

# Coke formation on platinum metals studied by Auger electron spectroscopy and secondary ion mass spectrometry

**Citation for published version (APA):**

Niemantsverdriet, J. W., & van Langeveld, D. (1986). Coke formation on platinum metals studied by Auger electron spectroscopy and secondary ion mass spectrometry. *Fuel*, 65(10), 1396-1399.  
[https://doi.org/10.1016/0016-2361\(86\)90112-2](https://doi.org/10.1016/0016-2361(86)90112-2)

**DOI:**

[10.1016/0016-2361\(86\)90112-2](https://doi.org/10.1016/0016-2361(86)90112-2)

**Document status and date:**

Published: 01/01/1986

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

# Coke formation on platinum metals studied by Auger electron spectroscopy and secondary ion mass spectrometry\*

J. W. Niemantsverdriet and A. D. van Langeveld<sup>†</sup>

Laboratory of Inorganic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

<sup>†</sup>Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

The combination of Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) can successfully distinguish between four types of carbonaceous deposits which may be present on a catalyst: molecular, carbidic, amorphous and graphitic carbon. Differences between Rh, Ir, and Pt with respect to carbon deposition from C<sub>2</sub>H<sub>4</sub> are discussed and correlated with catalytic properties of the metals.

(Keywords: coke; catalyst; surface deposition)

Carbonaceous deposits form an essential component of working catalysts in hydrocarbon reactions. These deposits, which influence catalytic activity, selectivity and stability, are formed immediately when hydrocarbons are passed over the catalyst<sup>1</sup>. Four types of carbonaceous deposits on metals can be distinguished; a, molecular: adsorbed hydrocarbons or hydrocarbon fragments; b, carbidic: dehydrogenated carbon atoms multiply bonded to the metal, which are reactive toward hydrogen; c, amorphous: largely dehydrogenated hydrocarbon fragments of aromatic nature with non-aromatic side chains, of which the latter are reactive toward hydrogen; d, graphitic: aromatic structures of low hydrogen content, unreactive toward hydrogen.

The characterization of carbonaceous deposits on metals requires techniques which reveal information on the nature of the carbon, its hydrogen content and the total amount of carbon. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) can supply much of the desired information<sup>2-4</sup>. AES investigations on carbonaceous deposits have been described in the literature<sup>5-10</sup>. Although several SIMS investigations on the adsorption of ethylene on metals have been reported in the literature<sup>11-15</sup>, studies of carbonaceous deposits formed at typical catalytic reaction temperature are scarce<sup>9</sup>.

In this paper, AES and SIMS are shown to form a powerful combination to quantify the state of carbonaceous deposits on metals with a few parameters, such as the total amount of carbon present, fraction of graphitic plus amorphous *versus* molecular plus carbidic carbon, hydrogen content and degree of polymerization. Differences between carbonaceous deposits formed under identical conditions on Rh, Ir, and Pt will be discussed in the light of known catalytic properties of these metals.

## EXPERIMENTAL

Experiments were carried out in an XPS/AES/SIMS spectrometer (Perkin Elmer, PHI 550). Auger spectra were measured in differential mode by using a 4.5  $\mu$ A beam of 2 keV electrons, with a spot diameter of 0.5 mm. In order to reduce possible effects of electron-induced alterations in the carbonaceous layers, the electron beam was defocused. SIMS spectra taken before and after measurement of Auger spectra were virtually identical, indicating that the effect of electron-beam induced damage was small.

SIMS spectra were measured with a 50 nA beam of 1 keV Ar<sup>+</sup> ions, which was rastered over the sample. The total exposure of the sample was  $<4 \times 10^{13}$  Ar<sup>+</sup>/cm<sup>2</sup>, corresponding to a few per cent of a monolayer.

The substrate metals were high purity rhodium, iridium and platinum foils of 15  $\times$  5  $\times$  0.1 mm, spot-welded on tantalum wires. The temperature was monitored by a chromel/alumel thermocouple spot-welded on the back of the sample. The foils were cleaned by applying several cycles of 5 keV Ar<sup>+</sup> sputtering and annealing at 1000 K.

The metal foils were exposed to 0.5 Torr ethylene (Messer Griesheim, research grade purity) at temperatures between 325 and 775 K for 5 min in a separate reaction chamber<sup>9</sup>. After reaction, the foil was cooled to room temperature, evacuated to about 10<sup>-6</sup> Torr and next transferred to the main chamber for AES and SIMS analysis.

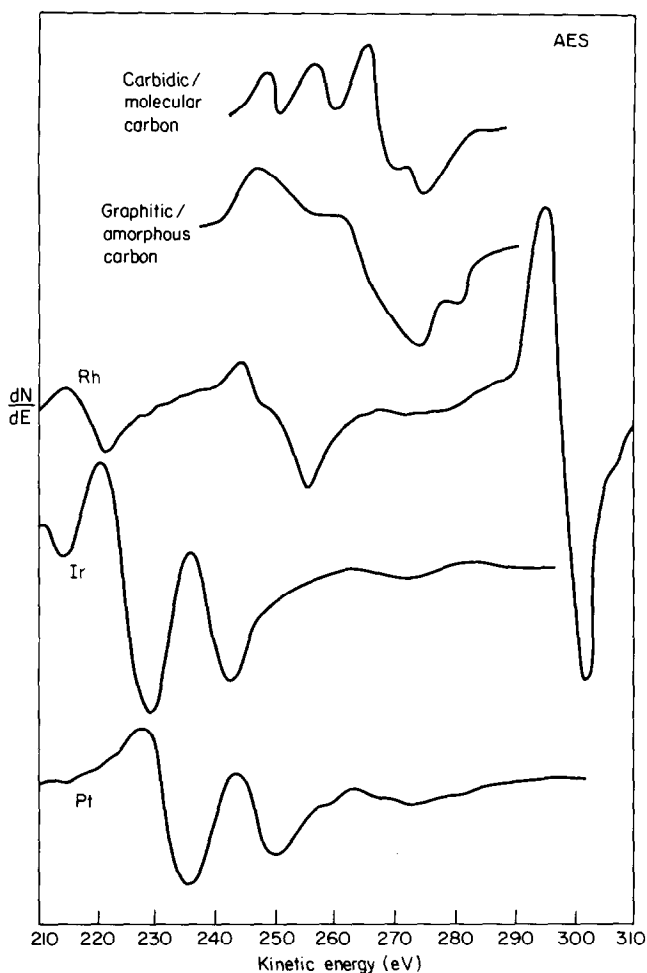
## RESULTS

Auger spectroscopy can distinguish between molecular or carbidic carbon on the one hand, and graphitic or amorphous carbon on the other. To illustrate this the two different Auger spectra of these types of carbon are shown in *Figure 1*, along with the spectra of the substrate metals considered in this paper.

\* This paper was presented at the International Symposium 'Fundamentals of Catalytic Coal and Carbon Gasification', Rolduc, The Netherlands, 5-7 May 1986

0016-2361/86/101396-04\$3.00

© 1986 Butterworth & Co. (Publishers) Ltd.



**Figure 1** Relevant parts of the Auger spectra of carbon, rhodium, iridium and platinum. AES does not readily distinguish between carbide and molecular carbon, or between graphitic and amorphous carbon. Note that the most characteristic region of the two carbon spectra overlaps with Auger features of the metals

In general, the Auger spectrum of a carbonaceous deposit on a metal is a combination of three spectra: two of carbon and one of the substrate. Note that, in particular with Pt and Rh substrates, the characteristic fine-structure of the carbon Auger spectra between 240 and 265 eV interferes with features in the spectra of the metals. The carbon Auger structure in the energy range between 265 and 285 eV, however, is not affected by features from the metals. Hence, visual inspection of this part of the Auger spectrum can be used to draw qualitative conclusions on the type of carbon in the deposit<sup>9,10</sup>.

A more quantitative interpretation can be obtained by fitting the spectrum of a carbonaceous deposit on a metal with a linear combination of the appropriate base spectra from *Figure 1*. The implicit assumption here is that changes in the spectra of the constituents due to chemical interactions can be ignored. It is not *a priori* clear that this requirement is fulfilled, as all Auger transitions of Rh, Ir, Pt, and C in the energy range between 200 and 300 eV involve valence electrons. Nevertheless, the approach has been used successfully before in spectrum subtraction techniques<sup>5-10</sup>, and also in this study the fits appeared to be of acceptable quality.

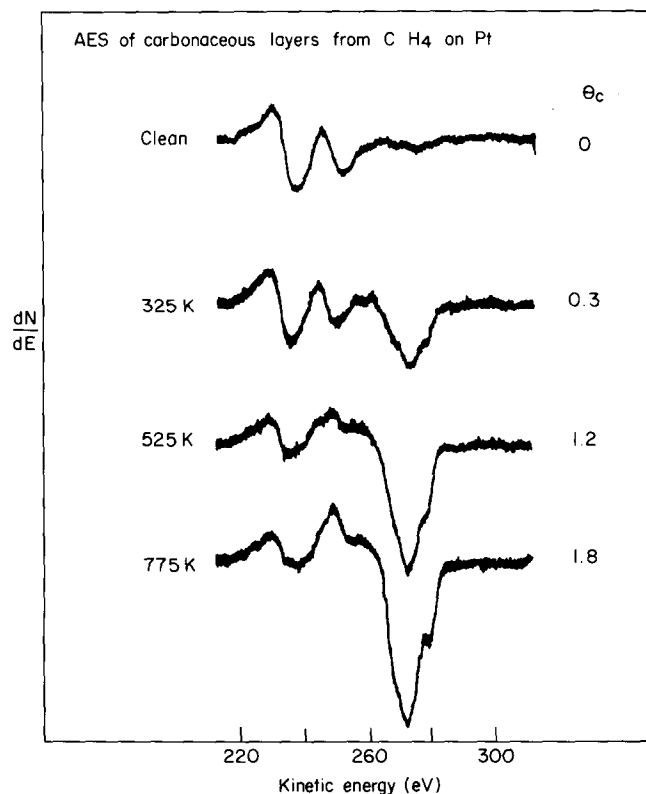
As an example of the AES analysis, Auger spectra of the Pt foil after treatment in 0.5 Torr  $C_2H_4$  at three different

temperatures are shown in *Figure 2*. The carbon coverage, indicated as a fraction of a monolayer, has been derived from the intensity ratio of the C peak at 273 eV and the Pt peak at 237 eV, by assuming that one monolayer corresponds to a ratio  $I(C)/I(Pt)$  of 2.8<sup>1</sup>. This method of estimating the carbon coverage is, although commonly applied, only approximately correct, as the carbon peak shape is not identical in all spectra. Nevertheless, the values are sufficiently accurate to justify the conclusion that the amount of carbon deposited on Pt increases with increasing reaction temperature.

Similar Auger experiments as with Pt have been done with Rh and Ir substrate foils. All spectra have been analysed by fitting them with a linear combination of the base spectra shown in *Figure 1*. The results are given in *Table 1*. For all substrate metals the amount of carbon deposited from ethylene, and the fraction amorphous/graphitic carbon (indicated as %ag in *Table 1*) in the deposit increase with increasing reaction temperature. At each reaction temperature used, the amorphous or graphitic fraction of the carbon is the highest for Pt and the lowest for Rh, with Ir in between.

As described above, AES cannot easily distinguish between molecular and carbide carbon, or between amorphous and graphitic carbon. An important difference between these types of carbon is their hydrogen content. As SIMS is among the few surface sensitive techniques which are capable of detecting hydrogen, SIMS spectra are expected to supply information on the hydrogen content of the deposits.

SIMS spectra of positive ions from adsorbed hydrocarbons<sup>11-15</sup> and carbonaceous deposits<sup>9</sup> on metals contain mainly peaks due to  $CH_n^+$  and  $C_2H_n^+$  ions, at amu 12-15 and 24-29, respectively. The most intense



**Figure 2** Auger spectra of a polycrystalline Pt foil after treatment in  $C_2H_4$  at the temperature indicated. Numbers on the right of the spectra represent the approximate carbon coverage in monolayers

hydrocarbon ions of the negative SIMS spectra are  $C_2^-$ ,  $C_2H^-$  and  $C_2H_2^-$  at 24–26 amu<sup>9,11–14</sup>. Smaller but detectable peaks are observed for  $CH_n^-$  (12–14 amu),  $C_3^-$  (36 amu),  $C_4^-$  (48 amu) and  $C_4H^-$  (49 amu). One of the characteristics of SIMS is that sensitivities can vary enormously between the elements. As a consequence, species present only in trace amounts, such as Na, Al, K, O and Cl, may appear quite clearly in the SIMS spectra. This limits the number of peaks which can be used to characterize hydrocarbon fragments. To avoid ambiguities, only the  $CH_n^+$  peaks of the positive SIMS spectra, and the  $CH_n^-$ ,  $C_2H_n^-$  and  $C_4H_n^-$  ions in the negative SIMS spectra of carbonaceous deposits will be used. It must be noted that secondary ion emission from Ir and Pt, or from Ir- $C_nH_m$  and Pt- $C_nH_m$  clusters could not be detected by our spectrometer when operating under static conditions. Rh and Rh- $C_nH_m$  ions, however, could be detected but have not been used in the present work.

The SIMS patterns of the  $CH_n^+$ ,  $CH_n^-$ ,  $C_2H_n^-$ ,  $C_4H_n^-$  ions are sensitive indicators for the nature of the carbonaceous

deposits. To illustrate this the distributions of secondary ion intensities for each of the substrate metals are shown in Figure 3. Note that the sum of the ion yields within each range has been set equal to 100%, and that comparisons of intensities for ions from different ranges cannot be made.

All hydrocarbons ions indicate that with increasing temperature at which the foils are treated in  $C_2H_4$ , the hydrogen content of the carbonaceous deposits decreases. This tendency is most clearly reflected by the intensity distributions of the  $C_2H_n^-$  and the  $C_4H_n^-$  ions.

It is useful to define a hydrogen content parameter  $h$  as the quotient  $(C_2H^- + C_2H_2^-)/(\sum C_2H_n^-)$ . This entirely empirical quantity varies between 0.8 for adsorbed hydrocarbons ( $CH_4$  on Ir at 300 K) and 0.03 for an almost completely dehydrogenated graphitic overlayer<sup>16</sup>. It is stressed that  $h$  is an empirical parameter which depends, among other things, on the extent of fragmentation caused by the ion beam. Thus, although  $h$  varies sensitively with the hydrogen content of

**Table 1** Carbon coverage, percentage amorphous/graphitic carbon, hydrogen-content parameter, and graphitization parameter of carbonaceous deposits formed from ethylene on Rh, Ir, and Pt

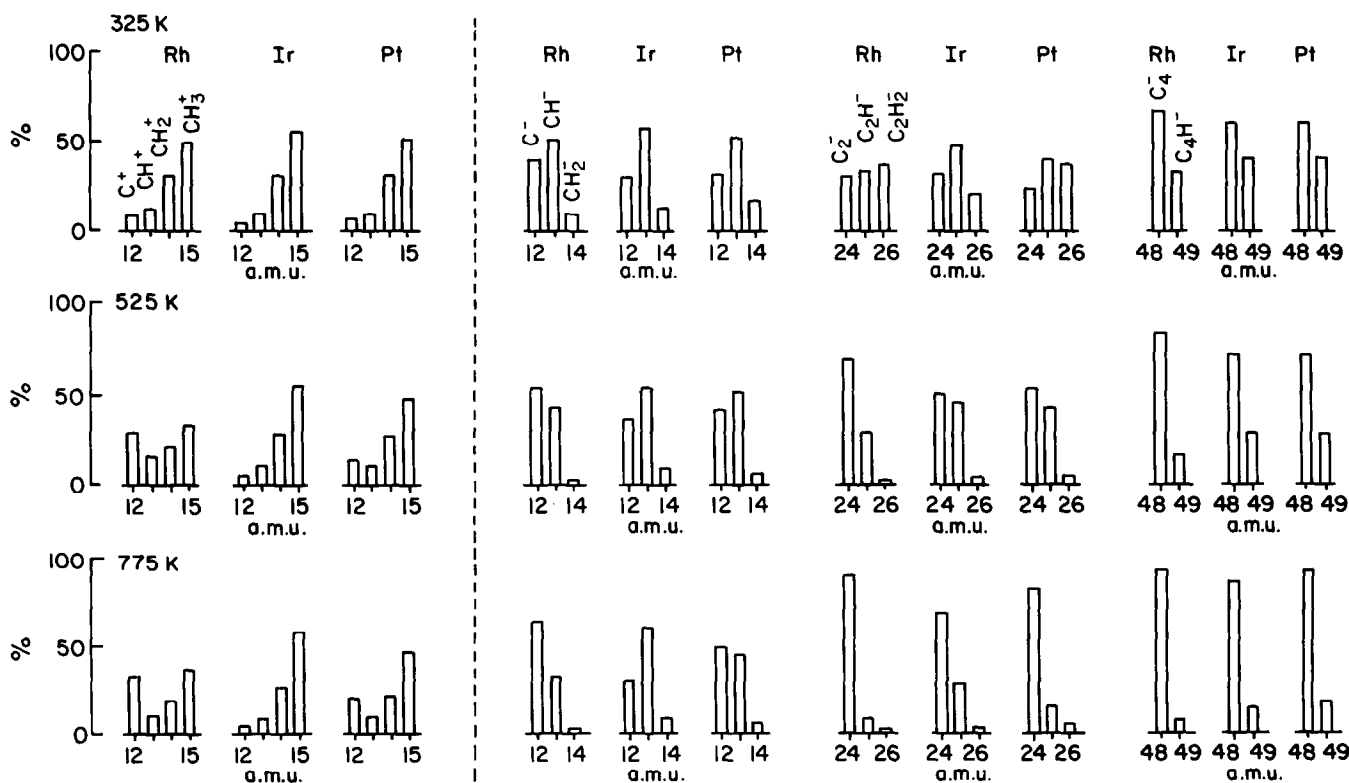
T (K)	Rh				Ir				Pt			
	$\theta_c$	%ag	$h$	$g$	$\theta_c$	%ag	$h$	$g$	$\theta_c$	%ag	$h$	$g$
325	0.4	10	0.70	0.011	0.5	30	0.68	0.014	0.5	35	0.77	0.012
525	0.7	30	0.32	0.020	1.2	50	0.49	0.024	1.2	60	0.47	0.031
775	1.2	70	0.10	0.015	1.4	80	0.32	0.030	1.8	90	0.20	0.047

$\theta_c$ : approximate carbon coverage in monolayers determined from Auger spectra

%ag: fraction amorphous + graphitic carbon determined from Auger spectra

$h$ : hydrogen content parameter determined from SIMS spectra;  $h=0.8$  for adsorbed methane, and about zero for dehydrogenated graphitic carbon

$g$ : graphitization parameter determined from SIMS spectra;  $g$  varies between about zero for a low coverage of adsorbed hydrocarbons and 0.05 for graphitic carbon on Pt



**Figure 3** Distribution of intensities of several hydrocarbon ions in the SIMS spectra of carbonaceous deposits on Rh, Ir, and Pt, formed by exposing the metals to  $C_2H_4$  at the temperatures indicated

carbonaceous overlayers on metals, it is not necessarily equal to the actual hydrogen content. The values of  $h$  for the carbonaceous deposits on Rh, Ir, and Pt are given in *Table 1*.

As was suggested before, the intensity ratio of  $C_4^-$  to  $C_2^-$  ions, called graphitization parameter  $g$  in the following, correlates well with the tendency of the carbon to polymerize into graphitic structures<sup>9</sup>. This parameter varies between  $g=0.01$  for  $C_2H_4$  adsorbed on Pt at 325 K, to 0.05 for graphitic overlayers on Pt. For carbidic carbon on Rh,  $g$  equals about 0.015. *Table 1* shows the  $g$  values for carbonaceous deposits on Rh, Ir and Pt.

## DISCUSSION

The combination of AES and SIMS can successfully distinguish between four types of carbonaceous deposits on metals mentioned in the introduction. AES indicates whether the carbon falls in the categories molecular/carbidic or amorphous/graphitic. Combination with data on hydrogen content and degree of polymerization from SIMS spectra enables further conclusions on the state of the carbonaceous deposits.

For example, as *Table 1* indicates, exposure of Rh, Ir, and Pt to  $C_2H_4$  at 325 K yields Auger spectra which are characteristic of either molecular or carbidic carbon. The high values of the hydrogen-content parameter,  $h=0.7-0.8$ , indicate that the deposit consists mainly of molecular carbon. This is consistent with the fact that  $C_2H_4$  adsorbs in the form of ethylidene,  $\equiv C-CH_3$ , on Rh<sup>17</sup> and Pt<sup>1,15,18</sup>, and most probably also Ir<sup>19</sup>, at 325 K. Note, however, that the Auger spectra indicate that the deposits formed at 325 K also contain some graphitic or amorphous carbon. Whether this is due to electron-beam induced degradation of the molecular carbon, or to chemical reactions in the overlayer, or to a combination of these effects, is not clear.

The data in *Table 1* suggest furthermore that the carbonaceous deposit formed on Rh at 525 K is a mixture of mainly carbidic carbon and some hydrocarbon fragments, whereas the deposit formed at 775 K contains, in view of the low hydrogen content and low degree of graphitization, mainly hydrogen-depleted amorphous and carbidic carbon. Deposits on Pt formed at 775 K are largely graphitic in nature. Carbon deposited on Ir at 775 K is characterized by a lower degree of graphitization and a higher hydrogen content, and has, consequently, a more amorphous character than on Pt. The carbonaceous deposits on Pt and Ir formed at 525 K are very similar, but remain difficult to characterize. The graphitization parameter  $g$  suggests that the amount of graphitic carbon on Pt is larger than on Ir. The hydrogen content for both deposits, however, is almost the same.

It is interesting to compare the properties of the metals with respect to carbon deposition with their catalytic properties. The SIMS data in *Figure 3* and *Table 1* show clearly that carbonaceous deposits formed on Rh contain significantly less hydrogen than on Pt and Ir. This is in agreement with the relatively high activity of Rh for C-H bond breaking reported by Merta and Ponec<sup>20</sup>. For Ir

and Pt substrates, the degree of polymerization of the carbon increases with increasing reaction temperature, for Rh substrates it remains at a low level. Pt is more sensitive for graphite formation than Ir, which is in agreement with work on alumina-supported Pt and Ir catalysts by Carter *et al.*<sup>21</sup>. According to these authors, the lower rate of deactivation caused by deposition of unreactive coke (graphitic carbon in our terminology) on Ir is due to the relatively high hydrogenolysis activity of this metal. The present AES and SIMS results show that the tendency of the substrate metals to promote graphitization decreases in the order Pt - Ir - Rh, which is indeed the order of increasing hydrogenolysis activity for these metals<sup>22</sup>.

The authors believe that AES and SIMS form a powerful combination to characterize carbonaceous deposits on metals. Finally, the techniques can be applied as well to investigate carbonaceous deposits formed from heavier hydrocarbon feedstocks such as naphtha, or even to characterize coal.

## ACKNOWLEDGEMENT

One of the authors (J. W. N.) is supported by a Huygensfellowship from the Netherlands Organization for the advancement of pure research (Z. W. O.).

## REFERENCES

- 1 Somorjai, G. A., 'Chemistry in Two Dimensions: Surfaces', Cornell Univ. Press, Ithaca 1981
- 2 Carlson, T. A., 'Photoelectron and Auger Spectroscopy', Plenum Press, New York, 1975
- 3 Benninghoven, A. *J. Vac. Sci. Technol.* 1985, **A3**, 451
- 4 Brown, A. and Vickerman, J. C. *Surf. Interface Anal.* 1984, **6**, 1
- 5 Hooker, M. P. and Grant, J. T. *Surface Sci.* 1977, **62**, 21
- 6 Smith, M. A., Sinharoy, S. and Levenson, L. L. *J. Vac. Sci. Technol.* 1979, **16**, 462
- 7 Netzer, F. P. *Appl. Surface Sci.* 1981, **7**, 289
- 8 Houston, J. E., Peebles, D. E. and Goodman, D. W. *J. Vac. Sci. Technol.* 1983, **A1**, 995
- 9 Van Langeveld, A. D. and Niemantsverdriet, J. W. *Surf. Interface Anal.*, in press
- 10 Van Langeveld, A. D., Van Delft, F. C. M. J. M. and Ponec, V. *Surface Sci.* 1983, **134**, 98
- 11 Benninghoven, A., Beckmann, P., Greifendorf, D. and Schemmer,
- 12 Benninghoven, A., Beckmann, P., Greifendorf, D. and Schemmer,
- 13 Lauderback, L. L. and Delgass, W. N., ACS Symp. Series 1984, **248**, 22
- 14 Lauderback, L. L. and Delgass, W. W. ACS Symp. Series 1985, **279**, 339
- 15 Creighton, J. R. and White, J. M. *Surface Sci.* 1983, **129**, 327
- 16 Niemantsverdriet, J. W. and Van Langeveld, A. D., unpublished results
- 17 Koestner, R. J., Van Hove, M. A. and Somorjai, G. A. *Surface Sci.* 1982, **121**, 321
- 18 Kesmodel, L. L., Dubois, L. H. and Somorjai, G. A. *Chem. Phys. Lett.* 1978, **56**, 267
- 19 Witt, J. and Nieuwenhuys, B. E. *Surface Sci.* 1982, **119**, 1
- 20 Merta, R. and Ponec, V., Proc. IVth Int. Congr. Catal., 1968, Moscow, 1971, **2**, 53
- 21 Carter, J. L., McVicker, G. B., Weissman, W., Kmak, W. S. and Sinfelt, J. H. *Appl. Catal.* 1982, **3**, 327
- 22 Gates, B. C., Katzer, J. R. and Schuit, G. C. A., 'The Chemistry of Catalytic Processes', McGraw-Hill, New York, 1979, p. 209