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Priority Communication

Facile, surfactant-free synthesis of Pd nanoparticles for heterogeneous catalysts

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ABSTRACT

A simple route to a highly active and selective Pd/C heterogeneous hydrogenation catalyst has been developed. The 1.5 nm Pd^0 nanoparticles (NPs) were synthesized at room temperature from the reduction of palladium acetate in methanol under anhydrous conditions. A powdered carbon support was added during the synthesis and dried to produce an active catalyst that did not require any additional treatment. This technique alleviates many of the difficulties reported in using colloidal NPs, such as residues left from the removal of capping agents or agglomeration during ligand removal.

1. Introduction

Supported Pd nanoparticles constitute the active phase in catalysts used for energy conversion, chemical synthesis, and pollution abatement. To achieve the highest selectivity and reactivity, it is desirable to have well-dispersed nanoparticles (NPs) that have identical properties and distribution of active sites [1]. Unfortunately, conventional synthesis routes do not provide the requisite degree of control, since they start from Pd salts that are first deposited on a support by impregnation or precipitation. Reduction is achieved by high-temperature treatments involving calcination and H_2 reduction, or chemical reduction by sodium borohydride [2]. The resulting broad distribution of particle size, shape, and composition is detrimental to catalyst performance. Hence, there has been considerable interest in developing colloidal routes to synthesize well-defined nanoparticles that could be used to prepare heterogeneous catalysts [3–5]. Typically, solution routes require various reducing agents such as hydrazine [6], alkaline borohydrides, [7], or amine groups [8] where the particles are protected by polymer groups, surfactants or ligands to prevent agglomeration and growth [7,9].

Polymer protecting agents such as poly(vinyl pyrrolidone) (PVP) and polyvinyl alcohol (PVA) allow preparation of metal colloids that can be stable for months with reasonable control over size as well as shape [10–14]. The synthesis involves addition of polymer to the metal salt followed by chemical or thermal reduction to produce a stable black suspension of Pd^0 particles. These polymer-capped nanoparticles have been shown to be capable of adsorbing probe molecules (i.e., CO) [12] and to be active in a variety of liquid-phase reactions, such as olefin hydrogenation [3] as well as alcohol oxidation [15]. However, when the polymer-capped nanoparticles are deposited on a support for gas-phase reactions, the capping agent must be removed to achieve catalytic activity [1,16,17]. The high-temperature oxidation and reduction treatments used can lead to particle growth and loss of monodispersity. Therefore, there is a need to develop novel routes that can provide metal nanoparticles without protective polymers or capping ligands.

In solvothermal synthesis, precursors, such as palladium chloride or palladium (bis acetyl acetonate), are added to high boiling solvents such as bromobenzene, toluene, or methyl isobutyl ketone in the presence of a surfactant to achieve reduction of the metal [18]. A more easily reduced precursor, such as palladium acetate (noted as $Pd(OAc)_2$) allows for colloidal synthesis at lower temperature using simple alcohols as reducing agents [4,5,19]. However, literature reports that utilize methanol (MeOH) without a capping agent indicate that large aggregates will form [19]. These aggregates can reach diameters of 50 nm and are not suited for catalytic applications. The uncontrolled reduction in Pd complexes at elevated temperatures has been described in the homogeneous catalysis literature as a nuisance [20]. These studies all suggest that capping agents or ligands are essential for the synthesis of nanoparticles in solution at elevated temperatures.

Recent work by Chen et al [21] has shown that graphene oxide can directly reduce K_2PdCl_4 to produce NPs. While this is an effective technique and yields Pd nanoparticles of about 3 nm in diameter, it is limited to reactions using graphene oxide as a support. We describe here a more general route for synthesizing nanoparticles that involves the reduction of the precursor by the solvent. In

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order to avoid capping agents, a mild reducing agent must be employed to limit rapid particle formation, growth, and coalescence. We have found that the room temperature reduction of $Pd(OAc)_2$ in MeOH is slow enough to produce a suspension of Pd NPs. These NPs can then be used as the metal phase of a heterogeneous catalyst without the need for thermal treatment prior to reaction. A Pd-NP/C catalyst was prepared by mixing the carbon support into the suspension of Pd NPs and evaporating the solvent. Aggregate formation was a concern, as there were no capping agents to prevent particle growth. Therefore, the nanoparticles were collected quickly before substantial aggregation could occur. As the reduction was not caused by the support, this technique is general and can be extended to other powder supports. The catalyst was active as-prepared and was found to be active and very selective for acetylene hydrogenation in the presence of excess ethylene.

2. Methods

2.1. Chemicals

All chemicals were used as received and stored under ambient conditions unless otherwise noted. Two separate containers of $Pd(OAc)_2$ were used, one stored and used in an argon-filled glovebox and the other stored and used under bench-top conditions. Anhydrous MeOH and bench-top MeOH, ethanol, 2-propanol, toluene, and acetone were reagent grade and purchased from Sigma Aldrich. Vulcan XC72R was obtained from Cabot Corporation. Hydrogen, nitrogen, and a mixture of 0.5% acetylene and 35% ethylene (balance nitrogen) were UHP grade from Matheson Trigas.

2.2. Synthesis

2.2.1. Preparation of colloidal nanoparticles

For a typical sample, Pd nanoparticles were synthesized by mixing $Pd(OAc)_2$ (5 mg) in MeOH (15 mL) in a scintillation vial and stirring for approximately 5 min with unobstructed exposure to room lighting. The vial was placed on an elevated stir plate for observation and allowed to react undisturbed for 20 min. After 20 min, a TEM grid was dipped into the vial and allowed to dry. Variations on this method were conducted with air-exposed precursors and solvents, including acetone, toluene, ethanol, and 2-propanol. The dependence upon light was evaluated by isolating a vial in an insulated container placed over a stir plate. The solution was stirred for 5 min in the dark and allowed to sit undisturbed over a 2 h period. Observations were conducted at 10 min intervals to minimize light exposure.

2.2.2. Preparation of supported catalyst

A supported catalyst was prepared by dissolving anhydrous $Pd(OAc)_2$ (20 mg) in anhydrous MeOH (30 mL) and stirring continuously for 10 min in a Schlenk flask under inert atmosphere. The flask was removed to ambient atmosphere and Vulcan XC72R carbon (1.0 g) was added. The slurry was mixed for an additional 10 min and subsequently attached to a rotovap, using the bath to maintain the flask at ambient temperature. The solvent was removed while the reaction continued to progress. After 30 min, the reaction was complete and the slightly damp powder was allowed to air dry prior to characterization. No additional treatments were performed prior to catalytic activity measurements. This sample will be referred throughout the manuscript as Pd-NP/C. A similar sample was prepared under identical conditions, except toluene was used as the solvent. As this sample did not form nanoparticles in solution, it will be referred to simply as Pd/C.

2.3. Acetylene hydrogenation

The catalyst was granulated by pressing the dried powder under ~7 metric tons with a Carver hydraulic press to produce a pellet. The pellet was ground and the powder sieved to between 106 and 250 μm using # 140 and # 60 US standard testing sieves from VWR. A sample of 15 mg of powder was mixed with 400 mg SiC (350 μm average grain size, Washington Mills) as an inert to minimize temperature non-uniformity. The mixed powder was packed in a 0.25 in. quartz tube between two plugs of quartz wool. A mixture of acetylene (0.5%) and ethylene (35%) in a balance of nitrogen was passed over the powder at a flowrate of 66 mL/min. Hydrogen was passed at 1.4 mL/min to produce a 5:1 ratio of hydrogen to acetylene. Product gases were sampled at temperature intervals of 10 °C by a Varian 3800 gas chromatograph equipped with a CP-PoraBOND U column and an FID detector.

2.4. Characterization

FTIR (Nicolet 6700, 32 scans, 4 cm^{-1} resolution) was used to probe for the presence of hydroxyl groups on each precursor. The prepared colloids were examined by transmission electron microscopy (TEM, JEOL 2010F) operated at 200 kV in scanning (STEM) and high- resolution (HRTEM) modes to determine the size and composition of the particles. X-ray diffraction (XRD, Panalytical X'Pert Pro, 45 kV 40 mA) was used as a complementary technique. An aliquot of the colloid was pipetted onto a zero-background Si wafer and allowed to dry at room temperature. As the solvent evaporated, the particles coalesced and produced a film, which was then analyzed to verify production of a metallic phase.

3. Results and discussion

The initial investigation involved the reduction of $Pd(OAc)_2$ in MeOH to produce a suspension of Pd NPs (Fig. 1). A systematic study of precursor conditions, light exposure, and solvent was undertaken. In the initial study, using an air-exposed precursor and solvent, the dissolution of the red–orange $Pd(OAc)_2$ in MeOH yielded a pale yellow solution that progressively darkened to a black solution after 60 min (Fig. 1a). Subsequent attempts to reproduce the reaction resulted in longer reaction times (up to days) and moderate variation in particle size. Under rigorously dry conditions, the color change was found to be both faster (dark green in 20 min, black in 30 min) and reproducible. A TEM grid was dipped into the solution at 20 min and a dark field STEM image is shown in Fig. 1b. The mean diameter of 1.5 nm (Fig. 1d) is remarkable in view of the simplicity of the preparation. Multiple tests were performed and it was found that the size distribution was very similar in each case. The Pd particles were so small that they were very difficult to detect via HRTEM on the carbon film and could only be imaged via dark field imaging in a STEM. Our estimate of precision in size measurement is based on the probe size used for our STEM imaging, 0.2 nm. The electron diffraction pattern is very diffuse in agreement with the small size and the low loading of the Pd NPs on the carbon film.

A sample of $Pd(OAc)_2$ in MeOH that was stored in a 'black box' was found to yield no color change after 2 h. Exposure to UV light only led to a similar reaction rate as the sample under ambient light. Larger chain alcohols (ethanol and 2-propanol) produced a color change in several hours, but non-alcohol solvents, such as acetone took one week to react. TEM samples prepared from the acetone preparation revealed that large Pd aggregates had formed. These observations indicated that alcohols were effective reducing agents, as noted by Hirai et al. [3]. Exposing a solution of $Pd(OAc)_2$ in anhydrous MeOH to ambient room light yielded optimal results.

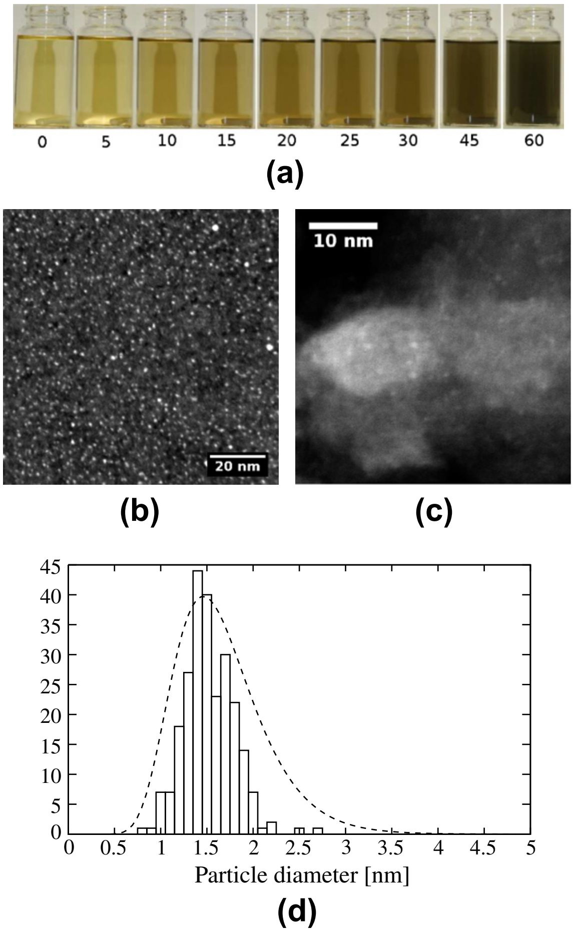

Fig. 1. (a) Time-progression (in min) of formation of air-exposed Pd NP solution in MeOH, (b) STEM image of colloid deposited on carbon film, (c) Pd-NP/C before reaction, (d) particle size distribution of Pd NP from MeOH.

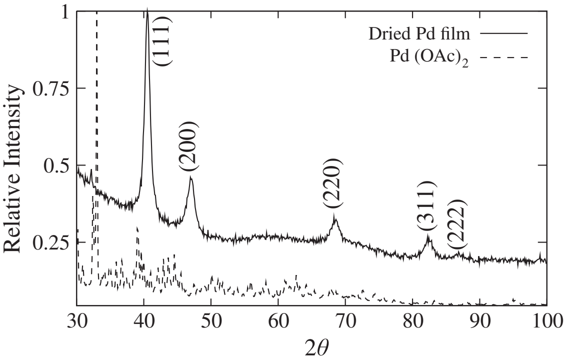

Fig. 2. XRD pattern of dried film colloid on a Si substrate matches Pd. The precursor, Pd(OAc)$_2$, shows a very different pattern, indicating that the organic precursor was reduced to fcc metal.

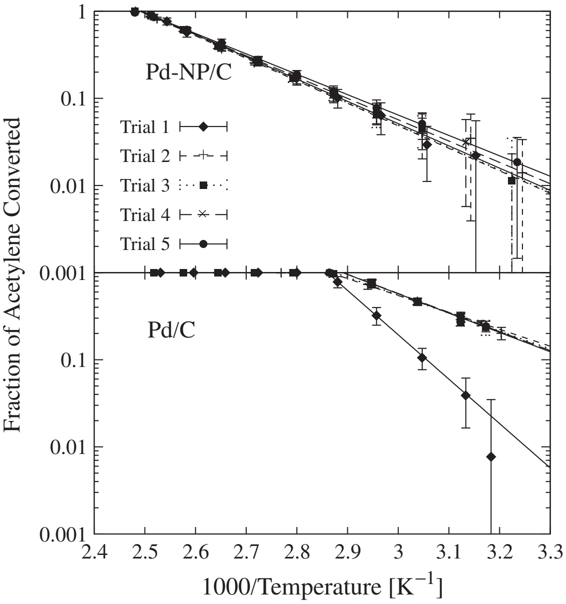

Fig. 3. Graph of fraction of acetylene generated over the reaction temperature range for Pd-NP/C (top graph) and Pd/C (bottom graph). Five repeat trials are shown for each catalyst.

Following these reaction conditions, a catalyst was prepared by mixing Vulcan XC72R carbon powder into the solution after 10 min of reaction. The suspension was stirred for an additional 10 min followed by drying *in vacuo* at room temperature. The powder was analyzed by TEM (Fig. 1c) and the nanoparticles were found to be similar in size to those noted in the previous synthesis (Fig. 1b). The Pd NPs in this colloid were confirmed to be metallic based on the XRD analysis of the dried colloid, which yielded the expected fcc Pd pattern. An XRD sample of the colloid was prepared by pipetting an aliquot of the suspension on a silicon wafer and allowing it to dry prior to analysis. As there were no surfactants, the metal dried to a thin film which produced peaks corresponding to metallic Pd. These peaks were indexed to ICCD card 89-4897 (fcc Pd) while the precursor did not display any metallic phase, shown in Fig. 2. The Pd-NP/C powder did not feature any prominent Pd peaks, which was expected due to the small crystallite size and low weight loading. EDS indicated that ~1 wt% loadings had been achieved.

Each as-prepared catalyst was subsequently tested for acetylene hydrogenation with a 70:1 mixture of ethylene to acetylene in a packed bed reactor. Interestingly, the Pd-NP/C catalyst was found to be selective (Eq. (1)) toward ethylene production at high conversion (Fig. 4) and active (Fig. 3, $E_a = 49$ kJ/mol) without any pre-treatment. Four subsequent trials showed similar results (Figs. 3 and 4, Table 1). The catalyst was therefore active without pre-treatment, and stable over the time interval studied. Pd is a well-known hydrogenation catalyst and is commonly diluted with other metals when used for selective hydrogenation of acetylene [22,23]. The Pd-NP/C catalyst yielded selectivity equivalent to the performance of the best catalyst reported in the literature, Pd$_3$Ga$_7$ [24]. The Pd/C catalyst exhibited an activation process where subsequent trials showed much greater activity in comparison with the initial experiment (Fig. 3, activation energies tabulated in Table 1). Each trial was significantly less selective (Fig. 4) at 100% conversion of acetylene. Both catalysts demonstrated activation energies within the reported values of 40–50 kJ/mol [25,23], except for trial 1 of Pd/C.

Selectivity was defined as the moles of ethylene generated per mole of acetylene consumed, as shown in Eq. (1). In the notation used, *f* denotes feed and *e* denotes effluent.

$$\text{Selectivity} = \frac{C_e^{\text{Ethylene}} - C_f^{\text{Ethylene}}}{C_f^{\text{Acetylene}} - C_e^{\text{Acetylene}}} \times 100\% \qquad (1)$$

The change $\Delta C^{\text{Ethylene}}$ is caused by production of ethylene from acetylene hydrogenation and consumption to ethane. Therefore, a positive selectivity indicates a net gain in ethylene compared with the feed. A negative value represents a loss due to consumption of

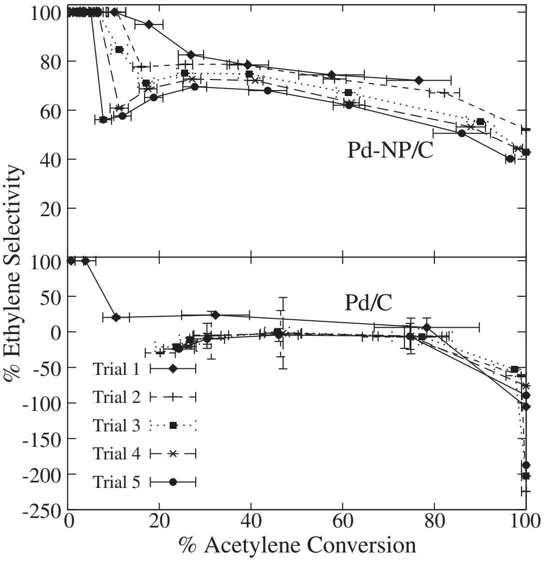

Fig. 4. Graph of ethylene selectivity showing excess C_2H_4 production as positive selectivity (consumption as negative values). As in Fig. 3, five repeat trials are shown for both Pd-NP/C (top) and Pd/C (bottom). Lines are added as a visual aid.

Table 1
Comparison of the performance of the Pd catalysts using selectivity as defined by Eq. (2).

Sample	E_a kJ/mol	Conversion (%)	Selectivity (%)
Pd-NP/C			
Trial 1	49	76	+72
Trial 2	47	100	+52
Trial 3	47	100	+43
Trial 4	45	98	+44
Trial 5	42	96	+40
Pd/C			
Trial 1	98	100	−105
Trial 2	37	100	−224
Trial 3	39	100	−203
Trial 4	42	100	−76
Trial 5	42	100	−89
Pd_3Ga_7 [24]		99	+71
Pd/Al_2O_3 [24]		43	+17

the feed ethylene in addition to total hydrogenation of acetylene to ethane. This definition of selectivity differs from an equation used by Osswald et al. [24] who consider the change in ethylene concentration $\Delta C^{\text{Ethylene}}$ to be unreliable, and use Eq. (2) instead.

$$Selectivity = \frac{C_f^{\text{Acetylene}} - C_e^{\text{Acetylene}}}{C_f^{\text{Acetylene}} - C_e^{\text{Acetylene}} + C_e^{\text{Ethane}} + 2C_e^{\text{other}}} \tag{2}$$

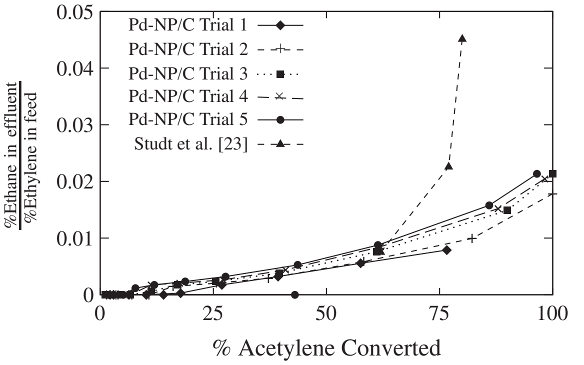

Fig. 5. Ethane content of outlet gas in the present work normalized to inlet ethylene for comparison to the literature [23]. Lines added as a visual aid.

This alternate definition of selectivity was used to compare our results with those of Osswald et al. [24]. The term C_e^{other} was omitted as there was no green oil detected in the present work. The comparison (Table 1) showed that the performance of Pd-NP/C was comparable with Pd_3Ga_7 and significantly better than Pd/Al_2O_3. Another study by Studt et al. [23] reported data in terms of ethane production, but using ~26× lower ethylene content in the feed. The ethane content of the present work is shown in Fig. 5 as moles of ethane in the effluent per mole of ethylene in the feed to compare the data on the same basis. Using this approach, it can be seen that the Pd-NP/C catalyst prepared in this work showed higher selectivity than the $Pd/MgAl_2O_4$ reported by Studt et al. [23]. The high selectivity of Pd-NP/C could be a result of the size of the nanoparticles, the carbon support, or possible carbonaceous species derived from the catalyst precursor and is under investigation. As the nanoparticles formed in solution, any carbonaceous impurities present could have deposited onto the particle as the sample dried. The presence of carbonaceous layers may have resulted in improved selectivity, as reported previously in the literature [26].

4. Conclusions

In summary, a simple route to a highly active and selective Pd-NP/C heterogeneous hydrogenation catalyst has been developed. The Pd^0 NPs were synthesized from the ambient temperature reduction of $Pd(OAc)_2$ in MeOH under anhydrous conditions. The inclusion of Vulcan XC72R during the synthesis led to isolation of the active catalyst that did not require any additional treatment. This technique alleviated the need to pre-treat the catalyst and provided a substantial improvement in selectivity. Additional work on understanding the performance of these catalysts, and Pd NPs on other supports, is being undertaken to explore the broader utility of this simple route to Pd^0 nanoparticles.

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