the literature about the effect of phosphorus. Although it has been suggested that introducing phosphorus to a NiMo/Al_2O_3 catalyst changes the type I NiMoS phase to the type II NiMoS phase [3,10], and that this is the explanation for the higher activity observed in the HDN of quinoline, a higher HDS activity of the type II NiMoS phase as initially proposed [11] was not observed over the P-containing catalyst. Moreover, both a decreased and an increased Mo dispersion over sulfided NiMo(P)/Al_2O_3 catalysts upon addition of phosphorus has been observed [3,8]. The effect of phosphorus on the acidity of the catalyst is not clear yet [4].

In the present study, the effect of phosphorus in the HDN of piperidine, decahydroquinoline (DHQ) and ortho-propylaniline (OPA) over a series of NiMo/Al_2O_3 catalysts with different phosphorus content (1–4 wt%) was studied. Direct evidences for the function of phosphorus in the C–N bond cleavage reaction were obtained.

2. Experimental

Catalysts were prepared by means of the incipient wetness impregnation method. γ-Al_2O_3 of particle size 0.25–0.45 mm was first co-impregnated with aqueous solutions of ammonium heptamolybdate and ortho-phosphoric acid. 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. The resulting Mo(P)/Al_2O_3 catalysts were further impregnated with an aqueous solution of nickel nitrate, dried and calcined as indicated above. The pH of the impregnating solution was in some cases adjusted by nitric acid or ammonium hydroxide. Further information of the catalyst preparation can be found elsewhere [12]. The original γ-Al_2O_3 (Condea, surface area 228 m^2/g, pore volume 0.49 ml/g) had an incipient water pore volume of 0.75 ml/g. Mo, Ni and P loadings, surface areas (SA) and pore volumes (PV) of the catalysts prepared are listed in table 1.

The HDN reactions were carried out in a continuous-flow microreactor. A sample of 0.5 g catalyst diluted with 9.5 g SiC was first sulfided in situ with a mixture of 10% H_2S and H_2 at 643 K and 1.5 MPa for 4 h. After sulfidation the reactor was cooled down in the flowing sulfiding gas to 593 K and the pressure was increased to 3.0 MPa. Liquid feed was fed to the reactor by means of a high pressure pump (Spectra Physics) at a rate of 0.1 ml/min. The space velocity was set at 1.0×10^{-2} mol-piperidine/h g-catalyst and 3.15×10^{-3} mol-DHQ(OPA)/h g-catalyst, and the hydrogen flow rate at 350 ml/min. Dimethyldisulfide was added to the liquid reactant to generate H_2S in the reaction mixture ($H_2S/H_2 = 3.0 \times 10^{-3}$ mol/mol). Reaction products were analysed by on-line gas chromato-

Table 1
Physical properties of the catalysts

Catalyst	SA (m^2/g)	PV (ml/g)	Composition (wt%)		
			Ni	Mo	P
γ-Al_2O_3	228	0.49	0	0	0
P(2)/Al_2O_3	200	0.45	0	0	2.0
NiMo/Al_2O_3	212	0.40	3.0	8.0	0
NiMo(1)/Al_2O_3	194	0.37	3.0	8.0	1.0
NiMoP(2)/Al_2O_3	174	0.35	3.0	8.0	2.0
NiMoP(4)/Al_2O_3	148	0.29	3.0	8.0	4.0

graphy with a Shimadzu GC-14A gas chromatograph equipped with a 50 m CP Sil-5 fused silica capillary column (Chrompack, 0.50 mm i.d. and 1.05 μm film) and a flame ionisation detector. Samples were taken after 6 h (piperidine) or 25 h (DHQ and OPA) on stream when the activity was relatively stable. HDN conversions were calculated from the formation of hydrocarbons per mole reactant fed, with *n*-nonane as the internal standard.

3. Results and discussion

3.1. PIPERIDINE

In the HDN of piperidine two C–N bond cleavage reactions are needed to remove the nitrogen atom (fig. 1). In the first C–N bond cleavage pentylamine (PA) is formed, which very easily undergoes a second C–N bond cleavage to C_5 hydrocarbons as shown by the low concentration of PA present in the reaction product (table 2). Pentenylamine ($C_5H_9NH_2$), which should be the first product formed by N-elimination from piperidine, was not observed. Once formed, it is probably immediately hydrogenated to pentylamine before desorbing from the catalyst surface.

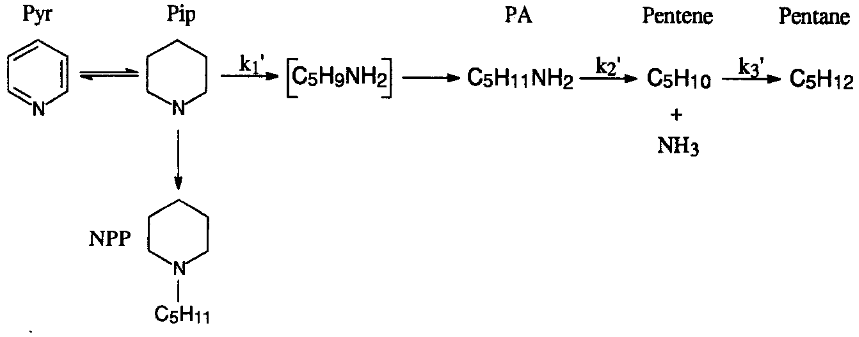

Fig. 1. HDN reaction network of piperidine.

Table 2
Effect of phosphorus in the HDN of piperidine

Catalyst	HDN (%)	Product composition (%)					
		pip.	PA	pentene	pentane	pyr.	others[a]
$P(2)/Al_2O_3$	0	99.4	0	0	0	0	0.6
$NiMo/Al_2O_3$	47.5	39.2	5.5	9.7	37.8	1.9	5.8
$NiMoP(1)/Al_2O_3$	39.8	46.4	4.9	11.3	28.5	1.7	7.9
$NiMoP(2)/Al_2O_3$	36.7	49.0	4.9	12.1	24.6	1.7	8.0
$NiMoP(4)/Al_2O_3$	26.7	58.9	5.7	11.5	15.2	1.6	7.5

[a] Sum of all by-products.

Phosphorus decreased the piperidine conversion as well as the HDN conversion to C_5 hydrocarbons of the $NiMo(P)/Al_2O_3$ catalysts (table 2), indicating that it diminished the C–N bond cleavage activity of the $NiMo(P)/Al_2O_3$ catalysts. The higher the phosphorus content in the catalyst, the lower the HDN activity. No HDN activity of P/Al_2O_3 was observed. This is contradiction to the dual bed results of Eijsbouts et al. [3], which were interpreted as indicating that phosphate on alumina increases the C–N bond breaking of alkylamines.

The results presented in table 2 can be quantitatively analyzed when it is assumed that the HDN reaction of piperidine over the $NiMo(P)/Al_2O_3$ catalysts follows a first-order Langmuir–Hinshelwood mechanism and that all reaction steps take place on one and same catalytic site. Then, for the reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{D},$$

where A stands for piperidine, B for pentylamine (PA), C for pentene and D for pentane, we have

$$\frac{\mathrm{dA}}{\mathrm{d}t} = -k_1 K_\mathrm{A} \mathrm{A}/P,$$

$$\frac{\mathrm{dB}}{\mathrm{d}t} = (k_1 K_\mathrm{A} \mathrm{A} - k_2 K_\mathrm{B} \mathrm{B})/P,$$

$$\frac{\mathrm{dC}}{\mathrm{d}t} = (k_2 K_\mathrm{B} \mathrm{B} - k_3 K_\mathrm{C} \mathrm{C})/P$$

with

$$P = 1 + \sum K_i \mathrm{I}.$$

In these expressions k_1 and k_2 are the rate constants of the first and second C–N bond cleavage, respectively, k_3 is the rate constant for the hydrogenation reaction of pentene to pentane, and K_i is the adsorption constant of compound I. Dividing the second and the third equation by the first one gives

$$\frac{dB}{dA} = -1 + \alpha\frac{B}{A} \qquad \text{with } \alpha = \frac{k_2K_B}{k_1K_A}\,,$$

$$\frac{dC}{dA} = -\alpha\frac{B}{A} + \beta\frac{C}{A} \qquad \text{with } \beta = \frac{k_3K_C}{k_1K_A}\,,$$

which leads to

$$\frac{B}{A_0} = \frac{1}{\alpha - 1}(a - a^{\alpha}) \qquad a = \frac{A}{A_0}\,,$$

$$\frac{C}{A_0} = \frac{\alpha}{(\alpha-1)(\beta-1)(\alpha-\beta)}[(\alpha-\beta)a + (\beta-1)a^{\alpha} - (\alpha-1)a^{\beta}]\,.$$

These equations were used to calculate the ratios α and β from the data presented in table 2. Under the assumption of first-order behaviour, the effective rate constants $k_1' = k_1K_A$ could be calculated from the piperidine conversions, which then afforded the effective rate constants $k_2' = k_2K_B$ and $k_3' = k_3K_C$. The results are presented in table 3.

Table 3 shows that k_2' and k_3' are much larger than k_1', which confirms the qualitative conclusion that the breaking of the second C–N bond and the subsequent hydrogenation of pentene are much faster than the breaking of the first C–N bond. Once the first C–N bond is broken (A → B), the final HDN product (D) will be quickly formed through fast successive reactions (B → C → D). This explains that, independent of the conversion level, the concentrations of the reaction intermediates (pentylamine and pentene) stay more or less constant, and that only the concentration of the final product pentane changes with the HDN conversion over the four catalysts (table 2). Introducing phosphorus to the NiMo/Al$_2$O$_3$ catalyst decreased the rate constant of the first C–N bond cleavage of piperidine, which is the rate-limiting reaction step. The higher the phosphorus content in the catalyst, the lower k_1'. The hydrogenation rate constants k_3' also decreased as the amount of phosphorus in the catalyst increased, suggesting that introducing phosphorus to the NiMo/Al$_2$O$_3$ catalysts inhibits the hydrogenation reaction of alkenes [13].

Table 3

Effective rate constants for the HDN reactions of piperidine and decahydroquinoline (10^2 mol reactant/h g-catalyst)

Catalyst	Piperidine			Decahydroquinoline		
	k_1'	k_2'	k_3'	k_1'	k_2'	k_3'
NiMo/Al$_2$O$_3$	0.82	7.4	4.8	0.87	18.7	8.6
NiMoP(1)/Al$_2$O$_3$	0.65	7.5	3.6	0.77	18.0	7.7
NiMoP(2)/Al$_2$O$_3$	0.60	7.3	3.2	0.71	16.8	6.5
NiMoP(4)/Al$_2$O$_3$	0.44	5.4	2.4	0.55	14.4	5.3

3.2. DECAHYDROQUINOLINE

In the HDN of piperidine, large amounts of by-products were formed (more than 20 by-products were observed in the gas chromatogram), which in some cases were partly denitrogenated products like N-pentylpiperidine (NPP). Products such as NPP, which can be thought to consist of one mole of pentene and one mole of the piperidine reactant, made the data analysis difficult. Because not all by-products can be identified and considered for the data analysis, the uncertainty of the data analysis may be large. To avoid such a problem, we studied the HDN of decahydroquinoline (DHQ) which contains a carbocyclic ring in addition to the heterocyclic ring (as in piperidine).

The HDN reaction network of decahydroquinoline (fig. 2) closely resembles that of piperidine (fig. 1). Again, only C–N bond cleavage reactions are needed to remove the nitrogen atom from the DHQ molecule. As in the case of piperidine, breaking the first C–N bond results in the formation of an intermediate (propylcyclohexylamine, PCHA), which easily undergoes breaking of the second C–N bond to the primary HDN product propylcyclohexene (PCHE). PCHE is then hydrogenated to the secondary HDN product propylcyclohexane (PCH). Just as piperidine can undergo dehydrogenation of the heterocyclic ring to pyridine, dehydrogenation of DHQ to 5,6,7,8-tetrahydroquinoline (THQ-5) also proceeds to an appreciable extent (fig. 2). Further dehydrogenation of THQ-5 to quinoline (Q) was not observed, and formation of 1,2,3,4-tetrahydroquinoline (THQ-1) was only observed in trace amounts (0.5–0.7%) under the present reaction conditions, indicating that dehydrogenation of the heterocyclic ring is much faster than that of the carbocyclic ring. The dehydrogenated secondary HDN product propylbenzene (PB) was never observed. In contrast to the HDN of piperidine, the formation of by-products (others) in the HDN of DHQ was small (table 4) which simplified the data analysis.

The high concentration of DHQ and low concentration of PCHA in the reaction products indicates that breaking the first C–N bond in a DHQ molecule is much more difficult than breaking the second C–N bond in a PCHA molecule, as in the case of piperidine. It is clearly seen from table 4 that phosphorus has a negative

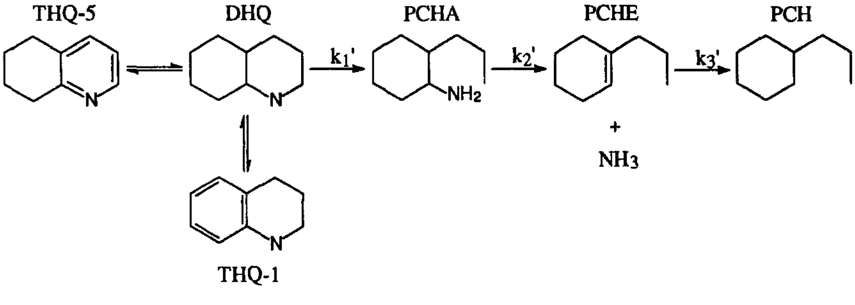

Fig. 2. HDN reaction network of decahydroquinoline.

Table 4
Effect of phosphorus content in the HDN of decahydroquinoline

Catalyst	HDN (%)	Product composition (%)						
		DHQ	PCHA	PCHE	PCH	THQ5	THQ1	others
NiMo/Al$_2$O$_3$	19.8	67.0	3.7	7.6	12.2	8.1	0.7	0.6
NiMoP(1)/Al$_2$O$_3$	17.6	69.6	3.5	7.5	10.1	8.0	0.6	0.7
NiMoP(2)/Al$_2$O$_3$	16.1	71.2	3.5	7.7	8.4	8.1	0.5	0.6
NiMoP(4)/Al$_2$O$_3$	12.2	75.5	3.3	6.8	5.4	7.8	0.7	0.6

effect on the HDN of DHQ over the NiMo/Al$_2$O$_3$ catalyst, i.e. a negative effect on the C–N bond cleavage reaction.

The results of table 4 were used for the same kinetic analysis as described in the foregoing for the piperidine results. The resulting effective rate constants k'_1, k'_2 and k'_3 for the first C–N bond breaking from DHQ to PCHA, the second C–N bond breaking from PCHA to PCHE, and the final hydrogenation of PCHE to PCH, respectively, are given in table 3. They allow similar conclusions as in the case of piperidine: k'_2 and k'_3 are much larger than k'_1, making the first C–N bond breaking the slowest reaction step. The effective rate constants k'_1 for DHQ are of the same magnitude as those for piperidine. The rates for the second C–N bond breakings are much faster than those of the first C–N bond breakings, and are larger for DHQ than for piperidine (table 3). This may be due to a stronger adsorption of PCHA than PA. The inhibiting effect of phosphorus on the hydrogenation reaction of the alkene does not contribute to the negative effect of phosphorus on the overall HDN reaction rate, because nitrogen was already removed in the preceding step.

To explain the enhanced HDN activity of quinoline over Ni–MoS$_2$/Al$_2$O$_3$ catalysts promoted with phosphorus, Eijsbouts et al. [3] suggested that phosphorus accelerates the N-elimination from DHQ. To prove their point, they carried out an experiment in which a P/Al$_2$O$_3$ catalyst bed was placed downstream of a Ni–MoS$_2$/Al$_2$O$_3$ catalyst bed and in which quinoline was used as the feed. They observed a decrease in the DHQ concentration and an increase in the hydrocarbon concentration at the reactor outlet, relative to the experiment in which only a single Ni–MoS$_2$/Al$_2$O$_3$ catalyst bed was used. Our experiments with DHQ over P/Al$_2$O$_3$ and Al$_2$O$_3$ showed no formation of hydrocarbons at all, however, at 593 K (table 5) or at 643 K (the temperature used by Eijsbouts et al.). The DHQ reactant, which consists of 3 : 1 cis/trans isomer mixture, isomerised over P/Al$_2$O$_3$ as well as Al$_2$O$_3$, probably via dehydrogenation and hydrogenation over metal impurities in the Al$_2$O$_3$ and SiC diluent. In agreement with this explanation, some dehydrogenation reaction of DHQ to THQ-5 and THQ-1 was observed. Furthermore, isomerisation to N-containing molecule (indicated by "others" in table 5) was also observed.

The results presented in table 5 demonstrated that in contradiction to the suggestion of Eijsbouts et al. [3], phosphate plays no direct role in the C–N bond cleavage.

Table 5
Activity of γ-Al_2O_3 and P/Al_2O_3 in the HDN of decahydroquinoline

Catalyst	Product composition (%)							
	HC[a]	*t*-DHQ	*c*-DHQ	PCHA	THQ5	Q	THQ1	others
feed[b]	0	23.1	75.1	0	0.1	0	0.1	1.7
blank[c]	0	24.6	73.2	0	0.3	0	0.1	1.8
γ-Al_2O_3 + SiC	0	35.5	56.4	0	1.1	0	0.4	6.6
P(2)/Al_2O_3 + SiC	0	33.4	59.0	0	1.1	0	0.4	6.1

[a] Nitrogen-free hydrocarbons.
[b] Composition of the DHQ feed.
[c] Empty reactor.

The negative effect of phosphorus in the HDN of piperidine and DHQ, and the positive effect of phosphorus on the HDN of quinoline must therefore be due to its effect on the Ni and Mo.

3.3. ORTHO-PROPYLANILINE

It is well known that phosphorus has a beneficial effect on the HDN reaction over NiMoP/Al_2O_3 catalysts in industrial [2] as well as laboratory operations [3]. Since basic nitrogen-containing heterocycles are the most difficult compounds to hydrodenitrogenate [14] and since the C–N bond cleavage reaction is usually the most difficult reaction step in the HDN process, our conclusion that phosphorus exhibits a negative influence on the C–N bond cleavage reaction over NiMoP/Al_2O_3 catalysts seems surprising. However, in the industrial HDN process aniline-type compounds are present in the feed or they are formed as reaction intermediates in the HDN of aromatic N-containing compounds such as quinoline and indole [14,15]. The HDN of anilines proceeds mainly through hydrogenation of the aromatic ring to a saturated amine (PCHA in the case of ortho-propylaniline, OPA). After hydrogenation of OPA to PCHA, the C–N bonds are broken and hydrocarbons are formed (fig. 3) as in the cases of DHQ and piperidine, while the direct C–N

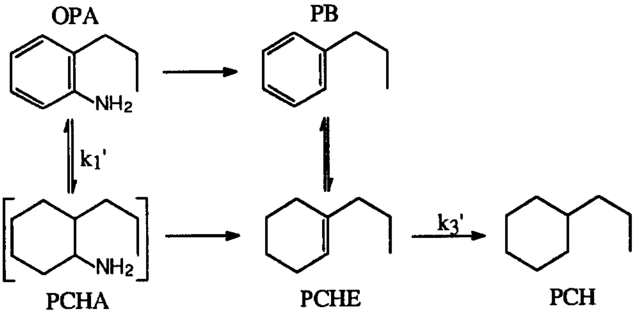

Fig. 3. HDN reaction network of ortho-propylaniline.

bond cleavage of the aniline (OPA) to the aromatic hydrocarbon (PB) occurs to a small extent only [16,17]. In the HDN of OPA, PCHA was either not observed or only in traces which indicates that the conversion of PCHA is very easy and that the hydrogenation of OPA to PCHA is the rate-limiting reaction step.

In contrast to its negative effect in the HDN of piperidine and decahydroquinoline, phosphorus exhibited a strong promotional effect in the HDN of ortho-propylaniline over NiMo(P)/Al_2O_3 catalysts (table 6). A kinetic analysis of the product composition, as performed for piperidine and decahydroquinoline, resulted in the effective rate constants k_1' for the hydrogenation of OPA and subsequent NH_3 elimination to PCHE, and the effective rate constants k_3' for the hydrogenation of PCHE to PCH (table 6). As to be expected from the product compositions, the k_1' values are much smaller than the k_3' values, and the k_1' values increase with phosphorus content up to 2 wt% P, indicating that phosphorus promotes the hydrogenation reaction of the aromatic ring. The decrease of k_1' for the NiMoP(4)/Al_2O_3 catalyst (table 6) may be due to a decreased dispersion of the Ni-Mo-S phase, because of the decrease in support surface area (table 1). The increase of k_1' up to 2 wt% P suggests that the promotional effect of phosphorus observed in the industrial HDN process [2] and model compound studies [3] might arise from the HDN of aniline-type compounds which is rate limiting. Although the concentration of aniline-type compounds in oil fractions is usually quite low and the HDN of anilines is quite easy when they react alone, their concentrations in the reaction effluent can be substantial due to the inhibiting effect of other nitrogen-containing compounds on their conversions, as has been reported both in model compound studies [18,19] and in industrial hydrotreating [20]. Limitation of the HDN process by the further conversion of aniline-type compounds is thus possible. Therefore, it can be expected that in industrial HDN processes phosphorus may exhibit a promotion effect over NiMoP/Al_2O_3 catalysts under mild hydrotreating conditions, when there is an accumulation of aniline-type compounds.

3.4. EFFECT OF PHOSPHORUS ON THE CATALYTIC SITE

Since the introduction of phosphorus to an NiMo/Al_2O_3 catalyst continuously

Table 6
Effect of phosphorus in the HDN of ortho-propylaniline

Catalyst	HDN (%)	Product composition (%)			Rate constant	
		PCH	PCHE	PB	k_1'	k_3'
P(2)/Al_2O_3	0	0	0	0	0	0
NiMo/Al_2O_3	23.5	17.8	4.8	0.9	0.84	14.1
NiMoP(1)/Al_2O_3	30.2	21.3	7.4	1.5	1.13	11.4
NiMoP(2)/Al_2O_3	34.6	23.7	9.1	1.8	1.34	10.4
NiMoP(4)/Al_2O_3	29.9	16.7	11.4	1.8	1.12	6.9

decreases the specific surface area and pore volume of the catalysts (table 1), the negative effect of phosphorus on the C–N bond cleavage reaction of saturated amines might simply be explained by a smaller number of catalytically active sites, due to the diminished support specific surface area available to disperse the active components. Another, or additional explanation would be that phosphorus has a negative influence on the sites on which N-elimination and olefin hydrogenation reactions take place.

The positive effect of phosphorus in the HDN of OPA can, however, only be explained by an increase in the number of sites which cause hydrogenation of aromatics, or by an increase in their intrinsic activity. An increased number of such sites might be possible when these sites are especially present in the top Ni–MoS_2 slab in a stack of Ni–MoS_2 slabs. An increase in the stacking of MoS_2 by the addition of phosphorus to $NiMo/Al_2O_3$ catalysts has been observed [8,21], and a special activity of the sites in the top MoS_2 slab has also been described [22].

An increase in the intrinsic activity for aromatic hydrogenation must mean that the sites are chemically modified. A reason for this might be the replacement of a sulfur atom by a phosphorus atom in the Ni coordination. Phosphorus which is close to Ni–MoS_2 particles might be reduced to PH_3 by spilt over H atoms, which induces a P–S exchange reaction at the catalyst surface. Evidence for such reaction has been presented [23].

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