

## Determination of the Near-Surface Elemental Composition of Catalysts by the Technique of Proton-Induced X-ray Analysis

J. A. CAIRNS,<sup>1</sup> A. LURIO, J. F. ZIEGLER

*IBM Research, Yorktown Heights, New York 10598*

AND

D. F. HOLLOWAY, AND J. COOKSON

*AERE Harwell, Didcot, Oxfordshire, England*

Received March 29, 1976

The technique of using an accelerated beam of protons to generate characteristic X-rays from elements is shown to be particularly useful for analyzing catalysts. The information comes from within the first few micrometers of the surface, so all elements in this region, i.e., the catalytic elements as well as trace impurities in the support, are detected. The technique is highly sensitive for all the main catalytic elements (down to at least  $10^{-12}$  g absolute and  $10^{-6}$  relative concentration) and is rapid, taking typically only a few minutes to obtain a sample spectrum. Unlike X-ray production by electron beam irradiation, advantage can be taken of the fact that the information may be rendered quantitative simply by preparing the sample in the form of small ( $<2 \mu\text{m}$ ) particulates: 3 MeV protons lose typically  $<2\%$  of their energy in traversing such a particle. No chemical information is obtained, but the technique, by virtue of its special features, is well suited for use in conjunction with other near-surface analytical techniques.

### 1. INTRODUCTION

The use of accelerated protons to generate characteristic X-rays on impact with solid targets is not in itself new, but there has been in recent years a dramatic resurgence in interest (1). This has been due partly to the increasing availability of suitable accelerators, which were designed originally for nuclear physics purposes but are now being used increasingly for materials characterization (2). However, the main reason was the realization that proton bombardment of a solid target produces a spectrum of X-rays which is relatively free from the continuous background electromagnetic

radiation (Bremsstrahlung) which accompanies X-rays produced by energetic electron bombardment. The result is a dramatic improvement in sensitivity. For example, it has been shown (3) that as little as  $10^{-12}$  g of many elements can be detected, in relative concentration as low as  $10^{-6}$  for a typical 1-mm<sup>2</sup> proton beam. A particularly striking example of the use of the technique is the work of Cahill (4) in analyzing the elemental composition of atmospheric particulates, collected on thin carbonaceous foils which are essentially transparent to a proton beam of a few MeV energy. The fact that the energy loss of a 3 MeV proton beam is less than 2% in passing through particulates ranging in size up to a few

<sup>1</sup> Present address: Metallurgy Division, AERE Harwell, Oxfordshire, England.

micrometers diameter means that quantitative data on the composition of the target can be obtained simply from the relative X-ray intensities, corrected for their respective ionization cross sections, fluorescence yields, and detector response. The correction for absorption of X-rays generated within the target is important only for those X-rays up to 3 keV, when the particulate size is greater than 1  $\mu\text{m}$  (4). It requires only a few minutes to obtain an X-ray spectrum, and indeed several thousand samples can be processed per day (4).

It is the purpose of the present study to demonstrate that the special attributes of the technique can be applied particularly well to the examination of catalysts. Most of the examples will be chosen from the large class of supported heterogeneous catalysts. It will be shown that elements can be detected with high sensitivity within the first few micrometers of the surface, thus revealing the catalytic metals, including those within the pores of the support which are not detected by true surface techniques such as Auger electron spectroscopy, as well as trace elements in the support itself. Since the supports most widely used, namely alumina, silica, and carbon, can be ground down readily to particles in the few micrometers range, the catalyst can be presented to the proton beam in the same manner as Cahill's atmospheric particulate samples, and so the elemental composition can be rendered quantitative.

The data thereby obtained contain no chemical state information, but represent a speedy, accurate means of monitoring the elemental composition of catalysts and of detecting the presence of undesired trace impurities.

## 2. EXPERIMENTAL

### 2.1 The Accelerator

The results presented here were obtained using two facilities, namely the IBM 3

MeV accelerator and the microprobe system of the Harwell 3 MeV IBIS accelerator, although in the latter case the small beam spot facility (down to 4  $\mu\text{m}$  diameter) was not used; on both machines the beam spot was of the order of 1 mm diameter. The basic features of a proton accelerator system are easily understood: the protons are produced in an ion source, then bent through an analyzing magnet, passed along a flight tube, then into a target chamber within which the sample is mounted. The whole system is maintained under modest vacuum (typically  $10^{-6}$  Torr) but the target chamber can be isolated from the flight tube by means of a vacuum valve, and targets interchanged readily. A more detailed description of these facilities has been presented elsewhere (5).

### 2.2 The X-Ray Detector

The X-rays generated by proton bombardment of the targets were detected by means of a Si (Li) solid state detector, mounted within the target chamber, on the same side of the target as the incoming proton beam. This yields a simultaneous X-ray spectrum of all the elements present, except for a limitation regarding light elements (described in section 3.1), for which a further procedure can be used.

### 2.3 Sample Preparation

As explained above, to obtain X-ray data which can be related to the sample elemental composition in a quantitative manner, the catalyst must be ground down to a particle size of less than a few micrometers diameter. This represents no difficulty with heterogeneous catalysts supported on alumina, silica, carbon, etc., all of which can be ground down readily. The supported catalysts examined here, which were all alumina-based, were ground to size in an air mill, then dispersed in a suitable reagent, such as 2% polyvinyl alcohol. A drop (0.01 ml) of the resulting

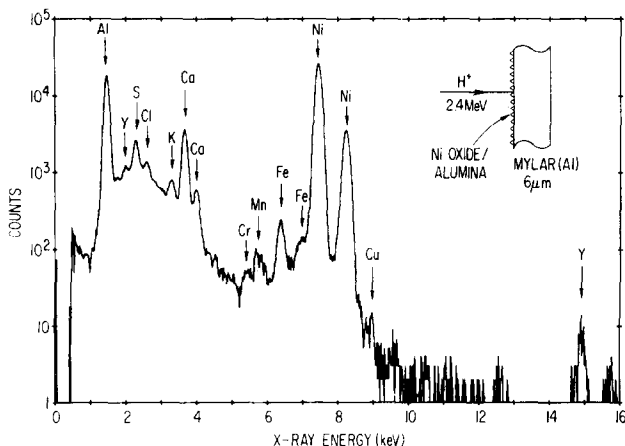


FIG. 1. X-ray spectrum, produced by 2.4 MeV proton bombardment of a nickel oxide/alumina catalyst.

dispersion, containing typically  $10^{-6}$  g of catalyst was placed on a  $6 \mu\text{m}$  aluminized Mylar foil, to form a spot of  $\sim 3$  mm diameter, i.e., equivalent to less than one layer of  $2 \mu\text{m}$  particles. (The Mylar foil had been treated previously with wetting agent, to ensure uniform spreading of the dispersion on its surface.)

### 3. RESULTS AND DISCUSSION

#### 3.1 Catalyst Spectra

The time required to accumulate a spectrum was typically 5 min. As an example

of a typical catalyst spectrum obtained by the use of proton-induced X-rays, Fig. 1 shows nickel oxide on alumina (Air Products Ltd.). Apart from the expected nickel and aluminum peaks, there are many others. Since the catalyst was unused, these additional elements could be postulated to have been included deliberately by the manufacturer, or to be undesired impurities. The background radiation in the lower energy region of the spectrum is due mainly to Bremsstrahlung radiation, caused by the presence of the relatively thick (6

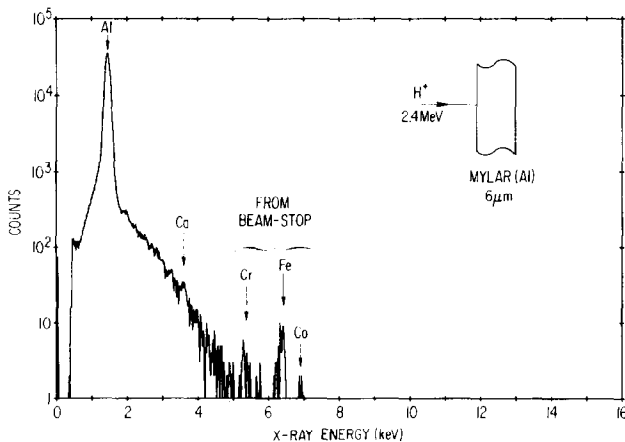


FIG. 2. X-ray spectrum, produced by 2.4 MeV proton bombardment of a  $6\text{-}\mu\text{m}$  aluminized Mylar foil.

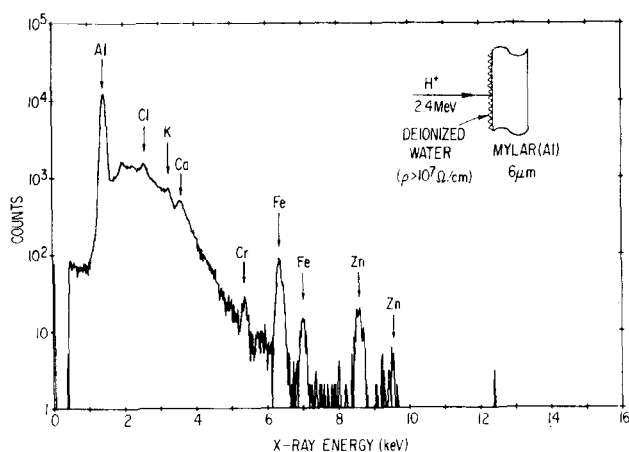


FIG. 3. X-ray spectrum, produced by 2.4 MeV proton bombardment of a drop (0.01 ml) of deionized water on a 6- $\mu\text{m}$  aluminized Mylar foil.

$\mu\text{m}$ ) Mylar backing film on which the catalyst was mounted. This may be appreciated from Fig. 2, which shows the spectrum obtained by bombarding the backing foil itself with the same dose of 2.4 MeV protons. The chromium, iron, and cobalt peaks arose by a stray fraction of the beam striking a steel beam stop. (The resultant X-rays were not shielded completely from the X-ray detector.)

However, most of the additional elements present in Fig. 1 were due to trace impurities in the deionized water which was used

to make up the catalyst dispersion. This is confirmed from Fig. 3, which was obtained by bombardment (with the same dose of 2.4 MeV protons) of the residue from a drop (0.01 ml) of deionized water on a 6- $\mu\text{m}$  aluminized Mylar foil, and indicates the high sensitivity of the technique.

As a further example, Fig. 4 shows a proton-induced X-ray spectrum of a 10% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst prepared at Harwell. The most significant additional impurities present in this catalyst are nickel and chromium.

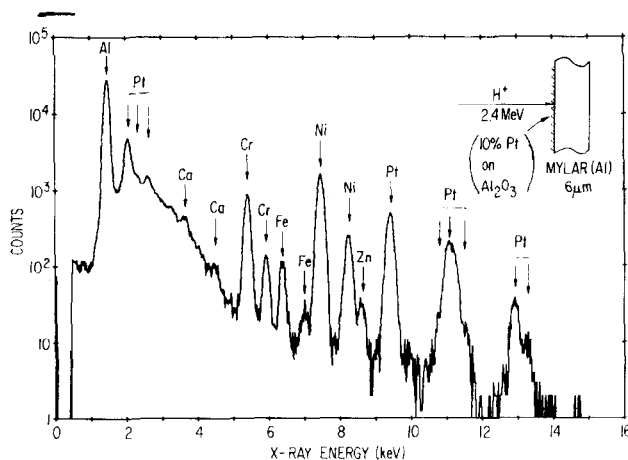


FIG. 4. X-ray spectrum, produced by 2.4 MeV proton bombardment of a platinum/alumina catalyst.

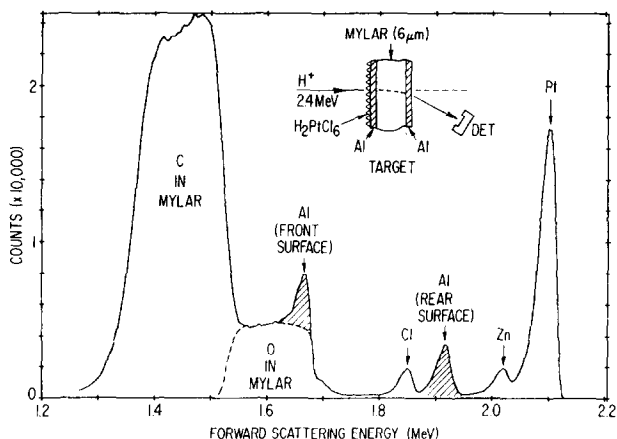


FIG. 5. Forward scattering spectrum arising from 2.4 MeV proton bombardment of a drop (0.01 ml) of chloroplatinic acid on 6- $\mu$ m aluminized Mylar foil. The experimental arrangement is shown in the insert (detector angle =  $41^\circ$ ).

The standard Si(Li) X-ray detector is relatively insensitive to the presence of X-rays from elements lighter than sodium, because of the absorption of such soft ( $<1$  keV) X-rays by its  $1.27 \times 10^{-3}$  cm thick beryllium window. For catalyst studies this is not likely to be a serious limitation, since such light elements tend to be of relatively modest interest in catalysis. However, these light elements *can* be detected very easily without disturbing the specimen by using the technique of forward proton scattering (4, 6), by which the proton beam, in scattering from the light nuclei, loses significant energy. This energy loss is a function of the mass of the nuclei, and so the energy spectrum of the scattered protons, which can be measured by means of a surface barrier detector, is seen to contain a series of peaks, corresponding to scattered protons having lost different fractions of their original energy to the various nuclei present in the target. An example of such a spectrum is shown in Fig. 5. The light elements in the foil are seen clearly. The sharpness of the platinum peak indicates that the layer being analyzed is thin, compared to the support film; in fact, the particle size range can be inferred from the sharpness of the forward

scattered peaks. This gives added confidence that the sample under examination will yield a quantitative measurement of the trace element concentrations. On the other hand, the peaks due to carbon and oxygen are relatively broad because of the thickness of the film. Note also that the aluminium film on the front of the foil is distinguished from that on the back.

### 3.2 Quantification

When a proton beam strikes an element, its probability of causing ionization may be expressed as the ionization cross section. This cross section can be calculated theoretically (1a) with considerable confidence for each element. However, since the precise value assigned to the ionization cross section depends on the proton energy, this means that when bombarding thick targets, the cross section will change rapidly as the incoming protons slow down within the target. There are further complications in the case of multielement thick targets, in that corrections have to be made for absorption of the various X-rays within the target itself.

All of these problems were avoided by preparing samples in the form of thin

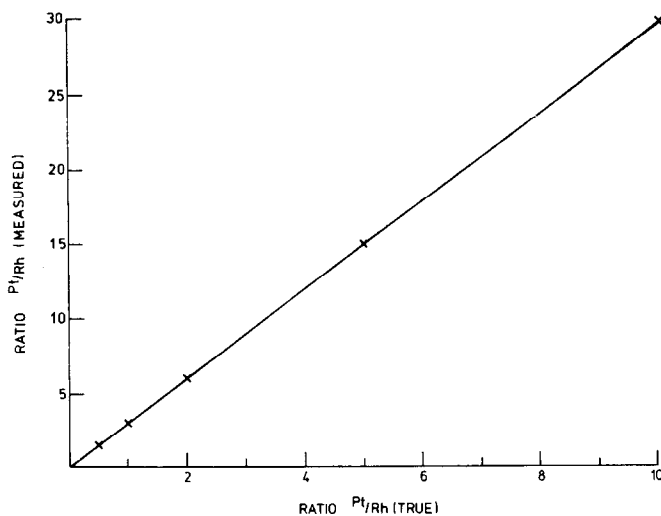


FIG. 6. Data obtained by bombarding a series of platinum/rhodium/alumina standards with 2 MeV protons.

targets, as described above (Section 2.3), for then the target is subjected to bombardment by protons of well-defined energy, and so the ionization cross section for each element is known. However, it must be recognized that an atom, having been ionized, may respond by emitting Auger electrons as an alternative to X-ray emission. Hence, it is necessary to know the relative probability of X-ray emission for each element. Values of this parameter, the fluorescence yield, usually denoted by the symbol  $\omega$  in the literature, can be obtained from standard literature references. Finally, we take account of the relative efficiency of the X-ray detector for characteristic X-rays from each element, including absorption of X-rays by its beryllium window. These considerations have been discussed at length elsewhere (4, 7) and so need not be considered further here.

However, there is a particular attribute of a typical catalyst which can be utilized to advantage: in general, the concentration of the main catalytic element is *known*, and so we can calculate the concentration of the other elements present by using the main element as a built-in standard, thus dispensing with the need to measure

the exact proton dose received by the sample and the solid angle subtended by the X-ray detector. More specifically, if we are interested in a particular contaminant, e.g., lead or sulphur, it is possible to provide an internal calibration which avoids the uncertainty involved in the calculation of cross sections.

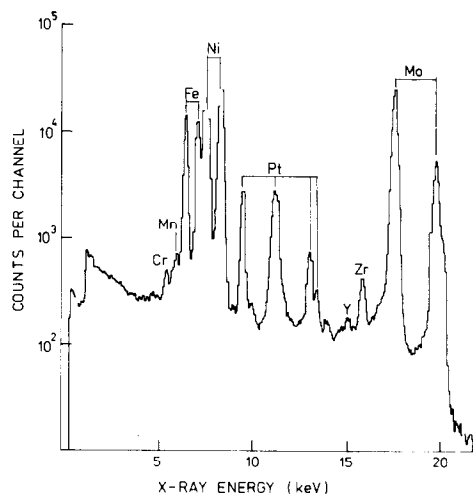


FIG. 7. X-ray spectrum obtained by 2 MeV proton bombardment of a 316 stainless steel specimen (composition detailed in Table 1), onto which had been evaporated a layer of platinum ( $52 \mu\text{g}/\text{cm}^2$ ).

TABLE 1  
316 Stainless Steel Composition, Wt%

Carbon	Chromium	Nickel	Molybdenum	Iron
0.03–0.06	16.5–17.5	13–14	2.0–2.75	Balance

It is simply necessary to add known amounts of an appropriate soluble salt of the contaminant to the catalytic dispersion and, by observing the change in its intensity relative to that of the main catalytic element, calculate the contaminant's true concentration. Figure 6 shows the observed relative X-ray peak heights of platinum and rhodium obtained by proton bombardment of some Pt/Rh/Al<sub>2</sub>O<sub>3</sub> standard dispersions. The straight line relationship demonstrates the reliability of this procedure. This concept of using internal standards has been employed by many authors including Ishii *et al.* (8), who used it in analyzing the trace elemental composition of tomato juice.

### 3.3 Comparison with Other Analytical Techniques

So far, we have examined catalysts which have been prepared as small particulate

specimens, so that the resultant X-ray information could be related quantitatively to the elemental composition. Naturally, if one were interested in obtaining simply an elemental survey, or if the catalyst was unsuitable for this pretreatment, it could be examined in the as-received state. In order to illustrate this point, we show (Fig. 7) a proton-induced X-ray spectrum of a 316 stainless steel specimen, onto which has been evaporated a layer of platinum (52  $\mu\text{g}/\text{cm}^2$ ). The composition of the steel is listed in Table 1, and indeed we see from Fig. 7 that all of the metals are detected, together with the platinum. Now it may be argued that this information could be obtained readily by the technique of X-ray fluorescence, and indeed we confirm this by showing in Fig. 8 two X-ray spectra obtained by irradiating with uranium L X-rays ( $\sim 13.5\text{--}20\text{ keV}$ ) the uncoated steel (on the right) and the platinum-coated steel (on the left). However, one drawback of the X-ray fluorescence technique for this application is that since the incoming exciting radiation is relatively penetrating, a fairly deep region of the specimen is sampled, and so the platinum signal from the surface does not stand out very clearly above background. Hence, we see the

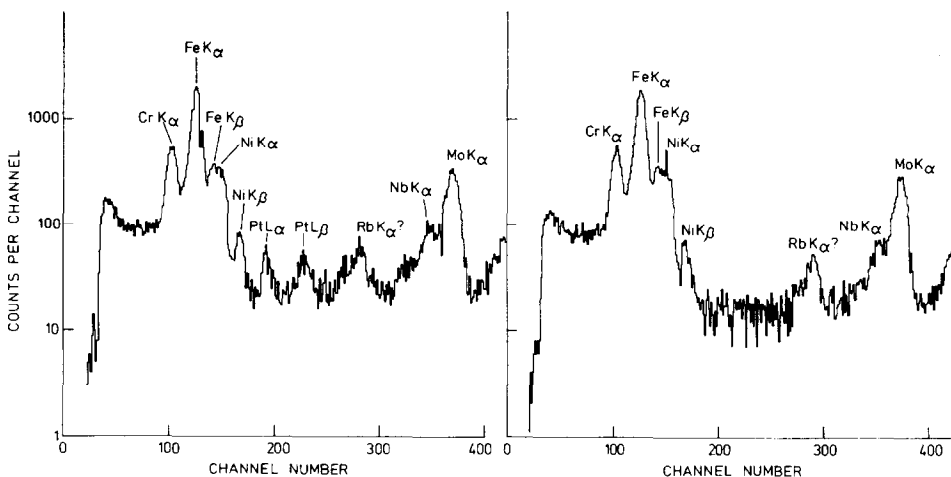


FIG. 8. X-ray spectrum obtained by X-ray fluorescence, using a uranium X-ray source, of the same steel as shown in Fig. 7.

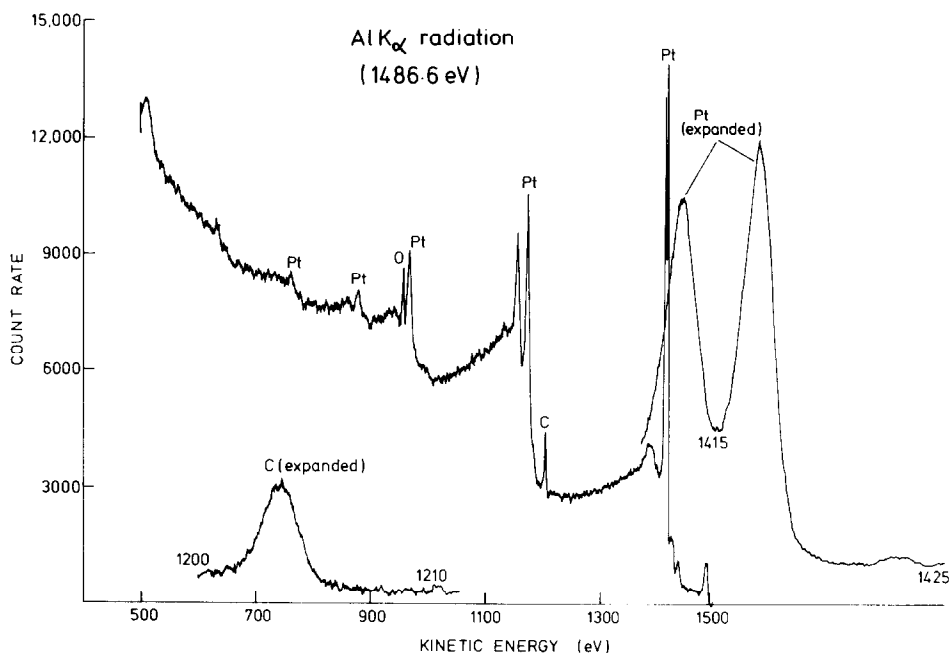


Fig. 9. XPS spectrum of the same platinumized steel as used for Figs. 7 and 8.

attraction of the proton probe: it has good, relatively uniform sensitivity for all elements within the first few micrometers of the surface.

Let us now consider the relative merit of a technique which is much more sensitive to the near-surface region, namely X-ray photoelectron spectroscopy (XPS or ESCA). Figure 9 shows the XPS spectrum obtained from the platinumized steel. This spectrum is dominated by the platinum signal, and shows none of the other elements present (apart from surface carbon and oxygen). Now it may be argued that since catalysis is a surface science, this is the ideal analytical technique, but it must be remembered that in supported catalysts a substantial fraction of the catalytic metal is dispersed within the pores of the support, and so will not be amenable to examination by XPS. Hence again we see the advantage of a technique which probes within the first micrometer or so of the surface and thus detects not only catalytic metal within porous supports, but also impurities within the support itself.

Incidentally, we see from Fig. 10, which is an XPS spectrum of the uncoated 316 stainless steel, that the *surface* is dominated by iron, carbon, oxygen, and chromium, and so one concludes that the maximum information benefit is to be obtained by *combining* proton-induced X-rays with XPS, particularly since the latter also provides chemical information.

#### 4. CONCLUSIONS

The purpose of this work has been to demonstrate that supported catalysts constitute a class of materials which, because of their physical characteristics, can be examined profitably by the technique of proton-induced X-rays.

One can obtain relatively quickly a spectrum showing all of the main elemental constituents, which can be rendered quantitative by recourse to the specimen preparation procedures described above. Indeed by recording simultaneously a forward scattering spectrum, it can be *confirmed* that the catalytic particles are sufficiently small to



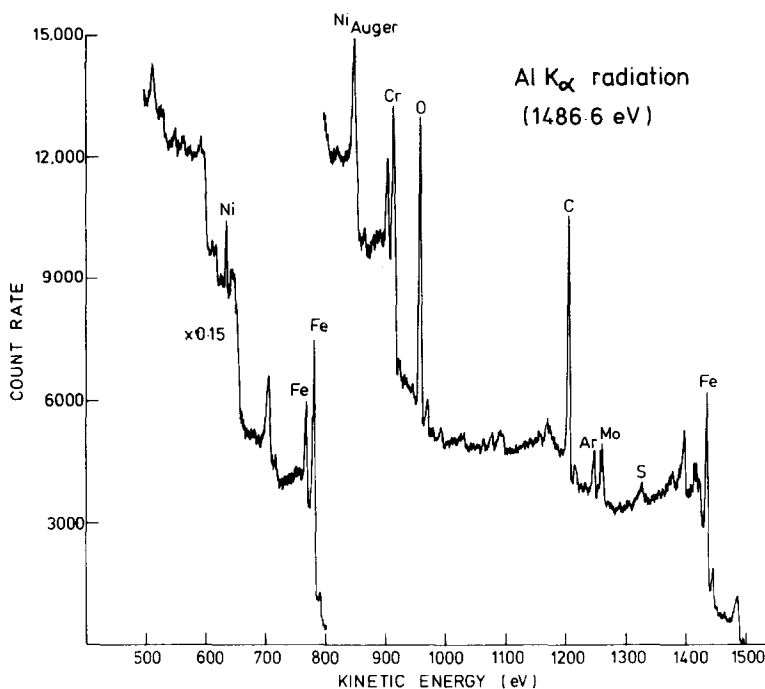


FIG. 10. XPS spectrum of the unplatized 316 stainless steel.

render the analytical data quantitative, as well as obtaining information about the light elements (hydrogen to chlorine), some of which cannot be observed by the use of the Si(Li) X-ray detector.

The sensitivity is adequate and the probing depth is relevant for detecting all of the elements which may influence the catalytic activity, including impurities within the support. On the other hand, the technique cannot distinguish easily true surface elements from near-surface ones, and gives no chemical information, so it can be used to greatest advantage when combined with the technique of X-ray photoelectron spectroscopy.

#### ACKNOWLEDGMENTS

It is a pleasure to express thanks to Johann Keller for assistance during the experimental work done at IBM, and to J. P. Coad of Harwell who took the XPS spectra shown in Figs. 9 and 10.

#### REFERENCES

1. (a) Garcia, J. D., Fortner, R. J., and Kavanagh, T. M., *Rev. Mod. Phys.* **45**, 111 (1973); (b) Kessel, Q. C., and Fastrup, B., in "Case Studies in Atomic Physics" (M. R. C. McDowell and E. W. McDaniel, Eds.), Vol. 1, p. 137. North-Holland, Amsterdam, 1973.
2. Ziegler, J. F. (Ed.), "New Uses of Ion Accelerators." Plenum Press, New York, 1975.
3. Johansson, T. B., Akselsson, R., and Johansson, S. A. E., *Nucl. Instrum. Meth.* **84**, 141 (1970).
4. Cahill, T. A., in "New Uses of Ion Accelerators" (J. F. Ziegler, Ed.), p. 1. Plenum Press, New York, 1975.
5. (a) Cairns, J. A., and Feldman, L. C., in "New Uses of Ion Accelerators" (J. F. Ziegler, Ed.), p. 431. Plenum Press, New York, 1975. (b) Reuter, W., Lurio, A., Cardone, F., and Ziegler, J. F., *J. Appl. Phys.* **46**, 3194 (1975).
6. Jolly, R. K., and White, H. B., *Nucl. Instrum. Meth.* **97**, 103 (1971).
7. Rickards, J., and Ziegler, J. F., *Appl. Phys. Lett.* **27**, 707 (1975).
8. Ishii, K., Morita, S., Tawara, H., Chu, T. C., Kaji, H., and Shiokawa, T., *Nucl. Instrum. Meth.* **126**, 75 (1975).