

# New model catalysts: uniform platinum cluster arrays produced by electron beam lithography

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Received 5 October 1995; accepted 17 November 1995

Platinum particles of 50 nm diameter and 15 nm height at 200 nm spacing have been prepared on an oxidized silicon wafer using electron beam lithography. These particles were cleaned of surface carbon with low energy (400 eV) neon ion sputtering. The rate of ethylene hydrogenation over this new model catalyst was measured in a UHV chamber equipped with a high pressure cell for catalytic reaction. Measured turnover numbers are in good agreement with previous work. Atomic force microscopy (AFM) and temperature programmed desorption (TPD) indicate the sample structure remains unaltered by the cleaning and the catalytic reaction.

**Keywords:** electron beam lithography; ethylene hydrogenation; model catalyst; platinum cluster arrays

## 1. Introduction

Single crystals of transition metals have been utilized successfully as model catalysts during the last 20 years. They were cut (with the proper surface orientation exposed) into disks of  $\sim 1$  cm diameter and 1 mm thick, cleaned in UHV by ion bombardment and chemical treatments, then transferred to a small volume ( $\sim 500$  cm<sup>3</sup>) reactor that could be pressurized to reaction conditions. The reaction rates and product distributions were then monitored by gas chromatography. After the reaction, the small area crystal was transferred back to UHV for surface analysis using a variety of electron scattering techniques (LEED, AES, XPS). These model catalysts have been used in studies of many reactions including hydrocarbon conversion, ammonia synthesis, and carbon monoxide hydrogenation [1,2]. Industrial high surface area transition metal catalysts are used in the form of small clusters (2–20 nm) deposited (usually from solution) on high surface area oxide supports. After suitable drying, oxidation, and reduction treatments, small clusters are produced that are dispersed all through the internal pores. Usually there is a broad particle size distribution and the distance between the particles is uncontrolled.

Many catalytic reactions proved to be sensitive to catalyst particle size, and there is evidence that surface species can diffuse between metal particles and the support [3] potentially influencing secondary reactions, including those leading to catalyst deactivation. Therefore, it appears important that we control the particle size as well as the distance between particles.

There have been attempts to fabricate model catalysts to better approximate industrial catalysts than single crystals [4–9]. One approach has been to evaporate metal on a flat oxide support and attempt to control the particle size distribution by careful control of the nucleation conditions. It is difficult to control the spatial distribution of the metal particles with this technique. Others have fabricated model catalysts using optical lithography which allows for spatial control over the metal particles but only in the micrometer size range.

Electron beam lithography can be used to pattern features of uniform size with a spatial resolution below 30 nm. We have used this technique to deposit platinum particles of 50 nm size, separated by 200 nm (center to center), over oxidized silicon single crystal wafers of 0.64 cm<sup>2</sup> surface area. Over  $10^9$  platinum clusters are produced this way in a square array. After preparation, a 0.4 cm<sup>2</sup> portion of this sample was cleaned by ion bombardment in a UHV chamber, then transferred to a high pressure reaction cell. We successfully carried out ethylene hydrogenation, proving that such a cluster array of uniform platinum particles can be used as a model catalyst.

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In this paper we describe the preparation of the platinum cluster catalyst system, the methods of cleaning the cluster surfaces, and their performance during ethylene hydrogenation.

## 2. Preparation of platinum cluster arrays on oxidized silicon wafers

Electron beam lithography was utilized to produce the platinum particles by the method shown schematically in fig. 1. A polymer (PMMA) was deposited by spin coating from solution to a thickness of  $\sim 100$  nm on the heavily oxidized silicon (100) oriented wafer. The wafer was then baked at 453 K for 1 h. Arrays of holes were patterned in the PMMA using an IBM Vector Scan electron beam lithography system operating at 25 keV. The arrays consisted of point exposures with a pitch of 200 nm, covering a  $1\text{ cm}^2$  area. The size of the holes was determined by the exposure dose which was controlled by the dwell time of the beam on each hole site. Area doses ranged between 20 and  $60\text{ }\mu\text{C}/\text{cm}^2$ . Following development in a mixture of isopropyl alcohol and methyl isobutyl ketone (3 : 1), we obtained holes in the PMMA of 50 nm. Platinum was then deposited from by electron beam evaporation to a thickness of 8 nm as measured with a quartz film thickness monitor. Then, the remaining PMMA was removed by an acetone rinse.

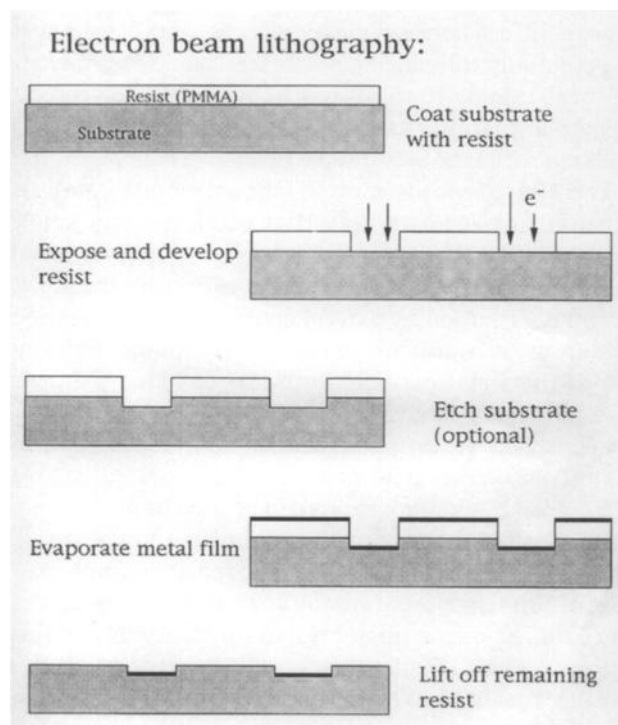


Fig. 1. A schematic diagram of sample preparation with the electron beam lithography process. The optional etching of the substrate was not carried out for our sample and so the Pt particles were deposited directly on the silicon oxide.

## 3. Characterization and cleaning of the platinum cluster arrays

The platinum arrays were characterized by various surface science techniques. Atomic force microscopy (AFM) was performed with a Park Scientific Instruments Autoprobe in air with micro fabricated silicon tips with a nominal radius of 10–15 nm (although more blunt tips were often formed after repeated scanning). Scanning electron microscopy (SEM) was performed with the Hitachi S-800 and an ISI DS 130C dual stage scanning electron microscope using the high resolution top stage. X-ray photoelectron spectroscopy (XPS) measurements were made using the PHI 5300 ESCA system. This UHV chamber has a smaller sample preparation chamber attached that is accessible via a transfer arm. This system is described by Boffa et al. [10]. Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and catalytic measurements were made using a UHV chamber equipped with a PHI 15-255G double pass cylindrical mirror analyzer, ion sputter gun, Balzers QMA 400 quadrupole mass spectrometer and a retractable high pressure cell attached to a gas chromatograph for kinetic measurements. The details of this apparatus are described elsewhere [11–13].

An electron microscope image of the platinum cluster array is shown in fig. 2. One can see the 200 nm periodicity of the square array as well as the 50 nm diameter of the Pt features.

The AFM picture of the platinum clusters is shown in fig. 3a. The clusters appear to be uniform in size and spatial distribution. The measured width of the feature is  $\sim 90$  nm which is appropriate for 50 nm particles given a tip radius of 20 nm. The height of the features was measured as  $\sim 15$  nm. With this thickness of the deposited Pt one calculates a geometrical surface area (assuming the particles take the shape of a cylinder) of  $0.04\text{ cm}^2$  Pt in a  $8\text{ mm} \times 5\text{ mm}$  array (the size of the sample used in the catalytic reactions).

The X-ray photoelectron spectrum of the platinum array before being subject to any treatments or reactions is shown in fig. 4. XPS showed the presence of platinum, silicon, oxygen and carbon, indicating that the platinum clusters are likely covered with a carbon deposit. The presence of a tenacious overlayer was also confirmed by thermal desorption studies using isotopically labeled carbon monoxide ( $^{13}\text{C}^{18}\text{O}$ ). By resistance heating a gold coated tantalum foil attached firmly to the back of the silicon wafer, we could heat the sample with a heating rate of 10–30 K/s. There was no evidence of CO desorption from the contaminated platinum particles detectable by the mass spectrometer.

The sample was bombarded with neon ions at 200 and 300 V for 10 min each without any changes apparent in the Auger spectrum. Spectra were taken in the differential mode with a primary beam energy of 1500 eV at normal incidence. Ion bombardment of the platinum

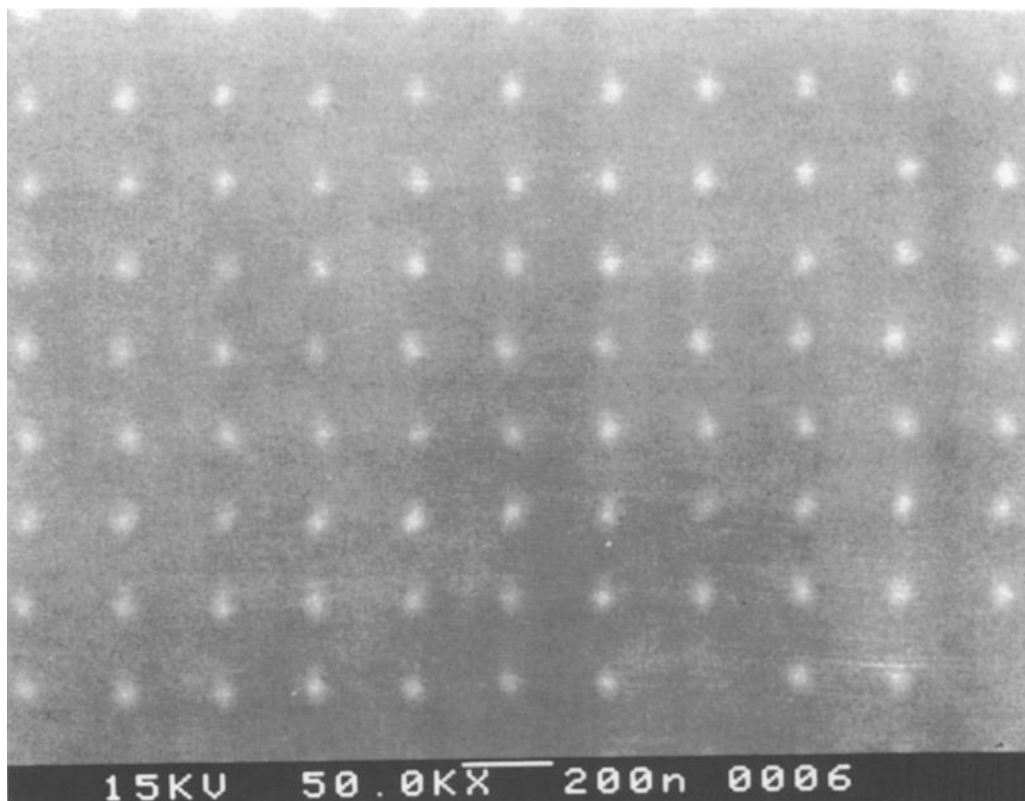


Fig. 2. SEM photograph of the platinum cluster array before cleaning. The white dots have a 200 nm period and a 50 nm diameter.

cluster array by a 400 eV neon ion beam at a pressure of  $10^{-5}$  Torr and a sample current of approximately 250 nA removed the carbon from the platinum. When the surface was heavily contaminated (multilayers of carbon), the carbon could be removed in about  $1\frac{1}{2}$  h of ion bombardment made in 15 min intervals with short ( $\sim 5$  min) periods of annealing in  $> 1 \times 10^{-6}$  Torr  $O_2$  at 200–250°C. AES was performed after each cycle. Over six such 15 min cycles the carbon (272 eV) to oxygen (510 eV) Auger ratio dropped from  $\sim 3$  to 0.8 indicating the removal of surface carbon. After a catalytic reaction, the light carbon layer (monolayer) could be removed in 10 min by 400 eV neon ion bombardment. After such set of ion sputtering cycles the sample was checked by AFM for damage and found to be in the same condition as previous to bombardment (see fig. 3b).

Temperature programmed desorption of isotopically labeled CO (mass 31) showed exposed metal that can readily adsorb and desorb CO. Exposures of  $> 20$  langmuirs were made with a dosing tube at chamber pressures of  $(1-3) \times 10^{-7}$  Torr. The sample was generally cooled to near  $-100^\circ\text{C}$  and the temperature was ramped at approximately 5 K/s. The area under the platinum desorption peak for the cluster array was measured to be  $5.2 \times 10^{-9}$  A s while that of a  $0.4\text{ cm}^2$  clean reference foil was measured to be  $5.6 \times 10^{-8}$  A s. The ratio of these CO titrations confirms the estimated geometric surface

area of  $0.04\text{ cm}^2$ . Furthermore, this small CO TPD signal from the platinum array indicates that neither the neon ion bombardment nor the annealing caused transport of the platinum from the clusters to the oxide support. If these treatments had caused a significant increase in platinum surface area, this would have been apparent by the increase of platinum in the Auger spectrum and the increased adsorption of CO.

We also tried to clean the platinum clusters using an oxygen plasma at 300 K. This was carried out by placing an aluminum electrode  $\sim 5$  mm in front of the sample in a small preparatory chamber attached via a gate valve to the UHV chamber. Oxygen gas was introduced to a pressure of 10–100 mTorr and high ac voltages were applied to the electrode with a tesla coil. The plasma completely removed carbon from the surface as determined by Auger spectroscopy. We found by helium ion scattering spectroscopy (ISS) and angle resolved XPS that exposure to oxygen plasma caused the silicon and oxygen to migrate over the platinum particles and encapsulate the metal. Previous to any plasma cleaning treatment the Pt/O and Pt/Si XPS peak height ratios were independent of the angle between the analyzer and the surface. After cleaning in an oxygen plasma the Pt/O and Pt/Si ratios were a factor of 5 smaller for photoelectrons leaving at a glancing angle ( $15^\circ$ ) than those leaving the surface near normal ( $75^\circ$ ). This indicates that the

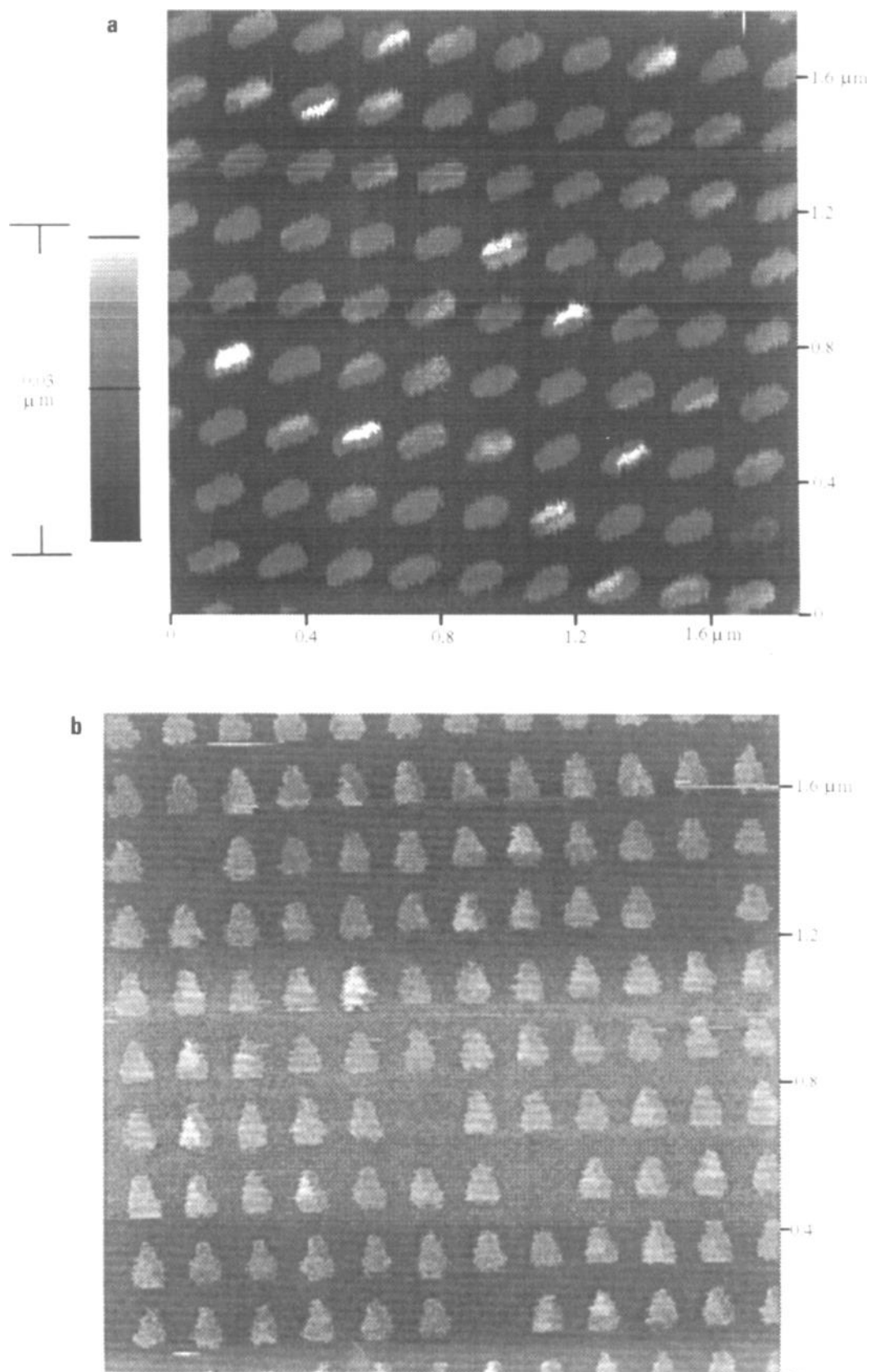


Fig. 3. (a) AFM of the Pt cluster array before either cleaning or reaction. Features are elongated due to convolution with the tip. The measured height is  $\sim 15$  nm and the features seem to be uniform across the sample. The period of the features is 200 nm. (b) AFM image of the sample after cleaning and reaction. The image was taken with a different tip and thus the shape of the features is different.

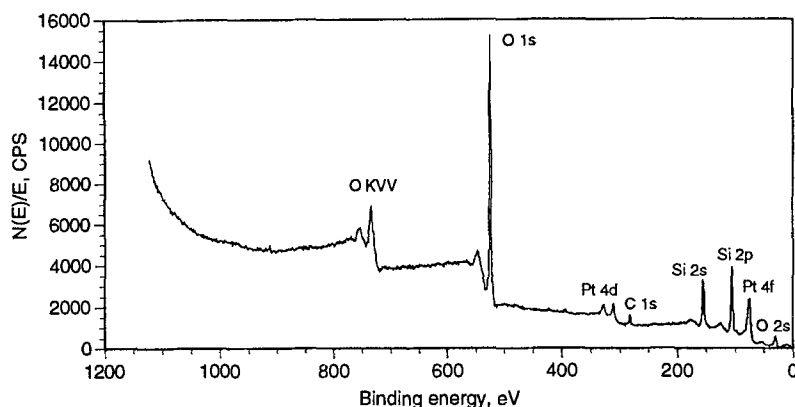


Fig. 4. XPS spectrum (Mg anode) of the cluster array before cleaning. Analyzed electrons were collected from a  $15^\circ$  angle with respect to the surface.

concentration of Si and O had increased at the surface because of the oxygen plasma.

The platinum clusters exhibited remarkable thermal stability in UHV. Neither flashing the sample to  $400^\circ\text{C}$ , nor heating the sample to  $400^\circ\text{C}$  in  $1 \times 10^{-6}$  Torr  $\text{O}_2$  for 5 min, nor  $80^\circ\text{C}$  in 1 atm of hydrogen and 0.016 atm of ethylene for  $\sim \frac{1}{2}$  h changed the surface structure. Such UHV thermal stability for bodies of this size ( $> 10^5$  atoms) may be expected considering a model in which the surface diffusion is controlled by the movement of the small numbers of periphery atoms [14]. Investigations of the thermal stability of the sample in various gases ( $\text{H}_2$ ,  $\text{O}_2$ ) will be carried out in the near future.

#### 4. Ethylene hydrogenation over the platinum cluster array model catalysts

After cleaning the metal clusters by neon ion bombardment the sample was enclosed in the reaction cell. The cell was then filled with 1 atm of hydrogen, followed by adding 12.5 Torr of ethylene (one reaction was performed with 8 Torr ethylene). The formation of ethane was monitored by gas chromatography. Fig. 5 shows the accumulation of ethane as a function of time at room temperature ( $297\text{ K}$ ), along with the background studies carried out on a blank silicon wafer that had been mildly ion bombarded. The activity of the blank was previously measured to be constant and unaffected by the temperature of the sample ( $20$ – $50^\circ\text{C}$ ). Also shown in the figure is an increase in rate of ethane formation upon heating the sample. This demonstrates that the sample is catalytically active. After reaction, Auger spectroscopy revealed little additional carbon that was irreversibly deposited on the sample.

Ethane is produced at a steady state rate of 30 molecules  $(\text{Pt atom})^{-1}\text{s}^{-1}$  and an initial rate of 140 molecules  $(\text{Pt atom})^{-1}\text{s}^{-1}$  over the platinum clusters using a geometric calculation of the surface area. Thus, the rate of ethane formation over the clusters compares well with

the rate of ethylene hydrogenation over platinum single crystals and polycrystalline foils [15–20]. Over a platinum polycrystalline foil a turnover rate of 80 molecules  $(\text{Pt atom})^{-1}\text{s}^{-1}$  was measured and others have measured turnover rates on single crystals in the 60–70 molecules  $(\text{Pt atom})^{-1}\text{s}^{-1}$  [15,16]. Over dispersed, supported Pt/ $\text{SiO}_2$  catalysts the turnover rate was measured in the 10–20 molecules  $(\text{Pt atom})^{-1}\text{s}^{-1}$  range [17,18,20].

Ethylene hydrogenation over foils and single crystals is known not to deactivate and indeed, when carried out over our platinum calibration foil, this was observed to be the case. However, when carried out on supported catalysts (Pt/ $\text{SiO}_2$ ) the group of Dumesic observed an initial deactivation of  $\sim 25\%$  over a period of tens of minutes before the steady state rate was reached [18,20].

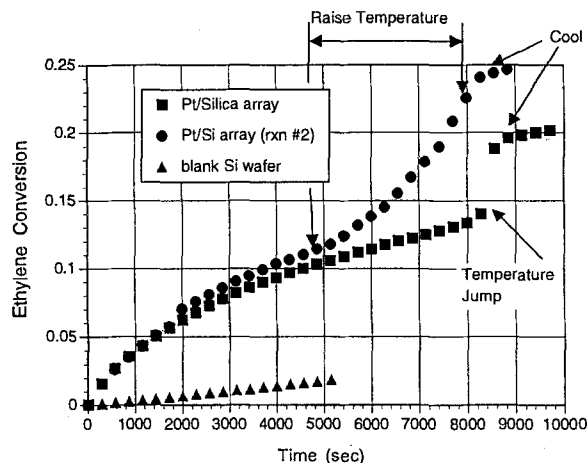


Fig. 5. Accumulation curves for ethylene hydrogenation over Pt/oxidized silicon array and silicon wafer blank: 0.016 atm ethylene, 1 atm hydrogen at  $24^\circ\text{C}$  (room temperature). The fraction of ethylene converted is plotted as a function of time. Arrows indicate changes in sample temperature. In the first reaction (squares) the sample temperature was increased quickly to  $75^\circ\text{C}$  for 4.75 min and then cooled quickly to room temperature. In the second reaction (circles) the sample temperature was slowly increased to  $75^\circ\text{C}$  over  $\sim 1$  h before being quickly cooled to room temperature.

The deactivation over the Pt array occurs over a similar time period but the initial reaction rate is much higher than over the dispersed catalyst.

## 5. Discussion

Electron beam lithography proved to be a useful new method to produce novel platinum model catalysts. Uniformly sized metal cluster arrays can be deposited over a large surface area ( $\sim 1 \text{ cm}^2$ ) within the spatial resolution accessible with this technique. Both the cluster size and the distance between clusters can be controlled over a wide range. Mild bombardment with 400 eV neon ions has been successful in cleaning surface carbon from the platinum clusters without damaging their array structure. Ethylene hydrogenation was utilized as a test reaction to demonstrate the activity of this new model catalyst.

Since ethylene hydrogenation over platinum is known to be surface structure insensitive, obtaining rates of reaction over the platinum cluster array that are comparable to foils and supported catalysts is gratifying. This indicates that our cleaning preparation allows these transition metal cluster arrays can be used as model catalysts after our cleaning procedure. Furthermore, TPD proved to be a useful technique for titrating such small surface areas ( $0.04 \text{ cm}^2$ ).

A "nanowriter" electron beam lithography system will become available soon at the Lawrence Berkeley National Laboratory which should permit the deposition of arrays of  $\sim 10^9$  platinum clusters with sizes in the 3–10 nm range such . These sizes overlap the catalyst particle size most commonly utilized in technology. We will be able to explore the particle size dependence of reaction rates using this smaller particle size regime.

Using electron beam lithography, the deposition of clusters using two or more different metals in the same cluster array sample is possible. We plan to explore the reactivity of these multi-metallic systems. Such metal particle arrays may also allow one to study the spatial extent of surface spillover by varying the amount of metal and support surface available as well as the amount of interfacial area between them. We plan to correlate these variables with kinetic data.

We will soon begin studies of hydrocarbon reactions that produce more than one product in order to explore the reaction selectivity of the platinum clusters. We will also explore the rate of deactivation and compare it to that of single crystal model catalysts. It is postulated that the support can act as a reservoir for unreactive species that might otherwise block active sites.

## Acknowledgement

We would like to thank Dr. Anthoni Tomsia for taking the images of the platinum array with the DS 130C SEM and James Bucchignano for carrying out the electron beam exposure and processing. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098.

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