Scanning tunnelling microscopy investigation of sintering in a model supported catalyst: nanoscale Pd on TiO_2(110)

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Vacuum annealing of metal vapour deposited Pd on TiO_2(110) results in particle formation and sintering with an increase in both the diameter and height of the particles measured using STM.

Metal vapour deposition on oxide single crystals provides a methodology for generating model catalysts which can be studied using conventional surface science techniques.[1,2] Of the wide range of techniques available scanning probe microscopy (SPM) is particularly valuable in that it allows the morphology and size distribution of metal particles on single crystal surfaces to be measured directly. The nucleation and growth of palladium on titania has previously been studied using STM by Goodman and coworkers[3] and Thornton and coworkers.[4] Here, we report the application of scanning tunnelling microscopy (STM) to the investigation of the sintering of Pd particles on TiO_2(110) upon heating in vacuum. STM is particularly advantageous compared to TEM as it measures the height of every particle in the scanned area. The magnitude of the reactivity relates to the area of supported particles which is available for reaction, and in this case particle–particle interactions in which size and shape distributions change will crucially affect the total reactivity. For example, sintering of small particles to form larger particles reduces the total surface area of the supported metal and results in a concomitant loss in catalytic activity. We present STM observations of the variation in particle size and height distributions and relate the observations to sintering. Annealing temperatures of 473 and 973 K correspond to the Hüttig and Tamman temperatures for Pd and roughly correspond to the expected onset of metal adatom and metal nanoparticle mobility respectively.[5] These observations represent the first analysis of the sintering process in this system by STM and the results are expected to be general for a wide variety of other systems.

Pd overlayers were prepared by Pd vapour deposition onto the TiO_2 surface at *ca.* 300 K. The Pd source consisted of a Pd wire wound tightly around a W filament. The TiO_2(110) surface was prepared by repeated sputter-anneal (>973 K) cycles to produce a slightly streaky (in the $<110>$ direction) (1×1) LEED pattern indicating the surface was slightly reduced. Pd deposition was monitored using Auger electron spectroscopy with the amount of Pd estimated from a calibration experiment of Pd deposition on Cu(110). The rate was estimated to be 2×10^{-3} ML s^{-1} where 1 ML is 1.1×10^{15} atoms cm^{-2}. The growth mode of Pd on TiO_2(110) at 300 K has been established to be of the classical nucleation type where Pd monomers are mobile while dimers form stable nuclei for subsequent growth in the Volmer–Weber mode (3D-islanding).[3]

Deposition of >1.5 ML Pd produced continuous, though rough Pd films which could be imaged in the STM. Annealing to 473 K produced particulate films, which is consistent with surface Pd mobility (Hüttig temperature) as small particles have been formed from a thin film. Deposition of <1.5 ML produces particles in the as-deposited overlayer. Fig. 1 shows STM images of 1.7 ML Pd on TiO_2 which has been vacuum annealed to (*a*) 473 K for 15 min and then (*b*) 973 K for a further 15 min. The Pd particles in Fig. 1(*a*) form a fairly homogeneous overlayer with some variation in particle size and height. This can be seen more quantitatively in Fig. 2 which shows (*a*) the particle size and (*b*) height distributions for this overlayer at this and two higher annealing temperatures (773 and 973 K). The same surface annealed to 973 K, Fig. 1(*b*), displays a significantly changed particulate array. The Pd particles show a reduction in particle number density from 7.5×10^{-2} to 6×10^{-3} nm^{-2} and display a much greater variety in size and height (Fig. 2). This change is characteristic of particle sintering as a result of mass transport of Pd particles on the surface (Tamman temperature). We believe that the mechanism of sintering in this system is by coalescence, that is, two or more particles join together to form the larger particles. Fig. 1(*b*) shows evidence of coalescence of the particles, in this image it is clear to see that some of the particles have merged together (see regions 1 and 2 on the image). In addition, if Ostwald ripening was the mechanism, we would expect to see smaller particles at some stage during the sintering process, which is not observed. The mean (s.d.) particle diameter varies between 42 (10 Å) after annealing at 473 K to 56 (11 Å) at 773 K and 87 (15 Å) at 973

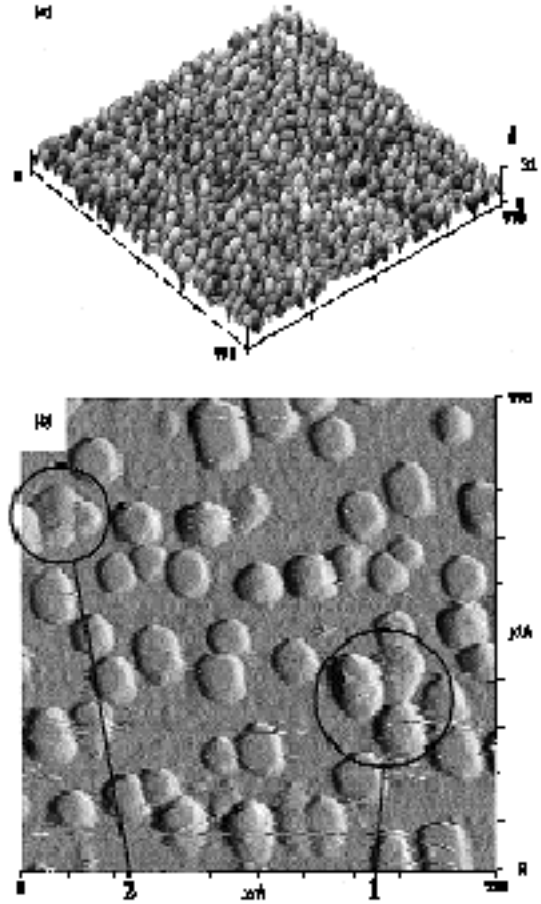

Fig. 1 STM images of 1.7 ML Pd on TiO_2(110) after annealing for 15 min at (*a*) 473 K (sample bias 0.5 V, tunnelling current 1 nA) and (*b*) 973 K (sample bias 2 V, tunnelling current 1 nA). The scan area of each image is 998×998 Å.

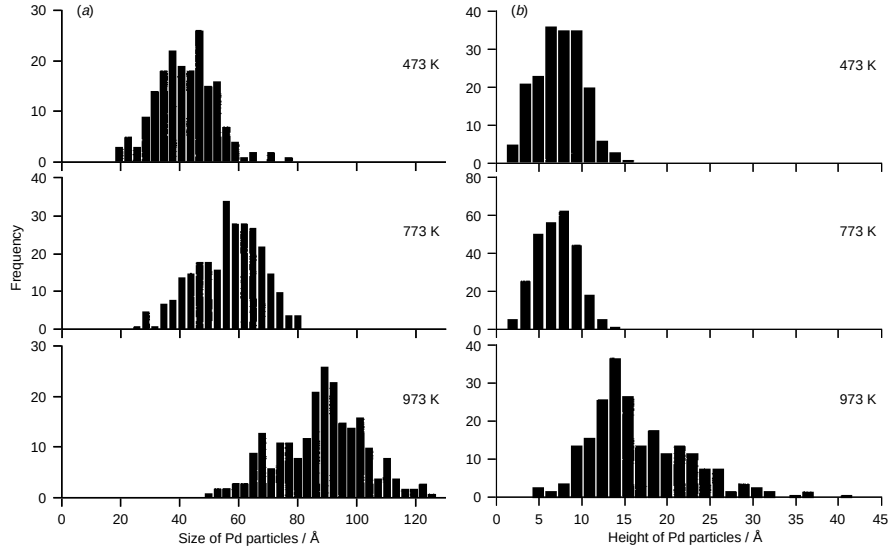

Fig. 2 Particle size distributions for 1.7 ML Pd on TiO_2(110) annealed to three different temperatures; 473, 773 and 973 K. (*a*) Size (diameter) and (*b*) height of particles.

K. The corresponding mean particle heights are 7.3 (2.7 Å), 6.8 (2.4 Å) and 16.6 (6.2 Å). The standard error for the mean particle diameter and height is (±1 Å) and (±0.5 Å) respectively.

At Pd coverages of 5 ML the same analysis of particle size with annealing temperature was not possible as well defined particulate arrays were not formed until the surface was annealed to 973 K. Other Pd coverages between 0.6 and 3 ML display the same trend on annealing as that shown above for the case of 1.7 ML though the measured particle densities after annealing to 973 K decrease with decreasing Pd coverage. After annealing at 973 K for lower Pd coverages it is possible to image the clean (1 × 1) surface between the particles.

In summary, we have investigated the sintering of particles in a model catalyst system, Pd on TiO_2. The as-deposited film displays little structure but annealing to 473 K produces distinct clusters, while further annealing at 973 K results in the sintering of these particles which we believe to be by the mechanism of coalescence.

Notes and References

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