X-RAY PHOTOELECTRON SPECTROSCOPIC (XPS) EXAMINATION
OF A SULPHIDED Co-Mo-ALUMINA (HDS) CATALYST

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MARCH 1982

For Presentation to the 8th Canadian Symposium on Catalysis,
University of Waterloo, May 27, 1982.

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by

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ABSTRACT

A hydrodesulphurization (HDS) Co-Mo-alumina catalyst was examined in its working state using x-ray photoelectron spectroscopy (XPS) and gas chromatography (G.C.).   The catalyst was exposed to 10% H_2S/H_2 and/or 1% thiophene/H_2 using a specially designed micro-reactor coupled directly to the XPS system.   The two chambers could be isolated when required.   The catalyst was manipulated between chambers using a transfer device, eliminating the risk of atmospheric exposure and catalyst alteration (ie. re-oxidation, surface contamination over-layers, etc.). In the activated (sulphided) state, the catalyst converted thiophene to C-4 hydrocarbons.   Molybdenum present on the surface of the sulphided catalyst exist as Mo VI and IV in approximately equal amounts.   The unconverted Mo VI was assigned to $Al_2(MoO_4)_3$ (Mo, tetrahedral sites) and the Mo IV was assigned to MoS_2. Some elemental as well as sulphide sulphur was detected on the surface.   Our results are in agreement with other studies that suggest there are at least two types of molybdenum species present.   One type would be MoS_2 crystallites and the other a molybdenum species which is bonded to the alumina, ie., possibly $Al_2(MoO_2S_2)_3$.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has been used to characterize the surface of hydroprocessing catalysts.   Extensive reviews of the theory and instrumentation of XPS, (1-7) and application to catalytic research have been published (8-22).   Catalysts used in hydroprocessing (hydrodesulphurization, HDS) are generally molybdenum supported on alumina with a promoter (cobalt or nickel) added to improve performance.

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To understand the mechanism responsible for catalyst activity, knowledge of the molybdenum interaction with the alumina support and the cobalt promoter is required. XPS can directly examine the catalyst surface to determine if new surface species are formed during activation. Determination of the surface chemical composition and identification of the compounds present on the fresh and reacted catalyst (ie. $MoO_3 \rightarrow MoS_2$, $CoO \rightarrow Co_9S_8$, etc.) are thus possible. Much of the published XPS work on HDS catalyst however has been controversial.

The XPS findings of several researchers have varied significantly although catalysts of the same bulk composition and similiar hydroprocessing exposure procedures were used. Thus, several hypotheses put forth to examine the mechanism of the Co-Mo-alumina catalyst have been developed using XPS data which can fluctuate widely between laboratories. Some of these contradictions may in fact be caused by different interpretations of the spectra or by inherent sample charging problems. Presently there is no standardized XPS procedure for handling catalyst samples prior to and following treatment or reaction studies. Thus each XPS laboratory may inadvertently introduce surface artifacts to varying degrees, caused by, for example, overlayer contamination, exposure to air etc. The preparation and storage history of the catalyst probably have the greatest effect on its activity. Specifically, the temperature and time of calcining as well as the impregnation sequence of molybdenum and cobalt have been found to drastically affect the resulting surface chemistry of the catalyst (10,13,20,23). Even slight variations in the preparation procedures are readily observable by XPS which is extremely sensitive to structural changes in the outmost few layers of a solid.

In this study an HDS catalyst was exposed to thiophene vapour (C_4H_4S) within a specially designed XPS reaction chamber. The catalyst's activity was tested in both the fresh (oxidic) and active (sulphided) form.. After thiophene exposure the catalyst was examined directly by XPS in-situ without breaking vacuum. Thus surface chemistry alterations, caused by exposure to the atmosphere, ie. oxidation, or contamination, were eliminated here. The activity of the HDS catalyst when exposed to thiophene was also monitored indirectly. The proportions of thiophene, hydrogen, hydrogen sulphide and C-4 hydrocarbons present in the product gases were measured using a gas chromatograph.

EXPERIMENTAL

The catalyst studied was a commerically available 3 wt. % CoO-15 wt. % MoO_3- γ-alumina extrudate (MB226) produced by impregnation. It was crushed and examined by XPS in pellet form. A Physical Electronics (PHI) model 548 x-ray photoelectron spectrometer with computer control was used in this study. The spectrometer is equiped with a Mg anode providing Mg K_α x-ray radiation (1253.6 eV) at 400 watts. All XPS peak positions reported here are accurate to ± 0.2 eV and are referenced to the hydrocarbon (C 1S) peak taken as 284.6 eV. This hydrocarbon component is deposited from either the XPS vacuum system (ie. pump oil) or from prior handling in air and is normally a layer approximately a monolayer thick. Gold is used to calibrate the binding energy (E_b) scale of the spectrometer (Au $4f_{7/2} = 83.8$ eV). The base pressure in the analytical chamber is $\simeq 2 \times 10^{-10}$ torr (ultra-high vacuum). Catalysts were usually analyzed at a pressure of $\simeq 10^{-8}$ torr. In this study all elemental (E_b) peak positions were cross checked using the aluminum and oxygen present in the γ-alumina support. The Al 2p and O1s peak positions are 74.0eV and 531.6eV respectivly. To eliminate sample charging responsible for XPS peak line broadening and the shift of element peak to higher binding energy, a charge neutralizer system (electron flood gun) was used. From observing the C 1S peak, it was found that this catalyst charged $\simeq 3.$eV. The C 1S peak position was then fine-tuned to occur at 284.6eV using the neutralizer. As a second precaution, the full width at half maximum (FWHM) and position of the Al 2p peak were closely monitored with and without the use of the

neutralizer for all specimens examined. The FWHM (2.7eV) and position (74.0eV) of Al 2_p did not vary during the study.

The XPS spectrometer is equipped with a custom designed micro-reaction chamber and gas handling system. The reactor is flange mounted to the analytical XPS chamber but isolated by means of a UHV gate valve. Transfer of a sample between chambers is done using a transport probe. The probe tip and sample can be heated up to 600°C and exposed to a gas, gas mixture and/or organic vapour in the micro-reactor under varying experimental conditions. The catalyst can therefore be reduced, sulphided, reacted in thiophene vapour or dry nitrogen purged in-situ sequentially or in various combinations. After exposure, the catalyst was inserted into the analytical chamber for XPS analysis. The gas handling system can be used in three operating modes as indicated in figure 1. A mixture of either 10% H_2S/H_2 or $\simeq 1.\%$ C_4H_4S/H_2 was introduced into the reactor at a flow rate of 50 ml. min^{-1}. Flow path A and B (Figure 1) were used to load and then inject a 100 ml. sample loop of hydrogen gas saturated with thiophene vapour. Flow path C was used to backfill the reactor with hydrogen gas to 5 psig or used to flush gases from the reactor and purge dry nitrogen over the sample. Hydrogen gas bubbled through thiophene (18°C) at 50 ml. min^{-1} produced an $\simeq 1.\%$ C_4H_4S/H_2 mixture as measured by gas chromatrography.

DISCUSSION

The results of exposing the oxidic and sulphided forms of this HDS catalyst with thiophene vapour/H_2 are shown in Tables 1,2. Note the experimentally determined XPS surface chemical composition of our catalyst agreed quite well with bulk theory (Table 2).

A.   Oxidic form.

No chemical conversion of thiophene occured in the presence of the oxidic catalyst (Table 1). Direct XPS analysis of the oxidic catalyst surface also revealed little or no changes in the element concentrations or in the amount of each compound present. Although the catalyst physically changed colour (bluish→black), no reduction in XPS peak intensities were observed. If the colour change was due to formation of a carbonaceous layer (coke) it must be very thin (ie. $\leq$ 100 A°); otherwise the peak intensities for the underlying species would quickly diminish. Other studies have also indicated the lack of activity of the catalyst in its fresh (oxidic) state (8,19).

B.   Sulphided form.

After sulphiding, the catalyst was active in promoting conversion of thiophene to C-4 hydrocarbons. The gas chromatrography analysis indicates the n-butane content of the product gases increased while the butene fractions decreased with longer reaction time (Table 1). It was found that a 10% H_2S/H_2 mixture, flowing at 50 ml. min^{-1} for greater than 30 minutes over the catalyst heated to 300°C or higher, resulted in nearly half of the molybdenum oxide initially present (MoVI, MoO_3) to be converted to molybdenum sulphide (MoIV, MoS_2) (Table 2, Figure 2).

Longer reaction times and higher temperatures did not increase this conversion ratio. Under indentical conditions, a pure MoO_3 pellet was nearly totally converted to MoS_2 (MoIV). Little or no chemical changes occurred at the catalyst surface after the initial sulphiding step. However, the gas chromatrographic analysis (Table 1) indicated clearly that thiophene is converted after sulphiding. Thus the sulphided catalyst is promoting the conversion but is not chemically altered itself by the exposure to thiophene.

The atom ratio of the total sulphur (S_T) to total molybdenum (Mo_T) present on the sulphided plus thiophene exposed catalyst surface is 2.1 (Table 2). This (S_T/Mo_T) ratio is theoretically close to that of MoS_2. However a closer examination

of the Mo 3d spectra (Figure 2) indicate only $\simeq 40\%$ of the molybdenum is sited as MoIV (ie. MoS$_2$), while $\simeq 80\%$ of the sulphur is sited as S(II). Thus the corrected SII/MoIV atom ratio is $\simeq 3.6$. Two explainations are possible: 1) the observed ratio may indicate a non-stoicheometric surface molybdenum sulphide (MoS$_3$) but the Mo 3d and S 2p peak positions indicate the presence of MoS$_2$ and not MoS$_3$. 2) excess sulphide is actually sited at the surface bonded to cobalt as CoS or Co$_9$S$_8$. Unfortunately direct XPS evidence is not available to support this hypothesis. If one assumes all cobalt initially present (0.7 At.%) is sulphided, the sulphide sulphur remaining available to bond to molybdenum yields a S(II)/Mo(IV) atom ratio of 2.2 (Table 2). Other studies have indicated MoS$_2$ and Co$_9$S$_8$ accompanied by excess elemental sulphur may exist on HDS catalysts when reacted in H$_2$S/H$_2$ (8,11,20). This calculated atom ratio which is in better agreement with theory (MoS$_2$), also collaborates the XPS (E$_b$) peak position data which indicate the presence of MoS$_2$.

The Mo 3d spectra (Figure 2) were computer curve fitted to 2 doublets labelled (A-A') and (B-B'). Peaks A - A' are assigned to MoVI (3d$_{5/2} \simeq 232.4$eV) indicative of either MoO$_3$ (octahedral MoVI) or Al$_2$(MoO$_4$)$_3$ (tetrahedral MoVI). XPS can not distinguish between these two species. Peaks B-B' are assigned to MoIV indicative of MoS$_2$ (3d$_{5/2} \simeq 228.7$eV). Peak D refers to the sulphur S 2s line which occurs at $\simeq 226$eV.
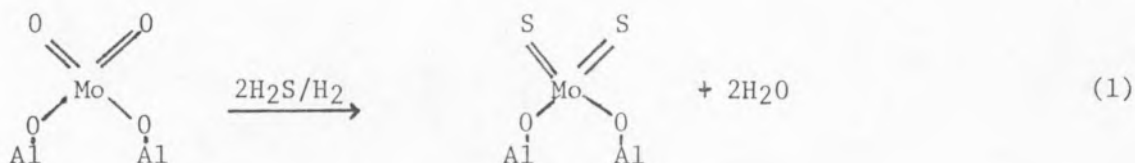
The S 2p spectra (Figure 2) have been fitted to 2 doublets labelled A-A' and B-B'. Peak A (S 2$_{p3/2} \simeq 161.7$eV) is assigned to sulphide sulphur (MoS$_2$). Peak B (S 2$_{p3/2} \simeq 163.8$eV) is assigned to elemental (amorphous) sulphur. The letters A,B and A', B' refer to S 2$_{p3/2}$ and 2$_{p1/2}$ peak doublets respectively. In another study with pure compounds, MoVI (MoO$_3$) was completely reduced to MoIV after 12 hours of reduction at 500°C in H$_2$ (10). It was also found that under those same conditions, Al$_2$(MoO$_4$)$_3$ (MoVI, tetrahedral) was only reduced to MoV. Our results with pure MoO$_3$ also showed that MoVI (MoO$_3$) was largely converted to MoIV (MoS$_2$), which is consistent with the above. Our results on the catalyst indicate that $\simeq 60\%$ of the MoVI present initially at the catalyst surface is not reduced or sulphided after reaction with 10% H$_2$S/H$_2$ or thiophene/H$_2$ at 300°C and 450°C. Based on the available information, it is suggested that this 60% unreacted MoVI present is tetrahedrially sited. Zingg et al. (10) found $\simeq 50\%$ of the original MoVI present in a MoO$_3$-Alumina catalyst was converted to MoIV with the remainder MoV. Our results indicate no intermediate MoV. The shape of the Mo 3d spectral envelope in both studies is quite similiar however; there is a large broad peak at $\simeq 232.5$eV and two reasonably well resolved shoulder peaks at $\simeq 235$eV and $\simeq 229$ eV. In our study, the MoVI 3d$_{3/2}$ peak (labelled A') in figure 2 at $\simeq 235.5$eV and the MoIV 3d$_{5/2}$ peak (labelled B) at $\simeq 228.7$eV are quite well defined. Thus the mid-portion of the 3d envelope is the major cause of uncertainty.

Using the well known 3d$_{3/2}$/3d$_{5/2}$ height intensity ratio (0.68) and the spin-orbit splitting (3.1 eV), this mid-region was curve fitted to 2 peaks (A,B' figure 2). If any MoV exists in these spectra, it is quite small. Note that the Mo 3d$_{5/2}$ peak position for MoVI and MoV are 232.4eV and 231.5eV respectively, Thus a small amount of either species is masked by a large amount of the other.

Our Mo 3d peak line widths (FWHM $\simeq 2.5$eV) were derived from the best Mo 3d doublet fit of the unreacted catalyst (Figure 2) and from the two peak shoulders (A', B'). The Al 2$_p$ peak position (74.0eV) and FWHM (2.7eV) were constant for the three samples shown in Figure 2.

The discrepancy between our results (ie. no MoV) and those of Zingg et al. (10) (ie. no MoVI) are not easily reconciled except that our catalyst contained 3 wt. % CoO which in some way may have stabilized the tetrahedral MoVI present. More importantly however, both studies indicate that $\simeq 45\%$ of the MoVI originally present on the alumina support is converted to MoIV. The remainder is assigned to higher oxidation state Mo(VI or V) which is probably bonded to the oxygen of alumina (tetrahedral sites). The existance of a surface MoO$_4^{2-}$ complex bonded to Al$_2$O$_3$ is

possible. Sulphiding can not readily break the Al-O-Mo bond resulting in a surface $MoO_2S_2^{2-}$ type complex as shown below (15,16).

$$\underset{\underset{Al}{\overset{|}{O}}\overset{O}{\underset{}{\backslash}}\overset{||}{Mo}\overset{O}{\overset{}{/}}\underset{\underset{Al}{\overset{|}{O}}}{}\qquad \xrightarrow{2H_2S/H_2}\qquad \underset{\underset{Al}{\overset{|}{O}}\overset{S}{\underset{}{\backslash}}\overset{||}{Mo}\overset{S}{\overset{}{/}}\underset{\underset{Al}{\overset{|}{O}}}{}\quad + 2H_2O \qquad\qquad (1)$$

The Mo 3d spectrum of pure $Al_2(MoO_2S_2)_3$ however has not been reported so this hypothesis can not presently be confirmed.

In this preliminary study, the elemental composition of the HDS catalyst was determined directly from the XPS spectra. The oxidation states of molybdenum and sulphur present on the surface were determined in-situ (without exposure to air) yielding a reasonable identification of the complexes present on the catalyst surface prior to and following exposure to H_2S/H_2 and C_4H_4S/H_2. The oxidic form of the catalyst was found to be inactive at 450°C but the sulphided state readily converted thiophene to C-4 hydrocarbons with the butane compound increasing at longer exposure times. This study also indicated that some elemental sulphur as well as MoS_2 exists at the sulphided catalyst surface after H_2S/H_2 exposure, however no additional increase in it was observed after the C_4H_4S/H_2 exposure.

The elemental sulphur in the catalyst, reported in this study, is experimental proof that additional sulphur can be added to the catalyst. Wise and co-workers (25,26) have used this concept to explain their reaction results. Non-stoicheometric sulphur has also been hypothesized to interpret coke formation on catalysts (27). The results reported here do not indicate whether, the additional elemental sulphur exists as adsorbed hydrogen sulphide (28) or as sulphur which is incorporated into the solid.

The fact that not all of the molybdenum in the catalyst was converted from MoVI to MoIV during either sulphiding or reaction, suggests that there are at least two types of molybdenum species present. One type would be MoS_2 crystallites and the other molybdenum species which is bonded to the alumina, for example, in accordance with Equation 1. Both crystallite (29) and epitaxial monolayer (30,31) structures have been suggested previously. The presence of both structures is consistent with the work of Pollack, Makovsky and Brown (32) who reported two dimensional (monolayer) MoS_2 after sulphiding at atmospheric pressure and three dimensional crystallites after the catalyst had been exposed to sulphur species at high pressures.

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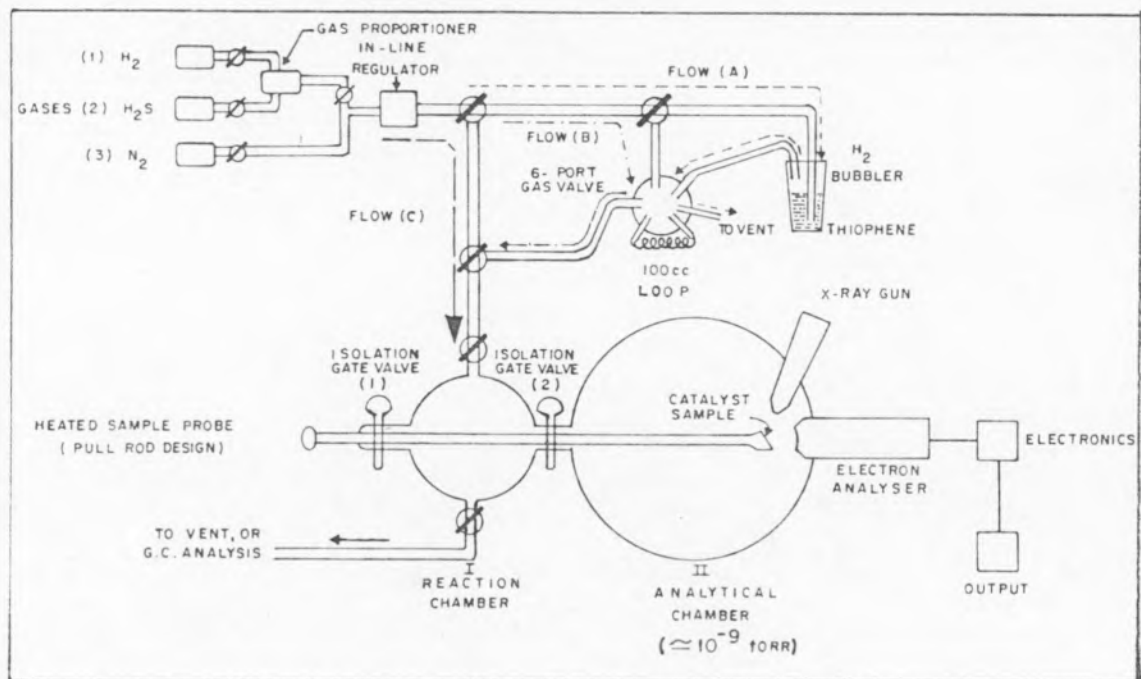
Figure 1

Schematic of the experimental configeration used for the direct surface
examination of reacted catalyst samples (MB226) by XPS. Flow (A)
(-----) is used to load the 100 ml loop with hydrogen gas saturated
with thiophene. Flow B (-·-·-·-) is used to flush the loaded loop
of thiophene/H$_2$ into the reactor. Flow C (——-) is used to pass
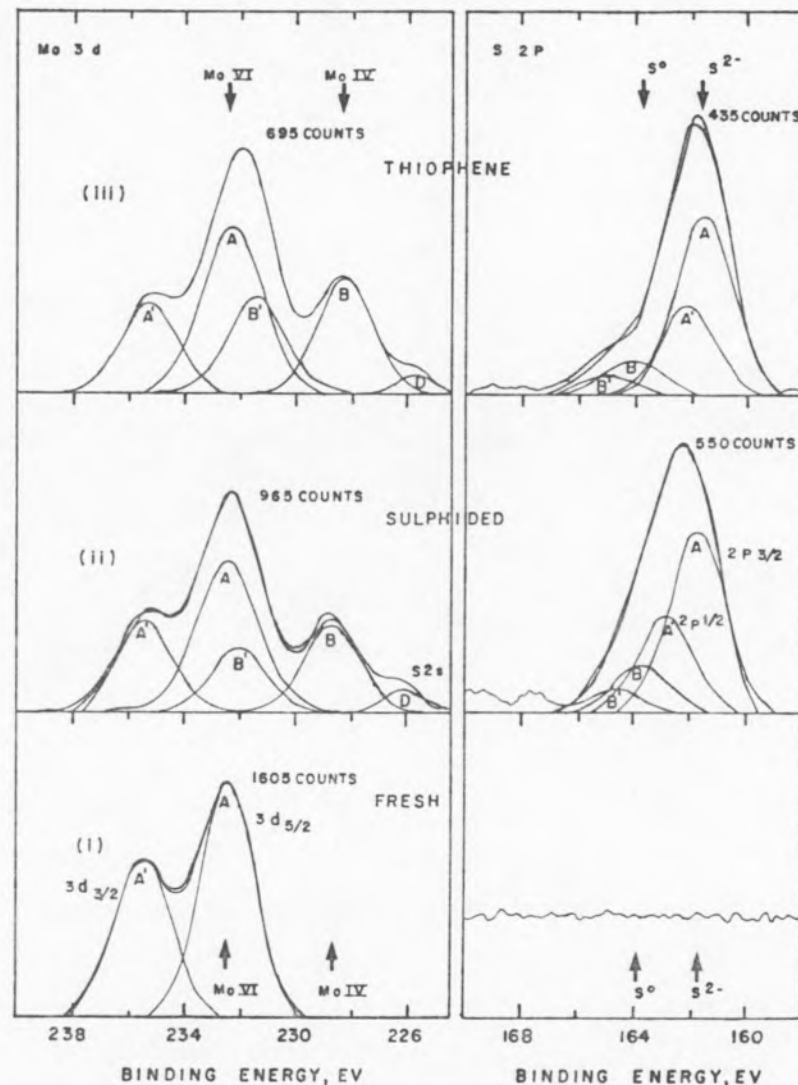H$_2$,H$_2$S/H$_2$ or N$_2$ directly into the reactor.

Figure 2

XPS spectra of Mo 3d and S 2$_p$ for (i) the fresh HDS catalyst (MB226) of composition
3 wt.% CoO-15 wt.% MoO$_3$-γ alumina (ii) fresh catalyst sulphided in flowing 10%H$_2$S/H$_2$
for 2 hours at 300°C (iii) sulphided catalyst exposed to thiophene/H$_2$ for 2 hours
at 450°C.

TABLE 1. Gas Chromatrography findings after Exposing MB226 Catalyst (Oxidic and Sulphided State) with Thiophene Vapour. (a)

Product Gas Composition (Vol %)	Oxidic State (b) Probe Temperature (°C)			Sulphided State (c) Reaction Time (hr.)	
	25	300	450	0.5	2.0
H_2	97.7	99.1	99.3	99.00	99.10
C_4H_4S	2.3	0.9	0.7	0.40	0.20
H_2S	-	-	-	0.20	0.19
C-4 Compounds					
n-butane	-	-	-	0.10(25)	0.17(33.3)
1-butene	-	-	-	0.05(12.5)	0.06(11.8)
trans 2-butene	-	-	-	0.15(37.5)	0.17(33.3)
cis 2-butene	-	-	-	0.10(25)	0.11(21.6)

(a) fresh catalyst reacted in 10% H_2S - in - H_2 changed colour from bluish-purple to grey black. Colour change also occured in presence of C_4H_4S/H_2.

(b) 100 ml loop of thiophene saturated hydrogen pulsed into XPS micro-reactor, pure hydrogen then added to attain a reactor pressure of 5 psig. Reaction time is 2 hours at the 3 temperatures indicated.

(c) fresh catalyst sulphided in the XPS micro-reactor using a 10% H_2S - in - H_2 gas mixture at a flow rate of 50 ml/minute for 2 hours and a probe temperature of 300°C. Thiophene vapour then introduced as per step (b) above while holding the probe temperature at 450°C for the two times shown. Values in brackets refer to C-4 compounds normalized to 100%.

TABLE 2. XPS Surface Analysis Results of Catalyst MB226 Reacted in C_4H_4S/H_2 (a)

XPS Surface Composition At % (±10%) Element	Species	Nominal Bulk Composition At% (±5%)	Oxidic State Unreacted	Reacted in C_4H_4S/H_2 (b) (2 hours) 25°C	300°C	450°C	Sulphided State Unreacted	Sulphided in H_2S/H_2 (c) 300°C 1.0 hr (e)	2.0 hr. (e)	Reacted in C_4H_4S/H_2 (b.d) 450°C 0.5 hr. (f)	2.0 hr. (f)
O	O^{2-} (Al_2O_3, MoO_3, CoO)	61.0	56.3	50.4	52.8	52.9	52.7	50.6	51.5	51.8	52.7
Al	Al^{3+} (Al_2O_3)	35.8	30.8	28.1	29.2	28.8	29.5	29.6	29.0	31.4	30.1
Mo	VI (MoO_3)	2.3	1.8	1.7	1.6	1.6	1.9	0.7 ⎫1.3	0.7 ⎫1.2	0.5 ⎫1.0	0.5 ⎫1.0
	IV (MoS_2)	-	-	-	-	-	-	0.6 ⎭	0.5 ⎭	0.5 ⎭	0.5 ⎭
S	$S°$ (S_8)	-	-	-	-	-	-	0.5 ⎫2.5	0.5 ⎫2.5	0.4 ⎫2.1	0.4 ⎫2.2
	S^{2-} (MoS_2)	-	-	-	-	-	-	2.0 ⎭	2.0 ⎭	1.7 ⎭	1.8 ⎭
Co	Co^{2+} (CoO)	0.9	0.8	0.8	0.6	0.8	0.7	-	-	-	-
C	$(CH_2)n$	—	10.3	19.0	15.8	15.9	14.9	15.3	15.1	13.7	14.0
$S^{2-}/Mo IV$ (g)			0	0	0	0	0	3.3(2.2)	4.0(2.6)	3.4(2.0)	3.6(2.2)

(a) As per table 1
(b) As per table 1: Note Mo is present as the VI species, no reaction occured between the oxidic catalyst and C_4H_4S/H_2.
(c) As per table 1: Reaction in H_2S/H_2 caused ≈ 45% conversion of Mo VI to Mo IV (ie. $MoO_3 \rightarrow MoS_2$) See figure 2.
(d) 2 hour sulphided sample used in this step.
(e) Mo3d spectrum (Figure 2ii) indicates ≈ 45% conversion of Mo VI → Mo IV; the S_{2p} spectrum indicates ≈80% sulphur present as sulphide (S^{2-}).
(f) Mo3d spectrum (Figure 2iii) indicates = 50% conversion of Mo VI → Mo IV; the S_{2p} spectrum indicates no change (ie = 80% sulphide (S^{2-})).
(g) Atomic ratio of sulphide sulphur to molybdenum IV; value in brackets assumes the Co present (0.7 At %) has been completely sulphided to Co_9S_8.