Structure of phosphorus containing CoO-MoO₃/Al₂O₃ catalysts

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Structure of Phosphorus Containing CoO–MoO₃/Al₂O₃ Catalysts

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ABSTRACT

The influence of phosphate (P) on the structure of alumina-supported Co–Mo catalysts was studied by means of temperature-programmed reduction (TPR). Conclusions deduced from these TPR measurements were supported by Fourier transform infrared (FT-IR) and Raman measurements. Phosphorus added by sequential impregnation or coimpregnation had a great influence on both Co and Mo surface structure. Addition of P to an alumina support resulted in the formation of a well dispersed AlPO₄ surface layer. Next to the phases already reported on Co/Al₂O₃ catalyst, cobalt can be present in interaction with the AlPO₄ species in Co–P/Al₂O₃ catalysts. Coimpregnation of Co and P increased the dispersion of the cobalt species. The influence of P on the distribution of the Mo species depends on the P content and the sequence of impregnation. On Mo–P catalysts, prepared by coimpregnation, the reducibility of a part of the Mo species decreased with increasing P content due to the formation of Mo–O–P species. On the catalysts prepared by sequential impregnation of P and Mo a part of the Mo was present in MoO₃ crystallites, the other part was very well distributed over the AlPO₄ surface layer. These results suggest that at high P loadings, Mo can be present as a Mo–AlPO₄ surface structure. Both sequential and coimpregnation of Co, Mo and P resulted in the formation of a Co–Mo–O–P phase, in which Co is in interaction with MoO₃ and AlPO₄ species. Due to the stronger polarization of the Co–O bond by P⁵⁺, the reducibility of the Co²⁺-ions in the Co–Mo–O–P phase is decreased compared to the reducibility of these ions in the Co–Mo–O phase. At a P-to-metal ratio of ≤ 1 , the AlPO₄ species were completely reduced to metalphosphides and alumina above 1000 K under TPR conditions. At higher P loadings, a part of the phosphates was reduced to P₄. The reduction of AlPO₄ is accelerated by both reduced Co and Mo species.

Key words: cobalt oxide-molybdenum oxide/alumina, phosphorus, phosphates, catalyst preparation (wet impregnation), catalyst characterization (FT-IR, Raman spectroscopy, TPR), hydrotreating catalysts.

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INTRODUCTION

Among the most important catalysts in oil-refining industry are hydrotreating catalysts such as alumina-supported Co-Mo, Ni-Mo and Ni-W.

Due to the high catalyst costs and increasing demands for better catalysts, it is worthwhile to improve the activity and selectivity and to reduce the catalyst costs. Adding a secondary promoter to the catalyst systems has proved to be one of the ways to attain this result. For instance, addition of phosphorus (often added as phosphate) can have a beneficial effect on hydrodesulphurization (HDS) and especially on hydrodenitrogenation (HDN) [1-8].

No common explanation for the promotive effect can be found in the literature. Improved dispersion [1,9,10], less deactivation [2] and decrement of the amount of inactive Co and Ni species [9,11] are explanations which have been put forward. The different effect of phosphates (P) on HDS and HDN [12] implicates that the function of P cannot simply be ascribed to one of the above mentioned explanations. To acquire a better understanding of the effect of P on the catalyst performance it is necessary to know the influence of P on the structure of the catalyst both in its oxidic and sulfidic state.

Despite the importance of phosphorus in hydrotreating catalysts only a few studies have been reported concerning the structure of these catalysts. Most information available is limited to P/Al₂O₃ and Mo-P/Al₂O₃ catalysts [13-19].

Gishti et al. [16] and López Cordero et al. [18] have shown that addition of phosphorus to alumina results in the formation of the stable AlPO₄ compound. X-ray photoelectron spectroscopy (XPS) data reveal that a monolayer of P is formed around 2.9 atoms/nm² [13].

Compared with the P/Al₂O₃ system, the structure of the Mo-P/Al₂O₃ catalysts is less well understood. XPS data show that addition of P can lead both to a better and to a worse distribution of the Mo species over the support [4,9,14,17,18]. This suggests that the structure of the Mo-P catalysts strongly depends on the preparation conditions used, such as pH, P loading and sequence of impregnation. Using NMR and electronmicroprobe analyses, Cheng and Luthra recently [14] investigated the influence of the P-to-Mo ratio and pH on the distribution of P and Mo on an alumina support. A low P-to-Mo ratio in combination with a relatively high initial pH [3.5] resulted in an inhomogeneous distribution whereas a high P-to-Mo ratio and/or a relatively low pH (1.7) resulted in a rather uniform distribution of P and Mo over the support. López Cordero et al. [18] showed recently that the impregnation procedure is another parameter which influences the partition of at least Mo. Sequential impregnation of P and Mo resulted in a worse distribution of Mo compared to coimpregnated catalysts.

Concerning the structure of Co and Ni in combination with P and Mo only few results are available [4,9]. These studies show that the Co and Ni disper-

sion is increased upon P addition but no more detailed structural information was obtained.

It was the aim of this study to understand the influence of P, added as phosphate, on the structure of alumina-supported Co–Mo catalysts.

Temperature-programmed reduction (TPR) will be the major technique to investigate the structure of the catalysts.

EXPERIMENTAL

Materials

AlPO_4 (Alpha Ventron) and $\text{Co}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ (Alpha Ventron) were used as model compounds. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ (Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck), phosphoric acid (85 wt.-% in water, Janssen Chimica) and $\gamma\text{-Al}_2\text{O}_3$ (Ketjen 000-1.5E high purity, surface area $200 \text{ m}^2/\text{g}$, pore volume $0.5 \text{ cm}^3/\text{g}$, particle size $100\text{--}150 \cdot 10^{-6} \text{ m}$) were used to prepare the catalysts.

The catalysts were prepared by pore volume impregnation of a $\gamma\text{-Al}_2\text{O}_3$ support. The samples were dried at room temperature and subsequently calcined in air ($0.68 \cdot 10^{-3} \text{ mol/s}$) with a heating rate of 0.167 K/s up to 773 K interrupted by isothermal stages at 323 K ($10.8 \cdot 10^3 \text{ s}$) and 373 K ($28.8 \cdot 10^3 \text{ s}$). The catalysts were calcined after each impregnation step at 773 K during $7.2 \cdot 10^3 \text{ s}$.

The Co–P and Mo–P catalysts were prepared in two different ways:

(1) By coimpregnation with an aqueous solution of the metal salts and phosphoric acid. The cobalt solutions were adjusted to a pH 1 by adding ammonium hydroxide or nitric acid, whereas the Mo solutions applied had a pH 1 or higher.

(2) By first impregnating the support with a phosphoric acid solution and subsequently adding solutions of Co, Co–P, Mo or Mo–P.

The Co–Mo–P catalysts were also prepared in several different ways. Most of the Co–Mo–P samples were prepared by coimpregnation except for the Co–Mo catalyst which was prepared by sequentially adding Co and Mo and the Co/Mo–P catalyst which was prepared by adding Mo–P and Co sequentially.

The catalyst will be denoted by the number of metal atoms per nm^2 of initial support area and a slash will denote separate impregnation steps, e.g. $\text{Mo}(1.9)/\text{P}(3.2)/\text{Al}$ contains $1.9 \text{ Mo atoms/nm}^2$ ($8.0\% \text{ MoO}_3$) and 3.2 P atoms/nm^2 ($3.0\% \text{ P}$) on $\gamma\text{-Al}_2\text{O}_3$ and is prepared by sequentially adding P and Mo. The metal contents given are calculated on the basis of the amounts used in the preparation. Table 1 lists the catalysts studied, together with the composition and surface area.

Surface area

Surface areas were determined from nitrogen adsorption–desorption isotherms using a Carlo Erba sorptomatic.

TABLE 1

Catalysts applied, their composition and surface area

n.d. = Not determined.

Catalyst	Co content		Mo content		P content ^a		Surface area (m ² /g)
	(wt.-%)	(atoms/nm ²)	(wt.-%)	(atoms/nm ²)	(wt.-%)	(atoms/nm ²)	
Co(1.2)P(0)/Al	3.0	1.2	—	—	—	—	253
Co(1.2)P(0.04)/Al	3.0	1.2	—	—	0.04	0.04	n.d.
Co(1.2)P(0.2)/Al	3.0	1.2	—	—	0.2	0.2	n.d.
Co(1.2)P(0.4)/Al	3.0	1.2	—	—	0.4	0.4	221
Co(1.2)P(0.9)/Al	2.8	1.2	—	—	0.9	0.9	179
Co(1.2)P(1.7)/Al	2.8	1.2	—	—	1.7	1.7	193
Co(1.2)/P(3.1)/Al	3.0	1.2	—	—	3.0	3.1	n.d.
Co(1.3)P(0.6)/P(3.1)/Al	3.0	1.3	—	—	0.6/3.0	0.6/3.1	n.d.
Co(1.1)P(4.0)/Al	2.5	1.1	—	—	3.9	4.0	169
Mo(2.0)P(0)/Al	—	—	9.1	2.0	—	—	213
Mo(2.0)P(0.5)/Al	—	—	8.8	2.0	0.4	0.5	179
Mo(2.1)P(0.9)/Al	—	—	9.1	2.1	0.9	0.9	196
Mo(2.1)P(1.9)/Al	—	—	9.1	2.1	1.7	1.9	176
Mo(1.9)/P(3.2)/Al	—	—	8.0	1.9	3.0	3.2	n.d.
Mo(2.1)P(4.7)/Al	—	—	8.8	2.1	4.2	4.7	156
Mo(2.1)P(1.2)/P(3.1)/Al	—	—	8.9	2.1	1.1/2.8	1.2/3.1	n.d.
Co(1.3)Mo(2.1)P(0)/Al	2.8	1.3	8.8	2.1	—	—	182
Co(1.2)Mo(2.2)P(0.4)/Al	2.6	1.2	9.1	2.2	0.4	0.4	159
Co(1.2)Mo(2.1)P(1.0)/Al	2.6	1.2	9.0	2.1	0.9	1.0	152
Co(1.3)Mo(2.2)P(2.1)/Al	2.7	1.3	9.1	2.2	1.8	2.1	145
Co(1.2)/Mo(1.9)P(3.2)/Al	2.6	1.2	7.8	1.9	2.9	3.2	160
Co(1.3)Mo(2.1)P(4.4)/Al	2.7	1.3	8.7	2.1	3.8	4.4	136

^aThe slash separates the amounts of P added during the first and the second impregnation step.

X-ray diffraction (XRD)

XRD was carried out on a Philips diffractometer PW 1130 using Ca $K\alpha$ radiation. A Fe filter was used to filter the Ca $K\beta$ radiation.

Raman

The powdered samples were pressed into self-supporting wafers. To avoid any laser-induced heat effects, the wafers were cooled to 113 K and the focussed laser beam was scanned over the surface by placing a rotating refractor plate between the sample and the focussing lens. The Raman spectra were recorded in the 90° configuration on a Jobin Yvon HG 2 S Ramanor using an argon laser, SP model 171, at 514.5 nm as excitation source.

Fourier transform infrared (FT-IR)

The IR spectra were recorded on a Digilab FT instrument using self-supporting disks of the sample (8 mg cm^{-2}). Prior to the measurements, the samples were calcined in situ at 800 K. In order to get quantitative data the absorbances were weight corrected.

Temperature-programmed reduction (TPR)

The TPR equipment is depicted in Fig. 1. 67% hydrogen in argon was used as reducing mixture (flow-rate $13.67 \mu\text{mol/s}$). The temperature was increased from room temperature up to 1270 K with a rate of 0.167 K/s. The temperature was kept at 1270 K for at least $3.6 \cdot 10^3 \text{ s}$. The changes in the hydrogen concentration were determined using a thermal conductivity detection (TCD) system. A flame ionization detection (FID) system was used to measure the methane production which can be produced due to the reduction of organics adsorbed on the support. The FID system can also detect other compounds as nitric oxide, PH_3 and P_4 . The TCD system was calibrated by reduction of CuO (Baker grade 99.99%). A more detailed description of the TPR equipment can be found in ref. 20.

Fig. 1. Scheme of TPR apparatus.

The solid-state NMR spectra were acquired on a Bruker MSL-300-machine.

RESULTS

TPR

Model compounds

$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, AlPO_4 . The TPR patterns of both compounds are shown in Fig. 2. The TPR patterns of other relevant model compounds such as CoO , Co_3O_4 , MoO_3 , CoMoO_4 and CoAl_2O_4 can be found elsewhere [20,21].

The reduction of $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ starts at 800 K and is completed around 1000 K. The total hydrogen uptake measured is 3.9 mol hydrogen/mol Co. After reduction XRD showed exclusively diffraction lines which could be attributed to CoP [22] and Co_2P [23] and not to Co metal which might have been expected.

The reduction of AlPO_4 starts around 1000 K and the reduction rate increases up to 1273 K. Even after $3.6 \cdot 10^3$ s at 1273 K the reduction is not completely finished. A hydrogen uptake of 0.6 mol hydrogen/mol AlPO_4 is measured after reduction ($3.6 \cdot 10^3$ s at 1273 K).

Fig. 2. TPR patterns of model compounds: (a) $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, (b) AlPO_4 , (c) $\text{P}(2.9)/\text{Al}$.

Catalysts

P/Al. The TPR pattern of *P/Al* is shown in Fig. 2. The reduction of *P/Al* looked very similar to the reduction of the AlPO_4 sample. A hydrogen uptake of 0.8 mol hydrogen/mol AlPO_4 was measured after $3.6 \cdot 10^3$ s reduction at 1273 K.

Co-P/Al, *Co/P/Al*, *Co-P/P/Al*. Coimpregnation: The TPR patterns of the *Co-P/Al* catalysts with different P loadings are depicted in Fig. 3. Both the FID

Fig. 3. TPR Patterns of coimpregnated Co-P catalysts. TCD signal (upper curve) and FID (lower curve). (a) $\text{Co}(1.2)\text{P}(0)/\text{Al}$, (b) $\text{Co}(1.2)\text{P}(0.04)/\text{Al}$, (c) $\text{Co}(1.2)\text{P}(0.2)/\text{Al}$, (d) $\text{Co}(1.2)\text{P}(0.4)/\text{Al}$, (e) $\text{Co}(1.2)\text{P}(0.9)/\text{Al}$, (f) $\text{Co}(1.7)\text{P}(1.7)/\text{Al}$, (g) $\text{Co}(1.1)\text{P}(4.0)/\text{Al}$.

(lower line) and TCD signals (upper line) are shown. The total hydrogen consumption can be found in Table 2, the values were corrected for the reduction of adsorbed organic material by making use of the FID signal.

All catalysts, except those with the highest P content, show a small hydrogen consumption around 570 K. A second TCD peak is found around 750 K, which coincides with an FID peak. These peaks are absent for the catalyst with the highest P loading. The major part of the reduction takes place above 900 K. In this region a large peak is observed around 1200 K, which shifts to higher

TABLE 2

Quantitative TPR results on total hydrogen consumption

When calculating the hydrogen amount the assumption was made that the metaloxides and P-oxides are reduced to metalphosphides or metals and phosphorus. The amount of methane produced, detected by FID, is used to correct the hydrogen uptake for the reduction of adsorbed organics.

Model compounds	$H_2(\text{exp})/H_2(\text{theo})^a$
$Co_3(PO_4)_2 \cdot 8 H_2O$	0.97
$AlPO_4$	0.24 ^b
Catalysts	$H_2(\text{exp})/H_2(\text{theo})^a$
Co(1.2)P(0)/Al	1.25
Co(1.2)P(0.04)/Al	1.00
Co(1.2)P(0.2)/Al	0.98
Co(1.2)P(0.4)/Al	1.07
Co(1.2)P(0.9)/Al	1.03
Co(1.2)P(1.7)/Al	0.71 ^a
Co(1.2)P(3.1)/Al	—
Co(1.1)P(4.0)/Al	0.86 ^a
Mo(2.0)P(0)/Al	1.02
Mo(2.0)P(0.5)/Al	1.06
Mo(2.1)P(0.9)/Al	0.94
Mo(2.1)P(1.9)/Al	0.86 ^a
Mo(1.9)P(3.2)/Al	0.90 ^a
Mo(2.1)P(4.7)/Al	0.86 ^a
Mo(2.1)P(1.2)/P(3.1)/Al	0.88 ^a
Co(1.3)Mo(2.1)P(0)/Al	0.92
Co(1.2)Mo(2.2)P(0.4)/Al	0.94
Co(1.2)Mo(2.1)P(1.0)/Al	0.92
Co(1.3)Mo(2.2)P(2.1)/Al	0.85 ^a
Co(1.2)/Mo(1.9)P(3.1)/Al	1.00
Co(1.3)Mo(2.1)P(4.4)/Al	0.90 ^a

^aThese values are too low since the reduction is not completed after $3.6 \cdot 10^3$ s at 1270 K.

Fig. 4. Influence of the sequence of impregnation on the reduction of Co-P catalysts. TCD signal (upper curve) and FID signal (lower curve). (a) Co(1.2)P(0)/Al, (b) Co(1.1)P(4.0)/Al, (c) Co(1.2)/P(3.1)/Al, (d) Co(1.3)P(0.6)/P(3.1)/Al.

temperatures with increasing P content. A shoulder is observed around 1050 K which is ascribed to the reduction of impurities of the support [24].

Sequential impregnation: In Fig. 4, the catalysts prepared by sequential impregnation are compared with the catalysts prepared by coimpregnation, which are already described above.

At a comparable P content, the TPR patterns of the catalysts prepared by sequential impregnation are similar to those prepared by coimpregnation except for some small differences: (1) The sequentially impregnated catalysts consume more hydrogen around 570 K and 760 K than the catalysts in which Co and P are coimpregnated, (2) In case of sequential impregnation, the high-temperature peak is observed at 1200 K whereas this peak appears at 1270 K for the coimpregnated catalysts.

Mo-P/Al, Mo/P/Al, Mo-P/P/Al. Coimpregnation: The TPR patterns for the coimpregnated catalysts are depicted in Fig. 5. Only the TCD signal is shown because nearly no FID peaks were present. Three peak maxima can be dis-

Fig. 5. TPR patterns of coimpregnated Mo-P catalysts. (a) $\text{Mo}(2.0)\text{P}(0)/\text{Al}$, (b) $\text{Mo}(2.0)\text{P}(0.5)/\text{Al}$, (c) $\text{Mo}(2.1)\text{P}(0.9)/\text{Al}$, (d) $\text{Mo}(2.1)\text{P}(1.9)/\text{Al}$, (e) $\text{Mo}(2.1)\text{P}(4.7)/\text{Al}$.

cerned in three different temperature regions: region 1 (660–690 K), region 2 (900–1100 K) and region 3 (1150–1270 K).

The peak in region 1 is observed for all catalysts. The amount of hydrogen consumed in this region is not changing very much for the different catalysts, except for catalyst (b) which shows a relatively large hydrogen uptake.

The peak in the second region diminishes with increasing P content and disappears nearly completely for the catalyst with the highest P loading. Simultaneously with the disappearance of the peak at 1000 K another peak appears around 1150 K which shifts to 1270 K with increasing P content.

Sequential impregnation: Fig. 6 shows the influence of the impregnation sequence. The sequentially impregnated catalyst ($\text{Mo}/\text{P}/\text{Al}$) differs in two respects from the coimpregnated catalyst: (1) The amount of hydrogen consumed in the peak around 675 K is diminished, (2) A new peak is observed at 745 K.

The TPR pattern of $\text{Mo-P}/\text{P}/\text{Al}$ is nearly the same as a coimpregnated Mo-P catalyst with a comparable P content.

Co-Mo-P/Al, Co/Mo-P/Al. Coimpregnation: The TPR patterns (TCD signal

Fig. 6. Influence sequence of impregnation on the reduction of Mo-P catalysts. TCD signal (upper curve) and FID signal (lower curve). (a) Mo(2.0)P(0)/Al, (b) Mo(2.1)P(4.7)/Al, (c) Mo(2.1)P(1.2)/P(3.1)/Al, (d) Mo(1.9)/P(3.2)/Al.

and FID signal) are depicted in Fig. 7. The pattern obtained for the sample without P agrees perfectly with the TPR measurements of Arnoldy et al. [21].

For all catalysts a similar reduction peak is observed around 680 K. A second peak is observed around 970 K which disappears with increasing P content. At higher P loadings two other peaks are appearing viz. at 1050 K and between 1200 and 1270 K. The position of the peak around 1050 K is independent of the P content whereas the position of the other peak shifts to higher temperatures with increasing P content.

Sequential impregnation: Fig. 8 shows the influence of the sequence of addition of Co, Mo and P. The TPR patterns of the Co/Mo-P/Al and Co-Mo-P/Al catalyst are almost identical.

The quantitative data are collected in Table 2. The amounts of hydrogen consumed agree very well with those expected on the basis of reduction of the oxides to Co, Mo and P with a formal valency of zero which suggests that P can be present as P_4 , P_{white} , P_{red} , P_{black} or in metalphosphides.

After subtracting the TCD patterns of Mo-P/Al and Co-Mo-P/Al samples

Fig. 7. TPR patterns of coimpregnated Co-Mo-P catalysts. TCD signal (upper curve) and FID signal (lower curve). (a) $\text{Co}(1.3)\text{Mo}(2.1)\text{P}(0)/\text{Al}$, (b) $\text{Co}(1.2)\text{Mo}(2.2)\text{P}(0.4)/\text{Al}$, (c) $\text{Co}(1.2)\text{Mo}(2.1)\text{P}(1.0)/\text{Al}$, (d) $\text{Co}(1.3)\text{Mo}(2.2)\text{P}(2.1)/\text{Al}$, (e) $\text{Co}(1.3)\text{Mo}(2.1)\text{P}(4.4)/\text{Al}$.

with the highest P content from each other, an area is obtained at 1100 K which agrees very well with the reduction of the amount of cobalt present.

The catalysts with the highest P contents, the model compound AlPO_4 and the P/Al catalyst showed an extremely broad FID peak (up to 9000 s) which appeared 4800 s after the reduction peaks around 1200 K (not shown). The height of this peak was about equal over the whole region i.e., the product partial pressure is such that the reaction/desorption is thermodynamically controlled at the flow-rate applied. From the total amount of P desorbed and the total FID peak area the partial pressure of PH_3 , P_4 or P_2O_3 was calculated. From the peak height the sensitivity of the FID for the P-compound was estimated.

During the reduction of the Co-P catalyst with the highest P loading a shiny red/orange deposit was formed around 1270 K which immediately started burning upon exposure to air.

Fig. 8. Influence of the sequence of impregnation on the reduction of Co-Mo-P catalysts. TCD signal (upper curve) and FID signal (lower curve). (a) Co(1.3)Mo(2.1)P(0)/Al, (b) Co(1.2)/Mo(1.9)P(3.2)/Al, (c) Co(1.3)Mo(2.1)P(4.4)/Al.

Surface area

The surface areas per gram of catalyst are shown in Table 1. If these values are normalised to the amount of alumina, in most cases we observe a decrease of the alumina surface area after addition of phosphorus, it amounts to 15–20% of the initial surface area for the catalysts with the highest P content. The surface area of the Co/Al catalysts is surprisingly high, probably caused by the fact that during preparation the pH was adjusted by adding nitric acid.

Raman

Co-P/Al

The coimpregnated samples showed a Raman peak at 690 cm^{-1} which disappeared for the catalysts with the highest P content.

Mo-P/Al, Mo-P/P/Al, Mo/P/Al

All catalysts showed an intense peak at 960 cm^{-1} which was asymmetric towards lower wavenumbers and two smaller peaks at 370 and 230 cm^{-1} . No

shift in peak position could be observed for the different catalysts. The Mo/P/Al catalyst showed sharp bands at 990, 820, 670 and 520 cm^{-1} .

Co-Mo-P/Al

All catalysts showed an intense band around 950 cm^{-1} and a broad shoulder around 850 cm^{-1} . Addition of P did not change the Raman spectra.

FT-IR

Fig. 9 reveals that the IR spectrum of P/Al is dominated by a sharp adsorption peak at 3675 cm^{-1} . Also several smaller peaks are observed around 3790, 3775 and 3730 cm^{-1} . Addition of Mo to this catalyst leads to a reduction of the band at 3675 cm^{-1} from 0.32 to 0.15 a.u. and disappearance of the smaller bands.

The IR spectrum of the Mo(2.1)P(1.7)/Al catalyst is also dominated by the peak at 3675 cm^{-1} , with a peak intensity of 0.12 a.u. and a few very small peaks at higher wavenumbers (Fig. 9c).

^{31}P -NMR

The P/Al and Mo-P/Al catalysts, both showed a single resonance at -20 ppm.

Fig. 9. FT-IR spectra of alumina-supported P and Mo-P catalysts. (A) P(2.9)/Al, (B) Mo(1.9)/P(3.2)/Al, (C) Mo(2.1)P(1.9)/Al.

DISCUSSION

A decrease in surface area after addition of phosphorus to an alumina support has also been observed by others [4,12]. This decrease is most likely explained by the formation of surface AlPO_4 which can result in pore plugging, especially of the smallest mesopores [4]. Due to the impregnation procedure applied, small amounts of the Al^{3+} surface ions are solubilised; upon drying small amounts of tri-dimensional compounds could be formed, containing Co and/or Mo, Al and P. The fact that the same structural changes are observed on the catalysts prepared by sequential impregnation confirms that these effects are of minor importance. The relative easiness of sulfiding of these catalysts [25] also supports the assumption that nearly no tri-dimensional Co- and Mo-containing compounds have been formed.

The total amount of hydrogen consumed between 300 and 1273 K agrees quantitatively with the reduction of phosphates to P with a formal value of 0, consequently excluding the formation of PH_3 and P_2O_3 as major reaction products. Due to the extremely high P_4 vapour pressure [26] of P_{white} , P_{red} , or P_{black} above 1000 K, the formation of these P-compounds can be excluded. Hence, we believe that phosphates are most likely reduced to P_4 and/or metalphosphides. In principle P_4 might dissociate to P_2 but thermodynamics showed that this is maximal 10% at 1270 K [26] and therefore the role of P_2 is only of minor importance. The major part of P_4 formed condensates in the cold part of the reactor. The shiny deposit which is formed in the cold part of the reactor started to burn upon exposure to air suggesting the presence of at least P_{white} but the presence of P_{red} and/or P_{black} can not be excluded. The low vapour pressure of P_{white} (5.66 Pa at 298 K) explains the extremely broad FID peak which was formed after reduction above 1000 K. Due to the relatively low vapour pressure of P_{red} or P_{black} at ambient temperature no sublimation is detectable at room temperature [26].

The fact that only a FID peak is observed in the high-temperature region for the catalyst with a P-to-metal ratio higher than 1 suggests that below this ratio P is present as phosphides.

Model compounds

The sharpness of the reduction peak around 850 K indicates that the reduction is accelerated by the formation of hydrogen dissociation centres, viz. small amounts of phosphides, which are known as hydrogenation catalysts [27], or reduced Co or P atoms for hydrogen dissociation. The catalytic involvement of reduced metal ions, called autocatalysis, is also observed in the reduction of other oxides [21,28,29]. It is not clear whether the reaction started by reduction of the P_2O_5 tetrahedra or of the CoO species.

Fig. 10. P_4 partial pressure at thermodynamic equilibrium for several cobalt phosphides. Curves 1: $\text{CoP}_3 \rightleftharpoons \text{CoP} + 1/2 P_4$, 2: $2\text{CoP} \rightleftharpoons \text{Co}_2\text{P} + 1/4 P_4$, 3: $\text{Co}_2\text{P} \rightleftharpoons 2\text{Co} + 1/4 P_4$. For an explanation of the crosshatched line see text.

XRD showed only diffraction lines attributable to CoP and Co_2P . In Fig. 10, the logarithm of P_4 partial pressure (pP_4), is plotted as a function of reaction temperature for three different reaction equations:

The partial pressure at thermodynamic equilibrium is calculated on the basis of data listed in ref. 30. The crosshatched line at $\log(pP_4) = -[4.5-5.5]$ denotes the partial pressure at which decomposition of the various cobalt phosphides can be observed under our TPR conditions. Since the curves for the decomposition of CoP and Co_2P are not crossing this line, it is concluded that no decomposition of CoP and Co_2P takes place on the time scale of the TPR experiments.

In comparison with Co_3O_4 [20], $\text{Co}_3(\text{PO}_4)_2$ is more difficult to reduce. This is in agreement with the assumption that the Co-O bonds are polarized by phosphorus ions analogous to the influence of Al^{3+} on the reduction of cobalt and molybdenum [21].

AlPO₄, P/Al

The reduction of bulk or surface AlPO_4 starts around 1000 K and increases very slowly up to 1270 K. Thermodynamic calculations suggest that the reduction is kinetically controlled. The large FID peak which appeared $4.8 \cdot 10^3$ s after the start of reduction at 1000 K indicates that P_4 was formed (see discussion above). Relevant to the interpretation of the AlPO_4 and P/Al reduction patterns is the reduction of P_2O_5 (H_3PO_4) on activation carbon, which

was observed already around 773 K in TPR [31]. Since no reduction was observed below 1000 K for the P/Al catalyst, it is concluded that all phosphate was present as AlPO_4 species and no “free” P_2O_5 existed.

FT-IR measurements showed that adsorption of P (as phosphate) on an alumina support resulted in the formation of an intense band at 3680 cm^{-1} which can be attributed to a P–OH bond [32]. Simultaneously, the IR adsorption of aluminium hydroxyl species (3790 , 3775 , 3730 and 3695 cm^{-1} [33]) was strongly reduced, indicating that P was mainly present as an AlPO_4 monolayer, which is in agreement with the literature [34].

Co-P/Al, Co/P/Al

The hydrogen consumption observed around 570 K has been attributed to the reduction of microcrystallites of cobalt oxide [20]. According to Arnoldy et al. [20] the presence of CoO is unlikely on the basis of XRD and thermodynamic data. In agreement with this, Raman spectra showed absorption peaks which could be attributed to Co_3O_4 [35] and, therefore, it is concluded that the reduction peak around 570 K is caused by the reduction of Co_3O_4 . The disappearance of both reduction- and Raman peaks, at 570 K and 690 cm^{-1} respectively, with increasing P content, shows that the cobalt dispersion has increased. The Co-dispersion is most likely increased due to the formation of a cobalt–phosphorus phase which prevents sintering of the cobalt species. Because of the low pH of the solutions it is not expected that the dispersion increased due to the formation of a cobalt–phosphorus phase during the impregnation step but more likely during the drying and/or calcination step. The hydrogen consumption at 750 K coinciding with methane production, is explained by reduction of organics adsorbed on the catalyst sample. This methane production is an indication for the presence of reduced cobalt species since hydrogen dissociation sites are prerequisite to reduce these organics. So the absence of a FID peak around 750 K for catalyst $\text{Co}(1.1)\text{P}(4.0)/\text{Al}$ supports the conclusion that no reduced cobalt species are present below 800 K.

The absence of a reduction peak below 1000 K shows that no crystalline or amorphous $\text{Co}_3(\text{PO}_4)_2$ species are formed.

The major part of the reduction takes place in the region from 1200 to 1270 K. The hydrogen consumption observed around 1190 K for the $\text{Co}(1.2)/\text{Al}$ catalyst is ascribed to the reduction of cobalt species with a large number of aluminum neighbours. This phase is described in reference [20] as phase IVa. The shift of this high-temperature peak from 1190 to 1270 K with increasing P content is due to the increased amount of reducible phosphates. The TPR patterns of the catalysts with a high P loading are completely dominated by the reduction of AlPO_4 . Therefore, it is impossible to conclude whether the reduction of the Co-ions takes place at the same temperature as in the P-free catalyst or is shifted to higher reduction temperatures.

Table 2 shows that the Co–P catalysts are completely reduced, in the region

from 1000–1273 K, on basis of reduction of cobalt phosphides or cobalt metal and phosphorus (P_{white} , P_{red} , P_{black} and P_4). In contrast with the reduction of surface AlPO_4 species on P/Al catalysts, AlPO_4 species on Co-P/Al catalyst were completely reduced to Al_2O_3 and P (as P_4 or Co_xP) obviously due to the presence of reduced cobalt species which initiate the hydrogen dissociation.

The catalysts with a P/Co ratio higher than 1.4 showed an FID peak after the reduction peak in the high-temperature region, probably caused by P_4 (see discussion above); this indicates that the major part of phosphorus is present as cobaltphosphides on the catalysts with a P/Co ratio of less than 1.4. Which cobaltphosphide is formed probably depends on the P content. On samples with a low P content Co_2P is formed whereas more and more CoP is formed with increasing P content. The equilibrium curve for the decomposition of CoP_3 crosses the line at $\log(pP_4) = [4.5-5.5]$ at about 1000 K showing that CoP_3 is not thermodynamically stable above this temperature. It is concluded that phosphorus present in excess of the P/Co ratio of 1 is reduced to P_4 above 1000 K.

Analogous to the coimpregnated samples, TPR results of the sequentially impregnated catalysts showed that the major part of the Co-ions were present in a highly dispersed state, only a small amount of Co_3O_4 crystallites has been observed. IR revealed (Fig. 9) that on a P(3.0)/Al catalyst the major part of the hydroxyl groups was present on the P rather than on the Al atoms, consequently it is most likely that the major part of the Co was in interaction with the AlPO_4 groups after calcination. The dispersive state of the cobalt species after calcination supports that cobalt is in interaction with the AlPO_4 groups. The disappearance of the reduction peak at 580 K for the Co-P/P/Al catalyst confirms the conclusion that the dispersion of cobalt is increased due to the formation of cobalt as a cobalt-phosphate phase.

The position of the high-temperature peak is influenced by the presence of reduced Co-species, therefore the absence of reduced Co atoms at around 1100 K, on the catalyst in which Co and P are impregnated simultaneously, results in a shift of the reduction peak at 1200 K.

Implications for the structure of the Co-P catalysts

All results from this work suggest that cobalt is present in contact with the AlPO_4 groups:

- (1) The complete reduction of the AlPO_4 phase in a Co-P catalyst,
- (2) The increase of the cobalt dispersion due to the formation of a cobalt-phosphate phase,
- (3) All cobalt species present react to phosphides.
- (4) Cobalt added to a P/Al "support" is very dispersed.

In the literature little experimental evidence is found for an interaction between transition metals and phosphates on a support. Ramselaar et al. [36]

showed the presence of a “Fe-PO₄” phase on a carbon support using Mössbauer spectroscopy. This suggests that also other transition metals might form a “metal-phosphate” phase. Several other authors could also explain their results by suggesting an interaction between the transition metals and the phosphate species [8,12].

Mo-P/Al, Mo/P/Al, Mo-P/P/Al

The large changes observed in reduction behaviour of Mo-P catalysts indicate that the distribution of molybdenum is strongly affected by the presence of phosphorus. The sharp reduction peak observed around 680 K present in all the samples is ascribed to the reduction of MoO₃ bilayer species as reported by several authors [28,37,38]. The fact that the height of this peak does not change with the P content (except for Mo(2.0)P(0.5)/Al) indicates that the amount of bilayer is nearly the same in all the catalysts. As the dispersion of the catalysts is not changing very much upon sulphiding, it is not likely that an increase of the stocking of the MoS₂ slabs after addition of P, as observed by Kemp et al. [15] will take place in the catalyst applied in this study.

The absence of sharp Raman lines around 990, 820 and 670 cm⁻¹ shows that no crystalline MoO₃ is present on the catalysts. This is confirmed by the absence of a reduction peak around 740 K which has been ascribed to the reduction of crystalline MoO₃ [18,28]. In contrast with our results, López Cordero et al. [18] observed reduction of crystalline MoO₃, probably due to a much lower flow-rate used during the calcination step leading to a higher water vapour partial pressure which is detrimental for the dispersion of metal oxides. Stepwise addition of phosphoric acid and Mo resulted in the formation of crystalline MoO₃, which was measured by TPR (740 K) and Raman (band at 990, 820 and 670 cm⁻¹). Limited adsorption of MoO₃ on a P/Al support was also reported in the literature [16,18]. Despite the loss of dispersion of MoO₃, IR showed that after addition of Mo to the P(2.9)/Al catalyst the intensity of the P-OH band was reduced by a factor 2 indicating that a large part of the molybdenum was still dispersed over the AlPO₄ surface after calcination. The disappearance of the remaining Al-OH species shows that a part of the molybdate species has been adsorbed on these alumina species. It was striking to observe that after addition of a Mo-P solution to the P(2.9)/Al support, the reduction peak at 740 K disappeared. Apparently, the adsorption of phosphomolybdate species inhibits the sintering of MoO₃.

Two explanations can be brought forward concerning the decrease of the reducibility of a part of the Mo-ions (decrease of the peak height around 1000 K accompanied by an increase of the peak height above 1200 K):

- (1) Part of the Mo which adsorbed as a phosphomolybdate complex does not decompose upon calcination,
- (2) After adsorption of the phosphomolybdate complexes, these complexes

react to AlPO_4 and Al-O-Mo species; after calcination at 773 K, a part of these Mo species are still in contact with the AlPO_4 species.

Evidence for an interaction between Mo and P is also obtained from IR spectroscopy. Assuming that the dispersion of the $\text{P}(2.9)/\text{Al}$ catalyst was almost 100%, we would expect a P-OH intensity of 0.18 a.u. for the $\text{Mo}(2.1)\text{P}(1.7)/\text{Al}$ catalyst, however a value of 0.12 a.u. has been found; this indicates that about 1/3 of the total amount of P-OH species is in interaction with Mo. The absence of Raman bands attributable to various phosphomolybdate complexes (P_2Mo_5 at 935 cm^{-1} , PMo_9 at 963 cm^{-1} and PMo_{12} at 995 cm^{-1}) suggests that the major part of the Mo-P species has an ill-defined structure compared to the phosphomolybdate complexes. In spite of this it cannot be excluded that a small amount of intact phosphomolybdate complexes is present (below detection limit in Raman). The ^{31}P -NMR spectra of the Mo-P/Al and P/Al catalysts were nearly the same indicating that ^{31}P solid state-NMR is not sensitive enough to discriminate between P with only Al neighbours and P with both Al and Mo neighbours.

More evidence for an interaction between Mo and P after adsorption and calcination can be found in the literature. With differential pulse polarography, Van Veen et al. [39] showed that a $(\text{P}_2\text{Mo}_5\text{O}_{23})^{6-}$ complex was not reducible suggesting that Mo in contact with a high number of phosphate groups can be extremely difficult to reduce. However, they also found that $(\text{NH}_4)_6\text{P}_2\text{Mo}_5\text{O}_{23}$ adsorbed on a P/Al (monolayer P) remained irreducible up to 950 K even after calcination at 773 K [33]. At a P loading less than a monolayer ($<2.9\text{ atoms nm}^2$), they observed that adsorption of ammonium heptamolybdate resulted in the formation of a Mo-P species, which decomposed after calcination at 773 K. The work of Cheng and Luthra [14] also supports these observations. By studying the adsorption of various Mo-P complexes they observed that the way in which these complexes adsorb strongly depends on the phosphate concentration, pH and the type of complexes in solution. In Mo-P solutions with a high P/Mo ratio Mo is mainly present as $[\text{H}_n\text{P}_2\text{Mo}_5\text{O}_{23}]^{n-6}$ ($n=0-2$) and $[\text{PMo}_9\text{O}_{23}(\text{OH})_3]^{6-}$ species [39,40]. In a solution with a P/Mo ratio of 0.4 Cheng and Luthra observed, using ^{31}P -NMR and an electron microprobe, that Mo and P mainly adsorbed separately instead of adsorbing as a phosphomolybdate. The strong increase of the pH, due to the adsorption of phosphate, molybdate and phosphomolybdate, shifted the equilibrium to the left of eqn. 5, leading to decomposition of the $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}$ complexes.

At higher phosphate concentrations ($\text{P}/\text{Mo} > 1$) no decomposition was observed suggesting that the major part of the molybdophosphate complexes adsorbed without decomposing. This was confirmed by the more homogeneous

distribution of molybdenum over the support. It is likely that after calcination Mo is still in contact with the phosphate species.

In conclusion, these results suggest that the decrement of the reducibility of the major part of the Mo-ions is caused by the formation of an ill-defined Mo-P phase; at high P/Mo ratios, it is possible that small amounts of intact phosphomolybdate complexes are present (P_2Mo_5 , PMo_6 , PMo_9 and PMo_{12}).

Table 3 shows that the amount of hydrogen consumed agrees very well with the reduction of MoO_3 and $AlPO_4$ to MoP_x or Mo^0 and P_4 . The complete reduction of the $AlPO_4$ groups is in line with the idea that part of Mo atoms are present in the vicinity of the phosphate species (in the absence of transition metals, P/Al_2O_3 is essentially stable under TPR conditions). The fact that only in the case of the $Mo(2.1)P(4.7)/Al$ catalyst a FID peak was found suggests that on the catalysts with a P/Mo ratio up to 1 molybdenum phosphides are formed (MoP_x ; $x=1, 1/3, 3/4$). The formation of MoP_2 is excluded due to its high equilibrium pressure at this temperature [26]. In contrast with our results, López Cordero et al. [18] found a hydrogen consumption which agreed with the reduction of the Mo-O species to Mo^0 , suggesting that Mo and P were distributed very inhomogeneously over the alumina support.

The dissimilarities between our results and those obtained by López Cordero et al. [18] stress the influence of minor differences in the preparation method of Mo-P-containing catalysts. The partition of Mo over the support strongly depends on the details of preparation.

Co-Mo-P/Al, Co/Mo-P/Al

The TPR pattern of $Co(1.3)Mo(2.1)/Al$ has already been reported by Arnoldy et al. [21]. By comparing the reduction behaviour of series of Co-Mo/Al catalysts the following species have been observed for a Co-Mo/Al catalysts with a moderate cobalt content and calcined at 773 K:

- (1) MoO_3 bilayer (reduction at 670 K),
- (2) Co-Mo-O phase (reduction at 800–850 K); Mo increases the reduction of the cobalt species due to a decrease of the interaction of the Co^{2+} species with the alumina support,
- (3) monolayer MoO_3 (peak maximum at 1000 K).

The disappearance of the peak around 1000 K with increasing P content is in agreement with the reduction patterns of the Mo-P samples (Fig. 5). Despite the fact that the whole TPR pattern is dominated by the reduction of MoO_3 and $AlPO_4$, the reduction of cobalt can clearly be discerned at 1100 K. The good agreement between the amount of hydrogen consumed at 1100 K and the amount of cobalt present on the catalysts with the highest P content, shows that in these samples nearly all the cobalt is quantitatively present in one well defined species.

Arnoldy et al. [21] showed that $CoMoO_4$ crystallites were reduced in the region from 800–1000 K, whereas the disperse Co-Mo-O species were reduced

between 800–850 K, so the reduction peak around 1100 K cannot be assigned to the reduction of a Co–Mo–O phase or CoMoO_4 crystallites. Also no evidence could be found for CoMoO_4 crystallites in Raman or XRD. Assignment of this reduction peak to Co^{2+} subsurface species is unlikely because this reduction peak is also observed in the catalyst which is prepared by adding stepwise Mo–P and cobalt (Fig. 8b). The reduction peak of these cobalt species, which are only present in a Mo–P/Al catalyst, is ascribed to Co^{2+} -ions bound to a monolayer of MoO_3 and AlPO_4 species, a Co–Mo–O–P phase. Due to the higher effective charge of P^{5+} -ions compared to the Al^{3+} -ions, the Co–O bonds were more polarized in the presence of P-ions than in the presence of Al^{3+} , resulting in a decrease of the reducibility of the Co-ions. The presence of a Co–Mo–O–P phase also implies that a part of the MoO_3 species is situated next to AlPO_4 species which is in agreement with the conclusion obtained for the Mo–P samples.

The presence of a FID signal indirectly proves the existence of reduced cobalt species. The appearance of an FID peak around 670–700 K (methane) indicates that a small amount of the Co-ions is present as another phase than the Co–Mo–O–P phase. It is not possible, only on the basis of these TPR patterns, to conclude which cobalt species are reduced in this temperature region.

Analogous to the discussion for the Co–P and Mo–P samples, the reduction of the metal oxides also proceeds to the matching metal phosphides.

CONCLUSIONS

TPR and FT-IR showed to be very sensitive techniques to characterize the structure of P-containing alumina-supported Co–Mo catalysts. P, added as phosphoric acid, strongly influences the surface characteristics of the Co, Mo and Co–Mo catalysts.

(1) The disappearance of nearly all Al–OH surface groups after addition of P (2.9 atoms/nm²) showed that phosphoric acid is well distributed over the Al_2O_3 surface layer. All the phosphoric acid added to the alumina support formed AlPO_4 .

(2) Phosphate species present up to a P-to-metal ratio of ≤ 1 were completely reduced to CoP, Co_2P or MoP_x ($x \leq 1$) above 1000 K. CoP, Co_2P and MoP are thermodynamically stable up to 1273 K. At P-to-metal ratios higher than 1, a part of the AlPO_4 phase was nearly completely reduced to P_4 and alumina.

(3) Coimpregnation of Co and P resulted in an increased dispersion of the Co species. At relatively high P contents, the major part of the Co-ions is in contact with the AlPO_4 surface species. Also after addition of Co to a P/Al catalyst, the major part of the CoO is highly disperse.

(4) Compared with a P-free Mo catalyst, coimpregnation of Mo and P changes the distribution of Mo over the support. After calcination at 773 K, a

part of the Mo-ions was present as Mo-O-P species. The amount of these species increases with the P content. On the catalysts prepared by sequential impregnation of P and Mo, a part of the Mo was present in MoO₃ crystallites, the other part was very well distributed over the AlPO₄ surface layer.

(5) After both sequential impregnation and coimpregnation of Co, Mo and P on alumina, the formation of a new phase viz. a Co-Mo-O-P phase is suggested. Compared with the Co-Mo-O phase, the reducibility of the Co-ions is decreased probably due to the stronger polarization of the Co-O bonds by P⁵⁺-ions than by the Al³⁺-ions.

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