Palladium catalysts for methane oxidation: old materials, new challenges

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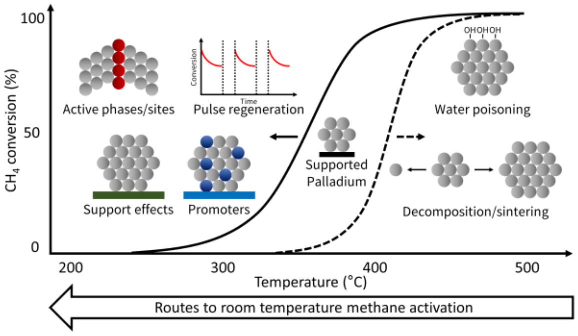
Conspectus

Methane complete oxidation is an important reaction that is part of the general scheme used for removing pollutants contained in emissions from internal combustion engines and, more in general, combustion processes. It has also recently gathered interest as an option for the removal of atmospheric methane in the context of negative emission technologies. Methane, a powerful greenhouse gas, can be converted into carbon dioxide and water via its complete oxidation. Despite burning methane is facile because the combustion sustains its complete oxidation after ignition, methane strong C-H bonds require a catalyst to perform the oxidation at low temperatures and in the absence of a flame as to avoid the formation of nitrogen oxides, such as those produced in flares. This process allows methane removal to be obtained in conditions that usually lead to higher emissions, such as in cold start conditions in the case of internal combustion engines. Among several options that include homogeneous and heterogeneous catalysts, supported palladium-based catalysts are the most active heterogeneous systems for this reaction. Finely divided palladium can activate C-H bonds at temperatures as low as 150 °C, although complete conversion is not usually reached until 400-500 °C in practical applications. Major goals are to achieve catalytic methane oxidation at as low as possible temperature and to utilize this expensive metal more efficiently.

Compared to any other transition metal, palladium and its oxides are orders of magnitude more reactive for methane oxidation in the absence of water. During the last few decades, much research has been devoted to unveiling the origin of the high activity of supported Pd catalysts, their active phase, the effect of support, promoters and defects, and the effect of reaction conditions with the goal of further improving its reactivity. There is an overall agreement in trends, yet there are noticeable differences in some details of the catalytic performance of palladium, including the

active phase under reaction conditions and the reasons for catalysts deactivation and poisoning. In this Account we summarize our work in this space using well-defined catalysts, especially model palladium surfaces and those prepared using colloidal nanocrystals as precursors, and spectroscopic tools to unveil important details about the chemistry of supported palladium catalysts. We describe advanced techniques aimed at elucidating the role of several parameters in the performance of palladium catalysts for methane oxidation, as well as in engineering catalysts through advancing fundamental understanding and synthesis methods. We report the state of research on active phases and sites, to then move to the role of supports and promoters, and finally discuss stability in catalytic performance and the role of water on the palladium active phase. Overall, we want to emphasize the importance of fundamental understanding in designing and realizing active and stable palladium-based catalysts for methane oxidation as an example for a variety of energy and environmental applications of nanomaterials in catalysis.



Key references

- Huang, W.; Johnston-Peck, A. C.; Wolter, T.; Yang, W.-C. D.; Xu, L.; Oh, J.; Reeves, B. A.; Zhou, C.; Holtz, M. E.; Herzing, A. A.; Linderberg, A. M.; Mavrikakis, M.; Cargnello, M. "Steam-created Grain Boundaries for Methane C-H Activation in Palladium Catalysts.", *Science*, **2021**, *373*, 1518-1523.[1] Demonstration of the high rates for methane oxidation on Pd sites located at a twin/grain boundary in supported Pd catalysts.

- Goodman, E. D.; Johnston-Peck, A. C.; Dietze, E. M.; Wrasman, C. J.; Hoffman, A. S.; Abild-Pedersen, F. A.; Bare, S. R.; Plessow, P. N.; Cargnello, M. "Catalyst Deactivation via Decomposition into Single Atoms and the Role of Metal Loading.", *Nature Catal.* **2019**, *2*, 748-755.[2] Identification of a deactivation mechanism induced by formation of atomically dispersed Pd species, which showed lower rates for methane oxidation compared to nanoparticles.

- Petrov, A. W.; Ferri, D.; Krumeich, F.; Nachtegaal, M.; van Bokhoven, J. A.; Kroecher, O. "Stable complete methane oxidation over palladium-based zeolite catalysts", *Nature Commun*. **2018**, *9*, 2545.[3] Combination of Pd-zeolite catalyst development and improved process control to run methane oxidation efficiently.

- Li, X.; Wang, X.; Roy, K.; van Bokhoven, J. A.; Artiglia, L. "Role of water on the structure of palladium for complete oxidation of methane", *ACS Catal*. **2020**, *10*, 5783-5792.[4] In situ XPS characterization of a Pd foil under methane oxidation reaction conditions.

1. Introduction

Methane is an important resource for energy and chemicals. It is widely used for power generation, and the availability of cheap natural gas reshaped the manufacturing of many chemicals that were once derived from crude oil.[5] Advances in methane conversion technologies also benefited from the renewed interest towards this abundant feedstock.[6–9]

Methane is also a powerful greenhouse gas.[10] Emissions of methane have increased greatly since the industrial revolution due to expanded oil and gas operations,[11] as well as from livestock and agricultural practices.[12,13] Reducing methane emissions is an imperative action required in mitigating this problem, and removing atmospheric methane represents a relevant strategy for negative emission technologies[14–16] that complements carbon dioxide removal.[17] Technologies for methane removal are needed since the transition from fossil fuels to renewable energy will require time to be completed.

Methane activation requires overcoming a high energy barrier.[18] Its oxidation is highly exothermic, and the reaction becomes self-sustaining at sufficient methane concentration (e.g., in a flame), but the high temperature leads to the production of nitrogen oxides that are harmful and potent greenhouse gases. Catalytic oxidation occurs at much lower temperatures[6,7] and represents an important technology in low-concentration methane streams, such as from vehicles, mines, and in the case of atmospheric methane.[17] It is thus important to develop catalysts for low-temperature methane activation in the challenging, realistic conditions that these applications require.[6,7]

Palladium is the most effective artificial methane oxidation catalyst, thanks primarily to the specific chemistry of its oxides.[19,20] There is a long-standing debate regarding the active phase for the reaction, and the effect of the reaction environment on activity and stability. Well defined model conditions help identifying critical ingredients that make a catalyst active. Using colloidal nanocrystals[21–23] in combination with advanced spectroscopic techniques is crucial in this field. Recent developments in *in situ* X-ray photoelectron spectroscopy methods, which are sensitive to the solid-gas interface and to the oxidation state of the catalyst, are of paramount importance.[24]

In this Account, we summarize recent research in the field of Pd-based catalysts for methane complete oxidation from our research groups at Stanford University and at ETH Zürich and Paul Scherrer Institute (PSI). We begin by discussing work on elucidating active phase and sites, then summarize recent results on the roles of supports and promoters for the reaction, on the stability of Pd-based catalysts, and finally discuss the role of water as inhibitor. Overall, our goal is to give the readers an overview of the field and the open questions and opportunities in this space through the lens of our research work.

2. Elucidation of the nature of active phase and sites in supported palladium catalysts

The active phase of Pd catalysts has received much attention in early studies.[25–27] Although PdO is known as the thermodynamically stable phase at temperatures lower than 700 °C in air, kinetic bottlenecks in oxidation-reduction processes of supported and unsupported Pd catalysts plague the measurements.[28] The group in PSI made use of ambient pressure X-ray photoelectron spectroscopy (APXPS). Thanks to its surface sensitivity and to the possibility to dose gas mixtures in the millibar pressure range, APXPS represents a suitable tool to characterize the solid-gas interface.[4,24,29–31] The investigation started with palladium foils used to lay the foundation for the understanding of powder catalysts.[31] Three different chemical species were identified: metallic palladium, surface palladium oxide, and bulk PdO, and their structural development was followed *in situ* as a function of time (Figure 1). Upon oxygen introduction into a stream of methane and a transient period, the catalyst structure equilibrated. A gradual oxidation of the foil surface was observed. The initial formation rate of the surface oxide was equal or higher than that of bulk oxide, which suggests that the former is a precursor of the latter. Our results demonstrate that, when the catalyst is active towards methane oxidation (between 250 and 500 °C), metallic palladium is quantitatively oxidized within the probing depth of XPS (approximately 5.5 Å). This proves that palladium oxide is directly involved in catalysis.

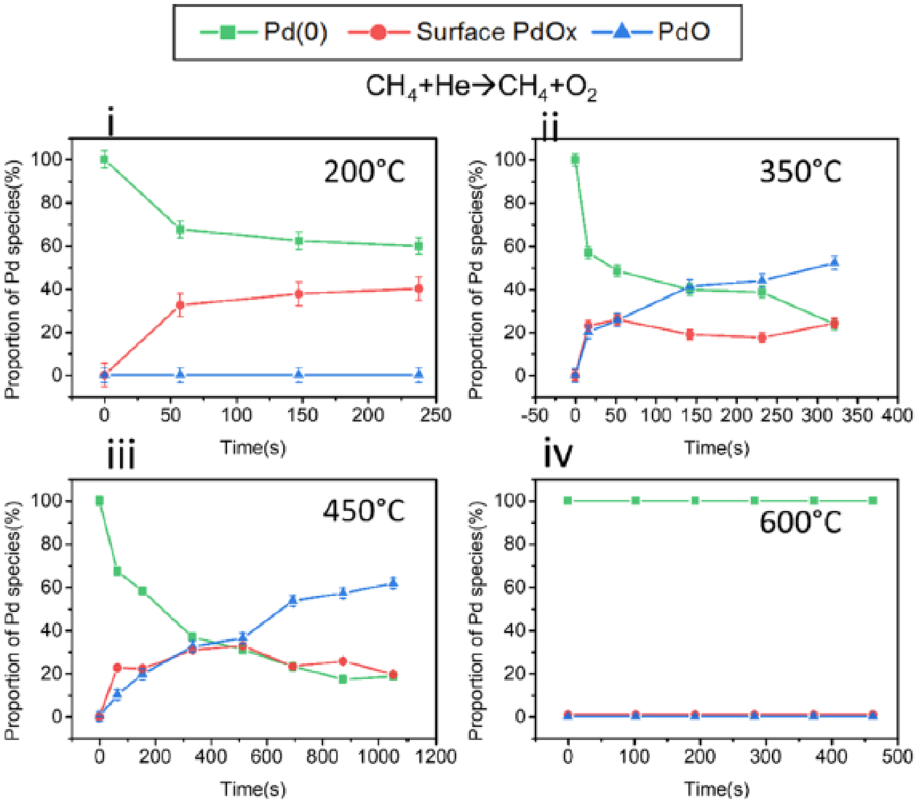


Figure 1: Time-resolved evolution of palladium species after switching from CH_4 + He to CH_4 + O_2. Adapted with permission from ref. 4. Copyright 2020 American Chemical Society.

The Stanford group utilized uniform Pd nanoparticles and *operando* quick scanning extended X-ray absorption fine structure (QEXAFS) techniques to also investigate the influence of Pd oxidation state on activity.[32] The relative fraction of PdO in three Pd/Al_2O_3 catalysts was quantified during light-off experiments (Figure 2a-f). Catalysts began to convert methane only after Pd became at least partially oxidized. Additional experiments supported this observation by showing that the temperatures needed to form (or reduce) the oxide were below the onset temperature for activity. In the absence of steam, H_2-pretreated Pd/Al_2O_3 started to oxidize methane at ~250 °C, the temperature at which Pd started to be oxidized in O_2-TPO experiments. In contrast, O_2-pretreated Pd/Al_2O_3 began to combust methane at ~160 °C, which was the onset temperature for methane reduction of PdO in CH_4-TPR experiments (Figure 2g-i). All these results suggested that the presence of an oxidized phase of Pd is essential for activity.

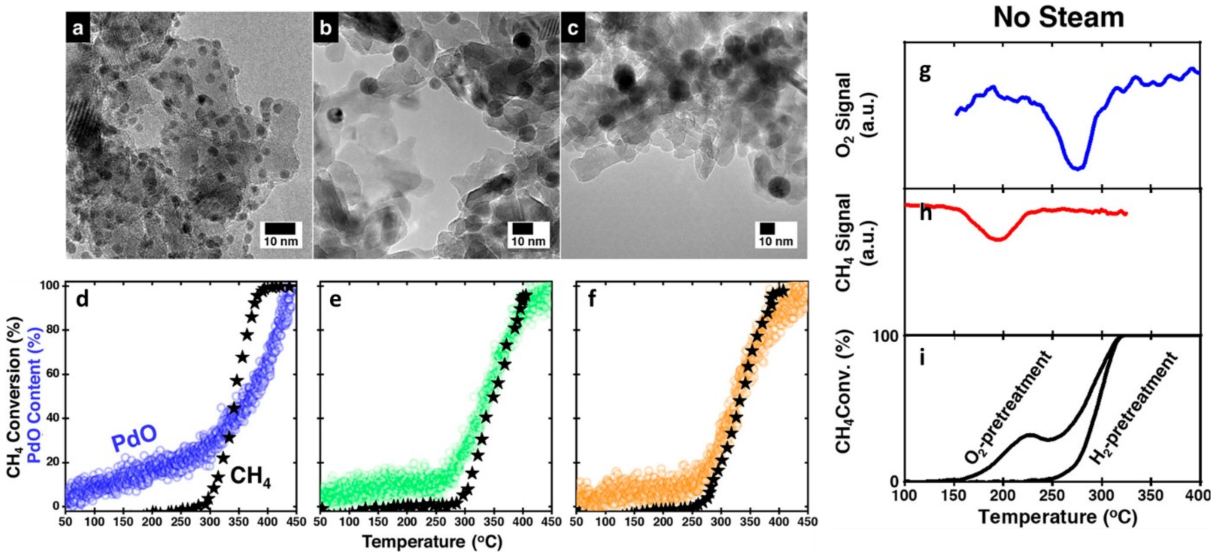


Figure 2. (a-c) Transmission electron microscopy (TEM) images and (d-f) *operando* x-ray absorption near edge spectroscopy of (a) 2.5 nm Pd/Al_2O_3, (b) 7.9 nm Pd/Al_2O_3, and (c) 14.7 nm Pd/Al_2O_3. Colored open circles plot the results of the relative amount of PdO in each catalyst. Black stars plot the corresponding methane combustion activity. Temperature-programmed oxidation (O_2-TPO) (g), reduction (CH_4-TPR) (h), and light-off experiment without steam (i) for

7.9 nm Pd/Al_2O_3 catalyst. Reproduced with permission from ref. 32. Copyright 2019 AIP Publishing.

Uniform colloidal Pd nanoparticles of sizes ranging from 2.5 nm to 8.2 nm were also used to identify optimum particle size in the reaction.[33] A mild structure sensitivity was observed when normalizing the rates by exposed Pd surface sites. Particles of intermediate size showed a rate that was 5 times higher than that of the smallest particles. The oxidation state of Pd, characterized by *in situ* X-ray absorption spectroscopy (XAS), was PdO for all catalysts. We hypothesized that the structure sensitivity resulted from different ratios of undercoordinated sites. Previous studies claimed that Pd step sites are the active sites.[34] However, the trend in turnover frequency did not follow the change in step site fraction. We concluded that further studies were required to identify the reasons for the activity difference, and literature work shed light on the potential role of the reducibility of Pd dependent on the type of support.[35]

In more recent work, we found a correlation between the density of twin boundaries and catalytic performance.[1] It was observed that high-temperature steam treatments on Pd/Al_2O_3 induced the formation of twin boundaries at higher density compared to other pretreatments (Figure 3a-j). The sample also showed a 12 times higher mass-specific rate (Figure 3k). CH_4-TPR and O_2-TPO experiments demonstrated that steam-treated Pd/Al_2O_3 was reduced and oxidized at lower temperatures. Environmental transmission electron microscopy (ETEM) showed that the twin boundaries in Pd transformed into general grain boundaries in PdO and that the boundaries were maintained even at high temperature. DFT calculations further demonstrated that expansive strain on PdO (101) and compressive strain on PdO (110) increases the intrinsic activity of Pd catalysts. Therefore, we concluded that grain boundaries are very active sites for methane oxidation.

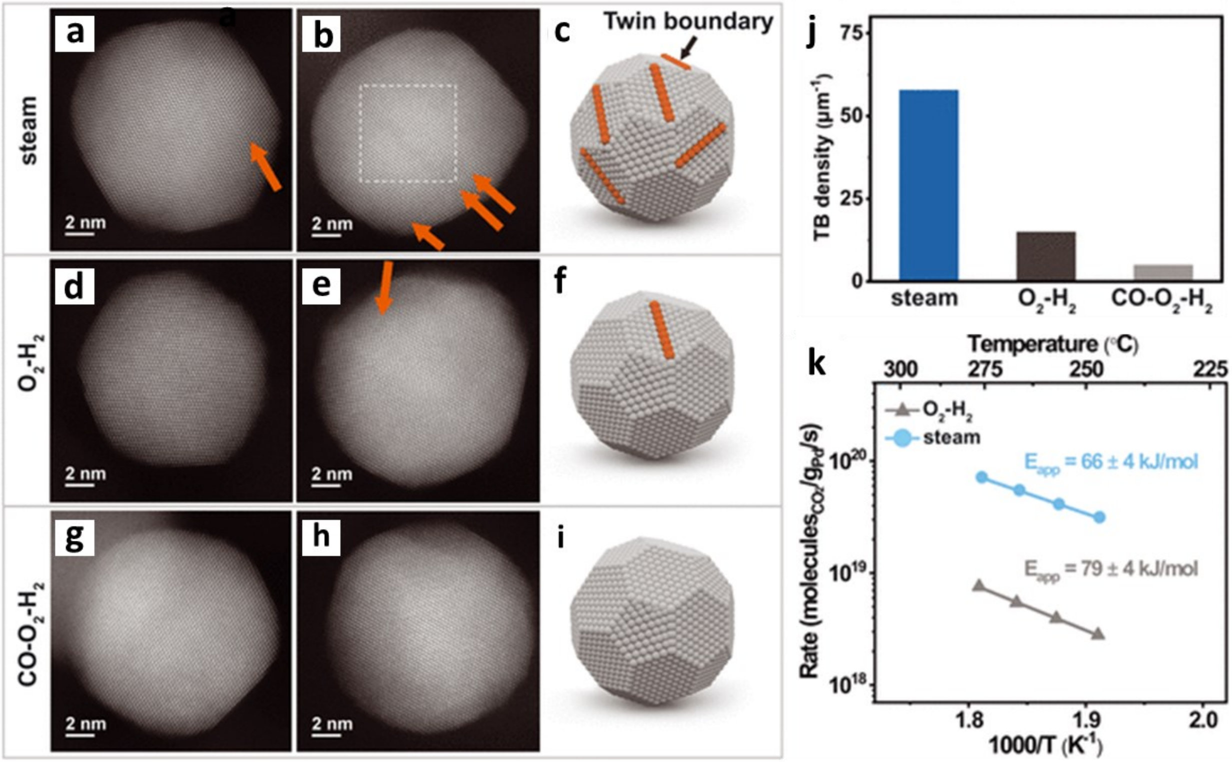


Figure 3. Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and schematics of steam-pretreated Pd/Al_2O_3 (a-c), O_2-H_2–pretreated Pd/Al_2O_3 (d-f), and CO-O_2-H_2–pretreated Pd/Al_2O_3 (g-i). (j) TB density histogram of Pd/Al_2O_3 after steam, O_2-H_2, and CO-O_2-H_2 treatment. (k) Arrhenius plots of methane oxidation. Reproduced with permission from ref. 1. Copyright 2021 AAAS.

3. The Role of Supports and Promoters

Supports play crucial effects in the observed catalytic performance of supported phases in multiple ways, either through charge-transfer, by modifying the particle morphology and reactive sites, or through strong metal-support interaction (SMSI).[36] Previous work suggested a distinction between supports that generate active (Al_2O_3, ZrO_2, and CeO_2) or inactive (SiO_2, MgO, La_2O_3,

TiO_2, NbO_2, and SnO_2) Pd catalysts.[35] Literature suggested that Pd particles on active supports are composed of a mixture of metallic and oxide phases,[19] but complete understanding of support effects is limited by the heterogeneity of catalysts and more work is required on this aspect even with the use of model systems.

The Stanford group utilized colloidal nanoparticles and atomic layer deposition (ALD) to study support effects.[37] Amorphous SiO_2 beads and Al_2O_3 were chosen as representative supports. Pd/SiO_2 resulted in 60 times lower rates compared to the same Pd particles supported on a commercial alumina (Figure 4a). Adding a single monolayer of alumina by ALD to SiO_2 significantly increased the reaction rate. The rate linearly increased with ALD cycles up to a monolayer (Figure 4b). Further deposition of Al_2O_3 layers linearly increased the activity of Pd, but with a smaller slope. The former change was therefore attributed to chemistry effects, whereas the latter to the crystallinity of the alumina support and potentially to changes in the geometry of the supported Pd particles.

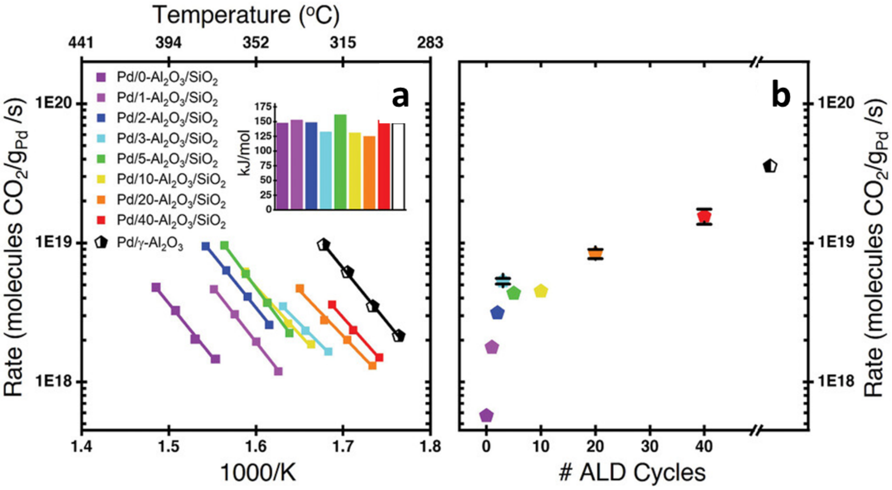


Figure 4. Methane oxidation activity of Pd/Al_2O_3/SiO_2 catalysts (and a Pd/γ-Al_2O_3 reference material). (a) Arrhenius plot. Inset shows activation barriers. (b) Extrapolated steady-state rate at 350 °C. Adapted with permission from ref. 37. Copyright 2021 Wiley-VCH GmbH.

An opportunity to increase the interface between Pd and an active support consists in the preparation of core-shell structures. By using this strategy, Pd@CeO_2/Al_2O_3 catalysts showed 200 times higher rates than parent Pd/CeO_2 catalysts.[38] The increased interface between Pd and CeO_2 changed the redox properties of Pd. In TPO experiments, PdO in Pd@CeO_2/Al_2O_3 decomposed into metallic Pd at a higher temperature than Pd/CeO_2 catalysts and consumed more O_2 during cool-down. The same method was applied to prepare a Pd@ZrO_2/Al_2O_3 catalyst, which demonstrated similar activity to Pd@CeO_2/Al_2O_3.[39] ZrO_2, known as a non-reducible support, was found to be partially reduced (especially on the surface) in the core-shell structure, and stabilized Pd in the PdO phase.

Zeolites have also been extensively explored as supports for Pd in methane oxidation.[40–43] Their hydrophobic/hydrophilic character has been hypothesized to affect the activity of Pd catalysts in the presence of water. The Stanford group utilized methods to produce mesoporosity in zeolites and introduce colloidal particles to study the influence of nineteen different mesoporous zeolite supports.[44] Water was efficiently transported off the Pd surface via adsorption/desorption processes at the interface with zeolites that possessed an intermediate hydrophilic/hydrophobic character by silanols and Brønsted acid sites, leading to the most active and stable catalysts.

In line with the above results, research at PSI focused on Pd supported on ZSM-5, MOR, and BEA zeolites.[45] To preserve the high dispersion of Pd nanoparticles within the framework, different pretreatments were carried out. Desilication of the parent zeolite, followed by dealumination under acid conditions, produced mesopores that acted as preferential nucleation and anchoring sites for Pd particles that were sinter resistant. This greatly improved the stability with respect to the same Pd loading deposited on the parent zeolite. Using specific ligands during the synthesis, the group at ETH-PSI synthesized small palladium oxide encapsulated in the micropores of silicalite-1.[46] The catalytic behavior of Pd@silicalite-1 is like that of the material synthesized using the same palladium loading deposited by means of incipient wetness impregnation (IWI) in silicalite-1. However, the optimized Pd@silicalite-1 catalyst exhibits long-time stability towards the complete methane oxidation. Encapsulated clusters are resistant towards sintering under reaction conditions.

Promoters can also be used to modify the geometric structure of Pd and affect redox properties. At Stanford, the effect of Pt in Pd catalysts was systematically studied by varying the Pd/Pt atomic ratio while using similarly sized nanocrystals.[47] In the absence of steam, the pure Pd catalyst showed ~2 orders of magnitude greater TOF than pure Pt and all other Pd/Pt (4/1, 2/3, 3/2, 1/4 atomic ratio) catalysts. However, in the presence of steam, the pure Pd catalyst rate decreased by ~3 orders of magnitude while all other bimetallic catalysts and the pure Pt catalyst were less affected. Increasing the Pt amount in the catalysts reduced the fraction of PdO phase. Therefore, Pt had a beneficial effect in keeping Pd more metallic, which led to increased stability in the presence of steam. Interestingly, the 4/1 Pd/Pt bimetallic catalyst was the most active and stable after aging at ~800 °C. EDS mapping showed that sintered particles were mainly composed of phase segregated PtPd/Pd/PdO structures, in agreement with recent results.[48] These results suggest that forming Pd alloys with Pt can increase the stability of Pd catalysts while maintaining their activity under steam conditions.

In addition to Pt, the Stanford group also explored the effect of base metal promoters (Figure 5a-h)[49]. In general, all PdM/Al_2O_3 catalysts showed only a slight activity improvement compared to pure Pd/Al_2O_3, except for PdSn/Al_2O_3 (Figure 5b), which formed a tin oxide layer covering the Pd surface and inhibiting the reaction. However, after aging at 850 °C, few samples (M = Fe, Co, Ni, Zn, and Sn) showed higher rates than pure Pd/Al_2O_3. Fe, Co, and Sn bimetallic catalysts maintained a higher metal dispersion after calcination. In the case of Ni, NiO stabilized the PdO phase and resulted in the best activity. In addition, all promoters (Fe, Co, Ni, Zn, and Sn) increased the amount of oxygen released compared to pure Pd catalysts. These studies indicated that these elements improved the redox properties of PdO, thus affecting the rates. Overall, rate increases were limited to 2-3 times those of Pd after the high-temperature aging.

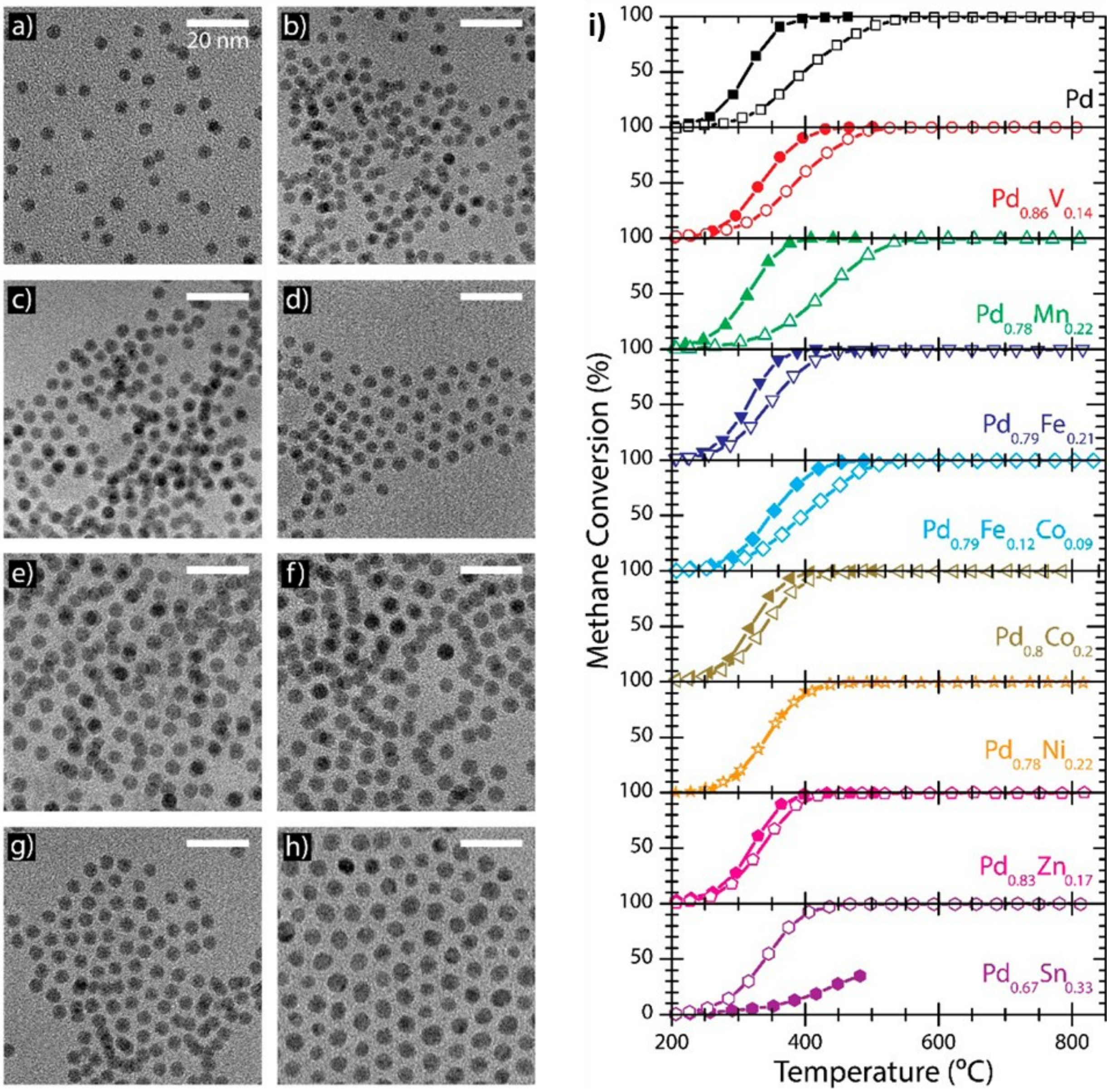


Figure 5. TEM images of (a) PdV, (b) PdMn, (c) PdFe, (d) PdFeCo, (e) PdCo, (f) PdNi, (g) PdZn, and (h) PdSn. Scale bars are all 20 nm. (i) Methane oxidation light-off curves for PdM/Al_2O_3 catalysts calcined at 500 °C (closed symbols) and 850 °C (open symbols). Adapted with permission from ref. 49. Copyright 2017 American Chemical Society.

4. Stability of Palladium-based Catalysts

Catalyst stability is a crucial factor for industrial applications. Catalysts can be deactivated in various ways,[50] requiring regeneration and/or replacement. Therefore, understanding deactivation mechanisms is essential to minimize expensive industrial practices.

A common deactivation mechanism in supported Pd catalysts is sintering, which causes loss of surface area.[50] Sintering can occur by two different mechanisms, which are particle migration and coalescence (PMC) and Ostwald (atomic) ripening (OR) depending on whether entire particles or atomic species are involved in the process. The two mechanisms could be differentiated by analyzing particle size distributions (PSDs) before and after aging.[51] Therefore, uniform PSDs can aid in distinguishing sintering mechanisms.

The Stanford group investigated sintering mechanisms of Pd catalysts using uniform nanoparticles with different sizes (3.0, 8.8, 14.8 nm) and particle density (2 nanoparticles/μm^2 to 367 nanoparticles/μm^2) on model SiO_2 supports composed of Stober silica beads.[52] Particle size distributions were analyzed after aging at increasing temperatures in air (Figure 6a). All samples showed only a slight increase in average particle size until 875 °C aging. The particle areas were measured, and the distribution changed from monodisperse to bimodal after 800 °C aging (Figure 6b), which indicated coalescence of entire particles. This observation demonstrated the density-dependence of coalescence through the PMC mechanism among particles, which experienced minor mobility.

Interestingly, particle size significantly and suddenly increased in the samples after aging at temperatures between 888 °C and 900 °C. High-resolution TEM (HRTEM) and X-ray diffraction analysis revealed the emergence of metallic Pd after aging at 900 °C, and nanoparticles that were smaller than the original particles were also observed (Figure 6c). These results suggested that metallic Pd is essential for sintering, and that Ostwald ripening occurred. Furthermore, it was found that the emission of atomic Pd species from nanoparticles was the rate-limiting step for sintering. This study therefore clearly revealed that sintering mechanisms of Pd catalysts proceed through minor PMC and then through OR likely via vapor phase at high temperatures and involving the PdO-Pd transition.

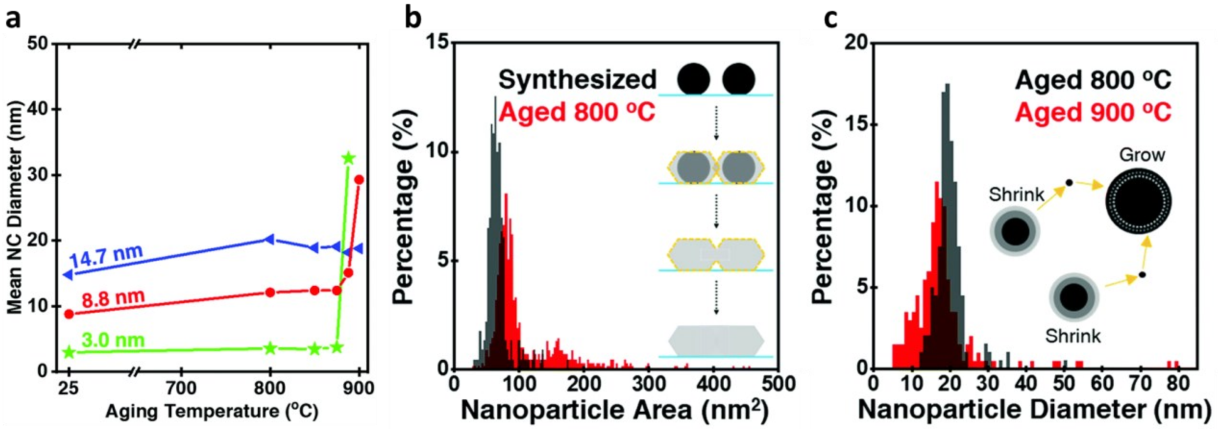


Figure 6. (a) Mean nanoparticle diameter as a function of aging temperature for Pd/SiO_2 catalysts. (b) Distribution of particle projected areas for a Pd/SiO_2 sample, as synthesized and after aging at 800 °C. (c) Particle size distributions after aging treatments at 800 °C or 900 °C. Adapted with permission from ref. 52. Copyright 2021 Royal Society of Chemistry.

The Stanford group also investigated whether surface-mediated OR is involved in sintering. Pt is known to sinter through formation of volatile platinum oxides.[53,54] At high temperatures in oxygen, PdO can trap mobile Pt species and form Pd/Pt alloys with larger particle sizes.[55,56] When Pt alloys with Pd, a drastic decrease in methane oxidation rate is observed.[47] We hypothesized that we could use the rates of methane oxidation on a Pd catalyst to infer whether Pt was sintering and alloying.[57]

We prepared a co-impregnated catalyst, where Pd and Pt nanoparticles were deposited on the same support grain (Figure 7a,c,d), and a physical mixture sample, where two distinct supported Pd and Pt catalysts were physically mixed (Figure 7b,e, and f). In this way, we surmised that surface and vapor phase-mediated ripening could occur in the co-impregnated catalyst, but only surface-mediated ripening could happen in the physical mixture due to the diffusion barrier imposed by the support grains. It was found that the co-impregnated catalyst and the physical mixture deactivated in different ways (Figure 7g). The co-impregnated catalysts deactivated significantly at relatively low temperatures (700 °C). The physical mixture started deactivating at higher temperatures (above 750 °C). STEM-EDS maps revealed that Pd and Pt in the co-impregnated catalysts formed an alloy at 700 °C aging conditions, while nanoparticles were mainly composed of either Pd or Pt in the physical mixture. After aging at 850 °C, both catalysts presented Pd and Pt in alloyed form. We concluded that Pd and Pt initially sintered by surface-mediated ripening, and that vapor phase-mediated ripening by PtO_2 started to occur at elevated temperatures, thus distinguishing between surface- and vapor-phase ripening.

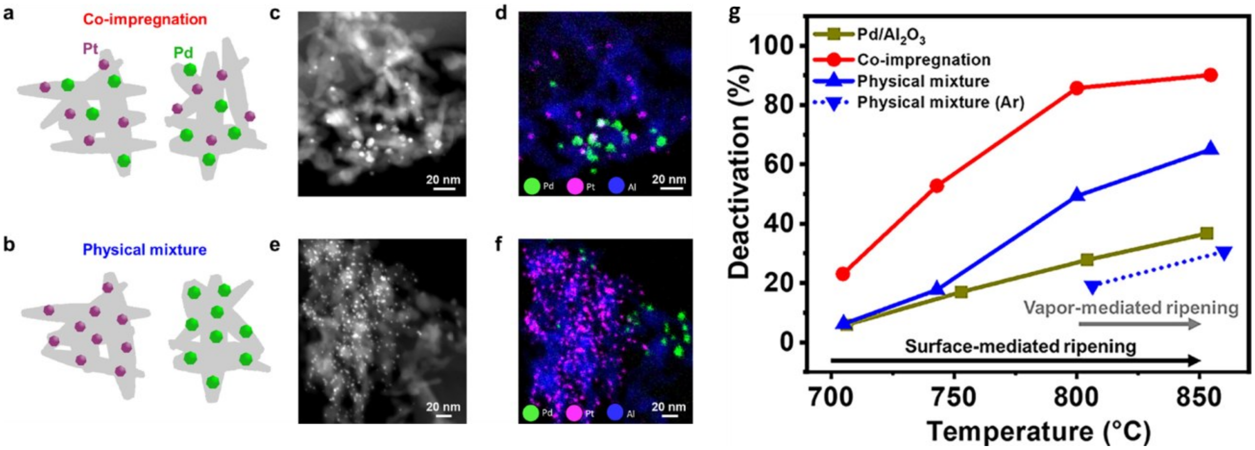


Figure 7. (a, b) Schematic representations of co-impregnated and physical mixture catalysts. Representative HAADF-STEM images (c, e) and corresponding EDS maps (d, f) of co-

impregnated Pd/Pt/Al_2O_3 catalyst and physical mixture Pd/Al_2O_3+Pt/Al_2O_3 catalysts, respectively. (g) Degree of catalyst deactivation (in percentage) reported as a function of aging temperature for Pd/Al_2O_3, co-impregnated catalyst, physical mixture catalyst aged under oxygen, and physical mixture catalysts aged under argon. Adapted with permission from ref. 57. Copyright 2023 American Chemical Society.

The Stanford team also discovered another unusual deactivation process in supported Pd catalysts where the redispersion of Pd nanoparticles into atomic species significantly deactivated the catalyst.[2] Pd decomposition depended on the density (metal loading) and size of particles (Figure 8a). The Pd/Al_2O_3 catalyst with the lowest density of nanoparticles (0.23 nanoparticles/μm^2) lost methane conversion activity from 85% to 20% after aging, while the catalyst with a 100x higher density of nanoparticles completely maintained its activity, despite sintering would predict the opposite. Only small Pd clusters could be observed in the low-density Pd/Al_2O_3 catalyst after aging (Figure 8b-c). The Pd-Pd coordination disappeared in XAS data. XPS demonstrated that the Pd evolved to a highly oxidized state (beyond PdO). All these elements pointed to particle disintegration, where defective alumina sites bind $Pd(OH)_2$ species formed by oxidation of Pd in the presence of steam. Only a small fraction of Al sites could bind and trap Pd species, so at higher Pd loadings, exchange of Pd species between particles was equilibrated and the catalyst was stable (Figure 8d). It was also found that nanoparticle disintegration deactivated the catalyst 100 times faster than sintering. The activity loss suggested that atomically dispersed Pd is less active than Pd nanoparticles for methane oxidation.

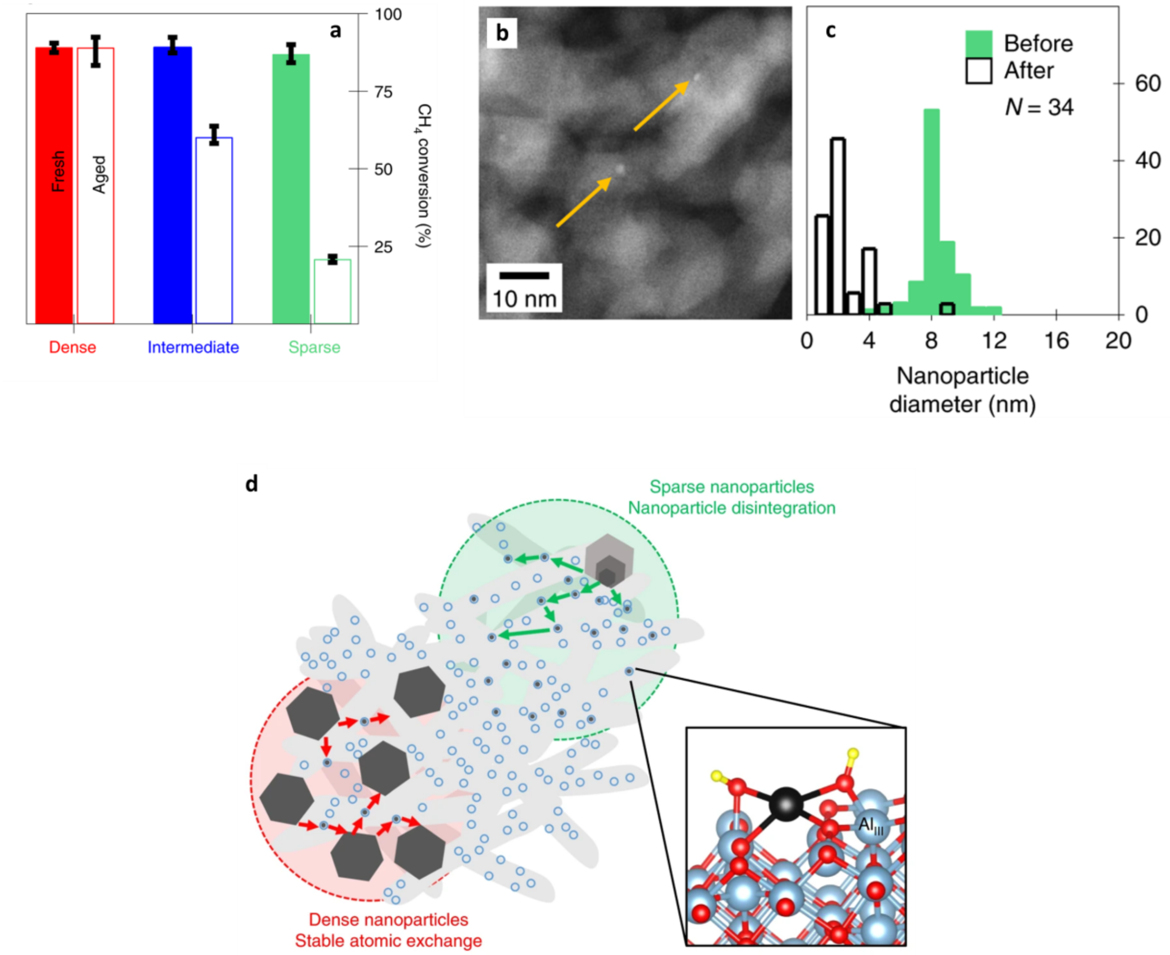


Figure 8. (a) Averaged CH_4 conversion values at 460 °C for the Pd/Al_2O_3 catalysts with different metal loading before (‘Fresh’) and after (‘Aged’) aging. (b) HAADF-STEM image of sparse Pd/ Al_2O_3 catalyst after aging in oxygen and (c) corresponding particle size distributions. (d) Schematic illustrating the density dependence of atomic redispersion. The inset shows the most stable adsorbate structure with $Pd(OH)_2$ binding to an Al_{III} site. Reproduced with permission from ref. 2. Copyright 2019 Springer Nature.

Zeolites can maintain small metal particle sizes because micropores (< 1 nm) allow the diffusion of reactants but hinder the migration of nanoparticles. However, Pd/zeolite catalysts tend to deactivate during the reaction because of sintering via OR mechanisms.[42,58] At PSI was performed a comprehensive characterization of Pd/ZSM-5 under methane oxidation conditions. Results indicated that, on a Pd (1 wt.%)/H-ZSM-5 (Si/Al=20) sample, deactivation occurred upon exposure to the reaction mixture for 30 minutes at 550 °C. While the zeolite framework only displayed small modifications, the average diameter of Pd nanoparticles increased from 1-2 nm to 5-10 nm, clearly indicating sintering.

In follow-up research, ZSM-5, BEA, and MOR zeolites were subjected to various chemical treatments (acid or acid-base) to modify the aluminum distribution and tune the pore structure.[45] Acid treatments of zeolites caused dealumination. While acid treatments did not improve the stability of Pd/H-Zeolites, desilication of zeolites in NaOH, followed by acid treatments (dealumination) turned out to be the best strategy to improve the catalytic stability of the investigated catalysts through removal of all acidity from the system. STEM did not show sintering of palladium nanoparticles. Physisorption isotherms proved that more mesopores with diameters ranging from 2 to 10 nm formed than on the acid treated zeolites. Palladium nanoparticles were mostly located in intercrystalline mesopores formed in dealuminated zeolites, which prevented Ostwald ripening, thus sintering and loss of activity, outlining a strategy for active and stable Pd catalysts in zeolites.

5. Effect of water on methane oxidation catalyzed by palladium catalysts

Palladium-based catalysts suffer from strong poisoning at temperatures below 450 °C in the presence of water.[59–65] The impact of water on methane oxidation reaction over palladium-based catalysts has been extensively studied and is a consequence of the competition between water and methane for adsorption sites on palladium oxide. Water has a negative reaction order in the kinetics, indicating inhibition. Despite the water inhibition effect disappearing at temperatures above ~450 °C, a full understanding of low-temperature inhibition is required for many applications.

As described in section 2, the PSI group used Pd foil as a model system to investigate structure-activity relationships during methane oxidation. When steam was co-dosed with the reactants, the oxidation rate of palladium was slowed down, in line with its role as surface adsorbate (Figure 9a). The impact of water was further observed at 600 °C: in the presence of water, the Pd foil remained oxidized. Water adsorbed on coordinatively unsaturated palladium sites adjacent to oxygen, filling oxygen vacancies and hindering the hydrogen abstraction process in C-H activation, thus PdO reduction. Oxygen 1s spectra unequivocally demonstrated that a relevant amount of surface hydroxyls formed, which delayed the formation of bulk oxide and negatively influenced the activity.

The same strategy was then used to investigate a 1 wt. % palladium catalyst supported on alumina (Pd/Al_2O_3).[31] Because the amount of palladium was low, the photoemission signal was lower than that detected on palladium foil (Figure 9b), making transient experiments unfeasible. Steady state APXPS measurements confirmed that a new component was detected in the Pd 3d signal, in addition to the species found in Pd foil. We attributed this higher binding energy speciea (>338 eV) to one related to the interaction between palladium and the alumina. In the literature, this signal was only observed at low metal loadings on Pd/Al_2O_3 and has been tentatively attributed to palladium aluminate or to Pd^{4+}.[66,67] We assigned it to palladium adatoms nucleating on alumina defects, in agreement with TEM highlighting well dispersed small nanoparticles.

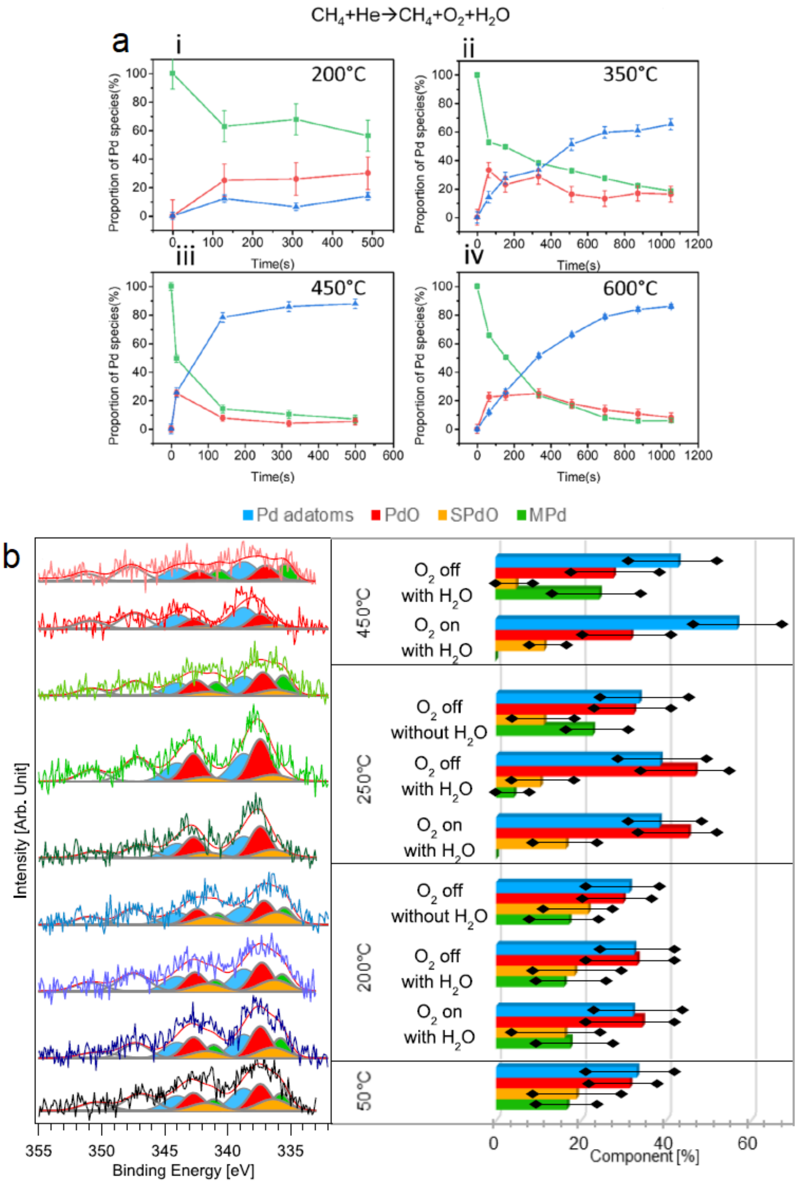


Figure 9. (a) Time-resolved evolution of palladium species after replacing CH_4 + He with CH_4 + O_2 + H_2O. Adapted with permission from ref 6. Copyright 2020 American Chemical Society. (b) Pd 3d photoemission spectra and their deconvolution acquired at hν = 890 eV at increasing temperature for a Pd/Al_2O_3 sample under methane oxidation conditions (left). Percentage of Pd 3d signals from different Pd species (right). Reproduced with permission from ref. 31. Copyright 2022 the authors. Published by Elsevier under a Creative Commons Attribution 4.0 International (CC BY 4.0) License.

The evolution of palladium species was followed by adding/removing oxygen from the reactant stream. Upon oxygen removal, palladium adatoms were reduced at a lower temperature than bulk palladium (II) oxide (Figure 9, top spectra). When steam was added to the reaction mixture, the initial amount of palladium adatoms present was lower than in the absence of co-dosed steam. The presence of water increased the temperature at which the catalytically active sites started to reduce. However, at 450 °C in the presence of water, the proportion of palladium adatoms was comparable to that of bulk palladium (II) oxide, indicating that the latter was more reactive. Additionally, when methane, oxygen and water were dosed, palladium adatoms represented the main species, suggesting that water favored nanoparticle redispersion at high temperature. In situ XPS measurements allowed the detection of different palladium oxide species. Under reaction conditions, palladium adatoms were more prone to poisoning than nanoparticles, demonstrating that the latter host active sites for methane oxidation.

Supports and diluents affect reaction rates at low temperatures by absorbing water in the reactor. Work from the Stanford group found that Pd/Al_2O_3 pretreated at 475 °C and diluted with alumina showed higher initial activity than the same catalyst pretreated at 275 °C.[68] The activity of high-temperature pretreated catalysts showed a dip at ~320 °C during light-off conditions. This trend was not observed when catalysts were pretreated at 275 °C, when water was co-fed in the reaction mixture, or when SiO_2 was used as a diluent. Thus, we concluded that γ-Al_2O_3 initially adsorbed the water generated by the reaction.[69,70] After its surface was saturated, the surface of PdO started to be poisoned by water, causing lower activity. High-temperature *in-situ* pretreatment desorbed water from the support/diluent. This study discovered that supports/diluents can significantly affect the activity of catalysts.

Using this knowledge, we proposed that water sorbents in the reactor could provide a transient improvement in catalytic performance (Figure 10a-b).[71] This concept was tested using zeolites, γ-alumina, and CaO that were mixed with a Pd/CeO_2 catalyst. All materials showed improved activity at 250 °C compared to when inert SiC was used as diluent. In the case of zeolites, activity differences at 300 °C were minor compared to the reference due to their weaker water sorption capability. CaO resulted in the greatest improvement thanks to its ability to capture both water and CO_2. The CaO-diluted catalyst showed a 6-fold higher maximum methane conversion compared to the SiC-diluted catalyst (Figure 10c-e). Although the effect of CaO sorption started to decrease once the adsorption sites became saturated, the activity was still higher than the reference over a 10 h reaction span. The CaO-diluted catalyst was completely regenerated after being exposed to dilute O_2 for 30 min at 500 °C, demonstrating that a regeneration step could maintain the high transient activity for many cycles.

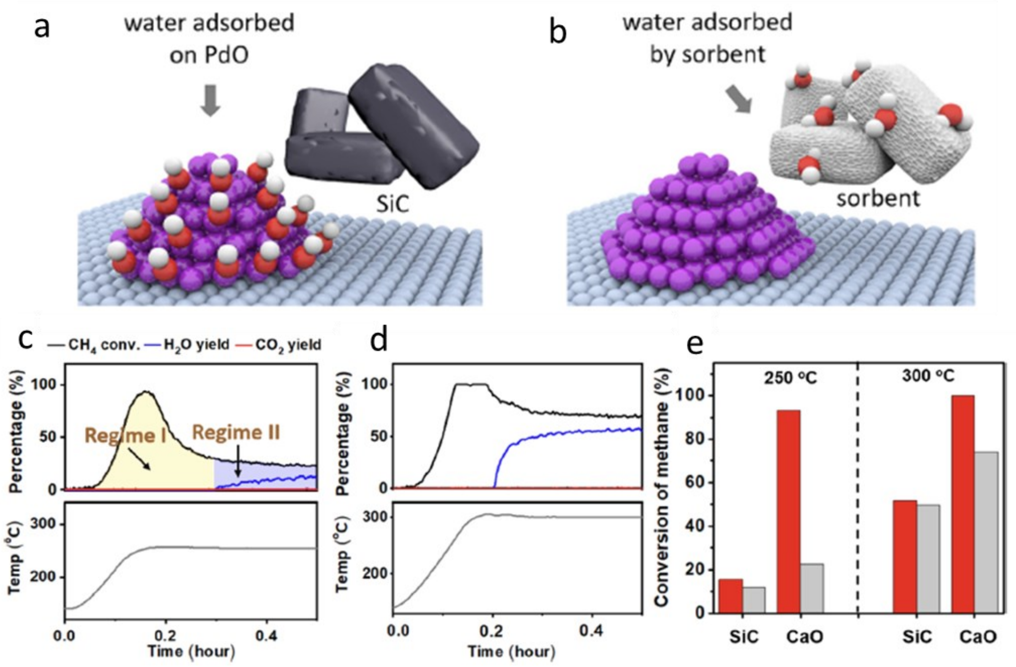


Figure 10. Schematic of sorption during methane oxidation: (a) using SiC as an inert diluent leads to water adsorbing on PdO surfaces and (b) using a water sorbent leads to active PdO surfaces with low water coverage. (c and d) CH_4 conversion, H_2O, and CO_2 yield over Pd/CeO_2 diluted with CaO at 250 and 300 °C, respectively, after 500 °C *in situ* pretreatment before the reaction. (e) Maximum conversion for the samples diluted with CaO at the peak of regime I (in red) and after 1 h (in gray). Adapted with permission from ref. 71. Copyright 2020 American Chemical Society.

Pd supported on zeolites like ZSM-5, prepared at PSI, showed higher activity than Pd/Al_2O_3.[72] However, the catalyst was still poisoned by water. Water was added/removed from the reaction mixture at one-hour periods and the results compared with constant water addition (Figure 11). The catalyst suffered from a rapid poisoning when water was constantly introduced due to the partial collapse of the zeolite lattice. Instead, with periodic removal of water, the deactivation rate was slower. The deactivation was however irreversible because of the gradual sintering of palladium oxide particles. In a following work, sintering was hindered by encapsulating small PdO particles in the pores of silicalite-1, opening the route for the development of more stable catalysts.[46]

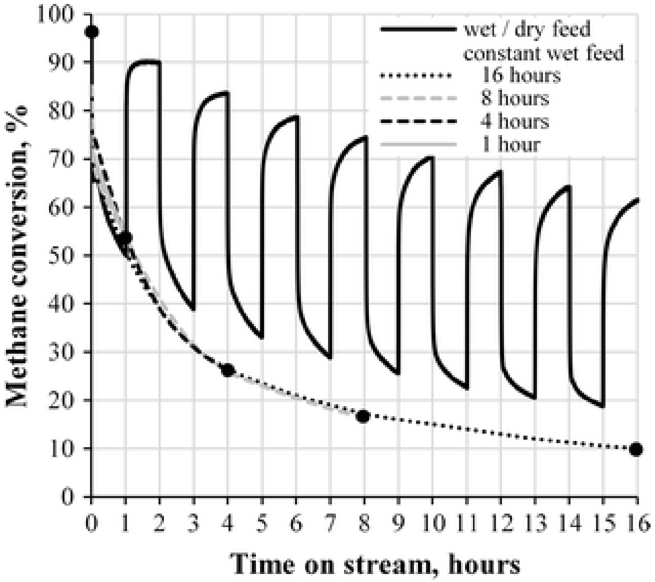


Figure 11. Time dependence of methane conversion on Pd/H-ZSM-5 at 450 °C with constant and periodic addition of steam to the feed. Feed composition: 1 % CH_4, 4 % O_2, 0 or 5 % H_2O in N_2. Adapted with permission from ref. 72. Copyright 2016 Springer Science Business Media New York.

Two new approaches to improve the catalyst stability were then explored. The first one consisted in improving support stability by treating the zeolite with acids and removing extra-framework aluminum, thus all acidity from the zeolite.[45] The second one consisted in the application of short reducing pulses, which produced a highly active transient state of the catalyst while being slowly poisoned by water in between them.[3] Oxygen was removed from the gas feed for 3 seconds every 10 minutes (Figure 12). The short pulses led to regeneration of the catalyst. HRTEM demonstrated prevention of sintering, and XAS proved the Pd reversible redox behavior, thus demonstrating the improved overall stability.

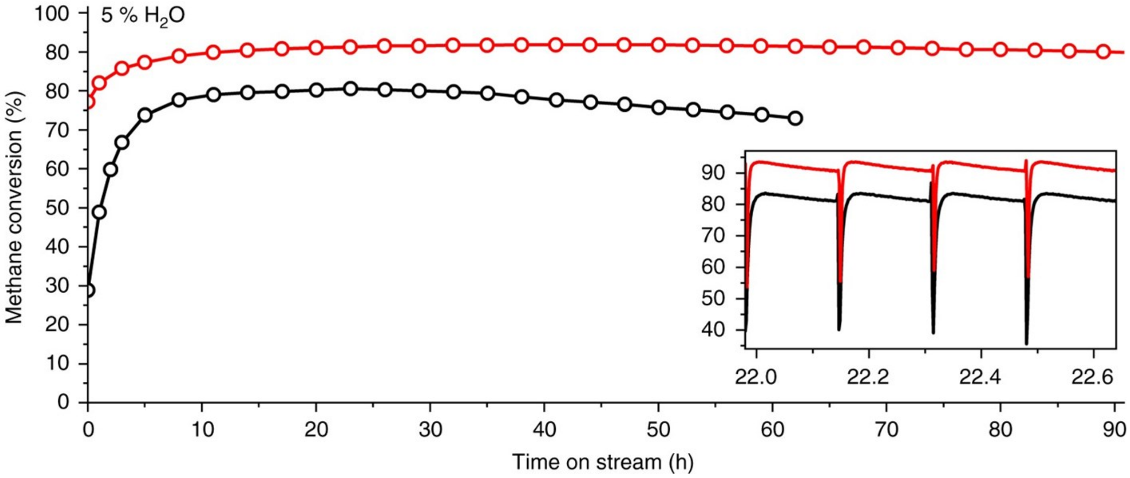


Figure 12. Stability test of Pd/zeolite catalyst with short pulse regeneration (top red curve) and compared to no regeneration (bottom black curve). Reproduced with permission from ref. 3. Copyright 2018 the authors. Published by Springer Nature under a Creative Commons Attribution 4.0 International (CC BY 4.0) License.

6. Summary and Perspective

In this Account, we have summarized recent research from our groups at Stanford and ETH/PSI related to methane oxidation using Pd-based catalysts. Besides the continued interest in reducing methane emissions from point sources and vehicles, there is heightened interest in tackling the removal of atmospheric methane, and palladium remains the most active catalyst for this reaction. Continued understanding of the fundamental reactivity of this material is necessary for emission control applications where low-temperature oxidation is relevant until society fully transitions to an energy system void of fossil fuels.

The active phase and sites of palladium catalysts have been a matter of debate for decades. We demonstrated that palladium oxide is a necessary phase for activity, and that support and promoters affect the fraction of oxide active phase. Defects and other under-appreciated aspects of Pd reactivity can disproportionately affect reaction rates. Further understanding of the relationship between surface features under reaction conditions and activity must be achieved. It remains uncertain whether large-scale applications of Pd catalysts like atmospheric methane removal are feasible, however, Pd promotion with base metals and the continued improvement of activity at lower temperatures will be crucial for many applications. In this respect, the use of active catalysts in pulsed experiments showed promising results. This work demonstrated that combining synthesis with engineering (e.g., continuous regeneration of poisoned active sites by short pulses under reducing reaction atmosphere) was a viable route to maintain high activity in the low temperature range.

Developing water-resistant catalysts represents another challenge of paramount importance. Our results showed that both catalysts and process modifications represent viable routes. Finding a mechanism and a catalyst composition that can take advantage of Pd specific reactivity for C-H activation in methane while not being inhibited by water at low temperatures is one of the most relevant challenges to overcome. Promising strategies, based on experimental results, include the control of support's hydrophobicity and the control of active sites' local structure in a way that leads to the destabilization of Pd hydroxide. Careful modifications of support materials may indeed favor active sites dispersion while preventing water adsorption, thus increasing low temperature performance.

The synergy between advanced synthesis methods and *in situ/operando* spectroscopic tools will continue to be paramount to assess the performance of newly developed materials under reaction conditions. It is necessary to expand the spectroscopy toolbox required to describe the detailed mechanism of catalytic reactivity at short timescales and higher spatial resolution. Because the concentration of active sites is often low and their lifetime limited, it will be important to further develop modulated excitation experiments coupled to time-resolved spectroscopies that are sensitive to interfaces and/or reaction intermediates (e.g., XPS, infrared, Raman). Introducing a perturbation to a catalytic system allows understanding the structure of active sites, deactivation pathways and how to hinder/prevent them. Concurrently, synthesis techniques that allow control of parameters that go beyond conventional size and shape control, such as crystalline defects and composition control, are needed to increase the precision in designing and realizing active sites for advanced catalysts.

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Luca Artiglia received his PhD from the University of Padova (UniPD) in 2011 in the field of surface science. From 2011 to 2015, as a post-doctoral researcher at UniPD, he was involved in different projects ranging from plasmonics to catalysis. He has been a scientist at the Paul Scherrer institute since 2015. His main research focuses on the application and development of ambient pressure X-ray photoelectron spectroscopy to characterize interfaces of relevance for catalysis and surface chemistry.

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Matteo Cargnello received his Ph.D. in Nanotechnology in 2012 at the University of Trieste, Italy, under the supervision of Prof. Paolo Fornasiero, and he was then a post-doctoral scholar in the Chemistry Department at the University of Pennsylvania with Prof. Christopher B. Murray before joining the Faculty at Stanford University in January 2015. He is currently Associate Professor of Chemical Engineering and, by courtesy, of Materials Science and Engineering and Vance D. and Arlene C. Coffman Faculty Scholar. The general goals of the research in the Cargnello group pertain to solving energy and environmental challenges through catalysis.

REFERENCES

(1) Huang, W.; Johnston-Peck, A. C.; Wolter, T.; Yang, W.-C. D.; Xu, L.; Oh, J.; Reeves, B. A.; Zhou, C.; Holtz, M. E.; Herzing, A. A.; Lindenberg, A. M.; Mavrikakis, M.; Cargnello, M. Steam-Created Grain Boundaries for Methane C–H Activation in Palladium Catalysts. *Science* **2021**, *373*, 1518–1523.

(2) Goodman, E. D.; Johnston-Peck, A. C.; Dietze, E. M.; Wrasman, C. J.; Hoffman, A. S.; Abild-Pedersen, F.; Bare, S. R.; Plessow, P. N.; Cargnello, M. Catalyst Deactivation via Decomposition into Single Atoms and the Role of Metal Loading. *Nat. Catal.* **2019**, *2*, 748–755.

(3) Petrov, A. W.; Ferri, D.; Krumeich, F.; Nachtegaal, M.; Van Bokhoven, J. A.; Kröcher, O. Stable Complete Methane Oxidation over Palladium Based Zeolite Catalysts. *Nat. Commun.* **2018**, *9*, 25455

(4) Li, X.; Wang, X.; Roy, K.; van Bokhoven, J. A.; Artiglia, L. Role of Water on the Structure of Palladium for Complete Oxidation of Methane. *ACS Catal.* **2020**, *10*, 5783–5792.

(5) Peplow, M. How Fracking Is Upending the Chemical Industry. *Nature* **2017**, *550*, 26–28.

(6) Monai, M.; Montini, T.; Gorte, R. J.; Fornasiero, P. Catalytic Oxidation of Methane: Pd and Beyond. *Eur. J. Inorg. Chem*. **2018**, *2018*, 2884−2893.

(7) Jiang, D.; Khivantsev, K.; Wang, Y. Low-Temperature Methane Oxidation for Efficient Emission Control in Natural Gas Vehicles: Pd and Beyond. *ACS Catal.* **2020**, *10*, 14304–14314.

(8) Narsimhan, K.; Iyoki, K.; Dinh, K.; Román-Leshkov, Y. Catalytic Oxidation of Methane into Methanol over Copper-Exchanged Zeolites with Oxygen at Low Temperature. *ACS Cent. Sci.* **2016**, *2*, 424–429.

(9) Dinh, K. T.; Sullivan, M. M.; Serna, P.; Meyer, R. J.; Dincă, M.; Román-Leshkov, Y. Viewpoint on the Partial Oxidation of Methane to Methanol Using Cu- and Fe-Exchanged Zeolites. *ACS Catal.* **2018**, *8*, 8306–8313.

(10) Montzka, S. A.; Dlugokencky, E. J.; Butler, J. H. Non-CO2 Greenhouse Gases and Climate Change. *Nature* **2011**, *476*, 43–50.

(11) Alvarez, R. A.; Zavala-Araiza, D.; Lyon, D. R.; Allen, D. T.; Barkley, Z. R.; Brandt, A. R.; Davis, K. J.; Herndon, S. C.; Jacob, D. J.; Karion, A.; Kort, E. A.; Lamb, B. K.; Lauvaux, T.; Maasakkers, J. D.; Marchese, A. J.; Omara, M.; Pacala, S. W.; Peischl, J.; Robinson, A. L.; Shepson, P. B.; Sweeney, C.; Townsend-Small, A.; Wofsy, S. C.; Hamburg, S. P. Assessment of Methane Emissions from the U.S. Oil and Gas Supply Chain. *Science* **2018**, eaar7204.

(12) Zhang, L.; Tian, H.; Shi, H.; Pan, S.; Chang, J.; Dangal, S. R. S.; Qin, X.; Wang, S.; Tubiello, F. N.; Canadell, J. G.; Jackson, R. B. A 130-year Global Inventory of Methane

Emissions from Livestock: Trends, Patterns, and Drivers. *Glob. Chang. Biol.* **2022**, *28*, 5142–5158.

(13) Howarth, R. W. A Bridge to Nowhere: Methane Emissions and the Greenhouse Gas Footprint of Natural Gas. *Energy Sci. Eng.* **2014**, *2*, 47–60.

(14) Jackson, R. B.; Solomon, E. I.; Canadell, J. G.; Cargnello, M.; Field, C. B. Methane Removal and Atmospheric Restoration. *Nat. Sustain.* **2019**, *2*, 436−438.

(15) Jackson, R. B.; Abernethy, S.; Canadell, J. G.; Cargnello, M.; Davis, S. J.; Féron, S.; Fuss, S.; Heyer, A. J.; Hong, C.; Jones, C. D.; Damon Matthews, H.; O'Connor, F. M.; Pisciotta, M.; Rhoda, H. M.; De Richter, R.; Solomon, E. I.; Wilcox, J. L.; Zickfeld, K. Atmospheric Methane Removal: A Research Agenda. *Philos. Trans. R. Soc.*, A **2021**, *379*, No. 20200454.

(16) Abernethy, S.; O'Connor, F. M.; Jones, C. D.; Jackson, R. B. Methane Removal and the Proportional Reductions in Surface Temperature and Ozone. *Philos. Trans. R. Soc.*, **2021**, *379*, 20210104.

(17) Brenneis, R. J.; Johnson, E. P.; Shi, W.; Plata, D. L. Atmospheric- and Low-Level Methane Abatement via an Earth-Abundant Catalyst. *ACS Environ. Au* **2022**, *2*, 223−231.

(18) Tang, P.; Zhu, Q.; Wu, Z.; Ma, D. Methane Activation: The Past and Future. *Energy Environ. Sci.* **2014**, *7*, 2580–2591.

(19) Chin, Y. H.; Buda, C.; Neurock, M.; Iglesia, E. Consequences of Metal-Oxide Interconversion for C-H Bond Activation during CH_4 Reactions on Pd Catalysts. *J. Am. Chem. Soc.* **2013**, *135*, 15425–15442.

(20) Chin, Y.-H. (Cathy); García-Diéguez, M.; Iglesia, E. Dynamics and Thermodynamics of Pd–PdO Phase Transitions: Effects of Pd Cluster Size and Kinetic Implications for Catalytic Methane Combustion. *J. Phys. Chem. C* **2016**, *120*, 1446–1460.

(21) Cargnello, M. Colloidal Nanocrystals as Building Blocks for Well-Defined Heterogeneous Catalysts. *Chem. Mater.* **2019**, *31*, 576–596.

(22) Losch, P.; Huang, W.; Goodman, E. D.; Wrasman, C. J.; Holm, A.; Riscoe, A. R.; Schwalbe, J. A.; Cargnello, M. Colloidal Nanocrystals for Heterogeneous Catalysis. *Nano Today* **2019**, *24*, 15–47.

(23) Huang, J.; Buonsanti, R. Colloidal Nanocrystals as Heterogeneous Catalysts for Electrochemical CO_2 Conversion. *Chem. Mater.* **2019**, *31*, 13–25.

(24) Roy, K.; Artiglia, L.; van Bokhoven, J. A. Ambient Pressure Photoelectron Spectroscopy: Opportunities in Catalysis from Solids to Liquids and Introducing Time Resolution. *ChemCatChem* **2018**, *10*, 666–682.

(25) Albers, P.; Seibold, K.; Thampi, K. R.; Grätzel, M.; Kiwi, J. Reduction of Supported and Unsupported Palladium Oxide Catalysts Using Methane. Characterization of Active Oxides. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3671–3677.

(26) Farrauto, R. J.; Hobson, M. C.; Kennelly, T.; Waterman, E. M. Catalytic Chemistry of Supported Palladium for Combustion of Methane. *Appl. Catal. A: Gen.* **1992**, *81*, 227–237.

(27) Ribeiro, F. H.; Chow, M.; Dallabetta, R. A. Kinetics of the Complete Oxidation of Methane over Supported Palladium Catalysts. *J. Catal.* **1994**, *146*, 537–544.

(28) Xiong, H.; Lester, K.; Ressler, T.; Schlögl, R.; Allard, L. F.; Datye, A. K. Metastable Pd ⇔ PdO Structures During High Temperature Methane Oxidation. *Catal. Letters* **2017**, *147*, 1095–1103

(29) Artiglia, L.; Sushkevich, V. L.; Palagin, D.; Knorpp, A. J.; Roy, K.; van Bokhoven, J. A. In Situ X-Ray Photoelectron Spectroscopy Detects Multiple Active Sites Involved in the Selective Anaerobic Oxidation of Methane in Copper-Exchanged Zeolites. *ACS Catal.* **2019**, *9*, 6728–6737.

(30) Artiglia, L.; Orlando, F.; Roy, K.; Kopelent, R.; Safonova, O.; Nachtegaal, M.; Huthwelker, T.; van Bokhoven, J. A. Introducing Time Resolution to Detect Ce^{3+} Catalytically Active Sites at the Pt/CeO_2 Interface through Ambient Pressure X-Ray Photoelectron Spectroscopy. *J. Phys. Chem. Lett.* **2017**, *8*, 102–108.

(31) Boucly, A.; Artiglia, L.; Roger, M.; Zabilskiy, M.; Beck, A.; Ferri, D.; van Bokhoven, J. A. Water Inhibition and Role of Palladium Adatoms on Pd/Al_2O_3 Catalysts during Methane Oxidation. *Appl. Surf. Sci.* **2022**, *606*, 154927.

(32) G Goodman, E. D.; Ye, A. A.; Aitbekova, A.; Mueller, O.; Riscoe, A. R.; Nguyen Taylor, T.; Hoffman, A. S.; Boubnov, A.; Bustillo, K. C.; Nachtegaal, M.; Bare, S. R.; Cargnello, M. Palladium Oxidation Leads to Methane Combustion Activity: Effects of Particle Size and Alloying with Platinum. *J. Chem. Phys.* **2019**, *151*, 154703.

(33) Willis, J. J.; Gallo, A.; Sokaras, D.; Aljama, H.; Nowak, S. H.; Goodman, E. D.; Wu, L.; Tassone, C. J.; Jaramillo, T. F.; Abild-Pedersen, F.; Cargnello, M. Systematic Structure–Property Relationship Studies in Palladium-Catalyzed Methane Complete Combustion. *ACS Catal.* **2017**, *7*, 7810–7821.

(34) Murata, K.; Mahara, Y.; Ohyama, J.; Yamamoto, Y.; Arai, S.; Satsuma, A. The Metal-Support Interaction Concerning the Particle Size Effect of Pd/Al_2O_3 on Methane Combustion. *Angew. Chem* **2017**, *129* (50), 16209–16213.

(35) Murata, K.; Kosuge, D.; Ohyama, J.; Mahara, Y.; Yamamoto, Y.; Arai, S.; Satsuma, A. Exploiting Metal-Support Interactions to Tune the Redox Properties of Supported Pd Catalysts for Methane Combustion. *ACS Catal.* **2020**, *10*, 1381–1387.

(36) van Deelen, T. W.; Hernández Mejía, C.; de Jong, K. P. Control of Metal-Support Interactions in Heterogeneous Catalysts to Enhance Activity and Selectivity. *Nat. Catal.* **2019***, 2,* 955−970*.*

(37) Goodman, E. D.; Asundi, A. S.; Hoffman, A. S.; Bustillo, K. C.; Stebbins, J. F.; Bare, S. R.; Bent, S. F.; Cargnello, M. Monolayer Support Control and Precise Colloidal Nanocrystals

Demonstrate Metal–Support Interactions in Heterogeneous Catalysts. *Adv. Mater.* **2021**, *33*, 2104533.

(38) Cargnello, M.; Delgado Jaén, J. J.; Garrido, J. C. H.; Bakhmutsky, K.; Montini, T.; Calvino Gámez, J. J.; Gorte, R. J.; Fornasiero, P. Exceptional Activity for Methane Combustion over Modular Pd@CeO_2 Subunits on Functionalized Al_2O_3. *Science* **2012**, *337*, 713-717.

(39) Chen, C.; Yeh, Y. H.; Cargnello, M.; Murray, C. B.; Fornasiero, P.; Gorte, R. J. Methane Oxidation on Pd@ZrO_2/Si-Al_2O_3 Is Enhanced by Surface Reduction of ZrO2. *ACS Catal.* **2014**, *4*, 3902–3909.

(40) Cui, Y.; Zhu Chen, J.; Peng, B.; Kovarik, L.; Devaraj, A.; Li, Z.; Ma, T.; Wang, Y.; Szanyi, J.; Miller, J. T.; Wang, Y.; Gao, F. Onset of High Methane Combustion Rates over Supported Palladium Catalysts: From Isolated Pd Cations to PdO Nanoparticles. *JACS Au* **2021**, *1*, 396–408.

(41) Lim, J. Bin; Jo, D.; Hong, S. B. Palladium-Exchanged Small-Pore Zeolites with Different Cage Systems as Methane Combustion Catalysts. *Appl. Catal. B* **2017**, *219*, 155–162.

(42) Okumura, K.; Matsumoto, S.; Nishiaki, N.; Niwa, M. Support Effect of Zeolite on the Methane Combustion Activity of Palladium. *Appl. Catal. B* **2003**, *40*, 151–159.

(43) Li, Y.; Armor, J. N. Catalytic Combustion of Methane over Palladium Exchanged Zeolites. *Appl. Catal. B* **1994**, *3*, 275–282.

(44) Losch, P.; Huang, W.; Vozniuk, O.; Goodman, E. D.; Schmidt, W.; Cargnello, M. Modular Pd/Zeolite Composites Demonstrating the Key Role of Support Hydrophobic/Hydrophilic Character in Methane Catalytic Combustion. *ACS Catal.* **2019**, *9*, 4742–4753.

(45) Petrov, A. W.; Ferri, D.; Kröcher, O.; van Bokhoven, J. A. Design of Stable Palladium-Based Zeolite Catalysts for Complete Methane Oxidation by Postsynthesis Zeolite Modification. *ACS Catal.* **2019**, *9*, 2303–2312.

(46) Li, T.; Beck, A.; Krumeich, F.; Artiglia, L.; Ghosalya, M. K.; Roger, M.; Ferri, D.; Kröcher, O.; Sushkevich, V.; Safonova, O. V.; van Bokhoven, J. A. Stable Palladium Oxide Clusters Encapsulated in Silicalite-1 for Complete Methane Oxidation. *ACS Catal.* **2021**, *11* (12), 7371–7382.

(47) Goodman, E. D.; Dai, S.; Yang, A. C.; Wrasman, C. J.; Gallo, A.; Bare, S. R.; Hoffman, A. S.; Jaramillo, T. F.; Graham, G. W.; Pan, X.; Cargnello, M. Uniform Pt/Pd Bimetallic Nanocrystals Demonstrate Platinum Effect on Palladium Methane Combustion Activity and Stability. *ACS Catal.* **2017**, *7*, 4372–4380.

(48) Porter, S.; Ghosh, A.; Liu, C. H.; Kunwar, D.; Thompson, C.; Alcala, R.; Dean, D. P.; Miller, J. T.; DeLaRiva, A.; Pham, H.; Peterson, E.; Brearley, A.; Watt, J.; Kyriakidou, E. A.; Datye, A. K. Biphasic Janus Particles Explain Self-Healing in Pt–Pd Diesel Oxidation Catalysts. *ACS Catal.* **2023**, *13*, 5456–5471.

(49) Willis, J. J.; Goodman, E. D.; Wu, L.; Riscoe, A. R.; Martins, P.; Tassone, C. J.; Cargnello, M. Systematic Identification of Promoters for Methane Oxidation Catalysts Using Size- and

Composition-Controlled Pd-Based Bimetallic Nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 11989–11997.

(50) Goodman, E. D.; Schwalbe, J. A.; Cargnello, M. Mechanistic Understanding and the Rational Design of Sinter- Resistant Heterogeneous Catalysts. *ACS Catal.* **2017***, 6,* 7156-7173.

(51) Datye, A. K.; Xu, Q.; Kharas, K. C.; McCarty, J. M. Particle Size Distributions in Heterogeneous Catalysts: What Do They Tell Us about the Sintering Mechanism? *Catal. Today* **2006**, *111*, 59−6.

(52) Goodman, E. D.; Carlson, E. Z.; Dietze, E. M.; Tahsini, N.; Johnson, A.; Aitbekova, A.; Nguyen Taylor, T.; Plessow, P. N.; Cargnello, M. Size-Controlled Nanocrystals Reveal Spatial Dependence and Severity of Nanoparticle Coalescence and Ostwald Ripening in Sintering Phenomena. *Nanoscale* **2021**, *13*, 930–938.

(53) Simonsen, S. B.; Chorkendorff, I.; Dahl, S.; Skoglundh, M.; Sehested, J.; Helveg, S. Ostwald Ripening in a Pt/SiO_2 Model Catalyst Studied by in Situ TEM. *J. Catal.* **2011**, *281*, 147–155.

(54) Challa, S. R.; Delariva, A. T.; Hansen, T. W.; Helveg, S.; Sehested, J.; Hansen, P. L.; Garzon, F.; Datye, A. K. Relating Rates of Catalyst Sintering to the Disappearance of Individual Nanoparticles during Ostwald Ripening. *J. Am. Chem. Soc.* **2011**, *133*, 20672–20675.

(55) Carrillo, C.; Johns, T. R.; Xiong, H.; Delariva, A.; Challa, S. R.; Goeke, R. S.; Artyushkova, K.; Li, W.; Kim, C. H.; Datye, A. K. Trapping of Mobile Pt Species by PdO Nanoparticles under Oxidizing Conditions. *J. Phys. Chem. Lett.* **2014***, 5,* 2089−2093.

(56) Xiong, H.; Peterson, E.; Qi, G.; Datye, A. K. Trapping Mobile Pt Species by PdO in Diesel Oxidation Catalysts: Smaller Is Better. *Catal. Today* **2016**, *272*, 80–86.

(57) Oh, J.; Beck, A.; Goodman, E. D.; Roling, L. T.; Boucly, A.; Artiglia, L.; Abild-Pedersen, F.; van Bokhoven, J. A.; Cargnello, M. Colloidally Engineered Pd and Pt Catalysts Distinguish Surface- and Vapor-Mediated Deactivation Mechanisms. *ACS Catal.* **2023**, *13*, 1812–1822.

(58) Okumura, K.; Shinohara, E.; Niwa, M. Pd Loaded on High Silica Beta Support Active for the Total Oxidation of Diluted Methane in the Presence of Water Vapor. *Catal. Today* **2006**, *117*, 577–583.

(59) Burch, R.; Urbano, F.; Loader, P. Methane Combustion over Palladium Catalysts: The Effect of Carbon Dioxide and Water on Activity. *Appl. Catal. A: Gen***.** **1995**, *123*, 173–184

(60) van Giezen, J. C.; van den Berg, F. R.; Kleinen, J. L.; van Dillen, A. J.; Geus, J. W. The Effect of Water on the Activity of Supported Palladium Catalysts in the Catalytic Combustion of Methane. *Catal. Today* **1999**, *47*, 287–293.

(61) Ciuparu, D.; Pfefferle, L. Support and Water Effects on Palladium Based Methane Combustion Catalysts. *Appl. Catal. A: Gen* **2001**, *209*, 415–428.

(62) Kikuchi, R.; Maeda, S.; Sasaki, K.; Wennerström, S.; Eguchi, K. Low-Temperature Methane Oxidation over Oxide-Supported Pd Catalysts: Inhibitory Effect of Water Vapor. *Appl. Catal. A: Gen.* **2002**, *232*, 23–28.

(63) Gholami, R.; Alyani, M.; Smith, K. Deactivation of Pd Catalysts by Water during Low Temperature Methane Oxidation Relevant to Natural Gas Vehicle Converters. *Catalysts* **2015**, *5*, 561–594.

(64) Mihai, O.; Smedler, G.; Nylén, U.; Olofsson, M.; Olsson, L. The Effect of Water on Methane Oxidation over Pd/Al_2O_3 under Lean, Stoichiometric and Rich Conditions. *Catal. Sci. Technol.* **2017**, *7*, 3084–3096.

(65) Velin, P.; Ek, M.; Skoglundh, M.; Schaefer, A.; Raj, A.; Thompsett, D.; Smedler, G.; Carlsson, P.-A. Water Inhibition in Methane Oxidation over Alumina Supported Palladium Catalysts. *J. Phys. Chem. C* **2019**, *123*, 25724–25737.

(66) Aznárez, A.; Gil, A.; Korili, S. A. Performance of Palladium and Platinum Supported on Alumina Pillared Clays in the Catalytic Combustion of Propene. *RSC Adv.* **2015**, *5*, 82296–82309.

(67) Ivanova, A. S.; Slavinskaya, E. M.; Gulyaev, R. V.; Zaikovskii, V. I.; Stonkus, O. A.; Danilova, I. G.; Plyasova, L. M.; Polukhina, I. A.; Boronin, A. I. Metal–Support Interactions in Pt/Al2O3 and Pd/Al2O3 Catalysts for CO Oxidation. *Appl. Catal. B* **2010**, *97*, 57–71.

(68) Huang, W.; Goodman, E. D.; Losch, P.; Cargnello, M. Deconvoluting Transient Water Effects on the Activity of Pd Methane Combustion Catalysts. *Ind. Eng. Chem. Res.* **2018**, *57*, 10261–10268.

(69) Castro, R. H. R.; Quach, D. V. Analysis of Anhydrous and Hydrated Surface Energies of Gamma-Al_2O_3 by Water Adsorption Microcalorimetry. *J. Phys. Chem. C* **2012**, *116*, 24726–24733.

(70) Lagauche, M.; Larmier, K.; Jolimaitre, E.; Barthelet, K.; Chizallet, C.; Favergeon, L.; Pijolat, M. Thermodynamic Characterization of the Hydroxyl Group on the γ-Alumina Surface by the Energy Distribution Function. *J. Phys. Chem. C* **2017**, *121*, 16770–16782.

(71) Huang, W.; Zhang, X.; Yang, A. C.; Goodman, E. D.; Kao, K. C.; Cargnello, M. Enhanced Catalytic Activity for Methane Combustion through in Situ Water Sorption. *ACS Catal.* **2020**, *10*, 8157–8167.

(72) Petrov, A. W.; Ferri, D.; Tarik, M.; Kröcher, O.; van Bokhoven, J. A. Deactivation Aspects of Methane Oxidation Catalysts Based on Palladium and ZSM-5. *Top. Catal.* **2017**, *60*, 123–130.