

Nucleation and growth kinetics of Pd and CuPd particles on NaCl(100)[†]

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Pd and CuPd nanometric particles have been grown by UHV condensation of the metal beams on UHV-cleaved NaCl(100) surfaces. The nucleation and growth kinetics have been determined from TEM measurements of the size distribution while the chemical composition has been determined by EDX. From these measurements the mechanisms of the nucleation and growth have been determined. The nucleation of the bimetallic particles is chiefly controlled by the Pd adatoms. The Pd atoms are essentially incorporated in the bimetallic clusters by a diffusion-capture mechanism while Cu atoms are mainly incorporated by direct impingement on the clusters. Thus the composition of the bimetallic particles changes during the deposition time from pure Pd in the early stages to a progressive increase of the Cu concentration. The difference between the adsorption and diffusion energies of an adatom on NaCl has been determined for the two metals.

Bimetallic catalysts are now used in industry. They are often based on Pd or Pt to which a second metal is added.¹ They are used mainly as reforming catalysts. Their advantages are a higher selectivity and being less prone to poisoning by carbonaceous deposits.^{1–3} Cu–Pd catalysts could be interesting as alternative catalysts for depollution⁴ or methanol synthesis.⁵ From a fundamental point of view it is interesting to know the origin of the particular catalytic properties of alloy catalysts. Numerous studies have been undertaken on bulk alloy surfaces in order to disentangle the geometric (site or ensemble) and electronic (ligand) effects.³ However, the results of these studies cannot be simply transferred to real catalysts, which are made from small particles in which the surface segregation can be very different and which also can be strongly influenced by adsorption, which is often size dependent. Therefore, surface science studies on particulate alloys are needed. Bimetallic catalysts are generally obtained by co-impregnation with metal salts⁶ or, more recently, by decomposition of organometallic compounds.^{7–9} However, these wet preparation methods are not well-suited for UHV studies with surface science techniques. Alternatively, it is possible to form alloy particles or thin films by condensing in vacuum vapour beams of the two metals. However, it is difficult to get a uniform collection of alloy particles by this method.^{5,10} From several studies on the nucleation of AuCu,¹¹ AuAg, AuPd and AgPd^{12–14} on NaCl(100), Anton and coworkers have clearly shown that the concentration in the bimetallic particles depends, in a complicated way, on the intensity of the vapour beams, on the deposition time and on the substrate temperature. In this paper we present new results on the nucleation and growth kinetics of PdCu particles on NaCl(100). We will show that the nucleation is mainly controlled by the palladium and that the copper atoms are incorporated essentially by direct impingement of the vapour atoms on the already formed particles.

Experimental

The experimental setup and the experimental methods used in this study are described in detail elsewhere,¹⁵ thus only a brief

description will be given here. NaCl single crystals are mechanically cleaved in the UHV deposition chamber at a base pressure of 3×10^{-9} Torr. The Pd and Cu atomic beams are obtained from two Knudsen cells in order to control independently the two fluxes by adjusting the two oven temperatures. The two evaporation cells have been calibrated, *in situ*, by a quartz microbalance. The deposition time for the two beams can be adjusted by two shutters. During the deposition the NaCl substrate was kept at a constant temperature between 300 and 700 K. At the end of the deposition the sample was covered *in situ* by a thin (few tenths of nanometers) carbon film. The carbon film containing the particles is separated from the substrate by interfacial dissolution in distilled water and mounted on electron microscopy nickel grids. The collections of particles have been subsequently observed in a JEOL 2000FX transmission electron microscope (TEM) operating at 200 KV. The size distributions of the particles were obtained from analysis of the TEM pictures on at least 1000 particles. The crystal structure of the particles and the epitaxial relationships were obtained by electron diffraction (TED) on several hundreds of particles. The structure of individual particles has been studied by HRTEM (high resolution TEM), these results are reported elsewhere.^{16,17} The composition of the particles was measured by energy dispersive X-ray analysis (EDX) coupled to TEM. It has been carefully checked that during the TEM observation no preferential evaporation of one component occurred. The homogeneity of the chemical composition in the collections of particles was checked by varying the analysed area. The smallest area corresponded to a few particles, or even one particle (for the largest ones). It has been checked that between CuPd particles separated by a large distance no metal was detected, within the detection limit of the apparatus. For the composition measurements the accuracy was between 3 and 6%, depending on the particle mean size.

Results

Pure Pd particles

In order to get well-shaped particles it is necessary to grow them at high temperature. However, to avoid evaporation of the NaCl substrate we have prepared the particles at a substrate temperature of 553 K. The nucleation kinetics of Pd on

[†] Non-SI units employed: 1 Torr \approx 133 Pa, 1 eV \approx 9.65×10^4 J mol⁻¹.

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NaCl(100) obtained at 553 K for a Pd beam intensity of 1×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$ is represented on Fig. 1. The number density of Pd clusters grows rapidly in the beginning of the condensation and saturates at about 150 s. The saturation density is 7.8×10^{10} particles cm^{-2} . The saturation density decreases when the substrate temperature increases. This behaviour is typical for the nucleation of metals on an insulator.¹⁸

Fig. 2 shows the growth kinetics obtained with the same conditions as for Fig. 1. The diameter of the particles follows a power law with deposition time, which is written as:

$$d = 0.84t^{0.4} \quad (1)$$

The Pd particles have a square outline and their 3D shape is a truncated pyramid.¹⁹ Knowing the shape of the particle it is possible to calculate the (integral) condensation coefficient, which is equal to the ratio of the number of atoms effectively condensed in the particles to the number of impinging atoms. At 553 K it is equal to 0.3 after 4 min deposition. It is noteworthy that this coefficient is smaller than unity, which is generally the case for the growth of metal on insulators at high temperature.¹⁸ From TED the Pd particles are perfectly epitaxial in the (100) orientation.

Pure copper particles

The study of the nucleation of Cu particles is difficult by TEM because, firstly, the contrast of the particles is very weak and, secondly, during the dissolution of the substrate in water to remove the carbon replica, the Cu particles are severely oxidized such that quantitative measurements cannot be achieved. However, in order to get some information on this

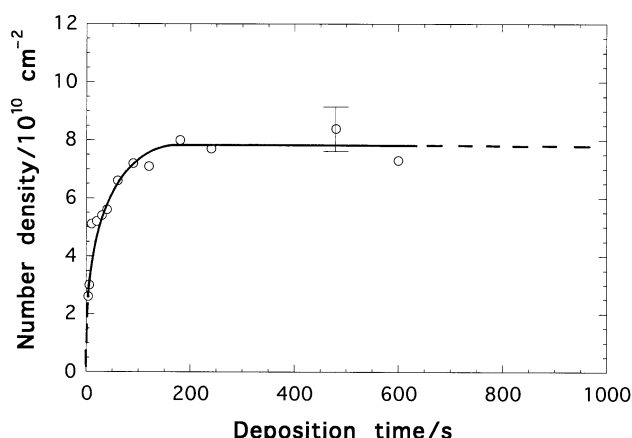


Fig. 1 Nucleation kinetics of Pd on NaCl(100) at 553 K and for a Pd flux of 1×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$

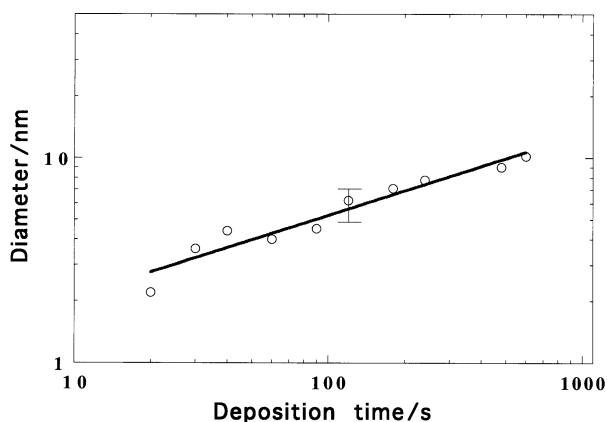


Fig. 2 Growth kinetics of Pd on NaCl(100) at 553 K and for a Pd flux of 1×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$

system we have used the microcleavage technique, which avoids the dissolution stage. In this case tiny parts of the NaCl support are observed by TEM; thus, both the Cu particles and the NaCl substrate are observed simultaneously. However, with this technique it is very time consuming to get statistically significant results because the parts of the sample that are sufficiently thin to be transparent to the electron beam are scarce. As the condensation coefficient of Cu on NaCl is much lower than the one of Pd we have increased the deposition rate by a factor of 8 in order to observe easily the particles by TEM. For the above mentioned reasons, it has not been possible to get complete nucleation and growth kinetics curves. The saturation density at 553 K was estimated to be around 6×10^{10} particles cm^{-2} . The condensation coefficient, at this temperature, after 4 min of deposition (mean cluster size: 3 nm, cluster density: $4.4 \times 10^{10} \text{ cm}^{-2}$) is only 0.0014.

CuPd particles

As seen in the previous sections the condensation coefficients of Pd and Cu on NaCl are very different. If we condense simultaneously Pd and Cu, using the same deposition rate for both metals, practically pure Pd particles are obtained. Alternatively, we can increase the deposition time for copper, but in this case HRTEM showed that the particles were inhomogeneous, probably with a core rich in Pd and a skin rich in Cu. As the objective of this study was to get homogeneous alloy particles we have condensed simultaneously the two metals but we increased progressively the intensity of the copper beam. All the following results have been obtained with a Pd flux of 1×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$ and a Cu flux of 8×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$. Fig. 3 and 4 present the nucleation and growth kinetics obtained at 553 K. The nucleation kinetics is very similar to the case of pure Pd but the saturation density is a little higher: 8.8×10^{10} particles cm^{-2} . The growth kinetics can be also expressed by a power law similar to that obtained with pure Pd:

$$d = 0.88t^{0.42} \quad (2)$$

Fig 5 displays the variation of the Cu concentration in the particles as a function of the deposition time. It is worth noting that the composition of the particles is not constant. The Cu concentration increases with the deposition time. After 10 min it is still below the proportion of Cu in the vapour beam (89%). Fig. 6(a) shows a micrograph of the CuPd particles. They have a square outline, like pure Pd, and probably the same truncated pyramid shape. The size distribution [see Fig. 6(c)] is rather broad. Its relative width $\Delta d/d = 26\%$, a little larger than for pure Pd. From the electron

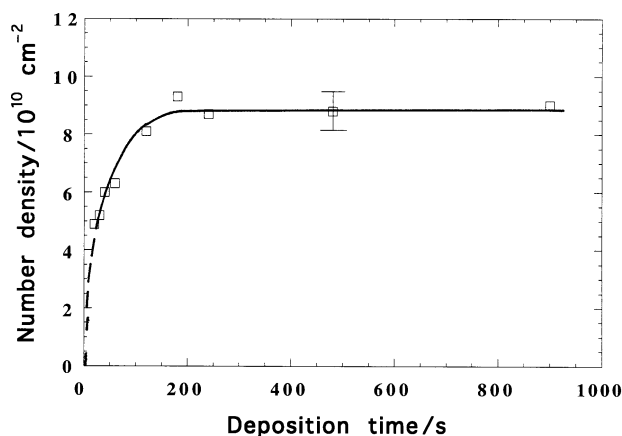


Fig. 3 Nucleation kinetics of CuPd bimetallic particles on NaCl(100) at 553 K. The intensities of the Pd and Cu beams were 1×10^{13} and 8×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$, respectively

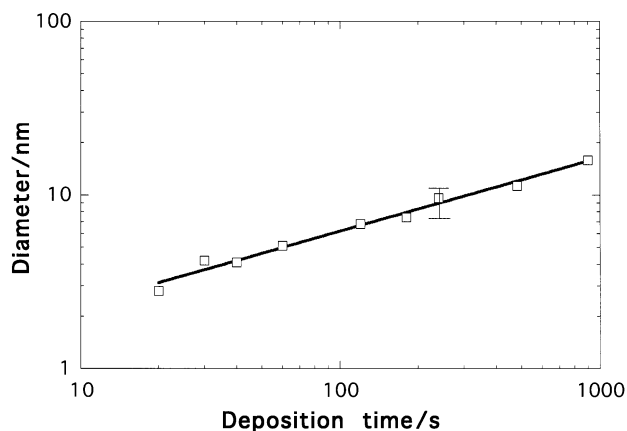


Fig. 4 Growth kinetics of CuPd bimetallic particles on NaCl(100) at 553 K. The intensities of the Pd and Cu beams were 1×10^{13} and 8×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$, respectively

diffraction diagram [see Fig. 6(b)] the structure of the CuPd particles is fcc. This means that they have the structure of the disordered alloy (solid solution), although from the bulk phase diagram²⁰ the disordered phase is obtained only at temperatures above 773–873 K for the considered concentration (around 50% Cu). HRTEM observations have confirmed the disordered alloy structure and have shown that the CuPd particles were homogeneous single crystals.^{16,17} The fact that the particles have the structure of the disordered alloy is probably due to a kinetic limitation related to the growth mechanism. With another preparation method ordered alloy particles have been obtained at low temperature.²¹ From TED, the CuPd particles smaller than 5 nm have the (100) epitaxial orientation while larger particles can be either in the (110) or (111) orientations.^{15,17} After annealing at 638 K the particles become chemically ordered (they adopt the bcc structure of the β -phase of bulk CuPd) but they lose their epitaxial orientation.^{15–17}

Discussion

From the above measurements the nucleation of CuPd particles resulting from the condensation of the two metals is not very different from the nucleation of pure Pd. The growth kinetics are also very similar. However, the most striking result is that the chemical composition of the bimetallic particles depends strongly on the deposition time. The concentration of copper increases continuously from about 20% to 60% and stays (for the considered range of deposition time) far below the composition expected from the ratio of the metal

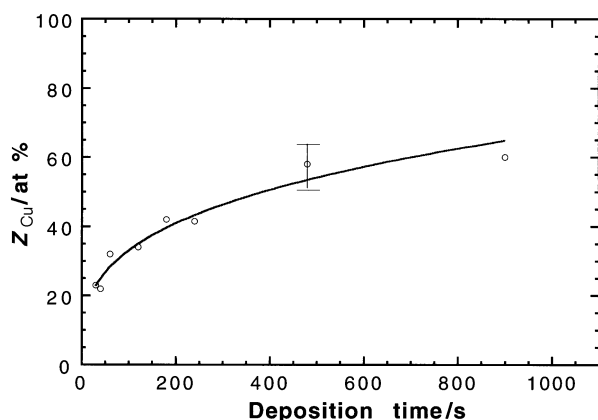


Fig. 5 Evolution of the Cu concentration in the CuPd particles as a function of the deposition time. The experimental conditions are the same as for Fig. 3 and 4

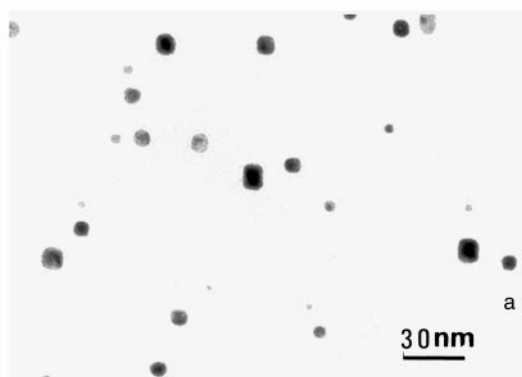
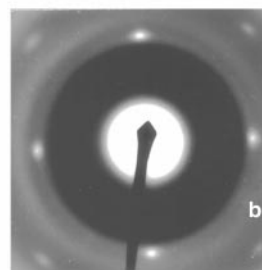
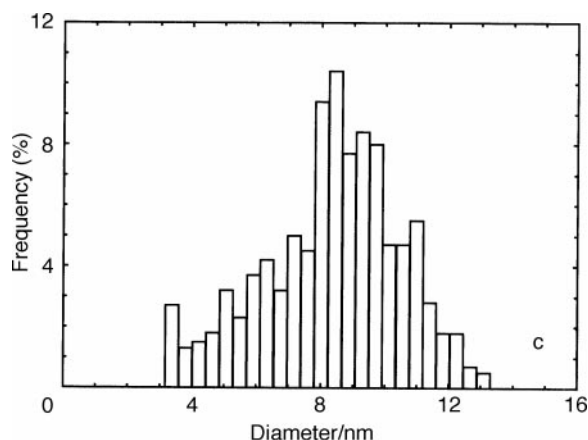


Fig. 6 A typical collection of CuPd particles obtained at 553 K: (a) micrograph, (b) electron diffraction diagram, (c) size distribution. The mean size and the size dispersion are 8.3 nm and 26%, respectively

fluxes (89% Cu). This result has to be related to the very low condensation coefficient of pure Cu compared to pure Pd. In fact, a large proportion of the Cu atoms reevaporate before being incorporated in the already formed metal particles. The low condensation coefficient of Cu on insulator substrates, such as MgO , SiO_2 and Al_2O_3 , has already been pointed out by several authors.^{22–24} The lack of condensation of Cu atoms can be due either to an imperfect accommodation on the substrate or to the small diffusion length of the adatoms, which desorb before reaching an existing cluster. It is known that some metals with low melting points like Cd, Hg or Zn are not completely accommodated on alkali halide substrates.^{25–28} This was directly evidenced by the presence of an important quasi-specular lobe in the angular distribution of the scattered metal atoms. Conversely, noble metals like Ag are scattered randomly on alkali halide single crystals²⁹ while the condensation coefficient is smaller than unity. In the last case the lack of condensation is attributed to the small residence time of the adsorbed atoms because the cosine distribution is indicative of complete thermal accommodation diffuse scattering on a rough surface leading to a cosine distribution²⁸ can be ruled out because the alkali halide crys-

tals were cleaved *in situ*²⁹). For Cu on NaCl a behaviour close to that of Ag is expected. This is also supported by the fact that the condensation of Cu decreases very quickly when the temperature increases, in agreement with nucleation theory in the incomplete condensation regime,³⁰ while for the case of non-thermal accommodation only weak variations are expected.²⁸

Now the mechanism of the nucleation and growth of the CuPd particles can be sketched as follows. The Pd and Cu impinging atoms adsorb on the NaCl substrate, where they stay for a lifetime τ varying exponentially with the adsorption energy:

$$\tau = (1/\nu)\exp(E_{ad}/kT) \quad (3)$$

where ν is the frequency factor (on the order of 10^{13} Hz), E_{ad} is the adsorption energy of an atom, T is the temperature of the substrate and k is the Boltzmann constant. During their stay on the substrate the adsorbed atoms diffuse with the diffusion coefficient D :

$$D = (a^2\nu/4)\exp(-E_d/kT) \quad (4)$$

where a is the distance between two neighbouring adsorption sites and E_d the diffusion barrier height. The mean distance travelled by an adsorbed atom before desorption is given by the Einstein relation:

$$\lambda = (D\tau)^{1/2} = (a/2)\exp[(E_{ad} - E_d)/2kT] \quad (5)$$

It is noteworthy that the diffusion length increases when the temperature decreases because it is limited by the desorption. Assuming that the adsorption energy of Cu is significantly lower than that of Pd (which is reasonable taking into account the *ab initio* calculations for Cu and Pd on MgO³¹) the lifetime and the diffusion length of Cu atoms must be much smaller than those of Pd. As a result, the density of Cu adatoms will be much smaller than that of Pd. If the size of the critical cluster is one atom (which is generally the case for the considered systems³⁰), the nucleation rate will be proportional to the probability of encounter of two adatoms. Taking into account the large difference of adatom density of the two metals, mainly pure Pd clusters will nucleate; thus the nucleation of CuPd will not be very different than that of pure Pd. The stable nuclei formed grow either by capture of diffusing adatoms or by direct impingement from the vapour.³⁰ The latter contribution, being proportional to the projected area of the clusters, becomes more important at the later stages of growth and it is proportional to the impinging flux of each metal (one assumes a unity metal-on-metal sticking coefficient). The former contribution will be proportional to the perimeter of the cluster and to the mean diffusion length; thus, it is relatively more important at the beginning of the growth and it is much more important for Pd than for Cu. Thus, the increase of the concentration of Cu with cluster size is now understandable. At the nucleation stage, mainly pure Pd clusters are formed because, when they grow, essentially Pd atoms are incorporated, direct growth being negligible at small sizes. As the clusters become bigger the fraction of direct growth increases and as the flux of Cu is eight times higher than that of Pd the concentration of Cu increases.

In order to be more quantitative we have tried to determine the mean diffusion lengths λ_{Pd} and λ_{Cu} corresponding to Pd and Cu adatoms, respectively. λ_{Pd} has been determined from the growth kinetics (Fig. 2). In the case of steady-state growth and for a constant density of clusters, the growth kinetics can be calculated from the atomistic nucleation and growth theory.³⁰ We have used the numerical model developed recently,³² which contains only one unknown parameter, the difference $E_{ad} - E_d$. This model assumes that the clusters are distributed on a square lattice and that the density of adatoms around a cluster is stationary but depends on the radial distance

from the clusters. Both direct and diffusion-capture growth mechanisms are taken into account. Fig. 7 shows the calculated growth kinetics for λ varying from 6 to 15 nm, together with the experimental radius of the Pd particles. We have started the calculation when the saturation density of clusters was reached (at 90 s). From the comparison between the experimental data and the calculated curves a value of $\lambda_{Pd} = 7.5 \pm 1$ nm is determined. From this value one can calculate two important parameters of the growth, $x = R/\lambda$ and $y = L/\lambda$, here R and L are the radius and the mean half-distance between two neighbouring clusters, respectively. L is calculated from the saturation density of clusters ($L = 1/\sqrt{n_s}$). Then $y = 4.7$, which means that the clusters are not in competition for the capture of adatoms or that the clusters behave like isolated clusters.³² From the value of x (between 0.20 and 0.66) the growth model³² predicts that the exponent of the power law, which expresses the growth kinetics, should be between 0.39 and 0.44, in good agreement with the experimental value of 0.40.

λ_{Cu} cannot be determined from the growth kinetics of pure Cu because of the experimental difficulties mentioned above. The mean diffusion length of the Cu adatoms has been determined from the variation with deposition time of the chemical composition in the CuPd clusters (Fig. 5). The Cu concentration is equal to the ratio of the number of Cu atoms, N_{Cu} , to the sum of the numbers of Cu and Pd atoms ($N_{Cu} + N_{Pd}$) in a CuPd particle. $N_{Cu} + N_{Pd}$ is calculated from the experimental size of the particle and assuming a hemispherical shape. The lattice parameter of the CuPd particles is assumed to be equal to those of the bulk fcc solid solution with the actual composition (measured experimentally). Then N_{Cu} is obtained from the experimental measurements of the Cu concentration. Alternatively, N_{Cu} can be calculated by a simple growth model. The direct growth contribution is easily calculated from the knowledge of the actual particle size, which is given by the experimental growth kinetics (Fig. 4). We have seen that for pure Pd the growing particles can be considered to be isolated ($L \gg \lambda$). In the case of Cu a smaller value of λ is expected because the condensation coefficient is much smaller, then the assumption of isolated clusters is also justified. The diffusion-capture contribution is calculated by taking an effective capture zone of width ρ around the clusters. By balancing the total number of Cu atoms in the cluster (from the experimental size and composition) and the sum of the two contributions for the growth, the capture width ρ is obtained. In a first approximation ρ can be taken to be equal to the mean diffusion

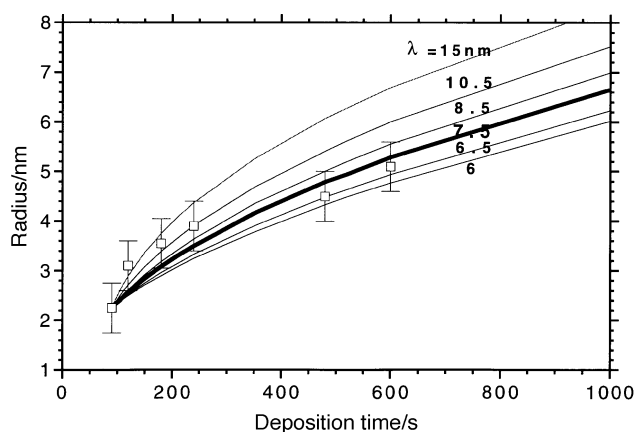


Fig. 7 Determination of the mean diffusion length of Pd adatoms on NaCl(100) at 553 K. The square symbols represent the experimental radius of the Pd clusters as a function of the deposition time after the saturation density of clusters has been reached. The continuous curves represent the theoretical growth kinetics calculated with different values of the mean diffusion length. The best fit (thick curve) is obtained for $\lambda = 7.5$ nm

length λ_{Cu} , this is justified in the present case because the radius of the clusters is larger than λ_{Cu} .³³ In practice, we have calculated the Cu concentration from the growth model for various values of λ_{Cu} . In Fig. 8 the experimental variation of the Cu concentration is plotted as a function of the deposition time, along with the calculated concentrations. The best fit with experimental data is obtained for $\lambda_{\text{Cu}} = 0.28$ nm. The theoretical curves have been calculated for some realistic values of λ_{Cu} corresponding to typical distances in the elementary cell of the NaCl lattice. In fact, the experimental curve is close to the case in which there is no diffusion-capture growth ($\lambda_{\text{Cu}} = 0$).

Knowing the mean diffusion length of Pd and Cu adatoms, it is now possible to calculate the proportion of growth by direct impingement, as a function of the deposition time, for Pd and Cu in the CuPd clusters. These variations are represented on Fig. 9. One can see that, as expected, the growth by direct impingement increases with the particle size but for Cu this contribution is around 80% while for Pd it stays below 30%, for the range of experimental conditions used. This is a clear confirmation of the qualitative picture described at the beginning of this section.

From eqn. (5) it is possible to calculate the difference between the adsorption and desorption energies of an adatom of Pd or Cu. These values are reported in Table 1. The energy difference is much larger for Pd than for Cu, which is indicative of a stronger bonding for Pd, in agreement with *ab initio* calculations on MgO(100).³¹ Anton and coworkers have

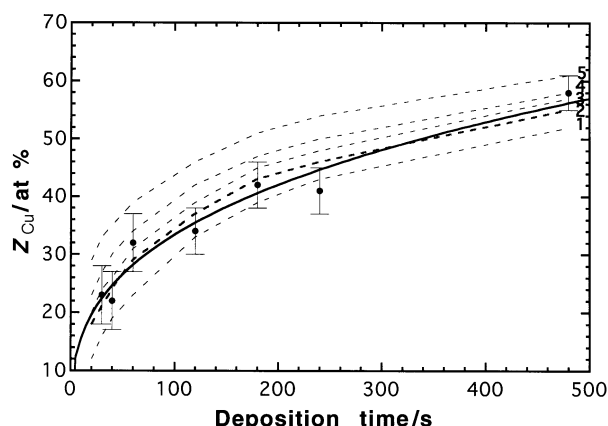


Fig. 8 Determination of the mean diffusion length of Cu adatoms on NaCl(100) at 553 K. The points represent the experimental variation of the Cu concentration in the CuPd particles, which is fitted by the solid line. The dashed curves have been calculated for various values of λ_{Cu} : (1) 0, (2) 0.282 nm, (3) 0.399 nm, (4) 0.564 nm, (5) 0.846 nm

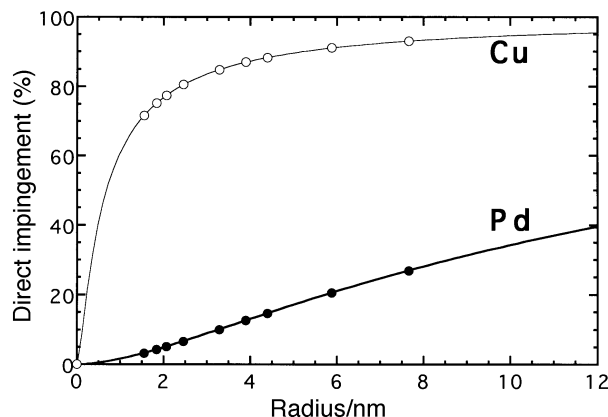


Fig. 9 Percentage of incorporation by direct impingement of Pd and Cu atoms during the growth of CuPd particles at 553 K. The solid curves were obtained by fitting with the growth model while the points correspond to the experimental radii

Table 1 Mean diffusion length and difference between the adsorption and diffusion energies of an adatom of Pd and Cu on NaCl(100)

Metal	λ/nm at $T = 553$ K	$(E_{\text{ad}} - E_{\text{d}})/\text{eV}$	$\Delta(E_{\text{ad}} - E_{\text{d}})/\text{eV}$
Pd	7.5	0.38	0.05
Cu	0.3	0.07	0.05

studied the nucleation and growth of Au–Pd on NaCl(100). They have fitted the experimental values of the composition and of the diameter by solving directly the kinetic equations given by the atomistic nucleation theory¹⁴ or by a Monte Carlo simulation.¹³ Unfortunately, due to a limitation of the calculation time, they have been able to fit only the experimental data corresponding to the smallest deposition times. Nevertheless, the trends observed experimentally were well-reproduced by the calculations. In this case a progressive enrichment in Au was observed because the binding energy of Au is smaller than that of Pd. From their fit they obtained a value for $E_{\text{ad}} - E_{\text{d}}$ equal to 0.45 eV for Pd and 0.33 eV for Au.¹⁴ Taking into account the accuracy of such measurements the agreement between the two studies is satisfactory.

Summary

The nucleation and growth of Pd and CuPd on UHV-cleaved NaCl(100) surfaces have been studied by TEM and EDX. The interaction of Cu atoms with the substrate is much weaker than that of Pd; thus the condensation coefficient, at high temperature, is much weaker for Cu than for Pd. The lower condensation coefficient of Cu results from a much lower concentration of Cu adatoms owing to a higher desorption rate. As a result, the nucleation of pure Pd clusters is favoured. Furthermore, at the beginning of the codeposition of Pd and Cu, when the growth occurs mainly by capture of diffusing adatoms, the incorporation of Pd is much easier than that of Cu; thus the concentration of Pd is very high even though the Pd flux is eight times smaller than that of Cu. As the particles become larger, growth by direct impingement becomes important and it is more efficient for Cu (because of the higher flux). As a consequence, the concentration of Cu in the particles increases. The successive steps for the formation of the CuPd particles can be summarized as follows.

- (1) Nucleation occurs by the encounter of two Pd adsorbed atoms, which form a stable nucleus.
- (2) The nucleus grows by incorporating atoms in two ways: by capture of diffusing adatoms, mainly Pd, and by direct impingement of evaporated atoms, mainly Cu.
- (3) The ratio between diffusion-capture of Pd and direct impingement of Cu depends on the particle size, thus determining the CuPd ratio in the particle.

From a quantitative fit of the growth kinetics and of the kinetics of the concentration evolution it has been possible to determine the mean diffusion length of the Pd and Cu adatoms on the NaCl substrate. From this quantitative model it was concluded that about 80% of the Cu was incorporated in the particles by direct impingement while more than 70% of the Pd was incorporated by the diffusion-capture mechanism. The difference between the adsorption and the diffusion energies has been determined to be 0.38 ± 0.05 and 0.07 ± 0.05 eV for Pd and Cu, respectively.

The CuPd particles grown at 553 K have the fcc structure of the chemically disordered alloy. They transform to the bcc ordered structure after annealing at 638 K.

In conclusion it was possible to get a homogeneous collection of bimetallic CuPd particles by condensing the two metals simultaneously. These uniform collections of CuPd particles are well-suited to be used as supported model catalysts.

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