# Binary and Ternary Transition-Metal Phosphides as HDN Catalysts

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Transition-metal phosphides ($Co_2P$, $Ni_2P$, MoP, WP, CoMoP, NiMoP) were prepared by reducing metal oxide/phosphate precursors in a flow of $H_2$. The solids obtained were tested in the hydrodenitrogenation of *o*-propylaniline at 643 K and 3 MPa. All the catalysts were active, with product selectivities resembling those of sulfidic catalysts. The influence of $H_2S$ on the activity and selectivities was tested and is discussed with regard to a possible surface modification. Based on the surface area of each catalyst, we estimated the relative intrinsic activities of the different phosphides. According to this estimation, MoP was intrinsically the most active catalyst. © 2001 Academic Press

*Key Words:* transition-metal phosphides; preparation; hydrodenitrogenation; *o*-propylaniline; comparison; hydrogen disulfide.

## 1. INTRODUCTION

Transition-metal phosphides have a wide range of interesting chemical and physical properties (1, 2). Phosphides may be classified in various ways, the usual being based on the stoichiometry, i.e., metal-rich phosphides (M/P > 1), monophosphides (M/P = 1), and phosphorus-rich phosphides (M/P < 1). Due to the thermal and chemical instability of phosphorus-rich phosphides, applications are more often reported for phosphides with a ratio of M/P ≥ 1. Metal-rich phosphides and, similarly, monophosphides are usually hard, brittle substances with relatively high thermal and electrical conductivities and thermal stability (3). Thus, transition-metal phosphides are applied as protective refractory coatings in electric lamps (4), as oxygen barrier layers in capacitors (5), and in coatings that are resistant to wear and corrosion (6).

Research on transition-metal phosphides in the field of heterogeneous catalysis focuses mainly on hydrogenation catalysis. The potential application of supported and unsupported crystalline transition-metal phosphides in hydrogenation catalysis was reported by various authors (7–10). Furthermore, amorphous nickel phosphorus alloys can be used as selective hydrogenation catalysts with a high activity (11–15). However, the amorphous catalysts deactivate at elevated temperatures due to the formation of less active crystalline compounds (16). Another drawback of the amorphous metal alloys is their sensitivity to sulfur-containing compounds, which leads to their deactivation (17). Yet the sulfur resistance of a catalyst is an important aspect of hydrodenitrogenation catalysis, because sulfur is always present in crude oil. Only few publications deal with the application of transition-metal phosphides in hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) catalysis. Robinson *et al.* showed that dinickel phosphide ($Ni_2P$) and dicobalt phosphide ($Co_2P$) are formed from the respective metal phosphates under reductive conditions, even in the presence of sulfur, and that these phosphides are active catalysts in the HDN of quinoline (18). Molybdenum phosphide (MoP) was prepared recently by reducing an amorphous molybdenum phosphate precursor and tested for catalytic activity in the HDN of quinoline (19). Using the same synthetic approach we prepared an unsupported MoP catalyst in a previous study and found that the catalyst was more active than an $Al_2O_3$-supported $MoS_2$ catalyst in the HDN of *o*-propylaniline (20). Despite the fact that *o*-propylaniline is a simple test molecule, it has enabled the in-depth study of several reactions involved in the HDN of N-containing aromatic compounds (hydrogenation of the phenyl ring, hydrogenolysis of the $C(sp^2)$–N bond, elimination of $NH_3$ from cyclohexylamine, and hydrogenation of cyclohexene) (21–24).

We prepared different binary transition-metal phosphides, ($Co_2P$, $Ni_2P$, MoP, and WP) by reducing an appropriate precursor in a flow of $H_2$. The preparation procedures were based on those reported in the literature (7, 9, 19, 20, 25, 26). The promoting effect of Co and Ni is known from HDS and HDN catalysis with $MoS_2$-type catalysts. To determine whether Co and Ni have similar effects on MoP, we also prepared the ternary phosphides CoMoP and NiMoP. All the phosphides were tested in the HDN of *o*-propylaniline at 643 K and 3.0 MPa in the presence and absence of $H_2S$.

## 2. EXPERIMENTAL

### Preparation of the Catalysts

The general procedure for preparing the phosphides was as follows: Di-ammonium hydrogen phosphate $(NH_4)_2$ $HPO_4$ was dissolved in deionized water. Subsequently a solution of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ ($x = 18$), nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, or cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ was added (all Fluka, puriss. p.a.). In the case of the two ternary phosphides, first a solution of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ followed by a solution of nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ or cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ was added to the phosphate solution. For all the compounds, the amounts of metal salt(s) and phosphate were chosen according to the stoichiometry of the corresponding phosphide.

After evaporation of the water, the solid obtained was calcined in air at 773 K for 5 h and then reduced in a stream of $H_2$ (99.999%, 300 mL $\cdot$ min$^{-1}$) at 823 K ($Co_2P$, $Ni_2P$), 923 K (MoP, WP, NiMoP), and 1023 K (CoMoP) (heating rate of 1 K $\cdot$ min$^{-1}$). Finally, the surface of the samples was passivated in a flow of 0.5% $O_2$/He (30 ml $\cdot$ min$^{-1}$) for 2 h at room temperature. The passivated phosphides can be handled in air.

XRD measurements were done with a Siemens D-5000 powder X-ray diffractometer (Cu K$_\alpha$ radiation). For the measurements, a sample was pressed into a flatbed sample holder. Nitrogen adsorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 or a Micromeritics Tristar 3000 instrument. The surface area was determined according to the BET method.

### HDN Activity Measurements

The catalytic tests for the HDN of $o$-propylaniline were carried out in a continuous-flow microreactor at a total pressure of 3.0 MPa. A sample (0.05–0.4 g) of the catalyst (Table 1), diluted with 8 g SiC, was used for each reaction. To remove the oxygen from the surface of the passivated catalysts, the catalysts were activated *in situ* with $H_2$ at 673 K and 0.2 MPa for 3 h. The liquid reactant was fed into the reactor by means of a high-pressure pump with $n$-octane as the solvent. A second pump made it possible to change to a feed of a different composition without interrupting the reaction. The catalyst was stabilized at 643 K and 3.0 MPa for at least 12 h before samples were taken. Variation of space time was achieved by changing the flow rate while keeping the ratio between the liquid feed and the $H_2$ gas flow constant. The product stream was analyzed online with a gas chromatograph equipped with a FID detector; $n$-heptane was the internal standard. Each set of experimental conditions was maintained for at least 4 h. Further details can be found in Ref. (21).

### TABLE 1

**Amounts of Catalyst Used for the Activity Test and BET Surface Areas of the Catalysts**

| Catalyst | Amount [mg] | BET surface area [m$^2 \cdot$ g$^{-1}$] |
|---|---|---|
| Co$_2$P | 150 | 3 |
| Ni$_2$P | 400 | 1 |
| MoP | 200 | 2 |
| WP | 300 | 6 |
| CoMoP | 100 | 5 |
| NiMoP | 50 | 8 |

The initial reactant partial pressure of $o$-propylaniline was 3 kPa. To study the HDN reaction of OPA in the presence of $H_2S$ (6 kPa), dimethyl disulfide (DMDS) was added to the feed that was pumped into the reactor by the second pump. After activation each catalyst was studied in the absence of $H_2S$; the reaction was continued in the presence of $H_2S$ by switching to the feed containing DMDS. Finally, DMDS was removed so that we could monitor the behavior of the catalyst again in the absence of $H_2S$. After removing DMDS, the catalysts were left to stabilize for 12 h before being subjected to one set of flow conditions for 12 h to check for further changes.

## 3. RESULTS AND DISCUSSION

### Characterization of the Phosphide Catalysts

The XRD patterns of all the synthesized phosphides (Figs. 1–3) are in agreement with literature data (27). CoMoP was the major component in a mixture, accompanied by small amounts of an unidentified crystalline phase. NiMoP contained small amounts of MoP. In all the other
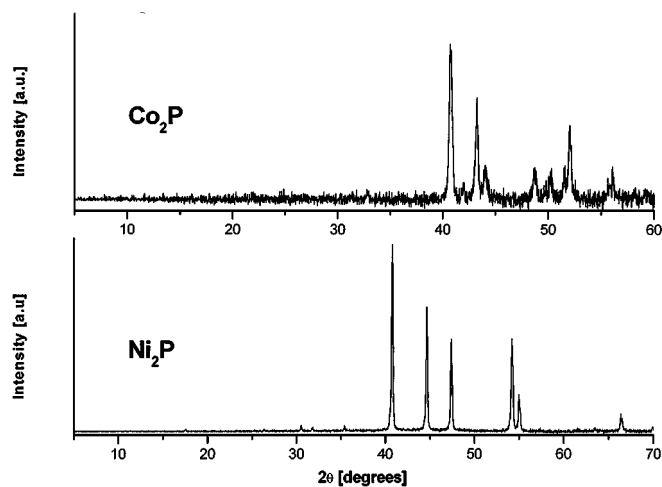


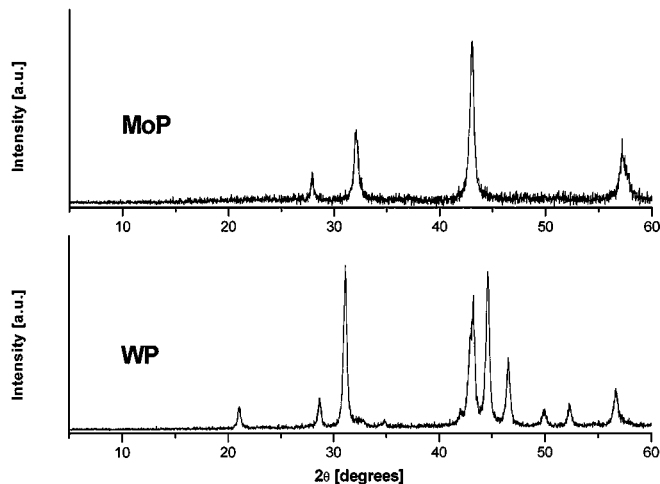**FIG. 1.** Powder XRD patterns of the passivated Co$_2$P and Ni$_2$P catalysts.

**FIG. 2.** Powder XRD patterns of the passivated MoP and WP catalysts.



**FIG. 4.** HDN conversion of $o$-propylaniline over $Co_2P$ in the absence ($a$) and presence ($b$) of $H_2S$ and after removal of $H_2S$ ($c$).

cases, only one crystalline phase was detected. The surface areas, as determined by $N_2$ adsorption, ranged from 1 to 8 $m^2 \cdot g^{-1}$ (Table 1).

### Activity Measurements

Prior to the determination of the catalytic activity, the sample was reactivated in a $H_2$ flow at 673 K for 3 h. Table 1 gives the amounts of catalyst. Amounts were adjusted to obtain comparable activities for the different catalysts at the beginning of the reaction. Activity measurements for the $o$-propylaniline HDN were performed in the absence, then in the presence of $H_2S$, and again in the absence of $H_2S$. Each experiment was performed in a continuous flow of feed while a constant total pressure of 3.0 MPa was maintained. The results of the activity measurements are pre-
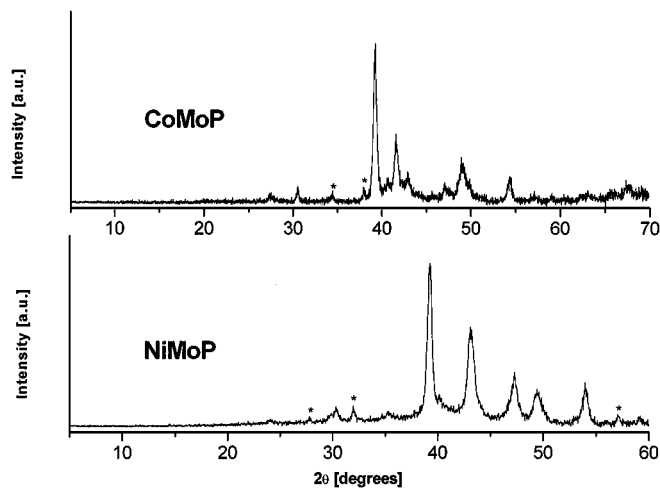
sented in Figs. 4–9. All the phosphides were active catalysts in the HDN of $o$-propylaniline. However, when $H_2S$ was introduced into the system, the catalysts behaved differently. With increasing space time the activity curves of all the catalysts level off the closer they get to equilibrium conditions. Below 20% conversion all the curves show a linear trend, that is, differential behavior can be assumed.

$Co_2P$ and $Ni_2P$ showed a clearly lower activity in the presence of $H_2S$ (Figs. 4 and 5), that is, the catalysts underwent deactivation. The deactivation appears to be partially irreversible; after the removal of $H_2S$, the activity increased again but did not reach its former level.



**FIG. 3.** Powder XRD patterns of the passivated CoMoP and NiMoP catalysts (reflections due to impurities are marked by asterisks).



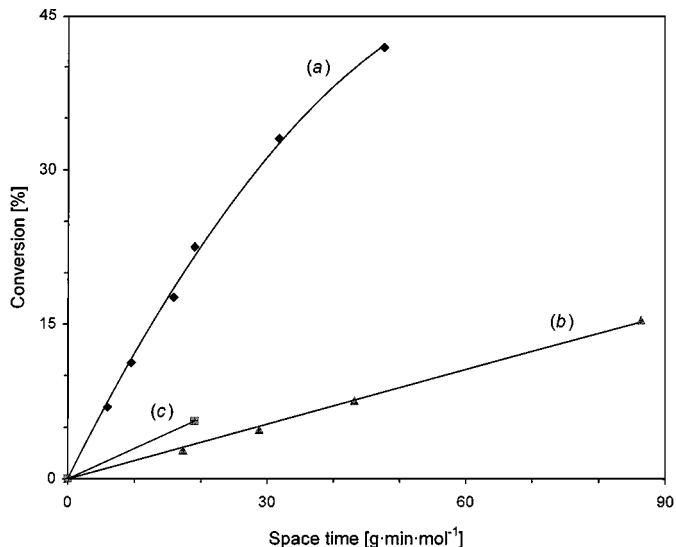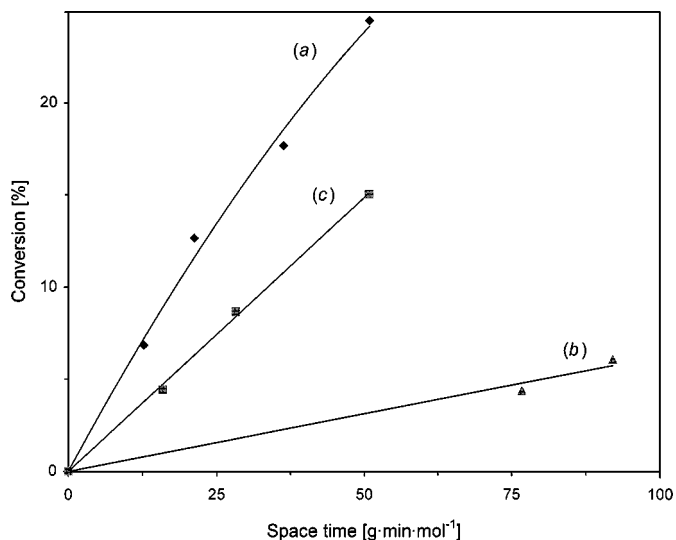**FIG. 5.** HDN conversion of $o$-propylaniline over $Ni_2P$ in the absence ($a$) and presence ($b$) of $H_2S$ and after removal of $H_2S$ ($c$).

**FIG. 6.** HDN conversion of *o*-propylaniline over MoP in the absence (*a*) and presence (*b*) of $H_2S$ and after removal of $H_2S$ (*c*).
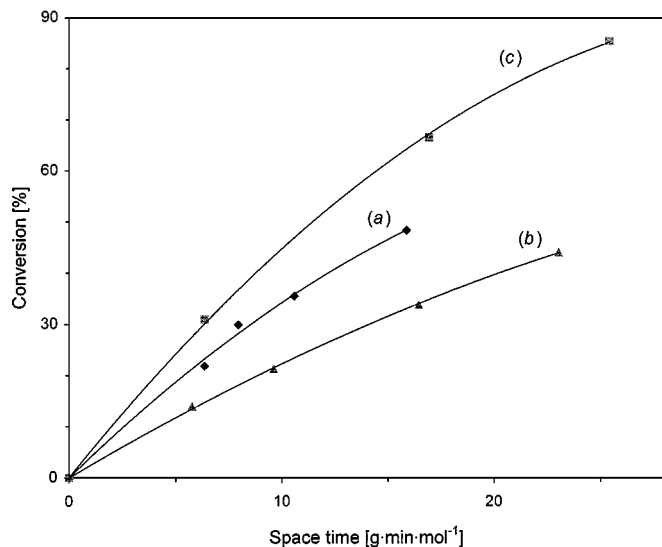


**FIG. 8.** HDN conversion of *o*-propylaniline over NiMoP in the absence (*a*) and presence (*b*) of $H_2S$ and after removal of $H_2S$ (*c*).

The activity of MoP was lower in the presence of $H_2S$. However, after the removal of $H_2S$ the activity increased to a higher level than that before the addition of $H_2S$. The activity of WP even increased in the presence of $H_2S$ compared with the activity before the addition of $H_2S$. After the removal of $H_2S$, the activity of the WP catalyst remained on a higher level.

The smallest influence of $H_2S$ on catalytic behavior was observed for CoMoP and NiMoP. The activities of these catalysts were somewhat lower in the presence of $H_2S$ and returned almost to their original levels after the removal of $H_2S$.
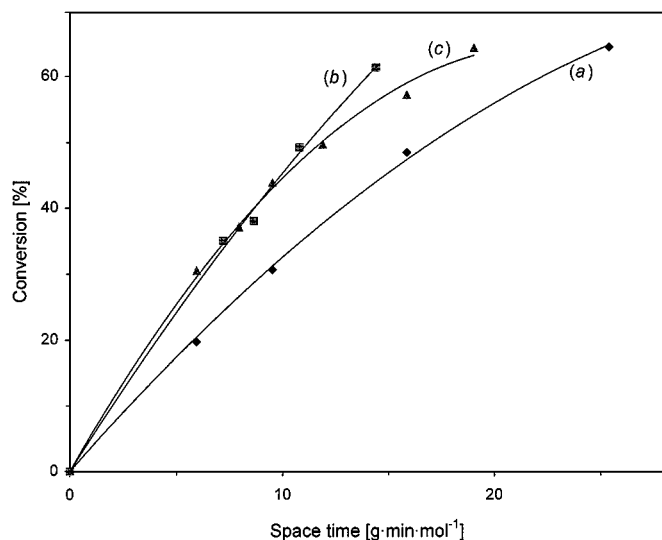
## Product Selectivities

For all the catalysts, the main products of the *o*-propylaniline HDN were propylcyclohexane (PCH), propylcyclohexenes (PCHE), propylbenzene (PB), and butylcyclopentane (BCP). The product selectivities, in the absence and presence of $H_2S$, plotted against the conversion are shown in Figs. 10–15. Hydrogenolysis products, such as ethylbenzene, toluene, and benzene, were not observed. This behavior differs from that of the molybdenum nitrides, as reported by Lee *et al.* (28). When they tested $Mo_2N$ in the HDN of quinoline, *o*-propylaniline was formed as an important reaction intermediate, which reacted further



**FIG. 7.** HDN conversion of *o*-propylaniline over WP in the absence (*a*) and presence (*b*) of $H_2S$ and after removal of $H_2S$ (*c*).
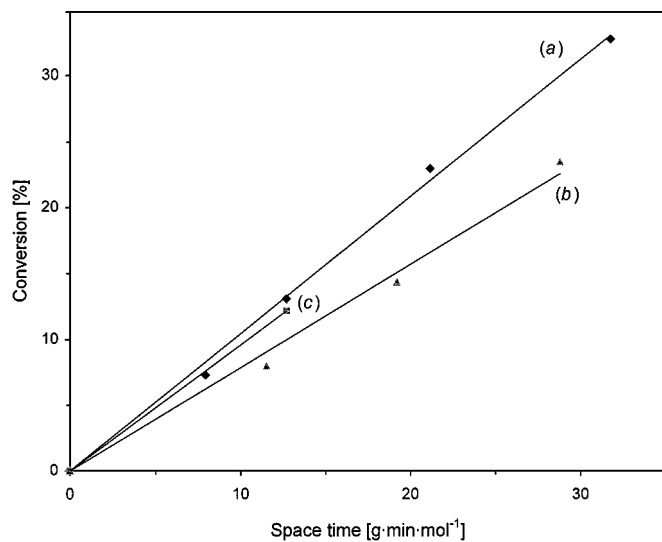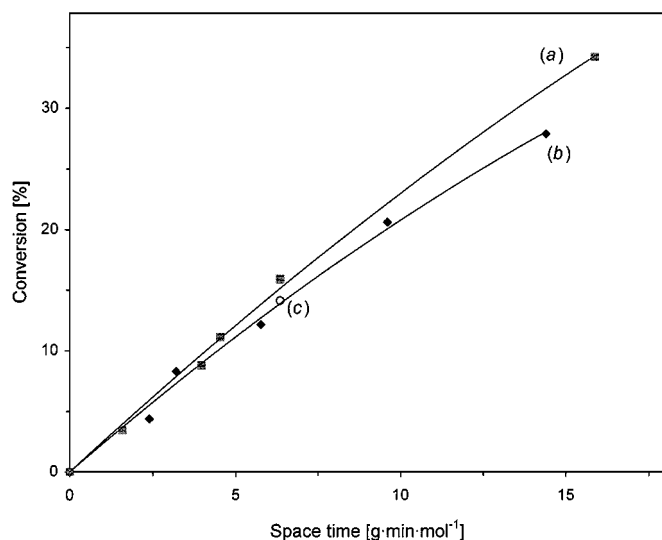


**FIG. 9.** HDN conversion of *o*-propylaniline over CoMoP in the absence (*a*) and presence (*b*) of $H_2S$ and after removal of $H_2S$ (*c*).

**FIG. 10.** Selectivities of products formed during the HDN of *o*-propylaniline over $Co_2P$ in the absence (closed symbols) and presence (open symbols) of $H_2S$.



**FIG. 13.** Selectivities of products formed during the HDN of *o*-propylaniline over WP in the absence (closed symbols) and presence (open symbols) of $H_2S$.
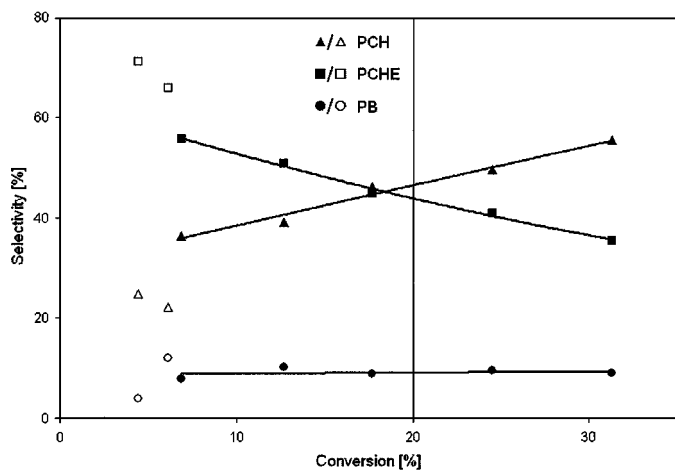


**FIG. 11.** Selectivities of products formed during the HDN of *o*-propylaniline over $Ni_2P$ in the absence (closed symbols) and presence (open symbols) of $H_2S$.



**FIG. 14.** Selectivities of products formed during the HDN of *o*-propylaniline over CoMoP in the absence (closed symbols) and presence (open symbols) of $H_2S$.
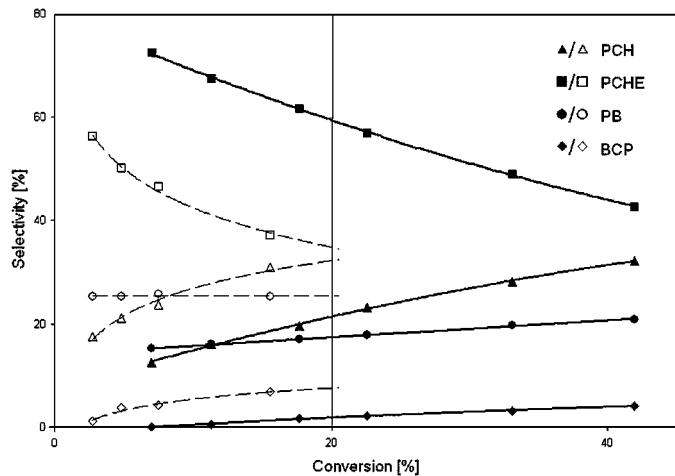


**FIG. 12.** Selectivities of products formed during the HDN of *o*-propylaniline over MoP in the absence (closed symbols) and presence (open symbols) of $H_2S$.



**FIG. 15.** Selectivities of products formed during the HDN of *o*-propylaniline over NiMoP in the absence (closed symbols) and presence (open symbols) of $H_2S$.
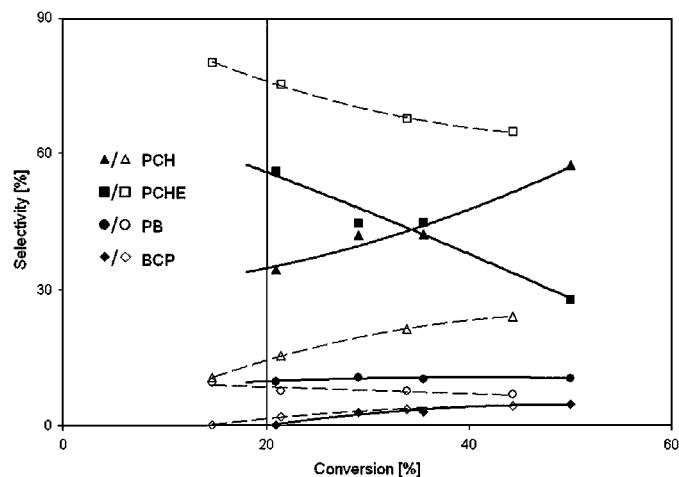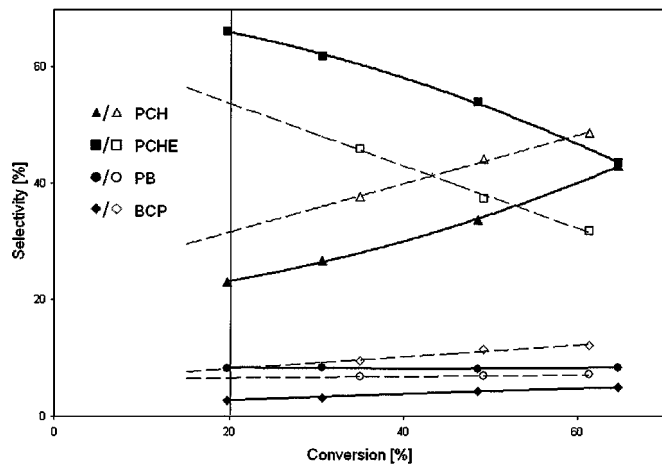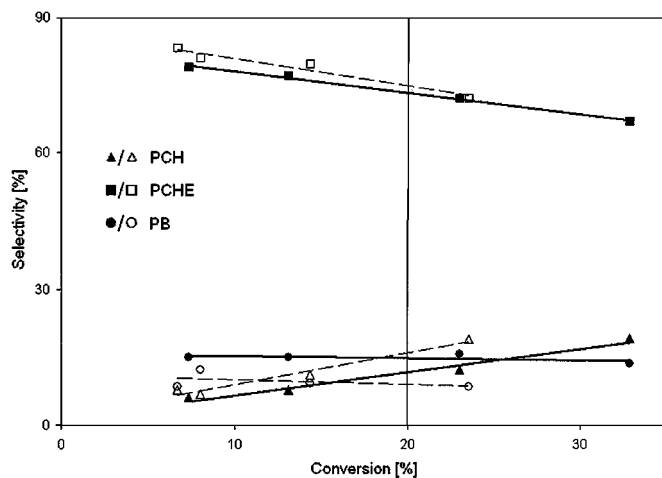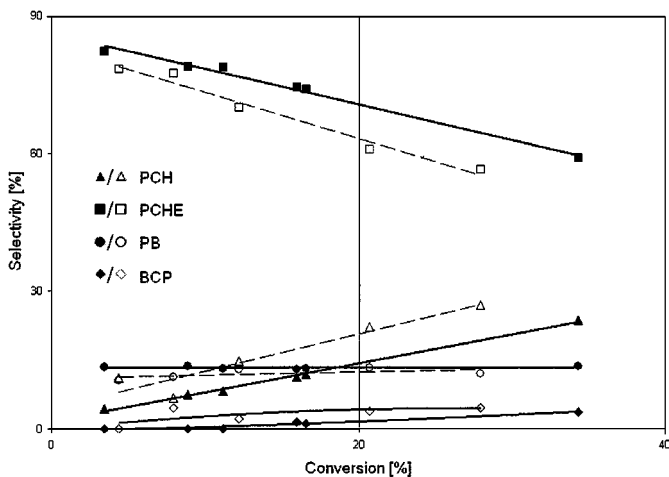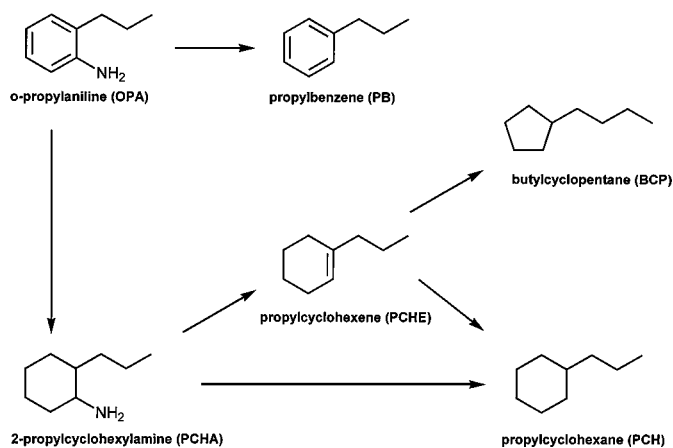
**FIG. 16.** HDN reaction network of *o*-propylaniline.

to N-free compounds. However, they also detected significant amounts of products, such as ethylbenzene, toluene, and benzene. These products formed as a result of the hydrogenolysis of C–C-bonds in the alkyl chain from the intermediate *o*-propylaniline. Thus, Mo₂N behaves more like a metallic catalyst with good hydrogenolysis properties. In our study, the products were the same as those observed for the HDN of *o*-propylaniline over sulfidic catalysts (29, 30).

The reaction network of *o*-propylaniline is shown in Fig. 16. Hydrogenation of the aromatic ring system is the main reaction pathway and leads to the formation of PCHE, PCH, and BCP as secondary reaction products. The intermediate propylcyclohexylamine was not detected because of its high reactivity (30). However, Rota and Prins reported that the structurally very similar intermediate methylcyclohexylamine in the HDN of *o*-toluidine was observed under certain reaction conditions (24). Propylcyclohexylamine either reacts via *β*-Hofmann elimination to propylcyclohexenes, or it reacts to propylcyclohexane. The latter can be formed directly by C–N bond hydrogenolysis from PCHA or by C–S bond hydrogenolysis from a thiol that is formed by replacing the amino group of PCHA by a thiol group in a nucleophilic substitution. It was shown that the intermediate thiol is present in the HDN of methylcyclohexylamine (23). In the HDN of *o*-propylaniline over a sulfided NiMo/Al₂O₃ catalyst, it was shown that PB forms mainly as a primary reaction product through C–N bond hydrogenolysis and that the dehydrogenation of PCHE to PB occurs to a much lesser extent as long as sufficient amine (*o*-propylaniline) is present (30).

For all the phosphides, the product selectivity of PB in the absence of H₂S did not change or changed very slightly with conversion. Thus, we assume that, under our reaction conditions, PB forms mainly through direct C–N bond hydrogenolysis. The influence of H₂S on the hydrogenolysis reaction to PB was usually not very prominent, that is, no change or only a small decrease in the PB selectivity was observed. An exception is Co₂P, where the selectivity of PB formation increased in the presence of H₂S (Fig. 10). At the same time, the selectivities of PCH and BCP also increased, while less PCHE was formed. Since the total activity of Co₂P is much lower in the presence of H₂S, it implies that the hydrogenation of the aromatic ring system is inhibited to a greater extent than the hydrogenolysis of the C(sp²)–N bond and the other reactions.

In the case of Ni₂P, only two flow conditions were measured in the presence of H₂S. Hence, the product selectivities measured in the presence of H₂S can only be regarded as trends. The formation of PCHE improved, whereas the formation of PCH was inhibited in the presence of H₂S.

In the case of MoP, more PCHE was formed in the presence of H₂S, whereas the formation of PCH strongly decreased and less PB was produced. There was a relative decrease in the total activity, which means that the absolute amount of PCHE formed is even higher than under the same flow conditions in the absence of H₂S. The addition of H₂S therefore favors the elimination pathway from PCHA to PCHE. In contrast to MoP, the selectivity of PCHE for WP decreased, while that of PCH increased when H₂S was added to the feed. The effect on PB is not very strong. The parallel increase in total activity implies that either new sites are formed or that existing sites are modified.

The influence of H₂S on the product selectivities of CoMoP and NiMoP was not very pronounced (Figs. 14 and 15). This fact, together with the weak influence of H₂S on the activities of the catalysts, led to the conclusion that the interaction of H₂S with the surface of CoMoP and NiMoP is weak. If a chemical reaction with the surface had occurred, then the selectivities would have changed.

### Comparison of the Phosphide Catalysts

In order to compare the activities of the different phosphides in the HDN reaction, we compared the activities of all catalysts based on their surface area. The structures of the phosphides are all different (1). Co₂P constitutes its own structure type. CoMoP crystallizes in the same structure type but with half of the Co atoms replaced by Mo atoms in an ordered fashion. Ni₂P and NiMoP belong to the Fe₂P structure type. In the NiMoP structure half of the Ni atoms are replaced by Mo atoms, but the Mo and Ni atoms form a different structure pattern than the Mo and Co atoms in the CoMoP structure. The Co₂P and Fe₂P structure types show certain similarities and both consist of interlinked tricapped trigonal prisms centered by P atoms. The metal atoms of all the structures show metal–metal interactions, because the M–M distances are only slightly larger than in the pure metals. MoP crystallizes in the WC structure type, which can be described as corner-sharing stacks of trigonal prisms of P atoms centered by Mo atoms. WP crystallizes in the MnP structure type, which can be understood

TABLE 2

**Conversion under the Same Reaction Conditions$^a$ and Activities Normalized to the Surface**

| Catalyst | Conversion [%] | | | Normalized activity [$10^{16}$ molecules $\cdot$ m$^{-2} \cdot$ s$^{-1}$] | | |
|---|---|---|---|---|---|---|
| | Before | With H$_2$S | After | Before | With H$_2$S | After |
| Co$_2$P | 4.6 | 0.6 | 0.9 | 4.8 | 0.6 | 0.9 |
| Ni$_2$P | 4.9 | 0.5 | 2.5 | 5.8 | 0.6 | 2.9 |
| MoP | 16.0 | 10.0 | 20.5 | 18.8 | 11.8 | 24.1 |
| WP | 21.5 | 30.0 | 31.0 | 5.6 | 7.8 | 8.1 |
| CoMoP | 2.2 | 1.7 | 2.0 | 2.1 | 1.6 | 1.9 |
| NiMoP | 2.8 | 2.5 | 2.6 | 3.3 | 2.9 | 3.1 |

$^a$ Flow rate of $o$-propylaniline $= 4.7 \times 10^{17}$ molecules(OPA) $\cdot$ s$^{-1}$.

as a variant of the NiAs structure with strongly distorted octahedral and trigonal prismatic coordination polyhedra. MoP and WP both contain trigonal prismatic coordination polyhedra, but since the metal-to-phosphorus ratio is 1 : 1 in MoP and WP no tricapped trigonal prisms are present.

All the phosphides were unsupported. None of the structures is a layered one, as is the case for MoS$_2$. Therefore, we assumed that the activities of the catalysts are proportional to their surface areas, implying that the activity of the surface sites is similar for different crystallographic surface planes. Thus, we made a direct comparison between the different catalysts by calculating their activities normalized to the surface areas. The $o$-propylaniline conversions under the same reaction conditions (643 K, 3.0 MPa, flow rate $= 7.84 \times 10^{-7}$ mol(OPA)/s) are presented in Table 2. Under the flow conditions chosen, we assumed differential behavior. Taking into account the amounts of catalyst used in the reaction and the surface areas (Table 1), normalized activities can be calculated for the different catalysts (Table 2).

According to this estimation, when H$_2$S is absent, MoP is by far the most active catalyst, followed by Ni$_2$P, WP, and Co$_2$P. The least active catalysts are NiMoP and CoMoP. Introducing H$_2$S leads to a strong decrease in the activity of Ni$_2$P and Co$_2$P, which are the least active catalysts in the presence of H$_2$S. MoP and WP are now most active, followed by NiMoP and CoMoP. After the removal of H$_2$S, MoP and WP remain the most active catalysts. Ni$_2$P recovers some of its activity and has an activity similar to NiMoP, followed by CoMoP, whereas the activity of Co$_2$P hardly changes.

The deactivation of Co$_2$P and Ni$_2$P is irreversible to a certain extent. A possible explanation for the lower activity might be the formation of a Ni or Co sulfide (e.g., Ni$_3$S$_2$ and Co$_9$S$_8$, which are known for their poor catalytic activity) (31). A recent article describes the reaction of [Co$_x$P$_y$]$^-$ cluster ions with H$_2$S in the gas phase (32). Depending on the type of cluster, the authors found that most clusters easily added S or exchanged P for S, whereas some did

not react at all. However, Mangnus et al. reported that, under TPR/TPS conditions, Co$_2$P forms as the only product detectable by XRD from Co$_3$(PO$_4$)$_2 \cdot$ 8H$_2$O (33). The formation of Co$_2$P as well as of Ni$_2$P from the respective phosphates in a H$_2$S/H$_2$ atmosphere was also observed by Robinson et al. (18). This means that Ni$_2$P and Co$_2$P are more stable than any sulfide that could be formed in the presence of H$_2$S. The formation of CoPS$_3$ and NiPS$_3$ is also unlikely, because Robinson et al. found that these compounds decompose to Co$_2$P and Ni$_2$P under the reaction conditions. That still leaves the possibility that the adsorption of H$_2$S to the surface is so strong that, even after removal of H$_2$S from the feed, some H$_2$S molecules remain adsorbed on the surface, thus diminishing the number of active sites.

The direct comparison of the structurally related CoMoP and NiMoP with Co$_2$P and Ni$_2$P shows that the latter were more active in the absence of H$_2$S at the beginning of the test. However, when H$_2$S is introduced, CoMoP and NiMoP are more active than Co$_2$P and Ni$_2$P and remain so even after H$_2$S was removed that is, Mo may have a beneficial effect under these conditions. Since this effect is evident only after H$_2$S was added to the system, H$_2$S may have induced a reconstruction of the surface. Surface Co atoms may react to form less active Co sulfides, which block the more active Mo active sites.

Pure MoP shows a decrease in activity in the presence of H$_2$S, but when H$_2$S is removed the activity increases to a higher level than that at the beginning of the reaction. WP even shows higher activity in the presence of H$_2$S with a further increase after the removal of H$_2$S. The decrease in the activity of MoP in the presence of H$_2$S was explained by the adsorption of H$_2$S. However, the increase in the activity of MoP as well as that of WP after the removal of H$_2$S implies that more active sites were formed and/or that the sites were modified by H$_2$S. In a recent article we showed that MoP is more active than $\gamma$-Al$_2$O$_3$-supported MoS$_2$ (20). If MoS$_2$ had formed on the surface of MoP, then the number of active sites would have been higher than on $\gamma$-Al$_2$O$_3$, that is, MoP would act as a support, providing a better dispersion of the MoS$_2$ phase than on $\gamma$-Al$_2$O$_3$.

Another possible explanation is the formation of a new mixed Mo-containing phase with the participation of both P and S. Poulet et al. and Jian and Prins proposed the participation of P in the MoS$_2$ surface structure for supported phosphate-containing MoS$_2$ catalysts (30, 34). They claimed that this modification would lead to active sites with different catalytic properties. Interestingly, MoP and MoS$_2$ show certain structural similarities. In both structures, Mo is trigonal prismatically coordinated by six P or S atoms; both structures have similar interatomic distances (first coordination shells in MoS$_2$: d(Mo–S) $= 2.43$ Å, d(Mo–Mo) $= 3.16$ Å; in MoP: d(Mo–P) $= 2.45$ Å, d(Mo–Mo) $= 3.19$–3.22 Å), the major difference being that MoS$_2$ has a layered structure. Unfortunately, there are no reports of defined ternary

Mo–P–S or W–P–S phases in the literature, which might have been further evidence of such phases in the catalyst. However, the chemical properties of P and S as well as the similarities of the MoP and $MoS_2$ structures leave the possibility open for the existence of a mixed Mo–P–S phase.

## 4. CONCLUSIONS

We prepared six different transition-metal phosphides and tested them under the same conditions in the HDN of OPA at 643 K and 3 MPa. From this comparison, we conclude that the cobalt compounds, $Co_2P$ and CoMoP, were the least active catalysts. $Ni_2P$ and NiMoP performed better, but $Ni_2P$ irreversibly lost some of its activity in the presence of $H_2S$. MoP and WP were the most active catalysts; MoP had the highest activity. Except for WP, all the phosphides lost activity in the presence of $H_2S$. This can be explained by reversible blocking of active sites by strongly adsorbed $H_2S$ molecules or by an irreversible surface reconstruction. The change in activity and selectivity in the presence of $H_2S$ and after the $H_2S$ was removed indicates a change in the surface structure.

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