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IN-SITU X-RAY PHOTOELECTRON SPECTROSCOPIC EXAMINATION OF A Co-Mo-ALUMINA HYDROTREATING CATALYST

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ABSTRACT

This study was performed in an attempt to examine a sulphided catalyst in its working state. The reactor containing the catalyst was bolted to the X-ray photoelectron spectrometer (XPS), but separated by an ultra-high vacuum gate valve. The catalyst was mounted on a heatable transfer rod. Reaction studies with thiophene were performed at atmospheric pressure and products from the reactor analyzed by gas chromatography. When the reaction study was complete, the catalyst was transferred to the XPS chamber for surface examination. This transfer permits the catalyst reactivity to be compared to its composition without exposing it to the atmosphere. Our findings indicate that under reaction conditions, the catalyst in its working state (sulphided) contains non-stoichiometric elemental sulphur in addition to stoichiometric sulphide anions. Approximately half the surface molybdenum cations are fully sulphided (MoS_2). The remainder is sited as an oxide associated with the alumina [i.e. $Al_2(MoO_4)_3$] or possibly an oxysulphide [$Al_2(MoO_2S_2)_3$]. A separate study in which pure MoO_3 (Mo-octahedral) was sulphided yielded nearly total conversion to MoS_2. The composition of the sulphided catalyst after reaction with thiophene vapour for periods up to 2 hours is much the same as after sulphiding alone, indicating the sulphiding process transforms the catalyst into its working state.

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INTRODUCTION

Fundamental catalytic studies often attempt to relate the reactivity of a catalyst to its structure and composition. One of the difficulties is that the catalyst composition before and after reaction may be different than its composition during reaction. For example, Mossbauer studies by Maksimov et al. (1975) have indicated that iron in a catalyst is transformed from Fe(III) to Fe(II) when oxidation reactions occur, but is restored to Fe(III) when they cease. The present work was performed in an attempt to examine a sulphided catalyst in its working state. X-ray photoelectron spectroscopy (XPS) is highly surface sensitive, direct and non-destructive and has been used extensively to characterize the surface of hydroprocessing catalysts. The outermost 1 → 5 nm region of a sample can be probed qualitatively to semi-quantitatively for all elements except hydrogen. Usually it is possible to confirm the chemical environment (oxidation state) of a surface sited element. Reviews of the theoretical aspects of, and instrumentation required for, XPS have been published by Carlson (1975), Delgass et al. (1970), Hercules and Hercules (1974) and Siegbahn (1982).

The recent publications of Apecetche et al. (1981), Breysse et al. (1981), Jepsen and Rase (1981) and Zingg et al. (1980) provide an excellent summary of the contributions of XPS to catalytic research and development. Catalysts used in hydroprocessing, for example hydrodesulphurization (HDS), are generally molybdenum supported on alumina with cobalt or nickel added (promoters) to improve performance. It has been found that for maximum activity, this type of catalyst must be sulphided. Jepsen and Rase (1981) reported the presulphiding requirement plays a dominant role in creating the essential surface changes required for optimum activity.

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 (i.e. $MoO_3 \rightarrow MoS_2$, $CoO \rightarrow Co_9S_8$, etc.) are thus possible. Much of the published XPS work on the HDS catalyst, however, has been controversial. The XPS findings of several researchers have varied significantly although catalysts of the same bulk composition and similar 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 vary 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 overlayer contamination, exposure to air, etc. The preparation and storage history of the catalyst probably have the greatest effect on its activity. Specifically, the findings of Zingg et al. (1980) and Jagannathan et al. (1981) clearly indicate that temperature and time of calcining as well as the impregnation sequence of molybdenum and cobalt drastically affect the resulting surface chemistry of the catalyst. Similar results have also been reported by Apecetche et al. (1981) and Okamato et al. (1979). 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 reactor is bolted directly to the analytical chamber of the spectrometer. The two chambers can be isolated using an ultra-high vacuum (UHV) gate valve when required. Manipulation of the catalyst between chambers is done using a heatable transfer rod. The catalyst's activity was examined in both the fresh (oxidic) and sulphided state. Reaction studies with thiophene were performed and products from the reactor analyzed by gas chromatography. The catalyst surface was then directly probed by XPS, eliminating the risk of atmospheric exposure and catalyst alteration.

EXPERIMENTAL

The catalyst studied was a commercially available 3 wt. % CoO-15 wt. % MoO_3-γ-alumina extrudate (HT-400) manufactured by Harshaw. It was crushed and examined by XPS in disc form. Analytical grade MoO_3 and MoS_2 powders (in disk form) were also examined and acted as internal standards. The discs were prepared using an IR type die and press. Each disc was dried at 105°C overnight prior to introduction into the XPS chambers. A Physical Electronics (PHI) model 548 x-ray photoelectron spectrometer with computer control was used in this study. The spectrometer was equipped with an Mg anode providing Mg K_α x-ray radiation (1253.6 eV) at 400 watts. Overlapping spectral peaks were "best fitted" using an iterative non-linear least square computer program available from PHI. All XPS peak positions reported 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 (i.e. pump oil) or from prior handling in air, and is normally only a few atomic layers thick. Gold is used to calibrate the binding energy (E_b) scale of the spectrometer ($Au4f_{7/2}$ = 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 O 1s peak positions are 74.0 eV and 531.6 eV respectively. To eliminate sample charging responsible for the XPS peak line broadening and the shift of element peaks 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 ≈2.0 eV. The C 1s peak position was set at 284.6 eV using the neutralizer control. 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 (2.7 eV) and position (74.0 eV) of Al 2p did not vary during the study. In the case of MoO_3, the O 1s line (530.6 eV) was used as a cross-check on the C 1s line to determine if the neutralizer was working effectively. The elemental composition of each sample was determined using XPS elemental sensitivity factors and the experimental peak area intensities recorded for each element present in the sample. Atomic sensitivity factors used were calculated according to theoretical photoelectron cross sections, the kinetic energy dependence of the PHI cylindrical mirror analyzer (CMA) and an average value for the dependence of the electron escape depth on kinetic energy. A discussion of factors affecting quantitative XPS determinations is available in the reviews by Powell and Larson (1978), Wagner (1977) and Wagner et al. (1979).

The XPS spectrometer is equipped with a micro-reaction chamber and gas handling system. The reactor is flange mounted on the analytical XPS chamber, but isolated by means of 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 is 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 ≈1.0% C_4H_4S/H_2 was introduced into the reactor at a flow rate of 50 ml min^{-1}. Flow paths A and B (Figure 1) are used to load and then inject a 100 ml sample loop of hydrogen gas saturated with thiophene vapour. Flow path C is 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 a ≈1.0% C_4H_4/H_2 mixture as measured by gas chromatography.

DISCUSSION

(I) Catalyst Study

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 occurred 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 component 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 (i.e. $\leq$ 100 Å); otherwise the peak intensities for the underlying species would quickly diminish. Our results are in agreement with those of Jepsen and Rase (1981) and Okamoto (1980) who also found the oxide form of Co, Mo-alumina catalysts of similar compositions were inactive.

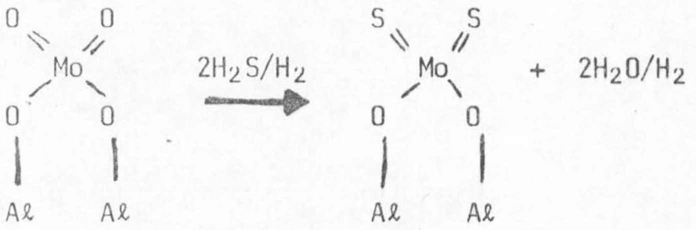
(b) Sulphided form

After sulphiding, the catalyst was active in promoting conversion of thiophene to C-4 hydrocarbons. The gas chromatographic analysis indicated 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 longer than 30 minutes over the catalyst heated to 300°C or higher, resulted in nearly half of the molybdenum oxide initially present [Mo(VI), MoO_3] to be converted to molybdenum sulphide [Mo(IV), MoS_2] (Table 2, Figure 2). Longer reaction times and higher temperatures did not increase this conversion ratio. Under identical conditions, a pure MoO_3 pellet was nearly totally converted to MoS_2, [Mo(IV)] (see part II). Little or no chemical changes occurred at the catalyst surface after the initial sulphiding step. However, the gas chromatographic 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 (2.1) is theoretically similar to that of pure MoS_2 (2.0). However, a closer examination of the Mo 3d spectra (Figure 2) indicates only ≈40% of the molybdenum is sited as Mo(IV) (i.e. MoS_2), while ≈80% of the sulphur is sited as S(II). Thus, the corrected S(II)/Mo(IV) atom ratio is ≈3.6. Two explanations are possible: 1) this observed ratio may indicate the presence of a non-stoichiometric surface molybdenum sulphide (MoS_3); however, the Mo 3d and S 2p peak positions favour MoS_2, not MoS_3 (Stevens and Edmonds, 1975); 2) excess sulphide is actually sited at the surface bonded to cobalt as CoS or Co_9S_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) atomic ratio of 2.2 (Table 2). Other studies by Declerck-Grimee et al. (1978), Jepsen and Rase (1981) and Okamoto et al. (1979) have indicated MoS_2 and Co_9S_8 accompanied by excess elemental sulphur may exist on HDS catalysts when exposed to H_2S/H_2. This calculated atomic ratio, which is in better agreement with theory (MoS_2), also corroborates 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 peak doublets labelled (A-A') and (B-B'). Peaks A-A' are assigned to Mo(VI) ($3d_{5/2}$ ≈ 232.4 eV) indicative of either MoO_3 [octahedral, Mo(VI)] or $Al_2(MoO_4)_3$ [tetrahedral, Mo(VI)]. XPS cannot distinguish between these two species. Peaks B-B' are assigned to Mo(IV) indicative of MoS_2 ($3d_{5/2}$ ≈ 228.7 eV). Peak D refers to the sulphur 2s line which occurs at ≈ 226 eV. The S 2p spectra (Figure 2) have been fitted to 2 doublets labelled A-A' and B-B'. Peak A (S $2p_{3/2}$ ≈ 161.7 eV) is assigned to sulphide sulphur (MoS_2). Peak B (S $2p_{3/2}$ ≈ 163.8 eV) is assigned to elemental (amorphous) sulphur. The letters A, B and A', B' refer to S $2p_{3/2}$ and $2p_{1/2}$ peak doublets respectively. In another study with pure compounds, Zingg et al. (1980) found MoO_3 Mo(VI) was completely reduced to Mo(IV) after 12 hours of reduction at 500°C in H_2. It was also found that under those same conditions, $Al_2(MoO_4)_3$ [tetrahedral, Mo(VI)] was only reduced to Mo(V). Our results on the catalyst indicate that ≈60% of the Mo(VI) present initially at the catalyst surface is not reduced or sulphided after reaction with 10% H_2S/H_2 or thiophene/H_2 at 300°C and 450°C. Based on the available information, it is suggested that this 60% unreacted Mo(VI) present is tetrahedrally sited. Zingg et al. (1980) found ≈50% of the original Mo(VI) present in a MoO_3-Alumina catalyst was converted to Mo(IV) with the remainder Mo(V). Our results indicate no intermediate Mo(V). The shape of the Mo 3d spectral envelope in both studies is quite similar, however. There is a large broad peak at ≈232.5 eV and two reasonably well resolved shoulder peaks at ≈235 eV and ≈229 eV. In our study, the Mo(VI) $3d_{3/2}$ peak (labelled A') in Figure 2 at ≈235 eV and the Mo(IV) $3d_{5/2}$ peak (labelled B) at ≈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' in Figure 2). If any Mo(V) exists in these spectra, it is quite small. Note that the Mo $3d_{5/2}$ peak position for Mo(VI) and Mo(V) are 232.4 eV and 231.5 eV respectively. Thus, a small amount of either species is masked by a large amount of the other. Our Mo 3d peak line-widths (FWHM ≈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 2p peak position (74.0 eV) and FWHM (2.7 eV) were constant for the three samples shown in Figure 2. The discrepancy between our results (i.e. no Mo(V) and those of Zingg et al. (1980) [i.e. no Mo(VI)] are not easily reconciled except that our catalyst contained 3 wt % CoO which in some way may have stabilized the tetrahedral Mo(VI) present. More importantly, however, both studies indicate that ≈45% of the Mo(VI) originally present on the alumina support is converted to Mo(IV). The remainder is assigned to higher oxidation state Mo (VI or V) which is probably bonded to the oxygen of alumina (tetrahedral sites). The existence of a surface MoO_4^{2-} complex bonded to Al_2O_3 is possible. If sulphiding at atmospheric pressure does not readily break the Al-O-Mo bond the result will be surface $MoO_2S_2^{2-}$ type complex as shown in equation 1. The existence of an oxysulphide Mo(VI) species has also been postulated to explain the findings of Brinen and Armstrong (1978) and Mitchell and Trifiro (1974). The Mo 3d spectrum of pure $Al_2(MoO_2S_2)_3$, however, has not been reported, so this hypothesis cannot presently be confirmed.



1)

Very recent experiments in our laboratory suggest that high pressure sulphiding causes a much higher proportion of the molybdenum cations to be bonded to sulphide anions rather than to oxygen anions.

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.

II. Molybdenum Oxide Study

MoO_3. was examined by XPS prior to and following exposure to 10% H_2S/H_2 at 300°C and 450°C. Changes in its surface composition are shown in Table 3. The unreacted MoO_3 examination indicates an oxygen/molybdenum atomic ratio of 2.9. Following two hours of exposure to the H_2S/H_2 mixture at 450°C, the surface chemistry has been greatly altered (Figure 3). The intensity and positions of the Mo 3d and S 2p spectra indicate the formation of MoS_2. For example, the S(II)/Mo(IV) atomic ratio is 2.05. Thus, sulphiding for two hours at 450°C converted ≈90% of the oxidic Mo(VI) (octahedral) to sulphidic Mo(IV); the remainder being unreacted oxidic Mo(VI) and Mo(V). The three Mo 3d doublets (AA', BB', CC') have been assigned to Mo(VI), Mo(IV) and Mo(V) respectively based on the Mo $3d_{5/2}$ peak positions (A,B,C) of 232.4 eV, 228.7 eV and 231.5 eV. The two S 2p doublets present (AA', BB') have been assigned to S(II) and elemental S(0) based on the S $2p_{3/2}$ peak positions (A,B) of 162.0 eV and 163.8 eV. The FWHM of the Mo and S peaks were determined to be 2.5 and 2.3 eV except for the fresh MoO_3 sample, where the "best" fit indicated a Mo 3d peak line width of 1.9 eV. These spectra were fitted using information from previously recorded pure MoO_3 and MoS_2 and the fact the largest Mo 3d doublet (BB') is well resolved yielding a line-width of 2.5 eV (Figure 3iii). Therefore, the two less-well defined doublets (AA', CC') were also fitted using this same value.

Interestingly, an intermediate stage of reduction/sulphiding was monitored at 300°C (Figure 3ii). Information from the S 2p spectrum indicated approximately one-third of the total surface sited sulphur (i.e. ≈9 At.%) exists as sulphide anions. The Mo 3d spectrum indicated the presence of ≈17 At.% molybdenum; however, only ≈4 At.% was sited as the sulphide [Mo(IV)]. This quantitative data yield a S(II)/Mo(IV) atomic ratio of 2.25 (MoS_2). Thus, the "fitted" peak positions and intensities of the Mo 3d and S 2p spectra (Figure 3) confirm that ≈67% of the total sulphur and ≈80% of the molybdenum surface sited on the MoO_3 pellet is present as elemental sulphur S(0) and molybdenum oxides (VI, V) after reaction in H_2S/H_2 at 300°C. The XPS results further indicate that sulphiding reduces some oxidic Mo(VI) to Mo(V) and Mo(IV); however, it is uncertain if some MoO_2 is formed as the XPS peak position of MoO_2 (Mo $3d_{5/2}$ = 229.2 eV) occurs close to the position of MoS_2 (Mo $3d_{5/2}$ = 228.7 eV). XPS evidence leads to the conclusion that a thick elemental sulphur layer coats the MoO_3 pellet during sulphiding at 300°C. Note, the surface molybdenum content decreased significantly from 26 At.% to 17 At.% after this reaction. Heating the pellet to 450°C again increased the observed molybdenum level to ≈25 At.% (Table 3). This piece of indirect evidence plus the direct information from the S 2p spectrum that ≈18 At.% S(0) exists, strongly indicate amorphous sulphur physically covers the pellet. This formation of elemental sulphur on MoO_3 as well as the proportionally increased water vapour (hydroxyl) levels generated during the reaction with H_2S/H_2 are being investigated using XPS and mass spectroscopy.

C. General Comments

One of the most interesting aspects of this catalyst study was the continued presence of substantial Mo(VI), probably as $Al_2(MoO_4)_3$, after sulphiding and after exposure to thiophene. Similar findings were reported in studies by Bancroft et al. (1979) and Zingg et al. (1980). However, in the present work the catalyst sample was sulphided, reacted and examined by XPS in-situ. No transfer of the catalyst from reacting equipment to the spectrometer was necessary. Therefore, there was no possibility of the catalyst being re-oxidized by even slight air exposure. The catalyst XPS molybdenum spectra show Mo(VI) (presumably $Al_2(MoO_4)_3$ is present after sulphiding and after thiophene reactions of 0.5 and 2.0 hours (Figure 2). Pollack et al. (1979) have reported X-ray diffractograms for used catalysts in which molybdenum oxides were identified at 2 θ values of 26 and 53.6. Their results support our findings that molybdenum oxides are likely present in the working state of the catalyst during reaction. The fact that not all of the molybdenum in the catalyst was converted from Mo(VI) to Mo(IV) during either sulphiding or reaction, suggests that there are at least two types of molybdenum species present. One type would be MoS_2 crystallites, formed during sulphiding in the same way that octahedral Mo(VI) in the pure MoO_3 powder was sulphided. The other molybdenum species is bonded to the alumina, possibly as a monolayer, in accordance with equation 1. The molybdenum in this structure may be similar to the tetrahedral molybdenum in $Al_2(MoO_4)_3$. The presence of bulk $Al_2(MoO_4)_3$ in the Mo-alumina catalyst has been suggested by the Raman studies of Medema et al.(1978). Furthermore, it has been reported by deBeer and Schuit (1976) and Zingg et al. (1980) that $Al_2(MoO_4)_3$ is difficult to reduce. It may be that the first type of molybdenum is octahedral Mo(VI) which is sulphided to form either two or three dimensional MoS_2 crystallites. The second type, molybdenum not sulphided, may be bonded to the alumina (either monolayer or as a bulk compound) in a structure related to $Al_2(MoO_4)_3$. Any molybdenum in the interior of a bulk aluminum oxide may be inaccessible to H_2S and impossible to sulphide. Both crystallite (deBeer and Schuit, 1976) and epitaxial monolayer structures (Frensen et al., 1979 and Massoth, 1977) have been suggested previously. The presence of both structures is consistent with the work of Pollack et al. (1979) who reported two dimensional MoS_2 (monolayer) after sulphiding at atmospheric pressure and three dimensional crystallites after the catalyst had been exposed to sulphur species at high pressures.

The elemental sulphur on the catalyst, reported in this study, is experimental proof that additional sulphur can be added to the catalyst. Aoshima and Wise (1974) and Wentrcek and Wise (1976) have used this concept to explain their reaction results. Non-stoichiometric sulphur has also been hypothesized by Ternan (1983) to interpret coke formation on catalysts. The results reported here do not indicate whether the additional elemental sulphur exists as adsorbed hydrogen sulphide, as postulated by Massoth et al. (1979), or as sulphur which is incorporated into the solid. The vacuum conditions in the spectrometer would be expected to remove much of the adsorbed H_2S. Therefore, the working state of the catalyst may contain even more H_2S than indicated in Figure 2. The decrease in elemental sulphur after reaction may be related to there being a lower partial pressure of H_2S in the reaction mixture than in the sulphiding mixture. All of this data show that under reaction conditions the working state of the catalyst does contain non-stoichiometric elemental sulphur in addition to the stoichiometric sulphide anions. The pure MoO_3 powder sulphided differently from the catalyst. The powder was almost completely sulphided to MoS_2. Ahuja et al. (1970) found the alumina support disperses the metal sulphides and provides acidity. Richardson (1964) determined the support interacts with some catalytic species. If this were not true, MoS_2 formed from pure MoO_3 should have the same catalytic effect as the Mo(IV) species in the catalyst. However, the Mo(VI) species which interacts with the alumina is different than the MoS_2 from pure MoO_3 and is not expected to have the same catalytic effect.

The data at 450°C, Table 1, indicated the major reactions were cleavage of carbon-sulphur bonds and hydrogenation. As expected from the previous studies, the reaction sequence was the conversion of thiophene to butenes and butenes to butane. Conversion did not occur on the catalyst in its oxide form. Hydrogen is known to adsorb on sulphur species (Wright et al., 1980). The paucity of sulphur in the oxide catalyst may have been responsible for the paucity of reaction with the oxidic catalyst. We have not established the hydrogen adsorption characteristics of either the sulphide anions or the non-stoichiometric elemental sulphur.

The major findings may be summarized as follows. Under reaction conditions at atmospheric pressure, the catalyst in its working state contains non-stoichiometric elemental sulphur in addition to the stoichiometric sulphide anions. Only some of the molybdenum cations are fully sulphided. A substantial fraction of the molybdenum remains as an oxide associated with the alumina. The composition of the catalyst after reaction with thiophene for periods up to 2 hours is much the same as after sulphiding and before reaction. This would indicate that sulphiding transforms the catalyst into its working state.

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FIGURE CAPTIONS

Figure 1: Schematic of the experimental configuration used for the direct surface examination of a reacted catalyst sample 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_2S/H_2 or N_2 directly into the reactor.

Figure 2: XPS spectra of (A) Mo 3d and (B) S 2p for (i) the fresh HDS catalyst (HT400) of composition 3 wt. % CoO-15 wt. % MoO_3-γ alumina, (ii) fresh catalyst sulphided in flowing 10% H_2S/H_2 for 2 hours at 300°C, (iii) sulphided catalyst exposed to thiophene/H_2 for 2 hours at 450°C.

Figure 3: XPS spectra of (A) Mo 3d and (B) S 2p for (i) the fresh MoO_3, (ii) fresh MoO_3 sulphided in flowing 10% H_2S/H_2 for 2 hours at 300°C, (iii) sulphided MoO_3 (from step ii), sulphided in flowing 10% H_2S/H_2 for 2 hours at 450°C.

TABLE I. Gas Chromatrography findings after Exposing HT 400 Catalyst (Oxidic and Sulphided State) with Thiophene Vapour (a)

Product Gas Composition (Vol %)	HT 400 + C_4H_4S/H_2				
	Oxidic State (b)			Sulphided State (c)	
	Probe Temperature (°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 occurred 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 products normalized to 100%.

TABLE II. XPS Surface Analysis Results of Catalyst HT 400 Reacted in C_4H_4S/H_2 [a]

XPS Surface Composition At. % (±10%)		Nominal Bulk Composition At. % (±5%)	CATALYST HT 400								
			Oxidic State				Sulphided State				
			Unreacted	Reacted in C_4H_4S/H_2 [b] (2 hours)			Unreacted	Sulphided in H_2S/H_2 [c] 300°C		Reacted in C_4H_4S/H_2 [b.d] 450°C	
Element	Species			25°C	300°C	450°C		1.0 hr [e]	2.0 hr [e]	0.5 hr [f]	2.0 hr [f]
O	Alumina + Mo(VI) and Co(II) oxides	61.0	56.3	50.4	52.8	52.9	52.7	50.6	51.5	51.8	52.7
Al	Alumina	35.8	30.8	28.1	29.2	28.8	29.5	29.6	29.0	31.4	30.1
Mo	1. oxide (VI) 2. sulphide (IV)	2.3 –	1.8 –	1.7 –	1.6 –	1.6 –	1.9 –	0.7 0.6 } 1.3	0.7 0.5 } 1.2	0.5 0.5 } 1.0	0.5 0.5 } 1.0
S	1. elemental (0) 2. sulphide (II)	– –	– –	– –	– –	– –	– –	0.5 2.0 } 2.5	0.5 2.0 } 2.5	0.4 1.7 } 2.1	0.4 1.8 } 2.2
Co	oxide or aluminate (II)	0.9	0.8	0.8	0.6	0.8	0.7	–	–	–	–
C	hydrocarbons	–	10.3	19.0	15.8	15.9	14.9	15.3	15.1	13.7	14.0
S(II)/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 no reaction occurred 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) → Mo(IV) (i.e. MoO_3 → 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 S2p spectrum indicates ≈80% sulphur present as sulphide, S(II).

(f) Mo3d spectrum (Figure 2iii) indicates ≈50% conversion of Mo(VI → Mo(IV); the S2p spectrum indicates no change [i.e. ≈80% sulphide, S(II)].

(g) Atomic ratio of sulphur (II) to molybdenum (IV); value in brackets assumes the Co present (0.7 At %) has been completely sulphided to Co_9S_8.

TABLE III

XPS Surface Analysis Results for MoO_3 Sulphided in H_2S/H_2(a)

XPS Surface Composition(b) At.% (±10%)		MoO_3(c)					
		Fresh (Unreacted) 25°C		Sulphided			
Element	Species			300°C		450°C	
Mo	1. oxide (VI)	26.1	26.1	6.7	17.1	2.5	25.3
	2. oxide (V), (IV)	–		6.3		3.8	
	3. sulphide (IV)	–		4.1		19.0	
O (d)	1. MoO_3	66.5	73.9	44.8	56.0	14.0	22.4
	2. OH	7.4		11.2		8.4	
S	1. Elemental (0)	–	Nil	17.8	26.8	13.4	52.4
	2. Sulphide (II)	–		9.0		39.0	
Atomic Ratio (e)	O(II)/Mo(VI,V)	2.9(MoO_3)		4.2		3.5	
	S(II)/Mo(IV)	Nil		2.2		2.05(MoS_2)	

(a) see text and Figure 3.

(b) The percentages of each species present at the surface are shown; values have been determined from curve fitted spectral envelopes shown in Figure 3. Note compositions are on a carbon-free basis.

(c) Pure MoO_3 powder sulphided in-situ in the XPS micro-reactor system using 10% H_2S in H_2 mixture at a flow of 50 ml per minute for 2 hours at the temperature shown. Dry nitrogen was used to quench to room temperature prior to analysis.

(d) XPS measured two species of oxygen; the major component is bulk MoO_3 oxygen; the remainder is oxygen indicative of structurally bound water.

(e) The O/Mo atom ratio exceeds 3.0 for the sulphided pellet and may indicate the formation of water at the MoO_3 surface during the H_2S/H_2 reaction. Note the increased proportion of OH type oxygen present as the sulphiding process went to completion.

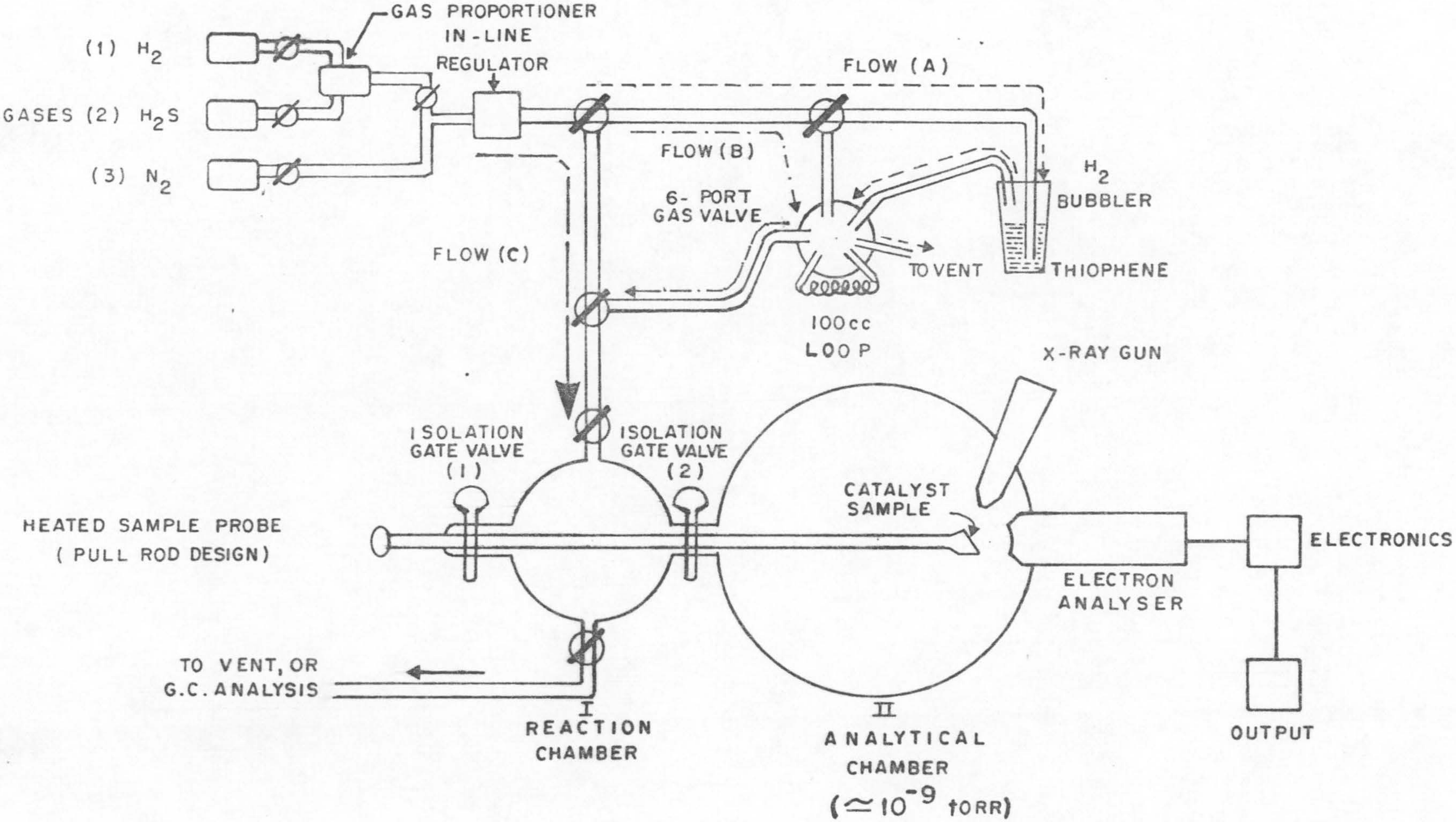

GAS PROPORTIONER
IN-LINE
REGULATOR
(1) H_2
GASES (2) H_2S
(3) N_2
FLOW (A)
FLOW (B)
6- PORT
GAS VALVE
H_2
BUBBLER
TO VENT
THIOPHENE
FLOW (C)
100cc
LOOP
X-RAY GUN
ISOLATION
GATE VALVE
(1)
ISOLATION
GATE VALVE
(2)
CATALYST
SAMPLE
HEATED SAMPLE PROBE
(PULL ROD DESIGN)
ELECTRONICS
ELECTRON
ANALYSER
TO VENT, OR
G.C. ANALYSIS
I
REACTION
CHAMBER
II
ANALYTICAL
CHAMBER
($\simeq 10^{-9}$ TORR)
OUTPUT

Figure 1

Figure 2

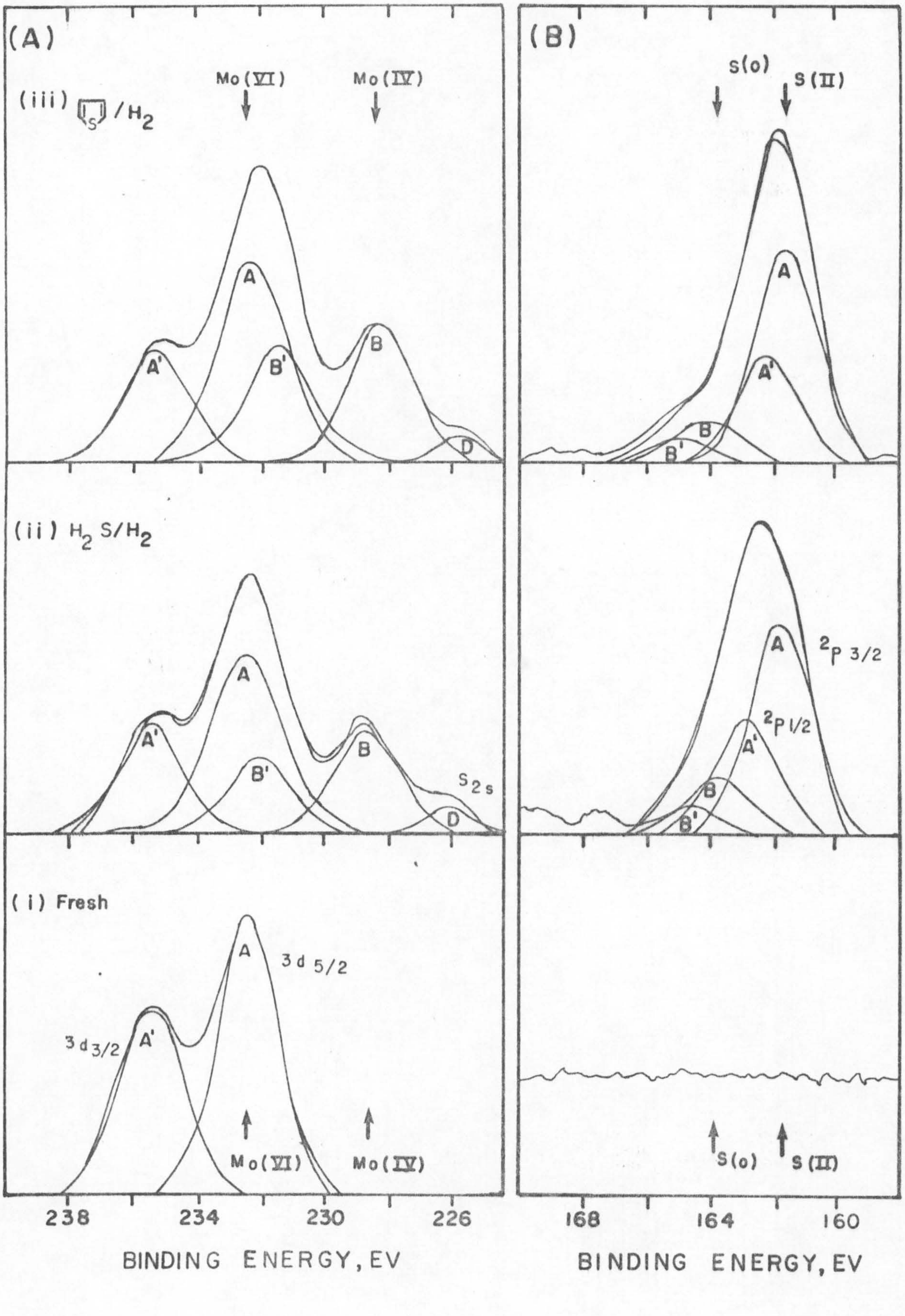
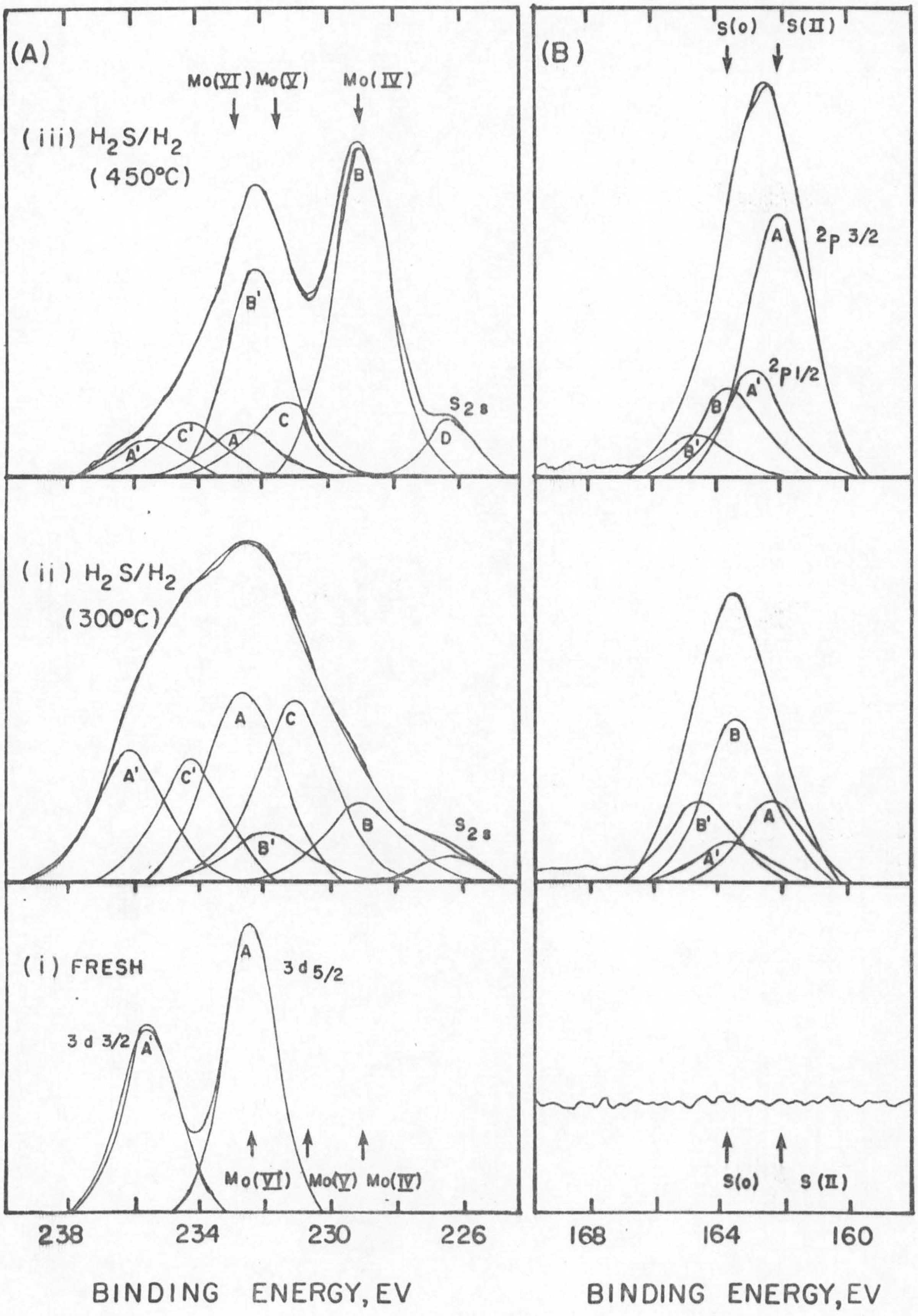

(A)
(iii) $\boxed{S}$/H_2
Mo(VI)
Mo(IV)
A
A'
B'
B
D
(ii) H_2S/H_2
A
A'
B'
B
S_{2s}
D
(i) Fresh
A
3d 5/2
3d 3/2
A'
Mo(VI)
Mo(IV)
238
234
230
226
BINDING ENERGY, EV
(B)
S(o)
S(II)
A
A'
B
B'
A
$^2P\ 3/2$
$^2P\ 1/2$
A'
B
B'
S(o)
S(II)
168
164
160
BINDING ENERGY, EV

Figure 3



(A)
Mo(VI) Mo(V) Mo(IV)
(iii) H_2S/H_2
(450°C)
B
B'
C
C'
A
A'
D
S_{2s}
(ii) H_2S/H_2
(300°C)
A
C
A'
C'
B'
B
S_{2s}
(i) FRESH
A
3d 5/2
3d 3/2
A'
Mo(VI) Mo(V) Mo(IV)
238
234
230
226
BINDING ENERGY, EV
(B)
S(o) S(II)
A
2p 3/2
2p 1/2
A'
B
B'
B
B'
A
A'
S(o) S(II)
168
164
160
BINDING ENERGY, EV