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Mechanism of the Hydrodenitrogenation of Quinoline over NiMo(P)/Al_2O_3 Catalysts

M. Jian and R. Prins

Laboratory for Technical Chemistry, Federal Institute of Technology (ETH), 8092 Zürich, Switzerland

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The hydrodenitrogenation (HDN) of quinoline and its reaction intermediates was studied over NiMo(P)/Al_2O_3 catalysts. Phosphorus exhibited a promotional effect on the HDN of quinoline and *ortho*-propylaniline and a negative effect on the HDN of decahydroquinoline and on the hydrogenation of 1-methylcyclohexene in its simultaneous reaction with quinoline. The HDN of quinoline was found to take place via two pathways: via the saturated intermediates decahydroquinoline and propylcyclohexylamine, and via the aromatic intermediates 1,2,3,4-tetrahydroquinoline and *ortho*-propylaniline. Although propylcyclohexane is the main HDN product in both reaction paths, formation of propylbenzene is relatively favored in the latter path. Thus, the relative contributions of the two reaction paths in the quinoline HDN network could be estimated from the HDN product composition. In contrast to previous suggestions, the 1,2,3,4-tetrahydroquinoline–*ortho*-propylaniline reaction path was found to be nonnegligible: About 40% of the quinoline HDN takes place via this reaction path at 643 K, 3.0 MPa, and $P_{H_2S} = 6.5$ kPa, and about 35% at 623 K. H_2S had an effect opposite that of phosphorus on the HDN of decahydroquinoline and *ortho*-propylaniline. H_2S as well as phosphorus had a small positive effect on the HDN of quinoline. This is due to a subtle balance between their opposite effects on the HDN of decahydroquinoline as well as *ortho*-propylaniline. Because of this, and of the opposite effect of phosphorus as well as H_2S on the HDNs of these two molecules, the effect of phosphorus and H_2S on the HDN of quinoline is a subtle balance between the two HDN pathways, the catalyst composition, and the reaction conditions.

INTRODUCTION

Quinoline (Q) has many advantages over other nitrogen-containing hydrocarbons as a model reactant in hydrodenitrogenation (HDN) (1, 2). Due to its molecular structure, all reactions that take place in an industrial HDN process also occur in the HDN network of quinoline, that is, C–N bond cleavage, hydrogenation of aromatic heterocyclic rings, and hydrogenation of benzenic rings. The reaction mechanism of the HDN of quinoline has been studied by several groups (1–8) and has been reviewed a few times (9–11). It is generally accepted that the HDN reaction goes through the intermediates indicated in the network presented in Fig. 1. Since the conversion of *ortho*-propylaniline (OPA) is strongly inhibited by the presence of quinoline-type molecules [quinoline, tetrahydroquinoline (THQ1 and THQ5), and decahydroquinoline (DHQ)] due to competitive adsorption (6, 8, 10, 12), it has been concluded that HDN of quinoline over NiMo/Al_2O_3 catalysts proceeds exclusively via the fully saturated intermediates decahydroquinoline and 2-propylcyclohexylamine (PCHA) (Q → DHQ → PCHA → hydrocarbons, see Fig. 1) (1–11).

A promotional effect of phosphorus on NiMo(P)/Al_2O_3 catalysts has been demonstrated in industrial HDN performance and in studies with model compounds such as quinoline (2, 13–16). It has been suggested that the positive effect of phosphorus originates from its accelerating effect on C–N bond cleavage which is often supposed to be the most difficult reaction step (2, 3, 17–19), although it has also been concluded that C–N bond breaking and hydrogenation of the aromatic ring are about equally slow (3, 7, 11). However, from direct evidence of the C–N bond cleavage of piperidine (20), it was concluded that phosphorus has a negative influence on C–N bond cleavage over NiMo(P)/Al_2O_3 catalysts, in contradiction to these suggestions in the literature.

To determine the role of phosphorus over NiMo(P)/Al_2O_3 catalysts, we have investigated the HDN of quinoline under various reaction conditions: in the presence as well as absence of H_2S, and at different temperatures. Important reaction intermediates of the HDN network (DHQ and OPA) were employed as reactants as well, to further study the effect of phosphorus on the different HDN steps and the reaction mechanisms. Simultaneous reactions of DHQ and 1-methylcyclohexene (MCHE), of DHQ and *ortho*-ethylaniline (OEA), and of Q and OEA were performed to understand the product composition and inhibitive adsorption effect in the HDN of quinoline.

EXPERIMENTAL

Catalysts used in this work had a composition of 3 wt% nickel, 8 wt% molybdenum, and 0–2 wt% phosphorus. They were prepared by incipient wetness impregnation, followed by drying at 393 K and calcination at 773 K (20). The

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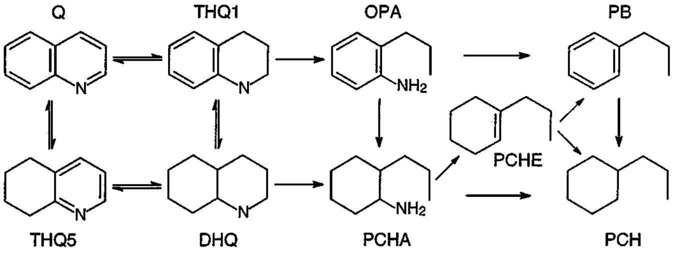

FIG. 1. HDN reaction network of quinoline. Q, quinoline; THQ5, 5,6,7,8-tetrahydroquinoline; DHQ, decahydroquinoline; THQ1, 1,2,3,4-tetrahydroquinoline; OPA, *ortho*-propylaniline; PCHA, 2-propylcyclohexylamine; PCHE, propylcyclohexene; PCH, propylcyclohexane; PB, propylbenzene.

reactions were carried out in a continuous-flow microreactor. A sample of 0.5 g catalyst diluted with 9.5 g SiC was used for each reaction. The catalyst was presulfided *in situ* with a mixture of 10% (mol) H_2S and H_2 at 643 K and 1.5 MPa for 4 h. The liquid reactant was fed to the reactor by means of a high-pressure pump, with *n*-octane as the solvent. The catalyst was stabilized at 643 K and 3.0 MPa for 18 h before samples were taken. The initial reactant partial pressure (P^0) of quinoline, DHQ, OPA, and OEA was 4.76 kPa in all cases, and that of MCHE was 1.6 or 13.5 kPa. The partial pressure of H_2S was set at 0 or 6.5 kPa by adding dimethyl disulfide (DMDS) to the liquid reactant. *n*-Nonane and *n*-dodecane were used as internal standards.

RESULTS AND DISCUSSION

HDN of Quinoline

Tables 1 and 2 and Fig. 2 present the results of the HDN of quinoline over the $NiMo(P)/Al_2O_3$ catalysts at 593, 623, and 643 K. The results demonstrate that in both the presence and the absence of H_2S, phosphorus promotes the HDN of quinoline at all reaction temperatures.

This overall behavior of the HDN of quinoline is quite different from that of each of the individual reaction steps involved in the HDN path via the fully saturated intermediates DHQ and PCHA: Thus, while the HDN activity of quinoline increased, the activities for the hydrogenation of alkenes, aromatics, and the aliphatic C–N bond cleavage decreased with the introduction of phosphorus into a $NiMo/Al_2O_3$ catalyst (20, 21). This demonstrates that the HDN of quinoline cannot simply by interpreted by one rate-limiting reaction step. Furthermore, since strong adsorption of molecules is involved in the HDN process (16, 22), inhibition effects due to the adsorption of the reactant, intermediates, or products must be taken into account in explaining the behavior of the catalysts.

According to Satterfield and Gültekin (1), the presence of H_2S increases the rate of aliphatic C–N bond breaking and decreases the rate of aromatic hydrogenation. Since H_2S promoted the HDN of quinoline (compare Figs. 2A and 2B), one could argue that the aliphatic C–N bond cleavage limits this HDN reaction under the present conditions. This, however, is in contradiction with the observation that phosphorus exhibits a negative influence on the aliphatic C–N bond cleavage of piperidine (20). It suggests that either the main HDN reaction of quinoline does not proceed through the fully saturated amine intermediates (DHQ–PCHA) or that the aliphatic C–N bond cleavage is not the only limiting reaction.

Figures 1 and 3 show that there are two possible paths for the HDN of quinoline: via DHQ–PCHA and via THQ1–OPA. The concentration of the intermediate DHQ was slightly lower, and that of OPA considerably higher, in the presence than in the absence of H_2S (Tables 1 and 2). The former can be understood from the increased consumption of DHQ through C–N bond cleavage to PCHA and hydrocarbons in the presence of H_2S, while the latter is due to the fact that the transformation of THQ1 to OPA is enhanced (an aliphatic C–N bond cleavage) and the further conversion of OPA inhibited by the presence of H_2S (see below). The higher concentration of OPA thus indicates that HDN via the THQ1–OPA path is limited by the transformation of OPA in the presence of H_2S.

Tables 1 and 2 also show that the hydrocarbon product distribution was different for different catalysts and

TABLE 1

Results of the HDN of Quinoline in the Presence of H_2S

Catalyst	*T* (K)	Product composition (mol%) HC	PCHA	OPA	DHQ	THQ5	Q	THQ1	PCH/PB ratio
$NiMo/Al_2O_3$	643	26.2	0	13.3	7.0	30.5	7.9	14.9	7.4
$NiMoP2/Al_2O_3$	643	32.5	0	10.9	6.3	27.8	7.4	14.5	5.2
$NiMo/Al_2O_3$	623	15.3	0	12.0	10.8	22.7	8.2	30.7	14
$NiMoP2/Al_2O_3$	623	18.1	0	10.4	10.1	24.8	8.7	27.5	8.6
$NiMo/Al_2O_3$	593	3.2	0.2	6.8	10.9	6.2	5.5	66.6	[a]
$NiMoP2/Al_2O_3$	593	4.8	0.3	6.6	13.9	8.5	6.7	58.6	[a]

[a] PB was not detected.

TABLE 2

Results of the HDN of Quinoline in the Absence of H_2S

Catalyst	T (K)	Product composition (mol%) HC	PCHA	OPA	DHQ	THQ5	Q	THQ1	PCH/PB ratio
$NiMo/Al_2O_3$	643	9.2	0	3.6	9.7	40.8	12.4	22.8	3.2
$NiMoP2/Al_2O_3$	643	20.8	0	2.3	12.3	35.8	10.6	19.9	2.8
$NiMo/Al_2O_3$	623	4.7	0	2.4	14.1	24.8	11.7	41.3	3.6
$NiMoP2/Al_2O_3$	623	9.0	0	2.3	12.3	22.5	10.5	42.3	2.4
$NiMo/Al_2O_3$	593	0.7	0	1.0	14.3	7.1	7.0	69.6	[a]
$NiMoP2/Al_2O_3$	593	1.7	0	0.9	13.9	6.5	6.5	70.3	[a]

[a] PB was not detected.

reaction conditions. Higher reaction temperatures, the presence of phosphorus, and the absence of H_2S favored the formation of PB, as shown by the lower PCH/PB ratio.

HDN of Decahydroquinoline

DHQ is a key intermediate in the HDN network of quinoline. Its molecular structure resembles that of piperidine for which only C–N bond cleavage is needed to remove the nitrogen atom. As in the HDN of piperidine (20), a negative effect of phosphorus prevailed in the HDN of DHQ at 593 K in the presence of H_2S. However, the negative effect became smaller at 623 K, and turned into a positive effect at 643 K (Table 3, Fig. 4A).

The PCH/PB ratio in the HDN of DHQ decreased with increasing temperature, and approached that of Q at the highest reaction temperature. This suggests that the HDN mechanism of Q and DHQ may be the same at higher reaction temperatures, but different at lower temperatures. In agreement with this, the relative yields of the quinoline-type compounds in the HDN product of DHQ also came close to those when quinoline was the reactant at higher temperatures. This would explain the positive effect of phosphorus on the HDN of DHQ, because the fast conversions of DHQ to Q, THQ1, and THQ5 at high temperatures caused this reaction to resemble that of Q (Tables 3 and 1). The total HDN conversion of DHQ increased only slightly when the reaction temperature was raised from 623 to 643 K, much less than when the temperature was raised from 593 to 623 K. This is another indication that the HDN reaction mechanism is different at high and low temperatures, or that the rate-limiting reaction steps have changed.

The HDN conversion of DHQ was much lower in the absence of H_2S (Table 4), and there was a strong promotional effect of phosphorus at all reaction temperatures (Fig. 4B). A comparison of the nitrogen-containing products shows that the concentrations of THQ1 and Q are higher in the absence than in the presence of H_2S, due to the faster dehydrogenation. It indicates that in the absence of H_2S, the HDN of DHQ proceeds partly through the THQ1–OPA

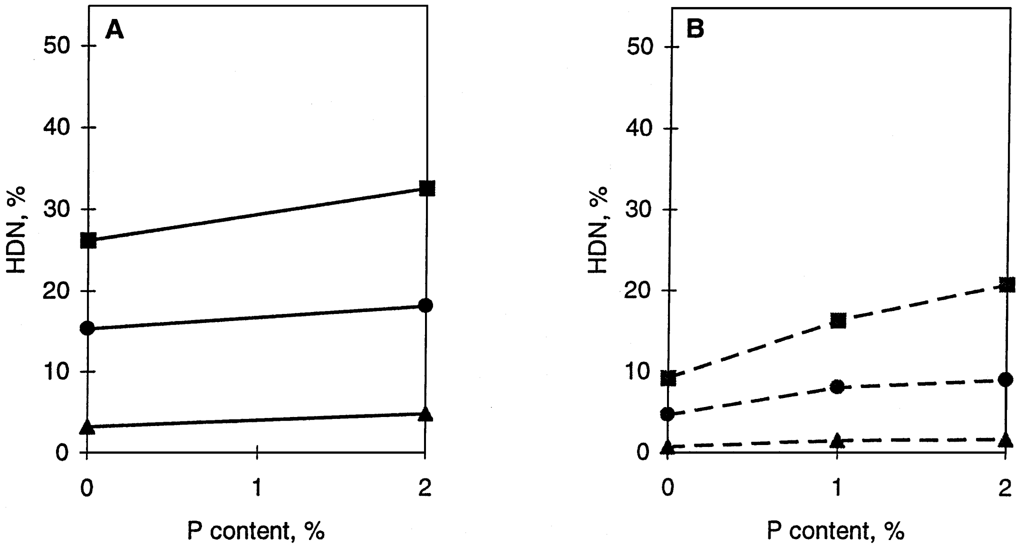

FIG. 2. Influence of phosphorus on the HDN conversion of quinoline over $NiMo(P)/Al_2O_3$ in the presence (A) and absence (B) of H_2S: ■, 643 K; ●, 623 K; ▲, 593 K.

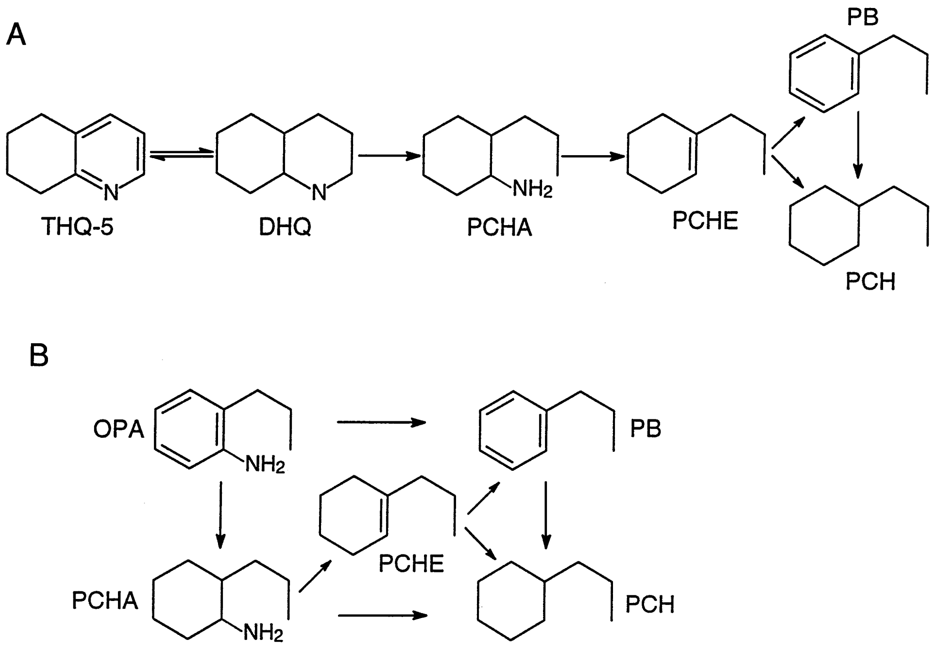

FIG. 3. HDN reaction networks of decahydroquinoline (A) and *ortho*-propylaniline (B).

path. The dehydrogenation of DHQ to THQ1 is promoted by the absence of H_2S, and as a consequence, the DHQ network as presented in Fig. 3A becomes coupled to that of OPA (Fig. 3B). Furthermore, HDN via the DHQ–PCHA path is slowed down in the absence of H_2S. That a substantial part of the HDN proceeds via THQ1–OPA also agrees with the fact that, although piperidine has a high C–N bond cleavage conversion in the presence and a very low one in the absence of H_2S (20), the difference in the HDN conversion of DHQ in the presence and absence of H_2S is much smaller, especially at high reaction temperatures (Tables 3 and 4, Fig. 4).

The PCH/PB ratios in the HDN product were much lower in the absence than in the presence of H_2S. These results resemble those of quinoline and again suggest that there might be a shift in the mechanism of the HDN of DHQ when the temperature is increased or when H_2S is omitted. One mechanism functions mainly at low temperature and is favored by the presence of H_2S, and the other functions at high temperature and is favored by the absence of H_2S. The latter might well be the HDN via the THQ1–OPA path, since a high temperature and the absence of H_2S favor the dehydrogenation of DHQ to THQ1 and Q, which will be further converted to OPA and hydrocarbons. The two mechanisms are working in opposite directions with respect to phosphorus; in the first phosphorus has a negative effect and in the latter a positive effect. The positive effect of phosphorus is associated with a low PCH/PB ratio, and the negative one with a high PCH/PB ratio.

The inhibition effect alone cannot account for the function of phosphorus. Since DHQ and THQ5 form the major part of the N-containing hydrocarbons in the products (Tables 3 and 4) and have the largest adsorption constants (22), one should expect that the major inhibition comes

TABLE 3

Results of the HDN of Decahydroquinoline in the Presence of H_2S

Catalyst	T (K)	Product composition (mol%) HC	PCHA	OPA	DHQ	THQ5	Q	THQ1	PCH/PB ratio
NiMo/Al_2O_3	643	46.9	0	4.2	6.2	27.4	5.3	9.6	8.8
NiMoP2/Al_2O_3	643	49.2	0	3.6	5.7	25.8	5.1	9.7	6.5
NiMo/Al_2O_3	623	45.7	0.5	0.9	17.6	27.6	1.7	5.2	25
NiMoP2/Al_2O_3	623	43.3	0.6	0.7	18.2	29.7	1.6	5.6	19
NiMo/Al_2O_3	593	19.8	3.7	0	66.7	8.2	0	0.7	[a]
NiMoP2/Al_2O_3	593	16.1	3.5	0	71.2	8.1	0	0.5	[a]

[a] PB was not detected.

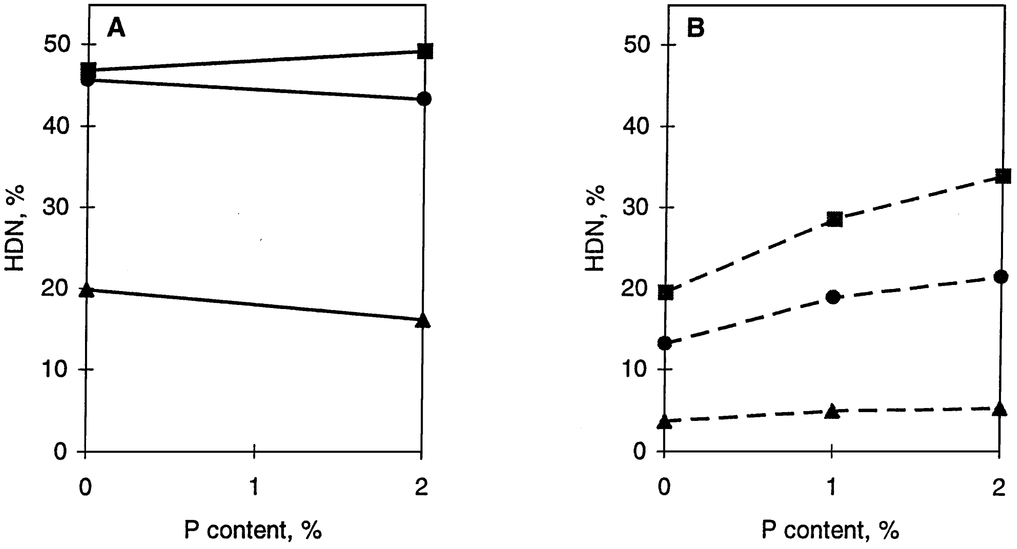

FIG. 4. Influence of phosphorus on the HDN conversion of decahydroquinoline over NiMo(P)/Al_2O_3 in the presence (A) and absence (B) of H_2S: ■, 643 K; ●, 623 K; ▲, 593 K.

from the adsorption of DHQ and THQ5. Tables 3 and 4 show that at 623 K the sum of DHQ and THQ5 is much higher in the absence than in the presence of H_2S. Nevertheless, phosphorus exhibits a positive effect in the former and a negative effect in the latter case. On the other hand, a positive effect of phosphorus prevails in both cases at 643 K where the sum of DHQ and THQ5 is still much higher in the absence of H_2S.

HDN of ortho-Propylaniline

OPA is the key intermediate in the HDN path via THQ1–OPA (Figs. 1 and 3B). If, as suggested above, the promotional effect of phosphorus in the HDN of Q and DHQ arises from the reaction path via THQ1–OPA, especially in the presence of H_2S, phosphorus should have an accelerating effect on the conversion of OPA. To demonstrate this suggestion, the HDN of pure OPA was studied under the same conditions as that of Q and DHQ. Indeed, a promotional effect of phosphorus was observed at all temperatures, in both the presence and the absence of H_2S (Tables 5 and 6).

The HDN product composition further supports the suggestion about the role of the THQ1–OPA path. The lowest PCH/PB ratio is generally observed in the HDN of OPA, the highest in the HDN of DHQ, while the PCH/PB ratio in the HDN of quinoline is inbetween (the PCH/PB ratio in the HDN of pure OPA might be somewhat overestimated in the absence of H_2S due to the hydrogenation of PB to PCH). Therefore, the HDN of quinoline might indeed be a combination of HDN reactions via DHQ–PCHA and THQ1–OPA. If the positive effect of phosphorus via the OPA path can compensate for the negative effect via the DHQ path, a promotional effect of phosphorus over NiMo(P)/Al_2O_3 catalysts will be observed, no matter which quinoline-type compound is used as the reactant. The higher HDN conversion of OPA in the absence of H_2S demonstrates that the relative low concentration of OPA in the HDN of DHQ and Q is at least partly due to an increased transformation of OPA to hydrocarbons under the corresponding conditions.

TABLE 4

Results of the HDN of Decahydroquinoline in the Absence of H_2S

Catalyst	*T* (K)	Product composition (mol%) HC	PCHA	OPA	DHQ	THQ5	Q	THQ1	PCH/PB ratio
NiMo/Al_2O_3	643	19.5	0	1.1	11.4	48.6	6.8	12.2	5.3
NiMoP2/Al_2O_3	643	34.0	0	1.1	8.7	38.8	6.3	11.0	4.3
NiMo/Al_2O_3	623	13.2	0	0	30.6	46.2	2.6	6.6	7.5
NiMoP2/Al_2O_3	623	21.5	0	0	24.7	44.6	2.3	6.3	5.3
NiMo/Al_2O_3	593	3.7	0	0	79.4	14.5	0.4	1.3	[a]
NiMoP2/Al_2O_3	593	5.4	0	0	78.8	13.0	0.4	1.5	7.7

[a] PB was not detected.

TABLE 5

Results of the HDN of *ortho*-Propylaniline in the Presence of H_2S

Catalyst	T (K)	HDN (%)	Product composition (mol%) PCH	PB	PCHE	PCH/PB ratio
NiMo/Al_2O_3	643	84.1	68.6	14.9	1.4	4.8
NiMoP2/Al_2O_3	643	99.7	76.5	21.5	0	3.6
NiMo/Al_2O_3	623	64.3	53.8	6.1	3.8	8.8
NiMoP2/Al_2O_3	623	90.9	75.3	12.2	2.7	6.1
NiMo/Al_2O_3	593	23.5	17.8	0.9	4.8	19
NiMoP2/Al_2O_3	593	34.6	23.7	1.8	9.1	13

Simultaneous Reaction of Quinoline and 1-Methylcyclohexene

Simultaneous hydrogenation of 1-methylcyclohexene (MCHE) and HDN of quinoline were performed to investigate the influence of phosphorus on the elementary reaction steps and the HDN product composition (Table 7). MCHE had no influence on the HDN of quinoline (the results are not listed here), but quinoline strongly inhibited the conversion of MCHE, from 100% in the absence of Q over all catalysts to values below 94% (Table 7). An increase in the initial partial pressure of MCHE by a factor of 8 had no influence on the conversion of MCHE, indicating pseudo-first-order hydrogenation behavior. Obviously, the catalyst surface was almost completely covered by the quinoline-type compounds and MCHE had little chance to compete with quinoline on the surface.

Table 7 shows that phosphorus exhibited a negative effect on the hydrogenation of MCHE over the NiMo(P)/Al_2O_3 catalysts, consistent with its negative effect on the hydrogenation of cyclohexene in the simultaneous reaction with piperidine (20). The MCH/T (MCH = methylcyclohexane, T = toluene) ratios were higher than the PCH/PB ratios, and were close to the equilibrium ratios of PCH/PB [11.5 at 643 K and 3.53 MPa and 24 at 623 K and 3.53 MPa (23)]. The PCH/PB ratio in the HDN product of DHQ was closer to the MCH/T ratio under the same reaction conditions than the ratios in the HDN of Q and OPA, while the PCH/PB ratio in the HDN product of OPA was the furthest from the MCH/T ratio.

TABLE 6

Results of the HDN of *ortho*-Propylaniline in the Absence of H_2S

Catalyst	T (K)	HDN (%)	Product composition (mol%) PCH	PB	PCHE	PCH/PB ratio
NiMo/Al_2O_3	643	90.5	66.2	21.8	1.0	3.0
NiMoP2/Al_2O_3	643	100	72.1	26.0	0	2.8
NiMo/Al_2O_3	623	76.5	61.7	12.6	1.8	4.9
NiMoP2/Al_2O_3	623	96.0	75.3	19.2	1.0	3.9
NiMo/Al_2O_3	593	37.2	28.6	5.0	3.7	5.7
NiMoP2/Al_2O_3	593	52.8	40.3	7.6	5.0	5.3

TABLE 7

Hydrogenation of 1-Methylclohexene in the Presence of Quinoline and H_2S ($P^0_{MCHE} = 1.6$ kPa, $P^0_Q = 4.76$ kPa)

Catalyst	T (K)	Conversion (%)	MCH/T
NiMo/Al_2O_3	643	94	11
NiMoP2/Al_2O_3	643	85	9.0
NiMo/Al_2O_3	623	79	25
NiMoP2/Al_2O_3	623	64	21
NiMo/Al_2O_3	593	51	[a]
NiMoP2/Al_2O_3	593	36	[a]

[a] Toluene was not detected.

The HDN path via DHQ–PCHA (Fig. 3A) should result in PCHE as the primary denitrogenation product which undergoes further (de)hydrogenation to PCH and PB just as MCHE. Therefore, the MCH/T ratio represents the extreme case in which the aromatic product can be formed only through dehydrogenation of the alkene intermediate. On the other hand, the HDN path via THQ1–OPA (Fig. 3B) enables the direct formation of PB by hydrogenolysis of OPA, and accounts for the relatively high PB concentration in the product (24). It has been demonstrated that PB can hardly be further hydrogenated in the presence of quinoline-type compounds (21). Therefore, the hydrocarbon product composition can be used to estimate the relative contributions of the two HDN pathways in the quinoline network. The high PCH/PB ratio in the case of DHQ suggests that a relatively large part of the HDN reaction takes place through PCHE.

Relative Contributions of the Two HDN Reaction Paths

The relative contributions of the two HDN pathways were calculated under the assumptions that the reaction path DHQ → PCHA → PCHE gives the same PCH/PB ratio as MCH/T in the simultaneous reaction of Q and MCHE (at 643 K: 11 for NiMo, 9.0 for NiMoP2; at 623 K: 25 for NiMo and 21 for NiMoP2), that the HC/PB ratio from the reaction path THQ1 → OPA → HC is the same as the HC/EB (EB = ethylbenzene) ratio of the HDN of *ortho*-ethylaniline (OEA) in the simultaneous reaction of OEA and Q, and that the amount of PCHE from each path is proportional to the extent of that reaction path. In that case one obtains

$$\mathrm{HC_{DHQ}} + \mathrm{HC_{OPA}} = \mathrm{HC_Q} \qquad [1]$$

$$\mathrm{PB_{DHQ}} + \mathrm{PB_{OPA}} = \mathrm{PB_Q} \qquad [2]$$

$$\mathrm{PCH_{DHQ}} + \mathrm{PB_{DHQ}} + \mathrm{PCHE_{DHQ}} = \mathrm{HC_{DHQ}} \qquad [3]$$

$$(\mathrm{PCH/PB})_{\mathrm{DHQ}} = \mathrm{MCH/T} \qquad [4]$$

$$(PB/HC)_{OPA} = (EB/HC)_{OEA} \qquad [5]$$

$$PCHE_{DHQ}/PCHE_{Q} = HC_{DHQ}/HC_{Q} \qquad [6]$$

In the above equations, HC_Q, PB_Q, and $PCHE_Q$ are the concentrations of total hydrocarbons (HC), PB, and PCHE in the HDN product of quinoline, respectively. PCH_{DHQ}, PB_{DHQ}, and $PCHE_{DHQ}$ are the contributions of PCH, PB, and PCHE in the HDN product of quinoline via the DHQ–PCHA path, and HC_{OPA} and PB_{OPA} are the contributions of HC and PB via the THQ1–OPA path, respectively. HC_{OEA} and EB_{OEA} are the HC and EB in the HDN product of OEA in the simultaneous reaction of OEA and Q under the corresponding reaction conditions.

In this way, the contributions from the DHQ–PCHA (path 1) and the THQ1–OPA (path 2) reaction paths in the HDN network of quinoline can be calculated (Table 8). The results show that under the present reaction conditions about 40% of the quinoline HDN proceeds via the THQ1–OPA path at 643 K, and 35% at 623 K. They confirm the qualitative conclusions obtained above that both reaction paths are important in the HDN of quinoline.

The $(HC)_{OEA}/EB$ ratio from the HDN of OEA in the simultaneous reaction of OEA and Q is independent of space time, while the $(HC)_{OPA}/PB$ ratio from the HDN of pure OPA decreases with increasing space time (Fig. 5), suggesting that the relative yield of the aromatic product is influenced by an inhibition effect. The inhibition effect on the HDN of OEA is so strong in the simultaneous reaction of OEA and Q that a decrease in inhibitor concentration by an increase in the space time has no influence on the different HDN steps of OEA. On the other hand, in the HDN of pure OPA the inhibition effect varies as the reaction proceeds, because OPA is much more weakly adsorbed than quinoline-type molecules. These results show that the above method of calculating the relative contributions of the two reaction paths can be used only when the conversion of quinoline is not too high, when most of the surface is still covered by strongly adsorbed species, otherwise different $(HC)_{OPA}/PB$ values have to be taken into account.

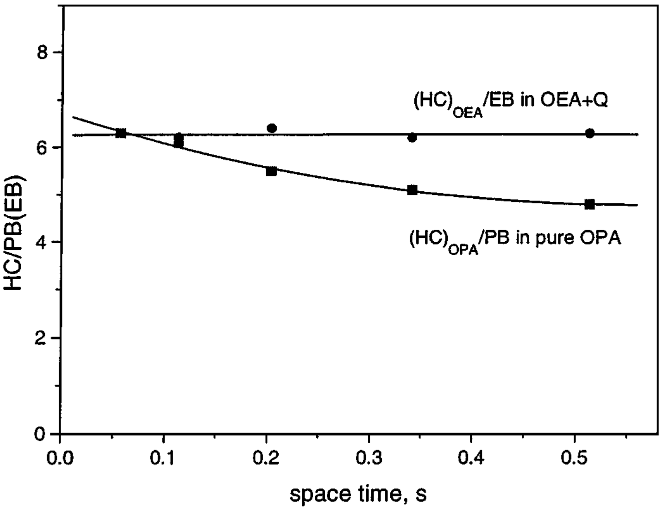

FIG. 5. $(HC)_{OEA}/EB$ ratio in the simultaneous HDN of OEA and Q and the $(HC)_{OPA}/PB$ ratio in the HDN of pure OPA as a function of space time at 643 K, 3.0 MPa, in the presence of H_2S.

Simultaneous HDN of Q and OEA and of DHQ and OEA was carried out to check the validity of the above calculations. Table 9 shows that the HDN conversion of OEA accounts for 30–40% of the total hydrocarbon production in the simultaneous HDN of Q and OEA. The simultaneous HDN of DHQ and OEA also demonstrates that 25–30% of the total hydrocarbon product originates from OEA and 70–75% from DHQ at 643 K (Table 10). At lower reaction temperature, however, the HDN contribution from OEA was considerably lower. This is due to a stronger inhibition, as the concentration of the inhibitors differed substantially from that when starting from Q + OEA (cf. Tables 3 and 1).

The HDN conversion of OPA is much higher than that of DHQ and Q, proving that pure OPA is much more reactive (3, 25). Comparing Tables 9 and 10 with Table 5 shows that the HDN of OEA is strongly inhibited by the presence of quinoline-type compounds. The stronger temperature dependence of the OEA conversion and the smaller effect of phosphorus on the HDN of OEA in the simultaneous reaction compared to when it reacted alone indicate

TABLE 8

Relative Contributions of the DHQ–PCHA Path (Path 1) and the THQ1–OPA Path (Path 2) in the HDN of Quinoline at 3.0 MPa and $P_{H_2S} = 6.5$ kPa

		Experimental result				Calculated result	
			Product composition (mol%)			Contribution (%)	
Catalyst	*T* (K)	HDN (%)	PCH	PB	PCHE	Path 1	Path 2
$NiMo/Al_2O_3$	643	26.2	19.9	2.5	3.8	62	38
$NiMoP2/Al_2O_3$	643	32.5	22.1	4.0	6.4	59	41
$NiMo/Al_2O_3$	623	15.3	10.7	0.7	3.9	67	33
$NiMoP2/Al_2O_3$	623	18.1	10.8	1.2	6.1	61	39

TABLE 9

Product Compositions in the Simultaneous HDN of Q and OEA in the Presence of H_2S ($P^0_{OEA} = P^0_{Q} = 4.76$ kPa)

		From OEA		From Q (mol%)						
Catalyst	*T* (K)	HC (mol%)	HC/EB	HC	PCHA	OPA	DHQ	THQ5	Q	THQ1
NiMo/Al_2O_3	643	15.7	7.5	20.6	0	12.4	8.4	30.6	9.5	17.6
NiMoP2/Al_2O_3	643	17.5	6.0	28.0	0	10.4	9.5	27.8	8.0	15.2
NiMo/Al_2O_3	623	8.9	12.7	12.8	0	10.8	14.7	21.3	9.2	30.9
NiMoP2/Al_2O_3	623	9.5	8.3	16.8	0	8.7	19.1	20.3	8.1	25.7

that it is mainly the inhibitive effect but not the intrinsic kinetics that controls the HDN of OEA in the simultaneous reactions. The negative effect of phosphorus on the HDN of DHQ results in a higher concentration of unconverted DHQ (THQ5) and, thus, in a stronger inhibition of the HDN of OEA, which more than compensates for its promotional effect. At the same time, OEA exhibits only a weak inhibition effect (about 10% less total conversion) on the HDN of DHQ (cf. Tables 3 and 10).

Influence of Phosphorus and H_2S

The influence of phosphorus and H_2S on the HDN conversion and PCH/PB product ratio in the HDN of Q, DHQ, and OPA is presented in Table 11. Phosphorus has a promotional effect on the THQ1–OPA path and an inhibitive effect on the DHQ–PCHA path in the presence of H_2S. The beneficial effect of H_2S on the overall HDN conversion of quinoline demonstrates that the majority of the HDN product was formed via the DHQ–PCHA path. The higher formation of HC via the DHQ–PCHA path in the presence of H_2S compensates for the lower formation of HC via the THQ1–OPA path. At the same time, the promotional effect of phosphorus on the THQ1–OPA path compensates for its negative effect on the DHQ–PCHA path. The result is a higher total HDN conversion and a small positive effect of phosphorus in the presence of H_2S.

The small change in HDN conversion of DHQ between 623 and 643 K is then due to the fact that at the higher temperatures more dehydrogenation of DHQ to THQ1 (and of THQ5 to Q) takes place. As a result of this coupling of the two networks shown in Figs. 3A and 3B, less HDN is possible via the quicker DHQ–PCHA path. In addition, depletion of DHQ due to its transformation to THQ5, which is thermodynamically favored at high temperature, is another limiting factor.

In the absence of H_2S, the contribution from the DHQ–PCHA path to HC production in the HDN of quinoline is suppressed and that of the THQ1–OPA path may hardly be changed, since decreased transformation of THQ1 to OPA can be compensated by an increased transformation of OPA to HC. As a result, a low HDN conversion is obtained. The negligible effect of phosphorus on the HDN of piperidine in the absence of H_2S (20) suggests that phosphorus should have a small effect on the DHQ–PCHA path in the absence of H_2S as well. Thus, the positive effect of the THQ1–OPA path in the HDN of Q will more than compensate for a small negative effect of the DHQ–PCHA path, and a strong promotional effect of phosphorus is observed.

The influence of phosphorus on the HDN of OPA is opposite that of H_2S, in both the HDN conversion and the PCH/PB ratio. Since the catalyst surface will be sulfur deficient in the absence of H_2S, this suggests that the introduction of phosphorus into a NiMo/Al_2O_3 catalyst may lead to a more reduced environment of the catalytic sites, to higher coordinative unsaturation, or to more sulfur vacancies in the NiMoS phase. Phosphorus and H_2S also exhibit

TABLE 10

Product Compositions in the Simultaneous HDN of DHQ and OEA in the Presence of H_2S ($P^0_{OEA} = P^0_{DHQ} = 4.76$ kPa)

		From OEA		From DHQ (mol%)						
Catalyst	*T* (K)	HC (mol%)	HC/EB	HC	PCHA	OPA	DHQ	THQ5	Q	THQ1
NiMo/Al_2O_3	643	15.9	7.8	41.1	0	3.6	9.3	28.6	5.5	9.6
NiMoP2/Al_2O_3	643	19.2	6.0	44.1	0	3.3	10.0	25.4	5.2	9.4
NiMo/Al_2O_3	623	7.4	12	41.7	0.5	0.9	18.8	27.9	1.6	5.2
NiMoP2/Al_2O_3	623	6.8	9.7	37.9	0.5	0.7	22.1	28.9	1.5	5.2
NiMo/Al_2O_3	593	1.9	[a]	18.7	3.1	0	66.8	8.4	0	0.8
NiMoP2/Al_2O_3	593	1.7	[a]	15.0	2.7	0	64.3	11.7	0.9	1.7

[a] EB was not detected.

TABLE 11

Influence of Phosphorus and H_2S on the Hydrocarbon Production and PCH/PB Product Ratio in the HDN of Q, DHQ, and OPA

	Hydrocarbon production				PCH/PB ratio			
	Effect of P		Effect of H_2S		Effect of P		Effect of H_2S	
	H_2S	No H_2S	With P	No P	H_2S	No H_2S	With P	No P
Q	+	++	+	+	−	−	+	+
DHQ	−	+	+	++	−	−	+	+
OPA	++	++	−	−	−	−	+	+

opposite effects on the PCH/PB ratio in the HDN of DHQ and Q, which can be explained by the fact that the yield of PB is low in all cases and comes mainly from the reaction path via OPA. Phosphorus and H_2S do not have an opposite effect on the HDN conversion of Q. This is explained by the fact that although phosphorus and H_2S have opposite effects on the HDN of OPA and DHQ (more or less), the influence of phosphorus as well as H_2S on the HDN of DHQ is (more or less) opposite that on the HDN of OPA. As a consequence, the influence of phosphorus and H_2S is a subtle balance between the two HDN paths (DHQ–PCHA and THQ1–OPA), catalyst composition, and reaction conditions.

In a study of the HDN of quinoline over a Mo_2N catalyst, Lee *et al.* (26) reported that HDN took place exclusively via the aromatic intermediates THQ1–OPA and that only aromatic hydrocarbons were present in the HDN product (benzene, toluene, ethylbenzene, and PB), suggesting that only aromatic C–N bond cleavage occurred. These experiments over Mo_2N represent an extreme case, however, because the sulfur-free Mo_2N catalyst behaves more like a metal than a sulfide, and the low pressure favors aromatic products. It does, however, indicate how strongly the catalyst properties can influence the HDN reaction network.

CONCLUSIONS

Phosphorus has a promotional effect on the HDN of quinoline over $NiMo(P)/Al_2O_3$ catalysts, even though it has a negative effect on aliphatic C–N bond cleavage. Two reaction paths are responsible for this HDN reaction: The reaction path via DHQ–PCHA is promoted by H_2S and inhibited by phosphorus, while the reaction path via THQ1-OPA is favored by the absence of H_2S and presence of phosphorus. The interpretation of the influence of reaction conditions and catalysts should thus take both paths into account. The former path results in a low PCH/PB ratio and the latter in a high PCH/PB ratio in the HDN products. At 643 K, 3.0 MPa, and $H_2S/H_2 = 2.2 \times 10^{-3}$ (mol/mol) about 40% of the quinoline HDN takes place via the THQ1–OPA path, while the proportion is 35% at 623 K.

Introduction of phosphorus into a sulfided $NiMo/Al_2O_3$ catalyst enhances the metallic properties of the catalyst, just like omitting H_2S from the reactant. The HDN results of quinoline and its reaction intermediates indicate that the properties and numbers of the catalytic sites are altered by phosphorus and reaction conditions. To fully understand the origin of the promotional effect of phosphorus and the HDN mechanism of quinoline, quantitative kinetic studies are necessary. These are described in another paper (27).

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