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Phosphorus Promotion of Ni(Co)-Containing Mo-Free Catalysts in Quinoline Hydrodenitrogenation

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Fresh and pretreated (in H_2S/H_2, H_2, or He) unsupported nickel– and cobalt–phosphorus compounds were characterized by XRD and EM/EDAX and tested in gas phase quinoline hydrodenitrogenation (643 K, 30 bar). During pretreatment or reaction, all compounds were transformed into Ni_2P or Co_2P. In addition, nickel supported on activated carbon, silica, silica/alumina, alumina, or NaY, to which phosphorus was added via three different methods, was tested in quinoline HDN. In most cases, the effect of phosphorus introduction was found to be strikingly beneficial, provided that the method of introduction was adjusted to the support: except with NaY, highly active molybdenum-free HDN catalysts could be prepared. The activity of the supported phosphorus promoted catalysts was ascribed to a new sulfur-free phase, consisting of highly dispersed Ni_2P.

INTRODUCTION

Mixed transition metal sulfides (TMS) are active catalysts for the removal of sulfur, nitrogen, oxygen, nickel, and vanadium from heterocyclic molecules, present in heavy oil fractions. Moreover, the thermal stability of these sulfides is such that they can be applied for the conversion of S-, N-, O-, Ni-, and V-contaminated heavy oil fractions to clean lower molecular weight hydrocarbon products. These catalysts are therefore extensively used for economically very important processes in the oil processing industry, so-called hydrotreating or hydroconversion (1).

Commercially applied catalysts usually contain a mixed Co–Mo or Ni–Mo sulfide phase. Mo is present as well dispersed MoS_2, which is often referred to as the basic sulfide ingredient, whereas Co or Ni, present in the form of a so-called "Co–Mo–S" or "Ni–Mo–S" promoter phase at the edges of the MoS_2 crystals, is considered the main active phase (2–4). On the basis of a detailed study, Crajé (5) and Crajé *et al.* (6) have deduced from Mössbauer spectroscopy (MES) and extended X-ray absorption fine structure spectroscopy (EXAFS) measurements that Co–Mo–S is a highly dispersed "Co-sulfide" species characterized by particle size and/or ordering. High surface area γ-Al_2O_3 is used as carrier material for the catalytic ingredients, which are typically introduced via impregnation with aqueous solutions of Co (or Ni) and Mo salts. Phosphate is often added to the impregnation solution: It improves stability and increases metal solubility which enables one to prepare promoted catalysts with high Co (or Ni)–Mo contents in just one impregnation step (7–9). Phosphate is also known to influence the catalyst performance: increased activity for heteroatom removal (especially N), improved mechanical and thermal stability, and decreased fouling and coke formation have been attributed to it (7, 9–14).

In earlier research we studied the effect of the addition of phosphorus on the structure and catalytic activity of supported transition metal sulfides (15–22). In a study with carbon-supported TMS from the first, second, and third row, it was found that the application of P by a P/C precatalyst bed generally has a negative effect on the thiophene HDS activity (17, 20). A clear exception was Ni on carbon, of which the activity was rather increased by P. The influence on the quinoline HDN activity was also tested, using carbon-supported catalysts which were supplied with P by a P/C precatalyst (16, 17). A strong promoting effect was found for Ni/C; for Mo/C the promotion was small, while for NiMo/C even a poisoning effect was observed. When phosphorus was applied by impregnation of the support with H_3PO_4, the effects were largely the same (16, 17): strongly promoting for Ni/C; neutral for Mo/C, and negative for NiMo/C. The nature of the support appeared to play an important role, as was demonstrated by a study on alumina-based catalysts (16, 18). The very low HDN activity of Ni/Al_2O_3 and Mo/Al_2O_3 was hardly improved by

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impregnation of the support with H_3PO_4, while the active $NiMo/Al_2O_3$ catalyst became even more active.

In the present study it is investigated whether this very interesting "P-promotion effect" for Ni/C can be realized to the same extent with nickel supported on silica, silica–alumina, alumina, and zeolites, since these carrier materials are considered more appropriate for industrial application than carbon. Several ways for introducing phosphorus were tested (impregnating the support with solutions of P-containing compounds, contacting the catalyst with volatile phosphorus-oxygen compounds, reacting the catalyst with gaseous PH_3), resulting in preparation methods for various Ni–P(–S)/support combinations. The activity of the catalysts was tested in gas phase quinoline HDN at 30 bar.

Moreover, it was attempted to identify the active Ni–P (–S) compound that is responsible for the observed activity increase. For this purpose, H_2 or H_2S/H_2 treated and spent supported catalysts as well as a number of unsupported Ni–P(–S) model compounds were studied. Both Ni and Co are used as so-called promoters in hydrotreating; therefore, several Co–P(–S) compounds were also included in order to investigate if they could be the active phase in P-promoted cobalt catalysts.

EXPERIMENTAL

Preparation of Unsupported Model Catalysts

Ni_2P (97%) and $Co_3(PO_4)_2 \cdot 8H_2O$ (purity unknown) were purchased from Alfa Ventron.

$Ni_3(PO_4)_2 \cdot 8H_2O$ was prepared by precipitation from freshly prepared $Ni(OH)_2$ and H_3PO_4 (23). The product was X-ray amorphous, but EM/EDAX showed it to be homogeneous with a Ni : P ratio corresponding to $Ni_3(PO_4)_2$ stoichiometry.

$NiPS_3$ was synthesized by reacting stoichiometric quantities of Ni (Johnson Matthey, special grade), red phosphorus (Merck, >98%), and sulfur (Carl Roth, sublimed) in an evacuated quartz–glass tube at 973 K for 3.5 days (24). In XRD, two very intensive peaks ($d = 6.33$ and 3.17 Å) and many others with low intensity were found (Fig. 1), matching the diffraction pattern of $Ni_2P_2S_6$ (JCPDS file 33-952); however, the intensity ratios of the bands were quite different.

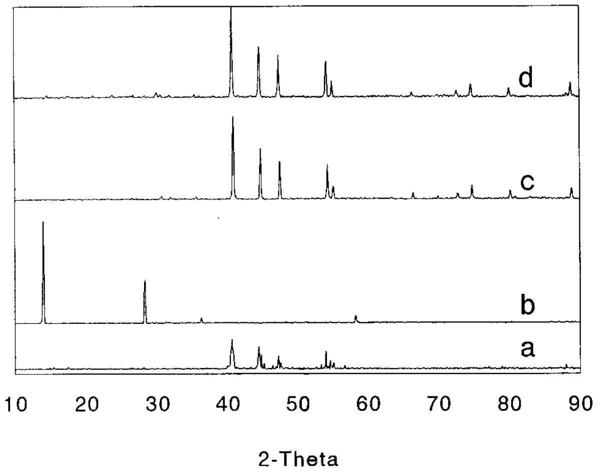


FIG. 1. XRD patterns of unsupported compounds. (a) Commercial Ni_2P. (b) Laboratory prepared $NiPS_3$. (c) Sulfided $NiPS_3$. (d) Sulfided $Ni_3(PO_4)_2$.

$CoPS_3$ was prepared in an analogous way (Co: Johnson Matthey, special grade) by heating at 973 K for 7 days (24). The XRD spectrum showed some broad, noisy peaks, but because of the lack of JCPDS reference data for $CoPS_3$, the sample could not be identified by XRD.

Preparation of Supported Catalysts

Table 1 summarizes the preparation of the supported catalysts and includes physical characteristics of the supports used.

TABLE 1

Support Materials and Preparation Methods for the Ni-Containing Supported Catalysts

Support	Notation	Surface area (SA), pore volume (PV)	Preparation method
Activated carbon (Norit RX3 Extra)	C	SA 1190 m^2/g PV 1.0 ml/g	Pore vol. impregnation H_3PO_4, $Ni(NO_3)_2$
SiO_2 (Degussa Aerosil 200)	Si^d	SA 200 m^2/g PV 0.76 ml/g	Pore vol. impregnation H_3PO_4, $Ni(NO_3)_2$
SiO_2 (AKZO Chemicals B.V.)	Si^a	SA 185 m^2/g PV 0.76 ml/g	Equilibrium adsorption $(NH_4)_2HPO_4$, $Ni(NO_3)_2$
SiO_2/Al_2O_3 (15% SiO_2)	SiAl	SA 269 m^2/g PV 0.50 ml/g	Equilibrium adsorption $(NH_4)_2HPO_4$, $Ni(NO_3)_2$
Al_2O_3 (Ketjen 001-1.5 E)	Al	SA 280 m^2/g PV 0.67 ml/g	Equilibrium adsorption $(NH_4)_2HPO_4$, $Ni(NO_3)_2$
NaY zeolite (LZY-52, AKZO Chemicals)	NaY		Ion exchange $NiCl_2$; impregnation NaH_2PO_2/H_3PO_4

Two NiNaY catalysts (ca. 8 wt% Ni) were prepared in which the nickel was introduced by ion exchange with 0.1 *M* $NiCl_2$ solutions. Phosphorus was introduced by impregnation with aqueous solutions of NaH_2PO_2 (pH 5.6) and H_3PO_4 (pH 1.6) at concentrations to obtain a $P/(Ni + P)$ molar ratio of 0.25 (designation: NaH_2PO_2/NiNaY and H_3PO_4/NiNaY).

For the preparation of the other supported catalysts, two procedures were used. The method of pore volume ("dry") impregnation, used for the carbon-supported catalysts, consisted of successive impregnation with appropriate volumes of H_3PO_4 or $(NH_4)_2HPO_4$ solutions and $Ni(NO_3)_2$ solutions of the desired concentration. After each impregnation step, the catalyst was dried in air at 393 K. In the equilibrium adsorption method, the support is suspended in an aqueous solution of $(NH_4)_2HPO_4$ (pH adjusted to 9.5 with ammonia), dried at 383 K, and subsequently suspended in a $Ni(NO_3)_2$ solution (pH adjusted at 12.0). All catalysts (except those supported on carbon) were calcined in static air for 2 h at 773 K. The nickel and phosphorus loading of the catalysts (in wt% P or wt% Ni) is indicated in brackets.

X-Ray Diffraction, EM/EDAX Analysis, and BET Measurements

XRD measurements were carried out on a Philips PW 1120 diffractometer using Cu$K\alpha$ radiation and a Ni filter.

Electron microscopy was performed in a Jeol JSM-840A scanning electron microscope equipped with energy dispersive analysis of X-rays (EDAX) facility. The samples were mounted onto carbon supports with carbon glue, without any further treatment.

BET surface areas were measured with a Carlo-Erba Sorptomatic apparatus. Before the BET measurement, the samples were conditioned for 1–20 h in vacuum at 293–353 K.

The samples were analyzed fresh or after a pretreatment analogous to pretreatments applied before the activity tests *(vide infra)*. All pretreated samples were stored in a N_2-filled recirculation type glove box (O_2 and $H_2O < 1$ ppm) until used for analysis.

Quinoline HDN Activity Tests

The activity of the samples for quinoline HDN was measured in a microflow reactor setup with a stainless steel reactor. Typically, the reactor was loaded with 0.5 g catalyst diluted with 9.5 g SiC. The sample was subjected to any of three standard pretreatments: (a) (SUL) treatment in a mixture of 10 vol% H_2S in hydrogen, (b) (RED) treatment in pure hydrogen, or (c) (NON) treatment in a nonreactive helium stream. In the following, treatment in H_2 or H_2S/H_2 are referred to as reduction (RED) or sulfidation (SUL) without implying that reduction (metal formation) or sulfidation (sulfide formation) actually takes place. In all three cases, the gas flow rate was 150 std $cm^3\ min^{-1}$; the pressure was either 15 bar (a and b) or 3 bar (c). The temperature was increased at 6 K min^{-1} to 643 K and held at this level for 4 h. After the pretreatment the gas flow was switched to hydrogen (950 std $cm^3\ min^{-1}$) and the reactor pressure increased to 30 bar; simultaneously, 12 $\mu l\ min^{-1}$ of liquid feed was evaporated in the hydrogen stream. The composition of the feed was 23.8 mol% quinoline (Janssen Chimica, 99%) and 3.8 mol% dimethyldisulfide (DMDS, Fluka, 99%) in 72.4 mol% *n*-decane (Janssen Chimica, >99%) The reaction mixture was analyzed after 30 min and at regular intervals, using a Hewlett-Packard 5890A GC equipped with a 50-m capillary CP Sil-5 fused silica column. In several cases, the catalyst activity was also measured at 663 and 623 K; at least 3 h was allowed for reaching steady state conditions.

Several techniques were applied for the *in situ* supply of phosphorus. In the combined-beds technique a P-containing prebed was placed upstream from the catalyst bed, separated by a layer of quartz wool. The prebed consisted of a mixture of 0.5 g H_3PO_4-impregnated activated carbon (4.8 wt% P on Norit RX3 Extra) and 1.5 g SiC. During the pretreatment of the catalyst, and possibly during the HDN reaction as well, P- containing compounds (presumably P_2O_5 or P_2O_3) which can interact with the catalyst sample downstream are released. Two other *in situ* techniques involved treatment with a PH_3-containing gas mixture. In the SUL/PH_3 technique a 5 : 5 : 90 $PH_3 : H_2S : H_2$ gas mixture was used (300 std $cm^3\ min^{-1}$, 15 bar). The PH_3 technique made use of a H_2S-free mixture (10% PH_3 in H_2, 150 $cm^3\ min^{-1}$, 15 bar).

RESULTS

Structure of Unsupported Model Catalysts after Pretreatment and HDN Reaction

The results of BET, XRD, EDAX, and EM analyses on the unsupported catalysts after pretreatment and HDN reaction are summarized in Table 2.

$Ni_3(PO_4)_2$ is converted into porous Ni_2P by a H_2S/H_2 treatment. This compound is stable under HDN conditions; no S-containing compounds were detected after pretreatment or after the HDN reaction. Reduction of $Ni_3(PO_4)_2$ also yields Ni_2P; the traces of Ni_5P_4 disappear after quinoline HDN. He-pretreated $Ni_3(PO_4)_2$ is reduced to Ni_2P during the HDN reaction by the hydrogen-containing gas.

$Co_3(PO_4)_2$ pretreated by either H_2S/H_2 or H_2 was X-ray amorphous; however, the EDAX analysis suggests the formation of Co_2P.

Treatment with H_2S/H_2 converts $NiPS_3$ into a sulfur-free product, possessing the crystal structure of Ni_2P.

Pure Ni_2P is both chemically and physically resistant to treatment with H_2S/H_2.

Quinoline HDN Reaction Scheme

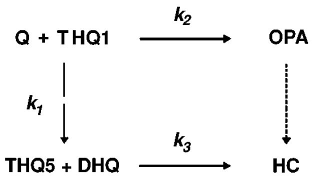
The conversion of quinoline (Q) to 1,2,3,4-tetrahydroquinoline (THQ1) is very fast; most likely equilibrium

TABLE 2

Analysis of Unsupported Ni–P and Co-P Compounds after Different Pretreatments

Compound	Pretr.	S_{BET} (m^2/g)	XRD	EDAX	EM
$Ni_3(PO_4)_2$	SUL	38	Ni_2P	Ni : P : S 2 : 1 : 0	Sponge-like structure of 1- to 3-μm particles
	SUL + HDN	11	Ni_2P	Ni : P : S 2 : 1 : 0	Gradual sintering
	RED	8	Ni_2P, Ni_5P_4 (wk)	Ni : P : S 2 : 1 : 0	As SUL
	RED + HDN		Ni_2P		
	NON	24	Amorph.		
	NON + HDN		Ni_2P		
$NiPS_3$	SUL		Ni_2P	Ni : P : S 2 : 1 : 0	As $Ni_3(PO_4)_2$ SUL
Ni_2P	SUL	17	Ni_2P	Ni : P : S 2 : 1 : 0	Rough, irregular particles
$Co_3(PO_4)_2$	SUL	12	Amorph.	Co : P : S 2 : 1 : 0	5- to 10- μm Lumps
	RED		Amorph.		More porous, sponge-like

is reached in every experiment (25). Therefore, we consider the conversion of Q + THQ1 (X_{Q+THQ1}) a more appropriate measure for the catalytic activity than quinoline conversion alone. Also, the hydrogenation products 5,6,7,8-tetrahydroquinoline (THQ5) and decahydroquinoline (DHQ) appear to be in equilibrium, and will therefore be lumped. Ring opening of THQ1 yields *o*-propylaniline (OPA), which is not further converted as long as strongly adsorbed double-ring nitrogen compounds are present, as was checked in a separate experiment, in which the contact time was varied in a wide range. The nitrogen-free hydrocarbons HC (propylcyclohexene, PCHE; propylbenzene, PBZ; and propylcyclohexane PCH) are formed by hydrogenolysis of DHQ. The resulting simplified reaction scheme is depicted in Scheme I. Besides the above-mentioned products, minor amounts of nitrogen-free cracking and isomerisation products were formed.



SCHEME I. Simplified quinoline HDN reaction scheme.

Due to the fairly high conversions obtained, and to the lacking of conversion data versus contact time, the initial rates of reaction could not be measured. However, assuming reaction rate equations of the Langmuir–Hinshelwood type,

$$r = k \cdot Y_i / \Sigma K_i \cdot Y_i,$$

where concentrations can be replaced by mole fractions Y_i, we can have access to selectivity parameters,

$$r_1 = k_1 \cdot Y_{Q+THQ1} / \Sigma K_i \cdot Y_i$$

$$r_2 = k_2 \cdot Y_{Q+THQ1} / \Sigma K_i \cdot Y_i$$

$$r_3 = k_3 \cdot Y_{THQ5+DHQ} / \Sigma K_i \cdot Y_i$$

where K_i is the adsorption constant and k_i the rate constant.

Dividing these rate equations by the rate of disappearance of Q + THQ1, the adsorption terms $\Sigma K_i \cdot Y_i$ cancel out, and the selectivities of THQ5 + DHQ and of OPA can be resolved by integration. This yields the theoretical values of the molar fractions of THQ5 + DHQ and OPA as a function of the conversion X of Q + THQ1:

$$Y_{THQ5+DHQ} = \alpha/(1-\beta) \cdot \{(1-X)^{\beta} - (1-X)\}$$

$$Y_{OPA} = (1-\alpha) \cdot X$$

with

$$\boldsymbol{a} = 1/(1 + (k_2/k_1)) \quad \text{and} \quad \beta = a \cdot (k_3/k_1).$$

The catalytic behavior of a catalyst can thus be characterized by its conversion of Q + THQ1 and by two selectivity parameters.

HDN Activity of Unsupported Model Catalysts

The results of the quinoline reaction test for the unsupported compounds are summarized in Tables 3 and 4, in which the activity and selectivity are reported after 2 and 16 h on stream.

TABLE 3

Activity and Selectivity in Quinoline HDN over Unsupported $Ni_3(PO_4)_2$ and $Co_3(PO_4)_2$ Catalysts (643 K, 30 bar)

Catalyst		TOS[a]	Conversion	Yield (%)			
No.	Notation	(h)	Q + THQ1	THQ5 + DHQ	OPA	HC	BY
1	$Ni_3(PO_4)_2$ (NON)	2	4.7	4.0	0.5	0.2	—
		16	31.6	17.1	6.8	7.8	—
2	$Ni_3(PO_4)_2$ (RED)	2	44.5	22.5	9.6	12.5	—
		16	41.9	24.3	7.8	9.8	—
3	$Ni_3(PO_4)_2$ (SUL)	2	31.7	17.5	6.6	7.6	—
		16	34.6	19.6	7.1	7.8	—
4	$Co_3(PO_4)_2$ (NON)	2	0.0	0.0	0.0	0.0	—
		16	1.3	1.3	0.0	0.0	—
5	$Co_3(PO_4)_2$ (RED)	2	1.4	1.3	0.1	0.0	—
		16	2.4	2.1	0.3	0.0	—
6	$Co_3(PO_4)_2$ (SUL)	2	21.3	14.3	2.4	4.5	—
		16	18.7	13.3	2.2	3.3	—

[a] TOS, time on stream.

$Ni_3(PO_4)_2$ and $Co_3(PO_4)_2$. Figure 2 gives X_{Q+THQ1} as a function of time on stream for the phosphate catalysts at 643 K. $Co_3(PO_4)_2$ (RED) and $Co_3(PO_4)_2$ (NON) hardly showed any activity. After sulfidation, however, a conversion of about 20% was reached which remained fairly constant during the entire run.

The $Ni_3(PO_4)_2$ samples were generally much more active than their cobalt-containing counterparts. The activity of $Ni_3(PO_4)_2$ (SUL) increased during the first few hours. After RED pretreatment an activity was obtained which was somewhat more constant in time at a level comparable to that of $Ni_3(PO_4)_2$ (SUL). Initially, the activity of $Ni_3(PO_4)_2$ (NON) was very low, but after about 6 h the activity climbed to a level which was barely lower than that of $Ni_3(PO_4)_2$ (SUL).

$NiPS_3$ and $CoPS_3$. The initial activity of all three $NiPS_3$ samples was high (yield of HC = 20–40%); however, after 16 h they were all strongly deactivated to a level of about 1% (Table 4). The initial order in activity (RED > SUL > NON) was preserved during the first 10 h of the test run.

The $CoPS_3$ catalysts had much lower initial activities than their Ni-containing counterparts, but they deactivated more

TABLE 4

Activity and Selectivity in Quinoline HDN over Unsupported $NiPS_3$, $CoPS_3$, and Ni_2P Catalysts (643 K, 30 bar)

Catalyst		TOS[a]	Conversion	Yield (%)			
No.	Notation	(h)	Q + THQ1	THQ5 + DHQ	OPA	HC	BY
7	$NiPS_3$ (NON)	2	48.9	10.6	14.8	22.7	0.8
		16	10.1	7.9	1.5	0.7	0.0
8	$NiPS_3$ (RED)	2	67.7	10.6	18.8	37.4	0.8
		16	16.7	12.5	2.7	1.3	0.0
9	$NiPS_3$ (SUL)	2	59.6	12.0	17.1	29.4	1.2
		16	15.7	12.1	2.2	1.4	0.0
10	$CoPS_3$ (NON)	2	23.4	15.2	3.8	4.4	—
		16	15.8	12.0	2.0	1.8	—
11	$CoPS_3$ (RED)	2	21.0	15.2	2.6	3.2	—
		16	15.0	11.6	1.8	1.6	—
12	$CoPS_3$ (SUL)	2	24.4	15.1	3.5	5.9	—
		16	19.4	14.0	2.1	3.5	—
13	Ni_2P (NON)	2	20.8	14.7	3.9	2.2	—
		16	13.1	10.2	2.0	0.9	—
14	Ni_2P (RED)	2	28.6	20.2	4.9	3.6	—
		16	18.9	14.8	2.7	1.4	—
15	Ni_2P (SUL)	2	23.1	16.3	3.6	3.1	—
		16	13.4	10.8	1.5	1.0	—

[a] TOS, time on stream.

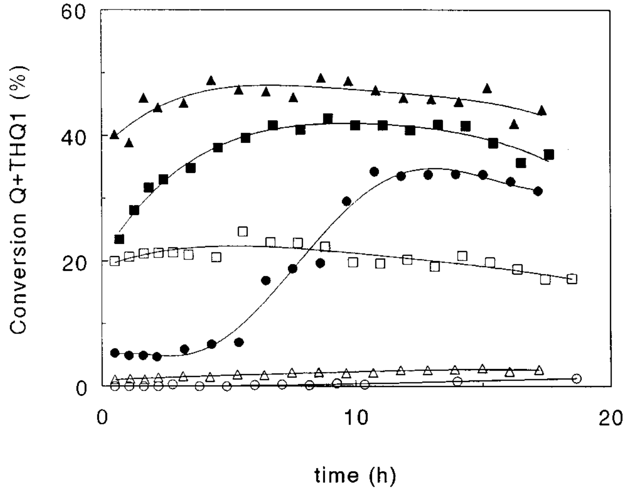


FIG. 2. Conversion of quinoline and THQ1 (X_{Q+THQ1}) versus time on stream for $Ni_3(PO_4)_2$ (filled symbols) and $Co_3(PO_4)_2$ (open symbols) (643 K, 30 bar) after sulfidation (SUL, ■, □), reduction (RED, ▲, △), and nonpretreatment (NON , ●, ○).

slowly (Table 4). The order in activity after 16 h is SUL > NON ≈ RED, but the differences are quite small.

Ni_2P. Again, all samples had a relatively low initial activity and showed slow deactivation during the run (Table 4). After 16 h, the order in activity is RED > SUL ≈ NON, with only small differences among the samples.

Selectivity of the Unsupported Model Catalysts

Figure 3 gathers the product selectivities of unsupported $Ni_3(PO_4)_2$, $NiPS_3$, and Ni_2P. The yields of THQ5 + DHQ and OPA, determined after 2 and after 16 h on stream (Tables 3 and 4), are plotted versus the Q + THQ1 conversion. The dashed lines join points with equal selectivity, calculated according to the quinoline reaction scheme with $k_2/k_1 = 0.17$ and $k_3/k_1 = 2$. It can be seen that the selectivity of all catalysts is very much alike, irrespective of pretreatment or time on stream. The one exception is the $NiPS_3$ catalyst, initially exhibiting a lower THQ5 + DHQ selectivity and a higher OPA selectivity, but joining the other catalysts after 16 h on stream.

HDN Activity of Supported Catalysts

The product distributions of the supported catalysts measured after 5 and about 18 h on stream are gathered in Tables 5 and 6. In the following, the catalysts included in these tables are referred to either by their notation or their number.

Carbon support. Normally, 1.0 g of catalyst was used, diluted with SiC to a total of 10 g. All catalysts were sulfided *in situ* according to the standard procedure, also in the case of the combined beds experiment. Figure 4 shows the evolution of the conversion of Q + THQ1 and the yield of HC with time on stream; the product distributions measured after 18–22 h on stream are shown in Table 5.

The Ni(6)/C catalyst showed a fairly stable Q + THQ1 conversion around 65%. The phosphorus impregnated catalyst Ni(4)P(5)/C was much more active; however, the conversion decreased slowly with time on stream. The conversion over P/C + Ni(6)/C was always close to 100%. The HC yield of Ni(6)/C decreased strongly in the beginning of the reaction and leveled off at a rather low level; the catalyst with phosphorus-impregnated support (Ni(4)P(5)/C) showed a marked decrease with time. In the combined beds

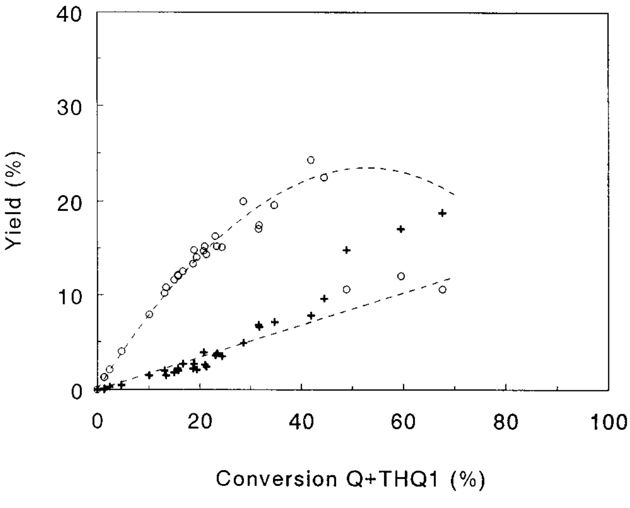


FIG. 3. Selectivity data for unsupported $Ni_3(PO_4)_2$, $NiPS_3$, and Ni_2P (643 K, 30 bar) after 2 and 16 h on stream: yield of THQ5 + DHQ (○) and yield of OPA (+) as a function of the conversion of Q + THQ1. The dashed lines represent calculated selectivity curves (see text).

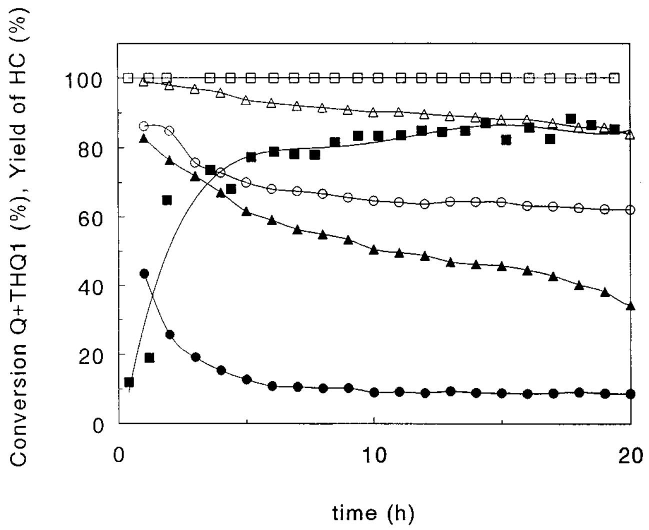


FIG. 4. Conversion of Q + THQ1 (open symbols) and yield of HC (filled symbols) versus time on stream (643 K, 30 bar) for sulfided Ni(6)/C (○, ●), Ni(4)P(5)/C (△, ▲), and P/C + Ni(6)/C (□, ■).

TABLE 5

Activity and Selectivity in Quinoline HDN over Carbon-Supported (Nos. 21–23), Degussa Silica-Supported (Nos. 24–25), AKZO Silica-Supported (Nos. 26–29), and Silica/Alumina-Supported (Nos. 30–31) Catalysts (643 K, 30 bar)

Catalyst		TOS[a]	Conversion	Yield (%)			
No.	Notation	(h)	Q + THQ1	THQ5 + DHQ	OPA	HC	BY
21	Ni(6)/C (SUL)	2	70.1	47.6	4.5	12.8	5.2
		8	66.9	49.5	3.9	9.2	4.3
22	Ni(4)P(5)/C (SUL)	5	93.7	14.5	9.3	61.7	8.2
		22	83.9	29.4	10.5	35.2	8.8
23	P/C + Ni(6)/C (SUL)	4	100.0	0.0	1.1	73.6	25.3
		18	100.0	0.0	1.2	86.7	12.1
24	Ni(7)/Si$^{\mathrm{d}}$ (SUL)[b]	5	70.1	36.0	4.7	18.7	10.7
		22	65.7	37.8	3.3	13.8	10.9
25	P/C + Ni(7)/Si$^{\mathrm{d}}$ (SUL)	5	98.8	2.2	12.3	70.5	13.8
		16	99.9	0.2	2.6	87.5	9.5
26	Ni(2)/Si$^{\mathrm{a}}$(SUL)	5	28.2	16.0	1.1	4.0	7.1
		14	27.0	15.3	1.0	3.6	7.1
27	Ni(2)/Si$^{\mathrm{a}}$ (SUL/PH$_3$)	5	92.8	11.8	6.3	70.0	4.7
		20	79.0	26.0	6.2	39.7	7.1
28	Ni(2)P(1)/Si$^{\mathrm{a}}$ (SUL)	5	81.5	23.1	8.1	43.6	6.7
		14	75.2	28.3	7.1	34.4	5.4
29	Ni(7)P(4)/Si$^{\mathrm{a}}$ (SUL)	5	91.1	6.2	7.5	73.3	4.1
		17	84.2	10.5	7.6	61.6	4.5
30	Ni(6)P(4)/SiAl (SUL)	5	39.7	28.0	1.4	5.5	4.8
		16	36.0	26.4	1.2	4.6	3.8
31	Ni(6)P(4)/SiAl	18	90.2	14.0	5.2	64.2	6.8
	(SUL/PH$_3$)	24	89.5	14.3	4.3	65.2	5.7

[a] TOS, time on stream.

[b] 2 g of catalyst.

TABLE 6

Activity and Selectivity in Quinoline HDN over Alumina-Supported (Nos. 32–36) and Zeolite-Supported (Nos. 37–38) Catalysts and over the Commercial Reference Catalyst KF 840 (643 K, 30 bar)

Catalyst		TOS[a]	Conversion	Yield (%)			
No.	Notation	(h)	Q + THQ1	THQ5 + DHQ	OPA	HC	BY
32	P/C + Ni(10)/Al (SUL)	6	52.8	29.2	3.8	9.7	10.1
		13	43.1	25.8	3.5	5.0	8.8
33	Ni(5)P(5)/Al (SUL)	6	45.6	32.9	2.4	7.2	3.1
		11	42.7	31.6	2.3	6.3	2.5
34	Ni(10)/Al (SUL/PH$_3$)	20	83.1	21.1	7.5	49.2	5.3
		34	67.5[b]	22.6	7.0	32.3	5.6
35	Ni(10)/Al (SUL/PH$_3$)	5-s	91.8[b]	12.0	3.5	68.4	7.9
		16-s	92.3[b]	21.4	3.6	58.5	8.8
36	Ni(10)/Al (PH$_3$)	5-s	94.3[b]	2.5	3.4	84.4	4.0
		14-s	97.2[b]	1.1	0.8	90.8	4.5
		24	66.4[c]	20.3	7.1	33.6	5.4
37	NaH$_2$PO$_2$/NiNaY	4	65.6	50.6	1.2	13.1	0.7
	(SUL)	16	67.6	51.8	1.2	13.9	0.7
38	H$_3$PO$_4$/NiNaY	3	47.9	42.0	1.0	3.8	1.1
	(SUL)	16	51.5	44.1	1.0	5.4	1.0
39	Ketjen KF 840	2	92.5	11.9	2.2	70.9	7.5
	(NiMoP/Al$_2$O$_3$)	16	86.3	22.6	3.5	55.0	5.2

[a] TOS, time on stream; -s, no DMDS present in feed.

[b] 623 K.

[c] 603 K.

experiment (P/C + Ni(6)/C) however, the HC fraction increased rapidly to a very high value (over 85%). Besides PCH and PBZ, only OPA and about 12% of N-free cracking and isomerization products (BY) were found in the product mixture.

SiO_2 support. The activity data of the Degussa silica-supported catalysts are given in Table 5. The performance of Ni(7)/Si^d (SUL) was moderate; by the use of the P/C prebed (No. 25), however, nearly complete Q + THQ1 conversion and a very high yield of HC were achieved. As in the case of the carbon-supported catalyst, the yield of HC increased slowly with time.

The AKZO silica-supported catalyst Ni(2)/Si^a (SUL) produced only 4% HC after 14 h on stream (Table 5). A fresh sample was subjected to the SUL/PH_3 treatment (1 h at 643 K) and afterward flushed with helium (No. 27). The yield of HC after 5 h on stream was as high as 70%, which, however, decreased to 40% after 20 h.

Ni(2)P(1)/Si^a (SUL) showed a fairly high initial yield of HC (44% after 5 h) which decreased only slowly with time (35% after 14 h).

The yield of hydrocarbons of Ni(7)P(4)/Si^a (SUL) was more than 50% higher than that of the former catalyst; however, a much larger increase was expected because the nickel and phosphorus content were about three times higher.

SiO_2/Al_2O_3 support. As can be seen from Table 5, the HDN activity of Ni(6)P(4)/SiAl (SUL) was low. Interestingly, a SUL/PH_3 treatment (1 h at 643 K) resulted in a dramatic increase in activity (No. 31).

Al_2O_3 support. For both P/C + Ni(10)/Al (SUL) and Ni(5)P(5)/Al (SUL), we note a low yield of HC (Table 6; Nos. 32–33), which is on the same level as for the sulfided Ni/SiO_2 catalysts.

A Ni(10)/Al catalyst was subjected to several pretreatments (Nos. 34–36). After successive sulfidation and phosphine treatment (SUL/PH_3; No. 34) the activity was clearly higher than of catalysts 32 and 33. The same pretreatment but with a DMDS-free feed mixture (No. 35) yielded a much higher activity (comparison temperature 623 K). Pretreatment in the absence of H_2S (No. 36) gave rise to an even higher activity when tested under the same (DMDS-free) conditions as No. 35. Upon addition of DMDS to the feed (at 603 K and 24 h run time), the activity of catalyst No. 36 dropped strongly; however, it was still higher than for catalyst No. 34, measured at 623 K with DMDS-containing feed.

It is interesting to compare the HDN activity of the P-promoted Ni/Al catalysts with that of a commercial NiMoP–catalyst (Ketjen KF 840). After standard sulfidation, the HDN activity was measured at the same conditions (643 K, 30 bar, DMDS-containing feed). We see that the activities of the phosphine-treated Ni/Al catalysts are at least comparable to that of the commercial catalyst (Table 6), which besides P also contains a considerable amount of Mo.

Zeolite support. The two NiNaY-supported catalysts, NaH_2PO_2/NiNaY and H_3PO_4/NiNaY were tested for their quinoline HDN activity with *n*-hexane instead of *n*-decane as solvent. The catalyst sample (0.25 g dry weight) was diluted with 4.75 g of SiC and dried in the reactor under a flow of helium at atmospheric pressure (heating rate 6 K min^{-1}, 1 h at 673 K). Next, the catalyst was sulfided according to the SUL procedure. Table 6 gives the relevant activity data. The activity of both catalysts was quite stable during the whole test run, which is in marked contrast with their rapid deactivation during thiophene HDS at atmospheric pressure (26). The highest activity appeared to be realized by impregnating the support with NaH_2PO_2.

Selectivity of the Supported Catalysts

Figure 5 shows the steady-state selectivity for THQ5 + DHQ of the supported catalysts measured at 643 K with a DMDS-containing feed. The numbers in the figure correspond to the catalyst numbers in Tables 5 and 6. The dashed lines join points with equal hydrogenolysis/hydrogenation selectivity ($k_3/k_1 = 0.35$, 0.90, and 1.45 with k_2/k_1 fixed at 0.05) calculated from the simplified reaction scheme.

It is clear that Ni/(6)/C and the zeolite-supported catalysts (Nos. 21, 37, 38) have a poor hydrogenolysis capacity ($k_3/k_1 \approx 0.35$), while Ni(2)/Si^a (SUL) and Ni(7)P(4)/Si^a (SUL) (Nos. 26, 29) have the highest values. All other catalysts have values for the selectivity ratio between 0.90 and 1.45, without a clear trend according to preparation or pretreatment. It should be noted that, because of their extremely high conversion, catalysts 23 and 25 could not be classified in a selectivity group.

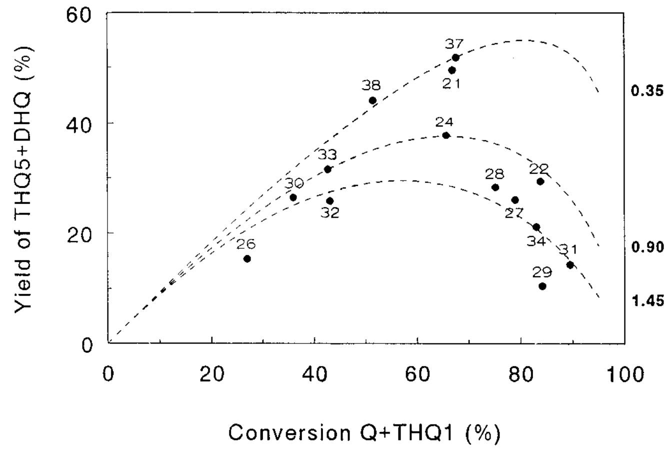


FIG. 5. Yield of THQ5 + DHQ versus conversion of Q + THQ1 for all supported catalysts (643 K, 30 bar, about 18 h on stream). The numbers correspond to the catalyst numbers in Tables 5 and 6. The dashed lines represent different values of the selectivity parameter k_3/k_1 (see text).

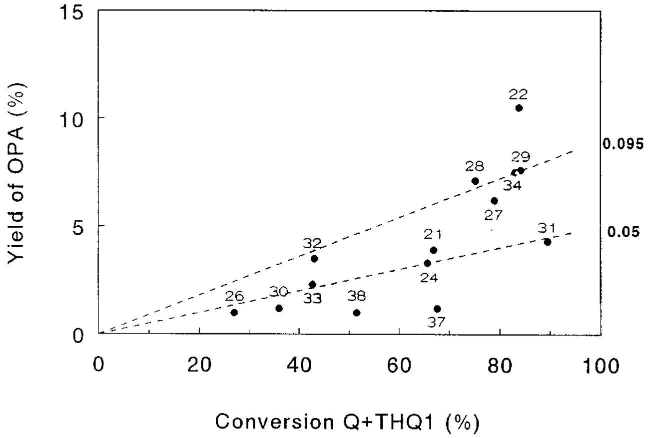


FIG. 6. Yield of OPA versus conversion of O + THO1 for all supported catalysts (643 K, 30 bar, about 18 h on stream). The numbers correspond to the catalyst numbers in Tables 5 and 6. The dashed lines represent different values of the selectivity parameter k_2/k_1 (see text).

The corresponding selectivity plot for OPA is shown in Fig. 6; here, the dashed lines are drawn for equal ring opening/hydrogenation selectivity ($k_2/k_1 = 0.05$ and 0.095). The zeolite-supported catalysts (Nos. 37, 38) have a very low OPA selectivity. Among the other catalysts, we can roughly distinguish two groups. The first group, with the lower OPA selectivity ($k_2/k_1 \approx 0.05$), comprises the catalysts Ni(6)/C (SUL), Ni(7)/Si^d (SUL), Ni(2)/Si^a (SUL), Ni(6)P(4)/SiAl (SUL), Ni(6)P(4)/SiAl (SUL/PH_3), and Ni(5)P(5)/Al (SUL) (Nos. 21, 24, 26, 30, 31, 33, respectively). The second group ($k_2/k_1 \approx 0.095$) consists of the phosphided catalysts Ni(2)/Si^a (SUL/PH_3) and Ni(10)/Al (SUL/PH_3), the double bed P/C + Ni(10)/Al (SUL) catalyst, and the phosphorus impregnated silica catalysts Ni(2)P(1)/Si^a (SUL) and Ni(7)P(4)/Si^a (SUL) (Nos. 27, 28, 29, 32, 34, respectively). The phosphorus impregnated carbon catalyst Ni(4)P(5)/C (SUL) exhibits a much higher OPA selectivity (No. 22).

DISCUSSION

Active Phase

It follows from the results presented in the Tables 5 and 6 that phosphorus-promoted nickel on various supports can be highly active for gas phase quinoline HDN. To elucidate the active phase of these Ni(Co)- containing Mo-free catalysts, unsupported Ni(Co)-containing phosphorus compounds were applied as model catalysts. From the XRD and EDAX results of these catalysts it has been found that the most active model catalysts contained under reaction conditions nickel (cobalt)–phosphorus compounds, in particular Ni_2P (Co_2P), and virtually no sulfur. This conclusion is supported by the results of a Mössbauer study on ^{57}Fe doped $Ni_3(PO_4)_2 \cdot 8H_2O$ (26). As shown in Fig. 7a similar high-spin Fe^{2+} (probing high-spin Ni^{2+}) compound is observed after a reduction as well as a sulfidation treatment at 673 K. Furthermore, this high-spin Ni^{2+} compound has been transformed into Ni_2P (determined by XRD) by an additional reduction or sulfidation treatment at 643 K and 15 bar (Fig. 7c).

It has been found that the presence of sulfur (H_2S) was not required to transform $Ni_3(PO_4)_2$, $NiPS_3$, and $CoPS_3$ into active catalysts, but only a sufficient reduction of the starting materials. However, H_2S facilitates the reduction process, as found in the Mössbauer spectroscopy study on ^{57}Fe doped $Ni_3(PO_4)_2 \cdot 8H_2O$ samples (26). The activation of $Co_3(PO_4)_2$ by the H_2S/H_2 mixture but not by pure H_2 may be another example of this effect. The finding that Ni_2P is not altered by heating in H_2 and H_2S/H_2 explains the fact why different pretreatments have only marginal effect on the HDN activity of the Ni_2P samples; this points also to the result that Ni_2P(Co_2P) will be the active phase for HDN in the Ni(Co)-containing catalysts. The similarity in the selectivity plot for the unsupported compounds (Fig. 3) also indicates that the same Ni_2P phase is responsible for the activity of the Ni-containing compounds, irrespective of the precursor. The low HDN activity of the unsupported Ni_2P samples is in our opinion due to the low surface area of these samples and not due to an intrinsic low HDN activity. A parallel may be drawn with transition metal carbides and nitrides, which combine high surface area with high HDN activity (27, 28).

From the above, it seems probable that for medium high-pressure reactions the promoting action of phosphorus to Mo-free nickel catalysts consists in the formation of chemically and physically stable nickel phosphide(s). Important parameters in this process are the pressure and the composition of the reducing medium. There are indications that the cobalt-containing compounds can also form (cobalt) phosphides, but the conditions required appear to be more severe (higher temperature and pressure) than for nickel.

The genesis of a Ni_2P phase in supported catalysts appears to be reflected in the selectivity behavior (Figs. 5 and 6). Although the trend is not completely unambiguous, the catalysts which were effectively promoted by P have a higher OPA selectivity (higher k_2/k_1 ratio) and approximately the same THQ5 + DHQ selectivity (k_3/k_1 ratio) compared to the nonpromoted (NiS_x containing) catalysts. However, the OPA selectivities of the P-promoted catalysts are low compared with the unsupported Ni_2P compound. A possible explanation of this effect can be that the phosphiding of the supported nickel is incomplete and that besides Ni_2P also NiS_x contributes to some extent to the HDN activity.

It should be emphasized that the described formation of Ni_2P occurred in Mo-*free* catalysts. In numerous other studies, however, (Ni)Mo/Al_2O_3 catalysts to which phosphorus was usually added in the form of phosphate anions were

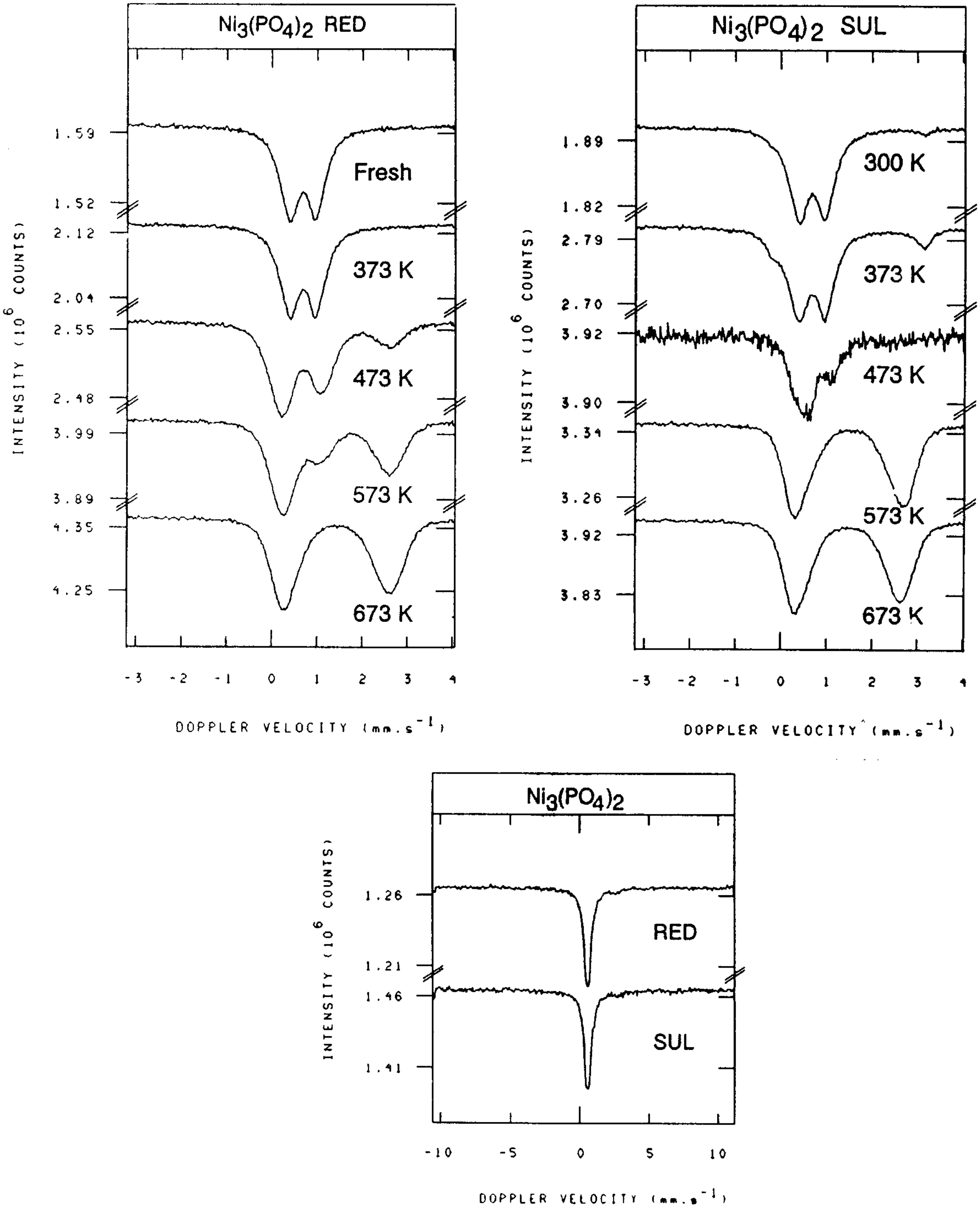


FIG. 7. Room temperature Mössbauer spectra of ^{57}Fe doped $Ni_3(PO_4)_2 \cdot 8H_2O$ after stepwise reduction in H_2 at 1 bar (RED, top), stepwise sulfidation in H_2S/H_2 at 1 bar (SUL, top right), and after a treatment at 15 bar (bottom) in H_2 (RED) or H_2S/H_2 (SUL).

studied. In these systems, phosphate appeared able to modify the surface properties of the alumina (29–31), to influence the structure and dispersion of the Mo surface species, both in the calcined (30–36) and sulfided catalyst (37, 38), and consequently influence the rate of the different reaction steps involved in HDN (39, 40). The formation of Ni_2P in these $NiMoP/Al_2O_3$ catalysts, however, may be just as unlikely as in impregnation-prepared Ni-P/Al_2O_3 catalysts (*vide supra*). Additional experiments with laboratory prepared impregnation-type $NiMo/Al_2O_3$ and $NiMoP/Al_2O_3$ catalysts resulted in $k_2/k_1 = 0.05$ and 0.055 and $k_3/k_1 = 0.6$ and 1.0, respectively. For the P-containing commercial catalyst, about the same selectivity ratios were found as for $NiMoP/Al_2O_3$. Thus, both selectivity parameters increase upon addition of P. The promotion of the supported Ni-catalysts in this work shows the inverse trend, i.e. an increase in k_2/k_1, while the effect on k_3/k_1 is less pronounced. This suggests that no Ni_2P was formed in the (commercial) $NiMoP/Al_2O_3$ catalyst.

Preparation Methods of Supported Nickel (Cobalt) Phosphide

It has been observed that the optimum method for preparing supported nickel phosphide is clearly dependent on the nature of the support. Therefore we will discuss our findings separately for each support applied.

Carbon support. The HDN activity of Ni supported on activated carbon could be strongly increased by impregnation of the support with H_3PO_4 prior to introduction of Ni. The application of a H_3PO_4/carbon prebed (P/C) also caused a large increase in activity. This increase is due to the release of volatile P-containing compounds which can react with the nickel catalyst. However, the increase in activity during the HDN test indicates that the transfer of P and/or formation of Ni_2P from the volatile P-containing compounds is a rather slow process, which continues after the pretreatment. Furthermore, it has been determined by phosphorus analysis (20) of the P/C prebed and the Ni/C catalyst that this way of preparing Ni_2P is rather inefficient: the major part of the H_3PO_4 passes the catalyst bed without reacting.

SiO_2 support. The same preparation methods were effective with silica; moreover, it was found that a pretreatment with a $PH_3/H_2/H_2S$ gas mixture promotes the HDN activity. The comparable selectivities (THQ5 + DHQ and OPA) of the H_3PO_4 impregnated and PH_3 pretreated Ni/SiO_2 catalysts suggest the formation of a similar active phase in these catalysts. The observed gradual deactivation of the $PH_3/H_2/H_2S$ prephosphided catalyst during the test run is most likely due to the loss of dispersion and not a chemical modification of the active phase, as from the experiments with the model compounds we know that Ni_2P is quite stable under reaction conditions.

SiO_2/Al_2O_3 and Al_2O_3 supports. For these supports only the $PH_3/H_2(/H_2S)$ method was an effective pretreatment. From the comparable selectivities it is concluded that the active phase formed will be the same as that on the phosphorus-treated Ni/silica catalysts. Applying the other phosphorus introducing techniques, P is supplied in the form of oxidic compounds, which likely form $AlPO_4$, rather than react with nickel. Indeed, the H_3PO_4 impregnated SiO_2/Al_2O_3- and Al_2O_3-supported Ni catalysts exhibit a selectivity comparable with that of the Ni/SiO_2 (SUL) catalysts, indicating that P is not involved in the active phase. Mössbauer studies on ^{57}Fe doped NiP/Al_2O_3 catalysts (26) also suggest that Ni and P do not have an interaction.

In creating the active phase on Ni/Al_2O_3, H_2S appears to play no important role; the Ni/Al_2O_3 catalyst becomes more active when pretreated in a S-free gas mixture (i.e., PH_3/H_2). This result strongly supports the idea that the high HDN activity should be ascribed to a Ni–P compound and not to a Ni–P–S compound. The presence of H_2S during HDN, formed from DMDS in the liquid feed, clearly has a negative influence on its activity.

NaY support. The two ion-exchanged/impregnated catalysts studied (NaH_2PO_2/NiNaY and H_3PO_4/NiNaY) showed a high THQ5 + DHQ selectivity while their selectivity for OPA was very low. This behavior is very different from the phosphided SiO_2- and Al_2O_3-supported catalysts, suggesting that no Ni_2P was formed and that another compound has to be responsible for the activity.

CONCLUSIONS

It has been demonstrated that phosphorus-promoted nickel on various supports is highly active for gas phase quinoline HDN. Effective phosphorus introduction methods were developed, depending on the nature of the support. Activated carbon was successively impregnated with aqueous solutions of H_3PO_4 and $Ni(NO_3)_2$; for SiO_2, equilibrium adsorption with the same solutions was applied. Reacting the Ni catalyst with volatile P-containing compounds, released by a H_3PO_4/carbon precatalyst bed, was also effective for both the carbon and the SiO_2 support. With SiO_2/Al_2O_3 or Al_2O_3 as support, an oxygen-free P-compound appeared to be required to activate the catalyst, which requirement could be fulfilled by pretreatment with a $PH_3/H_2/H_2S$ or PH_3/H_2 gas mixture. The latter (sulfur-free) pretreatment mixture resulted in the highest HDN activity. Also during the HDN experiment itself, the absence of sulfur from the feed appeared beneficial to the activity.

Based on the latter finding and the results obtained with the unsupported model compounds we conclude that a new sulfur-free phase, viz. highly dispersed Ni_2P, is responsible for the high catalytic activity. This activity can be even higher than that of a conventional commercial HDN catalyst which besides Ni also contains relatively large amounts of molybdenum (sulfide).

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