

C₂H₂ Treatment as a Facile Method to Boost the Catalysis of Pd Nanoparticulate Catalysts

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Supporting Information

ABSTRACT: A facile method to boost the catalysis of Pd nanoparticulate catalysts by simple C₂H₂ treatment is developed. During the C₂H₂ treatment, Pd nanoparticles serve as active catalysts to polymerize C₂H₂ into *trans*-polyacetylene. The deposition of *trans*-polyacetylene layer on Pd nanoparticles makes their surface hydrophobic. Such a hydrophobic surface modification helps to accumulate more hydrophobic substrates during catalysis, making the modified Pd nanoparticulate catalysts more active than untreated catalysts in the catalytic reaction involving hydrophobic substrates. Moreover, the coating of polyacetylene on Pd creates encapsulated Pd nanocatalysts, stabilizing Pd nanoparticles against sintering or aggregation. Since the catalytic polymerization of polyacetylene on Pd is not facet dependent, the development is readily applied to enhance the catalysis of commercial Pd nanoparticulate catalysts by simple C₂H₂ treatment.

The control over the surface wettability of heterogeneous catalysts is an important issue in catalysis because it regulates the interaction between substrates and catalysts and thus the activity and selectivity of the catalysts.^{1–9} For instance, hydrophobic solid acid catalysts were demonstrated as excellent catalysts for esterification reaction^{1–3} or trans-esterification of triglycerides to produce biofuels.^{4,5} Hydrophobic solid base catalysts exhibited high activity in trans-esterification.⁶ The epoxidation reaction catalyzed by hydrophobic molecular sieve led to enhanced activity and selectivity.^{7–9} As an important class of heterogeneous catalysts, heterogeneous metal catalysts with metal nanoparticles dispersed and stabilized on high-surface supports have been widely applied in industry. Recently, many studies have successfully demonstrated that the hydrophobic modification on supports helps to enhance the catalysis of supported metal nanoparticles.^{10–15} The hydrophobic mesoporous polymeric shell endowed the Au@polymer nanostructure with the selective catalytic activity by selectively allowing hydrophobic molecules to pass through the shell to reach the catalytic Au sites.¹⁰ Superhydrophobic SBA-15-supported Au nanoparticles using surface passivation displayed much improved catalytic activity and selectivity toward hydrophobic substrates.¹¹ In the catalytic hydrogenation of aromatic ketones by Pd/SiO₂, the silylation of the SiO₂ support improved the selectivity by weakening the interaction of alcohols on Pd and thus suppressing their consecutive reduction.¹² The hydrophobicity of high silica

zeolites was advantageous to the catalytic performances of noble metal catalysts for VOCs combustion.^{13–15}

Besides the modification on supports, the surface modification of organic ligands on metal nanoparticles has recently been emerging as an effective strategy to regulate the interaction between the metal surface and reactants^{16,17} and thus makes great influence on their catalytic selectivities. By regulating the interaction of reactants with noble metal surfaces, self-assembly monolayers (SAM) of appropriate organic ligands on noble metal nanoparticles enabled the control of chemoselectivity in various catalytic hydrogenation reactions.^{18–22} The coating of ionic liquids on Pt nanocatalysts improved their methanol tolerance in the electrochemical oxygen reduction reaction for fuel cell applications.²³ The modification of metal nanoparticles by chiral ligands promoted their applications in enantioselective catalysis.^{24–32} In most of the studies, the catalytic selectivity was emphasized. Studies on using organic coating to enhance catalytic activities by metal nanoparticles have been rarely reported.^{33,34}

Herein we report a facile method to boost the catalysis of Pd nanoparticulate catalysts through C₂H₂ treatment. Pd nanoparticles themselves can catalyze the polymerization of acetylene to produce *trans*-polyacetylene on their surfaces, modifying the surfaces of Pd nanoparticles to be hydrophobic. The created hydrophobic environment facilitates accumulation of hydrophobic substrates and thus enhances their interaction with Pd surfaces for boosting the catalysis. In the hydrogenation of styrene, Pd nanosheets (Pd NS) show significantly enhanced catalytic activity after C₂H₂ treatment. Moreover, the encapsulation of polyacetylene on their surfaces stabilizes the Pd nanoparticles from sintering. The C₂H₂-treated Pd nanoparticles are highly stable in catalysis. More importantly, the C₂H₂ treatment is readily applied to coat a thin-layer of hydrophobic *trans*-polyacetylene on Pd nanoparticles with morphology other than nanosheets to boost their catalysis, making the method useful to enhance the catalysis of commercial Pd/C catalysts.

By using CO as a surface confining agent, we have recently realized the successful synthesis of freestanding, ultrathin Pd NS.³⁵ The high specific surface area of those Pd NS has inspired us to further investigate their catalytic performances in various reactions. Considering Pd nanocatalysts have been well documented as excellent catalysts for the selective hydrogenation of alkynes and alkenes,³⁶ we first evaluated the catalysis of the Pd

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NS in those hydrogenation reactions. To our surprise, the high-surface area Pd NS dispersed in ethanol exhibited low catalytic activity toward the hydrogenation of acetylene (See Supporting Information for details). While the Pd NS were well dispersed in the solution at the beginning of the catalysis, they were precipitated out after 5 h reaction (Figure S1). To figure out why the Pd NS were poor catalysts for the reaction and changed their dispersion behavior during the catalysis, we have carefully characterized the Pd NS after the catalytic reactions. Compared with the nanosheets before catalysis (Figure 1a), TEM

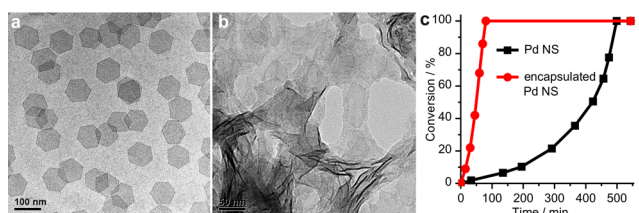


Figure 1. TEM of Pd NS (a) before and (b) after acetylene hydrogenation, and (c) their catalytic performances in hydrogenation of styrene.

measurements clearly showed that the Pd NS were encapsulated by a layer of less electron dense organics after the hydrogenation catalysis. More interesting was that the organic coating on the Pd NS significantly boosted their catalysis in the liquid-phase hydrogenation of styrene, although organic coating is typically considered deleterious to the catalytic performance of metal nanoparticles.^{37,38} In the hydrogenation of styrene, as in Figure 1c, the encapsulated Pd NS obtained from the hydrogenation of acetylene was able to achieve 100% conversion at 80 min. In comparison, it took up to 500 min for the original Pd NS to completely hydrogenate styrene into ethylbenzene under the same catalytic conditions.

To gain deep understanding of why the unexpected high catalytic activity was achieved by the organic coating, we first attempted to identify its chemical composition. As illustrated in the Raman spectrum (Figure S2), two strong peaks at 1117.4 and 1498.6 cm^{-1} together with two weak peaks at 1005.3 and 1294.6 cm^{-1} were observed from the encapsulated Pd NS. And these peaks were not present on the original Pd NS. Based on the literature data,^{39,40} all the four observed Raman absorption peaks are ascribed to the presence of *trans*-polyacetylene. The band assignments are as follows: 1498.6 cm^{-1} to the totally symmetric C=C stretching with considerable mixing of CH in-plane deformation; 1294.6 cm^{-1} to the C-C symmetric stretching vibration; 1117.4 cm^{-1} to CH in-plane deformation with large C=C stretch contributions and 1005.3 cm^{-1} to C-H out-of-plane wagging. The results clearly suggested that the encapsulating organic layer was made of *trans*-polyacetylene. During the hydrogenation of acetylene, the Pd NS served as a catalyst for polymerization of acetylene rather than a hydrogenation catalyst, which could be explained by the much higher solubility of acetylene in ethanol than that of hydrogen. It should be noted that using metal (e.g., Cu) to catalyze the growth of polyacetylene has been previously reported in the literature.⁴¹

When dispersed in ethanol, Pd NS catalyzed the polymerization of acetylene into *trans*-polyacetylene on their surfaces. The encapsulation of polyacetylene readily boosted the catalysis of Pd NS in the liquid-phase hydrogenation of styrene. These exciting results have motivated us to further generalize and simplify the encapsulation method to enhance the catalysis of Pd

nanoparticulate catalysts. In order to simplify the encapsulation of *trans*-polyacetylene on Pd nanostructures, we attempted to perform the polymerization process by simply treating the DMF dispersion of Pd NS with 0.1 MPa C_2H_2 for 2 h at 30 °C in the absence of H_2 . While TEM studies (Figure 2a) revealed no shape

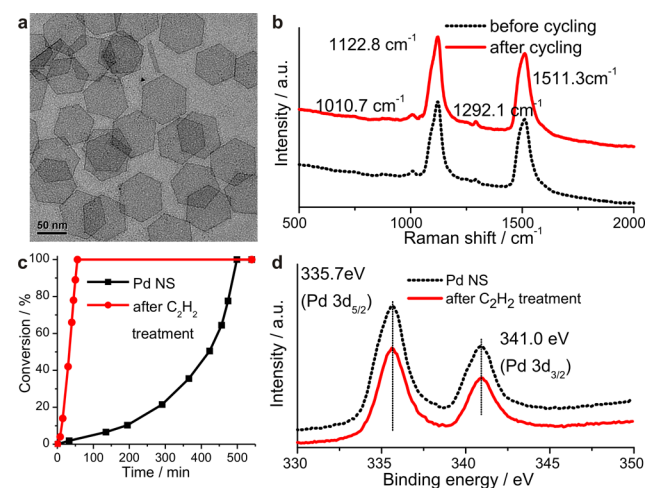


Figure 2. (a) TEM of Pd NS treated with C_2H_2 for 2 h. (b) Raman spectrum of Pd NS before and after C_2H_2 treatment. (c) Catalytic hydrogenation of styrene. (d) Pd 3d XPS spectrum.

change of Pd NS after the treatment, the Raman spectrum of the treated Pd NS (Figure 2b) clearly demonstrated the successful deposition of *trans*-polyacetylene on the Pd NS. All the peaks for *trans*-polyacetylene were nicely resolved. As shown in Figure 2c, the Pd NS treated by C_2H_2 also exhibited significantly enhanced catalysis in styrene hydrogenation as compared with untreated Pd NS. It took only ~56 min for the treated Pd NS to fully complete the hydrogenation of styrene.

To explain the enhanced catalysis by the polyacetylene encapsulation, X-ray photoelectron spectroscopy (XPS) was first applied to examine the possible change on the electronic states of Pd before and after encapsulation. However, as shown in Figure 2d, no observable shift in the binding energies of Pd 3d_{5/2} (335.7 eV) and Pd 3d_{3/2} (341.0 eV) of Pd NS was noted after the C_2H_2 treatment, suggesting that the enhanced catalysis was not caused by the change in the electronic structure of Pd NS. It should be pointed out that Pd NS treated by C_2H_2 alone became poorly dispersed in ethanol, similar to the Pd NS subjected to the mixture of H_2 and C_2H_2 . This phenomenon indicated the dramatic change of Pd NS from hydrophilic to hydrophobic after the polyacetylene encapsulation. We therefore measured the contact angles of water droplets on Pd NS to verify the change of their surface hydrophilicity. As shown in Figure 3a, the contact angle of water droplets on the Pd NS deposited on glass changed from 32.6° to 64.8° after the C_2H_2 treatment, implying that the polyacetylene on Pd NS made the NS more hydrophobic. We thus attributed the enhanced catalysis of the C_2H_2 -treated Pd NS in the hydrogenation of styrene to the hydrophobic modification of the surface of catalytic Pd sites by polyacetylene. The created hydrophobic environment allows more accumulation of hydrophobic substrates and thus enhances their interaction with Pd surfaces for boosting the catalysis.

Based on the proposed hypothesis, one would expect that the promoting effect by the polyacetylene encapsulation is closely determined by the hydrophobic nature of the reaction substrates. Experimentally, nitrobenzene was chosen as another hydro-

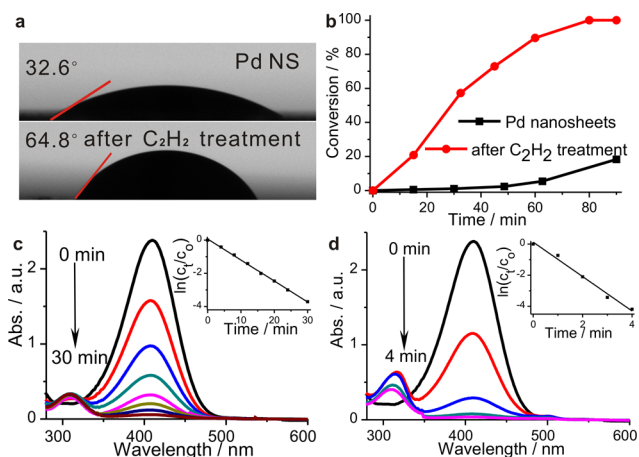


Figure 3. (a) Static water contact angle at the Pd deposits. (b) Catalytic hydrogenation of nitrobenzene by Pd NS and C_2H_2 treated Pd NS. (c and d) Time-dependent UV-vis spectra of the reaction mixture with 4-nitrophenol as the substrate catalyzed by Pd NS and C_2H_2 treated Pd NS, insert: plot between $\ln(C_t/C_0)$ versus time for the disappearance of 4-nitrophenol absorption at 410 nm.

phobic compound for evaluating the promoting effect. As expected, as shown in Figure 3b, the C_2H_2 -treated Pd NS were a far more active catalyst than untreated NS for the hydrogenation of nitrobenzene by offering 100% conversion at 80 min. In comparison, untreated Pd NS gave only a nitrobenzene conversion of 13.6% under the same condition. While the encapsulation can enhance the catalysis of hydrophobic substrates, it would not be effective to promote the catalysis of hydrophilic compounds. Indeed, in the catalytic hydrogenation of 4-nitrophenol by $NaBH_4$, the polyacetylene-encapsulated Pd NS exhibited a poorer catalytic activity than untreated Pd NS (Figure 3c,d). The reduction progress was monitored by UV-vis spectroscopy. As the catalytic reactions proceeded, the intensity of the characteristic absorption peak of 4-nitrophenol at 410 nm decreased and the characteristic absorption of the product (4-aminophenol) at 310 nm appeared accordingly. A linear relation between $\ln(C_t/C_0)$ and reaction time was observed (the insert of Figure 3c,d). The reaction rate constants (k) were calculated accordingly. While the untreated Pd NS offered a rate constant of 1.03 min^{-1} (Figure 3c), the polyacetylene-coated Pd NS gave a rate constant of only 0.13 min^{-1} (Figure 3d). Similarly, in the catalytic hydrogenation of *cis*-2-butene-1,4-diol, a hydrophilic substrate, the C_2H_2 -treated Pd NS exhibited lower catalytic activity than untreated Pd NS (Figure S3). These results demonstrated that the polyacetylene encapsulation on Pd NS can promote the catalysis of hydrophobic but not hydrophilic compounds.

We have known the reason of the enhanced catalysis by the polyacetylene encapsulation. Further, we study the influence of polyacetylene encapsulation thickness on the catalytic activity of Pd NS. Pd NS were treated by C_2H_2 for different time. Raman spectroscopic measurements revealed that even after only 5 min treatment, *trans*-polyacetylene was successfully grown on Pd NS (Figure S4a). As evidenced by the elemental analysis, the amount of polyacetylene deposited on Pd NS increased with the treatment time as indicated by the increased C/Pd ratio (Figure S4b). The more deposition of polyacetylene made the Pd NS more easily separated from the dispersion medium via centrifugation (Figure S5). But the catalytic activity of these catalysts is not as good as the 2 h's sample (Figure S6), indicating

that the presence of too much *trans*-polyacetylene on Pd NS was deleterious to their catalysis. This phenomenon can be explained by the blocking effect of *trans*-polyacetylene on the catalytic sites.

Although polyacetylene is a linear polymer, the polyacetylene coating layer was found not easily peeled off during the hydrogenation catalysis. As shown in Figure 4a, the C_2H_2 -

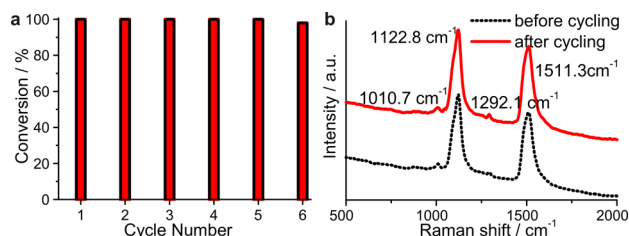


Figure 4. (a) Stability test of C_2H_2 treated Pd NS for the catalytic hydrogenation of styrene, reaction condition: 0.25 mg Pd, 10 mL ethanol, 1 mmol styrene, 1 atm H_2 , $30^\circ C$, time 1 h. (b) Raman of C_2H_2 -treated Pd NS before and after stability test.

treated Pd NS indeed exhibit stable catalytic performances. Not any decay in the activity was noted in the first five cycles of catalysis. After 6 cycles, 98% of the original activity was retained. As evidenced by Raman spectroscopic measurements, the signals of *trans*-polyacetylene on the C_2H_2 -treated Pd NS were not decayed even after 6 cycles of catalytic reactions (Figure 4b). The good stability of polyacetylene on Pd NS could be explained by the strong binding of C=C backbone with the Pd surface. No aggregation/sintering of Pd NS was observed after six cycles of catalysis (Figure S7).

The polyacetylene encapsulation enhanced the catalysis of Pd NS as well as their separability from the reaction medium, which was mainly due to the hydrophobic surface modification of Pd NS. By understanding such an enhancement effect, we have attempted to apply the concept to promote the catalysis of other Pd nanostructures. Pd nanocubes enclosed by Pd $\{100\}$ ⁴² were first chosen to check whether the effectiveness of the concept would be facet dependent. While no morphology change of Pd nanocubes was noted after the C_2H_2 treatment (Figure 5a), the growth of polyacetylene on Pd nanocubes was readily detected by Raman spectroscopy (Figure S8). As shown in Figure 5b, the

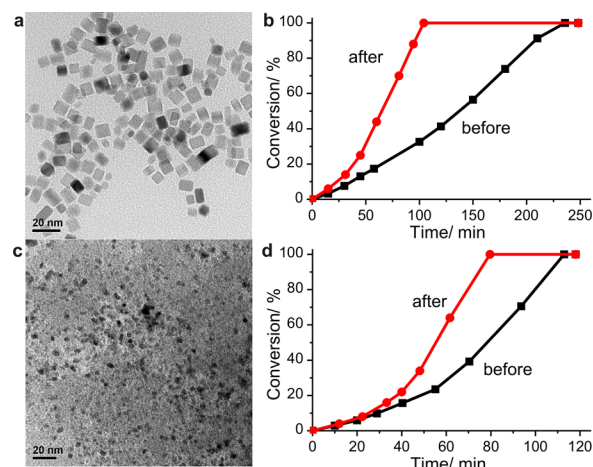


Figure 5. TEM images of Pd nanocubes (a) and commercial 5% Pd/C (c) treated with C_2H_2 for 2 h, and their catalytic performances (b, d) in hydrogenation of styrene.

polyacetylene coating on Pd nanocubes also significantly enhanced their catalysis in the hydrogenation of styrene. The C₂H₂-treated Pd nanocubes took only ~100 min to fully convert styrene into ethylbenzene. In comparison, it took Pd nanocubes without C₂H₂ treatment more than 200 min to complete the hydrogenation. This comparison suggested that the deposition of *trans*-polyacetylene on Pd nanoparticles via C₂H₂ treatment and the resulting promotional effect in catalysis are not facet dependent. It should be noted that such an enhancement was also revealed when surface-clean Pd NS were treated by C₂H₂ (Figure S9). All these positive results have further encouraged us to apply the concept to promote the catalysis of commercial Pd catalysts. Interestingly, an enhancement in catalysis was also observed on the commercial 5% Pd/C after the simple C₂H₂ treatment. The treatment did not result in any aggregation of Pd nanoparticles (Figure 5c) but dramatically promoted the catalytic activity in the reactions involving hydrophobic substrates. As illustrated in Figure 5d, while the untreated 5% Pd/C catalysts required more than 110 min to achieve a 100% conversion, the C₂H₂-treated catalyst took only 80 min to fully hydrogenate styrene into ethylbenzene. Therefore, we consider the polyacetylene encapsulation method developed in this work holds great potential to boost the catalysis of Pd nanocatalysts.

In conclusion, a facile method to boost the catalysis of Pd nanoparticulate catalysts has been developed. In the developed method, a thin layer of polyacetylene was successfully deposited on the surfaces of Pd nanoparticles by treating them with C₂H₂ at room temperature. The polyacetylene deposition changed the surface of Pd nanoparticles from hydrophilic to hydrophobic. Such a hydrophobic surface modification allowed more hydrophobic substrates to be accumulated on the Pd surface so that the catalysis was enhanced. The formation of polyacetylene by simple C₂H₂ treatment and the consequent catalysis enhancement were found independent of the facets of Pd nanoparticles. As a result, the developed facile method is applicable to enhance the catalysis of commercial Pd nanocatalysts for practical applications.

■ ASSOCIATED CONTENT

Supporting Information

Experiment details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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