

## XPS DETERMINATION OF DIMENSIONS OF METAL CLUSTERS ON SUPPORTS

Tomáš JUŠKA

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received November 26th, 1987

Accepted February 8th, 1988

The applicability of the XPS technique to the indirect determination of the size of metal clusters on supports was tested on two types of the Ag/Al<sub>2</sub>O<sub>3</sub> system. For clusters formed from vapour deposited layers, relations were derived enabling the size to be determined from photoemission line intensities of the metal measured after deposition at liquid nitrogen temperature and after heating to 25°C or 400°C. For metal clusters on supported Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts, their size was estimated by using two models, *viz.* the Kerkhof-Moulijn model and the Kuipers-van Leuven-Visser model. Spherical and hemispherical shapes of the clusters were assumed for the two Ag/Al<sub>2</sub>O<sub>3</sub> systems, and the results were confronted with electron microscopy photographs. The Kuipers-van Leuven-Visser model applied to the supported catalyst was found to fit the reality better than the Kerkhof-Moulijn model.

Metals dispersed on supports are known to frequently form clusters whose size depends on the strength of the metal-support interaction and also on the temperature of the support and amount of dispersed metal. Cluster size is an important parameter, the physical and chemical properties of tiny metal particles being often very different from those of the bulk metal<sup>1</sup>. Direct observation of small clusters whose size is in the order of nanometers is hampered by the insufficient resolving power of routine electron microscopes, not to mention problems arising from the fact that owing to their reactivity, clusters of some metals have to be kept in a high vacuum.

The aim of the present work is to examine the possibility of determining the cluster size indirectly, based on their photoelectron spectra (the XPS technique has been described, e.g., in refs<sup>2,3</sup>). The advantage of this approach is in the facts that the clusters can be prepared directly inside the spectrometer and that an XPS study affords information of various kind, of which the cluster size is only a part. The spectral characteristics that will be employed for the determination of the cluster size are the photoemission line intensities of the metal and of a suitable element of the support. The applicability of the XPS technique is tested on two somewhat different systems that will be treated separately, *viz.* a support-vapour deposited metal system and a supported catalyst system. Both contain Ag as the metal and Al<sub>2</sub>O<sub>3</sub> as the support, the catalyst being known to find wide application in the chemical industry.

## THEORETICAL

For establishing the cluster size of a vapour deposited metal, the photoemission line intensities  $I_M^0$  and  $I_M$  are determined for the metal at two different temperatures of the system,  $t_0$  and  $t$ , respectively. Temperature  $t_0$  is the temperature at which the metal is deposited, and it is so chosen that the metal is either dispersed in a form approaching the atomic state or it is arranged in layers whose thickness can be determined. Liquid nitrogen temperature was conceived to suit this purpose. Temperature  $t$  was room temperature (25°C) or 400°C. The line intensity decreases on heating because, due to aggregation, attenuation of photoemission from atoms that do not lie at the cluster surface starts to play a role. This attenuation can be described by an exponential function in the form

$$dI_M = (I_M^0/V_c) \exp(-z/\lambda_M) dV, \quad (1)$$

where  $V_c$  is the cluster volume,  $z$  is the distance of the emitting volume element  $dV$  from the cluster surface in the chosen direction of photoemission and  $\lambda_M$  is the mean free path of the electron in the metal. The description of the attenuation by means of a continuous function is only approximate, the metal being actually arranged in discrete layers of a thickness  $d_0$ , each of which reduces the photoemission to the value  $\exp(-d_0/\lambda_M)$ . The approximation can be improved by multiplying the right side of Eq. (1) by  $\exp(d_0/2\lambda_M)$ ; such a refined function is used in the subsequent treatment. For relating the experimental  $I_M/I_M^0$  ratio to the dimensions of the clusters formed, some assumptions concerning their shape must be made. A model was set up treating clusters of spherical or hemispherical shape deposited on a planar substrate. For spherical clusters of a radius  $R$ , the  $V_c$ ,  $z$  and  $dV$  quantities in Eq. (1) can be expressed in terms of spherical coordinates to obtain the relation

$$I_M/I_M^0 = (3\lambda_M/2R^3) \exp(d_0/2\lambda_M) \int_0^R (1 - \exp[-2\sqrt{(R^2 - r^2)}/\lambda_M]) r dr. \quad (2)$$

This equation is analytically unsolvable with respect to  $R$ , so that a numerical method has to be employed.

For hemispherical clusters, the relation is considerably more complex, *viz.*

$$\begin{aligned} \frac{I_M}{I_M^0} = \frac{3}{2\pi R^3} \exp\left(\frac{d_0}{2\lambda_M}\right) \int_0^R \int_0^\pi \int_0^\pi \exp\left(-\frac{\sqrt{(R^2 - r^2 \cos^2 \theta - r^2 \sin^2 \theta \sin^2(\alpha - \varphi))}}{\lambda_M} + \right. \\ \left. + \frac{r \sin \theta \cos(\alpha - \varphi)}{\lambda_M}\right) r^2 \sin \theta dr d\varphi d\theta, \quad (3) \end{aligned}$$

where  $\alpha$  is the angle between the direction of photoemission and the substrate plane. This equation is also analytically unsolvable and moreover, it has to be solved for

a particular angle  $\alpha$ , which is not included in Eq. (2) owing to the spherical symmetry of the clusters. The functional dependences  $I_M/I_M^0(R)$  for clusters of the two shapes are shown in Fig. 1.

The approach to the determination of the cluster size for supported catalysts is different from the above procedure because the aggregation of the metal has been accomplished during the catalyst preparation. Again, however, assumptions must be made concerning the cluster shape and support topography, and moreover, the catalyst composition must be available from independent measurements. Two models enabling the cluster size to be calculated will be dealt with. In the earlier Kerkhof–Moulijn model<sup>4</sup> (henceforth referred to as the KM model), the catalyst is considered as consisting of parallel support layers of equal thickness  $h$ , interspersed by cubic metal crystallites with the edge  $c$ . Thickness  $h$  is related to the specific surface area of the support  $\sigma_s$  and density  $\rho_s$  as  $h = 2/\sigma_s \rho_s$ . For  $c \gtrsim 3\lambda_M$ , the relation

$$c = (I_S/I_M) (M/S)_A (S_M/S_S) [\lambda_M / (2\lambda_S \sigma_s \rho_s)] \quad (4)$$

has been derived;  $I_S$  and  $I_M$  are the photoemission line intensities of a suitable element from the support and of the metal, respectively,  $(M/S)_A$  is the atomic ratio of the metal to the element from the support,  $S_M$  and  $S_S$  are sensitivity factors and  $\lambda_S$  is the mean free path of electrons in the support.

The more recent Kuipers–van Leuven–Visser model<sup>5</sup> (henceforth the KLV model) includes the effect of the random orientation of the support surface on which the metal is deposited in the form of a layer or spheres or hemispheres. In the case of spherical or hemispherical particles, their diameter  $D$  can be described by the relation

$$D = f[3c_M(P + P^\infty)]/[P\rho_M\sigma_s(1 - c_M)], \quad (5)$$

where  $P = I_M/I_S$ ,  $P^\infty = I_M^\infty/I_S^\infty$  (the superscript refers to the pure metal or pure sup-

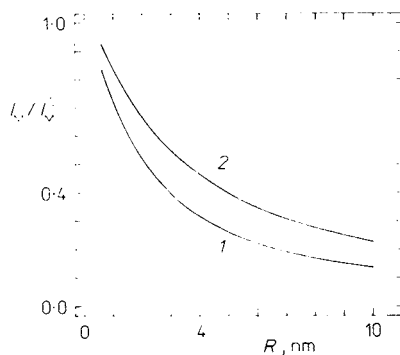


FIG. 1  
 $I_M/I_M^0(R)$  dependence for spherical (1) and hemispherical (2) Ag clusters on  $\text{Al}_2\text{O}_3$ . Eqs (2) and (3) are solved for  $d_0 = 0.257$  nm,  $\lambda_M = 1.78$  nm,  $\alpha = 45^\circ$

port),  $c_M$  is the weight fraction of the metal in the catalyst and  $\rho_M$  is the density of the metal; factor  $f$  is 1 for spheres and  $3/2$  for hemispheres. Eq. (5) again holds true assuming that  $D \gtrsim 3\lambda_M$ .

## EXPERIMENTAL

The applicability of Eqs (2) and (3) was tested in the following experiment. Silver in an increasing concentration series was vapour deposited at liquid nitrogen temperature onto a thin ( $\sim 6$  nm) layer of  $\text{Al}_2\text{O}_3$  obtained by oxidation on an aluminium sheet directly in the spectrometer. The surface concentrations of Ag were  $0.03d_0$ ,  $0.24d_0$  and  $10d_0$ . For Ag,  $d_0 = 0.257$  nm and the monolayer contains approximately  $1.2 \cdot 10^{15}$  atoms  $\text{cm}^{-2}$ . For all samples, the Ag 3d photoemission line intensities were measured at liquid nitrogen temperature, at  $25^\circ\text{C}$  and after heating, at  $400^\circ\text{C}$  for 30 min.

For verifying the validity of the KM and KLV models, a series of Ag/ $\alpha$ - $\text{Al}_2\text{O}_3$  catalysts containing 0.28 to 5.47 wt. % Ag was used. Samples were deposited onto the holder in a powder form, and the Ag 3d and Al 2s photoemission lines were measured.

The photoelectron spectra were measured on an ESCA 3 Mk II spectrometer (VG Scientific) at  $E_{\text{pass}} = 20$  eV,  $p = 10^{-7} - 10^{-6}$  Pa, Al  $K_\alpha$  excitation radiation. The photoemission line intensities were evaluated by area measurement.

## RESULTS AND DISCUSSION

We will first deal with the vapour deposited metal-support system. The  $I_M/I_M^0$  intensity ratios and calculated radii for spherical and hemispherical clusters are given in Table I; the value of 1.78 nm, obtained by calculation<sup>6</sup>, was taken for  $\lambda_M$ .

For the two lower depositions, the  $I_M/I_M^0$  ratio is unity at  $25^\circ\text{C}$ , which indicates that the metal remains dispersed in a form close to the atomic state. The marked intensity drop for the lowest deposition after heating to  $400^\circ\text{C}$ , on the other hand, is unexpected, and we feel that at so low concentration of Ag this drop cannot be accounted for by the formation of clusters of the given size; rather, it is due to diffusion of silver into the substrate; the cluster size then cannot be determined. This diffusion occurs probably in all cases, at higher depositions, however, its effect can be disregarded.

After finishing the experiment, the sample with the highest concentration of silver was investigated on a scanning electron microscope. The observed radius of the silver particles was about 10 nm. This value agrees very well with the calculated radius of hemispherical clusters  $R_h$  whereas it differs considerably from the calculated radius of spherical clusters  $R_s$ . From this we deduce that hemispheres approach the actual shape of clusters in the system studied more closely.

It should be noted that the described procedure for the determination of the cluster size has some limitations as follows. 1. If the cluster size is tens of nm, the  $I_M/I_M^0$  ratio varies very slowly with  $R$ , and the calculated value of  $R$  can involve a high error. 2. For clusters several tenths of nm in size, Eqs (2) and (3) will fail because

TABLE I

$I_M/I_M^0$  intensity ratios ( $t_0$  is liquid nitrogen temperature) and radii of spherical ( $R_s$ ) and hemispherical ( $R_h$ ) clusters (in nm) calculated from Eqs (2) and (3), respectively

Amount of Ag	$I_M/I_M^0$		$R_s$		$R_h$	
	25°C	400°C	25°C	400°C	25°C	400°C
0.03 $d_0$	1	0.5	— <sup>a</sup>	2.2	— <sup>a</sup>	3.9
0.24 $d_0$	1	0.924	— <sup>a</sup>	0.3	— <sup>a</sup>	0.6
10 $d_0$	0.286	0.239	4.5	5.5	7.5	9.3

<sup>a</sup> Atoms or clusters consisting of several atoms.

TABLE II

Comparison of size of Ag clusters (in nm) calculated from Eqs (4) and (5) and observed by electron microscopy for a series of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts

$w_{Ag}$ wt. %	Kerkhof–Moulijn model	Kuipers–van Leuven– –Visser model	Electron microscope
0.28	15	39	40
1.5	47	122	—
1.87	39	106	80–120
2.45	46	127	—
3.62	50	144	—
5.47	66	197	140–200

TABLE III

Effect of the shape of distribution of cluster size on the mean value of their diameter  $D_E$  (in nm) obtained from XPS data,  $D_{max} = 100$  nm;  $b$  is asymmetry parameter ( $-1 < b < 1$ )

Half width nm	Gaussian distribution	Lognormal distribution		
		$b = 0.25$	$b = 0.5$	$b = 0.75$
20	101.6	104.5	108.9	117.0
40	105.6	112.2	123.0	145.5
80	120.9	135.5	163.0	208.8

the attenuation of photoemission from atoms inside the clusters no more follows a continuous function (see Eq. (1)). 3. The procedure fails if the actual shape of the clusters does not approach spheres or hemispheres.

Now, let us deal with the supported  $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$  catalyst. This catalyst possesses a low specific surface area, about  $0.41 \text{ m}^2 \text{ g}^{-1}$  in our case, so that the surface concentration of silver is high enough for clusters of a size meeting the conditions of validity of Eqs (4) and (5) to be formed. The photographs give evidence that the shape of the clusters is nearly spherical. The calculated sizes and those found from microscopic investigation are given in Table II. It is evident that the observation agrees well with calculation in terms of the KLV model whereas it disagrees with the data obtained from the KM model. Clearly, the KM model is too crude approximation, inapplicable to the studied type of catalyst with a low specific surface area.

The KLV model was also used for other series of catalysts of  $\text{Ag}/\text{Al}_2\text{O}_3$  type, and we must admit that not always was the agreement between calculated and observed data so good as for the series treated above. We believe that one of the reasons for this is in the fact that the cluster size in a real catalyst is not unique for all clusters; rather, the size follows some distribution, dependent on the way of preparation. Microscopic observation affords the diameter of particles with the highest frequency of occurrence,  $D_{\text{max}}$ , and in some instances an estimate of the width of the distribution. Calculations from the XPS data, on the other hand, only give a mean value  $D_E$  for which the relationship  $D_E = (D^3)_{\text{mean}}/(D^2)_{\text{mean}}$  can be derived; i.e.,  $D_E$  is the ratio of the statistical means of the third and the second powers of the cluster diameters. The  $D_E$  value will be the more different from  $D_{\text{max}}$  the broader and more asymmetric the distribution is. This effect is demonstrated on a model case of a Gaussian and a lognormal<sup>7</sup> distribution of  $D$  at a constant  $D_{\text{max}}$ . The  $D_E$  values calculated for various parameters of the two distributions are given in Table III. It is clear that whereas for the symmetric Gaussian distribution the  $D_E - D_{\text{max}}$  difference is not too marked with respect to the accuracy of  $D_{\text{max}}$  determination, for the asymmetric lognormal distribution this difference, in dependence on the parameters, can be quite substantial.

It should be mentioned that also within the KM model, an analogous relation as for  $D_E$  in the KLV model can be derived for  $c_E$ , i.e.,  $c_E = (c^3)_{\text{mean}}/(c^2)_{\text{mean}}$ . However, the differences between the calculated and observed data are so high that they cannot be explained in terms of the cluster size distribution. Apparently, the  $\text{Ag}/\text{Al}_2\text{O}_3$  system fails to satisfy all assumptions underlying the KM model.

*The author wishes to express his thanks to Dr. M. Maryška of the Prague Institute of Chemical Technology for electron microscope photographs of the systems studied.*

#### REFERENCES

1. Petrov Yu. I.: *Klastery i malye chastitsy*. Nauka, Moscow 1986.
2. Carlson T. A.: *Photoelectron and Auger Spectroscopy*. Plenum Press, New York 1975.

3. Nemoshkalenko V. V., Aleshin V. G.: *Elektronnaya spektroskopiya kristallov*. Naukova dumka, Kiev 1976.
4. Kerkhof F. P. J. M., Moulijn J. A.: *J. Phys. Chem.* *83*, 1612 (1979).
6. Kuipers H. P. C. E., van Leuven H. C. E., Visser W. M.: *Surf. Interface Anal.* *8*, 235 (1986).
6. Seah M. P., Dench W. A.: *Surf. Interface Anal.* *1*, 2 (1979).
7. Fraser R. D. B., Suzuki E.: *Anal. Chem.* *41*, 37 (1969).

Translated by P. Adámek.