Deconvoluting Transient Water Effects on the Activity of Pd Methane Combustion Catalysts

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Supporting Information

ABSTRACT: It is well-known that water has a detrimental effect on the low-temperature methane combustion activity of palladium catalysts. However, when the transient activity (i.e., light-off or ignition—extinction experiments) of methane combustion catalysts is compared, the effects of water adsorption—desorption phenomena are seldom directly considered. While these effects are important to keep in mind when studying support-dependent methane combustion activity, they are crucial when selecting a catalyst diluent. In many cases, the water adsorption—desorption properties of “inert” reactor diluents may dominate the transient methane combustion activity of a Pd catalyst. In this contribution, we show how different catalyst pretreatments on various Pd catalysts can influence the presence of water and hydroxyl groups on the surface of catalyst supports, reactor diluents, and active phase, and how this process dramatically affects observed methane combustion activity. Transiently, alumina (both support and diluent), which strongly binds water that is produced in the reaction, can keep the PdO phase active and water-free. However, after alumina surfaces become saturated with water, the PdO surface also becomes hydroxylated, which decreases the catalyst’s methane combustion activity. Due to this time-dependent surface titration, care must be taken when comparing transient experiments between catalysts on different supports; comparable data for methane combustion must be collected while carefully checking for water adsorption on the surface of the catalyst and diluent. Finally, we propose that a channel for sustainable high combustion rates is possible if water is prevented from adsorbing on the highly active PdO surfaces.

1. INTRODUCTION

Methane combustion has been heavily investigated on palladium-based catalysts due to their high activity.1,2 While palladium is well-known as the best material for methane combustion,3 there is still the need to increase catalytic activity at low temperatures and in the presence of water, conditions which are especially important for the application of these materials in emission control catalysis.4 Although still debated, PdO is generally regarded as the most active phase for methane combustion due to a sigma-bond metathesis mechanism involving C–H bond activation on the Pd–O surface.5–7 Unfortunately, water, one of the products of the methane combustion reaction, dramatically hinders the activity of PdO materials at temperatures below 450 °C. This poisoning effect has been recognized through kinetic measurements showing a negative first order for water, indicating its strong coverage under conditions in which water adsorption is favored over its desorption.8 Water has been identified to hinder combustion rates due to either binding strongly on the PdO surface, or affecting oxygen transfer between the PdO and support surfaces.9–12 The alloying of Pd with other metals such as Pt reduces the water poisoning effect because of the formation of the metallic Pd phase, which is much less affected by water adsorption because methane activation proceeds through oxidative addition or homolytic H abstraction on the metallic or oxygen-covered surfaces.13,15

Support materials have also been shown to affect the catalytic activity of Pd for methane combustion. Recent studies from our group showed that rates normalized by the exposed Pd surface area do not drastically vary between Pd supported on alumina, ceria-zirconia or silica, but are lower on Pd/MgO.16 However, Pfefferle and co-workers reported that supports that are not considered “active”, such as alumina and magnesia, can still affect catalytic rates by oxygen transfer to the PdO phase during reaction conditions.17 In particular, alumina was found to provide oxygen to the PdO phase during the catalytic cycle, and this transfer is inhibited when hydroxyl groups accumulate on the support surface and the metal–support interface from water produced by the reaction.12 The
role of water in deactivating the catalyst was therefore ascribed to the blocked oxygen transfer mechanism, with water adsorption–desorption equilibrium playing an important role especially at temperatures below 450 °C, although in some cases providing further degradation mechanisms at higher temperatures.\textsuperscript{17} This effect had been previously recognized with a delay in water signal exiting the reactor during the combustion reaction.\textsuperscript{8,18} Therefore, measurements of the catalytic combustion of methane are highly sensitive to the state of the support surface, as we further corroborate in the present work via support modification with various in situ catalyst pretreatments. To our knowledge, we also demonstrate for the first time the high sensitivity of this reaction to the surface properties of the catalyst diluent. Previous contrasting results from the literature can therefore be reconciled by recognizing the important role of water remaining on the catalyst surface from pretreatments in determining reaction pathways in Pd-based materials. Two important conclusions arise from this work: pretreatment and thermal history of a sample can heavily affect catalyst performance studies in a predictable way due to water adsorption–desorption phenomena, and methods that prevent adsorption of water on the PdO active phase could provide sustainably high rates for the methane combustion reaction.

2. EXPERIMENTAL SECTION

2.1. Preparation of Pd-Based Catalysts. Solutions of 3 nm Pd nanocrystals and 16 nm Pd nanocrystals were synthesized using previously published procedures.\textsuperscript{16,19} Prior to impregnation, supports were calcined at temperatures at least 100 °C above reaction temperature. Alumina was prepared by calcining Puratex TH1/100/150 (kindly obtained from Sasol) at 900 °C for 24 h using heating and cooling ramps of 3 °C min\textsuperscript{-1} in static air. Silica was prepared by calcining silica gel (Davilis grade 643; 200–425 mesh) at 800 °C for 6 h using heating and cooling ramps of 3 °C min\textsuperscript{-1} in static air. Ceria was prepared by calcination of commercial CeO\textsubscript{2} powder (Treibacher Industries) at 600 °C for 6 h using heating and cooling ramps of 3 °C min\textsuperscript{-1} in static air. For impregnation of a desired loading of Pd nanoparticles onto Al\textsubscript{2}O\textsubscript{3}, metal concentrations of synthesized colloidal nanoparticle solutions were determined via thermogravimetric analysis (TGA). A nanoparticle solution was added dropwise into an aluminum TGA pan, which was heated via hot plate at ∼80 °C until 150 µL had been added. This pan was then further heated in the TGA in flowing air to 500 °C, and held until a steady mass was reached, indicating complete removal of solvents and organics. Dividing this final mass by initial solution volume gave the metal concentration. An appropriate amount of nanocrystals (to give a loading of 0.1 or 1.0 wt% Pd in the final catalysts) dissolved in hexanes was added to a dispersion of stirred support in hexanes. The same nanocrystal batch was used for all supports to ensure identical metal loadings and nanocrystal size/morphology across supports. Complete adsorption occurred immediately, and dispersions were left stirring no longer than 10 min after solution addition. The solid was recovered by centrifugation (8000 rpm, 1 min) and dried at 60 °C overnight. Prior to catalytic tests, all samples were sieved below 180 µm grain size, treated in a furnace at 700 °C for 30 s to remove ligands from synthesis as previously described,\textsuperscript{20} and sieved again below 180 µm grain size to avoid effects of mass transfer limitations. For synthesis of the deposition-precipitation catalyst, Pd(NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O (Sigma-Aldrich, ∼40% Pd basis; 0.125 g) was dissolved in deionized water (DI H\textsubscript{2}O) via a 50 mL volumetric flask. Al\textsubscript{2}O\textsubscript{3} (0.50 g) was dispersed in 50.0 mL of DI H\textsubscript{2}O under vigorous stirring. The prepared Pd(NO\textsubscript{3})\textsubscript{2} aqueous solution was slowly added by micropipette to the Al\textsubscript{2}O\textsubscript{3} suspension. The resulting solution was continuously stirred for 1 h to ensure a homogeneous distribution and preliminary natural adsorption of Pd\textsuperscript{2+} on the surface of Al\textsubscript{2}O\textsubscript{3}. The pH was then gradually adjusted to 9.5 by diluted ammonium hydroxide solution. Next, the solution was stirred overnight to reach an equilibrium for a thorough adsorption of Pd\textsuperscript{2+}. Then, the solution was centrifuged and washed by DI H\textsubscript{2}O. The obtained precipitate was dried in vacuum at 80 °C for 12 h and calcined in air at 550 °C for 4 h. For synthesis of the impregnation catalyst, the introduction of Pd\textsuperscript{2+} onto the Al\textsubscript{2}O\textsubscript{3} was achieved through impregnating a palladium nitrate solution (0.125 g Pd(NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O in 50 mL of DI H\textsubscript{2}O) in 0.50 g of Al\textsubscript{2}O\textsubscript{3}. The water was evaporated at 60 °C in a rotary evaporator under vacuum (200 mbar). After impregnation, the product was dried in a vacuum oven at 80 °C for 12 h and calcined in air at 550 °C for 4 h.

2.2. Characterization Techniques. Transmission electron microscopy (TEM) was performed on a FEI Tecnai operating at 200 kV. Samples were prepared by drop-casting dilute nanoparticle solutions in hexanes or isopropanol dispersions of powder catalysts directly onto carbon-coated Cu grids. All particle size distributions were calculated by measuring >100 nanoparticle diameters by hand using ImageJ software. For ex-situ post-catalysis TEM measurements, in order to preserve working catalyst state, the catalyst was immediately flushed with 45 mL min\textsuperscript{-1} pure Ar after reaction conditions, and rapidly cooled down to room temperature at ∼300 °C min\textsuperscript{-1}.

2.3. Catalytic Characterization. Because of the high temperatures required for this reaction, prior to nanocrystal impregnation, each of the catalyst supports were calcined to at least 600 °C, to ensure minimal change in support morphology during reaction conditions. To minimize thermal gradients and bed hot-spots, catalysts were mixed with large volumes of diluent. In general, each catalyst, postligand removal, was sieved below 180 µm grain size and mixed with Al\textsubscript{2}O\textsubscript{3} diluent (mass catalyst:diluent = 1:9), which was found to be sufficient to eliminate thermal effects by repeated tests; 200 mg of this diluted mixture was loaded into the reactor to give a bed length of about 1.0 cm; this bed rested between two layers of granular quartz which were used for preventing displacement of the catalyst powder and for preheating the reactant gases. The reactor was heated by a square furnace (Micromeritics) and the temperature of the catalyst was measured with a K-type thermocouple inserted inside the reactor, touching the catalytic bed. All experiments were conducted at atmospheric pressure. Ignition/extinction curves were obtained in a U-shaped quartz microreactor with an internal diameter of 10 mm, and a temperature ramp rate of 10 °C min\textsuperscript{-1}.

The reactant mixture composition was controlled by varying the flow rates of CH\textsubscript{4}(5%)/Ar, O\textsubscript{2}(5%)/Ar, H\textsubscript{2}(5%)/Ar and Ar (all certified mixtures with purity >99.999% from Airgas). In all catalyst tests, the catalyst was pretreated in the reactor without exposure to the environment, with described oxygen, hydrogen, or argon mixtures, before methane combustion conditions. These pretreatments occurred at either 475 or 275 °C, for 30 min, using 5% gases diluted in Ar. The reactor was then cooled to 200 °C, at which point the reactant mixture was
introduced, and the reactor was ramped to 500 °C at 10 °C min⁻¹. Unless specified, 2 mg of 1.0% Pd/Al₂O₃ catalyst (measured via serial dilution), or 20 mg of 0.1% Pd/Al₂O₃ catalyst were diluted with calcined Al₂O₃ to 200 mg, and loaded into the reactor bed. Unless specified, in all experiments, 23.5 mL min⁻¹ total gas reaction mixture was flowed over the bed, consisting of 0.5% CH₄ and 4.0% O₂, balanced with Ar (and in some cases, 4.2 vol % H₂O). Effluent was measured using an online mass spectrometer (Hiden HPR-20), retrieving one data point every 12 s. A 9-period moving average smoothing function was used in data processing, and all smoothed data were directly superimposable with raw data.

Water temperature-programmed-desorption (H₂O-TPD) was performed on the same setup described above. A 200 mg sample of pure, calcined (900 °C) alumina or silica (800 °C) support was added to the U-shaped quartz microreactor. The powder was set between two thin quartz wool plugs to avoid titration of any silanols. Prior to the TPD-measurement, the support was activated at 570 °C for 30 min (10 °C min⁻¹). Then water was adsorbed by flushing 4.2 vol % H₂O diluted in Ar for 30 min (20 mL min⁻¹ Ar-flow bubbling through a water saturator at 30 °C). Physically adsorbed water was removed by switching to dry Ar flow (20 mL min⁻¹) for a further 30 min. At each step complete isothermal water adsorption and desorption could be monitored by means of online MS. The H₂O-TPD measurement was performed between 110 and 570 °C with a 10 °C min⁻¹ ramp.

2.4. Calculations of Interface Atoms and CH₄ Consumption on-Stream. To calculate the fraction of interface sites present in 3 and 16 nm Pd nanocrystals supported on alumina, the number of Pd atoms in a sample was calculated based on the known Pd weight loading. Assuming that nanocrystals are spherical, the volume of a 3 or 16 nm sphere was calculated, and used to retrieve the number of Pd atoms present in such a sphere representing an individual nanocrystal. From the circumference of such a sphere it is then possible to calculate the number of Pd atoms residing at the interface with a support, and by multiplying the number of Pd interface atoms on each sphere by the total number of particles in a sample, the ratio of interface sites was retrieved.

In the case of the calculation of the moles of CH₄ reacted during the reaction before the water signal was detected, the decreased CH₄ signal from the mass spectrometer was normalized by the signal of Ar (inert gas) which is constant throughout the measurement. By measuring the time before the water signal is detected and by knowing total gas flow rate and concentration of CH₄ in the flow, it is possible to convert the CH₄/Ar ratio into the moles of CH₄ reacted during a certain time period.

3. RESULTS AND DISCUSSION

A 3 nm Pd/Al₂O₃ sample was prepared by impregnation of colloidal Pd nanocrystals with a uniform 3 nm diameter onto a commercial alumina support that was previously stabilized by calcination at 900 °C for 24 h. The alumina was mostly present in the gamma phase and had a surface area of 100 m² g⁻¹. Ligands on the Pd nanocrystals were removed by a fast thermal treatment that did not affect the size distribution of the supported nanocrystals according to previous work. Methane combustion experiments were performed by flowing a dry mixture of methane and oxygen over the catalyst and measuring methane conversion as a function of temperature using a mass spectrometer with a sampling time of 12 seconds. Temperature was ramped at 10 °C min⁻¹.

The nature of the in situ catalyst pretreatment was found to dramatically affect the catalyst performance: when the catalyst was pretreated in oxygen at 475 °C for 30 min, a much higher initial conversion was obtained compared to the same catalyst pretreated at a temperature of 275 °C for 30 min (Figure 1A). Specifically, the 475 °C pretreatment produced a local maximum conversion at about 320 °C, and then a decrease in conversion was observed, and finally conversion increased again to values that very closely followed the conversion curve for the 275 °C pretreated material. We found that hydrogen or pure argon pretreatments done at similar temperatures provided similar results, with pretreatment at higher temperatures always leading to a higher initial methane conversion (Figure 1B,C).

There is still debate whether the Pd, PdO, or a Pd/PdO interface is the most active phase for methane combustion. In asking this question, it is common to compare the activity of a calcined-and-stored catalyst (presumably containing a PdO phase) with the same material subjected to an in situ reducing pretreatment (aiming at producing a metallic Pd surface). The difference in activity is claimed to be related to the conversion of the PdO phase from oxide to metallic, or a mixture of the two. In our case, by performing such pretreatment in either diluted oxygen, diluted hydrogen, or pure argon at 275 and 475 °C for 30 min, we found that the activity patterns were very similar, if not equal: the pretreatment at 475 °C promotes the activity of the catalyst with a similar conversion profile in all cases. It is clear that the temperature of the pretreatment is more important than the nature of it, whether it is oxidizing or reducing. The same pretreatment-dependent activity profile, with higher pretreatment temperatures leading to increased...
low-temperature reactivity, was observed in catalysts synthesized via deposition–precipitation and wetness impregnation (Figure S3). The hydrogen treatment at either 275 or 475 °C is able to reduce the PdO phase, which is however likely oxidized back to PdO when the catalyst is placed under reaction conditions containing oxygen. Therefore, it is clear that a hydrogen pretreatment eventually leads to a catalyst active phase which is the same as the one obtained after an oxidation pretreatment (Figure 1).

An important element to clarify is that following pretreatment and catalysis, particle size distributions and particle morphology did not significantly change (Figure 2). This demonstrates the stability of the Pd/Al₂O₃ materials at temperatures of 500 °C and below. Therefore, as highlighted in a previous work, a permanent morphological change in the structure of the PdO active phase is unlikely to be the cause for the observed differences in catalytic behavior after the different pretreatment conditions. For this reason, the use of well-defined materials was crucial to rule out morphological change as a cause of different activity. Instead, we turn our attention to understanding how various pretreatments affect the properties of the catalyst support.

A common element between the 475 °C oxygen and hydrogen pretreatment experiments of Figure 1 is that water is observed to leave the reactor only after the appearance of a peak in activity at ∼310 °C (i.e., Figure 3). Previous work unequivocally demonstrated a lag in water production from the combustion reaction compared to CO₂ production. This delay was related to the desorption of water from the catalyst, which is considered one of the limiting steps of the combustion reaction. Therefore, two reactivity regimes can be identified under dry methane combustion experiments: the first, in which CO₂ is the only observed product of the combustion reaction and the catalyst is in its most active state (Regime I, Figure 3); and the second in which water starts to be detected, bringing the catalyst to a lower activity state (Regime II, Figure 3). The switch between these two regimes seems to be related to water production from the combustion reaction.

Previous work demonstrated that water accumulates on the support and PdO phase forming hydroxyl groups that were identified by infrared (IR) spectroscopy. It was proposed that the hydroxyl accumulation on the support blocks the oxygen exchange between support and PdO phase, thus reducing the activity of the system. Here we suggest that hydroxyl accumulation is the reason for the decrease in the activity. Water first adsorbs on the support until saturation and then hydroxyl accumulation on PdO takes place. Thus, the activity drop is due to accumulation on the PdO phase rather than the support. In the same previous work it was noticed that the water being produced as a product of the reaction was not as effective at stopping the oxygen transfer mechanism as the water being added in the feed mixed with methane and oxygen reactants. We propose that water formed during the combustion reaction can be adsorbed by either the PdO phase or the alumina support. Two general reactions can occur: (1) PdO reacts with water to form surface Pd hydroxide layers; (2) alumina surface adsorbs water (on Lewis sites) or reacts with water to form hydroxyl moieties. These reactions are likely to be under dynamic equilibria under the conditions of the reaction studied here, and is likely to lead to strong bonding of water on the alumina surface. A more detailed discussion on these equilibria processes can be found in Figure/Discussion S4. Previous
computational work on the hydroxylation levels of gamma-alumina facets suggested that the (100) surface is completely hydroxylated above 320 °C, whereas on the (110) surface the hydroxyl groups are stable even at higher temperatures. The (100) facet could therefore be responsible for sequestering the water produced by the combustion reaction, until this facet is saturated, at which point water exits the reactor and is detected (Figure 3, Regime II). It is at this point that the local excess of water molecules reacts with the PdO surface and causes the decrease in catalytic rates, since the sigma-bond metathesis pathway is likely more difficult in the presence of water.

Although it is clear from the above experiments that preferential water adsorption on the alumina causes an initially high activity, the reason for the decrease after water saturates the support is still not clear. Previous works suggest that excess water populates the Pd-support interface, blocking oxygen transfer and reducing reaction rates. However, if this was true, samples with a different Pd-support interface contribution might be expected to be more or less affected by the blockage of the oxygen transfer mechanism for methane combustion. To test this hypothesis, we prepared another Pd/Al2O3 catalyst by changing the particle size, moving from Pd nanocrystals of 3 nm to uniform Pd nanocrystals of 16 nm, while maintaining the same Pd metal loading of 0.1 wt %. Particles of different size may have drastically different reactivity at the metal-support interface. Despite the conversion over Pd(16 nm)/Al2O3 sample being lower than that of a sample containing smaller Pd nanocrystals, the light-off curve still showed an initial peak at about 350 °C and a slower increase in conversion over the following 50 °C during heat-up, before the conversion took off at higher temperatures (Figure 4A). Because of lower activity, peak activity during regime I of the reaction was observed at higher temperature compared to that of the sample containing 3 nm Pd particles. However, integrating the amount of CH4 consumed by the two samples before the water signal was detected provided a remarkably similar result, 13.9 micromoles for the 3 nm Pd sample and 9.1 micromoles for the 16 nm Pd sample (Table 1). The fact that the amount of CH4 consumed by the two samples during regime I is very similar is an indication that the reactivity at the Pd-support interface, whose length varies by a factor of 28 between the two samples, is not as important. In fact, the difference in these numbers can be quantitatively attributed to the equilibrium hydration levels of support as a function of temperature; indeed, integrating a temperature-programmed desorption (TPD, Figure 4B) experiment between the temperatures of interest shows that this difference in hydration is caused by equilibrium water coverages at different temperatures.

When 4.2% H2O is co-fed into the reaction mixture, the conversion inversion at 320 °C disappears (Figure 5). We hypothesize that this is due to immediate titration of the Al2O3 surface and subsequently the PdO surface, due to the presence of large quantities of H2O (i.e., compared to the small amount produced at low CH4 conversion without H2O co-fed). Even at higher temperatures (T > 320 °C), the addition of H2O decreases CH4 conversion; this second effect is because the water produced during the reaction (maximum 1 vol % at full methane conversion) is lower than the water that was introduced in the feed (4.2 vol %). The larger amount of water causes the equilibria involving Pd hydroxide formation and water adsorption by alumina to shift toward the products, thus causing stronger poisoning of the PdO surface.

Evidence that PdO surface poisoning by water is responsible for the decrease in activity, rather than the loss of oxygen transfer from the support, comes from an experiment in which the same 3 nm Pd nanocrystals are deposited onto silica instead of alumina. In the case of silica, it has been shown that there is no oxygen transfer given the very limited oxygen mobility on this inert support. Therefore, if limited oxygen...
transfer is the reason for the observed loss in activity, a Pd/SiO2 sample should not show a peak in activity even if the catalyst is diluted with a material that can adsorb water, such as alumina. The result of this experiment is reported in Figure 6.

![Figure 6](image)

Figure 6. Methane combustion activity over Pd/Al2O3 diluted in alumina (A), the same Pd/Al2O3 material diluted in silica (B), Pd/SiO2 diluted in alumina (C), the same Pd/SiO2 material diluted in silica (D). All samples were pretreated at 475 °C under oxygen for 30 min before the methane combustion reaction.

The performance of the Pd/SiO2 sample diluted in alumina is very similar to the Pd/Al2O3 material (Figure 6A,C): an initial high activity is observed with no water leaving the reactor, until water started to appear and the methane conversion peaks before increasing again, very close to what observed in Figure 3. This behavior clearly supports the hypothesis that it is the water produced during the reaction that reacts with the alumina support or diluent and is prevented from poisoning the PdO surface. Indeed, when the same Pd/SiO2 material is diluted using silica within the reactor, the activity is lower and does not show an intermediate peak in performance (Figure 6D). Likely, this is due to the inability of SiO2 to absorb any significant amount of H2O (Figure S5). These experiments are important because they show that dilution of the catalyst in the reactor should be performed with a truly inert powder; Figure 6A–D shows that the water adsorption–desorption properties may even dominate the transient activity of a combustion catalyst.

Transition aluminas, such as the γ-alumina used in the current and many other works, are known to provide strong binding for water molecules, in part due to surface rehydration or rehydroxylation and also to strongly binding Lewis acid sites.29–31 The fact that this chemistry is important for the transient activity observed for Pd/Al2O3 is further suggested by the fact that other supports do not exhibit such extreme behavior. Silica, for example, showed that water was being detected during methane conversion at temperatures very close to those at which reaction started (Figure 6D); diluting a small amount of Pd/Al2O3 in excess SiO2 (Figure 6B) shows only a small window between 200 and 300 °C where H2O is adsorbed, due to the limited quantity of Al2O3 (i.e., compared to Figure 6A, diluted in Al2O3). Finally, Figure S6 demonstrates that ceria-supported Pd diluted in more ceria showed initially some activity with no water being detected. Because the same batch of 3 nm Pd nanocrystals were used to prepare all these catalysts, it is clear that the ability of alumina to adsorb and sequester water formed by the reaction at low temperatures is highly beneficial for the activity of the PdO phase for methane combustion, leading to high transient conversions at low temperatures as long as water is removed from the PdO phase.

Following the above considerations, it becomes clear that the Pd loading also plays an important role in the transient activity of the samples, because in light-off experiments, the higher the activity at low temperature, the more the water “storage” on alumina can enhance the rates. Therefore, by impregnating the same 3 nm Pd nanocrystals on the alumina support but at higher metal loading (1 wt % compared to 0.1 wt %), we observed that the transient low-temperature activity was further increased, with complete methane combustion reached by 250 °C under dry conditions when the sample is pretreated at 475 °C (Figure 7). The lag in water detection allows the material to be only marginally affected by water produced during the reaction, because water saturates the support sites at temperatures when the catalyst is already at full conversion. However, these data confirm that unusually high activity of a sample could be measured if the transient effects of water and support hydration level are not taken into account. The high activity is in fact not stable but only transient: when the 0.1 wt % heating ramp was stopped while the catalyst was equilibrated (Figure 8).

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Overall, this work corroborates many previous studies on the effect of water on the activity of Pd catalysts for methane combustion, and in particular demonstrates that a lag in water detection during methane combustion is related to water adsorption by alumina supports and diluents that can result in very high activity for the reaction. This activity is, however, only transient. To be able to compare different samples it is therefore necessary to perform experiments with a truly inert diluent and under conditions where transient water effects are
not important, such as by adding water to the feed. It takes a specific set of conditions to identify this phenomena, which is why it may have gone unnoticed in the past: (1) enough high-surface area Al2O3 or other hydrophilic material in the bed (including catalyst and diluent), to act as a significant H2O absorber, (2) high-temperature in situ pretreatment without intermediate exposure to ambient conditions, (3) light-off experiments without steam, (4) a quick sampling outlet detector, such as a mass spectrometer and not a slowly sampling gas chromatograph, and (5) most importantly, catalytic conditions at which support H2O titration is reached before 100% CH4 conversion. This work also points to the fact that transient effects can go unrecognized depending on heating ramp rates and reaction conditions that are used during a particular experiment.

4. CONCLUSIONS
We describe the effect of water adsorption—desorption phenomena on the transient activity of Pd-catalyzed methane combustion as a function of pretreatment, particle size, catalyst support, and reactor bed diluent. It is crucial to understand these effects if one plans to make comparisons between methane combustion catalysts via transient ignition-extinction experiments (light-off curves). Our results highlight the fact that if these phenomena are not taken into consideration, high reactivity regimes could be claimed that are short-lived, since water adsorption on the PdO surface or at the Pd/alumina interface eventually removes this high activity pathway. Additionally, this work warns that the transient activity of methane combustion catalysts is strongly affected by the choice of reactor diluent, and this effect can be understood by considering the water adsorption—desorption properties of the support and diluent. In performing methane combustion studies it is therefore important to make sure that these transient water effects are not present by choosing an appropriate inert diluent (such as silica) and by adding water to the feed. This work also shows that if a method for keeping away water from the PdO surface was devised, the high activity regime could be sustained for a much longer time-on-stream.

ASSOCIATED CONTENT

Supporting Information
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Thermodynamic considerations; other figures as mentioned in the text (PDF)

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Notes
The authors declare no competing financial interest.

Biography

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 postdoctoral scholar in the Chemistry Department at the University of Pennsylvania (Philadelphia, USA) with Prof. Christopher B. Murray before joining the Faculty at Stanford University in January 2015. He is currently Assistant Professor of Chemical Engineering and, by courtesy, of Materials Science and Engineering and Terman Faculty Fellow. Dr. Cargnello is the recipient of several awards including the ENI Award “Debut in Research” in 2013, the European Federation of Catalysis Societies Award as best European Ph.D. thesis in catalysis in 2013, the Junior award from the European Rare Earth and Actinide Society in 2018, and the Sloan Fellowship in 2018. In the Cargnello group, uniform and tailored nanocrystals and nanostructures are synthesized, studied, and used for energy and environmental applications through catalytic processes, with emphasis on how to precisely control nanoarchitectures to understand and exploit interactions between well-defined building blocks.

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