Introduction
Small particles in the 1-20 nm range often exhibit significant deviations from bulk materials. Although the electronic band structure may approximate the bulk material in particles 8-10 nm in size, the optical, magnetic, mechanical, and chemical properties may be different from the bulk. Because these properties are promising for various practical applications, such as catalysis, electronics, imaging systems, etc., it is important to develop preparation methods that are simple, effective and flexible in controlling particle size distributions [1-4]. Pulsed laser deposition (PLD) has become one of the most versatile dry methods to deposit several classes of materials (metals, ceramics, and polymers) [5-6].
Pd resides within the series of transition metals used as dehydrogenation/hydrogenation (Pt, Pd, Ir, Rh) catalysts. The creation of metal nanoparticles through various means such as redox reactions, chemical vapor deposition, metal implantation/imregnation, and PLD can result in the development of new metal-deposited catalysts with a large surface area to volume ratio. The objective of this study is to correlate particle size with the various deposition parameters that can be controlled during laser ablation. Metal particle size, which is directly connected to the number of active catalytic sites present, is one major factor influencing the properties and performance of supported metal catalysts.

Experimental
The experiments were performed using an excimer laser (KrF, λ=248 nm, 25 ns FWHM). A high purity Pd target (99.95% at.) was ablated in an inert backfill gas of Ar at pressures of 1 to 100 mTorr and fluences ranging from 2 to 4 J/cm². Formation of nanoparticles and molecular clusters are largely facilitated by collisions both inter-plume and with the inert gas on the leading edge of the laser induced plume. Metal nanoparticles were collected on carbon grids and examined using bright-field (BF) and dark-field (DF) TEM, selected-area electron diffraction (SAED) Energy Dispersive X-ray Spectroscopy (EDXS) and High Resolution (HR) TEM in a JEOL 4000 EX TEM and in a JEOL 2010F AEM. Chemical analyses were performed using EDS with the JEOL 2010F with probe sizes of 0.5-2.4 nm. PEEL spectra were acquired in the image mode with 1.0-1.7 eV resolution at the zero-loss peak and 0.1 eV/pixel dispersion. After performing the detector gain calibration and dark current correction, plural scattering effects were removed from the spectra using a Fourier-log deconvolution [7].

Figure 1. (a) Experimental PLD system used for particle size analysis, (b) shows an actual PLD experiment in progress. The material system was YBCuO, deposited at 200 mTorr of O₂. (c) The modified PLD system for coating particulate and irregularly shaped materials (cellulose).

Background
Transition metals, which are most of the elements that occupy the middle section of the periodic table, have unfilled s and d orbitals and loosely held electrons that occupy these orbitals. This is why the electrons in transition metals have the ability to move freely, which gives rise to their high conductivity.

The electron configuration of palladium is 1s² 2s²2p⁶ 3s²3p⁶ 4s²4p⁶ 5s²5p⁶ 6s²6p⁶ 7s²7p⁶. The 5s orbital of palladium is empty because the electrons complete the 4d orbital first. Since hydrogen has one electron, two hydrogen atoms diffuse through palladium and fill the 5s orbital with their electrons making the palladium hydride stable.

The proton of hydrogen sits interstitially between the palladium atoms at octahedral sites in the lattice. While the hydrogen electrons lost to the 5s orbital of palladium revolve around the palladium lattice but they each electron spends more time about its proton because of attraction. So the hydrogen proton is rendered a neutral atom.

The crystal lattice of palladium must expand to hold the hydrogen proton. The lattice constant, d, expands from 0.3906nm before the inclusion of hydrogen, to 0.4049nm after the inclusion. Overall the expansion of the palladium lattice is 3% in length and 10% in volume as a result of hydrogen absorption.

One of the reasons palladium is most effective at holding hydrogen is because its bond enthalpy, 100 ±15 kJ mol⁻¹, is lower than any other metal surrounding it in the periodic table. Bond enthalpy is the energy required to break the metallic bond between two atoms of the same element (Pd-Pd). Lower bond enthalpy means that the hydrogen proton can “sit comfortably” between the palladium atoms with little energy devoted to pulling them apart. Another reason why palladium is most effective is that the crystal structure is face centered cubic, which is the most densely packed atomic spacing of a metal. The hydrogen proton is held tightly and in effect “trapped” because palladium atoms are blocking its path of motion on so many sides.

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The Development and Characterization of Palladium Dehydrogenation Catalysts

References
Figure 2. Deposited Pd particles (clockwise from top left): (a) HRTEM image, (250 pulses, 3 mTorr Ar) (b) HRTEM image and SAED pattern showing partially discrete Debye-Scherrer rings assigned to the FCC structure, enlarged inserts show individual typical multiply twinned particles and corresponding Fast-Fourier-Transforms (5K pulses, 100 mTorr Ar); (c) HRTEM image of Pd deposited onto TiO\textsubscript{2} (250 pulses, 3 mTorr Ar); (d) HRTEM image of Pd onto Al\textsubscript{2}O\textsubscript{3} (250 pulses, 3 mTorr Ar).

Figure 3. Size distributions of Pd particles (clockwise from top left): 250 pulses, 3 mTorr Ar; 5K pulses, 100 mTorr Ar; Pd on TiO\textsubscript{2} 250 pulses, 3 mTorr Ar; Pd on Al\textsubscript{2}O\textsubscript{3} 250 pulses, 3 mTorr Ar.

Figure 4. EDS and EELS performed on Pd particles: a) EDXS spectra of a Pd nanoparticle corresponding to 2.0x10\textsuperscript{-20} g or 1 atomic column for a 0.5 nm probe and 1.6x10\textsuperscript{19} g or 17 atomic columns for a 1.6 nm probe, respectively. Au and Ag represent 500 ppm impurities in the Pd target. b) PEEL spectra demonstrate distinct differences between Pd and Ag particles below 10 eV: a sharp intensity onset at 3.7 eV (Ag) and slowly increasing intensity reaching a maximum at 7.8 eV due to a strongly damped resonance. For energies above 10 eV the spectra reveal some similarities because of similar electron configuration of Ag and Pd with maxima between 17-44 eV corresponding to bulk plasmon at 26.1-26.2 eV and interband transitions from low-lying d-band to the conduction band [8].

Conclusions and Future Work

- Pd nanoparticles with sizes ranging from 1-40 nm were deposited using PLD without evidence of particle aggregation onto amorphous films as well as onto crystalline TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} supports.
- Pd particles were deposited with a mean diameter of 2 nm at 3 mTorr of Ar. Larger particles with some coalescence and fragmentation were obtained with increased pressures.
- Uniform Pd nanoparticles deposited onto the oxide carriers exhibited similar size distributions as particles deposited onto amorphous carbon films under the same ablation conditions.
- The elemental compositions of the Pd nanoparticles (with 500 ppm admixtures of Au and Ag) were confirmed by EDXS and PEELS.
- Low-loss PEEL spectra of the PLD-deposited particles show distinct features due to interband transitions and many-electron effects above 10 eV.
- Other supports will be used such as Avicel, silica, and zirconia.
- Catalytic testing under furnace pyrolysis conditions utilizing GC, TGA/DSC/MS, and \textsuperscript{1}H and \textsuperscript{13}C CPMAS NMR is under investigation at this time.

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