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Nanocluster formation by spin coating: Quantitative atomic force microscopy and Rutherford backscattering spectrometry analysis

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A recently developed spin coating method has been employed to produce a homogeneous distribution of nanometer-sized metal clusters onto a flat oxidic support. The particle size and distribution, and the total amount of material deposited has been studied by comparing the results of atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), and the appropriate hydrodynamic deposition equations. It is shown that the AFM is capable of producing a three-dimensional image of the surface which enables the particle number density and particle heights to be accurately determined. However, it is clear that as a result of tip convolution effects the particle diameter cannot be accurately determined. Using a hemispherical particle model the amount of material deposited during spin coating can be calculated from the AFM images. This calculation is shown to be accurate to approximately 50% in comparison with the results obtained from RBS. In contrast, it is shown that for a copper acetate precursor the predictions of the hydrodynamic equations are accurate to 2%. In the light of these results an assessment is made of the utility of AFM in the investigation of model catalyst systems and fundamental metal cluster studies. © 1996 American Vacuum Society.

I. INTRODUCTION

Over the last few years there has been considerable interest in developing alternative methods of producing nanometer-sized metal clusters. The reason for this is that the development of a technique which has the ability to produce particles with a narrow size distribution, and with control over the mean particle size is of considerable interest for catalysis and for more fundamental physical studies. In the field of catalysis a variety of techniques have been developed for the production of small metal particles on both real and model oxidic supports.¹ Recently Kuipers *et al.* introduced the spin coating technique to the field of catalysis for the preparation of model catalyst systems.² This process, which has long been used in the electronics industry for depositing thin films onto flat substrates, has the advantage of being able to produce small, relatively well defined metal particles on various substrates, with a considerable degree of control over the final particle size and distribution. For the purposes of catalysis it is clear that spin coating can be used to produce model catalyst systems which simulate real catalyst systems, since: (i) it is possible to spin coat onto any flat substrate (SiO_2 , Al_2O_3 , ZnO , etc.), (ii) the substrate chemistry can be modified to simulate the condition of real supports (i.e., hydrated/dehydrated), and (iii) a very wide variety of precursors can be employed (RhCl_3 , $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, $(\text{C}_6\text{H}_5\text{CN})_2\text{PtCl}_2$, etc.), including those employed in real catalytic applications. Furthermore, the ability to change the

particle size means that the catalytic activity of these deposited particles as a function of particle size can be monitored.

However, this technique offers an attractive alternative method of producing nanometer-sized clusters for more fundamental physical studies, since the ability to vary the particle size over several orders of magnitude, down to the order of 1 nm, provides the opportunity to study the change in the fundamental properties of metallic materials as the electronic structure changes from bulklike behavior to more atomlike (mesoscopic) behavior.^{3,4} Over the last few years considerable progress has been made in understanding the optical and magnetic properties of small free clusters⁵ and the influence of particle size on these clusters. Recently this research has produced the unexpected theoretical prediction⁶ and subsequent experimental confirmation⁷ of the onset of magnetism in 13 atom Ru, Rh, and Pd clusters, where the magnitude of the magnetic moment in these clusters was very sensitive to the particle size and particle morphology.

Further, there is considerable interest in determining whether these properties are maintained once the clusters are deposited onto a substrate, and in understanding what influence different substrates have on the clusters. For many purposes certain oxides (SiO_2 , Al_2O_3 , etc.) provide ideal support materials, since they are relatively inert, interact only weakly with the metal clusters and, in the case of anti-ferromagnetic oxides, provide opportunities for magnetic biasing. The use of nonconducting substrates, however, intro-

duces limitations on the types of analysis techniques that can be utilized to study the systems. In terms of the determination of the particle size, morphology and particle distribution following deposition the atomic force microscope (AFM) would appear to be an ideal tool for determining these properties.^{8,9}

However, although the AFM can routinely map out surface topography with nanometer resolution, including the imaging of surface steps and line defects,¹⁰ it has been unable to achieve the same extremely high resolution exhibited by the scanning tunnel microscope (STM). In particular, while "atomic" (lattice) images have been observed by the AFM in contact mode, there is no substantive evidence that true atomic resolution has been achieved. This is in contrast to the STM where atomic resolution of conducting and semi-conducting surfaces has routinely been obtained, as is evidenced by the presence of point defects in the images. This limitation is determined primarily by the principal difference of operation between the STM and AFM: the AFM tip being in "physical" contact with the surface under investigation. Even under the low loads typically used in AFM experiments (~ 1 nN) this results in a contact area of the order of 0.5 nm^2 , which sets a limit on the achievable resolution. This contact limitation can be avoided by operation of the AFM in close proximity to the surface, but in "out-of-contact" mode, as has recently been demonstrated by the work of Ohnesorge and Binnig,¹¹ Giessibl,¹² and Schaefer *et al.*¹³ However, at present most structural studies are still performed in contact mode where the resolution of the AFM is strongly influenced by tip structure and shape, and this clearly imposes limitations on the interpretation of the AFM images.

Therefore in this article spin coating has been used to produce small metallic clusters on oxidic supports. UHV-AFM in combination with Rutherford backscattering spectroscopy (RBS) was then employed to investigate whether spin coating is able to produce homogeneous distributions of nanometer-sized particles with a narrow size distribution on oxidic supports. A quantitative assessment of the AFM's abilities to characterize these metal-support systems, given the clear limitations inherent to the technique, has then been carried out within the context of catalysis and fundamental physical studies.

II. EXPERIMENT

The model system chosen for investigation was the Cu/SiO₂ system. A SiO₂ substrate was chosen since it offers a flat and well characterized oxidic surface which is readily accessible to AFM investigation. The Cu/SiO₂ system was selected since it has been shown to be capable of catalyzing a number of chemical reactions,¹⁴ and it was intended that this system would form the basis of a study to investigate the optical properties of small clusters.

A. Spin coating

The hydrodynamics of spin coating have previously been considered by Emslie *et al.*¹⁵ for a Newtonian liquid film. They calculated the inter-relationship between the liquid

shear force and the centrifugal force created by spinning, and modeled the reduction in film height with regard to changes in angular velocity and film viscosity; showing that the height of the films tended towards uniformity regardless of their initial distributions. This general theory was subsequently modified by Meyerhofer¹⁶ to include the effect of evaporation. He postulated that the initial reduction in film height was dominated by loss of the fluid through centrifugal outflow, and that evaporation is negligible, until a critical point h_c is reached. At this point the losses through centrifugal outflow become equal to losses through evaporation. When this critical thickness h_c has been reached, the subsequent reduction in film height is then dominated by evaporation. Therefore h_c is defined as the point where the rate of loss through radial outflow becomes equal to the loss through evaporation:

$$2 \cdot \left(\frac{\rho \cdot \omega^2}{3 \cdot \eta} \right) \cdot h_c^3 = \frac{\phi}{\rho}, \quad (1)$$

$$h_c^3 = \sqrt[3]{\frac{3 \cdot \eta \cdot \phi}{2 \cdot \rho^2 \cdot \omega^2}}, \quad (2)$$

where ρ is the density of the pure solvent, ω is the angular velocity, η the viscosity, and ϕ the mass flux as a result of evaporation.

During spinning the liquid film spreads out and is ejected from the edge of the sample, and the film height reduces rapidly. However, as the film height decreases the loss of solvent through edge ejection diminishes rapidly due to a balance between the centrifugal force and liquid shear force being attained, and consequently evaporation becomes the dominant loss mechanism. As the solvent evaporates the solution becomes supersaturated. In this supersaturated solution solute particles are able to nucleate and grow, and are subsequently deposited onto the support as the solvent evaporates.

In the catalytic spin coating technique the above analysis remains valid. A small amount of solute material, containing the element to be deposited, is dissolved into a volatile solution. This solution is dispensed onto a flat support substrate, which is then spun at rotational frequencies typically between 500 and 5000 rpm. During the initial stages of spin coating most of the solution is ejected from the substrate, due to centrifugal forces, and the film of solution formed across the substrate surface rapidly reduces in height until it reaches the critical thickness h_c . At this point the subsequent reduction in film height is governed primarily by the evaporation of the volatile solvent. As the solvent evaporates the solute concentration in the film increases, and the solvent becomes supersaturated, leading to nucleation of the solute particles. However, as the solute particles nucleate and grow, the solute concentration in the solution drops, causing nucleation to stop. The inter-relationship between these factors has been considered previously.^{2,17,18} Kuipers *et al.* argued that if the rate of concentration increase is large at the threshold for nucleation, the concentration will remain longer in the nucleation region (Fig. 1), favoring crystal nucleation over

FIG. 1. Change in the average solute concentration of a liquid film with time, due to evaporation of the solvent. Initial concentration (C_0) and the threshold concentrations for crystal growth (C_g) and nucleation (C_n) are shown.

growth. If, on the other hand, the rate of concentration increase is small at the threshold for nucleation, the solute concentration in the solution will quickly fall below the nucleation threshold and consequently growth of the previously nucleated particles will be favored. Therefore the rate of nucleation and growth is determined by both the initial concentration of the solution and the rate of evaporation, which is in turn dependent on the spin frequency and solvent (this behavior will be discussed further in Sec. III). Following nucleation the particles are deposited onto the substrate surface as the solvent evaporates. These particles are then transmuted into the metallic state using standard oxidation and reduction procedures.

It is also possible to make an estimate of the final loading of the sample (the number of metal atoms/cm²) using the hydrodynamic approach discussed above. Since the rate of evaporation is negligible up to h_c , the concentration of the liquid film at this point is the same as the initial film concentration C_0 , and, as the reduction in film height after h_c is dominated by evaporation, all the solute in this thin film will be deposited onto the substrate. The final loading (m) can therefore be estimated as

$$m = C_0 \cdot h_c = C_0 \cdot \sqrt[3]{\frac{3 \cdot \eta \cdot \phi}{2 \cdot \rho^2 \cdot \omega^2}} \quad (3)$$

The singular advantage of the spin-coating method is the fact that it is possible to affect a change in the mean particle size and distribution by adjustment of the initial solute concentration, spin speed, and choice of solvent. The particle size becomes smaller with lower initial concentration, increasing spin speed and higher solvent evaporation rate.

However, it has been suggested that the use of solutions containing acetate precursors can lead to the deposition of a layer of material, as opposed to small particles. The formation of particles from this layer is then dependent on the subsequent heat treatment. This has recently been shown to be the case for $\text{Cu}(\text{ac})_2$.¹⁹ This proffers an additional means of control over the final particle size, but also creates a greater degree of complexity in the process.

For the purpose of creating the small copper particles a solution of 0.01 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in ethanol or 1-butanol was used. The spin coating was performed in a glove box under dry atmospheric or inert N_2 conditions. The Si(100) wafers were oxidized at 500 °C for 24 h to produce a thicker oxide layer (5–10 nm), which was thought to be close to stoichiometric SiO_2 , and prior to deposition were spin cleaned in pure ethanol. Following deposition the Cu-acetate particles were transformed to CuO by calcination prior to imaging in the AFM. Details of the spin coating and calcination step are given in Table I.

B. Atomic force microscopy

All the AFM measurements were made using an Omicron UHV-AFM, and using Nanoscope cantilevers with integrated SiN_4 pyramidal tips.²⁰ All the measurements were made in contact mode, using the minimum force possible, typically of the order of 1 nN. The subsequent oxidation, reduction, and heat treatment of the samples was carried out in a high-pressure cell which was an integral part of the UHV chamber ($p \sim 1 \times 10^{-10}$ mbars) so that the samples were not exposed to ambient conditions between treatment steps.

C. Rutherford backscattering spectroscopy (RBS)

Surface loadings following spin coating were quantified with RBS using 4 MeV He^+ ions from the Eindhoven University of Technology AVF cyclotron. The beam guiding system was operated in the dispersive mode resulting in $\Delta E/E = 3 \times 10^{-3}$. Scattering experiments were carried out in a standard high-vacuum scattering chamber ($p \sim 1 \times 10^{-5}$ mbars), and the angle of the incoming beam with the sample surface normal was 5°. Scattered particles were detected with a standard passivated implanted planar silicon (PIPS) detector which was positioned at a scattering angle of 165° with respect to the direction of the incoming beam. The measured

TABLE I. Spin coating and calcination parameters.

Batch	Solution	Spin speed (rpm)	Calcination
1	0.01 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in ethanol	4000	300 °C/h–450 °C for 4 h
2	0.01 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in ethanol	5000	300 °C/h–450 °C for 4 h
3	0.01 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in butanol	5000	300 °C/h–450 °C for 4 h
4	0.01 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in butanol	4000	50 °C/h–450 °C for 4 h

FIG. 2. (a) AFM image of the Cu/SiO₂ sample, spin coated at 4000 rpm, and oxidized at 300 °C/h to 450 °C (300×300 nm). (b) Histogram plot showing the height distribution of the Cu clusters as determined by AFM.

overall energy resolution [full width at half maximum (FWHM)] was found to be 18 keV, sufficient to identify the ⁶³Cu and ⁶⁵Cu isotopes separately.

III. RESULTS

A typical image of the 300 °C calcined Cu/SiO₂ samples (samples 1 and 2) is shown in Fig. 2(a). Relatively densely packed small, roughly hemispherical, particles are observed to cover the surface. The size distribution of these particles is relatively well defined [Fig. 2(b)], the particles having a mean height of 5.6 nm [with a standard deviation (σ) of 1.6 nm] and a mean diameter of 18.7 nm (σ =4.6 nm). Generally, the samples exhibit a homogeneous distribution of particles over the surface, although sometimes sharply delineated areas free of particles were observed, these areas often extending over distances of several hundred nanometers (Fig. 3). It has been shown previously that the presence of water in the solvent or in the atmosphere during spin coating can stop the solution from wetting the surface fully as the solvent evaporates.¹⁷ This is particularly problematic in the case of solvents with high evaporation rates, since the rapid evaporation of the solvent leads to local cooling and hence water

FIG. 3. AFM image of the Cu/SiO₂ surface showing the interface between an area covered in particles and a region denuded of Cu particles (500×500 nm). The denuded region extends over several hundred nanometers.

condensation. The sharply delineated boundaries between those areas showing a high particle density and those with a low particle density lead us to conclude that water condensation and/or surface contamination was probably the cause of this inhomogeneous deposition, as discussed in a separate article.¹⁹

Consequently, a third set of samples was produced under low humidity conditions and with the same solute concentration as samples 1 and 2, but which was spun using butanol as a solvent. It was suspected that butanol may reduce the problems arising from water condensation, due to the fact that water is less soluble in butanol, and the lower rate of evaporation of butanol may reduce water condensation as a result of surface supercooling. Images of the samples made using butanol, and calcined at 300 °C/h, show a particle distribution almost identical to Fig. 1, except that no particle denuded zones were observed. However, the mean particle height of the Cu particles made using butanol was observed to be somewhat smaller (Table II).

In addition to studying the effect of changing the solvent, the effect of the calcination step was also studied. On imaging the surface immediately after spin coating no particles could be observed. However, on heating the same sample at a ramp rate of 300 °C/h to 450 °C a high density of small particles was observed to have formed (Fig. 1). In the case of a RhCl₃ precursor, spin coated under similar conditions, particles were observed to have formed immediately on spin coating.¹⁹ This confirms the proposition that in the case of acetate precursors the heat treatment step can be crucial in the particle formation process, whereas in the case of the simple salts particle nucleation and growth occur during evaporation. The influence of the temperature ramp rate during calcination was also investigated by reducing the ramp rate to 50 °C/h. The AFM images obtained on these samples revealed that the particle distribution obtained was not as

TABLE II. The number of particles (N_p) and mean particle height, determined by AFM, and a comparison of the total number of atoms per cm^2 ($n_{\text{atom}}/\text{cm}^2$) determined by AFM, RBS, and spin coat theory.

Sample	AFM			RBS	Spin coating theory
	No. of particles/ cm^2	Particle height (nm)	10^{15} atoms/ cm^2	10^{15} atoms/ cm^2	10^{15} atoms/ cm^2
1	1.52×10^{11}	5.6	2.82	2.05	2.11
2	0.99×10^{11}	6.6	3.00	1.91	1.88
3	1.67×10^{11}	3.0	0.47	1.43	1.49
4	0.11×10^{11}	4.0	0.07	1.69	1.68

reproducible as had been observed on the samples calcined at the higher ramp rate. The particles formed using a slow ramp rate calcination varied in size from 4–10 nm, and sometimes exhibited a very low particle density (see sample 4 and Fig. 4). The significance of these observations will be discussed later.

IV. ANALYSIS

A. Tip-surface convolution

During the AFM analysis of the samples it was observed that the mean particle diameter determined from a sample, measured with different tips, could vary significantly, and that the apparent sample diameter could even change in the course of one scan. This indicates that the particle diameter determination is dependent on the shape and size of the tip used, parameters which can change during scanning. This phenomenon is a consequence of the “contact” mode of operation of the AFM. If we take a Si_3N_4 tip which is in contact with a SiO_2 surface, with a force of 1 nN, it has a Hertzian contact area of $\sim 38 \text{ \AA}^2$, and a finite radius of curvature. For the standard pyramidal Si_3N_4 tips used in this investigation the manufacturer’s specifications define a typical tip radius

FIG. 4. AFM image of Cu/SiO_2 sample prepared using Copper (II) acetate in butanol, which has been calcined at $50^\circ\text{C}/\text{h}$ ($500 \times 500 \text{ nm}$). The sample shows a low density of very small particles. The changes in background contrast in the image is due to tip-surface interactions.

of 100 nm. However, in practice about 10% of these tips exhibit much sharper tip apexes, typically of the order of 10 nm or smaller.²¹ This means that the AFM images are strongly influenced by the convolution of the surface structure with the tip structure. The extent of this convolution can be illustrated by using a simple graphical representation of the tip and surface. By assuming that we have a tip with a hemispherical apex interacting with a hemispherical particle [Fig. 5(a)], then the dependency of the apparent particle size on the tip radius, as the tip traverses the particle, can be calculated from simple trigonometry. The apparent particle

(a)

(b)

FIG. 5. (a) Schematic of a hemispherical tip interacting with a hemispherical particle. (b) Plot of the apparent particle size vs true particle size, calculated using the model in a.

TABLE III. Comparison of particle parameters obtained on the same sample from AFM and HRSEM.

	Number particle density (N_p) $\times 10^{11}/\text{cm}^2$	Particle diameter/ nm	Particle height/ nm
AFM	1.5	19	5.6
HRSEM	1.3	8	...

size versus true particle size is plotted in Fig. 5(b) for several tip sizes. From the figure it is clear that as the particle diameter decreases the finite size of the tip causes a greater relative error in the particle diameter determination, and that small changes in tip radius create large changes in apparent particle diameter. This makes the determination of the true particle diameter unreliable, given the variable tip geometries encountered in AFM. This problem is demonstrated in Table III, where the particle number density and particle size determined from the same sample by AFM and high-resolution scanning electron microscopy (HRSEM) are compared. From the table it is clear that the AFM clearly overestimates the true particle diameter. By comparing the difference observed between the AFM and HRSEM images with Fig. 5 it is evident that the AFM tip must have had a tip radius of ~ 10 nm. What is also clear from this comparison though is that the AFM is capable of providing an accurate value of the particle height (provided that the tip is reasonably sharp) and that the number of particles per unit (N_p) area can also be reliably determined.

B. Quantification of AFM/RBS data

The important question which the above analysis raises is whether the AFM can provide quantitative information about the morphology and distribution of nanometer-sized particles, and if so what are the limitations of the technique. To answer this question it is necessary to be able to make a quantitative comparison of the data obtained by AFM with other quantitative techniques. To this end all the above samples were analyzed by RBS, which is capable of determining the surface concentration of copper to a high degree of accuracy. Figure 6 shows a typical RBS spectra obtained from a Cu/SiO₂ sample, exhibiting a sharp surface copper peak and a broad continuum due to the silicon substrate. The spectra were quantified using the computer code RUMP²² which implicitly applies normalization on the Si substrate continuum. Since the energy of the incoming He beam is 4 MeV instead of the more common 2 MeV, the validity of the Rutherford scattering cross sections should be assessed. The energy threshold for non-Rutherford behavior can be estimated theoretically²³ and was found to be 3.9 MeV for scattering on Si and 7.7 MeV for scattering on Cu at a scattering angle of 165°. Normalization on the Si continuum was therefore achieved in the spectrum interval between channel 200 and 400, corresponding to scattering with He particles with an energy between 3.3 and 3.7 MeV. Furthermore, stopping tables were also generated for this energy interval and used in the RUMP code. The resulting absolute accuracy in the

FIG. 6. RBS spectrum obtained from Cu/SiO₂ sample (sample 1).

measured Cu loading expressed in the number of atoms/cm² is estimated to be approximately 3%. For the purposes of comparison, the number of solute copper atoms deposited per cm² was also calculated using the hydrodynamic equations of Emslie *et al.* and Meyerhofer.^{15,16} The values for the evaporation rate of ethanol and butanol were calculated by extrapolating the relationship between evaporation rate and rotational velocity, determined by Hardeveld *et al.*¹⁸ to the slightly higher spin speeds used here.

To make a valid comparison between the AFM data and the two other calculation methods it is necessary to calculate the number of Cu atoms per unit area from the AFM images. Since the particle diameter, as determined by AFM, is not a reliable number, an assumption has to be made regarding the particle shape. This is done in the following manner: the particle height is taken as an indication of the true particle size, and the particles are assumed to have a hemispherical form.²⁴ The copper concentration is then calculated on the basis that the particles are composed of stoichiometric CuO following the calcination step. This assumption was confirmed by x-ray photoelectron spectroscopy analysis. In Table II the number of copper atoms per cm² calculated using the simple assumptions made above is compared with the results from both the RBS and theoretical spin coating calculations.

What is most striking about the data in Table II is the excellent agreement between the RBS and theoretical spin coating results, which agree to within 2% of each other. It is worth noting that the very good agreement observed between the RBS and hydrodynamic equations in the case of Cu(ac)₂ deposited on SiO₂ is significantly better than was found for MoO₂Cl₂ and copper ethylhexanoate [Cu(C₈H₁₅O₂)₂] by Hardeveld *et al.*¹⁸ In comparison the copper concentration, as determined from the AFM images of samples 1 and 2, is only accurate to approximately 50%. However, given the assumptions involved in the calculation this is not an unreasonable error. The error in the determination of $n_{\text{atoms}}/\text{cm}^2$ can be accounted for by an error in the mean particle radius

TABLE IV. Comparison of the AFM with other standard techniques. The key is as follows: ??? indicates a property that is well defined by the technique in question, V indicates a property that is used as a free variable in the standard quantification routines, while AFM indicates which properties are determinable once the value of N_p , determined from the AFM, is used as an input parameter. Question marks have been placed in the AFM column related to coverage, $n_{\text{atoms}}/\text{cm}^2$, and the particle size since these properties cannot be determined without some assumption being made regarding the tip convolution. In the above an assumption is nearly always made with respect to particle shape.

Property	RBS	XPS	LEIS	AFM
Coverage	AFM	AFM	???	?
$n_{\text{atoms}}/\text{cm}^2$	???	AFM	AFM	?
N_p	V	V	V	???
Particle size	AFM	AFM	AFM	?

determination by as little as 0.5 nm, although the height resolution of the AFM should be considerably better than that (~ 0.02 nm). In the case of samples 3 and 4, prepared using butanol, the copper concentration as determined by AFM is lower than in samples 1 and 2, consistent with the spin coating predictions. In the case of sample 3 there is clearly a reduction in the mean particle size, but the particle distribution remains approximately the same as in samples 1 and 2. However, in sample 4 there is also a clear change in the particle distribution, which has been attributed to the lower heating rate during calcination. RBS and x-ray photoemission spectroscopy (XPS) measurements performed on sample 4 revealed that the copper loading is higher than can be accounted for by the particle number density observed by AFM (Table II). This suggests that the copper is either in the form of isolated copper species or very small particles which are too small to be differentiated from the silicon oxide surface, given that this surface has a roughness of 0.5 nm. This phenomenon has been discussed in a separate article,¹⁹ but it would appear that during slow heating the $\text{Cu}(\text{ac})_2$ is mobile and can diffuse across the surface to form larger clusters, but can also react during the long heating time with the silica surface to form a dispersed Cu layer between the Cu clusters. Bonding of this nature has been discussed by Kohler *et al.*,²⁴ in the $\text{Cu}(\text{NH}_3)_4\text{-SiO}_2$ system, and by Xu *et al.* in Cu-SiO_2 model systems.²⁵ What is clear though is that a similar Cu distribution would have been anticipated for the 300 and 50 °C/h calcination treatment on the basis of RBS measurements alone. However, the application of the AFM to this system clearly shows the change in particle distribution following these two different heat treatments.

C. Evaluation of AFM in the study of model catalysts and nanometer-sized clusters

The above analysis raises a further important question about what information the AFM can provide in the study of model catalysts and small metal cluster support systems, and what implications this has, if any, on the quantification procedure of other analysis techniques. Table IV lists three other surface analysis techniques used for the quantification of model catalyst systems, and four properties determined by

these techniques. As can be seen from the table, the coverage, particle size, and total number of atoms per cm^2 ($n_{\text{atoms}}/\text{cm}^2$), determined by AFM, can only be ascertained by making certain assumptions with respect to the tip convolution, while the number of particles per cm^2 (N_p) can be determined to a high degree of accuracy. This statement, however, requires two qualifications to be made. First, for particles with a size significantly larger than nanometer dimensions, the tip/particle convolution becomes smaller, and consequently the need to make assumptions regarding the particle shape becomes unnecessary. Secondly, for sub-nanometer particles the ability to resolve the particles is dependent on both the size of the tip and the surface roughness, as is demonstrated by sample 4. Leaving these two qualifications aside for the moment, the AFM in combination with RBS can define all the properties considered, if an assumption is made regarding the particle shape. In fact, in all three additional techniques considered [low-energy ion scattering spectroscopy (LEIS), XPS, and RBS], where N_p is often taken as a variable parameter, the determination of this parameter by AFM allows the additional parameters to be calculated, again provided that an assumption is made regarding the particle shape. This is not an unreasonable requirement given that in many quantification routines an assumption of particle shape is made. Clearly many of these properties can already be determined by the application of a combination of different surface sensitive techniques²⁶ or, in the case of XPS, through the use of angle-dependent measurements.²⁷ However, the advantage of the AFM is that it can provide a value for N_p which is not readily available from other techniques, and which is obtained by making a few simple assumptions regarding the particle shape and the ability of the AFM to resolve the particles. Where these assumptions break down, such as in sample 4, this is immediately evident from a comparison of the loading determined by RBS and AFM, respectively, and indicates that very small clusters or atomic species have been deposited.

What is equally significant is that the AFM can produce “real-space” images of nonconducting surfaces following preparation, heat treatment, and reaction steps, providing direct information on changes in the particle distribution and dispersion, two parameters which can not be directly determined from other surface sensitive techniques. Clearly, a knowledge of the changes in these parameters is essential for understanding changes in the reactivity of catalytic systems and changes in the electronic structure of the particles.

V. CONCLUSIONS

UHV-AFM has been used to obtain 3D images of metal-oxide support surfaces, which show that a relatively homogeneous distribution of nanometer-sized metal clusters can be produced using the spin coating preparation technique. The major advantage of the AFM is that it produces direct real-space images of nonconducting surfaces, which means that the distribution of particles on these surfaces can be directly observed, and the total number of particles/ cm^2 (N_p) determined, a parameter which is not easily determinable by

other techniques. It has also been shown that the particle diameter, as determined by AFM, depends on the tip size, whereas the particle height is a parameter that can be determined independent of the tip. This therefore means that the dispersion, total number of particles/cm², and surface coverage cannot be determined without making some assumption regarding the particle shape. However, an assumption of particle shape is made in many quantitative routines. On the basis of a hemispherical particle shape, it has been shown that the other properties can be calculated, and that the number of atoms/cm² can be determined to an accuracy of 50% compared to RBS.

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