Dynamic metal-polymer interaction for the design of chemoselective and long-lived hydrogenation catalysts

Songhyun Lee1*, Seung-Jae Shin2*, Hoyong Baek1, Yeonwoo Choi1, Kyunglim Hyun1, Myungeo Seo1,2,3, Kyunam Kim1, Dong-yeun Koh1, Hyungjin Kim2†, Minkee Choi1†

Metal catalysts are generally supported on hard inorganic materials because of their high thermochemical stabilities. Here, we support Pd catalysts on a thermochemically stable but “soft” engineering plastic, polyphenylene sulfide (PPS), for acetylene partial hydrogenation. Near the glass transition temperature (~353 K), the mobile PPS chains cover the entire surface of Pd particles via strong metal-polymer interactions. The Pd-PPS interface enables H2 activation only in the presence of acetylene that has a strong binding affinity to Pd and thus can disturb the Pd-PPS interface. Once acetylene is hydrogenated to weakly binding ethylene, re-adsorption of PPS on the Pd surface repels ethylene before it is further hydrogenated to ethane. The Pd-PPS interaction enables selective partial hydrogenation of acetylene to ethylene even in an ethylene-rich stream and suppresses catalyst deactivation due to coke formation. The results manifest the unique possibility of harnessing dynamic metal-polymer interaction for designing chemoselective and long-lived catalysts.

INTRODUCTION

Supported metal catalysts are widely used in the chemical industry to produce bulk and fine chemicals. They can catalyze various reactions such as hydrogenation, dehydrogenation, hydrogenolysis, and aromatization (1). Typically, metal catalysts are supported on hard inorganic materials including metal oxides, zeolites, and carbons because of their high thermochemical stabilities. Metal particles deposited on inorganic supports typically form a rigid two-dimensional metal-support interface, and the remaining fresh metal surface acts as a catalytic active site. In these systems, support materials not only stabilize highly dispersed metal species but also substantially affect their catalytic properties by charge transfer, generation of perimeter sites, and strong metal-support interaction (SMSI) (2). Therefore, controlling metal-support interactions is one of the most important strategies to tune catalytic properties in heterogeneous catalysis.

The use of soft matter, organic polymers, as a support for metal catalysts is relatively scarce in previous researches (3–6). Even such studies almost exclusively used highly cross-linked polymers (3–6), which can be mainly attributed to the limited thermochemical stabilities of typical polymers. In this sense, truly “soft” polymers have not been widely investigated as a catalyst support. When metal catalysts are supported on soft polymers, however, very unique metal-support interactions and catalytic behaviors may be achieved, which are unlikely to be observed for conventional inorganic catalysts. For instance, mobile polymer chains can cover the entire surface of metal particles when a sufficiently strong metal-polymer interaction exists. The resultant three-dimensional metal-polymer interface can strongly affect the transport of reactants/products to or from the metal catalyst surface, similar to the case of enzymes that can be considered as metal catalysts embedded within biopolymers. The presence of functional polymers on top of metal catalysts can also alter the thermodynamic landscape of reaction intermediates, thereby substantially modulating catalytic properties (5). Because chemical functionalities and thermophysical properties of polymers can be controlled by the design of the polymer structure, it would be possible to systematically and widely tune the metal-polymer interactions and resultant catalytic properties.

In this study, we demonstrate unique catalytic properties of metal particles supported on a thermochemically stable but soft polymer. Such a catalyst is prepared by depositing premade Pd particles on a high-temperature engineering plastic, polyphenylene sulfide (PPS). PPS is a commercially available semicrystalline linear polymer consisting of benzene rings connected through sulfide linkages (7). PPS is thermally stable and insoluble in any of the known solvents below 473 K. In addition, it is mechanically stable and shows high dimensional stability even under elevated temperatures. Because of its commercial availability and remarkable thermochemical stability, PPS is a promising polymer support for metal catalysts. The resultant catalyst is tested for the partial hydrogenation of acetylene to ethylene in an ethylene-rich stream, which is industrially important for the downstream processing of ethylene produced by steam cracking (8–12). Combination of various experimental and theoretical investigations prove that PPS chains cover the entire surface of Pd particles near the glass transition temperature of PPS (~353 K) due to high polymer mobility and strong Pd-PPS interaction. The unique Pd-PPS interface enables the selective partial hydrogenation of acetylene to ethylene and suppresses harmful coke formation.

RESULTS

Synthesis and structures of supported Pd catalysts

For comparative studies, monodisperse Pd particles with a diameter of ~5 nm were synthesized using oleylamine as a stabilizer (13) and then deposited on three different supports (Fig. 1A). A commercially
available PPS powder, mesoporous silica SBA-15 (SiO$_2$) (14), and a thermally cured PPS at 823 K (c-PPS) were used as “soft organic,” “hard inorganic,” and “hard organic” support, respectively. According to differential scanning calorimetry (DSC), the pristine PPS showed clear melting and crystallization behaviors at 569 and 524 K, respectively, whereas c-PPS did not (fig. S1). This means that PPS is composed of discrete mobile polymer chains, whereas c-PPS has a highly cross-linked framework. c-PPS showed a somewhat lower S/C elemental ratio (0.12) than the pristine PPS (0.17), indicating that parts of the sulfide linkages were removed during curing. To support 0.3 weight % (wt %) Pd, the support materials were dispersed in a hexane solution of Pd particles and sonicated for 12 hours at room temperature. After collecting the sample by filtration and washing with hexane, the remaining oleylamine on the Pd surface was carefully removed by the treatment with concentrated acetic acid (13). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed a uniform dispersion of Pd particles with a surface-averaged mean particle diameter ($d_{\text{EM}}$) of 5.0 to 5.1 nm on all support materials (Fig. 1, B to D). Because all samples have the same Pd loading and particle size distribution, they can serve as the ideal model catalysts to unequivocally understand the catalytic effects of different metal-support interactions.

H$_2$ chemisorption on the Pd catalysts was carried out at 343 K to avoid the formation of $\beta$-hydride phase (15). Pd/SiO$_2$ showed an H/Pd ratio of 0.23, which corresponded to spherical Pd particles with a diameter ($d_{\text{chem}}$) of 4.9 nm (15). The good consistency between the Pd particle diameters determined by electron microscopy ($d_{\text{EM}} = 5.1$ nm) and chemisorption ($d_{\text{chem}} = 4.9$ nm) confirmed the successful removal of oleylamine stabilizer from the Pd surface (13). In contrast, Pd/PPS showed undetectable chemisorption (H/Pd < 0.01), although oleylamine was removed by the same acetic acid treatment. This implied that the Pd surface was still covered by some strongly binding species. We postulated that even the mild sample pretreatment temperature for chemisorption experiments (373 K) induced the surface coverage of Pd particles with mobile PPS chains. The possible formation of bulk palladium sulfide phases via polymer decomposition could be excluded, because extended x-ray absorption fine structure (EXAFS) analysis showed only the presence of Pd-Pd coordination (coordination number: 9.24) and negligible Pd-S coordination (fig. S2 and table S1). Pd/c-PPS exhibited a slightly smaller chemisorption (H/Pd = 0.19) than Pd/SiO$_2$ (0.23) presumably due to a minor Pd surface coverage with the polymer framework.

High-resolution transmission electron microscopy (TEM) was used to directly prove the Pd surface coverage by the polymer frameworks. To efficiently obtain the side-view images of Pd particles supported on PPS and c-PPS surfaces, we first coated PPS and c-PPS on globular $\alpha$-Al$_2$O$_3$ particles via melt coating and then supported the premade Pd particles (see Methods). The samples were treated similarly with acetic acid and then thermally treated in H$_2$ at 373 K. As shown in TEM image and elemental mapping (Fig. 1E), the Pd particles supported on the PPS-coated $\alpha$-Al$_2$O$_3$ were fully covered with a thin layer of the polymer. On the other hand, the Pd particles supported on the c-PPS–coated $\alpha$-Al$_2$O$_3$ (Fig. 1F) were mainly positioned on top of the polymer layer, showing only minor polymer coverage on the periphery of Pd particles. These results indicate that the mobile polymer chains of PPS could fully cover the surface of Pd particles at 373 K, while the cross-linked rigid framework of c-PPS exhibited only limited coverage. These results are consistent with the earlier chemisorption data.

To understand the temperature effect on the surface coverage of Pd particles with PPS chains, temperature-programmed H$_2$-D$_2$ exchange experiments were performed (Fig. 2A). Pd/SiO$_2$ showed monotonically increasing HD formation with increasing temperature. Compared to Pd/SiO$_2$, Pd/PPS showed substantially lower HD formation at the lowest temperature (313 K). This indicates that part of the Pd surface was already covered by PPS chains right after the catalyst preparation (note that final drying temperature during catalyst preparation was also 313 K). The HD formation over Pd/PPS
A mixture (100 kPa H\textsubscript{2}, 100 kPa D\textsubscript{2}, 800 kPa Ar) was flowed over Pd/PPS, Pd/SiO\textsubscript{2}, and SiO\textsubscript{2}.

The polymer chains start having sufficient mobility. Pd/PPS showed completely covered by PPS above 353 K. This temperature is close to the generally known glass transition temperature of PPS (358 K), where the Pd surface was partly covered by the polymer chains (fig. S6) because of strong Pd-PPS interactions.

**Thermochemical stabilities of PPS and Pd/PPS**

Thermochemical stabilities of the metal-free PPS and Pd/PPS catalyst were investigated by thermogravimetric analysis–mass spectrometry (TGA-MS) under H\textsubscript{2} atmosphere (fig. S7). The pristine PPS showed weight loss only above 673 K along with the generation of H\textsubscript{2}S, indicating its very high thermal stability compared to those of typical organic polymers. On the other hand, Pd/PPS showed a weight loss from a somewhat lower temperature (523 K). A small evolution of H\textsubscript{2}S was also detected at this temperature. This result indicates that the supported Pd particles can accelerate the degradation of PPS chains by catalyzing the desulfurization of sulfide linkages in the polymer backbone. Nevertheless, this result shows that Pd/PPS can be safely used up to 523 K under H\textsubscript{2} atmosphere, which is adequate for various selective hydrogenation reactions (8, 17).

**Selective and stable acetylene hydrogenation with Pd/PPS**

The prepared Pd catalysts were investigated for the partial hydrogenation of acetylene in an ethylene-rich stream (ethylene/acetylene = 82, H\textsubscript{2}/acetylene = 1.5) at 373 K. This reaction is very important in the petrochemical industry for removing acetylene impurity from ethylene, which would otherwise poison the downstream ethylene polymerization catalysts (8). In this reaction, high ethylene selectivity at complete acetylene conversion (>99%) is important for minimizing the ethylene loss. In industry, Pd-based catalysts have been widely used because of their high catalytic activity and good ethylene selectivity (9).

As shown in Fig. 3 (A to C), all Pd catalysts showed similar acetylene conversion as a function of contact time [1/weight hourly space velocity (WHSV)] and required the same minimum contact time (1/WHSV) of 4.83 hours for achieving full acetylene conversion (>99%). Pd/PPS exhibited substantially higher ethylene selectivity than Pd/SiO\textsubscript{2} and Pd/c-PPS. Even when the contact time (1/WHSV) was excessively increased above 4.83 hours, high ethylene selectivity could be maintained (>65%) and H\textsubscript{2} consumption did not increase noticeably above 80% (Fig. 3A). This means that ethylene was not substantially hydrogenated even after full acetylene conversion. In contrast, Pd/SiO\textsubscript{2} (Fig. 3B) and Pd/c-PPS (Fig. 3C) showed a steadily decreasing ethylene selectivity (down to 30 and 34%, respectively) and increasing H\textsubscript{2} consumption with increasing 1/WHSV. These results indicated that both Pd/SiO\textsubscript{2} and Pd/c-PPS substantially hydrogenated ethylene when acetylene was largely consumed.

Long-term reaction data at the 1/WHSV of 4.83 hours (i.e., minimum contact time enabling full acetylene conversion) are shown in Fig. 3 (D to F). Pd/PPS (Fig. 3D) showed complete acetylene
conversion and stable ethylene selectivity (>65%) for 200 hours. In contrast, Pd/SiO₂ (Fig. 3E) showed a rapid decrease in acetylene conversion (<75%) and ethylene selectivity (<22%) during the same period. This catalyst showed increasing selectivity to the full hydrogenation product, ethane, despite decreasing acetylene conversion. This means that the active sites for acetylene hydrogenation were deactivated, while the sites for preferential ethylene hydrogenation were newly generated during the reaction. To explain such behaviors, it was proposed that coke deposited on the catalyst surface can preferentially hydrogenate ethylene via hydrogen spillover (9).

Pd/c-PPS (Fig. 3F) also showed a substantial decrease in acetylene conversion with reaction time, indicating gradual catalyst deactivation. Compared to Pd/SiO₂, Pd/c-PPS showed a slower decrease in acetylene conversion and a more stable ethylene selectivity, indicating improved catalyst stability.

**Catalytic role of Pd-PPS interface**

As explained earlier, the reaction temperature for acetylene hydrogenation (373 K) was high enough to induce the full coverage of the Pd surface with mobile PPS chains in Pd/PPS. Therefore, the superior ethylene selectivity and long-term stability of Pd/PPS are likely to originate from the formation of a unique Pd-PPS interface. Another important question regarding Pd/PPS is how the catalyst with no apparent hydrogen activation capability (i.e., negligible H₂ chemisorption and H₂-D₂ exchange activity) could hydrogenate acetylene to ethylene in a similar rate to those of Pd/SiO₂ and Pd/c-PPS with fresh Pd surfaces.

To understand the reaction mechanism over Pd/PPS, we carried out H₂-D₂ exchange experiments with and without co-injection of acetylene or ethylene at 373 K (Fig. 4). When a simple H₂-D₂ mixture was flown over Pd/PPS (Fig. 4A), no HD formation was detected, confirming the absence of hydrogen activation capability. When acetylene was co-injected into the H₂-D₂ stream, a sudden formation of HD was observed along with the formation of ethylene (either deuterated or nondeuterated). These results indicate that H₂-D₂ cannot be activated (or dissociatively adsorbed) alone on the Pd surface but can be activated in the presence of co-adsorbed acetylene, thereby converting them into ethylene. This is a strong evidence indicating “cooperative” adsorption of acetylene and H₂-D₂ at the Pd-PPS interface. When ethylene was co-injected into the H₂-D₂ stream (Fig. 4D), no formation of HD and ethane was observed. This implied that cooperative adsorption of ethylene and H₂-D₂ did not occur.

These results can be interpreted that the acetylene-Pd interaction is strong enough to locally detach the PPS chains from the Pd surface, thereby providing accessible Pd sites for the adsorption of H₂-D₂. In contrast, ethylene-Pd interaction might be too weak to disturb the Pd-PPS interface. To support this postulation, we carried out DFT calculations to understand the adsorption thermodynamics of acetylene, ethylene, and hydrogen on the Pd surface (fig. S8), compared to that of diphenyl sulfide (a basic building unit of PPS; as an estimate of Pd-PPS interaction). The binding free energy (ΔGₐ) of diphenyl sulfide was calculated to be −22.05 kcal/mol, which was between that of ethylene (ΔGₐ of −7.75 kcal/mol) and

---

**Fig. 3. Acetylene hydrogenation in an ethylene-rich stream.** (A to C) Acetylene/hydrogen conversions and product selectivities over Pd/PPS (A), Pd/SiO₂ (B), and Pd/c-PPS (C) as a function of 1/WHSV (reaction conditions, 373 K; 0.9-kPa H₂, 0.6-kPa acetylene, 49.3-kPa ethylene, 0.6-kPa propane, 48.6-kPa N₂; WHSV = 0.031 to 1.9 gacetylene gcatalyst⁻¹ hour⁻¹). (D to F) Long-term reaction data for Pd/PPS (D), Pd/SiO₂ (E), and Pd/c-PPS (F) at the 1/WHSV of 4.83 hours.
acetylene ($\Delta G_B$ of $-37.58$ kcal/mol). $H_2$ dissociative adsorption exhibited $\Delta G_B$ of $-17.57$ kcal/mol, indicating a less favorable adsorption than that of diphenyl sulfide. These DFT energetics confirmed that only acetylene can effectively compete with the diphenyl sulfide units of PPS for adsorption on the Pd surface. This was further confirmed by the fact that the Pd/SiO$_2$ catalyst modified with diphenyl sulfide as a molecular promoter showed similar $H_2$-$D_2$ exchange behaviors to those of Pd/PPS (fig. S9). In addition to such thermodynamic aspects, it is also possible that the PPS overlayer further kinetically hindered the access of ethylene to the Pd surface. The kinetic diameter of ethylene (0.39 nm) is substantially larger than that of acetylene (0.33 nm), and its penetration through the PPS overlayer should be much slower. The gas permeability measurements through a commercial PPS film (100 µm thickness) revealed that ethylene permeability ($6.7 \times 10^{-11}$ mol µm m$^{-2}$ s$^{-1}$ Pa$^{-1}$) is five times smaller than acetylene permeability ($1.3 \times 10^{-11}$ mol µm m$^{-2}$ s$^{-1}$ Pa$^{-1}$).

To better understand the structural reorganization of PPS chains on the Pd surface during acetylene adsorption, we additionally performed MD simulations. Acetylene adsorption on Pd was modeled using a Lennard-Jones–type pairwise potential between Pd and C of acetylene and selecting LJ parameters to reproduce the adsorption energy from DFT (fig. S10). From MD trajectories, we sampled an instance when the gas-phase acetylene was adsorbed onto the PPS-covered Pd surface. As shown in Fig. 4G, (i) a small acetylene molecule first penetrates the void space between PPS chains, (ii) is adsorbed on the exposed Pd surface while enlarging the void space further, and then (iii) is loosely covered by PPS chains to maximize van der Waals (vdW) interactions. This result implies that the adsorption of small acetylene molecules can generate...

---

**Fig. 4. Adsorption behaviors of $H_2$, acetylene, and ethylene on Pd catalysts.** (A to C) $H_2$-$D_2$ isotope exchange at 373 K over Pd/PPS (A), Pd/SiO$_2$ (B), and Pd/c-PPS (C) with and without co-injection of acetylene. (D to F) $H_2$-$D_2$ isotope exchange at 373 K over Pd/PPS (D), Pd/SiO$_2$ (E), and Pd/c-PPS (F) with and without co-injection of ethylene. Products were analyzed with a quadrupole mass spectrometer. (G) MD simulation of acetylene adsorption on Pd/PPS, which shows that acetylene penetrates the void space between PPS chains and is adsorbed on the Pd surface, lifting the PPS chains and enlarging the pocket beneath them (C$_2$H$_2$ is indicated in magenta, and all other color codes are the same as in Fig. 2B).
accessible Pd sites for \( \text{H}_2 \) adsorption (i.e., sites for \( \text{H}_2-\text{D}_2 \) exchange) by lifting the PPS chains and widening the pocket beneath them.

In the \( \text{H}_2-\text{D}_2 \) exchange experiments with Pd/SiO\(_2\) (Fig. 4, B and E) and Pd/c-PPS (Fig. 4, C and F), a substantial amount of HD was immediately formed during the flow of a \( \text{H}_2/\text{D}_2 \) mixture, indicating the presence of fresh Pd surface. When acetylene was co-injected into the \( \text{H}_2/\text{D}_2 \) stream, HD formation was substantially reduced, while ethylene and ethane were produced (Fig. 4, B and C). When ethylene was co-injected into the \( \text{H}_2/\text{D}_2 \) stream, HD formation was again decreased, while the production of ethane was detected (Fig. 4, E and F). The reduced HD formation with the co-injection of acetylene/ethylene is in clear contrast to the case of Pd/PPS (i.e., HD formation was markedly enhanced with the co-injection of acetylene; Fig. 4A). Such behaviors can be interpreted that the surface coverage of Pd by acetylene/ethylene reduces the number of available sites for \( \text{H}_2-\text{D}_2 \) exchange (hydrogen chemisorption). This means that the adsorption of \( \text{H}_2/\text{D}_2 \), acetylene, and ethylene is all

---

**Fig. 5. Reversibility of Pd-PPS interaction and proposed acetylene hydrogenation scheme over Pd/PPS.** (A to C) Acetylene/ethylene conversions and product selectivities over Pd/PPS (A), Pd/SiO\(_2\) (B), and Pd/c-PPS (C) during repeated acetylene and ethylene hydrogenation cycles (reaction condition, 373 K; 0.9-kPa \( \text{H}_2 \), 0.6-kPa acetylene or ethylene, 98.5-kPa \( \text{N}_2 \); WHSV = 0.25 g\text{acetylene or ethylene g\text{catalyst}^{-1} \text{hour}^{-1}} \)). (D) Proposed scheme for the selective acetylene partial hydrogenation over Pd/PPS. (i) In the initial stage, PPS chains cover the entire surface of supported Pd catalysts due to strong Pd-PPS interaction. (ii) Acetylene, a strongly binding species on the Pd surface, can disturb the Pd-PPS interface and induce cooperative adsorption of \( \text{H}_2 \). (iii) Once acetylene is hydrogenated to ethylene (i.e., weakly binding species on Pd), PPS chains are readsorbed on the Pd surface while repelling ethylene into the gas stream. (iv) After full conversion of acetylene, ethylene and \( \text{H}_2 \) cannot be adsorbed on the Pd surface due to the stable Pd-PPS interface, thereby inhibiting the formation of a fully hydrogenated product, ethane.
This result indicates that the fresh Pd surface of Pd/SiO$_2$ allows unacetylene (>90%) in step (i) but also ethylene (>70%) in step (ii).

Our results demonstrate that the dynamic coverage of the metal catalyst surface with mobile polymer chains can critically affect the catalytic properties. We shall refer to this phenomenon as a dynamic metal-polymer interaction (DMPI). This can be roughly considered as the organic-version concept of SMSI observed in inorganic catalysts. SMSI occurs when transition metal oxide supports are partly reduced at high temperature (>700 K) to generate lattice oxygen vacancies, which can strongly interact with the metal catalyst surface by forming oxide overlayers (19, 20). Similar to DMPI demonstrated in this work, SMSI also leads to suppressed chemisorption.
and substantially affects the catalytic properties of supported metal particles (19, 20). Although both DMPI and SMSI are based on the high affinity between metal and support materials, they also differ substantially with regard to specific characteristics. SMSI requires high-temperature reduction of metal oxides to generate lattice oxygen vacancies, which disappear upon reoxidation of the support (19). SMSI is substantially affected by the reducibility and crystal structures of the support metal oxides. In contrast, DMPI is the interaction between metal catalysts and chemically intact polymer chains. DMPI can occur under relatively much milder conditions than those required for SMSI, and it depends on the polymer-metal interactions (i.e., chemical functionality of polymers) and the mobility of polymer chains. It is worth reminding that Pd/c-PPS with a rigid cross-linked polymer framework did not show substantial DMPI, although it should have sulfur functionalities similar to those of Pd/PPS. This implies that not only the chemical functionalities but also the thermophysical properties of polymers (e.g., glass transition and crystallinity) would play crucial roles in DMPI. As SMSI has been widely used for designing chemoselective catalysts for various reactions (21–26), DMPI may also be applied to diverse reactions other than acetylene hydrogenation. We believe that designed polymers with diverse functionalities, molecular weights, and crystallinity can be used to tune the catalytic properties of supported metal catalysts. Such polymers can be used alone as a catalyst support or introduced onto the surface of conventional inorganic catalysts to modulate their catalytic properties. In particular, the latter strategy will provide a more efficient way of synergistically combining the benefits of both inorganic (i.e., low price, commercial availability, easy porosity control, and high mechanical stabilities) and organic materials (i.e., designability of molecular structures and flexibility).

**METHODS**

**Synthesis of supported Pd catalysts**

Pd particles with a diameter of ~5 nm were synthesized using oleylamine as a stabilizer (13). In a typical synthesis, 0.075 g of Pd(acac)_2 was dissolved in 15 cm^3 of oleylamine. The solution was heated to 333 K under Ar atmosphere, and then 0.3 g of borane tert-butyllamine complex dissolved in 3 cm^3 of oleylamine was added under stirring. The solution was heated at 363 K for 1 hour. After cooling to room temperature, 30 cm^3 of ethanol was added and the solid precipitate was separated by centrifugation (8000 rpm, 10 min). The resultant Pd particles were then dispersed in 20 cm^3 of hexane. PPS (427268, Sigma-Aldrich), SiO_2 [mesoporous silica SBA-15, synthesized following the reported procedure (14)], and c-PPS (PPS thermally cured at 823 K in He for 2 days, followed by grinding) were used as a support for the premade Pd particles. For supporting 0.3 wt % Pd particles, the premade hexane solution containing Pd particles was further diluted with hexane so that 0.009 g of Pd particles was dispersed in 150 cm^3 of hexane. The diluted Pd solution was added dropwise into 150 cm^3 of hexane containing 3 g of the support materials (PPS, SiO_2, or c-PPS) under vigorous stirring. The resultant solution was sonicated for 12 hours at room temperature. The resultant solids were filtered, washed with ethanol, and dried at 303 K overnight. To remove the oleylamine stabilizer from the supported Pd particles, the solids were added into 200 cm^3 of acetic acid and stirred at 313 K for 12 hours. The samples were filtered, washed with ethanol, and dried under vacuum at 313 K. According to inductively coupled plasma mass spectrometry (ICP-MS; Agilent ICP-MS 7700S) analysis, the experimentally determined Pd loadings were 0.30, 0.32, and 0.31 wt % for Pd/PPS, Pd/SiO_2, and Pd/c-PPS, respectively. This means that the premade Pd particles could be fully deposited on the solid supports by simple wet adsorption. Diphenyl sulfide–modified Pd/SiO_2 was prepared by impregnating 2.6 wt % of diphenyl sulfide (diphenyl sulfide/Pd = 5 in a molar ratio) on Pd/SiO_2 by wet impregnation of a hexane solution. The sample was gently dried at 313 K for 12 hours.

**Characterization**

DSC analysis was carried out using a differential scanning calorimeter (DSC131, EVO). Before analysis, PPS and c-PPS were heated at 593 K under N\textsubscript{2} for 10 min to erase the thermal history of the samples. While measuring the heat flow, the temperature was decreased to 323 K (ramp: 5 K min\textsuperscript{-1}) and then increased to 593 K (ramp: 5 K min\textsuperscript{-1}). H\textsubscript{2} chemisorption was carried out using an ASAP 2020 (Micromeritics) volumetric analyzer. Before the measurements, samples were reduced at 373 K under H\textsubscript{2} for 3 hours, followed by evacuation for 3 hours at the same temperature. H\textsubscript{2} adsorption was carried out at 343 K to avoid the formation of a β-hydride phase (15). Chemisorption amounts were determined by extrapolating the high-pressure linear portion (7 to 30 kPa) of isotherms to zero pressure. Each sample was measured in triplicate and averaged. HAADF-STEM images of Pd/PPS, Pd/SiO\textsubscript{2}, and Pd/c-PPS samples were taken with a Titan Cubed G2 60-300 (FEI Co.) at 200 kV after the samples were mounted on a copper grid (300 square mesh) using an ethanol dispersion. Metal size distributions were determined by counting at least 200 metal particles. The surface area-weighted mean particle diameter was calculated using the following equation (15)

\[ d_{EM}(nm) = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \]  

where \( n_i \) is the number of particles with a diameter of \( d_i \) (15).

For efficiently obtaining side-view TEM images of Pd particles supported on PPS and c-PPS surfaces, PPS and c-PPS were precoated on globular α-Al\textsubscript{2}O\textsubscript{3} particles via melt coating. For PPS coating, a physical mixture of PPS and α-Al\textsubscript{2}O\textsubscript{3} (42573, Alfa Aesar) in a 1:3 mass ratio was ball-milled for 3 hours and then heated at 593 K (a slightly higher temperature than the melting point of PPS) for 1 hour under He flow. For the coating of c-PPS, the same ball-milled mixture of PPS and α-Al\textsubscript{2}O\textsubscript{3} was heated at 593 K for 1 hour and then at 823 K (elevated temperature for thermal curing) for 2 days under He flow. These composite materials were supported with 0.3 wt % of premade Pd particles, followed by the treatment with acetic acid as described above. After H\textsubscript{2} reduction at 373 K for 2 hours, the samples were mounted on a copper grid (300 square mesh) using an ethanol dispersion. TEM investigation and elemental mapping using energy-dispersive x-ray spectroscopy were carried out using a Titan Cubed G2 60-300 (FEI Co.) at 200 kV. EXAFS data over Pd K-edge were recorded in a fluorescence mode at Pohang Accelerator Laboratory (10C-Wide XAFS beamline) after pre-reduction at 373 K under H\textsubscript{2}. The EXAFS data were processed using Athena and analyzed using Artemis, part of the Demeter software package, interfaces for the IFEFFIT and FEFF6 codes. The \( K^3 \)-weighted EXAFS signal was Fourier-transformed to \( R \)-space to obtain the radial distribution function.

TGA-MS analyses of PPS and Pd/PPS were carried out using a TGA N-1500 thermogravimetric analyzer (Scinco) coupled with a...
quadrupole mass spectrometer (ThermoStar-GSD 320, Pfeiffer Vacuum). The temperature was increased from 373 K to 923 K with a ramping rate of 10 K min⁻¹ under H₂ flow (100 cm³ min⁻¹). H₂–D₂ isotope exchange experiments were carried out in a quartz plug-flow reactor connected to an online quadrupole mass spectrometer. Typically, 0.1 g of sieved catalysts (200 to 300 μm) was loaded into the reactor. For the temperature-programmed H₂–D₂ exchange, the catalysts were pretreated at 313 K under Ar for 30 min, and temperature was increased from 313 to 423 K with a ramping rate of 10 K min⁻¹ under a flow of H₂/D₂ gas (50 cm³ min⁻¹; 10-kPa H₂, 10-kPa D₂, 80-kPa Ar). The isothermal H₂–D₂ exchange experiments with and without co-injection of acetylene or ethylene were conducted at 373 K after pretreatment of the catalysts at the same temperature under H₂ flow for 2 hours. After purging with Ar for 30 min, H₂/D₂ gas mixture was flowed (50 cm³ min⁻¹; 10-kPa H₂, 10-kPa D₂, 80-kPa Ar) for 20 min. Then, the gas was switched to H₂–D₂ containing acetylene or ethylene (50 cm³ min⁻¹; 10-kPa H₂, 10-kPa D₂, 10-kPa acetylene or ethylene, 70-kPa Ar).

Gas permeation of a PPS film (100 μm thickness, Sigma-Aldrich) was measured using a constant-volume/variable-pressure single gas permeation system at 323 K. The PPS film was mounted on the sample cell with additional sealing using aluminum tape and epoxy (DP-100 from 3 M). Permeation system was evacuated overnight to decrease the pressure below 0.02 torr, and the upstream gas reservoir was charged with pure gases and allowed thermal equilibration for 30 min. The gas was dosed onto the PPS film, and the downstream pressure was logged with a high-resolution data logger via LabVIEW program.

**Catalytic reaction**

Acetylene hydrogenation in an ethylene-rich stream was carried out in a stainless-steel plug-flow reactor connected to an online gas chromatograph equipped with a GS-GasPro column. Typically, 0.067 g of sieved catalysts (200 to 300 μm) mixed with 1.9 g of sieved quartz particles was loaded into the reactor. The reaction was carried out at 373 K after pretreatment of the catalysts at the same temperature under H₂ flow. The reaction was carried out by flowing a gas mixture containing 0.9-kPa H₂, 0.6-kPa C₂H₂, 49.3-kPa C₂H₄, 0.6-kPa C₃H₈, and 48.6-kPa N₂ into the reactor. Propane (C₃H₈) was used as an internal standard. The WHSV was varied from 0.031 to 1.9 g acetylene g⁻¹ catalyst⁻¹ hour⁻¹. The reactant conversion and product selectivity were calculated using the equations given below

\[
C₂H₂ \text{ conversion} (\%) = \frac{C₂H₂_{\text{in}} - C₂H₂_{\text{out}}}{C₂H₂_{\text{in}}} \times 100
\]  

(2)

where \(C₂H₂\text{in}\) is the concentration of acetylene in the reactant and \(C₂H₂\text{out}\) is the concentration of acetylene in the product

\[
C₂H₆ \text{ selectivity} (\%) = \frac{C₂H₆_{\text{out}} - C₂H₆_{\text{in}}}{C₂H₂_{\text{in}} - C₂H₂_{\text{out}}} \times 100
\]  

(3)

where \(C₂H₆\text{in}\) is the concentration of ethane in the reactant and \(C₂H₆\text{out}\) is the concentration of ethane in the product

\[
C₄H₆ \text{ selectivity} (\%) = \frac{2(C₄H₆_{\text{out}} - C₄H₆_{\text{in}})}{C₂H₂_{\text{in}} - C₂H₂_{\text{out}}} \times 100
\]  

(4)

where \(C₄H₆\text{in}\) is the concentration of \(C₄\) in the reactant and \(C₄H₆\text{out}\) is the concentration of \(C₄\) hydrocarbon in the product. \(C₂H₂\) is the sum of the \(C₂\) hydrocarbons including butanes, butenes, and butadiene

\[
C₂H₄ \text{ selectivity} (\%) = \left\{1 - \frac{(C₂H₄_{\text{out}} - C₂H₄_{\text{in}}) + 2(C₂H₂_{\text{out}} - C₂H₂_{\text{in}})}{C₂H₂_{\text{in}} - C₂H₂_{\text{out}}}\right\} \times 100
\]  

(5)

**Analysis of the used catalysts**

After acetylene hydrogenation was carried out at WHSV = 0.21 g acetylene g⁻¹ catalyst⁻¹ hour⁻¹ (1/WHSV of 4.83 hours) for specified time intervals, the reactor was purged with N₂ (100 cm³ min⁻¹) for 2 hours at the reaction temperature (373 K). After cooling to room temperature, the used catalysts were collected and carefully separated from the quartz particles for further analysis. The total amount of carbonaceous deposits (green oil + coke) in the used catalysts was determined by combining elemental analysis (FLASH2000 elemental analyzer, Thermo Fisher Scientific) and TGA (TGA N-1500, Scinco). To separately determine the amounts of insoluble coke and soluble green oil deposited, the used catalysts were extracted with an excess amount of dichloromethane under stirring at room temperature for 2 hours. Then, the catalysts were filtered, washed with dichloromethane, and dried at 313 K. The remaining amounts of carbonaceous deposit (i.e., coke) were analyzed again by elemental analysis. The green oil amount was calculated by subtracting the coke amount from the total amount of carbonaceous deposits.

**Computational details**

We performed canonical ensemble (i.e., constant number of particles, volume, and temperature) MD simulations at 360 K and 300 K using the Nosé-Hoover thermostat (27, 28) by using a large-scale atomic/molecular massively parallel simulator (29). The valence interactions of PPS were modeled using a DREIDING 2.21 FF (30). The atomic charges of PPS were assigned using the charge equilibrium (Qeq) (31) method. The dielectric constant was set to 3 [experimentally determined value (32)] to model the electrostatic screening due to electronic polarization in an ad hoc but effective manner. The vdW interaction was then scaled by 0.3 from the original DREIDING FF parameters to reproduce the interchain interaction energy from DFT calculations (fig. S3). Current FF reproduces the experimental lattice parameters of crystalline PPS (fig. S3) and glass transition temperature (fig. S4), which validate the accuracy level of current FF parameters. The Pd particle was modeled using an icosahedral 55 atom cluster, and the metallic many-body interaction of Pd atoms was described using the EAM (16). To describe the nonbond vdW interaction between Pd particle and PPS, vdW parameters of the universal FF (33) were used for Pd and then the geometric mixing rule was used. However, for the interaction between Pd and S of PPS, where donor-acceptor interaction also exists, the vdW parameters were tuned to reproduce the DFT binding energy of diphenyl sulfide to Pd (111) surface (fig. S5). The MD simulation cell contains 1 Pd nanoparticle and 12 PPS layers, each of which has 10 polymer chains with 5 repeating units connected through the periodic boundary condition (fig. S4).

DFT calculations were performed using the Vienna Ab initio Software Package (VASP) 5.4.1 (34) with project augmented pseudopotentials (35). Perdew-Burke-Ernzerhof (36) exchange-correlation functional with dispersion correction by Grimme's scheme (D3) (37) was used, and the kinetic energy cutoff of the plane-wave basis
was set to 450 eV. A Γ-centered (3 × 3 × 1) mesh was used to sample the reciprocal space. An additional ~15-Å-thick vacuum regime was introduced to the slab models, and a dipole correction scheme was applied to electrostatically isolate the surface model from periodic images. During geometry optimizations, the convergences of the self-consistent field (SCF) and ionic relaxations were set to 10⁻⁴ and 10⁻³ eV, respectively. The binding free energy was calculated as ΔE_{SCF} + ΔZPE − TΔS, where ΔE_{SCF} is the electronic SCF energy, ZPE is the zero-point energy, and TΔS is the translational and rotational entropic contribution to the binding of gas-phase species such as ethylene, acetylene, and H₂.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/28/eabb7369/DC1

REFERENCES AND NOTES

Acknowledgments: We acknowledge the Pohang Accelerator Laboratory (PAL) for beamline use. Funding: This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF- 2020R1A2C1003694) and LG Chem. Author contributions: M.C. conceived and designed this study, S.L. and H.B. prepared the materials and performed structural and catalytic characterization. S.L., Y.C., K.H., M.S., and M.C. analyzed the experimental results. S.-J.S. and H.K. performed the DFT and MD studies. K.K. and D.-Y.K. performed gas permeation studies. S.L., S.-J.S., H.K., and M.C. wrote the paper. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 16 March 2020
Accepted 27 May 2020
Published 8 July 2020
10.1126/sciadv.aabb7369