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Quantitative Surface Analysis by XPS: Application to Hydrotreating Catalysts

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Résumé — Analyse quantitative de surface par XPS (X-ray photoelectron spectroscopy) : application aux catalyseurs d'hydrotraitement — La spectroscopie XPS est une technique de choix pour fournir la composition chimique de l'extrême surface de matériaux solides, très appliquée à l'étude des catalyseurs.

Dans cet article, nous montrons qu'une approche quantitative basée sur l'expression fondamentale du signal XPS a permis d'obtenir un jeu cohérent de facteurs de réponse pour tous les éléments du tableau périodique. Un travail de fond a été nécessaire pour connaître de façon précise la fonction de transmission du spectromètre utilisé à l'IFP. Le jeu de facteurs de réponse obtenu permet d'effectuer, en routine, une analyse quantitative avec une justesse relative d'environ 20 %, très acceptable pour une analyse de cette nature.

En utilisant cette approche quantitative, nous avons mis au point une méthode d'analyse spécifique aux catalyseurs d'hydrotraitement qui permet d'obtenir de façon fiable et reproductible le degré de sulfuration du molybdène. L'utilisation de cette méthode est illustrée par deux exemples pour lesquels la spectroscopie XPS a apporté des informations suffisamment précises et quantitatives pour permettre de comprendre des différences de réactivités entre certains catalyseurs d'hydrotraitement de type $\text{MoS}_2/\text{Al}_2\text{O}_3$ ou $\text{NiMoS}/\text{Al}_2\text{O}_3$.

Mots-clés : XPS, facteurs de réponse, fonction de transmission, analyse quantitative, catalyseurs d'hydrotraitement.

Abstract — Quantitative Surface Analysis by XPS (X-Ray Photoelectron Spectroscopy): Application to Hydrotreating Catalysts — XPS is an ideal technique to provide the chemical composition of the extreme surface of solid materials, vastly applied to the study of catalysts.

In this article, we will show that a quantitative approach, based upon fundamental expression of the XPS signal, has enabled us to obtain a consistent set of response factors for the elements of the periodic table. In-depth spadework has been necessary to know precisely the transmission function of the spectrometer used at IFP. The set of response factors obtained enables to perform, on a routine basis, a quantitative analysis with approximately 20% relative accuracy, which is quite acceptable for an analysis of such a nature.

While using this quantitative approach, we have developed an analytical method specific to hydrotreating catalysts that allows obtaining the sulphiding degree of molybdenum quite reliably and reproducibly. The usage of this method is illustrated by two examples for which XPS spectroscopy has provided with information sufficiently accurate and quantitative to help understand the reactivity differences between certain $\text{MoS}_2/\text{Al}_2\text{O}_3$ or $\text{NiMoS}/\text{Al}_2\text{O}_3$ -type hydrotreating catalysts.

Keywords: XPS, response factors, transmission function, quantitative analysis, hydrotreating catalysts.

INTRODUCTION

XPS spectrometry is a surface analysis technique capable of supplying the chemical composition of the first atomic layers below the surface of a solid sample. It is generally estimated that the depth of analysis ranges from 2 and 10 nm.

The ability of this technique to supply qualitative, and to a lesser extent, quantitative information on the chemical composition of the extreme surface has turned it into a widely used tool for characterisation of heterogeneous catalysts. For some twenty years, the launch on the market of commercial spectrometers, relatively reliable and user-friendly, has caused the explosion of the research and development works in catalysis, including XPS surface analyses.

Since the middle of the 1980's, important works have enabled better control of the quantitative aspect of the XPS measurement. Further to enhancements made, as well from a fundamental as from an instrumental viewpoint, the surface analyses available today are sufficiently quantitative to help interpret catalytic results and identify values responsible for the activity of catalysts.

In this article, we show that a quantitative approach based on the fundamental expression of the XPS signal has enabled to obtain a consistent set of response factors for all the elements of the periodic table. This set of response factors enables to perform, on a routine basis, a quantitative analysis with approx. 20% relative accuracy, which is quite acceptable for an analysis of such a nature.

While using this quantitative approach, we have developed an analytical method specific to hydrotreating catalysts that allows obtaining the sulphiding degree of molybdenum. The usage of this method is illustrated by two examples for which XPS spectroscopy has provided with information sufficiently accurate and quantitative to help understand the reactivity differences between certain $\text{MoS}_2/\text{Al}_2\text{O}_3$ or $\text{NiMoS}/\text{Al}_2\text{O}_3$ -type hydrotreating catalysts.

1 PRESENTATION OF THE TECHNIQUE

1.1 Principle of XPS

Subject to the irradiation of the E_0 -energy X-ray beam, the surface of the sample emits low energy electrons, ranging from 0 and E_0 , called photoelectrons.

Measuring the kinetic energy of the electrons (E_c) emitted enables to determine the binding energy (E_b) of the photoelectrons detected ($E_b = E_0 - E_c$, in a first approximation). The chemical analysis is possible by knowing the binding energies associated with the various atoms and with their electrons 1s, 2s, 2p_{1/2}, 2p_{3/2}... [1].

For a sample, XPS analysis enables to obtain a spectrum on which the binding energies are plotted on the abscissa axis

and the number of electrons detected on the ordinate axis. This spectrum comprises two sets of information:

- the position of the “peaks” in binding energy enables to determine the chemical elements making up the surface;
- the surface of each of these “peaks” enables to determine the concentration of these chemical elements.

The XPS spectrum of an $\text{MoS}_2/\text{Al}_2\text{O}_3$ -type catalyst is illustrated on Figure 1.

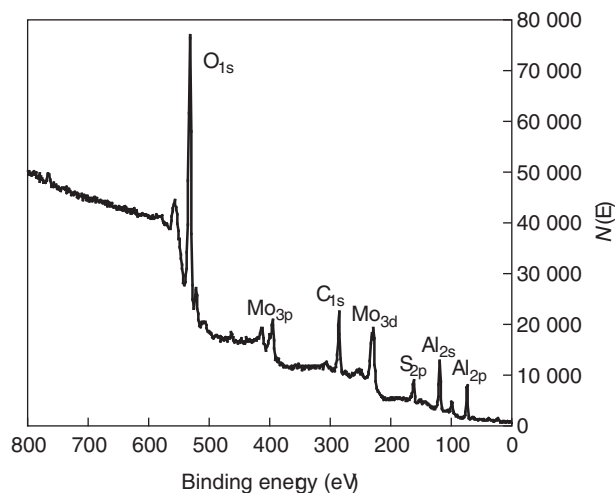


Figure 1
XPS spectrum of an $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst.

Both these sets of information, quantitative and qualitative, turn XPS spectroscopy into a technique that is quite suited for measuring the chemical composition of the extreme surface of a solid sample.

XPS is indeed a surface analysis technique since the photoelectrons emitted can only travel a few nanometres in the sample. The average distance that an electron can travel without losing a portion of its energy is called “mean free path”, a value that will be detailed below (§ 2.4) and which varies from 1 to 5 nm for the energies considered here.

1.2 Apparatus

Taking into account the low energies of the photoelectrons emitted, it is necessary to work under ultra-vacuum in order to reduce their interactions with the matter as far as possible. The ultra-vacuum required to perform XPS measurements must be lower than 10^{-8} torr. This pressure becomes sufficient to reduce notably interactions between the photoelectrons and the molecules making up the residual atmosphere. Analysis of certain samples may call for much better vacuums according to the reactivity of the surface analysed and the nature of the information sought.

Performing an XPS spectroscopy analysis requires the following equipments:

- an ultra-vacuum frame with its related pumping system;
- an X-ray source;
- an electron analysing/detecting system;
- computerised tools for data processing.

The X-ray sources used are X-ray tubes where the anode is, in most cases, covered with an aluminium or magnesium layer. The $K\alpha$ rays used for the analyses are approximately 0.5 eV full width at half maximum, compatible with the resolution required by XPS analysis. The related energies are 1486.6 eV for $Al_{K\alpha}$ and 1253.6 eV for $Mg_{K\alpha}$.

The purpose of the electron analyser is to sort the electrons according to their kinetic energy. The analyser used in this work is a hemispheric capacitor-type analyser. The potentials applied to the electrostatic grids are energy-scanned to enable energy sorting of the electrons. An electron multiplier placed at the output of the analyser enables to detect the electrons and to obtain kinetic energy distribution of the electrons emitted from the sample surface.

The spectrometer used in this work is an XSAM-800-type Kratos spectrometer.

1.3 Qualitative Analysis – Chemical Environment

The first information, directly accessible from an XPS spectrum, is the chemical nature of the atoms making up the surface. The presence of photoelectron peaks or photo-peaks at cleanly set binding energies reveals the chemical nature of the emitting atoms directly.

The second information is the accurate position in binding energy of the photo-peak. Indeed, the chemical environment of the emitting atom will alter the binding energy of the electrons. As a rule, the binding energy increases with the degree of oxidation. Table 1 shows the binding energies associated with an aluminium atom in different chemical environments.

TABLE 1
Influence of the chemical environment on the binding energy of the Al_{2p} electrons

Al chemical environment	Binding energy (eV)
Metal Al	72 to 73
Al_2O_3	74 to 75
$MeAl_2O_4$	74 to 75
AlF_3	76

The accurate measurement of the binding energy of a photo-peak is difficult when analysing electrically non-conducting samples. Indeed for these samples, XPS analysis causes a charge effect of the extreme surface linked to

the departure of the photoelectrons. This charge effect consequently alters the kinetic energy of the electrons that leave the solid and offsets XPS spectra. Positioning the signal C_{1s} , linked with the contaminating carbon, at 284.6 eV, a value generally admitted, makes energy recalibration of the spectra. In some cases, as we shall see for the catalysts supported on Al_2O_3 , the Al_{2p} photo-peak of the support will be used for recalibrating the whole spectrum.

The influence of the chemical environment of the emitting atom on the binding energy of the electrons is used to analyse the catalysts. It will thus be possible to characterise, while taking far-reaching experimental precautions when transferring and preparing the samples, the chemical environment of the catalyst-active sites, at the various steps of catalyst preparation. These pieces of information are often crucial to understand the catalytic activity. We shall see in the examples presented in this article, the application of this principle to ascertain the sulphiding degree of an Mo-based hydrotreating catalyst.

2 QUANTITATIVE ANALYSIS OF THE SURFACE COMPOSITION

2.1 Introduction

Generally in analysis, two types of approach are encountered to perform quantitative analyses. The first one consists in using synthetic samples of known composition and sufficiently “close” to the sample to be dosed. The unknown composition of the sample is determined from the calibration curve obtained with the samples of known composition. This is the approach used in elementary analysis, atomic absorption or X-ray fluorescence.

A second approach consists in knowing the relationship between the response of the measuring chain and the value to be measured in the sample. This implies knowing the experimental and physical values involved in the response measured.

In the case of XPS spectrometry, it is impossible to have “calibration solutions” in order to perform quantitative analysis. Indeed, the analysed volume of the sample consists of the first few atomic layers whose composition is difficult to control. It is precisely on these first atomic layers that phenomena such as oxidation, hydration or segregation occur. These chemical surface reactions alter the surface composition significantly and are hardly controlled.

It has appeared to us more appropriate and more practical to define response factors for each atom and each electronic level from relationships based on the processes involved from the creation of a photo-electron to its detection: ionisation cross-section, mean free path of an electron, transmission function of the analyser.

2.2 XPS Signal

The surface of a photo-peak in XPS spectroscopy depends on:

- the concentration of the chemical element associated with this emission ray;
- the probability of an incident X ray to transmit its energy to the electron affected and to cause its photoemission. The ionisation cross-section represents this probability;
- the distance that the photoelectron can travel without losing energy. This distance is called mean free path of the electron;
- the transmission function of the analyser/detector assembly. This function enables to obtain the energy spectrum at the output of the sample, i.e. the “real” spectrum, from that measured effectively, the “measured” spectrum;
- the instrumental conditions: source intensity, input window of the analyser.

Once the experimental condition have been set, the XPS signal can be expressed as follows [2]:

$$I_A = k \cdot I_0 \cdot \sigma_A(E_0) \cdot T(E_A) \cdot \int_0^{\infty} N_A(z) \cdot \exp\left(\frac{-z}{\lambda(E_A) \cdot \cos(\theta)}\right) \cdot dz \quad (1)$$

where:

- I_A surface of the photo-peak of the photoelectrons associated with the atom A ;
- k constant linked to the analysis conditions;
- I_0 current of incident X photons;
- $\sigma_A(E_0)$ ionisation cross-section of the photoelectron A for incident energy photons E_0 ;
- $T(E_A)$ transmission function of the spectrometer at kinetic energy E_A ;
- $N_A(z)$ atomic concentration at A at depth z below the surface;
- $\lambda(E_A)$ mean free path at kinetic energy E_A ;
- θ angle between the perpendicular at the surface and the collection axis of electrons.

The Expression (1) puts in evidence that the signal XPS depends on the composition profile below the surface, $N_A(z)$ and not directly on the mean composition over a certain depth. It also appears that it is not possible, from the measurement of the photo-peak area, to obtain the composition profile directly. There is no univocal relationship between I_A and $N_A(z)$.

In order to make a result representative of a mean surface concentration measured by XPS, it should be admitted that the sample is homogeneous over the volume analysed, in which case the Expression (1) of the XPS signal becomes:

$$I_A = k \cdot I_0 \cdot \sigma_A(E_0) \cdot T(E_A) \cdot \lambda(E_A) \cdot N_A \quad (2)$$

$$= I_A = k \cdot I_0 \cdot N_A \cdot F_A$$

with:

$$F_A = \sigma_A(E_0) \cdot T(E_A) \cdot \lambda(E_A) \quad (3)$$

The surface composition of the sample at the element A , C_A in atomic %, is obtained by 100-normalisation as follows:

$$C_A = (I_A/F_A) / \sum_i (I_i/F_i) \quad (4)$$

C_A composition in atomic % of element A ;

I_A surface of the photo-peak associated with A ;

F_A response factor of the photoelectron associated with element A ;

I_i surface of the photo-peak associated with element i ;

F_i response factor of the photoelectron associated with element i .

This expression shows that the response factors F_A of each photoelectron can be calculated from the ionisation cross-section, the mean free path of the electron and the transmission function of the spectrometer. We shall see how it is possible to choose values for each of these parameters and to conduct XPS spectrometry quantitative analysis.

2.3 Ionisation Cross-Section

The first process involved in XPS is the creation of the photoelectron when irradiated by the incident X photon. The creation probability of this photoelectron has a direct impact on the emission ray intensity of an electronic level. These probabilities are linked directly to the ionisation cross-sections, which have been calculated and published by J.H. Scofield for the electrons and the sources X used in XPS [3]. These values are acknowledged and universally used by various XPS laboratories. Table 2 presents a few values of cross-sections for a source $Al_{K\alpha}$. We can see in this table that the main reason for which hydrogen or helium analysis is impossible by XPS lies in the very low ionisation cross-section of 1s levels of H and He.

TABLE 2
Ionisation cross-sections for a source $Al_{K\alpha}$

Element	Electronic level	Ionisation cross-section according to Scofield [3] (standardised by C_{1s})
C	1s	1.0000
H	1s	0.0002
He	1s	0.0082
Li	1s	0.0568
Na	1s	8.52
S	2p	1.68
Mo	3d	9.50
Pt	4f	15.5

2.4 Mean Free Path of the Electrons

The mean free path of the electrons that represents the distance over which an electron can travel between two inelastic interaction (with a loss of kinetic energy) is still relatively unknown. It depends on the kinetic energy of the electron and on the nature of the sample. It has been shown that in a first approximation, this mean free path depends essentially on the kinetic energy of the electron [4] and rather little on the nature of the sample. A so-called universal curve (Fig. 2), plotting the evolution of the mean free path in relation to the kinetic energy puts in evidence this mean relationship in the field of XPS spectroscopy where the kinetic energy of the electrons ranges from 20 to 1500 eV. More recent works [5] confirm this hypothesis while mentioning, however, significant deviations according to the materials traversed.

Models for which λ varies only with the kinetic energy of the electron are often used in industrial laboratories. The models published until now supply functions in the form:

$$\lambda = k \cdot E_c^{0.5} \text{ according to [4]} \quad (5)$$

or
$$\lambda = k \cdot E_c^{0.7} \text{ according to [5]} \quad (6)$$

where k is a constant.

For routine analysis applications, we have chosen $\lambda = k \cdot E_c^{0.5}$. This choice is based essentially on the fact that this model is more universal. However, Figure 2 shows clearly far-reaching scattering of the points measured around the function $\lambda = k \cdot E_c^{0.5}$ and the limits of XPS quantitative analysis in terms of accuracy.

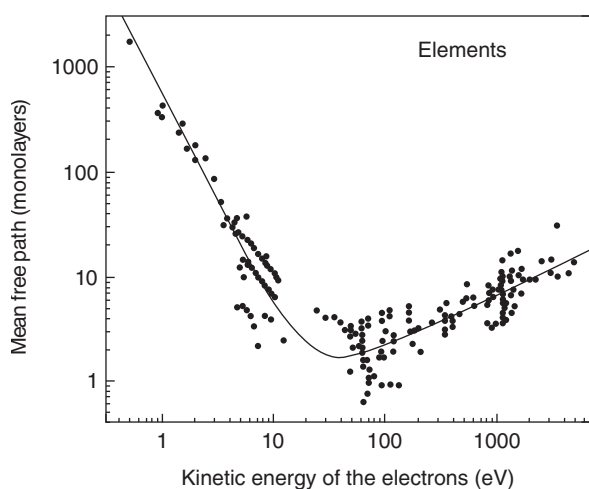


Figure 2

Variation of the mean free path in relation to kinetic energy of the electrons (according to [2]).

2.5 Transmission Function of the Spectrometer

The transmission function of the spectrometer represents the function $T(E_c)$ which enables to obtain the real spectrum $I_c(E_c)$ as it could be measured at the output of the sample from that actually measured via the analyser-detector system, $I_m(E_c)$. This function is defined as follows:

$$T(E_c) = I_m(E_c)/I_c(E_c) \quad (7)$$

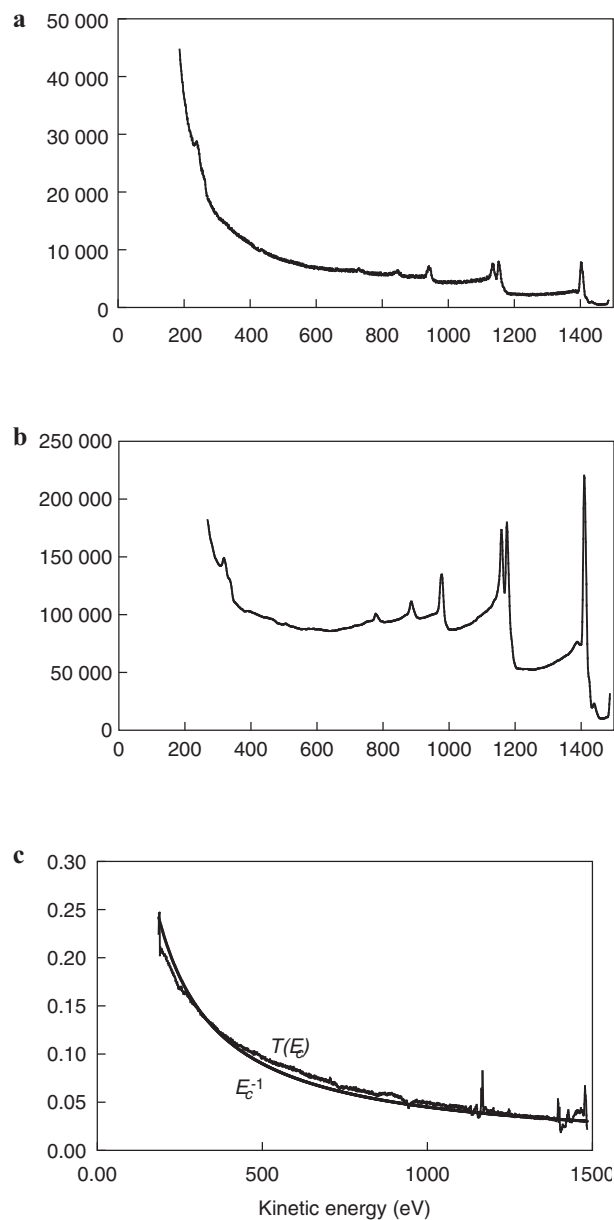


Figure 3

a: “IFP” spectrum of a pure gold leaf;
b: “real” spectrum of a pure gold leaf [6];
c: transmission function of IFP spectrometer.

This function depends on the spectrometer used and on the operating conditions of detection. An original method to determine this function has been suggested in the literature [6], which consists in measuring an XPS spectrum on a gold sheet of purity greater than 99.99%, and in comparing it with the “real” spectrum of the same sample.

This “real” spectrum, $I_c(E_c)$, has been published [6]. This has enabled us, while dividing the spectrum obtained on our apparatus for this golden sheet by the “real” spectrum, to determine the transmission function of our XPS spectrometer (Fig. 3). This function, in the conditions of analysis used at *IFP* for catalysts, is close to:

$$T(E_c) = k \cdot E_c^{-1} \quad (8)$$

This relationship shows that the electron detection efficiency is far from uniform over the whole kinetic energy range of the XPS spectrum and underlines how important it is to take the transmission function of the spectrometer into consideration in XPS quantitative analysis.

Regular follow-up of this function must be conducted to ensure its stability throughout the duration of the measuring chain.

2.6 Response Factors

The relationship that exists between the surface concentration of an element and the associated XPS signal was given at paragraph 2.2 with the relationships (3), (5) and (8) enable us to deduct a simple expression for these response factors:

$$F_A = \sigma_A \cdot E_c^{-1/2} \quad (9)$$

This expression was used for calculating the set of response factors of photoelectrons for our analysis conditions. Approximations were necessary to reach such a simple expression, in particular in the model used for the mean free path of the electrons. Using reference materials (Al_2O_3 , SiO_2 , MoS_2 , AlN , BN , MgO , NaF , MoSi_2), we could verify that the relative accuracy is approximately 20%, which is quite acceptable for the chemical analysis of the extreme surface. The repeatability of the method is approximately 10% in relative value.

3 SULPHIDING DEGREE OF MOLYBDENUM IN HYDROTREATING CATALYSTS

3.1 Description of the Problem

Hydrotreating catalysts are in most case in the form $\text{Mo}/\text{Al}_2\text{O}_3$, $\text{NiMo}/\text{Al}_2\text{O}_3$ or $\text{CoMo}/\text{Al}_2\text{O}_3$. After preparation of the catalyst, the elements Ni, Co or Mo are in oxide form. The active catalytic phase will only be obtained after sulphiding of these oxide precursors. An $\text{MoS}_2/\text{Al}_2\text{O}_3$ -type

phase is thus formed, for which Co or Ni are low-content promoters. It is acknowledged that these promoters Co or Ni are located at the periphery of the MoS_2 particles formed during sulphurisation.

This sulphiding step is an essential step since it will determine the quantity of Mo that will switch from the oxide state to the sulphur state. Partial sulphiding of the Mo will cause a loss of activity.

The characterisation methods of the sulphiding degree of molybdenum are relatively few. Elementary analytical methods, for example, require preparations that may alter the sulphur/sulphate ratio to a vast extent and prevent any measurement of the initial sulphur ratio. X-ray diffraction cannot be applied because of the amorphous character of the MoS_2 and MoO_3 phases present in these catalysts.

We will show below that XPS, avoiding any contact with air during the transfer from the reactor to the analysis chamber, enables to obtain the sulphiding degree of molybdenum.

3.2 Measuring Mo Sulphiding Degree by XPS

Numerous works using XPS spectroscopy [7-10] could demonstrate the capacity of this technique to assess the sulphiding degree of molybdenum. To this end, we use the fact that 3d-electrons of molybdenum have a variable binding energy when switching from an MoO_3 (Mo^{6+})-type oxide form to an MoS_2 (Mo^{4+})-type sulphur form (Fig. 4). The sulphiding degree of molybdenum is obtained by dividing the surface of the photo-peak associated with the MoS_2 form by the total surface of the Mo_{3d} photo-peak.

However, numerous problems are raised when analysing these catalysts by XPS spectroscopy:

- superficial oxidation problem when transferring catalysts from the catalytic reactor to the analysis chamber;
- the photo-peaks Mo_{3d} and S_{2s} interfere (Fig. 4), it is necessary to decompose the XPS signal to obtain their relative contributions. The resolution of the analyser must be sufficient to separate the various contributions linked with the forms of the molybdenum (Mo^{6+} , Mo^{4+} , possibly Mo^{5+});
- decomposing the XPS signal of molybdenum into S_{2s} , MoO_3 (Mo^{6+}) and MoS_2 (Mo^{4+}) contributions involves the sound knowledge of the positions in binding energy and full width at half maximum of each contributions;
- the XPS spectrum must be recalibrated in energy taking the isolating character of the samples into account;
- the binding energy of the MoO_2 species that can cohabit with the MoS_2 species in hydrotreating catalysts is rigorously identical to that of the MoS_2 .

All these problems imply that the results published in the literature exhibit certain heterogeneity according to the methods for processing raw data and the precautions taken to prepare and to analyse the samples (removal of continuous

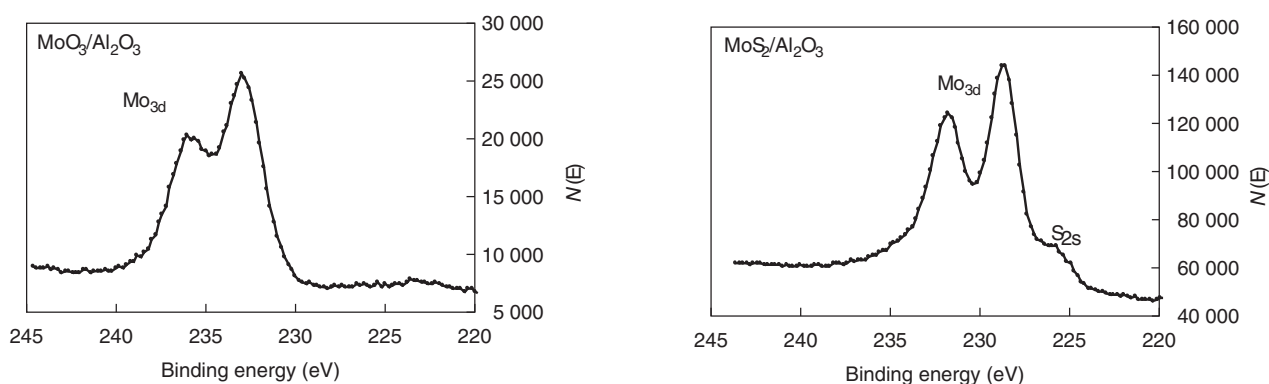


Figure 4

Influence of Mo chemical environment on the binding energy of Mo_{3d} electrons.

background, smoothing the raw spectra, parameters of decomposition of the molybdenum signal, energy recalibration of the spectrum, partial oxidation of the samples during transfers and preparation, etc).

A method has been developed at IFP [11] to analyse the signal of molybdenum in hydrotreating catalysts under the fairest and most repeatable possible conditions. We shall outline this method below.

The decomposition parameters of S_{2s} , MoO_3 (Mo^{6+}) and MoS_2 (Mo^{4+}) contributions were obtained from a large number of reference sample analyses: $\text{MoO}_3/\text{Al}_2\text{O}_3$, $\text{MoS}_2/\text{Al}_2\text{O}_3$. They are illustrated on Table 3. The XPS spectrum is energy recalibrated by placing the Al_{2p} photo-peak at 74.6 eV.

The superficial oxidation problems of sulphured catalysts are reduced as far as possible by using a glove box and a transfer lock under inert gas for, respectively, preparation and transfer of the samples from the glove box to the ultra-vacuum frame of the XPS spectrometer.

XPS spectra of $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalysts, totally or partially sulphured, are presented on Figure 5.

The sulphiding degree of Mo, TSMo, is assessed with the following formula:

$$\text{TSMO} (\%) = 100 * A(\text{Mo}_{3d} \text{ sulph.})/A(\text{Mo}_{3d} \text{ tot.}) \quad (10)$$

where:

$A(\text{Mo}_{3d} \text{ sulph.})$ surface of the Mo_{3d} photo-peak associated with the 4+ form of Mo
 $A(\text{Mo}_{3d} \text{ tot.})$ total surface of the Mo_{3d} photo-peaks associated with the oxide and sulphur forms of Mo.

This sulphiding degree can be calculated via the Formula (10) if the atomic ratio S/Mo^{4+} determined by XPS is greater than a value close to 1.8 (value significantly smaller than 2, a stoichiometric value of MoS_2). If this is not the case, the presence of molybdenum in the MoO_2 form will be very probable.

This method is used on a routine basis in our laboratory and enables, daily, measuring the sulphiding degree of molybdenum of hydrotreating catalysts under well-defined and reproducible conditions.

TABLE 3
Decomposition parameters of the Mo_{3d} signal of molybdenum [11]

	$\text{Mo}_{3d5/2}$ Sulphur	$\text{Mo}_{3d5/2}$ Sulphur	$\text{Mo}_{3d5/2}$ Oxide	$\text{Mo}_{3d5/2}$ Oxide	S_{2s} Sulphur
Position in binding energy (eV)	229.0 ± 0.1	232.15 ± 0.1	232.8 ± 0.1	236.0 ± 0.1	226.1 ± 0.2
Full width at half maximum (eV)	1.6 ± 0.2	1.6 ± 0.2	2.6 ± 0.2	2.6 ± 0.2	2.3 ± 0.2
Height of photo-peak (a.u.)	H_1	$H_1 \cdot 0.67$	H_2	$H_2 \cdot 0.67$	H_3
Forms of elementary photo-peaks	82% Gauss 18% Lorentz	82% Gauss 18% Lorentz	82% Gauss 18% Lorentz	82% Gauss 18% Lorentz	82% Gauss 18% Lorentz

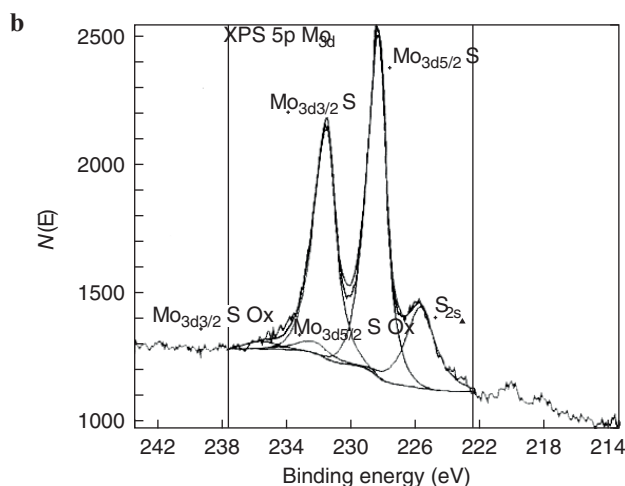
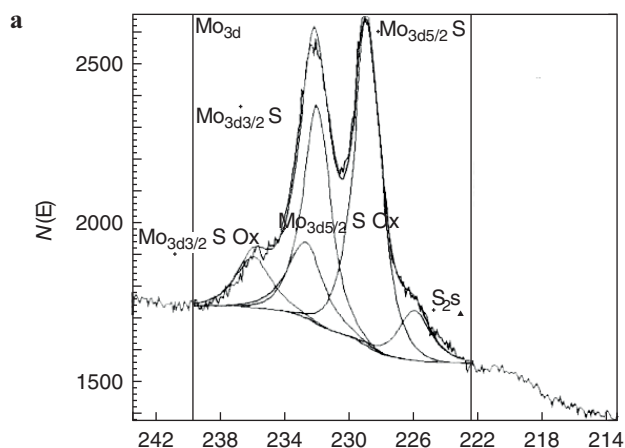


Figure 5

XPS spectra of $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalysts, partially or totally sulphured.

4 EXAMPLES OF APPLICATION

4.1 XPS Signal/ MoS_2 Particle Dispersion Relationship

These results are derived from works undertaken at IFP within the framework of optimising a sulphurisation process of hydrotreating catalysts. The catalysts obtained by this process exhibited quite variable catalytic activities, during standard valuation tests, with molybdenum iso-content.

XPS analysis has provided two types of information influencing the catalytic activity:

- surface concentration of molybdenum;
- sulphiding degree of molybdenum.

The molybdenum concentration measured by XPS is linked directly to the MoS_2 phase dispersion. The larger the particles, the smaller the molybdenum surface and the more the associated XPS signal decreases. Molybdenum

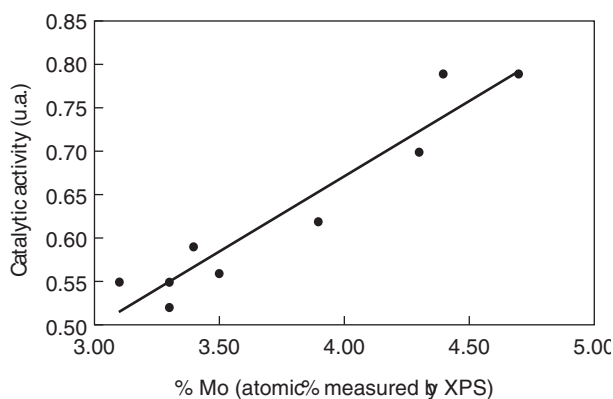


Figure 6

Catalytic activity in relation to Mo content measured by XPS.

concentrations have been determined by using the response factors presented previously (§ 2). It has been shown, besides, that the sulphiding degrees of these various catalysts were very close and approximately 90%.

Figure 6 shows the evolution of the catalytic activity in relation to the Mo surface contents as measured by XPS spectroscopy. It appears very clearly that activity deviations between the various catalysts are derived mainly from dispersions of the MoS_2 active phase that are quite variable according to the sulphiding procedure.

These XPS results have enabled to identify, over a consistent series of catalysts, the origin of significant deviations in catalytic activity. Later measurements conducted by transmission microscopy have confirmed the presence of very large particles of MoS_2 in the least active catalysts.

4.2 Evaluation of the Number of Active Sites

The results presented here are extracted from the thesis by P. Da Silva [12] prepared at IFP. The purpose of this work consisted in studying the influence of the size of molybdenum sulphur particles supported on alumina, on the activity of hydrodesulphurization or hydrogenation reactions of model molecules in conditions close to those of industry.

A set of molybdenum-based non-promoted catalysts supported on an alumina γ was prepared to obtain Mo-content catalysts ranging from 1.4 to 25% in weight.

The mean lengths of MoS_2 sheets were obtained by transmission electron microscopy (TEM) and it was found that this mean length increases linearly with total molybdenum content.

Each of these catalysts was tested in hydrogenation (HYD) and hydrodesulphurization (HDS) during catalytic tests on model molecules. They were tested after two different sulphiding procedures. After each catalytic test, the catalysts were characterised by XPS and by transmission electron

microscopy without air contact. TEM provided the histogram of the MoS₂ particle sizes. XPS spectroscopy enabled to ascertain the molybdenum sulphiding degree. The results of characterisation and of catalytic tests are given at Table 4.

TABLE 4
Results of XPS characterisation and of catalytic tests

Catalyst reference	Sulphiding degree (%)	HYD activity (mol/g/h)	HDS activity (mol/g/h)
Mo-4	76	2.5	1.0
Mo-6	81	4.8	1.8
Mo-9	88	7.3	2.7
Mo-12	83	9.5	3.4
Mo-14	78	9.5	3.4
Mo-22	63	9.1	3.4
Mo-4 (2)	92	3.3	1.2
Mo-6 (2)	92	5.8	2.2
Mo-12 (2)	91	9.8	3.4
Mo-17 (2)	88	12	4.0
Mo-22 (2)	73	12.5	4.2

One purpose of this work was to identify the active sites of the MoS₂/Al₂O₃-type catalysts and to try and check that only the atoms located at the periphery of the MoS₂ particles are active. To assess the number of edge atoms, it is necessary to model the form of the sulphur phase. In this work, this phase was modelled by MoS₂ hexagonal sheets as suggested by some authors [13-15].

The number of edge atoms was calculated by using the particle size histogram supplied by TEM and by supposing that the value measured in microscopy corresponds to the diagonal of the hexagon. This number of edge atoms was then corrected by the molybdenum sulphiding degree determined by XPS in order to take the various sulphiding degrees of the catalysts into account (Table 5).

Figure 7 shows that the hydrogenation and hydrodesulphurization activities are perfectly correlated with the number of Mo edge atoms if corrected by the Mo sulphiding degree as measured by XPS. This result puts directly in evidence the predominant role of the atoms at the periphery of the MoS₂ particles on the catalytic activity.

This example shows the importance of a reproducible and efficient technique to assess the sulphiding degree of molybdenum in hydrotreating catalysts, which sulphiding degree may vary quite significantly from one catalyst to another. Without measuring or taking into account the Mo percentage in the MoS₂ form, it would have been impossible to draw such a correlation between the number of edge atoms of MoS₂ particles supported on alumina and the catalytic activity of the catalysts in hydrogenation and hydrodesulphurization.

TABLE 5
XPS sulphiding degree and number of edge atoms

Catalyst reference	Sulphiding degree (%)	Mo edge ($\propto 10^4$)	
		Before correction	After correction
Mo-4	76	1.7	1.3
Mo-6	81	2.5	2.0
Mo-9	88	3.4	3.0
Mo-12	83	4.2	3.5
Mo-14	78	5.0	3.9
Mo-22	63	5.8	3.7
Mo-4 (2)	92	1.6	1.5
Mo-6 (2)	92	2.5	2.3
Mo-12 (2)	91	4.2	3.8
Mo-17 (2)	88	5.1	4.5
Mo-22 (2)	73	5.8	4.2

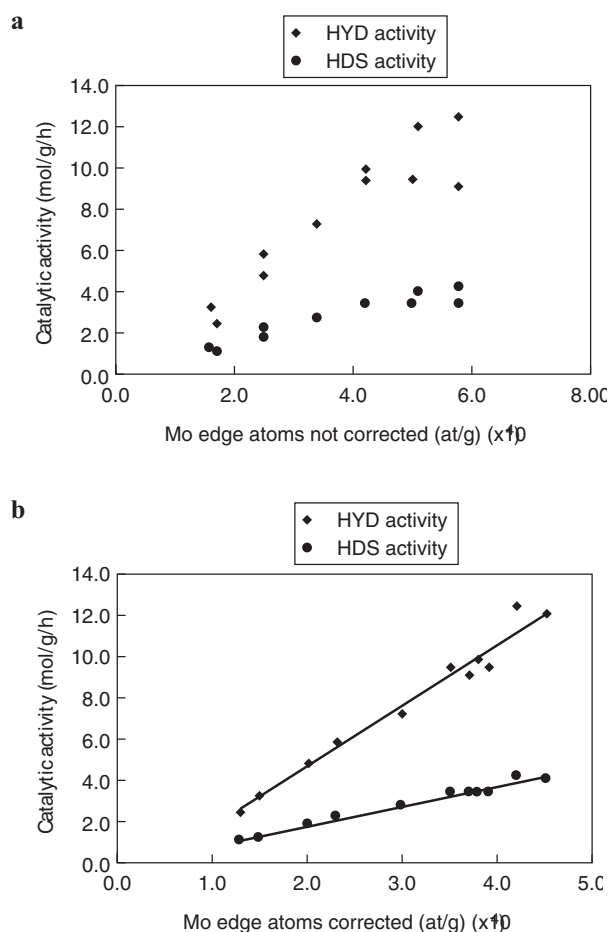


Figure 7

HYD and HDS activities in relation to the number of Mo edge atoms corrected or not by XPS sulphiding degree.

CONCLUSION

XPS is an ideal technique for providing quantitative information on the composition of the extreme surface of solid materials, extensively applied to the study of catalysts owing to the very high sensitivity of the catalytic activity to the composition of the extreme surface.

In-depth spadework was conducted on the spectrometer used at *IFP* in order to know its transmission function accurately. This function has enabled to define consistent response factors for all the elements of the period table. These response factors are, as of now, employed on a routine basis in the laboratory, for the analysis of all sample types.

The development of specific transfer and preparation tools as well as optimisation of the analysis and process conditions of the spectra have enabled to provide a reliable and reproducible analytical method of MoS₂/A₂O₃-type hydrotreating catalysts. This method of analysis enables to assess quantitatively the sulphiding degree of molybdenum, a primeval parameter in the activity of these catalysts.

Numerous examples of works carried out in XPS on industrial hydrotreating catalysts have enabled to lead to conclusions allowing identification of the origin of the activity differences observed.

Current work aims at improving the analysis of the signals associated with nickel and cobalt in order to measure more quantitatively their degree of sulphiding and of participation to the sulphur phase. This step is decisive to go further in the understanding of the promotion mechanisms of MoS₂/A₂O₃ catalysts by Co or Ni.

REFERENCES

- 1 Davis, L.E., Wagner, C.D., Riggd, W.M. and Moulder, J.F. (1978) *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics Division, Perkin Elmer, Minnesota.
- 2 Seah, M.P. (1990) *Practical Surface Analysis, Auger and X-Ray Photoelectron Spectroscopy*, Eds D. Briggs and M.P. Seah, Wiley, Chichester, 1.
- 3 Scofield, J.H. (1976) *J. Electron. Spectroscop.*, **8**, 129.
- 4 Seah, M.P. and Dench, W.A. (1979) *Surf. Interf. Analysis*, **1**, 2.
- 5 Tanuma, S., Powell, C.J. and Penn, D.R. (1993) *Surf. Interf. Analysis*, **20**, 77.
- 6 Seah, M.P. and Smith, G.C. (1990) *Surf. Interf. Analysis*, **15**, 751.
- 7 Morales, A., Martinez, N.P., Laine, J., Payen, E. and Grimblot, J. (1983) *Appl. Catal.*, **6**, 329.
- 8 Yoshimrora, Y., Shimada, H., Sato, T., Kubota, M. and Nishizima, A. (1987) *Appl. Catal.*, **29**, 125.
- 9 Patterson, T.A., Carter, J.C., Leyden, D.E. and Hercules, D.M. (1976) *J. Phys. Chem.*, **80**, 1700.
- 10 Tokamoto, Y., Maezawa, A. and Imanoka, T. (1989) *J. Catal.*, **120**, 29.
- 11 Hydrotreating Catalysts. sulphiding degree of Molybdenum. X-Ray Induced Photoelectron Spectroscopy, *Method IFP 9714*.
- 12 Da Silva, P. (1998) *Thesis*, Université Pierre et Marie Curie (PARIS VI).
- 13 Kasztelan, S., Toulhoat, H., Grimblot, J. and Bonelle, J.P. (1984) *Appl. Catal.*, **13**, 127.
- 14 Chianelli, R.R. and Daage, M. (1989) *Stud. Surf. Sci. Catal.*, **50**, 1.
- 15 Eijsbouts, S., Heinerman, J.L. and Eljerman, H.W. (1993) *Appl. Catal.*, **105**, 69.

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