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Polaron localization modulates lattice-oxygen transfer in Pd/CeO₂ methane oxidation

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ABSTRACT

Lean methane oxidation over Pd/CeO₂ depends on oxygen exchange across the metal-support interface, yet descriptors that connect the electronic structure of reducible supports to catalytic oxygen supply remain elusive. Here, we isolate the effect of ceria faceting using PdO_x/CeO_{2-y} catalysts with comparable PdO_x particle sizes and loadings. Contrary to the commonly reported preference for CeO₂(111)-rich nano-octahedrons, catalytic activity follows the order nanocubes > nanorods > nano-octahedrons. Kinetic isotope measurements show that C-H activation remains rate determining across all morphologies, whereas microkinetic analysis identifies a support-assisted pathway involving molecular O₂ activation at ceria vacancies and oxygen transfer to PdO_x. Density functional theory reveals that the open (100) and (110) surfaces stabilize localized Ce³⁺ small polarons, while the close-packed (111) surface delocalizes vacancy-derived charge over a Ce trimer, increasing the energetic penalty for oxygen removal and transfer. These findings suggest that polaron localization can be a mechanistic descriptor linking ceria faceting to lattice-oxygen availability and methane-oxidation activity, beyond conventional measures based solely on vacancy concentration. Reactor-scale simulations using the validated microkinetics translate these intrinsic energetics into design requirements, showing that more favorable ratios between the Gibbs free energy of activation and that of oxygen transfer from the support to the PdO_x ($\Delta G^\ddagger/\Delta G_{\text{lattice-oxygen transfer}}$) enable comparable conversion with reduced catalyst inventory. This framework links defect electronic structure to catalyst selection and reactor performance and may extend to oxidation catalysis over other reducible supports.

Keywords: Ceria, CeO₂, CH₄ oxidation, morphology-dependent properties, oxygen vacancies, polarons, oxygen transfer, strong metal-support interactions, nanorods, nanocubes, nano-octahedrons, DFT calculations, microkinetic model, reactor design.

Introduction

Lean methane oxidation catalysts offer a promising route for methane abatement, although their feasibility is limited by the low concentrations and mild exhaust gas temperatures[1,2]. Palladium (Pd)-based catalysts are among the most promising materials for this reaction[3]. Here, using reducible metal oxides like ceria (CeO₂) as a support contributes to a favorable concentration and distribution of reactive surface oxygen, increasing the activity[4–7]. This behavior is closely associated with electron localization and charge compensation during Ce⁴⁺ to Ce³⁺ reduction, often occurring via small polaron formation [8–15]. These characteristics result in synergistic effects that regulate both the electronic structure and the charge exchange processes at ceria surfaces to improve catalytic performance.

Several studies have compared Pd/CeO₂ catalysts with different ceria morphologies for lean methane oxidation, generally reporting higher mass-normalized conversion for nano-octahedrons that expose (111) facets primarily [16–20]. This enhanced activity has been attributed to stronger Pd-Ce interactions, higher concentrations of Ce³⁺, oxygen vacancies and adsorbed oxygen species, improved Pd dispersion, a larger fraction of Pd²⁺ species, and greater resistance to Pd sintering. Unfortunately, there is no clear consensus in the field because key descriptors such as Pd particle size were either not reported[16] or not consistently provided for all reference catalysts[19]. As a result, it remains difficult to separate the intrinsic effect of ceria morphology from changes in Pd particle size, oxidation state, dispersion, and stability. Nevertheless, the repeated observation of superior performance for CeO₂ nano-octahedrons has directed recent research toward this morphology, often reinforcing the assumption that the (111) surface is intrinsically preferred for lean methane oxidation[20].

Here, we hypothesize that controlling the polaron mobility on ceria, without altering the palladium cluster size, would allow us to modulate the reaction energy landscape of the C-H bond oxidation. To test this concept we have employed nanoshaping of CeO₂ to create distinct facet terminations, which can influence polaron formation, charge mobility, and substrate adsorption strength, as well as the oxidation state of Pd. In practice, ceria nano-octahedra predominantly expose the thermodynamically stable (111) facet, whereas nanorods preferentially present the more open (110) surface along with a smaller contribution from (100). In contrast, nanocubes are largely terminated by the (100) facet. [6,21–27] This shape-facet relationship establishes a systematic route to correlate ceria surface structure with the

oxygen vacancy formation, energetics of the resulting polaron, and chemistry of the Pd surface.

Contrary to the pervasive view that the close-packed CeO₂(111) surface is the most active, our results indicate that the delocalized nature of the (111) surface polarons increases the oxygen-vacancy formation energy, imposing the largest enthalpic penalty for supplying reactive oxygen to Pd. This also induces a large entropic penalty and concomitant stabilization of the activated complex [H₃C---H][‡] on the Pd under the influence of interfacial charge transfer from the (111) surface, further weakening the kinetics. The more open (100) and (110) surfaces presented the opposite trends, due to the more localized surface polarons and moderate Pd-metal oxide interactions.

To showcase the importance of these results, we investigated the interplay between the reactor length and washcoat thickness required for the removal of methane slip in the exhaust gas of a liquefied natural gas (LNG) engine. Here, we found that catalysts with more favorable oxygen-transfer thermodynamics and kinetics achieve higher conversion at a smaller washcoat thickness. More broadly, this framework of polaron-driven oxidation catalysis provides a unifying lens for metal-nonmetal compounds (oxides, nitrides, sulfides, carbides, borides), in which vacancy defects create localized electronic states that govern charge transfer and redox reactivity, and may extend beyond ceria-based materials.

Results and discussion

Probing the reactivity of faceted Pd/CeO₂ catalysts

In this work, the different morphologies of ceria, nanocubes, nano-octahedrons, and nanorods were studied to understand their influence on Pd/CeO₂ catalysts for lean methane oxidation. **Figure S3a** confirms the successful synthesis of distinct CeO₂ morphologies. HRTEM images of the catalysts (**Figure S3b1-b3**) show that impregnation followed by calcination did not significantly modify the support morphology. The lattice fringes in **Figure S3c1-c3** confirm the expected facet terminations. Pd/CeO₂ nanocubes exhibited an interplanar spacing of 0.27 nm, consistent with the (100) facet[17,28,29]. The nano-octahedrons showed a spacing of 0.31 nm, attributed to the (111) face[15,17,28,30]. The nanorods displayed spacings of 0.19 and 0.27 nm, assigned to the (110) and (100) facets, respectively[15,30–32].

To avoid biased benchmarking, wet impregnation was employed to obtain comparable Pd cluster sizes (~5 nm, size distribution in **Figure S6**) and metal loadings (0.5 wt.%), minimizing the influence of particle size effects (**Table 1**). No sodium contamination was detected by XRF, in agreement with the XPS results in **Figure S4**, confirming the effectiveness of the filtration step in the synthesis. This is important

because lean methane oxidation is structure-sensitive: the TOF increases with Pd particle size up to approximately 8 nm and then reaches a plateau[2].

Table 1. Properties of the supports, CeO₂ nanocubes (CeO₂ cub), nano-octahedrons (CeO₂ oct), and nanorods (CeO₂ rod); and catalysts, Pd/CeO₂ nanocubes (Pd/CeO₂ cub), nano-octahedrons (Pd/CeO₂ oct), and nanorods (Pd/CeO₂ rod).

	CeO ₂ cub	CeO ₂ oct	CeO ₂ rod	Pd/CeO ₂ cub	Pd/CeO ₂ oct	Pd/CeO ₂ rod
Surface area (m ² ·g ⁻¹) ^a	16	50	94	16	50	117
Metal loading (wt. %) ^b	-	-	-	0.50	0.49	0.50
PdO particle size (nm) ^c	-	-	-	5.4 ±2.1	5.3 ±1.5	5.1 ±1.8

^aUsing the BET method. ^bDetermined by XRF. ^cDetermined by HRTEM and HAADF-STEM analyses; values are reported as average ±standard deviation.

The electronic structure of the as-synthesized catalysts was characterized by XPS (**Figure S5**). The Ce 3d spectra (**Figure S5a**) indicate that the surface Ce³⁺ concentration follows the order nanocubes > nanorods > nano-octahedrons, with values ranging from 22 at.% for nanocubes to 17 at.% for nano-octahedrons. The Pd 3d spectra (**Figure S5b**) show no contribution from metallic Pd, indicating that calcination at 500 °C for 2 h fully oxidized the palladium species[17,33,34]. The main doublet at ~337 eV and ~342 eV is assigned to Pd²⁺ in PdO[33,35,36], while a second doublet at higher binding energies (~338 and ~343 eV) is attributed to Pd²⁺ species strongly interacting with the ceria support[36–38]. The relative contribution of this high-binding-energy Pd²⁺ component follows the same trend as the Ce³⁺ concentration: nanocubes > nanorods > nano-octahedrons. This correlation suggests that oxygen-deficient ceria surfaces promote stronger Pd–CeO₂ interactions and stabilize more electron-deficient Pd²⁺ species. The O 1s spectra (**Figure S5c**) were deconvoluted into three components: lattice oxygen (O_{latt.}) at ~529 eV[16,39–42], surface hydroxyl groups at ~531 eV[39–41,43]. The contribution of surface hydroxyl groups (OH_{surf.}) followed the same trend observed for Ce³⁺ and Pd²⁺ components. Overall, the XPS results indicate that the more open faceting promotes higher Ce³⁺ and Pd²⁺ ratios.

The differences among the shaped catalysts (**Figure 1a₁-c₁**) are more evident in the TGA analysis performed in the presence of oxygen. This experiment provides insight into the extent to which oxygen can be removed from PdO_x under oxidative conditions, thereby enabling the evaluation of the influence of support morphology on PdO_x reducibility. Pd/CeO₂ nanocubes showed the lowest onset temperature (993 °C), while nano-octahedrons showed the highest (1079 °C), with nanorods displaying intermediate behavior (**Figure 1a₂-c₂**). Overall, this trend indicates that PdO_x reducibility is sensitive to the exposed CeO₂ facets, with the different morphologies affecting the stability of oxygen species associated with PdO_x.

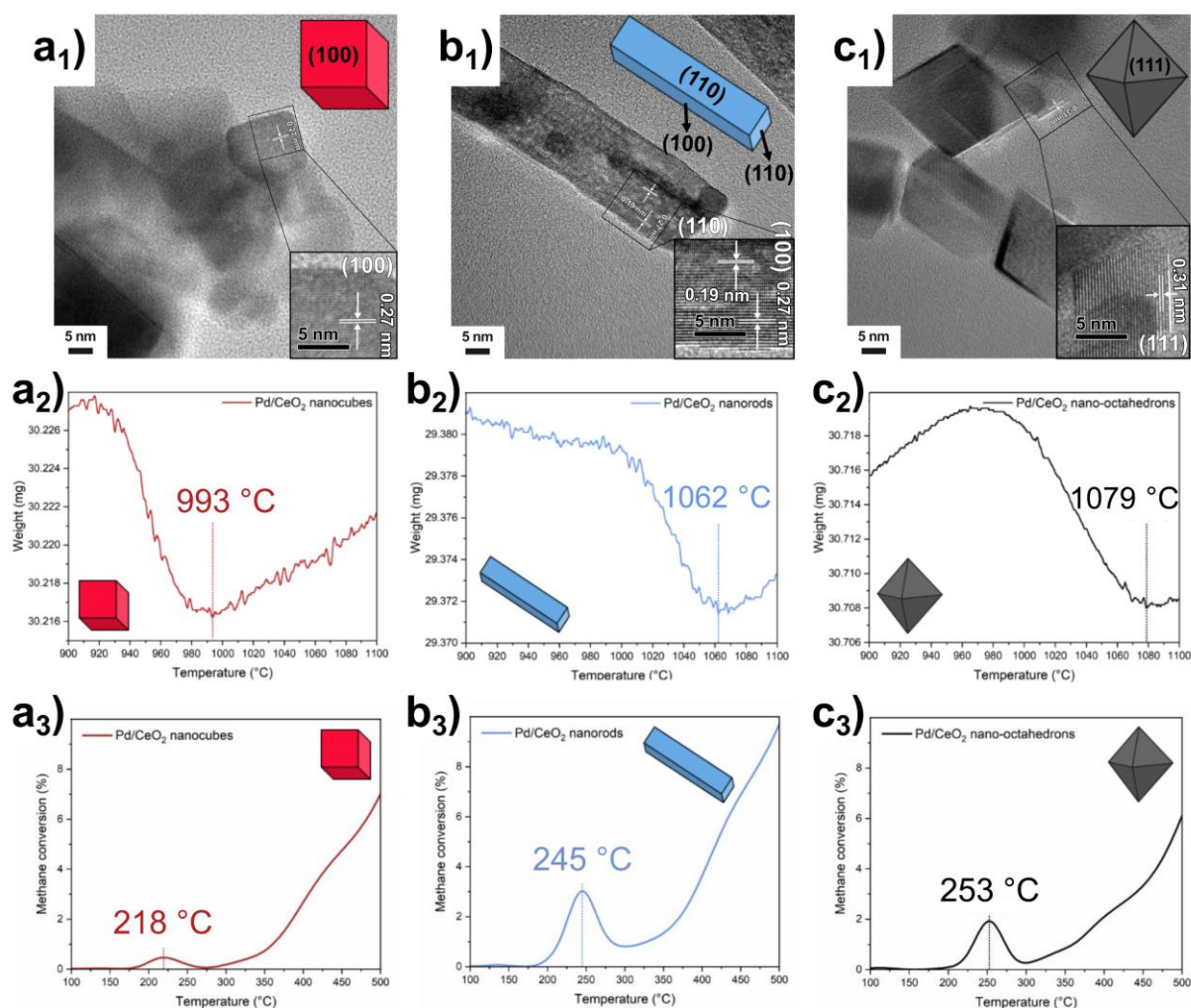


Figure 1. (1) HRTEM of the Pd/CeO₂ catalysts and graphical representation of the nano-shaped materials; (2) TGA profile of the catalysts from 900-1100 °C in 9.52% O₂; (3) CH₄-TPR profile from 100-500 °C in 1 vol.% CH₄ at 30 000 mL·g_{cat}⁻¹·h⁻¹ for (a) nanocube-, (b) nanorod-, and (c) nano-octahedron-based catalysts.

Next, we studied the CH₄-TPR profiles of the Pd/CeO₂ catalysts (**Figure 1a₃-c₃**). The first reduction feature at 170-300 °C is assigned to PdO_x reduction

1 to metallic Pd, while the sustained methane consumption above 300 °C is attributed to
2 Pd-assisted ceria reduction, involving near-surface lattice oxygen removal, oxygen
3 vacancy formation, and partial reduction of Ce⁴⁺ to Ce³⁺.

4 Bare CeO₂ supports showed negligible methane conversion under the same
5 conditions, confirming that methane activation and ceria reduction are promoted by Pd.
6 The PdO_x reduction onset follows the same trend observed for PdO autoreduction,
7 indicating that methane interacts more readily with PdO_x on nanocubes, promoting
8 CO₂ and H₂O formation at lower temperatures. Despite comparable PdO_x loadings and
9 similar particle sizes, the integrated PdO_x reduction areas varied significantly among
10 the morphologies. The apparent PdO consumptions were 104 % for nanocubes, 354 %
11 for nano-octahedrons, and 513 % for nanorods relative to the nominal PdO content,
12 indicating that the additional oxygen likely originates from the support. This trend
13 correlates with the bulk oxygen vacancy concentration estimated from the I₅₉₈/I_{F2g}
14 (intensity at 598 cm⁻¹ divided by the intensity of the F_{2g} peak at ~462 cm⁻¹) Raman
15 ratio (**Figure S7**) and agrees with previous reports [44–46]. In general, higher bulk
16 oxygen vacancy concentrations increase the oxygen storage capacity[47]. A possible
17 transfer of lattice oxygen from CeO_{2-y} to PdO_x species [48] may enable repeated Pd
18 redox cycling, resulting in apparent PdO consumption exceeding the theoretical 100 %
19 for all morphologies.

20 To rationalize these differences in the reducibility of the different catalysts, we
21 conducted differential kinetic measurements in the absence of internal and external
22 heat and mass transfer limitations (experimental and theoretical calculations and mass
23 transfer analysis in **Section S4**). In every experimental campaign, the catalyst was
24 initially equilibrated under reaction conditions for 2.5 h, and the start-of-run conversion
25 was compared to the end-of-run conversion to ensure that there was no major
26 deactivation during the experiment (**Figure 2a**). Surprisingly, the Pd-based catalyst
27 supported on nanocubes, which has the lowest surface area, was the most active
28 across all the conditions explored, followed by the nanorods and nano-octahedrons
29 (**Figure 2b**). This trend contrasts with literature reports in which CeO₂ nano-
30 octahedron-based catalysts are often described as the most active morphology[16–
31 20]. However, active metal cluster size was not kept constant across these reports,
32 complicating benchmarking because the reaction is structure-sensitive[2].

33 Kinetic tests at varying partial pressures of oxygen (**Figure 2c**) and methane
34 (**Figure 2d**) were performed at increasing temperatures to estimate apparent reaction
35 orders. For nano-octahedron-supported catalysts, the apparent methane reaction
36 order increased with temperature, whereas nanorod- and nanocube-supported
37 catalysts showed weaker temperature dependence and a slight decrease. Similarly,
38 for Pd-CeO₂ nanorods and nanocubes, the reaction order for oxygen

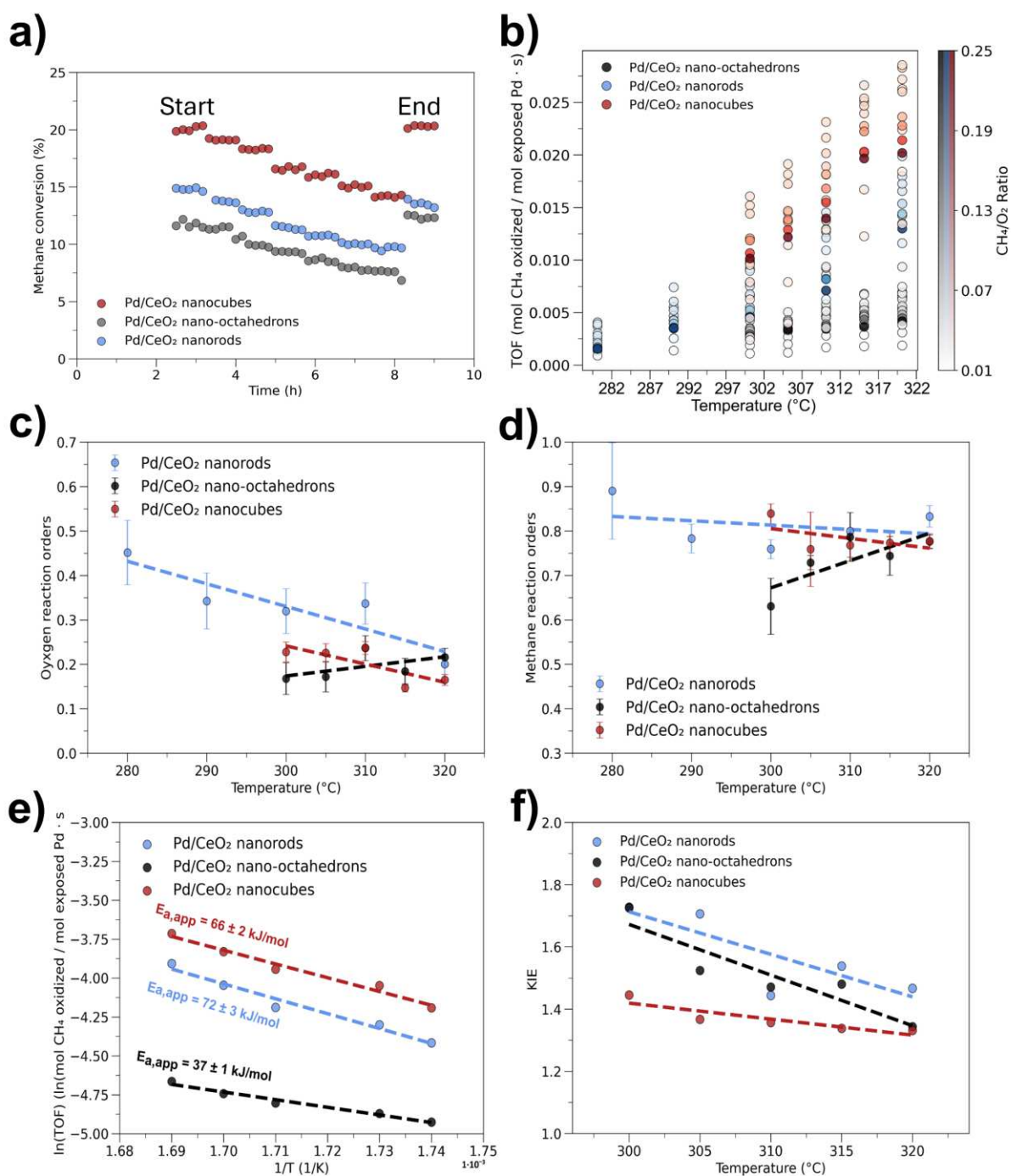


Figure 2. (a) Methane conversion as a function of time at 320 °C, with the oxygen concentration varied stepwise between 12.0 and 1.6 vol.% at a constant methane concentration of 0.40 vol.%. (b) TOF as a function of temperature for different CH₄:O₂ ratios. (c) Oxygen reaction orders as a function of temperature. (d) Methane reaction orders as a function of temperature. (e) Arrhenius plots. (f) Kinetic isotope effect. Error bars and parameter uncertainties represent ± 1 standard error from the linear regression.

decreased with increasing temperature, suggesting saturation kinetics. In stark contrast, the Pd-based catalyst supported on nano-octahedrons exhibited the opposite trend, although with less pronounced variation, where increasing the temperature raised the apparent reaction order.

These results are difficult to rationalize, as one would expect that increasing temperature would lead to lower surface coverages, which in turn would lead to higher reaction orders. In fact, these results suggest that on nanocubes and nanorods, where (100) and (110) surfaces dominate, the availability of oxygen and, to a lesser extent, methane increased with temperature.

Arrhenius analysis (**Figure 2e**) showed that Pd/CeO₂ nano-octahedrons had approximately half the apparent activation energy of the nanorod- and nanocube-supported catalysts. However, this lower $E_{a,app}$ was accompanied by a decrease of ~3 orders of magnitude in A_{app} . The nanocube-supported catalyst showed intermediate $E_{a,app}$, and A_{app} values.

In this scenario, one might argue that these differences could be due to a change in the rate-determining step depending on the faceting. To investigate this, we employed kinetic isotope effect (KIE) experiments using deuterated methane (CD₄) at different temperatures. The comparison of the CD₄ reaction rates with those of CH₄ (**Figure 2f**) demonstrated a significant KIE (>1.3) for all morphologies. As expected, the KIE decreased with increasing temperature because added thermal energy reduced the relative importance of the zero-point-energy difference between C–H and C–D, making isotope substitution less rate-influential at higher temperature. This observation strongly supports that C–H bond dissociation is the RDS across all catalyst supports, consistent with previous studies[49–53]. Thus, we can reject the hypothesis that these differences in apparent reaction orders and activation barriers are due to changes in the RDS.

Interplay between surface energetics and activity

The premise of this study is that specific electronic features of faceted ceria may dictate the observed activity trends. To probe these trends and the role of support faceting, we therefore conducted DFT calculations, as direct characterization of such electronic features, particularly under operando conditions, remains challenging. DFT calculations were performed on the energetics of oxygen-vacancy formation, polaron localization, and electronic metal-support interactions for CeO_{2-y} (100), (110), and (111) ceria surfaces. In general, the (111) faceted surface was the most stable, with a surface energy of 1.22 J·m⁻², followed by (110) with 1.67 J·m⁻², and (100) with 2.23 J·m⁻². This trend agrees with the O 1s XPS results (**Figure S5c**), which showed surface hydroxyl ratios of 59, 52, and 24 at.% for catalysts predominantly exposing the (100), (110), and (111) facets, respectively. The higher hydroxyl coverage on the (100) and (110) surfaces is consistent with their higher surface energies and greater number

of undercoordinated surface atoms. Hydroxyl adsorption can stabilize these high-energy surfaces by saturating surface cations and lowering the excess surface energy[54]. The lower surface energy of CeO₂(111) is related to its close-packed O-Ce-O trilayer termination, which preserves a near-bulk coordination environment. Surface Ce atoms remain sevenfold coordinated, close to the eightfold coordination in bulk CeO₂, minimizing undercoordinated sites and dangling bonds. In contrast, the more open (100) and (110) surfaces contain more undercoordinated cations, resulting in higher surface energies.

Polaron formation is an intrinsic feature of reduced ceria[55], arising from oxygen vacancies that leave two excess electrons, which can localize on Ce cations. The neutral vacancy-polaron complex ($[V_{O^{2+}} - 2 e^-]^0$), containing two parallel-spin 4f electrons, is the most stable configuration compared with the bare vacancy (VO^{2+}) and the single-polaron complex ($[V_{O^{2+}} - e^-]^+$)[56]. As summarized in **Table S3**, vacancy formation is least favorable under O-rich conditions and becomes progressively more favorable under reducing conditions. The calculated reducibility follows the trend (100) $\approx$ (110) < (111), indicating that oxygen removal is easier on the (100) and (110) facets than on the close-packed (111) surface. This ordering describes the formation of a single, isolated vacancy; as shown in **Table S6**, the same ranking does not hold once a second vacancy is introduced adjacent to the first. This trend can be explained by the distinct polaronic structures formed upon oxygen-vacancy creation on each facet. On the (100) and (110) surfaces, each oxygen vacancy localizes two excess electrons on two nearby Ce centers, forming two distinct small polarons, **Figure 3a₁** and **Figure 3b₁**, respectively. This is reflected in the band structure by two occupied mid-gap states in the same spin channel, corresponding to two parallel-spin electrons (**Figure 3a₂** and **Figure 3b₂**). In contrast, on the highly symmetric and densely coordinated (111) surface, the excess charge is delocalized over a Ce trimer rather than forming two separate small polarons (**Figure 3c₁**). This is evidenced by one fully occupied and two partially occupied mid-gap states (**Figure 3c₂**). The delocalized charge distribution reduces local lattice relaxation but increases the energetic penalty for oxygen-vacancy formation on the (111) facet. Because the excess charge on (111) is already spread over three Ce centers rather than concentrated on two, this facet accommodates a second, adjacent vacancy at a smaller additional energetic cost than either (100) or (110) (**Table S6**), despite being the most resistant of the three to forming the first vacancy. (100) and (110), by contrast, must localize a third and fourth electron onto already-reduced, spatially separated Ce centers, which is comparatively more costly. Close-packed (111) is therefore best described as protected against initial reduction but comparatively permissive toward vacancy clustering once reduction is underway, rather than uniformly resistant to oxygen-vacancy formation.

Since these electronic descriptors were obtained from support-only models, they do not fully capture the catalytic interface. Therefore, PdO-supported models with

identical PdO-cluster sizes and comparable PdO coverages were constructed for each morphology, as shown in **Figure S11**. Bader charge analysis confirms electronic metal–support interaction for all terminations, with net electron transfer from reduced ceria to PdO of -0.33 e for (111), -0.93 e for (110), and -0.56 e for (100). This establishes the hierarchy (110) > (100) > (111) for interfacial charge transfer. The strongest charge injection on (110) is consistent with its highly negative Fermi level, and notably occurs despite this facet hosting the most deeply bound polaron state of the three surfaces (1.06 eV below the CBM, **Table S5**). This indicates that the thermodynamic driving force set by the Fermi level, rather than local polaron binding depth, governs charge injection on (110). This may also lead to an electronically saturated PdO interface where charge becomes strongly stabilized and less available for dynamic redox steps. The (111) surface shows the weakest charge transfer. This is not attributable to polaron binding depth, since the (111) donor state (0.80 eV below the CBM, **Table S5**) is intermediate between the (100) (0.70 eV) and (110) (1.06 eV). Instead, the delocalized character of the excess charge itself determines this effect: distributed as partial occupancy over a Ce trimer rather than concentrated in two fully occupied, single-center polarons as on (100) and (110), this charge is less available for a discrete one-electron transfer event, consistent with the structural rigidity and near-bulk coordination of the (111) termination. By contrast, the (100) surface exhibits intermediate charge transfer and shallower, more accessible donor states. This moderate reduction may allow PdO to exchange charge more reversibly during catalysis, avoiding both deep polaron trapping on the (111) surface and possible over-reduction on the (110) surface. Therefore, the (100) surface likely offers the most favorable balance between charge mobility and redox flexibility, providing a rationale for the superior performance often reported for ceria morphologies dominated by this surface.

A key limitation of the model is that only oxygen vacancies near PdO are explicitly considered, whereas real surfaces contain vacancies at different distances from the metal–support interface. Distal vacancies may preserve the intrinsic polaronic character of defective ceria and act as electron reservoirs for O_2 activation. This suggests a cooperative mechanism in which distal polaronic sites promote O_2 activation and oxygen transfer toward the interface. In this context, the moderate electron depletion at the (100) interface is beneficial, as it reduces charge trapping while preserving redox flexibility and oxygen replenishment capacity.

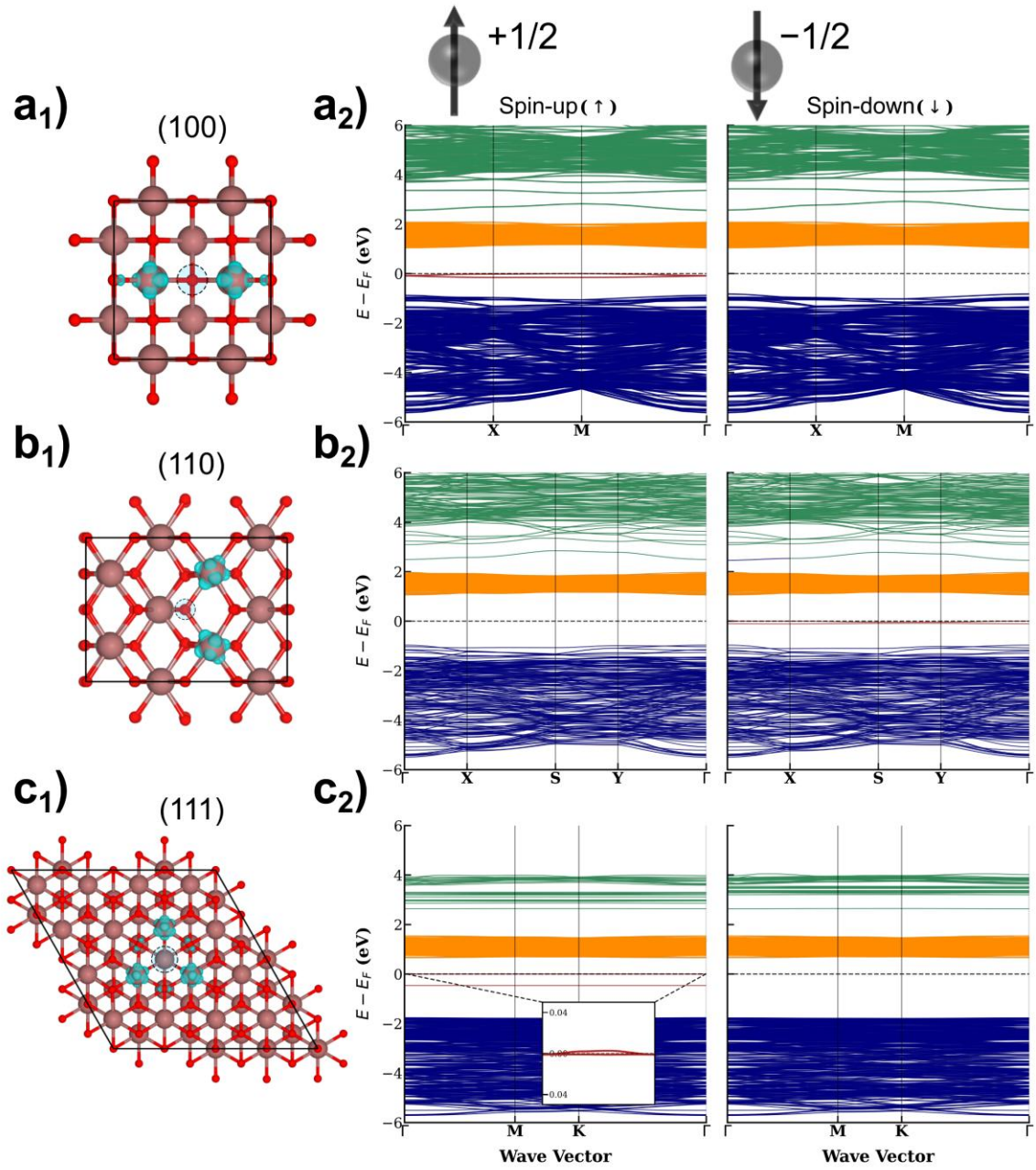


Figure 3. (1) Isosurfaces in blue (10 % of maximum density) corresponding to the polaronic states arising from the creation of a single oxygen vacancy in each surface with neutral charge. Dashed lines indicate the oxygen vacancy site. Ce and O atoms are represented in wine and red colors, respectively. (2) Corresponding calculated spin-resolved band structures for spin-up and spin-down configurations. Results are shown for the (a) (100), (b) (110), and (c) (111) ceria surfaces with one neutral oxygen vacancy. Blue, orange, and green bands correspond to O 2p, Ce 4f, and Ce 5d states, respectively, while the red bands indicate localized Ce³⁺ polaronic states arising from oxygen-vacancy formation. Full, dot, and dashed lines represent occupied, unoccupied, and partially occupied bands, respectively. The zero is set to the valence band maximum, and the systems were aligned to the vacuum level energy.

To challenge this postulate, we interrogated the catalyst using microkinetic modeling with four different mechanisms. In all cases, the first hydrogen abstraction step was considered the RDS, as supported by **Figure 2f**, and the overall pathway was described by a Mars-van Krevelen mechanism. **Figure S16** summarizes the four mechanisms considered: dissociative O₂ adsorption on PdO_x (M1), dissociative O₂ adsorption on ceria followed by transfer to PdO_x (M2), molecular O₂ adsorption on PdO_x (M3), and molecular O₂ adsorption on ceria followed by transfer to PdO_x (M4). The detailed development of the models is provided in **Section S5**. By combining microkinetic modeling, kinetic data from lean methane oxidation, and DFT calculations, this approach allows the contribution of individual elementary steps to be evaluated and helps decouple polaron-induced oxygen transfer from other effects involved in C–H bond activation on PdO_x surfaces.

Table S1 summarizes the model fitting results using the kinetic data, evaluated by RSS and AIC. Since M1 contains fewer adjustable parameters, AIC is particularly useful because it penalizes model complexity. Among all models, M4 consistently gave the lowest RSS and most negative AIC, indicating the best overall performance. Models including support participation, M2 and M4, fitted the data more accurately than those excluding the support, M1 and M3, highlighting the importance of explicitly accounting for ceria in the microkinetic model. Among the models without support participation, M3 provided a significantly lower RSS than M1. Although M1 has fewer adjustable parameters, M3 still showed better performance after AIC penalization. Therefore, M3 and M4, both based on molecular O₂ adsorption and containing the same number of adjustable parameters, were selected to evaluate the effect of support participation. **Figure S8** shows the corresponding fits for Pd/CeO₂ nanocubes, comparing models without support participation, M3 (**Figure S8a,c**), and with support participation, M4 (**Figure S8b,d**). The color gradients represent variations in temperature (**Figure S8a,b**) and CH₄/O₂ ratio (**Figure S8c,d**). As shown in **Figure S8**, including the support clearly improves the model predictions. In particular, the parity plots as a function of CH₄/O₂ ratio (**Figure S8c,d**) show that models neglecting the support increasingly underpredict the experimental rates at higher CH₄/O₂ ratios. This suggests that without support participation, the mechanism cannot sustain the higher rates without creating an imbalance in the PdO_x oxidation state. Including ceria support resolves this limitation by providing an additional oxygen-transfer pathway to the PdO_x active phase. The same trend is observed for the other catalysts (**Figure S9**).

To assess the feasibility of model M2 via DFT calculations, which would require a divacancy to incorporate the dissociation of molecular oxygen at oxygen vacancy sites of the ceria support and transfer to PdO_x active sites, the formation energies of paired surface vacancies (divacancies) were evaluated (**Table S6**). Divacancy complexes magnify facet-specific contrasts and reveal key mechanistic trade-offs: although divacancy formation is substantially more costly than single-vacancy

formation (**Table S3**), it drives distinct facet-dependent reconstructions. On (110) and (111) surfaces, the divacancy stabilizes two localized polarons (total magnetization of 4 μB). In contrast, the divacancies at the (100) surface induce an electronic collapse; the magnetization falls to 0 μB , polarons delocalize, and the excess electrons redistribute over the surface. Crucially, the high thermodynamic cost of forming divacancies, together with the superior statistical fit of model M4 (RSS and AIC, **Table S1**), indicates that the M2 pathway is unlikely to dominate under the present catalytic conditions.

Figure 4a shows a simplified version of the best-fitting mechanism, M4, highlighting the transition state and the redox cycles on PdO_x and ceria, including lattice and surface oxygen exchange; the complete mechanism is provided in **Figure S10**. Based on the previously explained DFT analysis and statistical metrics, M4 (**Equation S92**) was selected for further analysis of the different catalysts.

$$\frac{-r_{\text{CH}_4}}{N} = k_{sr} \cdot p_{\text{CH}_4} \cdot \frac{1}{1 + \frac{1}{K_a^{0.5} \cdot K_{2b}^{0.5} \cdot K_9^{0.5} \cdot pO_2^{0.5}}} \cdot \frac{1}{1 + \frac{K_a^{0.5} \cdot K_{2b}^{0.5} \cdot pO_2^{0.5}}{K_9^{0.5}}} \quad (\text{Eq. S92})$$

The enthalpy and entropy changes associated with the equilibrium constants, together with the transition-state parameters ($\Delta^\ddagger H$ and $\Delta^\ddagger S$) derived from the reaction rate constants, are summarized in **Table S2**. The equilibrium constant K_9 , related to oxygen transfer from the PdO_x surface to the PdO_x lattice, remains essentially unchanged among the catalysts. This indicates that this step is not affected by the CeO_2 facet termination, consistent with its occurrence exclusively on PdO_x . Moreover, this step is thermodynamically favorable under typical lean methane oxidation conditions. In contrast, K_a describes a coupled process involving molecular O_2 adsorption at ceria oxygen vacancies followed by oxygen transfer to PdO_x . This process is most favorable for Pd/CeO_2 nano-octahedrons due to its highly exothermic character and relatively small entropy loss. However, because K_a combines two sequential events; its direct mechanistic interpretation is limited. If the assumption of a similar transfer of oxygen from the ceria lattice to the surface of PdO_x is made, a very exothermic molecular adsorption of oxygen is observed for the nano-octahedrons. This could result in oxygen trapping, thereby reducing the oxygen mobility of the support even further due to the strong oxygen binding.

A deeper analysis of the reaction rate constant and the equilibrium constant governing the transfer of oxygen from the ceria lattice to the PdO_x lattice is presented in **Figure 4**. In **Figure 4b**, it is evident that the energy required for oxygen transfer in the case of octahedrons is significantly higher than for the other morphologies, as reflected in their more endothermic enthalpic change. Moreover, the octahedrons exhibit a lower entropic gain relative to the other supports. In contrast, the nanocubes display the least positive enthalpic change combined with the highest entropic gain,

1 making them the most favorable morphology for oxygen transfer among those
2 investigated in this study. Notably, this oxygen transfer occurs even though the Gibbs
3 free energy remains positive, since the reaction consuming oxygen from the PdO_x
4 lattice drives the equilibrium toward additional oxygen transfer from the ceria support
5 to the PdO_x active sites.

6 The observed differences in reaction orders (**Figure 2**) can be rationalized by
7 the interplay of enthalpic and entropic contributions to lattice oxygen transfer. For
8 nanocube- and nanorod-based catalysts, lattice oxygen transfer is less endothermic
9 and associated with a larger entropy increase than for the nano-octahedrons
10 (**Figure 4c**). This places the nano-octahedrons, which predominantly expose the (111)
11 facet termination, in a distinct regime compared to the other two morphologies. The
12 greater intrinsic oxygen-transfer propensity of nanocubes and nanorods alters the
13 dependence of the overall rate on the external oxygen concentration. In addition, as
14 temperature increases, the mobility of lattice oxygen within both the ceria support and
15 the PdO_x phase is expected to increase. This higher oxygen mobility facilitates faster
16 vacancy replenishment and accelerates oxygen exchange, thereby reducing the
17 sensitivity of the reaction to the external oxygen partial pressure. This explains the
18 temperature-dependent decrease in the oxygen reaction order observed for
19 nanocubes and nanorods. In contrast, the nano-octahedrons, with their partial polaron
20 delocalization, hinder oxygen transfer and retain their dependence on external oxygen
21 concentration, displaying the opposite temperature trend. On the other hand, analysis
22 of the transition state (**Figure 4d**) shows that nano-octahedron-based catalysts have
23 the lowest activation enthalpy, but this is offset by a large unfavorable entropic penalty.
24 Nanocube-based catalysts exhibit an intermediate activation enthalpy, lower than that
25 of nanorods but higher than that of nano-octahedrons, while maintaining a much
26 smaller entropy loss than nano-octahedrons.

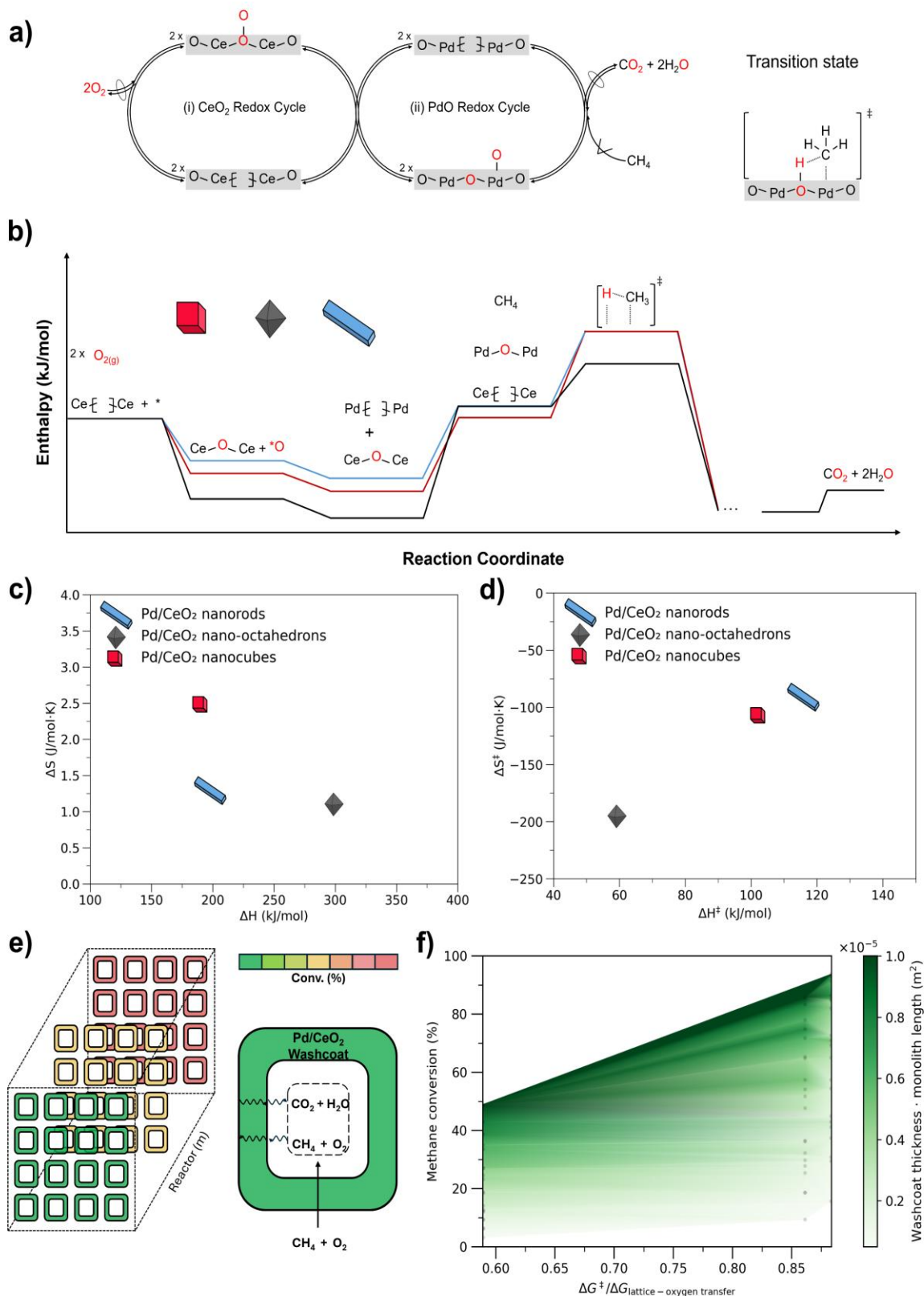


Figure 4. (a) Simplified mechanism M4. (b) Energy profile diagram. Enthalpic and entropic contributions to (c) the equilibrium constant governing oxygen transfer from the ceria lattice to the PdO_x lattice, and (d) the transition state of the reaction rate constant. (e) Schematic of the reactor. (f) Methane conversion versus $\Delta G^{\ddagger}/\Delta G_{\text{lattice oxygen transfer}}$; the washcoat thickness · channel length (m²) is shown as a continuous color map generated by triangulation-based interpolation of the measured points.

The microkinetic results also correlate with experimental characterization. The higher surface oxygen-vacancy concentration of nanocubes may contribute to a larger fraction of high-binding-energy Pd^{2+} species (**Figure S5**). This behavior is intrinsic to the CeO_2 (100) surface, as supported by DFT calculations, and corresponds to the dominant facet in nanocubes (**Figure S3c₁**). The strong interaction between Pd^{2+} and the vacancy-rich (100) surface promotes oxygen transfer, consistent with the microkinetic model and with the lower-temperature PdO autoreduction and CH_4 -TPR profile observed experimentally (**Figure 1**). Nanocube- and nanorod-based catalysts exhibit apparent pre-exponential factors approximately three orders of magnitude higher than those of the nano-octahedron-based catalyst. However, nanocubes also exhibit a lower activation barrier than nanorods (**Figure 2e**), which, combined with enhanced lattice oxygen transfer, explains their higher turnover frequencies across the investigated conditions (**Figure 2b**).

The microkinetic model was further applied to monolith reactor design. The simulation parameters are listed in **Table S7**, and the monolith scheme is shown in **Figure 4e**. **Figure S12a** presents the methane concentration profile along the gas channel for 90 % methane conversion. The required channel length is 0.24 m for nanocubes, while the other two morphologies presented a much lower conversion with the same length. Pressure drop was around 10 Pa across all simulations. The advantage of nanocubes is also evident in the washcoat concentration profiles (**Figure S12b**), where steeper methane gradients reflect higher reaction rates. The calculated reactor volume for Pd/ CeO_2 nanocubes is only 19 % of that required for Pd/ CeO_2 nano-octahedrons, indicating potential reductions in both CapEx and OpEx.

Finally, **Figure 4f** links the thermodynamic descriptors from **Figures 4c and d** to reactor-scale performance. A parametric set of reactor simulations was performed in which the washcoat thickness (10 to 50 μm) and channel length (0.05 to 0.20 m) were systematically varied, while all remaining inputs were fixed to the values of **Table S7**. This analysis was carried out for each ceria-supported catalyst, and the resulting methane conversion was plotted as a function of $\Delta G^\ddagger/\Delta G_{\text{lattice-oxygen transfer}}$, a combined kinetic–thermodynamic descriptor relating the activation barrier of the rate-determining step to the Gibbs free energy of lattice-oxygen transfer from CeO_{2-y} to PdO_x . The color scale represents the product of washcoat thickness and channel length (**Figure 4f**). The resulting map highlights a coupled support-morphology reactor dependence, in which conversion is controlled both by support-specific properties and by the washcoat thickness and channel length. Catalysts with more favorable oxygen-transfer thermodynamics and kinetics achieve higher conversion at a smaller washcoat thickness · channel length, whereas less favorable supports require increased catalyst inventory to reach comparable conversion. Thus, **Figure 4f** provides a numerical scaling relationship that connects morphology-dependent transition-state and lattice-

oxygen transfer energetics to the required reactor dimensions, highlighting the importance of support engineering in reactor design.

Conclusions

In this work, PdO_x/CeO_{2-y} catalysts were synthesized with comparable PdO_x particle sizes but different dominant ceria facet terminations, allowing particle-size effects to be decoupled from support morphology. The catalytic activity followed the order nanocubes > nanorods > nano-octahedrons. Microkinetic analysis indicated that these differences arise from facet-dependent oxygen-transfer energetics between ceria and PdO_x, which modulate the availability and replenishment of reactive oxygen at the active phase rather than changing the identity of the rate-determining C-H activation step. The lower activity of the nano-octahedron-supported catalyst was associated with less favorable enthalpic and entropic contributions to lattice-oxygen transfer and a larger entropic penalty in the transition state. DFT calculations showed that these differences are linked to the nature of the surface polarons formed upon oxygen-vacancy generation. On the CeO₂ (100) and (110) surfaces, vacancy formation is more favorable and the two excess electrons localize on two Ce centers as Ce³⁺ small polarons, producing two mid-gap states. In contrast, the close-packed CeO₂ (111) surface resists initial oxygen removal and delocalizes the excess charge over a Ce trimer, producing one fully occupied and two partially occupied mid-gap states. These facet-dependent polaronic configurations regulate lattice-oxygen availability and transfer to PdO_x. The resulting kinetic-thermodynamic descriptor, $\Delta G^\ddagger/\Delta G_{\text{lattice-oxygen transfer}}$, was subsequently related to reactor requirements, with more favorable energetics enabling comparable methane conversion at lower catalyst inventory. Overall, the results demonstrate that facet engineering of CeO₂ can tune polaron-mediated lattice-oxygen transfer and improve both catalytic performance and reactor efficiency.

Materials and methods

Materials

CeO₂ nano-octahedrons, Ce(NO₃)₃·6H₂O (99 wt.% pure), and NaOH (≥ 98 wt.% pure) were purchased from Sigma-Aldrich. Pd(NO₃)₂·xH₂O (99.8 wt.% pure, ≥ 39 wt.% of Pd) was purchased from Alfa Aesar.

Preparation of CeO₂ supports

CeO₂ nanorods and nanocubes were prepared through hydrothermal synthesis, as reported in previous studies[31,44,57]. A typical synthesis started with the agitation of NaOH 17.1 M at 700 RPM using a magnetic stirrer. Subsequently, a solution composed of 2.17 g Ce(NO₃)₃ and 5 mL of ultrapure water was dripped into the NaOH solution, leading to a milky slurry solution. The stirring process continued for over 30 minutes. Following this duration, 60 mL of ultrapure water was introduced into the solution and stirred for more than 10 minutes. The resulting mixture was then transferred to a 150 mL Teflon-lined autoclave, filling only up to 2/3 of its maximum volume. The Teflon-lined autoclave was placed in an oven and allowed to undergo a reaction for 24 hours at a temperature of 100 °C for nanorods or 180 °C for CeO₂ nanocubes. The reaction precipitate was filtered and rinsed with ultrapure water until the post-filtration water attained a pH of 7. The CeO₂ nano-octahedrons were purchased from Sigma-Aldrich. All different CeO₂ shapes were dried for 24 h at 100 °C, followed by calcination in stagnant air at 500 °C (heating rate of 5 °C·min⁻¹) for 5 h, and then gradually cooled to room temperature.

Preparation of PdO_x/CeO_{2-y} catalysts

For simplicity, PdO_x/CeO_{2-y} is referred to as Pd/CeO₂ throughout this thesis. The catalysts were produced using a wet impregnation technique. In a standard procedure, 25.7 mg of Pd(NO₃)₂, containing at least 39 wt.% of Pd, was mixed with 200 mL of water and stirred at 700 RPM for 30 minutes. Following this, 2 g of CeO₂ (previously dried overnight at 100 °C) was introduced into the solution, which was then stirred for an additional hour. The resulting solution was then transferred to a rotary evaporator to allow gradual water evaporation. The catalyst was extracted from the flask and dried overnight at 100 °C. Finally, the catalyst underwent calcination at 500 °C (heating rate of 5 °C·min⁻¹) in a tube furnace with a synthetic air flow rate of 100 mL·min⁻¹ for 2 h (supplementary information, **Figure S1**).

Characterizations

The surface area of the support and catalysts was assessed through N₂-adsorption at -196 °C using the Brunauer–Emmett–Teller (BET) isotherm in a Micromeritics Tristar equipment (Micromeritics Instrument Corporation, United States).

1 Before analysis, the samples underwent a 24-hour out-gassing process in a vacuum
2 at 300 °C.

3 High-resolution scanning electron microscopy (HRSEM) imaging was
4 performed using a Zeiss MERLIN field emission scanning electron microscope (Carl
5 Zeiss Microscopy GmbH, Germany), operated at an accelerating voltage of 1.4 kV. The
6 HRSEM was equipped with a high-brightness Schottky field emission gun (FEG),
7 enabling sub-nanometer-resolution imaging, particularly suitable for detailed
8 morphological and structural analysis at the nanometer scale.

9 High-resolution transmission electron microscopy (HRTEM) images were
10 acquired using a Tecnai F30 (FEI Company, The Netherlands) transmission electron
11 microscope at a working voltage of 300 kV. Samples were prepared by dispersing the
12 powders in ethanol, followed by sonication for 2 min. A drop of the resulting suspension
13 was then deposited onto a holey carbon TEM grid. After evaporation of the ethanol,
14 the material remained on the grid for TEM analysis. Images were recorded from
15 representative electron-transparent regions to evaluate the lattice fringes and
16 microstructural features of the material.

17 High-angle annular dark-field scanning transmission electron microscopy
18 (HAADF-STEM) was performed using a probe-corrected Titan transmission electron
19 microscope (Thermo Fisher Scientific, United States), operated at an accelerating
20 voltage of 300 kV. The instrument was equipped with a high-brightness X-FEG electron
21 source and a spherical aberration (Cs) corrector (CEOS GmbH) for the condenser lens
22 system, enabling the formation of a sub-ångström electron probe suitable for high-
23 resolution imaging. Elemental analysis was conducted via energy-dispersive X-ray
24 spectroscopy (EDS) using an Ultim Max silicon drift detector (Oxford Instruments,
25 United Kingdom), allowing for spatially resolved compositional mapping.

26 X-ray fluorescence (XRF) analysis was conducted using a TIGER S8 XRF
27 Series 1 spectrometer (Bruker Corporation, United States). The samples were
28 measured as powder, in a sample cup with a Mylar film, in a Helium environment. The
29 concentrations of each element were calculated from the $K\alpha$ or $L\alpha$ lines of all elements,
30 using the internal database. Data acquisition and analysis were performed using
31 SPECTRA Plus software, version 3.0.2.5.

32 Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo
33 TGA/SDTA 851 system (Mettler-Toledo International, Switzerland). Approximately
34 30 mg of catalyst was weighed and placed in a high-purity alumina crucible. The
35 sample was subjected to a controlled gas atmosphere composed of synthetic air
36 ($45.4 \text{ mL} \cdot \text{min}^{-1}$) and argon ($50 \text{ mL} \cdot \text{min}^{-1}$), resulting in a feed gas containing 9.5 vol.%
37 O_2 . The temperature was ramped from 20 °C to 250 °C at a rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and
38 held isothermally at 250 °C for 3 hours to remove physisorbed water and surface

1 moisture. Following this step, the temperature was increased to 1100 °C at a constant
2 heating rate of 10 °C·min⁻¹, while the mass loss was continuously recorded.

3 X-ray photoelectron spectroscopy (XPS) analyzes were performed on the fresh
4 catalysts, which had been exposed to ambient atmosphere before measurement. The
5 spectra were acquired using a Kratos Axis Supra spectrometer (Kratos Analytical,
6 United Kingdom), equipped with a monochromatic Al K α radiation source (1486.6 eV,
7 8 mA, 15 kV). A charge neutralization system was employed throughout all analyzes
8 to mitigate surface charging effects. Survey spectra were acquired over an analysis
9 area of 300 × 700 μm^2 using a pass energy of 160 eV and a step size of 1 eV. High-
10 resolution spectra were collected over the same area with a pass energy of 20 eV and
11 a step size of 0.1 eV. Binding energies were referenced to the C 1s peak of adventitious
12 carbon, set at 284.6 eV. Spectral analysis and peak fitting were performed using
13 CasaXPS software[58]. The Shirley background method[59] was applied for baseline
14 correction of all spectra. During the fitting of the Ce 3d and Pd 3d XPS spectra, the
15 theoretical spin-orbit area ratios of 3:2 for Ce 3d_{5/2}:3d_{3/2} and 3:2 for Pd 3d_{5/2}:3d_{3/2} were
16 maintained. The spin-orbit splitting values were fixed at 18.6 eV for Ce 3d and 5.4 eV
17 for Pd 3d, in accordance with literature values[60,61]. Peak positions were permitted
18 to vary within defined bounds to prevent overlap with adjacent components. The full
19 width at half maximum (FWHM) values were also allowed to vary, subject to fitting
20 windows of 1-5 eV for ceria species, 0.9-2.2 eV for palladium species, 0.3-3 eV for
21 oxygen species, and 0.4-6 eV for carbon species. The baseline was manually adjusted
22 to minimize residuals, and deconvolution was performed using the automatic fitting
23 function in the software to minimize deconvolution errors.

24 Raman spectra were collected at room temperature and ambient pressure using
25 a Senterra Raman spectrometer (Bruker Optics GmbH & Co. KG, United States)
26 equipped with a cooled charge-coupled device (CCD) detector. Spectra were recorded
27 with a 532 nm laser operating at 10 mW, a spectral resolution of 3-5 cm⁻¹, an
28 integration time of 3 s, and 5 accumulations.

29 Temperature-programmed reduction with methane (CH₄-TPR) was carried out
30 using a Compact GC 4.0 online gas chromatograph (Global Analyzer Solutions, The
31 Netherlands), equipped with a flame ionization detector (FID). The system was
32 configured with two analytical columns: an RTX-Wax column (1 μm film thickness, 3 m
33 length, 0.32 mm internal diameter) and an Alox Na₂SO₄ column (10 m length, 0.32 mm
34 internal diameter), optimized for hydrocarbon separation and quantification.
35 Approximately 50 mg of catalyst was loaded into a quartz tubular reactor (inner
36 diameter: 4 mm) and subjected to a pre-treatment in a 25 mL·min⁻¹ N₂ stream. The
37 temperature was ramped from ambient to 200 °C at 10 °C·min⁻¹, and held for 2 hours
38 to remove physisorbed species and moisture from the catalyst surface. Subsequently,
39 the temperature was decreased to 50 °C using the same ramp rate (10 °C·min⁻¹), and
40 the carrier gas was switched from nitrogen to 1 vol.% CH₄ in nitrogen, maintaining the

total flow rate at $25 \text{ mL} \cdot \text{min}^{-1}$. The CH_4 -TPR experiment was then initiated by increasing the reactor temperature from $50 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, while monitoring the outlet methane concentration at regular sampling intervals using the online GC system. To quantify the baseline CH_4 signal, the reactor temperature was subsequently decreased to $150 \text{ }^\circ\text{C}$, a condition under which no methane conversion occurs, allowing for the determination of the initial inlet concentration.

Catalytic testing

Catalytic tests were conducted in a quartz tubular reactor having a 4 mm internal diameter under atmospheric pressure conditions. The axial temperature profile inside the quartz reactor was first calibrated using seven thermocouples inserted at 1 cm intervals. This calibration allowed identification of the isothermal zone, which was subsequently selected as the position for the catalytic bed. After calibration, the thermocouples were relocated to the exterior of the reactor tube to monitor and verify temperature stability during the catalytic experiments. GF040 mass flow controllers (MFCs) (Brooks Instrument, United States) were employed to control the gas flow rate. A typical experiment involved 50 mg of catalyst with a particle size of 38-45 μm , thoroughly mixed with 100 mg of quartz having a particle size of 100-150 μm to prevent excessive heating of the bed due to exothermic reactions. The flow rate was set at $25 \text{ mL} \cdot \text{min}^{-1}$, resulting in a weight hourly space velocity (WHSV) of $30\,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at $20 \text{ }^\circ\text{C}$. Due to their lower observed activity, the Pd/CeO₂ nano-octahedron catalysts were operated at a reduced WHSV of $18\,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at $20 \text{ }^\circ\text{C}$ to obtain methane conversions above 1 % and minimize experimental uncertainty.

The outlet gases were characterized using an Agilent online Varian CP-3800 Gas Chromatography (GC) (Agilent Technologies, United States) equipped with two thermal conductivity detectors (TCD) and one flame ionization detector (FID). The GC columns were 15 m $\times$ 0.32 mm ID J&W GS-GasPro GC column 113-4312, 1 m $\times$ 2 mm ID UltiMetal 80/100 mesh HayeSep Q, 0.5 m $\times$ 2 mm ID UltiMetal 80/100 mesh HayeSep Q, 1 m $\times$ 2 mm ID UltiMetal 60/80 mesh MolSieve 5Å. Methane conversion was determined based on the actual and initial methane concentrations measured at $150 \text{ }^\circ\text{C}$. A scheme of the experimental setup is shown in **Figure S2**.

During the kinetic experiments, the catalyst was first equilibrated at the reaction temperature under a gas feed composition of 0.4 vol.% of methane and 9.52 vol.% of oxygen using the same WHSV of $30\,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at $20 \text{ }^\circ\text{C}$ for 2.5 hours. The methane conversion was below 30 % under all tested conditions, which minimizes the formation of concentration and temperature gradients within the catalyst bed. Catalyst deactivation was evaluated by returning to the initial reaction conditions after completion of the experimental sequence. For all catalysts tested, the average loss in activity did not exceed 10 %. The concentration of oxygen was varied from 1.60 to

12.00 vol.% with methane fixed at 0.40 vol.%. The methane concentration was varied in the range of 0.08-0.44 vol.% while maintaining the oxygen concentration at 9.52 vol.%. Nitrogen was used as the balance gas, and the temperature range was 280-320 °C.

The apparent activation energy ($E_{a, app}$) and apparent pre-exponential factor (A_{app}) were determined using an aged catalyst pretreated for 3.5 h. The reactant gas feed consisted of 0.4 vol.% CH₄ and 9.52 vol.% O₂, balanced with N₂, at a total flow rate corresponding to 30 000 mL·g_{cat}⁻¹·h⁻¹ for Pd/CeO₂ nanocubes and Pd/CeO₂ nanorods, and 18 000 mL·g_{cat}⁻¹·h⁻¹ for Pd/CeO₂ nano-octahedrons, at 20 °C. The measurements were conducted over the temperature range of 300-320 °C, and conversions remained below 20 % for all runs.

The kinetic isotope effect (KIE) was evaluated by repeating the above procedure, replacing methane with deuterated methane (CD₄). KIE values were calculated at each temperature by taking the ratio of the reaction rate with CH₄ to that with CD₄.

Fitting of the microkinetic models

The microkinetic modeling of methane oxidation over Pd-based catalysts was conducted using Python, employing a combination of thermodynamic principles and statistical optimization techniques (information about the Python scripts and data is available in **Section S5.8**). Four mechanistic models (M1-M4) were developed to represent distinct pathways for oxygen activation and methane oxidation at the catalyst surface.

Experimental turnover frequency (TOF) data were acquired from a structured CSV file (information about the CSV files is available in **Section S5.8**). This dataset included the reaction temperature (T, in K), the partial pressures of methane (pCH₄, in Pa) and oxygen (pO₂, in Pa), and the corresponding TOF values, expressed as moles of CH₄ oxidized per mole of surface-exposed PdO_x per second. All data were preprocessed to ensure consistency before modeling. TOF values were calculated by dividing the experimental methane reaction rate (in mol) by the number of exposed PdO_x (in mol). The average PdO_x particle diameter was obtained from TEM, and spherical particle geometry was assumed. The total number of PdO_x atoms was determined from the measured catalyst mass and PdO_x metal load, together with the PdO_x molar mass and Avogadro's number. The number of surface PdO_x atoms was then estimated using a geometric model in which the particle surface area is divided by the atomic cross-section of PdO_x, yielding the corresponding surface atom density. The resulting metal dispersion was applied to the total PdO_x atom count to obtain the number of exposed PdO_x.

The mechanistic models were formulated based on different hypotheses regarding the activation and transport of oxygen. In all four models, equilibrium constants (K_i) and rate constants (k_j) were computed using transition state theory. The kinetic parameters were estimated by minimizing the residual sum of squares (RSS) of the logarithmic errors between predicted and experimental TOF values.

The objective of the data fitting procedure is to determine the enthalpic and entropic contributions to the equilibrium constants, as well as the rate constants, for each proposed mechanism. This approach enables a simultaneous assessment of the mechanism that best reproduces the experimental data while providing access to thermodynamic parameters associated with individual reaction steps. The initial parameter estimates were derived from our DFT calculations and relevant literature values; the reasoning is available in **Section S5.7**.

To ensure thermodynamic consistency and physical plausibility, the parameter search space was constrained to $\pm 60\%$ of the initial estimates. A global grid search strategy was used to exhaustively sample the parameter space, followed by local optimization using the Nelder-Mead algorithm as implemented in `scipy.optimize.minimize`, with a convergence tolerance of 10^{-9} and a maximum of 10^5 iterations.

To account for model complexity and penalize models with more adjustable parameters, the Akaike Information Criterion (AIC)[62,63] was also calculated (**Equation 1**):

$$AIC = n \cdot \ln\left(\frac{RSS}{n}\right) + 2 \cdot k \quad (Eq. 1)$$

Where: AIC is the Akaike Information Criterion (dimensionless), RSS is the residual sum of squares (total squared difference between measured and predicted values) (dimensionless), n is the number of data points (dimensionless), and k is the number of fitted parameters (dimensionless). A lower AIC indicates that the model fits the data better without overfitting, because it rewards a good fit but penalizes unnecessary complexity.

Parity plots and error distributions were generated using Matplotlib to visualize model performance, with data points color-coded according to either temperature or the pCH_4/pO_2 ratio. All computations were performed in Python using the NumPy, SciPy, Pandas, and Matplotlib libraries. The Python scripts are available in **Section S7.1**.

DFT calculations

All DFT calculations were performed using the VASP code[64,65] with the PBEsol exchange-correlation functional[66]. A Hubbard U correction ($U-J = 5.1$ eV)

was applied to Ce-4f states following Dudarev et al.[67] formalism, with the parameter determined via a linear response method[68]. Dispersion interactions were included using Grimme's D3 method with Becke-Johnson damping[69]. All simulations were spin-polarized. Ion-electron interactions were treated using the projector-augmented wave method[70,71] with cutoff core radii of 2.700 a.u. for Ce and 1.520 a.u. for O.

The plane-wave cutoff energy was set to 500 eV, using Ce ($5s^25p^64f^15d^16s^2$) and O ($2s^22p^4$) valence configurations. Brillouin zone integrations employed a Γ -centered k-point grid with a spacing of $0.03 \text{ \AA}^{-1}$ applied only to the in-plane directions for slab models. Geometry optimizations proceeded until all atomic forces were below $0.02 \text{ eV}\cdot\text{\AA}^{-1}$.

Bulk modulus values were obtained by fitting total energy-volume data to the third-order Birch-Murnaghan equation of state[72,73]. The calculated lattice constant ($5.37 \text{ \AA}$) and bulk modulus (199.2 GPa) agree with literature and experimental data[56,74–76], validating the model's structural reliability. The band gap (2.5 eV) shows a 45 % improvement over standard PBE[77] but remains underestimated compared to HSE06[78] and experiment (3.3 eV). This methodology balances computational efficiency and accuracy for surface chemistry studies, maintaining reliable relative energetics for adsorption and reaction modeling.

Slab convergence was evaluated using the surface energy as a function of layer thickness, expressed as the number of 12-atom CeO_2 unit cells in a 1×1 cell. Convergence was achieved for all surfaces from three repetition units, with bulk energies differing by less than 10 meV. The CeO_2 (110) and (111) surfaces were modeled as 2×2 supercells with a $15 \text{ \AA}$ vacuum gap, yielding no net dipole along the surface normal. For defective slabs, dipole corrections were applied to remove spurious electrostatic effects. The (100) surface exhibited a net dipole upon cleavage; to cancel it, half the terminating oxygen atoms were shifted from one side to the other, following a tested correction scheme[79]. Convergence tests using a 4×2 supercell confirmed that the 2×2 supercell model correctly describes the oxygen vacancy formation energy. The formation energy of a vacancy in charge state q was computed, as shown in **Equation 2**:

$$\Delta_f E(V_O^q) = E_T(V_O^q) - E_T(\text{CeO}_2) + \frac{1}{2}E(O_2) + \mu_O + q(\epsilon_F + E_{VMB}) \quad (\text{Eq. 2})$$

Where $\Delta_f E(V_O^q)$ is the formation energy of a vacancy in charge state q (eV), $E_T(V_O^q)$ is the energy of the slab containing an oxygen vacancy in charge state q (eV), $E_T(\text{CeO}_2)$ is the energy of the CeO_2 slab (eV), $E(O_2)$ is the energy of an isolated O_2 molecule (eV), μ_O is the oxygen chemical potential (eV), ϵ_F is the Fermi energy (eV), and E_{VMB} is the energy of the highest occupied electronic state (eV).

To correct DFT overbinding of O₂, μ_O was shifted by +0.5 eV[80,81]. Entropy and zero-point energy corrections were omitted, as they are negligible for extended solids, owing to their low vibrational energy scales and minimal configurational entropy differences[82]. The applied μ_O shift does not affect relative trends, serving only to align absolute values with the experiment.

Electrode potentials (V), referenced to the Standard Hydrogen Electrode (SHE) at pH 0, were calculated from vacuum-referenced electronic energies (eV) (**Equation 3**):

$$V_{vs\ SHE} = -(E_{edge} - E_{vac} + 4.44) \quad (Eq. 3)$$

Where E_{edge} denotes the electronic energy level of interest (for example, conduction or valence band edge), E_{vac} corresponds to the vacuum level energy, and 4.44 eV represents the Trasatti absolute potential of the SHE, which bridges the vacuum and electrochemical scales[83]. This conversion enables a direct comparison between computed energy levels and experimental electrochemical potentials, which is essential for assessing catalytic performance in applied catalysis studies.

To model the catalyst surface, 10 % PdO coverage was used, with a fixed PdO-cluster size, and the slab supercell size was chosen based on the surface area of each ceria morphology. This resulted in a 2×2, 4×2, and 4×4 expansions for the (111), (110), and (100) facets, respectively. This scaling maintains a consistent PdO density across the different terminations and enables a direct comparison of facet-dependent stability and electronic restructuring of the Pd-based catalysts.

Reactor design

To elucidate the influence of the support morphology on the operational performance of a monolithic reactor, a numerical simulation of a monolith channel was developed. This model is based on the numerical solution of the governing partial differential equations for transport phenomena within both the gas flow and the porous washcoat. To this end, the conservation equations for mass, momentum, and energy were solved for the gas phase. The mass transport of the gaseous species within the channel was modeled using **Equation 4**, as follows:

$$\frac{\partial(\rho_g Y_k)}{\partial t} + \frac{\partial(U \rho_g Y_k)}{\partial z} = \frac{J_k W_k}{t_{ch}} \quad (Eq. 4)$$

Where: ρ_g is the total gas density (kg·m⁻³), Y_k is the mass fraction of k species (dimensionless), t is the time (s), J_k is the species molar flux coming from the washcoat (mol·m⁻²·s⁻¹), W_k is the molecular weight of the species k (kg·mol⁻¹), U is the gas velocity (m·s⁻¹), and t_{ch} and z are the axial coordinates for the channel gas flow (m).

The momentum equation is given by **Equation 5**, as follows:

$$\rho_g \frac{\partial U}{\partial t} + U \rho_g \frac{\partial U}{\partial z} + \frac{\partial P_g}{\partial z} + \frac{U}{t_{ch}} \sum_{k=1}^n J_k = - \frac{2 \rho_g U^2 f}{D_h} \quad (\text{Eq. 2.5})$$

Where P_g is the gas absolute pressure at the washcoat gas phase (Pa), f is the Fanning friction factor (dimensionless), and D_h is the channel hydraulic diameter (m).

Equation 6 was used to calculate the energy balance for the gas phase, as indicated below:

$$\frac{\partial (T_g C_{p_g} \rho_g)}{\partial t} - \frac{\partial (P_g)}{\partial t} + \frac{\partial (T_g C_{p_g} \rho_g U)}{\partial z} = \frac{T_s}{t_{ch}} \sum_{k=1}^n J_k C_{p_k} + \frac{h_s (T_s - T_g)}{t_{ch}} \quad (\text{Eq. 6})$$

Where: T_g and T_s are the gas and washcoat temperature (K), respectively, C_{p_g} is the gas specific heat at constant pressure ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and h_s is the convection heat transfer coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$).

In addition, pressure can be computed after considering the ideal gas law (**Equation 7**), as shown below:

$$P_g = T_g \sum_{k=1}^n \rho_k R_k \quad (\text{Eq. 7})$$

Where: R_k is the universal gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). In addition, the washcoat solid-phase temperature has to be estimated. **Equation 8** shows the energy balance for the washcoat:

$$C_{s,eff} \rho_{s,eff} \frac{\partial T_s}{\partial t} = \lambda_{s,eff} \frac{\partial^2 T_s}{\partial z^2} + \frac{T_s}{t_{ch}} \sum_{k=1}^n J_k C_{p_k} - \frac{h_s (T_s - T_g)}{t_{ch}} + \frac{J_{\text{CH}_4} \Delta H_{\text{CH}_4}}{t_{ch}} \quad (\text{Eq. 8})$$

Where ΔH_{CH_4} is the enthalpy of reaction ($\text{J} \cdot \text{mol}^{-1}$), and $\lambda_{s,eff}$ is the effective thermal conductivity for the washcoat ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

To achieve closure for this system of partial differential equations, a set of constitutive relations is required to define the gaseous species fluxes within the washcoat. The formulation for these fluxes is derived from a molar-based species conservation equation (**Equation 9**):

$$\phi \frac{\partial c_k}{\partial t} + \frac{\partial J_k}{\partial y} = \dot{r}_k \nu d_{se} \quad (\text{Eq. 9})$$

Where ϕ is the gas phase porosity at the washcoat (dimensionless), c_k is the gas species concentration ($\text{mol} \cdot \text{m}^{-3}$), $\dot{r}_k$ is the reaction rate ($\text{mol} \cdot \text{m}^{-3}$), ν is the

stoichiometric coefficient (dimensionless), and d_{se} is the molar palladium density in the washcoat ($\text{mol} \cdot \text{m}^{-3}$).

The solution of the governing transport equation requires a constitutive model to evaluate the molar fluxes of all species throughout the washcoat domain. To this end, the dusty-gas model (DGM) is employed, chosen for its rigorous formulation and proven efficacy in describing multicomponent mass transport coupled with reaction in porous catalytic media[84]. The DGM provides a comprehensive framework that unifies multiple transport mechanisms within a single formulation. It rigorously couples molecular (or bulk) diffusion with Knudsen diffusion while also incorporating contributions from Darcy viscous flow. The molar flux for a given species, as described by the DGM, is expressed in **Equation 10**:

$$J_k = - \left[\sum_{l=1}^{K_g} D_{kl}^{DGM} \frac{\partial c_l}{\partial y} + \left(\sum_{l=1}^{K_g} \frac{D_{kl}^{DGM} c_l}{D_{l,Kn}^e} \right) \frac{B_g}{\mu} \frac{\partial P_g}{\partial y} \right] \quad (\text{Eq. 10})$$

Where D_{kl}^{DGM} is the DGM diffusion coefficient matrix ($\text{m}^2 \cdot \text{s}^{-1}$), $D_{l,Kn}^e$ is each species' Knudsen diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), B_g is the washcoat permeability (m^2), and μ is the gas dynamic viscosity ($\text{Pa} \cdot \text{s}$).

The pressure inside the pores of the washcoat was evaluated using the ideal gas law. The formulation requires two coupled domains: the bulk gas phase and the porous washcoat. This leads to a system of partial differential equations (PDEs) (**Equations 4-6** and **Equations 8-9**), which are solved numerically. In this work, the PDEs are solved using the method of lines. Spatial derivatives in both domains are discretized with second-order centered finite differences, while the resulting system of temporal ordinary differential equations is integrated using the IDA solver from the SUNDIALS suite, interfaced through Julia. This constitutes a transient, coupled 1D+1D problem.

A fully transient simulation of both domains, however, results in a significant computational burden. To address this, the washcoat domain is treated under a quasi-steady-state assumption. This simplification is justified by the disparity in characteristic time τ scales (s) between gas-phase convection in the channel and diffusion-reaction phenomena in the washcoat ($\tau_{\text{conv}} \approx 10^{-1}$ s and $\tau_{\text{diff}} \approx 10^{-4}$ s). To further reduce simulation time while preserving numerical accuracy, the washcoat is represented by a surrogate model. This model employs a three-dimensional bicubic interpolation scheme, constructed from pre-computed solutions tabulated as functions of the key operating parameters: oxygen partial pressure ($p\text{O}_2$), methane partial pressure ($p\text{CH}_4$), and temperature (T).

CRedit authorship contribution statement

Martim Chiquetto Policano was responsible for the conceptualization of the study, the design and execution of the experiments, catalyst synthesis, microkinetic modeling, data analysis, data fitting, and the writing and editing of the manuscript. Felipe Lipsky and Samantha Custódio carried out the DFT calculations. Julian Camilo Restrepo contributed to the data fitting and reactor modeling. Leon Lefferts and Jimmy Alexander Faria Albanese supervised the project, with additional supervision provided by Juan Andrés for the DFT calculations and Aayan Banerjee for the reactor modeling. All authors contributed to manuscript revision and provided feedback on the text.

Declaration of competing interests

The authors declare no competing interests.

Data Availability

Data will be made available on request.

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