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A SEMI-QUANTITATIVE XPS STUDY OF MODEL Co/Mo-ALUMINA HYDROTREATING REFINERY CATALYSTS

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JULY 1986

For presentation at the 11th International Conference on X-ray Optics and Microanalysis, London, Canada, August 4-8, 1986 and for publication in proceedings

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 86-46 (OPJ)

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Removal of sulphur from fuel prior to use is presently carried out in oil refineries by catalytic hydrodesulphurization (HDS). HDS catalysts, usually Mo supported on alumina with Co or Ni added to improve performance, are among the most important of multifunctional industrial catalysts. However, basic research efforts concerning the nature of the catalyst's activity including the form in which cobalt and molybdenum exist has only recently received extensive attention. Pre-sulphiding plays a dominant role in creating the essential surface changes required for optimum HDS activity. Knowledge of the Mo and Co interaction with the alumina support is also required to explain catalyst activity.

Modern spectroscopic techniques have rapidly improved the fundamental understanding of the active structures and active sites at the HDS catalyst's surface.

A recent review summarized the progress to date in HDS catalysis basic research[1]. The active HDS structure is postulated as the "CoMoS" phase. The amount of cobalt in this phase was found to correlate with the HDS reaction rate constant[2]. The pronounced promotional effect of cobalt on HDS catalytic activity was recently explained using electronic concepts[3]; cobalt donates electrons to molybdenum sited as highly dispersed MoS_2 crystallites on the alumina. A scanning auger microscopy study of a cobalt doped MoS_2 single crystal indicates cobalt surface segregates to MoS_2 edge planes[4]. Thus, one can postulate that optimizing the active phase,

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"CoMoS", in the working catalyst requires the formation of highly dispersed MoS_2 crystallites on the alumina support with a large edge plane to basal plane ratio and with all cobalt sited at edge plane sites. The method of fabricating the precursor metal oxide HDS catalyst so this active "CoMoS" phase is preferentially created during the activation stage (sulphiding) is the key to improvements in HDS catalytic behaviour. To achieve this goal requires measuring the structures and content of Co and Mo present in the calcined oxide state and in the pre-conditioned working state of the catalyst. X-ray photoelectron spectroscopy has been used extensively to study the surface chemistry of HDS catalysts prior to and following refinery use[5-9]. X-ray photoelectron spectroscopy (XPS) can directly probe, and chemically characterize the outermost 5-10 atomic layers of most solids, offering a rapid, qualitative analysis of all elements except hydrogen and helium. Semi-quantitative analysis is possible, with an ultimate sensitivity approaching 0.1 At % (10^{-9}g cm^{-2}) using peak intensities and empirically derived sensitivity factors. A discussion of factors affecting semi-quantitative surface analysis is available in several reviews [10-12]. Peak shape and peak binding energy values are then used to determine element oxidation states and, where possible, to aid in compound identification.

The objective of this work was to prepare thin film analogues of the oxide precursor of the alumina-supported Co-Mo catalyst used in HDS reactions. There are several reasons for studying the catalyst in a flat, thin film form rather than as bulk extrudate or powder. The deposition of active metals in thin films affords a better control over the surface composition than the usual bulk precipitation or impregnation reactions. Study of the films by surface spectroscopic techniques is much easier since the films are deposited on an electrically conducting substrate and are not subject to surface charging effects. Therefore, XPS line shapes and positions are much easier to identify.

The present paper describes the XPS results of exposing a Co/Mo containing alumina thin film to HDS process conditions. A commercial HDS catalyst subjected to identical process conditions served as the reference.

Experimental

The fabrication and characterization details of the Co-Mo-Al oxide thin films (50 nm) used here were reported previously.[13] A microactivity catalyst testing unit designed to allow sample transfer to the XPS spectrometer without air exposure was used.

Reduction, sulphidation and thiophene HDS steps were done sequentially with XPS analysis performed after each. Each specimen was reduced in flowing hydrogen for 30 min (120 mL min^{-1}) at 623 K, sulphided in flowing 10% H_2S/H_2 for 30 min (120 mL min^{-1}) at 623 K then exposed to thiophene by direct injection of 10 μL of the feed into the cool reactor followed by hydrogen gas to a final pressure of 172 KPa while rapidly heating to 623 K. Gas samples were withdrawn for GC analysis after 1 h and, in several cases, after 6 h. Matheson ultra-high purity grade gases further purified by moisture and oxygen traps were used.

Details of the XPS spectrometer, manufactured by Physical Electronics Division, Perkin-Elmer Corporation and its operating parameters were reported previously .[14]

Results

Analysis of many thin film specimens revealed that calcination at a constant set of conditions produced Co-Mo-Al oxide films having similar surface chemistry regardless of the metal deposition sequence. However, surface composition and compounds vary greatly with calcination conditions. Examination of the model catalyst's surface by XPS (Table 1, Fig. 1-A) reveals Mo present only as Mo(6+) oxide (MoO_3 or $Al_2(MoO_4)_3$ whereas Co sites as Co(2+) and Co(3+) oxide (probably Co_3O_4). After reduction (Fig. 1-B), 80% of the Mo is present as Mo(4+) oxide, the remainder as Mo(5+) oxide with the mixed Co oxide reduced to metal and to a Co(2+) species (likely CoO) in nearly equal amounts (Fig. 1-C). The sulphiding step readily converted the Mo(4+,5+) to Mo(4+) sulphide. Only ≈10 At % of the Mo(5+) and Co(2+) oxides still remains after sulphidation. This unsulphided Co(2+) was likely sited as $CoAl_2O_4$. Examination of the surface by XPS after thiophene exposure indicated that no Co or Mo oxide remained, (Fig. 1-D). The S 2s peak located at 225.6 eV in the Mo 3d spectrum (Fig. 1-D), is nearly half the Mo 3d peak intensity indicating sulphide anions are associated with the second metal. An XPS Mo 3d spectrum of pure MoS_2 indicated a S 2s/Mo 3d ratio of 0.1. Also, the surface composition of this thiophene-exposed sample (Table 1) indicates a Co+Mo/S ratio of 0.62, in good agreement with a two-phase mixture of MoS_2 and CoS compounds (0.67). These XPS determined results however, do not preclude the existence of the "CoMoS" phase on the model catalyst[1,2].

The surface sited Co and Mo contents of the model catalyst are nearly equal and did not change drastically during the reduction, sulphidation and HDS steps. The absolute amount of sulphur, [S(2-)], measured by XPS after sulphidation and the HDS test is very close to that required for the total conversion of surface sited Mo and Co oxides to sulphides (MoS_2 + CoS). This model HDS catalyst had HDS catalytic activity. After a 6h exposure the model catalyst converted 17% of the injected thiophene into C_4 hydrocarbons.

An examination of the commercial catalyst by XPS, shown in Table 1 and Fig. 2-A, indicates the presence of Mo sited as Mo(6+) and Co as Co(2+). The XPS Co/Mo ratio 0.30 is very similar to the value expected from the manufacturer's formula (0.39). After the reduction step, three surface Mo states are present: Mo(6+), Mo(5+) and Mo(4+) in the ratio 15:3:2 whereas only 10% of the Co was reduced to Co metal. Sulphidation further changed these ratios; only Mo(4+) and Mo(5+) are now present and in nearly equal amounts whereas half the Co(2+) and probably all the Co metal has been sulphided (Fig. 2-B). Exposure to thiophene for 1 h resulted in conversion of half the Mo(5+) oxide to Mo(4+) sulphide; after a further 6 h, 80% of the Mo present was sited as a Mo(4+) sulphide species, (Fig. 2-C1). This desulphurization step also increased the CoS-type component to nearly 60% of the total Co present (Fig. 2-C2). Note the Co sited in the commercial catalyst is much more difficult to reduce or sulphide than Co in the model thin film catalyst although the Mo components behaved similarly. This effect was probably the result of the larger Co/Mo ratio present in the model catalyst thin film causing less Co-Al-O interaction. The reduction and sulphidation behaviour of several Co-Al oxide films was very similar to that of the commercial catalyst, a catalyst with a large $CoAl_2O_4$-like component.

Conclusion

Some sulphided Co-Mo/alumina thin films have been found to possess HDS activity superior to a commercial catalyst (on a unit surface area basis) leading one to speculate that inexpensive bimetallic alumina supported catalysts of high activity might be manufactured using advanced thin film technology. XPS has shown that the initial Co and Mo concentrations and the particular oxide phase in which they are present determine the ease of sulphide formation and HDS catalytic activity. All the surface sited Co and Mo in the active model catalysts were sulphided at the process conditions employed; however, nearly half the surface sited Co and Mo present in the commercial catalyst remained unsulphided at identical conditions.

These XPS results suggest that a commercial HDS catalyst's activity can be improved substantially by a preparation process that allows all the Co and Mo constituents to be accessible to sulphidation and results in the largest density of dispersed, strongly anchored bimetallic sulphide crystallites per square metre of alumina surface.

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FIGURE CAPTIONS

FIG. 1.--XPS spectra (Mo 3d, Co 2p, S 2p) of model thin film catalyst: (A) fresh, (B) reduced, (C) sulphided and (D) after HDS.

FIG. 2.--XPS spectra (Mo 3d, Co 2p, S 2p) of commercial catalyst: (A) fresh, (B) sulphided and (C) after HDS.

TABLE 1 - SEMI-QUANTITATIVE XPS ANALYSIS OF A Co-Mo-AL MODEL CATALYST AND A COMMERCIAL CATALYST PRIOR TO AND FOLLOWING HDS TESTING

I. XPS SURFACE COMPOSITION (A) ATOMIC % (±10%)	CATALYST TYPE							
	MODEL CATALYST(B)				COMMERCIAL CATALYST(C)			
	FRESH	H_2 (30 MIN)	H_2S/H_2 (30 MIN)	C_4H_4S/H_2(D) (360 MIN)	FRESH	H_2 (30 MIN)	H_2S/H_2 (30 MIN)	C_4H_4S/H_2(E) (360 MIN)
Co (2.50)	7.0	5.0	7.0	6.0	0.5	0.5	0.5	0.4
Mo (2.80)	7.0	6.0	8.0	7.0	2.0	1.5	1.0	1.3
AL (0.17)	3.0	12.0	8.0	6.0	28.5	30.0	30.5	31.5
O (0.67)	41.0	45.0	24.0	20.0	62.0	62.0	59.0	59.0
C (0.25)	42.0	32.0	30.0	34.0	7.0	6.0	7.0	4.8
S (0.48)	-	-	23.0	21.0	-	-	2.0	3.0
II. SURFACE SPECIES(F)								
Co	Co_3O_4	CoO_x (.5) Co^0 (.5)	CoO_x (.1) CoS_x (.9)	CoS_x	$CoAL_2O_4$ $Co(OH)_2$	$CoAL_2O_4$ (.9) CoO_x Co^0 (.1)	$CoAL_2O_4$ (.4) CoO_x CoS_x (.6)	$CoAL_2O_4$ (.4) CoO_x CoS_x (.6)
Mo	MoO_3	Mo_2O_5(.2) MoO_2 (.8)	Mo_2O_5(.1) MoS_2 (.9)	MoS_2	MoO_3	MoO_3 (.8) Mo_2O_5 (.15) MoO_2 (.05)	Mo_2O_5 (.4) MoS_2 (.6)	Mo_2O_5 (.2) MoS_2 (.8)

(A) DETERMINED FROM XPS PEAK INTENSITIES AND ELEMENTAL SENSITIVITY FACTORS (SHOWN IN BRACKETS)

(B) MODEL CATALYST SURFACE AREA (APPARENT) IS 1 CM^2

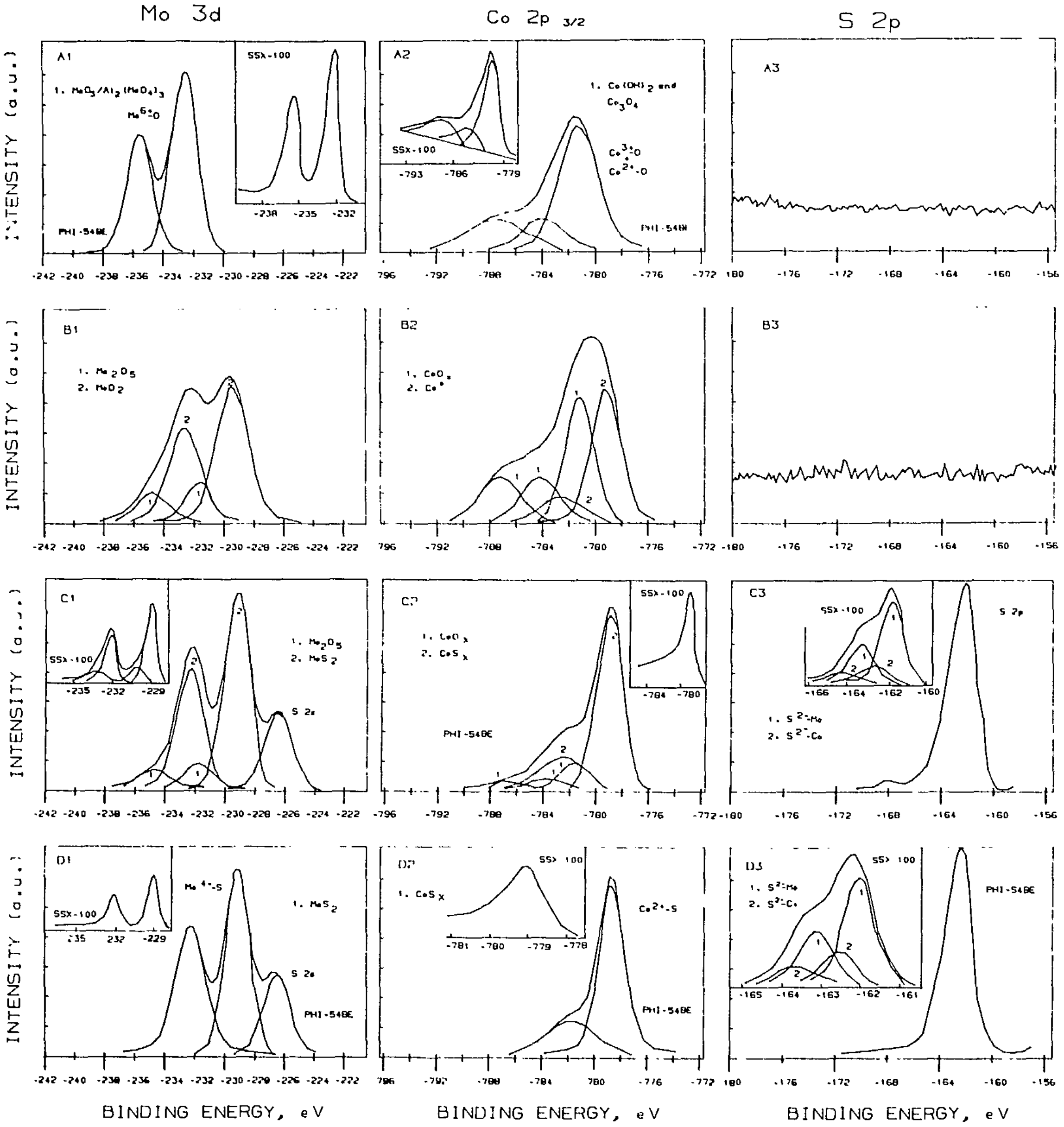
(C) BULK COMPOSITION IS REPORTED AS 0.9 AT % Co, 2.3 AT % Mo; SURFACE AREA OF THE SAMPLE IS $47M^2$ (0.225G) OR MEASURED BY BET METHOD

(D) CONVERSION OF C_4H_4S WAS 17 VOL %

(E) CONVERSION OF C_4H_4S WAS 52 VDL %

(F) MOST PROBABLE SURFACE SITED COMPOUNDS DETERMINED FROM XPS FINGERPRINTS (PEAK POSITION AND SHAPES). VALUES SHOWN IN BRACKETS REFER TO THE PERCENTAGE OF THAT SPECIES MEASURED.

MODEL CATALYST



COMMERCIAL CATALYST