Grain Boundaries Created by Steam Treatment are Active Sites for Methane C-H Activation in Palladium Catalysts

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Abstract

The structure and arrangement of atomic ensembles play a critical role in heterogeneous catalysis. Defects may display high reactivity due to the specific arrangement of atoms that differs from crystalline surfaces. In this study we demonstrate that high-temperature steam treatment of palladium catalysts provides a twelve-fold increase in the mass-specific reaction rate for C-H activation in methane oxidation compared to conventional treatments. Through a combination of experimental and theoretical methods, we demonstrate that an increase in the grain boundary density is achieved during the steam treatment and oxidation and is responsible for the increased reactivity. The grain boundaries are highly stable during reaction and show specific rates at least two orders of magnitude higher than other sites on the Pd/Al₂O₃ catalysts, predominantly because of strain introduced by the defective structure.

One-Sentence Summary: Grain boundaries in palladium nanocrystals show two orders of magnitude increase in rates for methane combustion due to strain.

Supported metal nanoparticles have been widely used as catalysts in heterogeneous reactions. Their catalytic activities are highly dependent on the surface structure of nanoparticles because the different surface sites display diverse reactivity (1-5). Exploring the nature of the active site is critical for understanding structure-property relations in catalysis. Recent studies have shown that specific types of surface sites (e.g., terrace sites, steps, grain boundaries, and metal-support interface sites) can be manipulated to improve catalytic activity (6, 7). For instance, tetrahexahedral platinum (Pt) nanoparticles with high-index facets exhibit enhanced catalytic activity in electro-oxidation of formic acid and ethanol compared to Pt nanospheres (8). A silver catalyst with a high density of stacking faults showed superior activity and durability in the hydrogen evolution reaction (9). These examples highlight how specific atomic-scale surface motifs can display increased catalytic performance compared to more stable, low-energy surface facets.

Twin and grain boundaries, some of the most stable defects on metal surfaces, have been demonstrated to be active sites in certain electrocatalytic reactions and especially CO_2 electroreduction (10–12). It has been shown that the improvement in performance results from the lattice strain and structural perturbations in the vicinity of the grain boundaries at the catalyst surface (13), and that this effect can lead to orders of magnitude higher catalytic rates (14). Although grain boundaries have been recognized as promising defects for the activity of electrocatalysts, little is known about how grain boundaries alter the catalytic properties in gas-phase heterogeneous reactions. This correlation is essential for establishing valuable structure-property relationships in heterogeneous catalysts to develop more efficient systems.

In this work, we demonstrate that steam treatment of a Pd/Al_2O_3 catalyst provides an enhancement in its methane combustion activity, with the mass-specific reaction rate increasing

by \approx 12 times compared to the same sample treated in O₂. A direct correlation between the extent of formation of twin and grain boundaries with the activity of these Pd catalysts was revealed, and density functional theory (DFT) calculations show that changes in reactivity can be explained by surface strain present in the immediate vicinity of grain boundaries. Given that the specific active sites show two orders of magnitude higher intrinsic rates, this work provides a clear motivation to use bulk defects to improve catalysts.

Uniform colloidal palladium nanoparticles with an average particle size of 15 nm were deposited onto a commercial Al₂O₃ support (Fig. 1A). The catalytic performance of the Pd/Al₂O₃ catalyst was evaluated for methane combustion in the presence of steam after several gas treatments [O₂, H₂, Ar, and steam, (15)]. Negligible changes in light-off curves were observed for the Pd catalyst after conventional treatments (O₂, H₂, and Ar atmospheres) (fig. S1A). The T₅₀ values, which are the temperatures needed to achieve 50% conversion of CH₄ to CO₂, were similar for the catalyst after all these treatments. Strikingly, upon treatment in steam at 300 °C, the catalyst showed a noticeable improvement in catalytic activity leading to the lowest T₅₀ value (fig. S1A). The Pd/Al₂O₃ catalyst was then treated in either steam or O₂ at increasing temperatures (300 $^{\circ}$ C, 500 °C, 600 °C, and 700 °C). No catalytic enhancement was found for the catalyst treated in O₂ (fig. S1B). Upon treating with steam, however, the catalyst exhibited improved catalytic activity with increasing treatment temperature up to 600 °C (Fig. 1B), with the catalyst showing a T_{50} of \approx 373 °C, which was 50 °C lower than the one treated in oxygen (\approx 423 °C) (Fig. 1D). Even though no further improvement was observed for the catalyst treated in steam at 700 °C, the results indicated that the Pd/Al₂O₃ catalysts could be considerably activated during the steam treatment. It is well known that co-feeding of steam in the reaction mixture has a detrimental effect on the methane combustion activity of Pd catalysts (16, 17). Therefore, it was surprising that the steam

pre-treatment could increase the activity of the catalyst. The higher performance after steam treatment was stable for at least five cycles, which is equal to 5 h spent on stream (fig. S2). We also considered the variability in steam concentration and processing time during the treatment. The improved activity was achieved at a water concentration as low as 0.8 % (by volume) and did not change at increasing concentrations (fig. S3A), and treatment duration of 0.5 h or 2 h did not have a major effect (fig. S3B). These experiments suggest that the treatment temperature is more important than its duration and steam concentration.



Fig. 1. Characterization and performance of Pd/Al₂O₃ catalysts upon different gas treatments. (A)
Representative HAADF-STEM image of the pristine Pd/Al₂O₃ (inset: size distribution of Pd nanoparticles).
(B) Light-off curves for methane combustion (0.4% CH₄, 4.0% O₂, 4.2% H₂O, balance Ar) on pristine
Pd/Al₂O₃ and after treatment in steam at increasing temperatures. (C) Pd 3d photoelectron spectra of

Pd/Al₂O₃ after O₂ (600 °C), O₂-H₂, steam (600 °C), and steam-O₂ treatments. The spectral fittings are shown in fig. S5. (D) Light-off curves and (E) T₅₀ values of Pd/Al₂O₃ after O₂ (600 °C), O₂-H₂, steam (600 °C), and steam-O₂ treatments. Error bars represent the minimum and maximum measured values of at least three repeated experiments. (F) Arrhenius plots of methane combustion on Pd/Al₂O₃ after O₂-H₂ treatment and steam treatment (600 °C).

Using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis, we confirmed that there was no appreciable change in particle size distributions after any of the treatments (fig. S4). Therefore, particle sintering or redispersion could not explain the activity improvement in the steam-treated catalyst. X-ray photoelectron spectroscopy (XPS) measurements demonstrated that in the O₂-treated catalyst, Pd 3d_{5/2} peak was located at 336.6 eV (Fig. 1C and fig. S5), consistent with PdO phase. Instead, the steam-treated catalyst showed the peak at 335.0 eV, attributable to metallic Pd(0). This result was consistent with X-ray diffraction (XRD) data (fig. S6). There is still a debate as to whether Pd, PdO, or a Pd/PdO mixed phase is the active phase for methane combustion (18). To fairly compare catalysts with the same oxidation state, a Pd/Al₂O₃ sample was prepared through sequential oxygen and hydrogen treatments [labeled as O₂-H₂-treated Pd/Al₂O₃, (15)] to convert the Pd oxide phase into metallic Pd, as revealed by XPS (Fig. 1C). However, the activity for this sample was similar to the one treated exclusively in O₂ and much lower than the steam-treated catalyst (Fig. 1, D and E). Furthermore, the steam-treated sample was subjected to an oxygen treatment [labeled as steam-O₂-treated Pd/Al₂O₃, (15)] to convert the metallic Pd phase into PdO and test whether the oxidation would reduce its activity to that of the oxidized sample. The XPS spectrum of the steam-O₂-treated Pd/Al₂O₃ demonstrated the exclusive presence of PdO after this treatment (Fig. 1C). However, no evident activation/deactivation in light-off performance was found as compared to the steamtreated sample (Fig. 1D). Clearly, the initial Pd oxidation state before catalysis does not correlate with the methane oxidation activity of the samples, and the steam treatment drastically improves the Pd activity regardless of its initial oxidation state.

Kinetic rate measurements were collected on the Pd/Al₂O₃ catalyst subjected to the different treatments under varying conditions. Steam was not added to the reaction mixture to avoid catalyst changes during kinetic experiments (fig. S7). The steam-treated catalyst demonstrated \approx 12 times higher mass-specific rate than the O₂-H₂-treated catalyst (Fig. 1F). An Arrhenius plot showed an apparent activation energy for the O₂-H₂-treated catalyst of \approx 81 kJ·mol⁻¹, in line with previous work (*19*). The steam-treated catalyst displayed lower activation energy (\approx 68 kJ·mol⁻¹), indicating a lower-energy pathway for C-H activation in this catalyst.

The first C–H bond activation is recognized as the rate-limiting step in methane oxidation, and the PdO redox properties are an important parameter that affects catalyst activity. Methane temperature-programmed reduction (CH₄-TPR) was performed to evaluate the reducibility of Pd/Al₂O₃ catalysts after different treatments (fig. S8A). CH₄ oxidation was observed at \approx 180 °C for the steam-treated catalyst, while it appeared at a higher temperature of \approx 215 °C for the O₂treated catalyst, in line with the improved catalytic activity of the former sample observed in lightoff curves (Fig. 1D). Furthermore, Pd oxidation in temperature-programmed oxidation (O₂-TPO) experiments was observed at \approx 295 °C for the steam-treated catalyst, lower than that for the O₂treated one (\approx 330 °C) (fig. S8B). The TPR/TPO results illustrate that the palladium phase in the steam-treated catalyst is more easily oxidized and reduced by O₂ and CH₄, respectively, and thus can be more active in the relevant steps of methane oxidation. Changes in the support after steam treatment, including support hydroxylation, have been documented to promote reactivity of supported metal phases (20). To explore this possibility, the alumina support was treated in steam before depositing Pd nanoparticles (15). However, the Pd/Al₂O₃ sample prepared in this way showed an even higher T_{50} than that of conventional Pd/Al₂O₃ with the same particle size (fig. S9). The decreased activity might be attributed to different metal-support interactions between Pd and the hydroxylated alumina. The role of the support in the improved steam-treated activity was further excluded by proving that Pd/SiO₂ catalysts showed the same improvement in activity when treated in steam, oxygen, or oxygen-hydrogen atmospheres (fig. S10). Another possibility for the activity improvement is that of synthesis byproducts being removed from the catalyst surface by the steam treatment. Phosphorus is present as an impurity in the initial Pd nanoparticles; however, it is mostly removed after steam or O₂-H₂ treatments and there is no difference in its concentration between the samples (fig. S11 and table S2). Taken together, all these results suggest that the observed activity enhancement is solely related to the structural evolution of Pd nanoparticles following the steam treatment.

High-resolution HAADF-STEM was used to characterize the structure of the supported palladium nanoparticles (Fig. 2 and figs. S12 to S17). It was not possible to characterize oxidized palladium because of its fragility under the beam which caused drastic changes to the particles, and hence only Pd in the metallic state was investigated. The pristine Pd nanoparticles on alumina consisted of a mostly amorphous structure (fig. S12). However, after being treated in steam or O₂-H₂, the nanoparticles crystallized and became highly faceted. We initially focused on the different Pd exposed facets to determine whether this parameter was responsible for the change in reactivity. HAADF-STEM images in fig. S17 highlight the surface facets of Pd nanoparticles upon different gas treatments. The distances from the particle center to the outermost surface planes were

measured (table S3). On the basis of these values, the corresponding three-dimensional crystal shape was derived using the Wulff construction. From the Wulff shape, the occurrence of different types of surface facets was extracted (fig. S18). Even though samples showed different fractions of exposed facets, no trend was found that correlated with the difference in catalyst activity (figs. S18 and S19). The presence of voids in the particles due to Kirkendall effects (figs. S12 to S15 and table S4) did also not relate to the observed reactivity.

Interestingly, it was found that both the steam- and O_2 -H₂-treated samples presented twin boundaries (TBs) that lay parallel to {111} planes (also referred to as Σ 3 {111} twin boundaries, arrows in Fig. 2, A, B, and E). Separated by a coherent twin boundary, the surface structure shows a symmetrical lattice arrangement, forming an ABCICBA stacking sequence. The fast Fourier-Transform (FFT) diffractograms in Fig. 2J show two sets of patterns, in which the (111), (200) spots in grain G2 are mirrored, across the plane parallel to (111), by (111), (002) in grains G1 and G3, forming a typical coherent twin boundary pattern. To assess the relationship between the presence of TBs and catalytic activity, we measured the TB surface density, which was taken to be the sum of the TB surface length over all measured particles divided by the sum of the particle surface areas (*15*). Experimental data on samples following different treatments were used to estimate the twin boundary density to be \approx 58 µm⁻¹ for the steam-treated sample and \approx 15 µm⁻¹ for the O₂-H₂-treated sample (Fig. 2K and table S5). This result correlates well with the observed catalytic activity trend, thus suggesting that the TBs could be responsible for the change in catalytic activity.



Fig. 2. Microstructure investigation. Atomic-resolution HAADF-STEM images of (A and B) steamtreated (600 °C) Pd/Al₂O₃, (D and E) O₂-H₂-treated Pd/Al₂O₃, (G and H) CO-O₂-H₂-treated Pd/Al₂O₃. (C, F and I) Schematic of the TB density change in Pd nanoparticles after different gas treatments. (J) The area marked by the boxes in (B), revealing the detailed arrangements of Pd atoms. The dash lines highlight Σ 3{111} twin boundaries. Corresponding FFT images of grains (G1, G2, and G3) labeled in the top panel. (K) Twin boundary density statistical histogram of Pd/Al₂O₃ after steam (600 °C), O₂-H₂, and CO-O₂-H₂ treatment.

To confirm this hypothesis, a new pristine Pd/Al_2O_3 sample was subjected to dilute CO treatment to cause Pd nanoparticles to restructure into vicinal stepped surfaces (4), thus decreasing the possibility of TB formation. The sample was further subjected to O_2 and H_2 treatments to

remove the carbon coating induced by the CO treatment (fig. S20), reduce the Pd to metallic state and create a fully accessible and active Pd surface [labeled as CO-O₂-H₂-treated Pd/Al₂O₃, (15)]. TEM characterization of the catalyst after the full treatment did not show an appreciable change in particle size, and XPS analysis confirmed the metallic state of Pd (fig. S21). In line with our hypothesis, the CO-O₂-H₂ treated sample had the lowest populations of TBs among all the samples at a density of $\approx 4.9 \ \mu m^{-1}$, as revealed by high-resolution HAADF-STEM images (Fig. 2, G to I and fig. S15). Furthermore, the CO-O₂-H₂-treated catalyst was found to be less active than both the steam-treated catalyst and the O₂-H₂ catalyst with a higher T₅₀ (Fig. 3A and fig. S22). As such, these results confirm that the increased activity of the Pd/Al₂O₃ catalysts is associated with twin boundaries that form when the catalyst is treated in steam at high temperature, while instead TBs are not formed under oxygen, hydrogen, or CO atmospheres (Fig. 3B). By calculating the intrinsic reaction rate on the atoms at the twin boundary given the TB density in the steam-treated sample and comparing it to all the other plane atoms (15), this rate is measured to be \approx 785 times larger than that on the plane Pd atoms, thus demonstrating a dramatic increase in rate for C–H activation at the twin boundaries.



Fig. 3. Identifying twin boundaries as the origin of increased catalytic activity and exploring their thermal stability. (A) Light-off curves of Pd/Al₂O₃ after steam (600 °C), O₂-H₂ and CO-O₂-H₂ treatments. (B) Relationship between reaction rate/T₅₀ and twin boundary density. (C) Representative surface strain mapping for an individual Pd nanoparticle on in the stream-treated catalyst relative to the reference values. The arrows denote the twin boundaries. (D) and (E) Representative environmental TEM (E-TEM) images of the same Pd nanoparticle in the steam-treated Pd/Al₂O₃ sample that was exposed to O₂ at 23 °C and 500 °C, respectively, with the twin/grain boundaries highlighted by orange lines. FFT diffractograms (insets in (E)) indicating that the "cap" region separated by GB is preferentially oxidized at 500 °C. (F) Zoom-in of the area marked by the white dashed box in (E) showing the exposed Pd and PdO facets in the vicinity of the grain boundary (orange line).

The enhanced catalytic activity at twin boundary sites could be related to two factors: a change in the coordination environment of those Pd atoms that are part of the grain boundary, or strain effects related to the presence of the grain boundary. For face-centered cubic (fcc) structures, the coordination numbers of atoms on $\{111\}$, $\{100\}$, and $\{110\}$ surfaces are 9, 8, and 7, respectively (21). The atoms on Σ 3{111} twin boundaries have the same coordination number as those on $\{110\}$. Hence, the former reason could be excluded based on the fact that different exposed facets did not correlate with reactivity (fig. S18) despite the different coordination environment of the Pd atoms. The exit-wave power-cepstrum (EWPC) transform was applied to scanning nanobeam electron diffraction data to explore the distribution of lattice strain in the steam- and CO-O₂-H₂-treated Pd/Al₂O₃ catalyst (22). The strain values are relative to a reference value (i.e., Lagrange strain), which is the sum of all the diffraction patterns for individual particles (Fig. 3C). Analysis revealed a radial lattice expansion near surfaces in both stream- and CO-O₂-H₂-treated samples regardless of the presence of a TB, and no correlation between the presence of a TB and a change in strain was identified in the Pd samples (figs. S23 and S24). A previous report analyzing atomic resolution images of supported Pt particles reported a 1% to 2% expansion in the lattice planes immediately adjacent to the TB (23). It is unclear if the difference in results reported here originates from the material system and synthesis or if the lower spatial resolution of the strain routine implemented here lacks sensitivity. However, analysis of the pre-reaction particles may not be sufficient due to restructuring under reaction conditions and oxidation of the metallic surface. We therefore determined the thermal stability of the twin boundaries under oxidizing conditions using environmental transmission electron microscopy (E-TEM). Initially, the Pd/Al₂O₃ was exposed to an O₂ environment at a pressure of ≈ 0.87 Pa at room temperature (Supplementary Video 1), and then the catalyst was heated at a rate of $100 \, {}^{\circ}\text{C} \cdot \text{s}^{-1}$ and stabilized at \approx 500 °C (Supplementary Video 2). We detected no apparent boundary segregation or disappearance as annealing temperature increased (from Fig. 3D to E). Instead, surface oxidation on the nanoparticle was observed during this process: the "cap" separated by the {111} TB was preferentially oxidized (Fig. 3, E and F), suggesting that the TB may promote oxygen dissociation and serve as the precursor structure to the formation of a grain boundary (GB) between the Pd core and the surface PdO region. A slow heating rate experiment (200 °C·min⁻¹) showed that the "cap" region was preferentially oxidized at ≈ 391 °C in the same O₂ environment (fig. S25). The E-TEM identification explains the O₂-TPO data, in which the steam-treated catalyst was found to be oxidized at a lower temperature compared to the O2-treated catalyst. These observations lead us to the conclusion that the original twin boundary transforms into a general grain boundary, indicating that these planar defects are maintained in an oxidizing condition at a high temperature of at least 500 °C. Importantly, the conversion of Pd to PdO transforms the crystalline lattice from cubic to tetragonal and the resulting mismatch in lattice parameter between the Pd and PdO will generate strain in the Pd/PdO heterostructure and in the fully oxidized PdO particle containing the grain boundary.

Planewave DFT calculations were performed to assess the effect of strain generated by the GBs on the activity of the catalyst. The first C-H bond-breaking step in methane combustion was studied on PdO(110) and PdO(101), chosen because the oxidized phase was found to form under reaction conditions (Fig. 3E) and pre-oxidation of the nanoparticles did not hinder catalytic activity (Fig. 1D). These facets were specifically chosen because they were observed with ETEM (Fig. 3F). The catalyst surfaces were modeled as bulk PdO surfaces because the nanoparticles that were placed under reaction conditions were measured to have PdO phases that were at least 4 nm thick, which corresponds to approximately 13 atomic layers. At this PdO thickness, there should be a

sufficient number of PdO layers so that they would resemble the properties of a bulk PdO surface, while the contribution from the supporting metallic Pd substrate is effectively screened. Gibbs free energy diagrams and energy-optimized structures for adsorbed CH_{4*} , the transition states (TS), and the final states $(CH_3^* + H^*)$ were computed (Fig. 4). The calculation of the Gibbs free energy assumed a temperature of 400 °C, at which the largest difference in methane conversion between steam-treated and O_2 -treated catalysts was observed (Fig. 1D). Calculations were performed for each surface at -5% (i.e., 5% compressive), 0%, and +5% (i.e., 5% expansive) strain, so that the effects of both types of strain were explored and a trend could be established between the reactivity and the applied strain level. The Gibbs free energies of adsorbed methane on PdO(101) with -5%, 0%, and 5% applied strain were -0.03 eV, -0.07 eV, and -0.25 eV, respectively (Fig. 4A). These values indicate that CH₄ binds stronger to the surface with expansive strain, which is consistent with previous observed strain effects on metallic surfaces(24). The Gibbs free transition state energies relative to gas-phase CH₄ were 0.89 eV, 0.85 eV, and 0.63 eV for -5%, 0%, and 5% applied strain, respectively. These energy values are effectively the Gibbs free energy differences between the C-H activation barrier and the desorption barrier of adsorbed CH₄. Expansive strain is therefore able to increase the activity for C-H activation (as opposed to CH₄ desorption) on the PdO(101) surface. To give a sense for the magnitude of this effect, a difference of ca. 0.13 eV in activation energy corresponds to one order of magnitude change in reaction rate constant at 400 °C. Consequently, imposing a 5% expansive strain on PdO(101) would yield: (i) an intrinsic reactivity enhancement corresponding to a 0.22 eV transition state energy difference, and (ii) a coverage term enhancement due to stronger CH₄ binding by 0.18 eV. Combined, this leads to ≈ 3 orders of magnitude in intrinsic rate enhancement for the expansively strained PdO(101) surface, an estimate that is very close to the factor of 785 estimated from our experiments.



Fig. 4. Theoretical calculations for the effect of surface strain on the C-H breaking Gibbs free energy. (A) and (C) Calculated Gibbs free energy diagrams for breaking the first C-H bond in CH₄ on PdO(101) and PdO(110), respectively. The Gibbs free energies were calculated using a temperature of 400 °C and referenced a clean surface and gas-phase CH₄ at infinite separation. (B) and (D) Top view of structures for adsorbed CH₄ (CH₄*), transition state (TS), and co-adsorbed CH₃ and H (CH₃* + H*) on PdO(101) and PdO(110), respectively. Light black rectangle denotes the unit cell.

For comparison, the Gibbs free energy diagram for methane activation on the PdO(110) facet was also calculated (Fig. 4C). The reactivity of this surface was probed at its oxygen-termination that corresponds to a lower surface energy compared to its Pd-termination under the experimental conditions used in this study (25). The application of expansive or compressive strain

did not show a large effect on the binding energy of CH₄* or CH₃* + H* on this surface, where only narrow ranges of variances in the energies of CH₄* (0.05 eV) and CH₃* + H* (0.03 eV) were observed (Fig. 4C). The transition state energies on the PdO(110) surface showed a different trend than that observed on the PdO(101) surface as expansive or compressive strain was applied. The transition state energies are 0.57 eV, 0.61 eV, 0.79 eV for -5%, 0%, and 5% applied strain, respectively (Fig. 4C). These results suggest that a 5%-compressed PdO(110) can lead to an increased intrinsic reactivity corresponding to a total of \approx 0.09 eV, which is less than an order or magnitude at 400 °C, compared to 0% strain on that facet. Expansive strain would decrease reactivity on that facet.

The DFT results for PdO(101) and PdO(110) together demonstrate that a strained surface causes higher methane oxidation rates. As mentioned previously in the ETEM experiment, the PdO phase tends to form a "cap" region on one side of the grain boundary, so the PdO phase could experience compressive or expansive strain due to the existence of grain boundaries or to lattice mismatch between Pd and PdO phases, which, in turn, can lead to increased reactivity. This idea is consistent with the experimental results showing higher activity for nanoparticles that have a higher number of twin boundaries. Our DFT results strongly indicate that the enhanced activity for the steam-treated Pd catalyst stems from a concerted effect of PdO formation and local strain due to the presence of grain boundaries. In fact, based on the reactivity enhancement estimates calculated on the stretched Pd(101) and on the compressed PdO(110), and the respective comparisons with experimental rate measurements, we conclude that stretched Pd(101) is likely the dominant active site on the steam-treated catalysts. This assertion offers a potential avenue for improving Pd methane oxidation catalysts through better control of the facets and strain during PdO growth.

It is important to note that the activity enhancement by steam treatment was not exclusive of the Pd(15 nm)/Al₂O₃ catalyst. The same treatment-dependent activity profiles were observed in a Pd/Al₂O₃ catalyst prepared by conventional wet impregnation, and Pd/Al₂O₃ catalysts prepared from 8 nm and 12 nm colloidal Pd nanoparticles (figs. S29 to S31). In all these cases, the steam-treated catalysts exhibited higher activity than the O₂-treated catalysts. It was also interesting to observe that the particles with a larger size showed greater improvement in rates upon the steam treatment (fig. S32). This observation may be explained by the more energetically favorable formation of TBs in larger particles that can more easily accommodate defects. Despite a lower magnitude in rate increase likely due to the smaller particle sizes and a less uniform surface structure in the wet-impregnated catalyst, these experiments confirm the generality of the effect of steam treatment on Pd catalysts.

Finally, the identification of GBs as highly active sites for methane combustion provides the opportunity to engineer Pd/Al₂O₃ catalysts for even improved reactivity if the density of such defects can be increased. With this goal in mind, a laser ablation process was used to fabricate nanocrystals rich in grain boundaries (Fig. 5 and figs. S33-S34) following previous reports (*9*) and were deposited on the same alumina used for the colloidal NPs. As predicted by our observations, the turnover frequency (TOF) of the laser-generated Pd/Al₂O₃ catalyst was found to be 4 times higher than that of the steam-treated Pd(15 nm)/Al₂O₃ catalyst, and hence nearly 25 times higher than a conventional catalyst treated in just oxygen and hydrogen (Fig. 5). On the basis of these results, we believe that our work provides not only a general strategy for the rational design of the surface structure in heterogeneous nanocatalysts, but also can help explain previous work on Pd-based catalyst for methane combustion that demonstrated improved reactivity upon aging or disparate thermal treatments (*26*). We propose that engineering of the surface structure as well as

of defects in catalytic materials provide new opportunities for improving the performance in several areas of heterogeneous catalysis.



Fig. 5. Grain-boundary density effect investigation. (A) High-resolution TEM image of laser ablationgenerated Pd nanoparticles. The orange dash lines highlight $\Sigma 3\{111\}$ twin boundaries and the blue dash lines highlight general grain boundaries. (B) Grain boundary density statistical histogram of laser-generated Pd/Al₂O₃ and Pd/Al₂O₃ after steam (600 °C) and O₂-H₂ treatments. (C) Arrhenius plots of methane combustion on laser-generated Pd/Al₂O₃ and Pd/Al₂O₃ after steam (600 °C) and O₂-H₂ treatments.

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Supplementary Materials for

Grain Boundaries Created by Steam Treatment are Active Sites for Methane C-H Activation in Palladium Catalysts

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Materials and Methods Figs. S1 to S34 Tables S1 and S6 Video S1 and S2 (and captions) References

MATERIALS AND METHODS

Chemicals and Materials

Pd(acac)₂ (acac=acetylacetonate, 35% Pd) was purchased from Acros Organics. Oleylamine (OLAM, 70%), 1-octadecene (ODE, 90%), 1-tetradecene (TDE, 90%), and trioctylphosphine (TOP, 97%), Davisil (Grade 643) silica gel and tetraamminepalladium nitrate (10% (by weight) in H₂O) were purchased from Sigma-Aldrich. Isopropyl alcohol, ethanol and methanol were purchased from Fisher Scientific. The alumina support was kindly donated by Sasol.

Synthesis of palladium nanoparticles (NPs) with different sizes

All syntheses were performed using standard Schlenk techniques. In a typical synthesis, Pd(acac)₂ was mixed with solvent mixture, OLAM and OLAC in a three-neck flask (see Table S1 for further details). The mixture was evacuated at room temperature for 15 min under magnetic stirring. TOP was then added under evacuation and the mixture was heated to 50 °C. The solution was left under vacuum for 30 min to remove water and other impurities. At this point, the reaction mixture was a transparent colored solution. The reaction flask was then flushed with nitrogen and heated quickly (≈ 40 °C min⁻¹) to the desired temperature (T_{rxn}). After 15 min of reaction at the appropriate temperature under magnetic stirring, the solution was quickly cooled to room temperature (RT) by removing the heating mantle. The particles were purified three times by precipitation with a mixture of isopropanol, ethanol and methanol, and separated by centrifugation (838 rad/s (8000 rpm) for 3 min). A size selection is required for 12 nm and 15 nm Pd sample before purification. Nanoparticles were first dispersed in 10 mL hexanes and 2 mL IPA, and then separated by centrifugation (838 rad/s (8000 rpm) for 3 min). Finally, the particles were dispersed in hexanes producing a black solution and stored at room temperature. A small volume of OLAM $(50 \ \mu L)$ was generally needed to ensure the complete redissolution of the particles. The sizes of nanoparticles obtained by TEM are well controlled with a standard deviation <10%.

Preparation of supported catalysts

Prior to impregnation, alumina was prepared by calcining Puralox TH100/150 (obtained from Sasol) at 900 °C for 24 h using heating and cooling ramps of 5 °C min⁻¹ in static air (named as conventional Al₂O₃). Silica was prepared by calcining silica gel (Davisil Grade 643; 200-425 mesh) at 800 °C for 6 h using heating and cooling ramps of 5 °C min⁻¹ in static air.

For impregnation of a desired loading of Pd nanoparticles onto Al₂O₃, metal concentrations of synthesized colloidal nanoparticle solutions were determined via thermogravimetric analysis (TGA). Before TGA measurement, centrifugation ((838 rad/s (8000 rpm), 1 min) was applied to seperate isolated nanoparticles and agglomerated nanoparticles. After removing the precipitate, a nanoparticle solution was added dropwise into an aluminum TGA pan, which was heated via hot plate at \approx 80 °C until 150 µL had been added. This pan was then further heated in the TGA in flowing air to 500 °C, and held until a steady mass was reached, suggesting complete removal of organic molecules. Dividing this final mass by initial solution volume gave metal concentration. An appropriate amount of nanocrystals (to give a loading of 0.5–1.0% (by weight) of Pd in the final catalysts) dispersed in hexanes was added to a dispersion of stirred support (Al₂O₃ or SiO₂) in hexanes. Complete adsorption occurred immediately, and dispersions were left stirring for 5-10 minutes after particle addition. The solid was recovered by centrifugation ((838 rad/s (8000 rpm), 1 min) and dried at 60 °C overnight. Prior to catalytic tests, all samples were sieved below 180 µm grain size, treated in air at 700 °C for 30 seconds in a furnace to remove ligands from synthesis as

previously described (1), and sieved again below 180 µm grain size to avoid effects of mass transfer limitations. Metal concentration of synthesized colloidal nanoparticles was determined via Inductively coupled plasma mass spectrometry (ICP-MS).

Support hydroxylation was achieved by treating conventional Al_2O_3 at 600 °C for 0.5 h under 4.2% (by volume) H_2O in Ar (labeled as hydroxylated Al_2O_3). An appropriate amount of nanocrystals (to give a loading of 1.0% (by weight) of 8 nm Pd in the final catalysts) dispersed in hexanes was added to a dispersion of stirred support (conventional or hydroxylated Al_2O_3) in hexanes.

For the synthesis of the impregnation catalyst, 0.142 g of tetraamminepalladium nitrate $(Pd(NO_3)_2 \cdot 4NH_3, 10 \text{ wt. }\% \text{ in } H_2O)$ was deposited onto 0.50 g of Al_2O_3 using incipient wetness impregnation. After impregnation, the product was dried in a vacuum oven at 70 °C for 12 h and calcined in air at 500 °C in O_2 for 3 h.

Preparation of Pd nanoparticles from laser ablation and supported catalysts

A 1/8" thick, 1 inch diameter Pd sputtering target was rinsed in acetone and deionized water. The target was mounted into a standard threaded 2.54 cm diameter optical lens mount using two threaded retaining rings to keep the target standing on its edge during ablation. The mounted target was set into a 30 mL rinsed Pyrex beaker and covered with 10 mL of deionized water, resulting in approximately 1 cm of water between the target and glass wall, before sealing the beaker mouth with aluminum foil. The assembly was set near a 50 mm focal length, anti-reflection coated, plano-convex lens, such that the Pd surface was normal to the optical axis and approximately one centimeter upstream of the lens' focal point. This short focal-length lens was used to keep the intensity low at the glass surface. After checking the ablation point position on the target and for stray reflections with a few long pulse-mode laser pulses, the beaker was further encased in aluminum foil to minimize risks of inadvertent reflections, and the Pd was ablated with nominally 8 ns to 12 ns full width half-maximum, Q-switched, 1064 nm, 0.3 J Nd:YAG laser pulses at 10 Hz for 20 minutes. The beam profile before focusing is shown in figure S34 (left); diffraction spots would rotate with neutral density filters present only during imaging. Also shown in fig. S34 is a bright field optical image of the deep pit on the Pd surface that formed by laser ablation (right).

Image analysis (Fiji) was used to estimate the ovular pit area to be 0.008 cm^2 , which taken as the average area for the 0.3 J pulses yields an average fluence of $4 \cdot 10^2 \text{ J} \cdot \text{cm}^{-2}$. In this configuration, no back-focused reflections damaged any optics, and the water steaming and spitting, along with concomitant nanoparticle carryover, were contained inside of the ablation assembly. The final black, opaque solution was poured into a glass container, sealed, and walked between laboratories. Future work will use quartz beakers to avoid potential glass fracturing; the laser interaction increases at the liquid|glass interface as the nanoparticle density increases.

10 ml of as-made Pd nanoparticle solution was added to a dispersion of stirred conventional Al_2O_3 in water (800 mg of Al_2O_3 in 40 ml of water) and further stirred for 5 h. Then, the supported particles were collected by centrifugation (838 rad·s⁻¹ (8000 rpm), 30 min) and dried at 60 °C overnight. Metal weight loading was determined by x-ray fluorescence (XRF) measurement.

Different gas treatments

The heat treatment (O₂, H₂, CO, and Ar) was carried out at a target temperature (300 °C - 700 °C) for 0.5 h under the 25 ml min⁻¹ flow of 5% (by volume) O₂ in Ar, 5% (by volume) H₂ in Ar, 5% (by volume) CO in Ar, and pure Ar, respectively.

Unless specified, the sample labeled 'steam' treatment was treated at 600 °C for 0.5 h under 4.2% (by volume) steam in Ar (25 ml min⁻¹ Ar-flow through a saturator with Milli-Q water at 30 °C). The concentration of steam was controlled by adjusting the saturator temperature. Likewise, 0.8% (by volume) and 10% (by volume) steam were achieved by cooling and heating the saturator at 4 °C and 47 °C, respectively.

The sample labeled 'O₂-H₂' treatment was treated at 600 °C for 0.5 h under O₂ (5% (by volume))/Ar and subsequently reduced using 5% (by volume) H₂/Ar at 600 °C for 0.5 h. The sample labeled 'steam-O₂' treatment was treated at 600 °C for 0.5 h under 4.2% (by volume) H₂O in Ar and subsequently oxidized at 600 °C for 0.5 h under O₂ (5% (by volume))/Ar. The sample labeled 'CO-O₂-H₂' treatment was first treated at 675 °C for 0.5 h under CO (5% (by volume))/Ar, then was oxidized using 5% (by volume) O₂/Ar at 600 °C for 0.5 h, and subsequently was reduced using 5% (by volume) H₂/Ar at 600 °C for 0.5 h.

Catalytic testing

The catalytic tests were carried out using a fixed-bed flow reactor. For the reaction, typically 10 mg of 1% (by weight) Pd/Al₂O₃ catalysts and 190 mg of Al₂O₃ (or 20 mg of 0.5% (by weight) Pd/Al₂O₃ and 180 mg of Al₂O₃) were physically mixed and loaded into a U-shaped quartz microreactor with an internal diameter of 1 cm to give a bed length of about 1 cm. The catalysts were rested between two layers of granular quartz, which were used for preventing displacement of the catalyst powder and for preheating the reactant gases. The reactor was heated by a Micromeritics Eurotherm 2416 furnace, and the temperature was recorded by a K-type thermocouple inserted inside the catalytic bed. All heat treatment and catalytic reactions were conducted at atmospheric pressure.

After the appropriate treatment, the reactor was cooled down to 150 °C, at which point the reactant mixture was introduced. The reactant mixture composition was controlled by varying the flow rates of CH₄ (5% (by volume))/Ar, O₂ (5% (by volume))/Ar, and Ar (all certified mixtures with purity >99.999% from Airgas) and passed through a H₂O saturator at 30 °C before reaction. The reactor was heated up to 600 °C with a ramp rate of 10 °C min⁻¹. Unless specified, in all experiments, gas hourly space velocity (GHSV) was held at 141,000 mL·g_{catalyst}⁻¹·h⁻¹, and the flow rate was 23.5 mL min⁻¹, consisting of CH₄ (0.4% (by volume)), O₂ (4.0% (by volume)), and H₂O (4.2% (by volume)) diluted in Ar. Effluent was measured using an online mass spectrometer (Hiden Analytical HPR20), using a Faraday detector following the parent molecular ions for CH₄ (15 amu), O₂ (32 amu), CO₂ (44 amu), and H₂O (18 amu) and retrieving one data point every 9 seconds.

Kinetic rates were measured by a gas chromatograph (Buck Scientific model 910) using flame ionization detector (FID) with a methanizer and thermal conductivity detector (TCD) with Ar as the carrier gas. The data were collected at steady state as determined by a stable CO₂ production signal at 240-300 °C. For kinetic rates, in order to correctly measure the intrinsic activity of the catalysts, conversions of the limiting reactant were always kept below 15% conversion to guarantee differential working conditions. In all experiments, the total gas flow rate was 62.2 mL min⁻¹, consisting of CH₄ (0.4% (by volume)) and O₂ (4.0% (by volume)) diluted in Ar. Reaction rates and turnover frequency were calculated on the basis of Pd mass and accessible Pd surface area calculated from CO chemisorption measurements.

Characterization (TEM, XPS, XRD, XRF, Chemisorption, TPR and TPO)

Low-magnification TEM was conducted on a Tecnai system operating at 200 kV. Samples were prepared by drop-casting dilute Pd nanoparticle solutions or isopropanol dispersions of Pd/Al₂O₃ or Pd/SiO₂ catalysts directly onto Cu grids. XPS spectra were recorded under vacuum conditions with a PHI VersaProbe 3 spectrometer (Al K α , 1486.6 eV). All samples were deposited onto conductive carbon tapes on top of an aluminum holder. All spectra were calibrated to their corresponding C 1s (284.8 eV) to account for small charging effects, and binding energy values for all fitted and assigned spectral peaks are stated with an accuracy of 0.2 eV. Analyses of XPS peaks were performed with a Casa program. XRD measurements were performed on a Bruker D8 Venture X-ray Diffractometer using a Cu K α source in transmission mode (Debye-Scherrer geometry). The powder catalysts were studied by XRD inside a 0.5 mm Kapton HN-type polyimide capillary. XRF measurements were collected on a XEPOS X-ray spectrometer. The spectrometer is equipped with a Solid-State Detector (SSD) and samples are run at 4 different energies.

CO Chemisorption experiments were carried out on a Micromeritics 3Flex. Typically, 250 mg of samples were placed in a U-shaped quartz reactor, heated in flowing 5% (by volume) O_2 in Ar at 300 °C for 0.5 h and reduced in flowing 5% H₂ (by volume) in Ar at 300 °C for 0.5 h, and then evacuated at 300 °C for 4 h. All CO chemisorption experiments were conducted at 35 °C in the pressure range from 100 to 450 Torr, using a double isotherm to remove the contribution from physisorption.

For temperature-programmed reduction with methane, CH₄-TPR, and temperatureprogrammed oxidation, O₂-TPO, 200 mg of pure 1% (by weight) Pd/Al₂O₃ was introduced into the quartz reactor. The catalyst was ramped in 23 ml min⁻¹ of 4% (by volume) O₂/Ar to 500 °C at 10 °C min⁻¹ and back to 100 °C in an oxidative cleaning step. Next, 23 ml min⁻¹ of 0.5% (by volume) CH₄/Ar was introduced, the feed was stabilized, and the catalyst was ramped until \approx 400 °C and cooled back down to 100 °C in CH₄/Ar. Next, 4% (by volume) O₂/Ar was reintroduced, and the catalyst was ramped to 450 °C in the O₂ mixture. All temperature ramps were performed at 10 °C min⁻¹.

Scanning transmission electron microscopy characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired on an aberration corrected instrument operated at accelerating voltage of 300 kV. The convergence semi-angle was 14.0 mrad and the detector inner collection semi-angle was 70 mrad. Stacks of images were acquired using a script implemented in Digital Micrograph (2). Image stacks were aligned using rigid registration and summed in Fiji (3–5).

The fraction of surface facet coverage as function of treatment (Figure S18) was determined using the Wulff construction. Particles containing twins were excluded from the analysis. Distances from the particle center bisecting each facet of the particle surface were measured and then normalized by the $\{111\}$ lengths to control for differences in particle size. The ratios are shown in Table S3. Subsequently, these values were entered into the Wullfman program (6, 7) as surface energies setting $\{111\}$ as a baseline of 1.0 and the area of each facet was extracted from the resulting Wulff shape.

Surface grain boundary densities were measured using the routine described below. Both the particle perimeter and the length of any GBs present were measured. Assuming a spherical geometry the surface density is calculated using the following equation

 $\frac{Grain\ boundary\ surface\ length}{Nanoparticle\ surface\ area} = \frac{\sum \pi L}{4\pi R^2}$, where *L* is the length of the grain boundary and *R* is the particle radius. For the analysis of 15 nm Pd nanoparticles, only particles orientated to <110> type zone axes were considered. For the laser-generated nanoparticles, both twin grain boundaries and general grain boundaries were observed and were taken into consideration for the GB density calculation.

Scanning nanobeam electron diffraction data was acquired with a convergence semi-angle of \approx 1.3 mrad corresponding to a diffraction-limited probe size of approximately \approx 0.9 nm FWHM. Diffraction patterns were recorded on a detector with (256 X 256) pixels applying a 72 X 72 raster with a pixel size of \approx 0.25 nm. Strain information was extracted using the exit wave power cepstrum routine implemented in MATLAB (8). The indicated strain values are relative to an internal reference value (i.e., Lagrange strain), the sum of all the diffraction patterns of the particle.

The estimation of specific rates on the twin boundary atoms

In this calculation, a simplified Pd nanoparticle model is proposed, in which only two kinds of atoms (i.e., plane atoms and TB atoms) are assumed on Pd surface. The calculation of specific rate on the TB sites on the steam-treated Pd sample can be derived as follows:

 $A \times N_1 + B \times N_2 = C \times (N_1 + N_2)$

where A is the specific rate on the TB sites, B is the specific rate on the plane sites, N₁ and N₂ are the number of TB and Pd plane sites and C is turnover frequency (C = 0.051 molecules CO₂ formed/exposed metal atom/s, from Table S6). To calculate the specific rate on the TB site present in Pd nanoparticle supported on alumina, the number of Pd TB sites in a sample was calculated based on the known TB density and the diameter of Pd atom (N₁= 0.015 × (N₁+N₂), and N₂= 0.9841 × (N₁+N₂)). Furthermore, the CO-O₂-H₂-treated Pd/Al₂O₃ sample has a negligible TB density compared to O₂-H₂-treated and steam-treated one. Therefore, we assume this rate to be that of the specific rate on the TB sites (A) is then computed to be 3.14 molecules CO₂ formed/atom/s, from Table S6). The specific rate on the TB sites is 785 times higher than the plane Pd atoms.

In-situ experiments of steam-treated Pd/Al₂O₃ in an oxidizing environment

Experiments were carried out in an environmental transmission electron microscope (ETEM) equipped with a differentially pumped system and a field-emission electron gun operated at 300 kV. The differentially pumped system is used to maintain a pressure difference between the sample region (≈ 0.87 Pa) and the TEM column ($\approx 10^{-6}$ Pa) by the means of a series of differential pumping aperture and additional pumping capacity (9, 10), so that an optimal spatial resolution of ≈ 0.07 nm can be achieved for high-resolution TEM (HRTEM) imaging. The electron dose rate was controlled during the in-situ experiments at ≈ 6.0 A/cm² to avoid the electron beam induced surface oxidation in Pd nanoparticles, reported elsewhere (11).

Pd nanoparticles were prepared as described in the "Synthesis of palladium nanoparticles (NPs) with different sizes" section. The Pd/Al_2O_3 catalysts underwent the steam treatment, as indicated in the "Catalytic testing" section, and were removed from the reactor without experiencing the methane combustion reaction. The steam-treated Pd/Al_2O_3 catalysts were

dispersed in IPA and drop-cast onto a micro-electromechanical system (MEMS) chip for a doubletilted TEM heating holder. On the MEMS chip, arrays of through-holes have been patterned on the thin silicon nitride window membrane using a focused ion beam (FIB) milling process.

In a typical experiment, a baseline pressure inside the E-TEM sample region was reached at $(\approx 10^{-6} \text{ Pa})$ after the Pd/Al₂O₃ catalysts were inserted. Pd/Al₂O₃ catalysts, sitting inside the throughholes and showing no background contrast of silicon nitride, were chosen for the experiment. A constant flow of O₂ was then leaked into the sample region to obtain an oxygen partial pressure at ≈ 0.87 Pa. All images acquired during the ETEM experiments were recorded using a direct electron detector. Wiener filtering was applied to the experimental images to mitigate the amorphous-like image background due to the O_2 environment (12, 13). In Supplementary Video S1, a series of HRTEM micrographs, captured using a frame rate of 100 milliseconds (ms), shows that a Pd nanoparticle is oriented along the $[1\overline{1}0]$ zone axis and located on top of and near the edge of Al₂O₃ support at ≈ 23 °C. Two $\Sigma 3\{111\}$ twin boundaries (TB's) are seen in the Pd nanoparticle (Fig. 3D). During the recorded period of 21.8 s, the structure of Pd stayed consistent (space group: $Fm\overline{3}m$) and showed no sign of surface oxidation in the O₂ environment at ≈ 23 °C. Following that, Supplementary Video S2 begins 13 s after the start of heating at a rate of 100 °C/s to reach and stabilize at \approx 500 °C. During the 13 s, the Pd nanoparticle was re-centered and refocused in response to the sample drift caused by the temperature change. The Pd nanoparticle tilted slightly but still aligned closely to the original zone axis. A part of the Pd nanoparticle has been oxidized when heated to 500 °C in the O₂ environment (Fig. 3E). The fast Fourier transform diffractograms (insets in Fig. 3E), derived from the blue and turquoise squares indicated in Fig. 3E, respectively, show that the "cap" region separated by the original GB in Pd (orange line in Fig. 3D) has been transformed preferentially into the PdO phase (space group: P42/mmc), whereas the other side across the boundary remained the Pd phase. This finding suggests that the grain boundary in Pd nanoparticles can promote oxygen diffusion in an oxidizing environment. This agrees with the O2-TPO result (fig. S6B) that indicates that the steam-treated catalyst us oxidized at a lower temperature than the O₂-treated catalyst. The phenomenon may contribute to the improvement in catalytic activity, which is consistent with the observed low T₅₀ for Pd nanoparticles experience either steam or steam-O₂ treatment (Fig. 1E). Notably, the Pd nanoparticle was slightly tilted and remained partially oxidized during the recorded period of 158.8 s (Supplementary Video S2), indicated by the noticeable $Pd(\overline{1}\overline{1}1)$ lattice fringes.

Partial oxidation in the steam-treated Pd nanoparticles were typically seen during the ETEM experiments. In one example, only Pd{111} lattice fringes with an interplanar spacing of ≈ 0.23 nm were initially present in a steam-treated Pd nanoparticle on top of the Al₂O₃ support at 23.6 °C (fig. S25A). The sample was then heated slowly at a rate of 200 °C/min toward 500 °C. At ≈ 391 °C, the presence of PdO{101} lattice fringes with an interplanar spacing of ≈ 0.265 nm indicated the oxidation of the cap region (fig. S25B). The Pd nanoparticle remained partially oxidized when the temperature reached at ≈ 500 °C (fig. S25C).

Density Functional Theory (DFT) methods

Plane-wave density functional theory (DFT) calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP) (14, 15). The PBE(16) parameterization of the generalized gradient approximation (GGA) was used along with Grimme's D3 dispersion correction method.(17) The Hubbard U parameter is commonly used as a correction (+U correction) in DFT studies for metal-oxide systems to obtain more accurate band structures. A previous DFT study by Chin and co-workers showed that the addition of +U corrections resulted in minimal differences

(less than 0.02 eV) in the calculated activation energy barriers of C-H bond-breaking steps on PdO surfaces (18). Since the primary goal of our study is to evaluate the reaction energetics for C-H activation during methane oxidation on PdO surfaces, we did not apply +U corrections to our calculations. The electron wave function was expanded using plane waves with an energy cutoff of 400 eV. A vacuum layer of at least 12 Å was used to separate periodic images in the vertical direction. Adsorption was allowed on only one side of the metal slab, and the electrostatic potential was adjusted accordingly (19, 20). An 8×8×1 gamma-centered Monkhorst-Pack (21) k-point mesh was used for all surface calculations. A 1×2 surface unit cell with 4 PdO layers (see Fig. S26A) for slab geometry and the definition of a single PdO layer) was used for the PdO(101) facet, and a 1×1 surface unit cell with 4 PdO layers (see Fig. S26B) for slab geometry and the definition of a single PdO layer) was used for the PdO(110) facet. Convergence with respect to energy cutoff, kpoint set, and layer thickness was confirmed. Forces were converged to 0.01 eV/Å for all energy minimization and vibrational frequency calculations. Nudged elastic band (NEB) (22, 23) calculations were converged to 0.05 eV/Å to find geometries close to transition states for C-H bond breaking steps. The transition states were then determined by performing a local optimization with the geometry with the highest energy from the NEB calculations. The local optimization employed the RMM-DIIS algorithm (24) and forces were converged to 0.005 eV/Å. Vibrational frequency calculations were used to verify that the states determined that way were indeed transition states by the existence of a single imaginary mode. This method was compared to climbing image-NEB calculations for test cases and was found to be in good agreement. Lattice parameters were calculated by optimizing the cell volume for bulk PdO. The bulk cell used the rectangular PdO unit cell repeated twice in both the x and y directions. This calculation used a $14 \times 14 \times 14$ k-point mesh. The lattice parameters were found to be a = 3.01 Å and c = 5.45 Å which agree reasonably well with the experimental values of a = 3.04 Å and c = 5.33 Å (25).

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Figure S1. Methane combustion light-off curves of (A and B) Pd/Al₂O₃ treated in different conditions (O₂, H₂, Ar, and steam) at 300 °C, 500 °C and 600 °C, respectively.



Figure S2. Cyclic stability test of steam-treated Pd/Al_2O_3 for methane combustion.



Figure S3. Methane combustion light-off curves of (A) Pd/Al_2O_3 treated in 0.8%, 4% and 10% (by volume) steam at 600 °C, respectively, and (B) Pd/Al_2O_3 treated with steam at 600 °C for 0.5 and 2 hours, respectively.



Figure S4. HAADF-STEM images of (A) Pd/Al₂O₃ treated in steam at 600 °C, (B) Pd/Al₂O₃ treated in O₂ and H₂ sequentially at 600 °C, (C) Pd/Al₂O₃ treated in O₂ at 600 °C, and (D) Particle size distributions of these samples.


Figure S5. Spectral fitting and peak assignments for Pd/Al_2O_3 after O_2 , O_2-H_2 , steam and steam- O_2 treatments.



Figure S6. XRD patterns of Pd/SiO₂ after O₂, O₂-H₂, and steam treatments.



Figure S7. The CO₂ signal of steam-treated and O₂-treated samples as a function of time at different temperatures when steam (4.2 vol. %) was added to the reaction mixture of CH₄ and O₂. Clear, slow activation is visible in the O₂-treated sample that was attributed to the effect of steam.



Figure S8. (A) CH₄-TPR and (B) O_2 -TPO profiles of Pd/Al₂O₃ catalysts after steam or O_2 treatments. Triangles indicate the peak centers of reduction or oxidation temperatures measured by equally dividing the peak area.



Figure S9. (A) Methane combustion light-off curves and (B) T_{50} values of Pd(8 nm)/Al₂O₃ catalysts prepared on conventional Al₂O₃ and steam-treated Al₂O₃.



Figure S10. (A) TEM image of Pd(8 nm)/SiO₂. (B) Methane combustion light-off curves of Pd/SiO₂ catalysts after treatment in O₂, O₂ followed by H₂, and steam at 600 °C, respectively.



Figure S11. EDS-STEM mapping of (A) pristine Pd/Al₂O₃, (B) Pd/Al₂O₃ after steam treatment, and (C) Pd/Al₂O₃ after O₂-H₂ treatment. The mapping areas marked by the boxes in the ADF-STEM images, indicating the regions where EDS mapping is performed.

A few studies found out that phosphorus poisoning of noble metal catalysts can dramatically decreases the catalysts activity (26, 27). In our case, the existence of phosphorus in Pd nanoparticles is possible due to the use of trioctylphosphine (TOP) as the reducing agent during Pd nanoparticles synthesis. Figure S11 shows energy-dispersive X-ray spectroscopy (EDX) mapping of pristine, O_2 –H₂ treated, and steam treated Pd/Al₂O₃. Indeed, the elemental mapping shows the appearance of phosphorus signal in the pristine catalyst. The signal, however, reduces similar to background in both O_2 -H₂ treated and steam treated samples. Because counting statistics of the chemical maps is poor further comparisons were made. EDX spectra were acquired while the beam was rastered over a fixed area containing many Pd nanoparticles. This measurement was

repeated 12 times across each sample while keeping experimental parameters (e.g., sample tilt, probe current, live time) consistent. Spectra were processed in Hyperspy to remove the background and determine the integrated peak intensity (28). The ratio of phosphorous to palladium intensity was computed and then compared using a *t*-test. A two-tailed test resulted in a P-value of 0.311 indicating there is not a significant difference in the phosphorus content between the O_2 -H₂ treated and steam treated samples. Analogous results are obtained from inductively coupled plasma–mass spectroscopy (ICP–MS), where the change in phosphorus content among these catalysts was recorded (Table S2). Phosphorus removal is therefore not responsible for the rate enhancement. The similar P/Pd ratios in both O_2 –H₂-treated and steam-treated samples further eliminate this possibility.



Figure S12. Atomic-resolution HAADF-STEM images of pristine Pd/Al_2O_3 . The inset is a fast Fourier transform (FFT) pattern from the nanoparticle. Note that the ring in the FFT (left image) illustrates the amorphous nature of the nanoparticle. The ring is slightly elliptical due to sample drift. In addition, 6 of 38 particles ($\approx 16 \%$) have some degree of long-range order (right image), but no particle was entirely crystalline.





Figure S13. Atomic-resolution HAADF-STEM images of steam-treated Pd/Al₂O₃. The dash lines highlight Σ 3{111} twin boundaries.



23

2 nm

Figure S14. Atomic-resolution HAADF-STEM images of Pd/Al₂O₃ upon O₂-H₂ treatment. The dash lines

5 nm

5 nm

highlight Σ 3{111} twin boundaries.





Figure S15. Atomic-resolution HAADF-STEM images of Pd/Al_2O_3 upon CO-O₂-H₂ treatment. The dash lines highlight Σ 3{111} twin boundaries.



Figure S16. A ball model representing a Pd particle containing a twin boundary is shown from two different orientations. Both these orientations are present in the data (Figures S13 to S15) used to quantify the density of TBs. In (A) both sides of the twin boundary are orientated to <110> type zones. After a 90-degree rotation, (B) one side remains orientated to a <110> type zone while the other side is orientated to a <114> type zone. HAADF-STEM images representative of these two situations are shown in (C) and (D). A dashed red line depicts the twin boundary. Note, while in (D) the twin boundary is depicted as being orthogonal to the plane of the image, it is inclined as exemplified in the ball model. In (D) fast Fourier transforms from the two sides are included.



Figure S17 Atomic-resolution HAADF-STEM images of (A and B) steam-treated Pd/Al_2O_3 , (C and D) O_2 -H₂-treated Pd/Al_2O_3 , (E and F) CO-O₂-H₂-treated Pd/Al_2O_3 . The terminating lattice fringes are highlighted in different colors corresponding to the {100}, {110}, {111} and {113} planes of Pd, viewed along the 110 zone axis. The distances from the particle center to different outermost surface planes were measured (Table S3).



Figure S18. Occurrence of different surface facets as a function of the gas treatment as derived from the information in Table S3.



Figure S19. (A) Two consecutive light-off curves of the steam-treated Pd/Al_2O_3 catalyst. (B) Pd 3d photoelectron spectra of the catalyst before the 1st and 2nd light-off experiments.

It has been reported that certain facets on a Pd catalyst can be more easily oxidized compared to others (29), which can lead to the enhancement of methane combustion rates. To explore this possibility, two light-off tests were conducted on the steam-treated catalyst. The two light-off curves were nearly over imposable, which demonstrates that the catalytic improvement does not result from the difference in oxide formation on palladium surfaces.



Figure S20. Bright-field (BF) STEM images of Pd/Al_2O_3 upon treatment with CO at 675 °C for 0.5 h. Note that few thin layers of a material coating the particles were observed, and the interplanar spacings measured (0.33 nm) matched reasonably with graphitic carbon.



Figure S21. TEM image of (A) Pd/Al₂O₃ after CO-O₂-H₂ treatment, (B) and (C) Particle size distribution and XPS spectrum of the sample.



Figure S22. Arrhenius plots of methane combustion on Pd/Al₂O₃ after CO-O₂-H₂, O₂-H₂, O₂(600 °C), and steam (600 °C) treatments.



Figure S23. Strain mapping for Pd nanoparticles on the stream-treated catalyst relative to the internal reference (i.e., Lagrange strain). HAADF-STEM images of the particle are included. The red dash lines denote the twin boundaries. In each nanoparticle images, the top row depicts the principal strain vectors while the bottom row visualizes that data by the strain ellipse construction.



Figure S24. Strain mapping for a Pd nanoparticle on the $CO-O_2-H_2$ -treated catalyst relative to the internal reference (i.e., Lagrange strain). A HAADF-STEM image of the particle is included. The top row depicts the principal strain vectors while the bottom row visualizes that data by the strain ellipse construction.

Figure S25. Partial oxidation of the steam-treated Pd/Al₂O₃ in O₂ environment ($P_{O2} \approx 0.87$ Pa) at 500 °C. (A) Only Pd{111} lattice fringes were present in the Pd nanoparticle at ≈ 23.6 °C. (B) During heating toward 500 °C, a cap region was seen oxidized at ≈ 391 °C, whereas the rest of the nanoparticle, separated by the orange line, remained in the metallic phase. (C) The nanoparticle stayed partially oxidized as the temperature was stabilized at ≈ 500 °C. Insets 1 to 3 of each panel show the line-profiles of the lattice fringes for interplanar spacing measurements at the indicated areas (turquoise boxes).



Figure S26. Structures for the clean (A) PdO(101) and (B) PdO(110) surfaces. Blue circles represent Pd atoms and red circles represent O atoms. Unit cell is shown in black lines.



Figure S27. Top views of the (A) PdO(100) plane and the (B) PdO(001) plane of the bulk PdO lattice structure at the optimized lattice parameters. The bulk structure has been repeated once in the [100] and [010] directions in these images. Blue circles represent Pd atoms and red circles represent O atoms. Unit cell is shown with a black box.



Figure S28. Side views of initial, transition, and final state structures for methane activation on (A) PdO(101) and (B) PdO(110). Blue, red, brown, and pink circles represent Pd, O, C, and H, respectively.



Figure S29. (A) Arrhenius plots of methane combustion for O_2 and steam-treated Pd/Al₂O₃ prepared by wet impregnation. (B) Corresponding particle size distributions for the pristine and steam-treated Pd/Al₂O₃ prepared by wet impregnation. TEM images of (C) pristine Pd/Al₂O₃, (D) Pd/Al₂O₃ treated in steam at 600 °C. Note that the corresponding TEM results reveal no appreciable change of the Pd particle size for wet-impregnated samples upon steam treatment.



Figure S30. (A) TEM images of 8 nm Pd nanoparticles (insets in A: size distribution of Pd nanoparticles). (B) Methane combustion light-off curves for 8 nm Pd/Al₂O₃ catalysts, after different treatments. (C) Arrhenius plots of dry combustion kinetics for Pd/Al₂O₃ catalysts after treatment in O₂ and steam at 600 °C.



Figure S31. (A) TEM images of 12 nm Pd nanoparticles (insets in A: size distribution of Pd nanoparticles). (B) Methane combustion light-off curves for 12 nm Pd/Al₂O₃ catalysts, after different treatments. (C) Arrhenius plots of dry combustion kinetics for Pd/Al₂O₃ catalysts after treatment in O₂ and steam at 600 °C.



Figure S32. Increase in reaction rates for Pd/Al_2O_3 catalysts after steam treatment. Note that 4 nm Pd was prepared from wet impregnation, whereas the 8, 12 and 15 nm samples were prepared from colloidal nanoparticles. (Increase in reaction rates = rate (steam-treated catalyst)/ rate (O₂-treated catalyst))



Figure S33. TEM images of Pd nanoparticles prepared from laser ablation in water. The orange dash lines highlight Σ 3{111} twin boundaries and the blue dash lines highlight general grain boundaries.



Figure S34. Left, a measured beam image before focusing onto the Pd target. Right, the pit created by the ablation process. The ovular pit volume was measured to be 0.008 cm² by image analysis and used for fluence estimates.

Seed Size (nm)	Pd(acac) ₂ (mmol)	Solvent Mixture (mL:mL)	OLAM (mL)	OLAC (mL)	TOP (mL)	T_{rxn} (°C)
8.0 nm	0.25	ODE : TDE = 6.6 : 3.4	3.4	0.8	2.4	290
12.0 nm	0.25	ODE = 5	-	5	0.56	250
15.0 nm	0.25	ODE = 5	-	5	0.56	280

Table S1. Reaction conditions for the synthesis of Pd nanoparticles with different sizes.

Table S2. Concentration of Pd and P in Pd/Al₂O₃. The values from the pristine sample are included as a reference.

	Pd (wt%)	P(wt%)	P/Pd	
Pristine (after FT)	0.70	0.0245	0.12	
O ₂ - H ₂	0.62	0.0024	0.01	
steam	0.68	0.0039	0.02	

Table S3. The surface facets distributions on Pd/Al₂O₃ after different treatments.

	STEAM	O ₂ -H ₂	CO-O ₂ -H ₂
Number of particles	5	15	17
{110}/{111} (o)	1.055 (±0.015)	1.085 (±0.037)	1.043 (±0.024)
{100}/{111} (o)	1.061 (±0.018)	1.046 (±0.054)	1.040 (±0.041)
{113}/{111} (o)	1.068 (±0.016)	1.088 (±0.039)	1.060 (±0.037)

	PRISTINE	STEAM	O ₂ -H ₂	CO-O ₂ -H ₂
Number of particles	310	325	375	357
Diameter (σ) nm	14.6 (±1.7)	15.1 (±2.6)	15.7 (±3.8)	15.2 (±2.8)
# Containing a Void (%)	0 (0)	0 (0)	128 (34.1)	72 (20.2)
Void Diameter (σ) nm	-	-	7.3 (±1.5)	6.2 (±2.2)

Table S4. The data of particle size distributions.

Table S5. Grain boundary surface density on Pd/Al₂O₃ after different treatment.

	STEAM	O_2 - H_2	CO-O ₂ -H ₂
Total Number of particles	42	27	33
Number with a GB	35	7	4
Percent	83.3	25.9	12.1
Number with two or more GBs	12	2	0
Percent	28.6	7.4	0
Surface Density (µm ⁻¹)	57.78	14.94	4.94

Table S6. Turnover frequency results for Pd/Al2O3 after different treatment and Pd/Al2O3 prepared fromlaser ablation.

	STEAM	O ₂ -H ₂	CO-O ₂ -H ₂	LASER ABLATION
Turnover frequency at 250 °C (molecules CO ₂ formed/	0.051	0.0086	0.0039	0.21
exposed metal atom/s)				

SUPPLEMENTARY VIDEO CAPTIONS

Supplementary Video 1: video of a representative individual Pd nanoparticle in the steam-treated Pd/Al₂O₃ that was exposed to an O₂ environment at a pressure of ≈ 0.87 Pa at room temperature in the Environmental TEM.

Supplementary Video 2: video of a representative individual Pd nanoparticle in the steam-treated Pd/Al₂O₃ that was exposed to an O₂ environment at a pressure of ≈ 0.87 Pa and then heated at a rate of 100 °C·s⁻¹ and stabilized at ≈ 500 °C in the Environmental TEM.

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