

Model Catalysts Fabricated Using Electron Beam Lithography and Pulsed Laser Deposition

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Supported metal nanoparticles have been fabricated using electron beam lithography (EBL) and pulsed laser deposition (PLD). EBL produced ordered two-dimensional arrays with particle diameters of 40 ± 0.5 nm, uniform interparticle distances (230 ± 2 nm), and uniform height (20 ± 0.5 nm). Due to the narrow size distribution of the particles and the long-range (cm^2) order, the arrays produced using EBL were applied as models for supported metal catalysts. Smaller particle sizes can be obtained using PLD, but with larger size and spatial distributions of the particles. Particles fabricated with PLD have mean sizes ranging from 2 to 50 nm, depending on the ambient pressure during deposition. The nanoparticles have been characterized using TEM, AFM, UPS, and SEM. Reaction studies of ethylene hydrogenation on Pt nanoparticle arrays have demonstrated that detectable amounts of ethane are produced, despite the low surface area of the model catalysts.

Introduction

It is well-known that the surface structure of transition metal catalysts can influence and, in some cases, determine the turnover rate and selectivity of reactions. This structure sensitivity has been studied in this and other laboratories using transition metal single crystals as model catalysts (Pt, Rh, Fe, Re, etc.).¹ Both the rates and selectivity of hydrocarbon conversion (hydrogenolysis, dehydrogenation, dehydrocyclization, and isomerization) and ammonia synthesis were changed when the surface orientation, i.e., the crystal face, was changed.^{2–4} In many cases, the concentration of atomic steps and kinks controlled elementary reaction steps leading to changes in turnover rates and selectivity. The dependence of reaction pathways on the surface structure of single crystals was a consequence of the different activities of the various surface sites.

While single crystals provide ideal studies of the effect of surface structure on catalyst performance, many industrial catalysts are metal nanoparticles (1–100 nm diameters) on oxide supports. Changing the particle size can affect many properties of a catalyst including (1) particle surface structure, (2) metal dispersion, and (3) electronic interactions between the support and the particle. In addition, changing the distance between particles on a support affects the stability of spillover species.⁵ To identify the effects of particle size and interparticle distance on reaction activity and selectivity in supported catalysts, uniform particles with uniform interparticle distances must be produced. In this paper, we review the methods of electron beam lithography (EBL), utilized for fabrication of uniform metal nanoparticle arrays, and of pulsed laser deposition (PLD), which has been recently applied to prepare model catalysts. The target particle size of these techniques was 1–100 nm diameter particles, which overlaps the particle size range of most industrial metal catalyst systems. Various techniques used to characterize the model catalysts are introduced, as well as some initial studies of catalytic reactions.

There have been several methods reported to produce particles with very narrow size distributions but without regular spatial distribution. Evaporation of metals in vacuum onto a well-defined substrate at submonolayer coverage was one of the first methods to prepare model catalysts.^{6–12} Catalysts with mean particle sizes ranging between 1.5 and 30 nm could be easily obtained. Metal particles encapsulated in the supercages of zeolites were found to be considerably more uniform. Here, the growth of the metal particles was controlled by the size of the cage in the range 1–2 nm.^{13–18} A novel method called “microemulsion technique”, using a mixture of surfactant, oil, and water, was developed to prepare metal catalysts with particle sizes of 2–5 nm and narrow size distributions.^{19–21} A similar method was developed to prepare supported metal catalysts using metal sols with uniform size.^{22,23} Advantages of these methods include the ability to produce very small size particles with narrow size distributions. A disadvantage of these techniques is that uniform arrays are not produced.

In other fabrication techniques, uniform arrays are produced, but the total area of fabrication is limited generally to a few micrometers.^{24,25} The recently introduced “spin-coating technique” utilizes a spinning disk onto which a solution of catalyst precursor is dispensed. Most of the solution was ejected from the disk, but a thin layer remained which could be used, after proper treatments, to prepare a model catalyst with uniformly distributed particles.^{26–29} In another study, using dodecanethiol bound to 2.8 nm diameter Ag particles, an ordered array covering a submicrometer area was formed.³⁰ Ordered arrays were also produced by filling ionic vacancies in a AgBr(111) lattice.³¹ The application of these techniques toward the fabrication of model catalysts is limited by the small area (generally micrometers) encompassed by the uniform particle arrays or the materials that can be employed.

The methods of particle preparation presented above have pieces of the necessary characteristics to make model catalysts, but a single technique does not provide all of the necessary attributes. A supported model catalyst must have (1) a large enough metal surface area ($>1 \text{ mm}^2$) to produce measurable amounts of product, (2) uniformly spaced particles which have diameters between 1 and 100 nm, (3) uniform interparticle distances, and (4) a suitable combination of metal/support

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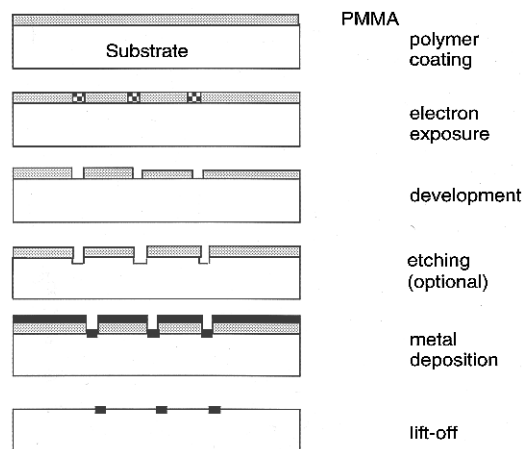


Figure 1. Schematic diagram of the electron beam lithography process.

materials, e.g. Pt on SiO₂. Therefore, in the present article, we review the fabrication of model catalysts using electron beam lithography (EBL) and pulsed laser deposition (PLD). EBL, which can produce nanoparticles with uniform size and spatial distribution over large (cm²) areas, is a technique that is largely independent of the materials used. PLD is also largely independent of the materials required and is a novel method for nanoparticle fabrication.

Results and Discussion

Nanoparticle Arrays Fabricated with Electron Beam Lithography. Electron beam lithography has been used extensively to fabricate sub-100 nm features.^{32–34} The main advantages of electron beam lithography (EBL) over other lithographic techniques (X-ray, UV) are (1) high spatial resolution, (2) long field of focus, and (3) reasonable beam generation requirements (a synchrotron source is not needed). Modern EBL systems, like the one at the Lawrence Berkeley National Laboratory (LBNL) Nanofabrication Facility, are capable of fabricating lines as thin as a few nanometers and particles as small as 10 nm.³³ A schematic diagram of the EBL process is presented in Figure 1. Briefly, the first step in the process is to spin-coat an electron-sensitive polymer (typically polymethyl methacrylate (PMMA)) onto a substrate. Computer-designed patterns are then “written” into the polymer layer by a highly collimated electron beam followed by a selective dissolution of the polymer damaged by the electron exposure. A thin metal film is then coated on the sample by thermal evaporation. Finally, the remaining polymer resist is removed (“lifted-off”) by dissolution, and the metal particles of the prescribed pattern remain on the substrate.

At IBM (Yorktown Heights), electron beam lithography was used to fabricate an array of 50 nm Pt particles with a 200 nm

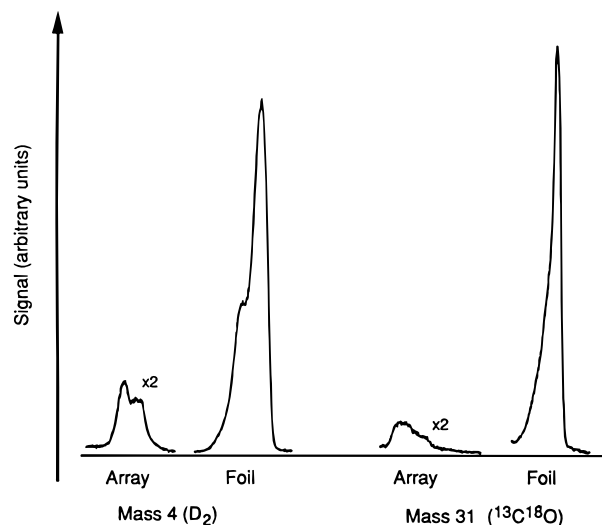


Figure 3. Temperature-programmed desorption spectra of deuterium and ¹³C¹⁸O desorbed from a platinum foil and a platinum nanoparticle array.^{34,35}

periodicity on an oxidized Si substrate (Figure 2).^{34–36} Temperature-programmed desorption of deuterium and ¹³C¹⁸O was used to characterize the number of metal surface atoms for the Pt nanoparticle array produced by IBM (Figure 3). By assuming that the particles were cylinders with 1×10^{15} surface atoms/cm², the calculated Pt surface area on the entire area was 0.04 cm². The measured area of the CO peak from the particles was 10% of the area of a CO peak measured from a 0.4 cm² Pt foil, showing good agreement with the calculated surface area. The ratio of the amount of CO chemisorbed over platinum foils and Pt/SiO₂ nanoparticle array is about 10, whereas the same ratio for deuterium is about 5. The difference in the ratios suggested that deuterium dissociated on the Pt array and migrated to the support.

The Pt/SiO₂ array catalyzed ethylene hydrogenation at 25 °C in a 64 cm³ batch reactor.³⁴ H₂ (760 Torr) and C₂H₄ (12.5 Torr) were used, and a steady-state turnover of 30 molecules ethane (Pt site)^{−1} s^{−1} was obtained. The reaction rate was comparable to those obtained using conventional catalysts. This work demonstrated that catalysis on 10⁹ Pt nanoparticles produced enough product to be easily detected using gas chromatography, despite the fact that the actual metal surface area (about 0.04 cm²) was far less than that of current industrial catalysts.

At LBNL, an array of 40 nm Pt particles with a 230 nm periodicity was fabricated on an oxidized Si(100) substrate and characterized with transmission electron microscopy (TEM) and atomic force microscopy (AFM). Bright field TEM images showed that the Pt particles were uniform in size (40 ± 0.5 nm) and periodicity (230 ± 2 nm) (Figure 4a). Dark field

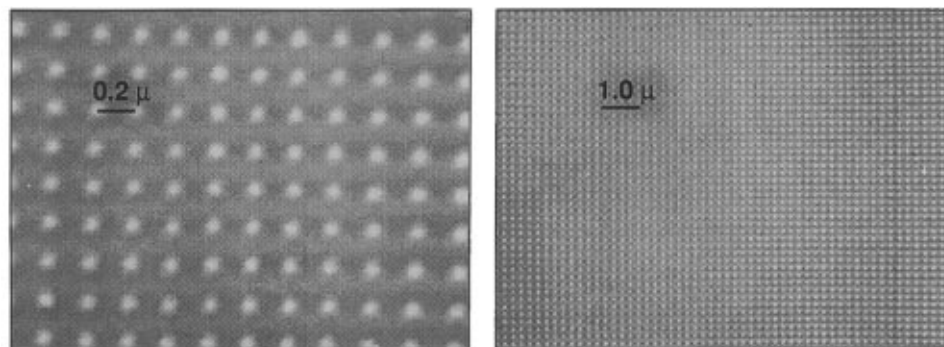


Figure 2. SEM image of platinum particles on an oxidized silicon wafer.³⁴ The particles were 50 nm in diameter, and the interparticle distance was 200 nm. This array was fabricated using electron beam lithography.

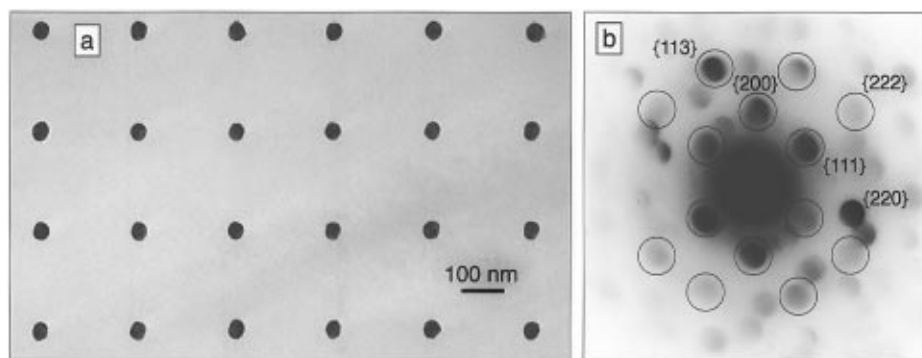


Figure 4. (a) TEM image of Pt particles on a silica substrate. The diameter of the particles was 40 nm, and the interparticle distance was 230 nm. (b) Microdiffraction pattern of a single Pt nanoparticle. Reflections originating from a [110] oriented crystalline grain within the Pt particle are marked by circles. For reference, the interplanar distance of Pt(111) is 2.27 Å.

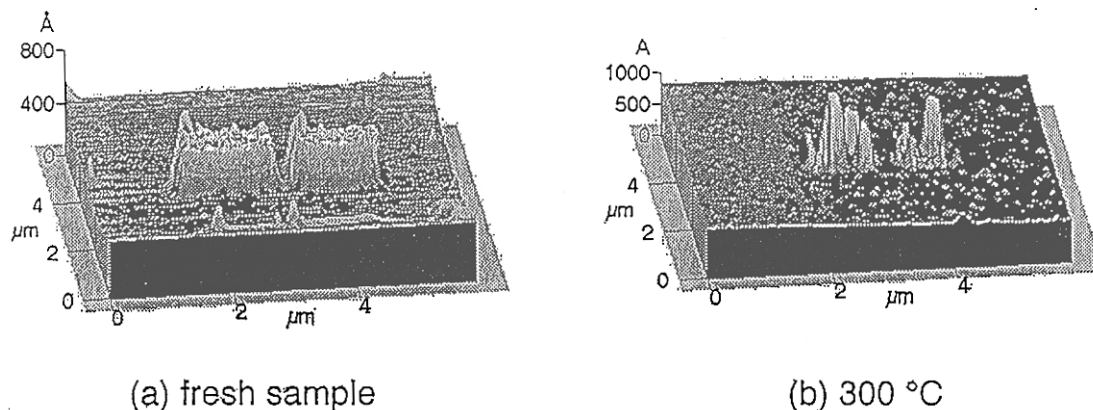


Figure 5. AFM picture of Ag particles: (a) a fresh sample and (b) after oxidizing the sample at 300 °C.³⁶

images indicated that the particles were polycrystalline with domain sizes of approximately 4 nm. Microdiffraction patterns of *individual* particles obtained with scanning TEM (beam diameter of 20 nm) confirmed that the particles were polycrystalline and that, as expected, no epitaxy existed between the particle and the support (Figure 4b). AFM line scans of the LBNL sample showed that the particles had uniform heights of 20 ± 0.5 nm.³⁷

In anticipation of ethylene epoxidation reactions, the thermal stability of 100–750 nm Ag particles on a SiO₂ support has been investigated. The Ag particles supported by SiO₂ were stable up to 300 °C in air and O₂ atmospheres and up to 700 °C in a H₂ atmosphere (Figure 5). Using scanning Auger microscopy, it was observed that Si from the substrate migrated onto the Ag particles when heated to 300 °C in O₂. Under the same oxidizing conditions, when Al₂O₃ was used as the support, Al did not migrate onto the Ag particles.³⁸

Nanoparticles Fabricated with Pulsed Laser Deposition.

A new technique called pulsed laser deposition (PLD) has recently been used to fabricate metal nanoparticle arrays.^{39–44} In PLD, material is ejected from the surface of a target metal by laser ablation (Figure 6). A pulsed Nd:glass laser with 2 J pulse energy and 35 ns pulse length was used to form a plasma on the surface.⁴³ The base pressure in the evaporation chamber was 3×10^{-7} mbar. The deposition of the particles was monitored with a quartz crystal oscillator. The increase in surface temperature of the target metal depended on the penetration of the laser beam, thermal diffusivity, and the rate of energy deposition on the target (laser pulse width). With proper alignment, nanoparticles were deposited on a substrate located in front of the target.

One of the crucial parameters that controls the size distribution of the deposited metal particles was the ambient pressure under which PLD was performed. Cu particles were deposited on

Interaction of High Power Laser with Target

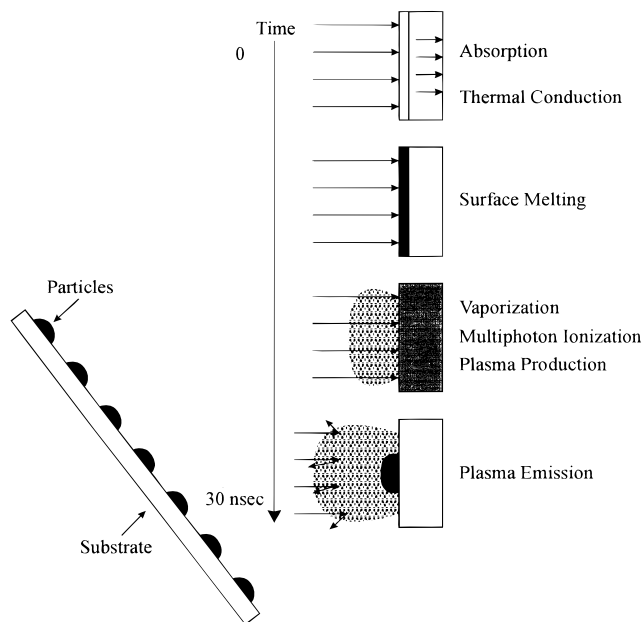


Figure 6. Schematic diagram of pulsed laser deposition, adapted from ref 40.

Si(100) in vacuum (Figure 7a), 1 mbar Ar (Figure 7b), 2 mbar Ar, and 4 mbar Ar. Particles deposited in vacuum had an average diameter of 40 nm, while particles deposited under 1 mbar Ar had an average diameter less than 5 nm. At pressures higher than 1 mbar, the appearance of the deposited particles did not differ significantly from Figure 7b.⁴²

Ag particles formed in vacuum were sputtered with Ar⁺ (at energies varying between 0.5 and 1.5 keV) to produce particles

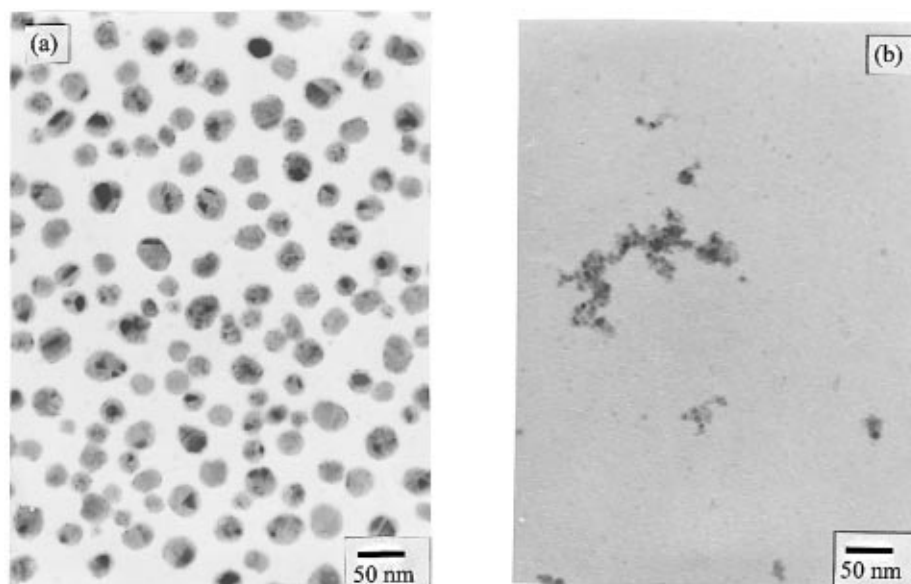


Figure 7. TEM images of Cu films deposited in (a) vacuum and (b) 1 mbar Ar atmosphere.

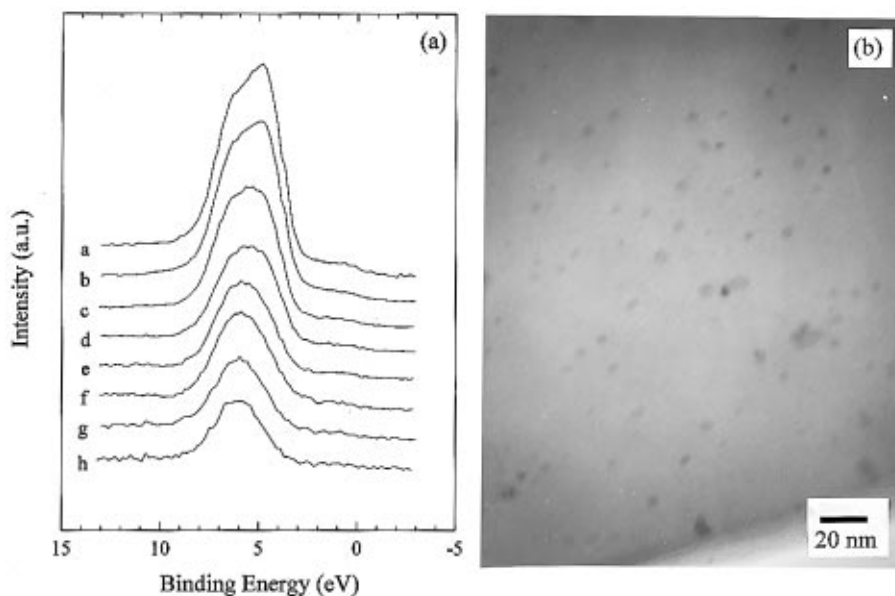


Figure 8. (a) UPS spectra of Ag particles deposited on Si(100) in 2 mbar Ar. Spectrum (a) was bulk Ag. Spectra b–h were after 2, 7, 10, 30, 33, 39, and 42 min sputtering with 1 keV Ar ion bombardment, respectively. (b) TEM image of the Ag particles after 42 min sputtering with 1 keV Ar ions.⁴³

with a size distribution of 4–6 nm (Figure 8).⁴⁰ The Ag 4d UPS peak (using 21.2 eV He (I) and 40.8 eV He (II) excitations) was measured as a function of sputtering time (Figure 8). The fwhm of the valence band UPS peak of Ag 4d was narrowed by 0.7 eV and the Ag 4d band shifted by 1.1 eV from the bulk Ag value toward higher binding energy as sputtering time was increased. Similar results were found for Co⁴² and Pt.⁴³ Lee and Davis discussed the change in the local density of states with diminishing metal particle size.^{45,46} When the size of particles was reduced, the binding energies measured by UPS for electrons in the valence band and by XPS for the core level electrons shifted toward higher value. The shift in the UPS peaks of Ag, Co, and Pt toward higher binding energies was an indication that the particle size was reduced as the Ag particles were sputtered.

Conclusions

To better understand working metal catalyst systems that consist of nanoparticles dispersed on oxide supports, we need

to fabricate model catalysts for which we have control over particle size and interparticle distance. Electron beam lithography (EBL) can be used to fabricate large area (cm²) metal nanoparticle arrays, and the technique provides a method for the systematic variation of size and interparticle distance. EBL is therefore ideally suited to create model catalysts that can be used to explore the effects of particle size, interparticle distance, and catalyst composition on reaction activity and selectivity. Pulsed laser deposition (PLD) is a new technique for deposition of metal nanoparticles with diameters of 1 nm and larger. The use of PLD to create ordered model catalysts is an intriguing possibility. Both of these fabrication methods are independent of the material used for the metal or for the support, and thus a wide range of metals and supports can be combined.

Further studies must explore the thermal and chemical stability of the nanocluster arrays as a function of particle size and the nature of the oxide support. In addition, reactions, such as hydrocarbon isomerization and ethylene epoxidation, that

depend on particle size and interparticle distance should also be investigated.

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