Fabrication of platinum nanoparticles and nanowires by electron beam lithography (EBL) and nanoimprint lithography (NIL): comparison of ethylene hydrogenation kinetics

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Electron beam lithography (EBL), size reduction lithography (SRL), and nanoimprint lithography (NIL) have been utilized to produce platinum nanoparticles and nanowires in the 20–60-nm size range on oxide films (SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}) deposited onto silicon wafers. A combination of characterization techniques (SEM, AFM, XPS, AES) has been used to determine size, spatial arrangement and cleanliness of these fabricated catalysts. Ethylene hydrogenation reaction studies have been carried out over these fabricated catalysts and have revealed major differences in turnover rates and activation energies of the different nanostructures when clean and when poisoned with carbon monoxide. The oxide-metal interfaces are implicated as important reaction sites that remain active when the metal sites are poisoned by adsorbed carbon monoxide.

KEY WORDS: ethylene hydrogenation; CO poisoning; electron beam lithography; size reduction lithography; nanoimprint lithography; platinum nanoparticles; platinum nanowires.

1. Introduction

Metal single crystals have long been used as model catalysts in combined surface science and catalytic reaction studies. Platinum single crystals of different orientation crystal faces have been used for H\textsubscript{2}/D\textsubscript{2} exchange \cite{1–3}, CO oxidation \cite{4,5}, and hydrocarbon conversion reactions like ethylene hydrogenation \cite{6–16}. They revealed the surface structure sensitivity or insensitivity of different catalytic reactions, the roles of surface defects such as steps and kinks, and additives that are bonding or structure modifiers. Many industrial platinum catalysts are nanoparticles that are dispersed on high surface area porous oxide supports. The resistance of these industrial catalysts to poisoning under industrial conditions has been the focus of much research, and it has been postulated that this may be due to the presence of an oxide-metal interface. Single crystals provide a wealth of information about adsorbate bonding to different crystal faces and catalytic reaction mechanisms, but are unable to successfully model reactivity intrinsic to industrial catalysts that involve the oxide-metal interface or the oxide surface. One direction of research in our laboratory is to bridge this gap between the catalytic chemistry of model single crystals and high surface area platinum nanocluster catalysts used in the chemical technologies. There has been considerable effort to create a model catalytic system with an oxide-metal interface that can be tuned precisely in the nanometer size range. While turnover frequencies are measured under many conditions for various oxide-metal systems, the nature of the catalytically active sites in industrial catalysts is not well understood. With precise control of the fabrication of a catalyst comes the ability to systematically vary different parameters of the metal structure such as size and spacing as well as a choice of the oxide-metal interface of the catalyst. Control of these parameters in the nanoscale regime is difficult to obtain, but lithography lends itself nicely to this task. To this end, we first explored the use of electron beam lithography (EBL) to construct platinum nanoparticle arrays on oxide surfaces as new model platinum catalysts \cite{17,18}. Approximately 10 \textsuperscript{[9]} nanoparticles could be produced using this technique on a 1-cm\textsuperscript{2} silicon wafer in about a day. This corresponds to a platinum surface area of about 0.1 cm\textsuperscript{2}. However, the study of low turnover reactions \textsuperscript{(}<10\textsuperscript{−4} s\textsuperscript{−1}) requires \sim 1 cm\textsuperscript{2} of platinum surface area for practical detection of reaction products. Because of the sequential nature of electron beam exposure, the production of \sim 1 cm\textsuperscript{2} of exposed platinum surface area would require approximately 10 days to fabricate, which is not practical. While the EBL-fabricated platinum samples could be used to study high turnover reactions (such as ethylene hydrogenation) or the thermal and chemical stability of the platinum nanoparticles, we turned to another technique, photolithography, to fabricate higher surface area nanoarrays of platinum cata-

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lysts. Photolithography techniques have been used successfully in the microelectronic industry for years and have proven successful in creating sub-\( \mu \)m structures with high degree of uniformity and reproducibility [19–21]. Size reduction lithography (SRL), developed in our laboratory, couples photolithography with low-pressure chemical vapor deposition and reactive-ion etching techniques to create structures smaller than the normal diffraction limits of photolithography. When this size-reduction technique is used multiple times, it can drastically increase feature density. SRL has previously demonstrated the ability to produce a silicon mold with nanowire structures of 7-nm diameter [22,23]. It has also been shown, that a silicon mold can be used in nanoimprint lithography (NIL) to reproduce sub-10 nm features by using the mold to imprint its features into a polymer resist and depositing the desired material into the negative of the mold pattern [24–26]. The NIL process is a practical fabrication method, which offers a high-throughput method with low production cost, and a choice of deposition materials and substrates. Here, SRL has been used in conjunction with NIL to fabricate arrays of platinum nanowires. After using photolithography and SRL to produce a silicon mold with nanowire features, the mold was used to imprint its features into a polymer resist. This imprint was followed by platinum deposition through the imprinted features to produce platinum replicas of the original silicon mold on either a SiO\(_2\) or Al\(_2\)O\(_3\) surface.

This paper describes the production of platinum nanocatalyst arrays fabricated by EBL and NIL to create nanoparticle and nanowire arrays, respectively. We use these platinum nanoarrays to carry out ethylene hydrogenation with and without the presence of carbon monoxide. Surprisingly large differences in turnover rates and activation energies were found for the different nanocatalysts even for this structure insensitive reaction. The collected experimental data points to the important catalytic role of the oxide-metal interface especially when the platinum sites are poisoned using carbon monoxide.

2. Experimental

2.1. Platinum nanoparticle arrays on alumina and silica: fabrication by EBL and characterization

The EBL fabrication process of platinum nanoparticle arrays has been reported elsewhere [17,18], and the general scheme is shown in figure 1a. Briefly, a thin layer of electron sensitive polymer resist is spin cast onto a Si(100) wafer coated with a 15-nm thick film of either alumina (Al\(_2\)O\(_3\)) or silica (SiO\(_2\)). The photoresist used was poly-methyl methacrylate (PMMA) with \(M_w = 950\) k. The resist is exposed to a highly collimated electron beam (Leica Nanowriter) in a computer-generated dot-like pattern across the polymer surface. The electron beam is generated by a field emission source that exposed the polymer with a beam current of 600 pA and an accelerating voltage of 100 kV giving the beam a diameter of approximately 3 nm. Upon exposure to the electron beam, the polymer undergoes bond scission, which renders it more soluble in a developer solution. After developing the pattern, 15 nm of Pt is vacuum deposited onto the exposed underlying oxide substrate by means of electron beam evaporation using a quartz crystal microbalance thickness monitor. Lift off of the remaining polymer is achieved by ultrasonication in acetone for 5 min, leaving an array of Pt nanoparti-

![Figure 1](image-url)