# Chapter 3

# **Preparation and Hydroprocessing Properties of Molybdenum Phosphide Supported on γ-Alumina**

# 3.1. Introduction

Although hydroprocessing catalysts have been widely studied, their compositions have changed little since their introduction by I. G. Farben Industrie (1) in the 1920s. They are typically alumina supported molybdenum sulfides with nickel or cobalt promoters- NiMoS/Al<sub>2</sub>O<sub>3</sub> or CoMoS/Al<sub>2</sub>O<sub>3</sub>. In recent years, phosphorus has come to be used as a secondary promoter in commercial catalysts (2). The use of phosphorus in hydroprocessing catalyst formulations was introduced in a series of patents dating back to the 1950s (3, 4, 5). The phosphorus in these catalysts is in oxidized form dispersed on the catalyst surface, as shown by studies with x-ray photoelectron spectroscopy (6), nuclear magnetic resonance (7), and infrared spectroscopy (8). The effect of phosphorus depends on its concentration and physical form, but in general it increases the HDN performance of Ni-Mo sulfides, and poisons Co-Mo HDS catalysts (9).

The previous chapter described the synthesis and properties of tungsten phosphide. This chapter describes the preparation and properties of a molybdenum phosphide dispersed on alumina. The alumina supported phosphide catalyst studied here is distinguished from the phosphate promoted sulfide counterpart, in that the active phase contains P in a reduced state associated directly with the active metal component. The MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts studied here were also distinct from their bulk phosphide

counterpart, in that the temperature programmed reduction profiles show at least two new events in the reduction process. Furthermore, in contrast to the bulk material, the active component in our MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was found to have a bimodal size distribution. There were large, ~140 nm diameter, x-ray diffracting crystallites similar to the bulk, and there were very small, ~1.2 nm diameter, x-ray invisible crystallites well dispersed on the alumina surface.

# 3.2. Experimental

Oxidic catalyst precursors were prepared in the following manner. Desired quantities of ammonium paramolybdate tetrahydrate, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O (Aldrich, 99%) and ammonium phosphate, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Aldrich, 99%) were dissolved in 1:1 stoichiometric mixtures to form clear solutions in distilled water. These solutions were used to fill the pores of an alumina support (Degussa, Aluminumoxid C) by incipient wetness impregnation. The moist paste was calcined in air at 773 K for 6 h, ground with a mortar and pestle, pressed, broken, and sieved to particles between 650 and 1180  $\mu$ m diameter for use. Samples were prepared with loadings between 0 and 39 wt% MoP (0 and 3.1 mmol g<sup>-1</sup>). Specific compositional characteristics for the series of catalysts are reported in Table 3.1. The highest loading sample was prepared by a double impregnation, due to a solubility limit of the metal phosphate solution. Much of the work carried out in this study used the 13 wt% MoP/Al<sub>2</sub>O<sub>3</sub> material. Reference samples containing only 1.16 mmol Mo g<sup>-1</sup> Al<sub>2</sub>O<sub>3</sub> (11.1 wt% Mo) or P (3.6 wt% P) were prepared in a similar manner, while aluminum phosphate (99.999%) was obtained from Johnson-Matthey. Temperature programmed reductions and CO uptake measurements were carried out as described in Chapter 2 for the bulk WP. Unless otherwise noted, the space velocity was set at 650  $\mu$ mol H<sub>2</sub> s<sup>-1</sup> g<sup>-1</sup> of sample loaded (1000 cm<sup>3</sup> min<sup>-1</sup> g<sup>-1</sup>), and the heating rate was 0.0833 K s<sup>-1</sup>. BET specific surface areas (S<sub>g</sub>) of the supported sample were measured with a Micromeritics 2000 sorption unit.

wt% MoP	mmol MoP g <sup>-1</sup> Al <sub>2</sub> O <sub>3</sub>	molecule MoP nm <sup>-2</sup> Al <sub>2</sub> O <sub>3</sub>
2.5	0.20	1.0
3.5	0.29	1.9
6.8	0.58	3.8
13	1.16	7.7
23	2.3	15
39	3.8	25

**Table 3.1**: Compositional characteristics of MoP/Al<sub>2</sub>O<sub>3</sub> samples.

X-ray diffraction (XRD) patterns were obtained using a Scintag XDS-2000 diffractometer. The x-ray source was Ni-filtered Cu K<sub> $\alpha$ </sub> ( $\lambda = 0.1541$  nm) radiation used at a scan rate of  $0.035^{\circ} 2\theta$  s<sup>-1</sup>. Crystallite sizes were estimated using the Scherrer equation,  $D_x = K\lambda / \beta \cos\theta$ . The constant K was taken here to be 0.9, and the average of the first three reflections was used to determine the reported values (10). The value  $\beta$  in this equation is the linebreadth of the XRD peak at half maximum, adjusted for instrumental linebroadening as  $\beta = B \cdot (1 - b^2/B^2)$ . Here b is the linebreath of a nearby peak of a highly crystalline reference material, and B is the measured linebreadth of the material under investigation. Activation energies for reduction reactions were estimated by the heating rate variation method of Redhead (11), assuming first order processes. Hydrotreating activity was evaluated in the same manner as described in Chapter 2. To review briefly, a model oil described in detail in Table 2.1, and which contained 2000 wppm N as quinoline (Aldrich, 99%), 500 wppm O as benzofuran (Aldrich, 99%), and 3000 wppm S as dibenzothiophene (Aldrich, 99%) in an aliphatic-aromatic solvent, was hydroprocessed at 673 K and 3.1 MPa to test the activities of the catalysts. An amount of catalyst corresponding to 70  $\mu$ mol of CO sites (measured *ex situ*) was loaded in each reaction. To start the reaction, the catalysts were pretreated in flowing hydrogen (100  $\mu$ mol s<sup>-1</sup>) at 723 K and 1 atm pressure for 2 h.

## **3.3. Results and Discussion**

#### **3.3.1.** Synthesis of MoP/γ-Al<sub>2</sub>O<sub>3</sub>

Oxidic catalyst precursors were reduced to phosphide catalysts by temperatureprogrammed reduction in hydrogen. Corresponding reduction profiles, as a function of loading, are presented in Figure 3.1. There are five peaks associated with the reduction process corresponding to different stages in the synthesis. The reaction sequence was followed by XRD of quenched intermediates of the 13 % MoP/Al<sub>2</sub>O<sub>3</sub> and these results are shown in Figure 3.2. The first reduction peak seen in Figure 3.1, at 373 K, is due to physically adsorbed water. The second peak, near 650 K, is labeled  $\alpha$  and represents the onset of the reduction process. It is visible in the lowest loading sample, and is likely due to well-dispersed molybdenum oxide species, as no new XRD peaks are seen in Figure 3.2 at 673 K. The intensities of the third and fourth reduction peaks, labeled  $\beta$  and  $\gamma$  respectively, increase with loading. Figure 3.2 shows the sequential reduction of MoO<sub>3</sub> to MoO<sub>2</sub> for the  $\beta$  peak, and MoO<sub>2</sub> to Mo metal for the  $\gamma$  peak. The final reduction peak, labeled  $\delta$ , is large and broad with a maximum between 1100 and 1200 K. Figure 3.2 reveals that the  $\delta$  peak is accompanied by the disappearance of molybdenum metal and the appearance of molybdenum phosphide above 1123 K. The  $\delta$  peak is assigned to reduction of well-dispersed, x-ray amorphous aluminum phosphate, accompanied by transfer of phosphorus to Mo metal to form MoP. The presence of aluminum phosphate in standard phosphorus promoted catalysts is well established (12, 13). One of the effects



Figure 3.1: Temperature programmed reduction profiles for various  $MoPO_x/Al_2O_3$  samples reduced to 1223 K at 5 K min<sup>-1</sup>.



Figure 3.2: Evolution of MoP during the reduction of MoPO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (13 % MoP).

Samples were reduced to intermediate temperatures, quenched in helium, and

characterized by *in-situ* CO uptake before passivation.

(o) MoO<sub>3</sub>; (y) MoO<sub>2</sub>; (+) Mo<sup>o</sup>; (x) MoP, and (\*) Al<sub>2</sub>O<sub>3</sub>.

of phosphorus is to block nucleation sites for the high temperature transition between high surface area  $\gamma$ -alumina and low surface area  $\alpha$ -alumina (14), a finding that is substantiated in this study.

The development of the *in situ* CO uptake during the reduction process on the quenched intermediates from 13 % MoP/Al<sub>2</sub>O<sub>3</sub> is shown in Figure 3.3, superimposed on its reduction profile. (*In situ* CO uptakes were collected on samples quenched immediately following the attainment of the stated temperature according to the temperature program.) Reduction of MoO<sub>3</sub> to Mo metal (i.e. the  $\alpha$ ,  $\beta$ , and  $\gamma$  peaks) only slightly increases the CO uptake. In contrast, the peak resulting from aluminum phosphate decomposition, along with the transition from Mo to MoP, is accompanied by a large increase in the CO uptake. This increase in chemisorption is approximately proportional to the degree of completion of the  $\delta$  peak, and exhibits a similar maximum with temperature.

Comparisons of the reduction profile of the 1.16 mmol MoP  $g^{-1}$  Al<sub>2</sub>O<sub>3</sub> material (i.e. 13 %) with reference samples containing either 1.16 mmol phosphate  $g^{-1}$  Al<sub>2</sub>O<sub>3</sub>, 1.16 mmol molybdate  $g^{-1}$  Al<sub>2</sub>O<sub>3</sub> (with otherwise similar conditions), and bulk AlPO<sub>4</sub>, are made in Figure 3.4. The three peaks between 600 and 900 K are found only in the molybdenum containing samples, and, thus, these are confirmed to be due to the supported Mo species. The high temperature reduction, i.e. the  $\delta$  peak, in 13 % MoP/Al<sub>2</sub>O<sub>3</sub> overlaps the P/Al<sub>2</sub>O<sub>3</sub> and AlPO<sub>4</sub> reductions, and this feature does not occur at all in the Mo/Al<sub>2</sub>O<sub>3</sub> sample. This confirms that the high temperature peak is associated with the aluminum and phosphorus components. Similar results have been found previously for high temperature TPR of P/Al<sub>2</sub>O<sub>3</sub> samples (8).



**Figure 3.3**: Evolution of *in-situ* CO uptake sites of quenched intermediates during the preparation of 13 wt% MoP/Al<sub>2</sub>O<sub>3</sub>.



**Figure 3.4**: Reduction profiles for 'blank' alumina samples reduced to 1223 K at 5 K min<sup>-1</sup>. (a) 1.16 mmol g<sup>-1</sup> PO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>; (b) AlPO<sub>4</sub>; (c) 1.16 mmol g<sup>-1</sup> MoPO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>; and (d) 1.16 mmol g<sup>-1</sup> MoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>.

The presence of molybdenum species appears to reduce the peak temperature compared with the  $P/Al_2O_3$  and  $AIPO_4$  samples, possibly by providing spillover hydrogen. It is also possible that the high temperature peak results from a complex species containing phosphorus, molybdenum, and aluminum. It was observed that

reduction of (molybdenum free) aluminum phosphate materials resulted in the release of vapor phase phosphorus, which deposited downstream in the reactor. This has been reported earlier for phosphorus containing materials undergoing high temperature TPR (8). Owing to their high vapor pressure, it is likely that the species formed is either  $P_2$  or  $P_4$  (15, 16).

X-ray diffraction spectra showing the evolution of MoP with loading in samples reduced at 1223 K are presented in Figure 3.5. MoP is the only crystalline product formed, becoming visible at 6.8 wt%, and increasing intensity with loading. MoP has a hexagonal WC type structure, space group =  $P_{\overline{6}m2}$ , with bulk lattice parameters  $a_0 = 322$  pm and  $c_0 = 319$  pm (17). MoP is a metallic conductor with properties similar to ordinary intermetallic compounds (18). The lattice constants for the supported MoP are reported in Table 3.2 along with the crystallite sizes calculated from them using the Scherrer equation

Sample	Lattice	Lattice	Crystallite
	Parameter a	Parameter c	Size <sup>a</sup>
	pm	pm	nm
13% MoP/Al <sub>2</sub> O <sub>3</sub>	321	318	141
23% MoP/Al <sub>2</sub> O <sub>3</sub>	322	319	143
39% MoP/Al <sub>2</sub> O <sub>3</sub>	322	319	173
MoP	322	318	74
MoP reference <sup>c</sup>	322	319	-

**Table 3.2**: X-ray diffraction results for MoP/Al<sub>2</sub>O<sub>3</sub> catalysts.

<sup>a</sup> average of <1 0 0>, <1 0 1>, and [0 0 1] directions

<sup>b</sup> calculated from the crystallite size using the experimentally determined site density of bulk MoP.

<sup>c</sup> PDF 24-771

The lattice parameters agree very well with the literature values, indicating that fairly pure supported MoP is formed. The particles sizes of the diffracting crystallites found on the supported MoP are about twice as large as the particles in the bulk MoP. This is probably because the supported samples were reduced at a much greater temperature (1123 K vs. 923 K), and the free MoP crystallites had greater opportunity for grain growth by sintering. Sintering is typical of metal crystallites at elevated temperature.

The effect of loading on *in situ* CO uptakes, of samples reduced to 1223 K and quenched, are reported in Figure 3.6. These values are for the same samples whose XRD are included in Figure 3.5. The *in situ* CO uptakes rise initially with loading, then level off , and begin to fall at high loadings. This behavior is consistent with the approximate proportionality between CO uptake and the amount of MoP at low loadings ( $\leq 6.8$  wt%). The *in situ* uptake then goes through a maximum as dispersion is optimized, and drops off at higher loadings. The decrease at high loadings is probably due to the loss of surface area due to pore filling, as see in Table 3.3.

The proportionality of *in situ* uptake with loading at low concentrations of MoP, is explained by the formation of a highly dispersed MoP phase on the alumina surface. These dispersed MoP crystallites are distinct from the diffracting particles seen at higher MoP loading. This idea can be developed as well by considering theoretical CO uptakes calculated from particle sizes estimated from the linebreadths of the XRD peaks. These results are compared to each other, along with surface areas and *ex situ* uptakes, in Table 3.3.



**Figure 3.5**: X-ray diffraction results showing increased amounts of MoP with loading for samples reduced to 1223 K at 5 K min<sup>-1</sup>. (x) MoP, and (\*)  $Al_2O_3$ .

A theoretical CO uptake can be calculated from the crystallite size, density, and loading as follows:

Theoretical CO Uptake =  $S_x \cdot n_{CO} \cdot \%$  MoP

where  $S_x$  is the specific surface area calculated from the crystallite size and density by

$$S_x = \frac{6}{D_{hkl} \cdot r}$$

while the value  $n_{CO}$  is the site density, calculated as the CO uptake divided by the surface area for the bulk material, and % MoP is the wt% loading of the sample. Here, D<sub>hkl</sub> is the average diameter of the crystallite in the hkl directions, as calculated from the Scherrer equation (which was described on page 47). The experimental ratio of CO uptake to surface area is taken here to be 18/15, or 1.2 µmol m<sup>-2</sup>, as reported previously (19). As reported in Table 3.3, the theoretical uptakes for the diffracting crystallites are very small in comparison to the measured values. In contrast, the theoretical CO uptake is equal to 16 µmol g<sup>-1</sup> for the bulk sample, in good agreement with the experimental results. It is reasonable to conclude that the diffracting crystallites represent only a small contribution to the total uptake. We explain that the remainder of the CO uptake sites are associated with very small crystallites of MoP derived from the x-ray amorphous surface layer. Using the

Sample	Surface	Theoretical <sup>a</sup>	in situ <sup>b</sup>	ex situ <sup>c</sup>	ex situ <sup>c</sup>
	Area	CO Uptake	CO Uptake	CO Uptake	CO Uptake
	fresh <sup>d</sup>			fresh <sup>d</sup>	spent <sup>e</sup>
	$m^2 g^{-1}$	µmol g⁻¹	µmol g⁻¹	µmol g⁻¹	µmol g⁻¹
Al <sub>2</sub> O <sub>3</sub> blank	91	-	1	0	-
6.8 wt% MoP	75	$67^{\mathrm{f}}$	70	26	20
13 wt% MoP	71	1.1	81	36	31
23 wt% MoP	60	1.9	76	28	29
39 wt% MoP	49	2.7	60	36	26

Table 3.3: Surface area and chemisorption properties of MoP/Al<sub>2</sub>O<sub>3</sub> samples.

<sup>a</sup> calculated from XRD particle size, loading, and density.

<sup>b</sup> Reduced to 1223 K ( $\beta = 5$  K min<sup>-1</sup>, H<sub>2</sub> flow = 650 µmol g<sup>-1</sup>), then quenched.

<sup>c</sup> Pretreated in H<sub>2</sub> at 723 K for 2 h ( $\beta$  = 5 K min<sup>-1</sup>, H<sub>2</sub> flow = 650 µmol g<sup>-1</sup>).

<sup>d</sup> Prepared by reduction to 1123 K for 2 h ( $\beta = 5$  K min<sup>-1</sup>, H<sub>2</sub> flow = 650  $\mu$ mol g<sup>-1</sup>).

<sup>e</sup> Spent catalysts washed in hexane and dried in air.

<sup>f</sup> Calculated from loading and density assuming spherical particles of 1.2 nm.



**Figure 3.6**: Development of *in-situ* CO uptake as a function of loading. The samples were reduced to 1223 K at 5 K min<sup>-1</sup> in hydrogen flow at 1 dm<sup>3</sup> min<sup>-1</sup> g<sup>-1</sup>.

above procedure in reverse, it is calculated from the *in situ* CO uptake of the x-ray amorphous 6.8% MoP/Al<sub>2</sub>O<sub>3</sub> that the average diameter of a highly dispersed phosphide particle, as found on the 6.8% MoP/Al<sub>2</sub>O<sub>3</sub> catalyst, is about 1.2 nm.

A heating-rate variation study was performed on the reduction forming 23 % MoP/Al<sub>2</sub>O<sub>3</sub>. The resulting reduction profiles are displayed in Figure 3.7. Table 3.4 reports the first order activation energies calculated for each of the four reduction peaks,

 $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The kinetic fits are good for the  $\alpha$ ,  $\beta$ , and  $\delta$  peaks. The  $\gamma$  peak is shown in Figure 3.7 to be resolved into three smaller peaks as the heating rate is reduced.

Furthermore, the peak maxima in the  $\gamma$  peak do not conform to a linear activation energy



**Figure 3.7**: Effect of heating rate on the temperature programmed reduction forming 23% MoP/Al<sub>2</sub>O<sub>3</sub>.

peak	activation energy kJ mol <sup>-1</sup>	
α	152	
β	157	
γ	130 <sup>*</sup>	
δ	160	

**Table 3.4**: Apparent first order activation energies of reduction events in the preparation of 23 % MoP/Al<sub>2</sub>O<sub>3</sub>.

<sup>\*</sup> Not linear. Estimated using heating rates of 2 K min<sup>-1</sup> and 5 K min<sup>-1</sup>. See text.

relationship. This suggests an overlap of processes in this temperature range, probably due to overlap of  $MoO_2 \varsigma$  Mo reduction peaks with coincidental reduction of free molybdenum phosphate  $MoPO_x \varsigma$  MoP. The latter reaction is demonstrated to occur in the same temperature range during the preparation of bulk MoP (19), and its occurrence is understandable given the doubling in loading of MoP to 23% compared to the 13% material studied in Figures 3.1 and 3.2. That is, following the abstraction of a surface layer of Mo and P species by the alumina, additional Mo-P-O species deposited to the Mo-P-O/Al<sub>2</sub>O<sub>3</sub> surface are expected to behave similarly to the bulk phosphate. In this report, we demonstrate surface layer saturation in the 6.8 wt % to 13 wt % range, based on *in situ* CO uptake and x-ray diffraction data.

## 3.3.2. Catalytic Activity of MoP/γ-Al<sub>2</sub>O<sub>3</sub> Samples

A temperature variation study was undertaken for the synthesis of the 13%  $MoP/Al_2O_3$  catalyst. Of four temperatures tried, successful samples were produced only at 1023 K and 1123 K. A sample reduced at 873 K for 2 h had insufficient *ex situ* CO uptake (= 12 µmol g<sup>-1</sup>) to load 70 µmol of sites, and the sample reduced at 1223 K for 0.5 h exhibited daily aging in its CO uptake and therefore was also not used.

The catalysts were evaluated for activity in hydrotreating of a simulated light oil containing quinoline (2000 wppm N) and dibenzothiophene (3000 wppm S) at 643 K and 3.1 MPa. Importantly, for direct comparison of activity, amounts of catalysts were loaded into the reactor that corresponded to 70  $\mu$ mol of sites as titrated by *ex situ* CO uptake. Table 3.3 provides a summary of these uptakes obtained after pretreatment in hydrogen at 723 K for 2 h.

The hydrotreating performances of the MoP/Al<sub>2</sub>O<sub>3</sub> samples are reported in Table 3.4. The values reported were stable and were averaged over the final 30 h of reaction. There was only a slight effect of loading on the HDN and HDS performances, which averaged 56 % and 52 %, respectively, for most conditions. The decreased HDS (44 %) for the high loading sample might be due to size exclusion of the relatively large dibenzothiophene molecules from pores which are increasingly plugged with MoP. Note the considerable decrease in surface area with loading (Table 3.3). Overall, the consistency in conversions indicate that CO uptakes are a good measure of the surface sites involved in catalytic reactions. The amount of hydrogenated quinoline products was stable near 30% for all samples, including the blank. This is consistent with equilibration between quinoline and 1,2,3,4-tetrahydroquinoline. The activity of the supported MoP/Al<sub>2</sub>O<sub>3</sub> samples is high, especially in HDN, and can be compared to that of a

commercial Ni-Mo-S/Al<sub>2</sub>O<sub>3</sub>, which at the same conditions has HDN conversion of 38% and HDS conversion of 79 % (20).

Sample	% HDN	% HYD	%HDS
Al <sub>2</sub> O <sub>3</sub> blank	2.4	32	1.1
6.8 wt%	54	31	51
13 wt%	52	33	57
13 wt% <sup>b</sup>	62	29	57
23 wt%	58	28	53
39 wt%	54	33	44

**Table 3.5**: Hydroprocessing conversions of MoP/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>a</sup>.

<sup>a</sup> Reduced to 1123 K ( $\beta$  = 5 K min<sup>-1</sup>, H<sub>2</sub> flow = 650 µmol g<sup>-1</sup>) for 2 h <sup>b</sup> Reduced to 1023 K ( $\beta$  = 5 K min<sup>-1</sup>, H<sub>2</sub> flow = 650 µmol g<sup>-1</sup>) for 1.5 h <sup>c</sup> m<sup>2</sup> g<sup>-1</sup> MoP/Al<sub>2</sub>O<sub>3</sub> <sup>d</sup> *ex-situ* CO uptake sites g<sup>-1</sup> MoP/Al<sub>2</sub>O<sub>3</sub>

As bulk and silica supported MoP were also prepared and tested in conjunction with other aspects of this study, reported in chapter 5, it is of interest to compare the results to each another. This is done in Table 3.6, on the basis of specific rates per CO site. This basis was used to compensate for the different loading requirements adopted for supported (70  $\mu$ mol of sites) and bulk (30 m<sup>2</sup>) materials. It can be seen from Table 3.6 that the MoP/Al<sub>2</sub>O<sub>3</sub> performs similarly to the bulk material for both HDN and HDS, while the MoP/SiO<sub>2</sub> had lower activity than its counterparts. This is suggestive that the sites on the well dispersed MoP crystallites on the alumina support have similar activity to the bulk material.

Sample	HDN mol auinoline mol site <sup>-1</sup> s <sup>-1</sup>	HDS mol dibenzothiophene mol site <sup>-1</sup> s <sup>-1</sup>
13 wt% MoP/Al <sub>2</sub> O <sub>3</sub>	1.21E-03	8.54E-04
13 wt% MoP/SiO <sub>2</sub>	7.21E-04	2.95E-04
bulk MoP	1.49E-03	5.24E-04

**Table 3.6**: Comparison of specific hydroprocessing rates of 13% MoP/Al<sub>2</sub>O<sub>3</sub> with 13% MoP/SiO<sub>2</sub> and bulk MoP.

In situ EXAFS measurements on the 6.8 % MoP/Al<sub>2</sub>O<sub>3</sub> sample (24) identified the dispersed phase as clusters of MoP between 0.5 nm and 1.2 nm size. These results are in excellent agreement with the particle size of 1.2 nm calculated from the *in situ* CO uptake above.

It is interesting that the CO uptake is proportional to the aluminum phosphate ( $\delta$ ) reduction peak, because CO uptake is expected to be proportional to coordinatively unsaturated sites at the molybdenum metal atoms. This feature implies that the dispersed MoP phase is formed directly from the phosphate sites on the surface, perhaps occupying a position close to those sites upon reduction of the phosphorus compound. That is, perhaps the  $\delta$  peak corresponds to the reduction of an alumina coordinated molybdenum phosphate glass, having properties distinct from the bulk form.

Table 3.3 also reports the *ex situ* CO uptake values for the spent catalysts. For these measurements the samples were removed from the catalytic reactors, washed with hexane, and dried in air. Subsequently, they were reduced in hydrogen (0.3 g of sample,  $300 \text{ cm}3 \text{ (NTP)} \text{ min}^{-1} \text{ flow}$ ), using a temperature ramp of 0.0833 K s<sup>-1</sup> (5 K min<sup>-1</sup>) to a final temperature of 723 K, which was held for 2 h. Following the reduction, the flow

was switched to helium (80 cm<sup>3</sup> (NTP) min<sup>-1</sup>), the sample was cooled rapidly to room temperature, and the chemisorption begun. It is evident that the *ex situ* CO adsorption sites are stable toward reaction conditions and exposure to air. The *ex situ* CO uptakes were roughly constant with loading, but the surface area dropped dramatically as loading increased. A blank alumina sample subjected to incipient wetness impregnation of distilled water, pelletization, and reduction in hydrogen at 1023 K, was tested as a reference. Of the samples considered, only the 3.2 % sample, the P/Al<sub>2</sub>O<sub>3</sub> references, and the alumina blank had insufficient *ex situ* CO uptake to load 70 µmol of sites.

X-ray diffraction patterns for fresh and spent 13 % MoP/Al<sub>2</sub>O<sub>3</sub> catalyst reduced to 1123 K are presented in Figure 3.8. MoP and Al<sub>2</sub>O<sub>3</sub> were the only crystalline phases observed, and the catalyst XRD pattern was not significantly affected by reaction. Similar results were found for catalysts of other loadings, whose XRD patterns were unaffected by the catalytic test, and resembled those shown in Figure 3.5.

For the 13 % MoP/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 1023 K, the x-ray diffraction patterns for fresh and spent catalyst contain lines of both Mo and MoP, as shown in Figure 3.9. This material was also unaffected by the catalytic reaction conditions. This catalyst was prepared at 1023 using a 1.5 h soak, as noted in Table 3.4. Compared to the intermediate sample which was quenched at 1023 K, whose XRD spectrum is shown in Figure 3.2, and which contained only Mo metal , the diffraction trace of the catalyst sample reduced at 1023 K contained mostly MoP. Thus, the molybdenum phosphide in the catalyst sample appeared as a result of the 1.5 hour soak time. During this time, a slow reduction of aluminum phosphate (the  $\delta$  peak) led to the phosphidation of the metal.



**Figure 3.8**: X-ray diffraction of fresh and spent 13 wt% MoP/Al<sub>2</sub>O<sub>3</sub> catalyst prepared at 1123 K. MoP is the only observed crystalline phase of Mo, and it is not significantly affected by reaction study.



**Figure 3.9**: X-ray diffraction of fresh and spent 13 wt% MoP/Al<sub>2</sub>O<sub>3</sub> catalyst prepared at 1023 K. MoP and Mo are both present in the material, and are not significantly affected by reaction study.

### **3.3.3.** Relationship to Previous Results in the Literature

Although the nomenclature "MoP/Al<sub>2</sub>O<sub>3</sub>" has appeared before in the literature (21), the materials studied were in fact phosphate promoted molybdenum sulfides. Such phosphate promoted sulfidic hydrotreating catalysts have been widely investigated, as described in an extensive review by Iwamoto and Grimblot (2), but are not the same materials investigated in the present study. In our catalysts, the phosphorus is in a reduced state and the active molybdenum phosphide is metallic. Aside from the presence of Ni or Co promoters, comparison of the preparative conditions reveals that the relative amount of P to Mo in the promoted system is small, whereas in the present system it has exactly 1:1 molar proportions. For example, optimal activity for thiophene HDS in an alumina supported sulfide catalyst containing 3.0 wt% NiO and 15 wt% MoO<sub>3</sub> was achieved with a phosphorus content of 1 wt% (0.24 mol P: mol Mo) (22). Furthermore, the activation procedure for the promoted system typically involved low temperature (c. 723 K) reduction in a sulfidic atmosphere, whereas in the present study the reduction is at high temperature (1123 K) in pure hydrogen. No definitive evidence for phosphide formation has been given for the promoted system, whereas we demonstrate by XRD and EXAFS the presence of hexagonal MoP in our materials.

Despite the differences between the two systems, there are also similarities. Both systems exhibit a strong interaction between phosphate and alumina resulting in the formation of aluminum phosphate (12, 13). Additionally, the presence of phosphate

results in moderate reductions in the surface area of the catalysts. As noted earlier, the phosphate blocks the transformation of  $\gamma$ -alumina to  $\alpha$ -alumina (14), which would result in a catastrophic loss of surface area. It has been found that the interaction of alumina and phosphate increases the dispersion of the metals in the Ni-Mo-S system (23). Molybdena also interacts strongly with alumina, suggesting that the phosphate group alters the interaction of molybdenum with the surface (23).

The *in situ* CO uptake was roughly proportional to the progress of the aluminum phosphate reduction (Figure 3.3), and the *in situ* and *ex situ* CO uptakes were roughly independent of loading in the catalyst samples (Table 3.3). The catalyst with well dispersed phosphide (6.8 wt%) has similar activity for the hydrotreating reaction as do the higher loading samples. The dispersion of aluminum phosphate is necessarily high, because alumina is immobile and has a high surface area. These facts suggest that the majority of active centers are located on highly dispersed sites.

Because the catalytic activity is roughly independent of loading from 6.8 wt% to 39%, while the XRD of MoP increases dramatically in intensity, it is reasonable to conclude that the majority of active sites are associated with highly dispersed P and Mo, associated with  $Al_2O_3$ . Characterization of this active phase using extended x-ray absorption fine structure is reported in another study (24).

This is the first report of the use of alumina supported MoP for hydroprocessing reactions. The nature of phosphorus in MoP/Al<sub>2</sub>O<sub>3</sub> catalysts reported here is quite different from its state in commercial phosphorus promoted sulfides. A strong interaction was found between phosphorus and alumina, which resulted in highly dispersed active sites with better hydroprocessing activity than bulk MoP.

# 3.4. Conclusions

A series of MoP catalysts supported on γ-Al<sub>2</sub>O<sub>3</sub> was prepared and tested for hydroprocessing activity under simulated industrial conditions. Dispersion of the molybdenum phosphate precursor on alumina resulted in an interaction between alumina and phosphate, evidenced by the presence of MoO<sub>3</sub> in the oxidic precursor form of the catalyst, and by new peaks in the TPR profile. As reduction proceeds, MoO<sub>2</sub> occurred at 763 K, molybdenum metal was seen between 863 and 1073 K, and MoP was formed above 1173 K. The catalysts were active for hydroprocessing of both dibenzothiophene and quinoline, and were stable under hydroprocessing conditions. The MoP/Al<sub>2</sub>O<sub>3</sub> catalysts had similar activity to the bulk MoP when compared on the basis of CO chemisorption sites. Analysis suggests that the active species are associated with well dispersed sites on the alumina carrier.

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